

Homogeneous-Phase Electron-Transfer Reactions of Polyoxometalates†

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Contents

I. Introduction	113	VII. Reduction of Inorganic Oxidants by Reduced POM Anions	156
II. Outer-Sphere Electron-Transfer Reactions	115	A. Introduction	156
A. Debye-Smoluchowski and Marcus	115	B. Hydrogen Cations	156
B. Marcus Equation	116	C. Nitrite	157
1. Applications	116	D. Nitronium Ion	158
2. Theoretical Calculation of Outer-Sphere Electron-Transfer Rate Constants	117	E. Peroxodisulfate	159
3. Outer-Sphere Electron Self-Exchange	117	F. Chlorate and Periodate	159
4. The Marcus Cross-Relation	117	G. Permanganate	160
C. Ion Pairing between Electrolyte Ions and Electron Donors or Acceptors	118	VIII. Reduction of Dioxygen by Reduced POM Anions	161
D. Outer-Sphere Electron Transfer within Stable Donor-Acceptor Complexes	119	A. Introduction	161
III. Electron Self-Exchange between POM Anions	121	B. Single-Electron Reduction of O ₂	161
A. Keggin Tungstocobaltate Anions	121	C. The O ₂ /O ₂ ^{•-} Self-Exchange Reaction	161
B. Keggin and Wells-Dawson Metallophosphate Anions	122	D. Reduction of O ₂ by Reduced Isopoly- and Heteropolytungstates	162
C. Reevaluation of the Reorganization Energy of the [Co ^{III} W ₁₂ O ₄₀] ⁵⁻ /[Co ^{II} W ₁₂ O ₄₀] ⁶⁻ Couple	125	E. Reduction of O ₂ by d-Electron-Containing, Transition-Metal-Substituted Heteropolytungstates	164
D. One-Electron Oxidation of [Cu ^{II} W ₁₂ O ₄₀] ⁷⁻ to [Cu ^I W ₁₂ O ₄₀] ⁶⁻	129	F. Reduction of O ₂ by Reduced Vanadomolybdophosphates	166
IV. Oxidation of Organic Electron Donors by POM Anions	129	IX. Acknowledgments	167
A. Alkylaromatic Compounds	129	X. References	167
B. Cyclohexadienes	136		
C. Organic Acids, Esters, Aldehydes, and Ketones	138		
D. Aromatic and Aliphatic Alcohols	142		
E. Carbon-Centered Organic Radicals	143		
F. Thiols and Organic Sulfides	145		
V. Oxidation of Inorganic Electron Donors by POM Anions	148		
A. Introduction	148		
B. Inorganic Electron Donors	150		
C. Hydrogen Sulfide	150		
D. Luminescence Quenching of Electronically Excited [Ru(bpy) ₃] ²⁺ Cations	152		
VI. Reduction of Halogenated Alkanes by Reduced POM Anions	153		
A. Carbon Tetrabromide	153		
B. Halomethanes	154		
C. Carbon Tetrachloride, Halomethanes, and Haloalkanes	155		

I. Introduction

Many isopoly- and heteropolyoxometalate (POM) anions are ideal candidates for the observation of homogeneous-phase outer-sphere electron-transfer processes and for comparison of experimentally determined rate constants with those predicted by the theoretical models of Marcus, Sutin, and others. At the same time, where one or more addendum atoms—usually V(v), Mo(VI), or W(VI)—of the POM cluster have been substituted by d-electron-containing first- or second-row transition-metal cations, more rapid inner-sphere electron-transfer pathways are often accessible. The purpose of the present article is to provide a comprehensive and critical analysis of published data concerning the mechanisms of homogeneous-phase electron-transfer reactions between POM anion pairs, and between POM anions and organic or inorganic electron donors or acceptors.

The elegance and utility of Marcus's theory of outer-sphere electron transfer were recognized in 1992 with a Nobel Prize in chemistry, and its historical development was outlined in his Nobel Lecture.¹ Shortly after publication of Marcus's seminal papers on this topic,²⁻⁴ it was recognized that POM anions were likely to exchange electrons via an outer-sphere mechanism: (1) As a class, POM anions possess

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†Dedicated to Dr. J. Hodge Markgraf, Ebenezer Fitch Professor of Chemistry at Williams College, on the occasion of his retirement.



Ira A. Weinstock was born in Ithaca, NY, in 1959. He received a B.A., magna cum laude, from Williams College in 1988 and earned an M.A. under the direction of Carlo Floriani in 1986 from Columbia University. As an NSF Graduate Fellow at M.I.T., he earned a Ph.D. under the guidance of Richard R. Schrock in 1990. At M.I.T. he synthesized complexes containing metal-carbon, -nitrogen, and -oxygen multiple bonds and studied the mechanism of alkyne metathesis by rhenium(VII) alkylidyne complexes. He subsequently spent one year at Sandia National Laboratory, Albuquerque, NM, where he developed metal oxide thin films for applications in electronics and catalysis. In 1991 he joined the staff of the USDA Forest Service, Forest Products Laboratory, Madison, WI, the National Laboratory of the U.S. Forest Service. There, he initiated a program in the use of water-soluble polyoxometalate salts as selective catalysts for the oxidative delignification (bleaching) of commercial wood pulp. The goal was to replace the chlorine compounds used in papermaking by dioxygen, the least expensive and most environmentally attractive oxidant available. The program, now supported by a partnership between the U.S. Forest Service, the U.S. Department of Energy, and private industry, and which includes collaborations with the University of Wisconsin and Emory University, was recognized in 1996 with the U.S. Secretary of Agriculture's National Honor Award for Excellence in Research. In addition to the design of versatile water-soluble catalyst systems for the development of environmentally sustainable chemical technologies, the authors research interests include the kinetics and thermodynamics of polyoxometalate duster formation and the mechanisms of catalytic oxidations by dioxygen.

charge densities considerably lower than those observed in traditional low-charge-density (noncoordinating) anions, such as ClO_4^- and NO_3^- ; (2) the partial negative charges on the oxide anion ligands within POM structures are quite low (the pK_a values of many POM anions are below 1, and the partial negative charges residing on the outermost terminal oxide ligands, $\text{M}=\text{O}$, are generally lower than those on the bridging oxide anions embedded within the clusters); and (3) many POM anions, and in particular those possessing the Keggin structure, are close to spherical in shape, a geometric consideration important for application of the electrostatic laws upon which much of Marcus's development was predicated.

The first detailed kinetic study and theoretical analysis of electron transfer involving POM anions was reported by Rasmussen and Brubaker in 1964, only shortly after the foundations of Marcus's work had been laid.⁵ Rasmussen and Brubaker studied the self-exchange reaction between $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ (abbreviated $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$) and its 1- e^- -oxidized derivative, $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ ($\text{Co}^{\text{III}}\text{W}_{12}^{5-}$). In addition to the general considerations listed above, both these complexes are substitutionally inert with respect to the ligand environments of the cobalt ions.⁶ In 1970 Chester recognized the potential utility of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$

as a well-defined probe for determining the nature of outer-sphere oxidations of alkyl aromatic hydrocarbons.⁷ His aim was to determine whether such processes were feasible.

An additional rationale for using $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ was the expectation that reduction of tetrahedrally coordinated $\text{Co}(\text{III})$ ions (ground-state electronic configuration $e^3 t_2^3, {}^5\text{E}$) to tetrahedral $\text{Co}(\text{II})$ ($e^4 t_2^3, {}^4\text{A}$) would occur rapidly in the absence of electronic excitation. In contrast, addition of an electron to an e_g orbital of low spin octahedral $\text{Co}(\text{III})$ ($t_2^6 e_g^0, {}^1\text{A}$) is formally a spin-forbidden process. Hence $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ anions were expected to be more kinetically facile oxidants than the octahedral cobaltoorganic complexes, such as cobalt(III) acetate, typically used in the oxidation of organic substrates. The possible effects of Jahn-Teller distortion on the inner-sphere reorganization energy associated with the 1- e^- reduction of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ were not considered. These, and related structural and electronic issues, will presently assume greater importance in evaluation of the role of inner-sphere reorganization energies, and of the potential for nonadiabatic behavior, in electron self-exchange between $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ and between other POM anion pairs.

Since publication of Chester's work in 1970, $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and related POM anions have been used as well-defined outer-sphere electron-transfer agents in over 50 published studies. Indeed, the $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ anion has, with good reason, been referred to as a "soluble anode".⁸ Meanwhile, the potential utility of numerous POM anions as electron-transfer agents in the selective catalytic oxidations of inorganic and organic substrates of practical importance has been recognized. Despite these developments, the handful of studies specifically concerned with defining the nature of electron-transfer reactions of the POM anions themselves reach conflicting conclusions regarding issues of fundamental significance.

After Marcus and Sutin's early treatments of electron-transfer reactions, they and others continued to improve upon a number of initial approximations and assumptions in the theory.^{1,9-14} More than three decades of interaction between theoreticians and experimentalists have resulted in a dramatic refinement of classical and semiclassical approaches, and empirical observations have led to important conclusions regarding the scope and limitations of the theoretical models.^{11,15-22}

In parallel with progress in the theoretical arena, new, more accurate and versatile spectroscopic techniques for observing the rates of electron self-exchange between POM anions were developed. These techniques have made it possible to obtain, and more thoroughly verify,²³⁻²⁶ the accuracy of key theoretical parameters. The new kinetic techniques were a natural outgrowth of spectroscopic studies concerning the nature of reduced POM anions (heteropoly "blues").²⁷⁻³⁴ In particular, however, the use of NMR to determine key theoretical parameters followed the observation by Kozik and Baker that 1- e^- -reduced heteropoly blues, although paramagnetic, gave sharp NMR signals.²³⁻²⁶ (Detailed studies concerning the nature of reduced POM anions, al-

though pertinent to electron-transfer reactions of POM anions, are outside the scope of the present review. Nevertheless, important findings from that body of work will be included as necessary.)

Given these developments, critical evaluation of the literature concerning the nature of electron-transfer reactions of POM anions (section III) is now possible. Indeed, it is a necessary prerequisite to understanding the use of POM anions as electron-transfer probes (i.e., "soluble anodes") in physical or physical-organic chemistry or as catalysts for selective oxidations. First, however, some introductory comments regarding theories of electron transfer are in order. Although the interested reader will find considerably more detail and depth in the original articles cited, it is hoped that familiarity with the mathematical forms of the theories and with the physical phenomena represented by specific mathematical relationships, as conveyed in the following brief introduction (section II), will make the intellectual matter covered in the present review more readily accessible to the nonexpert.

Within the context of electron-transfer reactions, a number of issues pertinent to analysis of reaction rates of charged species in solution, such as ion-pairing and donor-acceptor complex formation, are discussed. Here too, the intent is to provide the reader with an appreciation for phenomena commonly encountered in homogeneous-phase electron-transfer reactions of POM anions.

Beginning with section IV, published data concerning the mechanisms of electron-transfer reactions of POM anions are critically evaluated. Because the primary focus is on reaction mechanisms, many reports concerning stoichiometric and catalytic homogeneous-phase reactions of POM anions are not discussed. The review is limited, rather, to discussion of kinetic or other published data pertinent to understanding the mechanisms of electron-transfer reactions.

Because of this focus, relatively short portions of much longer published studies are sometimes given disproportionate attention. Nonetheless, considerable effort has been made to place mechanistic data within the context defined by the larger significance of the reactions under discussion. On the other hand, POM anions have frequently been used to address issues of fundamental significance, or of considerable interest with respect to important industrial or biological processes. In some of these cases, the chemistry of the POM anions has taken a back seat to discussion of the conclusions reached through their use.

Finally, because discussion of reaction mechanisms requires familiarity with the behaviors of all the species involved, brief summaries or clarifications of the chemistries of key substrates have been included. A good example is the brief review of experimental data and attendant theoretical considerations pertinent to determination of the outer-sphere reorganization energy of the $O_2/O_2^{\bullet-}$ reactant pair presented in section VIII.C.

Oxidations of organic electron donors by POM anions are covered in section IV, followed by oxidations of inorganic substrates in section V. Reactions

of reduced POM anions with halogenated alkanes are presented in section VI, and with inorganic oxidants in section VII. Because of its importance and complexity, the reduction of dioxygen by reduced POM anions is treated separately in section VIII. To aid the reader, all chemical potentials have been referenced to the normal hydrogen electrode (NHE) and all energies have been reported in units of kilocalories per mole (kcal mol^{-1}).

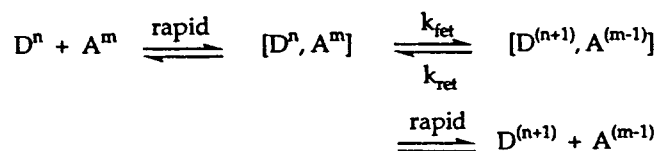
II. Outer-Sphere Electron-Transfer Reactions

A. Debye-Smoluchowski and Marcus

In 1942 Debye extended Smoluchowski's method for evaluating fundamental frequency factors, which pertained to collision rates between neutral particles D and A, freely diffusing in solution, to include the electrostatic effects of charged reacting species in dielectric media containing dissolved electrolytes.³⁵⁻³⁷ Debye's colliding-sphere model assumed that the reactant pairs formed during collisions between D^n (electron donor with a charge of n) and A^m (electron acceptor of charge m) possessed no inherent stability such that contact between colliding D^n-A^m pairs was shortlived.

When Marcus³ and others⁴ extended this model to include the occurrence of adiabatic electron transfer during collisions between donor and acceptor species, Debye's transient D^n-A^m pairs were referred to as "precursor" complexes ($[D^n, A^m]$ in Scheme 1). The Debye-Smoluchowski model for the diffusion-controlled collision frequency between D^n and A^m (and between $D^{(n+1)}$ and $A^{(m-1)}$) was retained.

Scheme 1



Marcus's theoretical treatment of outer-sphere electron-transfer reactions³ related the free energy of activation for electron transfer, ΔG^\ddagger (and thus implicitly k_{fet} , k = rate constant, fet = forward electron transfer), to the corrected free energy of the reaction, ΔG° , via a quadratic equation (eq 1),^{4,38}

$$\Delta G^\ddagger = \frac{z_1 z_2 e^2}{D r_{12}} \exp(-\chi r_{12}) + \frac{\lambda}{4} \left(1 + \frac{\Delta G^\circ}{\lambda} \right)^2 \quad (1)$$

where χ is the reciprocal Debye radius,^{15,37}

$$\chi = \left(\frac{4\pi e^2}{D k T} \sum_i n_i z_i^2 \right)^{1/2} \quad (2)$$

in which D is the dielectric constant of the medium, k is the Boltzmann constant, and $\sum n_i z_i^2 = 2\mu$, where μ is the total ionic strength of an electrolyte solution containing molar concentrations, n_i , of species i of charge z ($\mu \equiv (1/2) \sum n_i z_i^2$).

The first term in eq 1 was retained from the colliding-sphere model: The electron-donor and electron-acceptor molecules were viewed as spheres of

radii r_1 and r_2 , which possessed charges of z_1 and z_2 , respectively (e is the charge of an electron). This term defines the electrostatic energy (Coulombic work) associated with bringing the two spheres, initially infinitely removed from one another, to a distance $r_{12} = r_1 + r_2$ (formation of the precursor complex, $[D^{\ddagger}, A^{\ddagger}]$ in Scheme 1). The magnitude of the Coulombic term is modified by a factor $\exp(-\chi r_{12})$, which encompasses the attenuating effects of the dielectric medium (of dielectric constant D) and total ionic strength, μ , of the solution (eq 2).

The thermodynamic driving force for the electron-transfer reaction was represented by the corrected standard free energy, $\Delta G^{\circ'}$, which is the standard free energy, ΔG° , adjusted to account for the free-energy change associated with the changes in charge, z , of reactants and products, upon electron transfer between the donor and acceptor molecules in the reaction medium:

$$\Delta G^{\circ'} = \Delta G^{\circ} + (z_1 - z_2 - 1) \frac{e^2}{Dr_{12}} \exp(-\chi r_{12}) \quad (3)$$

From the standard reduction potentials, E° , of the donor and acceptor species, where $E^{\circ} \equiv -\Delta G^{\circ}/nF$ (n is the number of electrons transferred, and F is the Faraday constant), eq 3 can be used to calculate $\Delta G^{\circ'}$ from electrochemical data.

The term I (eq 1) is the reorganization energy associated with electron transfer within the precursor complex. Electron transfer induces changes in bond lengths and bond angles (in-plane and torsional) of the donor and acceptor molecules and in the arrangement of solvent molecules around the reacting pair. These inner-sphere (bond-length and -angle) and outer-sphere (solvent) reorganization processes are associated with enthalpic and entropic "costs", which present an activation barrier to electron transfer. According to the Franck-Condon principle, electron transfer within the transition-state complex occurs at a much greater rate than bond or solvent reorganization. Thus, the lowest energy pathway for electron transfer involves a transition-state complex in which inner- and outer-sphere rearrangements have occurred so as to minimize the combined potential energies of the incipient reduced and oxidized products. The energetic cost incurred en route to the transition state is the sum of the inner- and outer-sphere reorganization energies, $I = I_{\text{in}} + I_{\text{out}}$, of the donor-acceptor-electrolyte-solvent system.

In contrast to the substantial bond and solvent reorganization associated with electron transfer, very little electronic coupling between donor and acceptor species (<1 kcal mol⁻¹) occurs along the reaction coordinate leading to the transition state. This is the fundamental difference between outer-sphere processes and inner-sphere reactions, which often, but not always, involve ligand exchange or atom (e.g., oxygen, hydrogen, or hydride) transfer.³⁹⁻⁴⁴

B. Marcus Equation

1. Applications

For a series of reactions possessing similar I values and differing only in Coulombic terms and in ΔG°

(E°), the Marcus equation (eq 1) can be fitted to a plot of ΔG^{\ddagger} vs $\Delta G^{\circ'}$ by nonlinear regression, using I as an adjustable parameter. A good fit between calculated and experimental curves for a set of like reactions can be used to provide evidence for an outer-sphere electron-transfer mechanism and to estimate I for the reactions. Often ΔG^{\ddagger} is not known, but bimolecular rate constants, k , for the electron-transfer reaction have been measured. In these cases, the Eyring equation,

$$k = Z \exp(-\Delta G^{\ddagger}/RT) \quad (4)$$

can be applied, where ΔG^{\ddagger} is defined by eq 1 and Z is the collision frequency in units of per molar per second (M⁻¹ s⁻¹). Expansion of eq 1 gives

$$\Delta G^{\ddagger} = W(r) + \frac{\lambda}{4} + \frac{\Delta G^{\circ'}}{2} + \frac{(\Delta G^{\circ'})^2}{4\lambda} \quad (5)$$

where the Coulombic work term is abbreviated as $W(r)$. Substituting eq 5 into eq 4, taking the natural logarithm, and rearranging gives

$$RT \ln Z - RT \ln k = W(r) + \lambda/4 + \Delta G^{\circ'}/2 + (\Delta G^{\circ'})^2/4\lambda \quad (6)$$

For a series of reactions possessing similar I values, eq 6 can be fitted to a plot of $\ln k$ vs $\Delta G^{\circ'}$ by nonlinear regression, using I as an adjustable parameter.

In more limited cases, the Marcus equation can be approximated by a linear free-energy relationship. If $|\Delta G^{\circ'}| \ll I$ the last term in eq 5 can be ignored, such that

$$\Delta G^{\ddagger} = W(r) + \frac{\lambda}{4} + \frac{\Delta G^{\circ'}}{2} \quad (7)$$

If the reorganization energies, I , of a set of like reactions are similar and $W(r)$ is small or constant, a plot of ΔG^{\ddagger} vs $\Delta G^{\circ'}$ will be linear and have a slope of 0.5. By using eq 4 and the definition of the equilibrium constant, $K = A \exp(-\Delta G^{\circ}/RT)$, where A is a constant, a plot of $\ln k$ vs $\ln K$ will be linear and have a slope of 0.5:

$$\ln k = \ln Z - W(r)/RT - (\lambda/4)/RT + 0.5 \ln K + \ln A \quad (8)$$

Alternatively, given that $\Delta G^{\circ} = -nFE^{\circ}$, a plot of $\ln k$ vs E° for the series of reactions will have a slope of $0.5(nF/RT)$, and a plot of $\log k$ vs E° will have a slope of $0.5(nF)/2.303RT$ or 8.5 V⁻¹ for $n = 1$ at 25 °C. Observation of a linear free-energy relationship (cf., $\ln k$ vs $\ln K$) whose slope is 0.5, or in the electrochemical case $\log k$ vs E° , 8.5 V⁻¹, is an indication that the electron-transfer step is outer-sphere in nature.³ Because of confusion in the literature regarding the application of Marcus theory to intramolecular electron transfer within stable donor-acceptor complexes, alternative definitions of E° and the effect of sign convention on the slope (+

or -), and terminology, these linear free-energy relationships are discussed in greater detail in section II.D.

2. Theoretical Calculation of Outer-Sphere Electron-Transfer Rate Constants

The free energy of activation (ΔG^\ddagger) of the elementary electron-transfer step of an outer-sphere reaction can be calculated using the Marcus equation (eq 1). The calculation of ΔG^\ddagger (henceforth, $\Delta G^\ddagger_{\text{calc}}$) requires thermodynamic data (ΔG° or information from which (ΔG°) can be calculated, such as E° , or the equilibrium constant, K); the dielectric constant of the solvent, D ; the ionic strength, μ , of the reaction solution; the charges, z ; and radii, r , of the reactants; and a means for calculating I . If the preexponential factor, 2 , in eq 4, can be estimated or calculated, $\Delta G^\ddagger_{\text{calc}}$ from eq 1 can be used to obtain a theoretical bimolecular rate constant, k_{calc} . Theoretical k_{calc} values are often compared to experimentally determined rate constants of suspected outer-sphere electron-transfer reactions. Good agreement between k_{calc} and k_{obs} is often viewed as evidence of an outer-sphere mechanism. Poor agreement is often rationalized on the basis of uncertainties in the assumptions required for the theoretical calculation or is viewed as evidence that the electron-transfer reaction is not outer-sphere in nature.

Rate constants can also be calculated by means of Sutin's semiclassical (partly quantum-mechanical) approaches. Here, electron transfer is handled within a broad theoretical framework common to processes that occur rapidly on the nuclear time scale, such as electronic energy transfer and a number of nonradiative processes.^{14,45,46} Within these frameworks, observed rate constants are expressed as a combination of diffusion-controlled rate constants for the formation of transient "precursor complexes" and activation-controlled rate constants, k_{act} , for the bimolecular electron-transfer reaction:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{act}}} \quad (9)$$

The bimolecular rate constant, k_{act} , in turn is expressed as the product (eq 10) of an "equilibrium constant", $K(r)$ (in M^{-1}), for formation of reactant pairs separated by a distance r (more exactly, a radial distribution function is used, eq 11) and a first-order rate constant, $k_{\text{el}}(r)$ (in s^{-1} , for electron transfer within the reactant pairs:

$$k_{\text{act}} = K(r)k_{\text{el}}(r) \quad (10)$$

$$K(r) = \frac{4\pi N r^2 \delta r}{1000} \exp\left(\frac{-W(r)}{RT}\right) \quad (11)$$

Finally, the first-order rate constant for electron transfer is expressed as a product of nuclear, electronic, and frequency factors:

$$k_{\text{el}}(r) = \nu_n(r)k_{\text{el}}(r)\kappa_n(r) \quad (12)$$

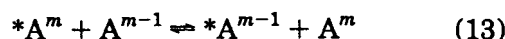
The product in eq 12 is a quantum-mechanical

description of phenomena encountered in classical Marcus theory.

In at least one case,²³ rate constants of electron-transfer reactions involving POM anions have been estimated using Sutin's semiclassical method. However, there is a more compelling reason for briefly describing Sutin's approach in this introductory overview. As discussed more fully later in this section (section II.D), it must be recognized that the "equilibrium constants" described here are radial distribution functions and not the formation constants typically associated with stable, if not always readily observable, donor-acceptor reactant pairs.

3. Outer-Sphere Electron Self-Exchange

The reorganization energy, 1 , associated with electron transfer to, or from, a molecule can be determined experimentally from the rate constant for electron self-exchange between that molecule and its 1-e-oxidized or -reduced form. In self-exchange reactions, such as that between A^m and A^{m-1} , $\Delta G^\circ = 0$:



In these cases, the Marcus equation (eq 1) reduces to

$$\Delta G^\ddagger = W(r) + \frac{\lambda}{4} \quad (14)$$

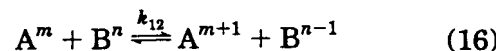
Given the charges and radii of the reactions, the dielectric constant of the solvent, and the ionic strength of the solution, the work term, $W(r)$, can be estimated. Given ΔG^\ddagger , the reorganization energy for electron self-exchange, I_{11} , can then be calculated using eq 14.

Alternatively, I_{11} can be calculated from the observed rate constant, k , of the reaction shown in eq 13 by using eq 15, obtained by substituting eq 14 into eq 4. For reactions in solution, Z is often taken to be $\sim 6 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$.³⁸

$$k = Z \exp\{-\{(W(r) + \lambda/4)/RT\}\} \quad (15)$$

4. The Marcus Cross-Relation

The rate constant associated with a particular self-exchange reaction (and hence the reorganization energy, I_{22} , of that self-exchange reaction) can often be inferred from the rate constant of the cross-reaction, k_{12} , between the species of interest, B, and another donor or acceptor, A, whose reorganization energy, I_{11} , is known:



Provided the reorganization energy associated with the cross-reaction (I_{12}) is the mean of those associated with the A^m/A^{m+1} and B^{n-1}/B^n self-exchange reactions (i.e., $\lambda_{12} = 1/2(\lambda_{11} + \lambda_{22})$), then^{14,45,46},

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}C_{12} \quad (17)$$

where

$$\ln f_{12} = \frac{1}{4} \left(\ln K_{12} + \frac{W_{12} - W_{21}}{RT} \right)^2 \quad (18)$$

$$\ln \left(\frac{k_{11}k_{22}}{Z^2} \right) + \frac{W_{11} - W_{22}}{RT}$$

and

$$C_{12} = \exp[-(W_{12} + W_{21} - W_{11} - W_{22})/2RT] \quad (19)$$

As above (eq 4), Z is the preexponential factor, and W_{ij} are the Coulombic work terms (eq 1) associated with all four combinations of the reacting species. If k_{ji} is known, then experimentally determined values of k_{12} can be used to calculate k_{22} and its associated reorganization energy, I_{22} .

C. Ion Pairing between Electrolyte Ions and Electron Donors or Acceptors

Catalytic and inhibitory effects of ion pairing on the rates of outer-sphere electron-transfer reactions are well documented.¹⁷⁻¹⁹ In a study of the kinetics of electron self-exchange between the ferri- and ferrocyanide anions, $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$, Shporer observed rate increases in aqueous solution corresponding to the series H^+ to Cs^+ and Mg^{2+} to Sr^{2+} .¹⁷ In alkaline aqueous solutions at constant ionic strength, Wahl¹⁹ observed decreasing rates of self-exchange between $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ with increasing size of the tetraalkylammonium cations, Me_4N^+ , Et_4N^+ , $n\text{-Pr}_4\text{N}^+$, $n\text{-Bu}_4\text{N}^+$, and $n\text{-Pent}_4\text{N}^+$. Similar effects were observed in acetic acid.¹⁸

Shporer¹⁷ attributed the specific cation effects, which paralleled increasing ionic radii of the electrolyte cations, to ion pairing with the negatively charged iron complexes. The factors that dictate the extent of interaction of electrolyte cations with POM anions in aqueous solution were summarized nicely by Kirby and Baker.⁴⁷ The ionic radii of Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ are, respectively, 0.60, 0.95, 1.33, 1.48, and 1.69 Å. However, because the smaller cations attach water molecules more firmly, the hydrated radii of these ions in water decrease with increasing cation size: 3.40, 2.76, 2.32, 2.28, and 2.28 Å for the above series.^{48,49} Corresponding hydration numbers for Li^+ through Cs^+ are in the ratios: 25.3:16.6:10.5: ...9.9, which reflect hydration energies in the ratios: 123:97:77:70:63. These data reflect larger ion-induced-dipole terms in the interactions between the smaller cations and the negatively charged and highly polarizable oxygens of water. In ion-pair formation, Coulombic driving forces are counterbalanced by losses in hydration energy of the cation and of the POM anions. For the cations, losses in hydration energies decrease with ion size, and formation constants for ion pairing increase in parallel. As a whole, however, the POM anions possess very low charge densities and low negative charge densities on their surface ($\text{M}=\text{O}$) oxygens ($\text{M} = \text{V}(\text{V})$, $\text{Mo}(\text{VI})$, $\text{W}(\text{VI})$; the terminal oxide, O^{2-} , anions actually donate more than four electrons to the oxophilic d addendum atoms). Thus, the extent of ion-pairing between electrolyte cations and POM anions is

largely governed by the balance of energetic factors associated with the cations.

In analyzing the $\text{Fe}(\text{CN})_6^{3-/4-}$ self-exchange reaction, Shporer¹⁷ considered the possible effects of ion pairing on electrostatic terms, on reorganization energies, and on the mechanics of electron transfer itself. Three issues were addressed: (1) the effect of ion pairing on the Coulombic terms associated with bringing together similarly charged species (Coulombic term in eq 1); (2) the effect of ion pairing on the reorganization energies, I , associated with electron transfer; and (3) the possibility that electron transfer might occur via the ion-paired cation, with the cation serving as a lower energy pathway between the donor and acceptor species. Of these, the first is undoubtedly important, while the second is more difficult to assess.¹⁹ With regard to the third proposal, recent work by Kirby and Baker suggests that simple alkali, alkaline-earth, or tetraalkylammonium cations do not serve as conducting bridges between POM anions.⁵⁰

Kirby and Baker investigated rates of electron transfer through cationic bridges by observing the ^{31}P NMR spectra of reduced tilacynary Keggin and Wells-Dawson derivatives (heteropoly blues) rigidly linked by diamagnetic ($\text{Zn}(\text{II})$ or $\text{Cd}(\text{II})$) or paramagnetic ($\text{Co}(\text{II})$ or $\text{Ni}(\text{II})$) cations and of reduced monolacynary Wells-Dawson anions flexibly attached via a single $\text{Th}(\text{IV})$ atom. When the paramagnetic linking cations, $\text{Co}(\text{II})$ or $\text{Ni}(\text{II})$, were present, substantial antiferromagnetic interaction between the "blue" electrons and the unpaired electrons of the paramagnetic cations was observed (see original article⁵⁰ for details of the spectroscopic evidence).

In similarly rigid structures linked by diamagnetic $\text{Zn}(\text{II})$ or $\text{Cd}(\text{II})$, no electronic interaction between the reduced tungstophosphate clusters could be discerned by ^{31}P NMR. However, in the flexible $\text{Th}(\text{IV})$ -linked complex, $\text{syn-}[(\alpha_2\text{P}_2\text{W}_{17}\text{O}_{61})\text{Th}^{\text{IV}}]^{16-}$, in which the two reduced lacynary $\alpha\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ units were in close contact with one another, significant electronic interactions between electrons located on opposite sides of the $\text{Th}(\text{IV})$ ion were observed. This interaction, however, appeared to result from direct exchange between the reduced clusters rather than from electron transfer via the $\text{Th}(\text{IV})$ bridge: When the complex assumed the anti conformation, wherein close contact between the reduced tungstophosphate structures was not possible, no electronic interactions were observed.

Kirby and Baker's studies do, however, point to a role for electrolyte cations not mentioned by Shporer. The cations might catalyze electron transfer between negatively charged species by facilitating the formation of ternary $[\text{X}^{m-}\text{-M}^+\text{-X}^{n-}]^{(m+n-1)-}$ complexes. Such complexes are particularly relevant to the study of electron-transfer reactions of highly negatively charged POM anions. In addition, the formation of ternary complexes is particularly likely when reactions between POM anions, or between cations and other charged species, are carried out in solvents of low dielectric constant.^{26,51} The application of Marcus theory to outer-sphere electron transfer within binary, or higher order, donor-acceptor complexes is discussed in section II.D, immediately below.

Finally, ion pairing between cations (H^+ , alkali-metal, alkaline-earth, or tetraalkylammonium cations) and POM anions can strongly influence the electrochemical reduction potential, E° , of the latter.⁵² Because the rate of outer-sphere electron transfer is exponentially dependent upon thermodynamic driving force (i.e., ΔG°), small changes in reduction potential (recall that $E^\circ = -\Delta G^\circ/nF$) can have large effects on reaction rates.

D. Outer-Sphere Electron Transfer within Stable Donor-Acceptor Complexes

The Marcus equation (eq 1) and its derivatives (eqs 7, 14, and 17), as well as Sutin's semiclassical approach, were based upon a colliding-sphere model in which reactant pairs (precursor complexes) possessed no inherent stability. Sutin has noted, however, that although preequilibrium formation of precursor complexes was not explicitly postulated in Marcus's formalism, "stability constant" of precursor "complexes" were implicated by his mathematical treatment.⁵³ In Sutin's semiclassical treatment (eq 10), these "equilibrium constants" were described more explicitly. However, despite the mathematical similarity of radial probability distribution functions^{13,46} (with units of M^{-1}) to formation constants of stable donor-acceptor pairs, no departure from the colliding-sphere model is intended.

At the same time, the quadratic dependence of ΔG_{et}^\ddagger on ΔG° and I , developed by Marcus (and inherent in Sutin's quantum-mechanical treatment) and which describes the activation barrier to outer-sphere (adiabatic) electron transfer, is applicable whether electron transfer occurs within transiently formed reactant pairs (colliding-sphere model) or within stable donor-acceptor complexes. In each of these cases, however, k_{obs} values measured for the overall electron-transfer reactions have different meanings. In the classical (colliding-spheres) case, k_{obs} is equivalent to k_{et} , the bimolecular rate constant described by the Marcus equation (eq 1), or to k_{act} in Sutin (eq 10). For adiabatic (outer-sphere) electron transfer within stable donor-acceptor complexes, the relationship between k_{obs} and k_{et} (or k_{act}) is not always straightforward. This point has caused confusion among some who have used POM anions, particularly $[Co^{III}W_{12}O_{40}]^{5-}$, as outer-sphere oxidants.

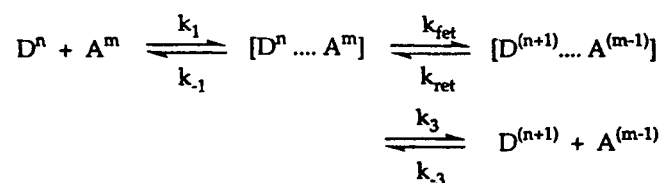
In particular, lack of agreement between k_{calc} values obtained using the Marcus equation (eq 1) and experimentally determined rate constants, k_{obs} , need not imply that electron transfer is inner sphere in nature; intramolecular outer-sphere electron transfer within stable donor-acceptor pairs must also be considered. A brief evaluation, using $[Co^{III}W_{12}O_{40}]^{5-}$ as an example, follows.

The $Co(III)$ ion in $[Co^{III}W_{12}O_{40}]^{5-}$ is substitutionally inert. Thus, it is reasonable to expect that this ion will be reduced via outer-sphere pathways. At the same time, the $[Co^{III}W_{12}O_{40}]^{5-}$ anion possesses a high negative charge. As a result, three phenomena that might complicate the kinetic analysis of reactions of this and related anions with electron donors must be considered. These phenomena are (1) effects of

ionic strength, (2) ion pairing between $[Co^{III}W_{12}O_{40}]^{5-}$ and any cations present in solution, and (3) the formation of stable complexes between $[Co^{III}W_{12}O_{40}]^{5-}$ and electron donors. In the simplest case (1), increasing ionic strength simply attenuates the Coulombic term in eq 1. In the second case, $[Co^{III}W_{12}O_{40}]^{5-}$ reacts with cations, M^+ (most often, alkali-metal cations such as Li^+ , Na^+ , and K^+), to give ion-paired anions of the form $[(M^+)(Co^{III}W_{12}O_{40})^{5-}]^{4-}$. Ion pairing of this type has two consequences: It reduces the Coulombic work term in eq 1 by decreasing the charge product, $z_1 z_2$, of the reacting species, and it changes the reduction potential, E° , of the POM anion, thus altering the thermodynamic driving force, ΔG° .

Both ionic strength and ion pairing can impact the third phenomenon: the formation of stable complexes between $[Co^{III}W_{12}O_{40}]^{5-}$ and electron donors. Evaluation of the effects of the formation of donor-acceptor complexes on the relationship between experimentally measured k_{obs} values and bimolecular rate constants, k_{et} , predicted by the Marcus equation requires consideration of the reaction steps and associated rate constants shown in Scheme 2.^{14,54-56} Unlike the transient ion pairs $[D^n, A^m]$ and $[D^{(n+1)}, A^{(m-1)}]$ described in Scheme 1, the ion pairs described in Scheme 2, $[D^n \cdots A^m]$ and $[D^{(n+1)} \cdots A^{(m-1)}]$, refer to association complexes with negative enthalpies of formation.

Scheme 2



In the most general case, no restrictions are placed on the values of rate constants or associated equilibrium quotients: $K_1 = k_1/k_{-1}$, $K_{et} = k_{fet}/k_{ret}$, or $K_3 = k_3/k_{-3}$, where k_{fet} and k_{ret} are the rate constants for forward and reverse outer-sphere electron transfer, respectively. The rate constant for formation of donor-acceptor pairs of formation constant K_1 is given by k_1 ; the rate constant for dissociation of the successor complex, $[D^{(n+1)} \cdots A^{(m-1)}]$, formed via intramolecular electron transfer within $[D^n \cdots A^m]$, is k_3 .

Usually, however, one of three situations, depending on the energetics of the electron-transfer step, applies:⁵⁷ **Case 1.** The electron-transfer step is highly exergonic and rapid, such that $k_{fet} > k_1$, $k_{fet} > k_{-1}$, and $k_3 \gg k_{ret}$. **Case 2.** The electron-transfer step is slightly endergonic or exergonic ($|\Delta G_{et}^\circ|$ is small) and reversible ($k_{ret} \approx k_{fet} \ll k_1$ and $k_{ret} \approx k_{fet} \ll k_3$). **Case 3.** The electron transfer step is substantially endergonic and reversible, such that $k_{fet} \ll k_1$ and $k_{ret} \gg k_3$.

Case 1. In this case, the reaction is diffusion controlled and $k_{obs} = k_1 K_1 [D^n][A^m]$. In this regime, no correlation between k_{obs} and ΔG_{fet}° (or E_{fet}°) is observed.

Case 2. The reaction is activation controlled: $k_{obs} = K_1 k_{fet} [D^n][A^m]$. The term "activation control" refers to the dependence of k_{obs} on k_{fet} . Despite this dependence, however, k_{obs} does not obey the Marcus equation.

tion (eq 1). There are two reasons why. First, the Coulombic work term, $W(r)$, in eq 1, taken from the colliding-sphere model, does not apply here. Rather than a transient "precursor" complex such as that depicted in Scheme 1, $[D^n \cdots A^m]$ is a stable complex whose concentration at equilibrium is dictated by K_1 . The remainder of eq 1, however, which includes the reorganization energy, I , and describes the quadratic dependence of $\Delta G^\ddagger_{\text{fet}}$ (and hence k_{fet} on $\Delta G^\circ_{\text{fet}}$, is still applicable. A complication arises, however, in that k_{obs} is not equal to k_{fet} . Nonetheless, provided K_1 is independent of ΔG° for the electron-transfer reaction, then k_{obs} is linearly proportional to k_{fet} over a range of ΔG° values. Making use of this relationship, the quadratic portion of the Marcus equation can be used to evaluate k_{obs} (eqs 20-31).

Case 3. In this case, the reaction is under thermodynamic control. Because $k_{\text{ret}} \gg k_3$, $k_{\text{obs}} = K_1 K_{\text{et}} k_3$ and $k_{\text{obs}} \propto K_{\text{et}}$ (i.e., $k_{\text{fet}}/k_{\text{ret}}$). However, while directly proportional to K_{et} , and hence under thermodynamic control, k_{obs} is also a linear function of k_3 . For this reason reactions of this type, while very different from those described by case 1, are sometimes also referred to as "diffusion controlled".⁵⁷ When encountered in the literature, reference to reactions of the type described in case 3 as "diffusion controlled" can lead to confusion.

In cases 2 and 3, in which k_{obs} is proportional to k_{fet} , determination of k_{fet} requires knowledge of K_1 (case 2) or of K_1 , K_{et} , and k_3 (or more generally K_3) (case 3). For reactions between charged species, K_1 and k_3 or K_3 (each functions of the parameters associated with the Coulombic work terms defined in eqs 1 and 2) can be evaluated both theoretically⁵⁸ and experimentally. Experimentally, values of K_1 and K_{et} can be obtained by fitting integrated rate expressions to raw kinetic data by means of nonlinear regression techniques in which K and/or k are adjustable parameters.⁵⁹ In unique cases, such as in the oxidative electron-transfer luminescence quenching of photoexcited donors within donor-acceptor ion pairs, k_{fet} can be measured more directly.^{60,61}

In case 1, no correlation between kinetic and thermodynamic parameters is observed. In cases 2 and 3, however, linear relationships exist between specific functions of k_{obs} and ΔG° (or E°), and the slopes of the lines obtained by plotting these functions can be used to differentiate between the two cases:

Case 2: $k_{\text{obs}} \propto k_{\text{fet}}$. Because k_{obs} is proportional to k_{fet} , the quadratic term in the Marcus equation (eq 1) applies. Because the electron transfer is occurring within a stable complex, the first term in the Marcus equation drops out, as does the need to apply an electrostatic correction to ΔG° . This leaves only the quadratic dependence of ΔG^\ddagger on ΔG° :

$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G^\circ}{\lambda} \right)^2 \quad (20)$$

For limited ranges of ΔG° , an expression analogous to eq 7 applies:

$$\Delta G^\ddagger = \frac{\lambda}{4} + \frac{\Delta G^\circ}{2} \quad (21)$$

Combining eq 21 and the Eyring equation (eq 4) gives

$$k \propto \exp(-\Delta G^\ddagger/RT) \propto \exp(-\Delta G^\circ/2RT) \quad (22)$$

in which nonessential constants have been omitted. The equilibrium constant, K , is defined by a similar exponential relationship:

$$K \propto \exp(-\Delta G^\circ/RT) \quad (23)$$

The natural logarithms of eqs 22 and 23 are

$$\ln k \propto -\Delta G^\ddagger/RT \propto -\Delta G^\circ/2RT \quad (24)$$

and

$$\ln K \propto -\Delta G^\circ/RT \quad (25)$$

Thus, returning to Scheme 2, if $k_{\text{obs}} \propto k_{\text{fet}}$, then

$$\frac{\ln k_{\text{obs}}}{\ln K_{\text{et}}} = \frac{-\Delta G^\circ/2RT}{-\Delta G^\circ/RT} = +0.5 \quad (26)$$

such that a plot of $\ln k_{\text{obs}}$ vs $\ln K$ gives a straight line with a positive slope of 0.5.

Because electrochemical reduction potentials are often experimentally accessible, it is useful to consider the above relationships in electrochemical terms. The standard thermodynamic potential of a reversible galvanic cell (electromotive force, *emf*) or of an electron-transfer reaction (i.e., the sum of two half-reactions) is defined as

$$\Delta G^\circ = -nFE^\circ \quad (27)$$

and

$$E^\circ = \Delta G^\circ/-nF \quad (28)$$

Thus, returning to eq 25,

$$\ln K_{\text{et}} \propto -\Delta G^\circ/RT \propto nFE^\circ/RT \quad (29)$$

and using eq 24 for $\ln k$,

$$\frac{\ln k_{\text{obs}}}{E^\circ} = \frac{-\Delta G^\circ/2RT}{\Delta G^\circ/-nF} = +0.5 \left(\frac{nF}{RT} \right) \quad (30)$$

For $n = 1$ and in \log_{10}

$$\frac{\log k_{\text{obs}}}{E^\circ} = +8.5 \text{ V}^{-1} \quad (31)$$

Thus, if $k_{\text{obs}} \propto k_{\text{fet}}$, plot of $\log k_{\text{obs}}$ vs E° gives a straight line with slope of $+8.5 \text{ V}^{-1}$.

Case 2: $k_{\text{obs}} \propto K_{\text{et}}$. By definition,

$$\ln K_{\text{et}} \propto -\Delta G^\circ/RT \quad (32)$$

Because k_{obs} is proportional to K_{et} , rather than to k_{fet} ,

$$\ln k_{\text{obs}} \propto \ln K_{\text{et}} \propto -\Delta G^\circ/RT \quad (33)$$

such that

$$\frac{\ln k_{\text{obs}}}{E^\circ} = \frac{-\Delta G^\circ/RT}{\Delta G^\circ/-nF} = +1.0 \left(\frac{nF}{RT} \right) \quad (34)$$

Plot of $\log k_{\text{obs}}$ vs E° now gives a straight line with a slope of $+16.9 \text{ V}^{-1}$.

Note that the signs of the slopes of lines obtained in plots charted using electrochemical data can be either positive or negative depending on how E° is defined. The above relationships were derived in terms of the standard thermodynamic potentials, E° , of electron-transfer reactions. By convention $E^\circ = -(E^\circ_{\text{donor}} - E^\circ_{\text{acceptor}})$.^{54,55} (In the more general case E°_{donor} or $E^\circ_{\text{acceptor}}$ can be electrode potentials).⁵⁷ By definition (i.e., eq 27), if an electron-transfer reaction is spontaneous, E° is greater than zero. Hence, if for a series of outer-sphere electron-transfer reactions involving a common donor or acceptor species, one plots $\log k_{\text{obs}}$ vs E° , the slope of the plot will be positive (i.e., +8.5 V⁻¹ or +16.9 V⁻¹).

However, values of $\log k_{\text{obs}}$ for electron-transfer reactions of a given species are also plotted as a function of standard reduction potentials (also E°), of individual electron-donors or acceptors (usually a set of donors or acceptors are used). This is equivalent to plotting $\log k_{\text{obs}}$ as a function of a varying electrode potential. In these cases, slopes of lines obtained in plots of $\log k_{\text{obs}}$ vs E° can be either positive or negative, depending on one's frame of reference. For example, if the species under investigation is an electron donor, rates of electron transfer to the acceptors increase as the standard reduction potentials (E° of the acceptors shift to more positive values. Hence, the sign of the slope of the plot of $\log k_{\text{obs}}$ vs E° is positive. However, if the species under investigation is an electron acceptor, rates of electron transfer increase as the E° values of the donors shift to more negative values. The sign of the slope of the plot of $\log k_{\text{obs}}$ vs E° is now negative (i.e., -8.5 V⁻¹ or -16.9 V⁻¹).

III. Electron Self-Exchange between POM Anions

A. Keggin Tungstocobaltate Anions

Rasmussen and Brubaker carried out the first direct measurements of self-exchange rates for electron transfer between POM anions in water using $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ ($\text{Co}^{\text{II}}\text{W}_{12}^{6-}$) and its one-electron-oxidized derivative $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ ($\text{Co}^{\text{III}}\text{W}_{12}^{5-}$).⁵ The reduced anion, $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$, first synthesized and characterized by Baker and co-workers,⁶²⁻⁶⁴ was prepared using small amounts of ⁶⁰Co, an unstable isotope of cobalt. The extent of electron transfer from $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ to $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ was determined after selectively precipitating $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ by addition of tetra-*n*-butylammonium iodide. Rates of electron transfer were then calculated from the specific activities of the insoluble tetra-*n*-butylammonium salts of $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$. At 0 °C, pH 2 (HCl), and an ionic strength of $\mu = 0.6$ M (LiCl), the reaction was first-order in both $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ and $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ with $k = 0.63$ M⁻¹ s⁻¹ (eq 35).



The rate constant was independent of $[\text{H}^+]$ over a pH range of 0.10 to 1.6 but showed a marked dependence on ionic strength, $k_{(\mu=0.015\text{M})} = 0.03$ M⁻¹ s⁻¹ and $k_{(\mu=0.81\text{M})} = 0.93$ M⁻¹ s⁻¹. The rate constant for the self-exchange reaction decreased as the di-

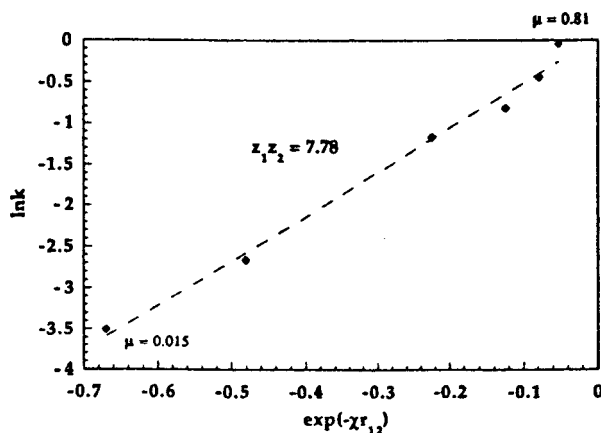


Figure 1. Plot of $\ln k$ vs $\exp(-\chi r_{12})$ (eq 1) for the electron self-exchange reaction between $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$.

electric constant, D , of the reaction medium was reduced by addition of dioxane. In addition, at constant ionic strength, replacement of Li^+ ions by K^+ ions resulted in a nearly 10-fold increase in k .

From a plot of $\ln k$ vs the Debye term, $\exp(-\chi r_{12})$ (eq 1), an experimental value of $k_0 = k_{(\mu=0\text{M})} = 4.5 \times 10^{-3}$ M⁻¹ s⁻¹ was obtained by extrapolation to $\exp(-\chi r_{12}) = 1$ ($\mu = 0$ M). From the slope of the plot of $\ln k$ vs $\exp(-\chi r_{12})$, a charge product of $z_1 z_2 = \sim 8$ was calculated (Figure 1).

Had the reactions been carried out within the ionic strength limit of the Debye equation ($\mu < \sim 0.001$ M), a charge product of 30, corresponding to $z_1 z_2 = (-5)(-6)$, would have been expected. Nonetheless, in calculation of a theoretical value for $k_{(\mu=0\text{M})}$, the experimentally determined charge product of 8 was used to calculate the Coulombic contribution to ΔG^\ddagger at infinite dilution ($W(r)$ in eq 1 with $z_1 z_2 = 8$ and $\exp(-\chi r_{12}) = 1$), which gave $W(r)_{(\mu=0\text{M})} = 3.0$ kcal mol⁻¹.

The inner-sphere reorganization energy, $I_{\text{in}} = 11.05$ kcal mol⁻¹ (converted from the published value of 7.68×10^{-13} erg), was calculated using Pauling crystal radii after a ligancy correction from six to four: 1.97 Å for four-coordinate $\text{Co}^{\text{II}}\text{-O}$ and 1.87 Å for four-coordinate $\text{Co}^{\text{III}}\text{-O}$. The latter value compared well with that determined by X-ray diffraction for $\text{K}_5[\text{Co}^{\text{III}}\text{O}_4\text{W}_{12}\text{O}_{36}]$.⁶⁵ An outer-sphere reorganization energy of 18.4 kcal mol⁻¹ was obtained using a $[\text{CoW}_{12}\text{O}_{40}]^{n-}$ radius of 5.0 Å. The total calculated reorganization energy was 29.5 kcal mol⁻¹.

These values gave $\Delta G^\ddagger_{(\mu=0\text{M})} = 10.4$ kcal mol⁻¹ (eq 1). Equation 4, with $Z = 10^{11}$ M⁻¹ s⁻¹, gave a theoretically predicted value of $k_{0\text{calc}} = 4.7 \times 10^2$ M⁻¹ s⁻¹, which was 10^5 to 10^6 greater than that obtained experimentally ($k_0 = 4.5 \times 10^{-3}$ M⁻¹ s⁻¹).

Rasmussen and Brubaker suggested that the disparity between experimentally observed and calculated k values might have resulted from the use of too many simplifying assumptions. Alternatively, the authors proposed that because the cobalt cations were embedded in $[\text{W}_{12}\text{O}_{40}]^{8-}$ shells, electron transfer between the $\text{Co}(\text{II})$ and $\text{Co}(\text{III})$ ions might not have met the requirements of the theory. These alternatives are further evaluated in section III.C.

B. Keggin and Wells-Dawson Metallophosphate Anions

The next direct measurements of the rates of outer-sphere electron self-exchange between POM anions were reported in 1986.²⁵ Rate constants were calculated by analysis of the NMR spectra of equimolar mixtures of fully oxidized and 1-e⁻-reduced POM anions (1-e⁻ heteropoly blues). On the basis of line broadening observed in ³¹P NMR spectra, rate constants were determined for self-exchange between the Keggin anions α -[PW₁₂O₄₀]³⁻ (PW₁₂³⁻) and 1-e⁻-reduced α -[PW₁₂O₄₀]⁴⁻ (PW₁₂⁴⁻), between the Wells-Dawson anions α -[P₂W₁₈O₆₂]⁶⁻ (P₂W₁₈⁶⁻) and α -[P₂W₁₈O₆₂]⁷⁻ (P₂W₁₈⁷⁻), and between the trimolybdenum-capped derivatives α -[P₂Mo₃W₁₅O₆₂]⁶⁻ and α -[P₂Mo₃W₁₅O₆₂]⁷⁻. (In 1975 rate data for electron self-exchange between [PMo^VW₁₁O₄₀]⁴⁻ and [PMo^{VI}W₁₁O₄₀]³⁻ in *nonaqueous* solvents was obtained using electron-spin resonance (ESR) spectroscopy.⁵¹ Observed rate constants were reportedly greater than those predicted by diffusion control, a result that suggested²⁵ the formation of charge-transfer complexes between the POM anions.)

A key difference between self-exchange between Co^{II}W₆⁶⁻ and Co^{III}W₆⁵⁻ and between PW₁₂⁴⁻ and PW₁₂³⁻ is that in Co^{II}W₆⁶⁻ the exchanged electron is localized at the center of the POM anion within the d orbitals of a tetrahedrally coordinated Co(III) ion. On the basis of spectroscopic (ESR) and magnetic properties of 1- and 2-e⁻-reduced [Co^{II}W₁₂O₄₀]⁶⁻ (i.e., [Co^{II}W₁₂O₄₀]⁷⁻ and [Co^{II}W₁₂O₄₀]⁸⁻), it was concluded that the central (Co(II)) heteroatoms are effectively electronically isolated from the reduced tungsten framework.³⁰ By contrast, in the 1-e⁻-reduced tungstophosphate anion, PW₁₂⁴⁻, the exchanged electron, located in a predominantly nonbonding b₂ orbital of the C_{4v} distorted WO₆ octahedron, is delocalized over all 12 tungsten atoms (rates of intramolecular electron transfer are ~10¹¹ to 10¹² s⁻¹ at room temperature) via a thermal hopping mechanism.^{25,33,66} In the 1-e⁻-reduced Wells-Dawson anion P₂W₁₈⁷⁻, the blue electron is rapidly delocalized (1.7 × 10¹¹ s⁻¹) over only the 12 "belt" tungsten atoms of the complex,^{25,33} and in α -[P₂Mo₃W₁₅O₆₂]⁷⁻ delocalization of the added electron is limited to the trimolybdenum cap and is 25 times slower than in P₂W₁₈⁷⁻.

In a preliminary investigation, ³¹P NMR spectra were acquired from solutions prepared from the free acids of PW₁₂³⁻ and PW₁₂⁴⁻ (pH 1), from the lithium salts of P₂W₁₈⁶⁻ and P₂W₁₈⁷⁻ (pH 1 and pH 4), and from the potassium salts of α -[P₂Mo₃W₁₅O₆₂]⁶⁻ and α -[P₂Mo₃W₁₅O₆₂]⁷⁻ (pH 2.5). No ionic-strength effects were seen when the overall concentrations of equimolar mixtures of PW₁₂³⁻ and PW₁₂⁴⁻ were increased from 0.002 to 0.02 M. On the basis of reported diffusion coefficients,^{31,67,68} the rate constant for electron transfer between the Keggin anions appeared to be diffusion controlled (i.e., greater than ~10⁷ M⁻¹ s⁻¹, based on a hydrodynamic radius of 5.6 Å)⁶⁷ as was that for electron transfer between P₂W₁₈⁶⁻ and P₂W₁₈⁷⁻ (greater than ~10⁴ M⁻¹ s⁻¹, based on a hydrodynamic radius of 10 Å).⁶⁸ The line broadening observed in ³¹P NMR spectra of mixtures of

[P₂Mo₃W₁₅O₆₂]⁶⁻ and [P₂Mo₃W₁₅O₆₂]⁷⁻ corresponded to an exchange rate of ~2 × 10³ M⁻¹ s⁻¹, about 1 order of magnitude smaller than the diffusion-controlled rate limit. The slower rate was attributed to localization of the blue electron in the Mo₃O₁₃ triad.

Well-resolved ¹⁷O NMR spectra obtained from acetonitrile solutions of oxidized and 1-e⁻-reduced POM anions (free-acid forms) were also used to estimate POM self-exchange rate constants.⁶⁹ However, only limiting (minimum) values were obtained: At room temperature, a rate constant of greater than ~5 × 10³ M⁻¹ s⁻¹ was estimated for self-exchange between [PMo₁₂O₄₀]⁴⁻ and [PMo₁₂O₄₀]³⁻ and a rate constant of greater than ~4 × 10⁴ M⁻¹ s⁻¹ was estimated for self-exchange between [SiW₁₂O₄₀]⁵⁻ and [SiW₁₂O₄₀]⁴⁻. At 65 °C the rate constant for electron transfer between the metatungstates [H₂W₁₂O₄₀]⁷⁻ and [H₂W₁₂O₄₀]⁶⁻ was estimated to be greater than ~4 × 10⁴ M⁻¹ s⁻¹. Because the nature of solutions of the free acids of POM anions in acetonitrile (extent of ion pairing, diffusion coefficients, etc.) were not reported, it is difficult to draw conclusions from these data. However, these results are consistent with those obtained by analysis of the ³¹P NMR spectra of aqueous solutions of related tungstophosphates.²⁵

In a detailed investigation,²³ Kozik and Baker performed a variable ionic strength study of the rates of electron transfer between PW₁₂³⁻ and 1-e⁻-reduced PW₁₂⁴⁻ and between PW₁₂⁴⁻ and the diamagnetic 2-e⁻-reduced anion PW₁₂⁵⁻. In PW₁₂⁵⁻ the two d electrons, although residing on different tungsten atoms and thus widely separated from one another, are completely paired by a "multiroute super-exchange" mechanism.^{23,24,26,31} A more limited study of the rate of self-exchange between α -[P₂W₁₈O₆₂]⁶⁻ and 1-e⁻-reduced α -[P₂W₁₈O₆₂]⁷⁻ at several high ionic strengths was also performed.⁷⁰ Theoretical outer-sphere rate constants were predicted using Sutin's semiclassical method.^{14,45,46}

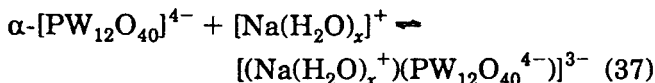
Rate constants for 1:1 mixtures of α -[PW₁₂O₄₀]³⁻ and α -[PW₁₂O₄₀]⁴⁻ (1.0 mM of each in their free-acid forms), the most thoroughly studied system, were determined by ³¹P NMR over a range of ionic strengths (μ = 0.026–0.616 M). Ionic strength was adjusted by addition of HCl and NaCl (pH values ranged from 0.98 to 1.8). Observed rate constants, k_{obs} , were fitted to the Debye-Hückel equation⁷⁰ (eq 36), which is conceptually related to the Debye term, $\exp(-\gamma r_{12})$, in eq 1. An internuclear distance of r = 11.2 Å or twice the ionic radius of the PW₁₂ⁿ⁻ anions, was used; at 25 °C in water, α = 0.509 and b = 0.329 Å⁻¹.

$$\log k = \log k_0 + 2z_1 z_2 \alpha [\mu^{1/2} / (1 + \beta r \mu^{1/2})] \quad (36)$$

A linear relationship was observed (correlation coefficient of 0.998), from the slope of which a charge product of $z_1 z_2$ = 12.5 (12.0 is the theoretical value) was calculated. The linearity and close-to-theoretical slope was surprising in that the Debye-Hückel expression (eq 36) for rates of reaction in solution was derived for univalent ions at low ionic strengths (up to 0.01 M). Agreement at much higher ionic strengths (greater than 0.5 M) was attributed to the fact that

POM anions,^{71–73} “owing to the very pronounced inward polarization of their exterior oxygen atoms, have extremely low solvation energies and very low van der Waals attractions for one another”.²³ For the α -[PW₁₂O₄₀]^{4–}/ α -[PW₁₂O₄₀]^{5–} system, fairly good agreement with the Debye-Hückel expression was observed up to $\mu = 0.125$ M (slope consistent with the predicted charge product of $z_1 z_2 = 20$) before significant deviation from linearity was observed.

Agreement with the Debye-Hückel expression, and slopes near theoretically predicted values, indicated that the “precursor complexes” (contact ion pairs) that formed prior to electron transfer likely involved “free” aqueously solvated α -[PW₁₂O₄₀]^{3–}, α -[PW₁₂O₄₀]^{4–}, and α -[PW₁₂O₄₀]^{5–} anions rather than alkali metal cation paired species such as those shown in eq 37.



Theoretically predicted self-exchange rate constants for the α -[PW₁₂O₄₀]^{3–}/ α -[PW₁₂O₄₀]^{4–} system were $k_0 = 3.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at infinite dilution ($\mu = 0$ M) and $k_{(\mu = 0.616\text{M})} = 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at $\mu = 0.616$ M. The effect of added electrolyte (higher ionic strength) was to decrease electrostatic repulsion between the negatively charged POM anions, which attenuated the contribution of the Coulombic work term to ΔG^\ddagger for electron transfer (eq 1). Experimentally determined values were $k_0 = 1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (by extrapolation using eq 36), and $k_{(\mu = 0.616\text{M})} = 8.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

It has been stated that “the crux of the electron-transfer problem is the fact that the equilibrium nuclear configurations of species changes when it gains or loses an electron”.⁴⁶ It is not surprising, then, that inconsistent conclusions reached concerning the outer-sphere electron-transfer reactions of POM anions can, to a large extent, be attributed to assumptions made with regard to pertinent inner-sphere reorganization energies. The physical properties of the oxidized and reduced anions α -[PW₁₂O₄₀]^{3–} and α -[PW₁₂O₄₀]^{4–} have been well studied. Thus, Kozik and Baker’s detailed analysis of the inner-sphere reorganization energy associated with this system²³ provides a useful starting point for analysis of other, more complex, heteropolyanions.

Reorganization energies for the α -[PW₁₂O₄₀]^{3–}/ α -[PW₁₂O₄₀]^{4–} system were calculated according to literature methods.⁵³ The inner-sphere reorganization energy, I_{in} , is a function of bond-length and -angle changes and their associated force constants (eq 38, d_1 and d_2 are atomic coordinates, and f is a force constant).

$$\lambda_{\text{in}} = (1/2) \sum f_i (d_1^\circ - d_2^\circ)_i^2 \quad (38)$$

Bond lengths of oxidized and reduced Keggin anions were obtained from X-ray crystallographic data. On the assumption that I_{in} would result primarily from changes in W–O bond lengths, slight changes in bond angles upon reduction were ignored. Force constants of individual W–O bonds in oxidized and reduced

Keggin anions were estimated from IR data in combination with normal coordinate analyses, which was reported for two hexametalate anions.⁷⁴ With the use of eq 38, a value of $I_{\text{in}} = 6.1 \text{ kcal mol}^{-1}$ was calculated. The authors suggested that if small changes in bond angles had been included, a slightly higher I_{in} value would have been obtained and slightly better agreement with experimentally determined rate constants achieved.

Calculation of the outer-sphere reorganization energy is straightforward, provided that accurate values of the hydrodynamic radii of the reacting species are available (eq 39).

$$\lambda_{\text{out}} = (\Delta e)^2 [1/(2r_1) + 1/(2r_2) + 1/r_{12}] (1/\eta^2 - 1/D_s) \quad (39)$$

In eq 39, e is the charge transferred during reaction; h is the refractive index, and D_s the dielectric constant of the reaction medium; r_1 and r_2 are the radii of the reacting species; and r_{12} is the internuclear distance at which the probability of electron transfer is at a maximum (usually set equal to $r_1 + r_2$). It is noteworthy, because not intuitively obvious, that I_{out} is neither an explicit function of the ionic strength in a given reaction medium nor of the charges of the reacting species. Thus, unlike the Coulombic work term, which is highly sensitive to charge- and ionic-strength effects, the contribution of outer-sphere reorganization energy to the free energy of activation, ΔG^\ddagger , is often, to first approximation, regarded as a constant property of the reactant pair. For the α -[PW₁₂O₄₀]^{3–}/ α -[PW₁₂O₄₀]^{4–} system at 25 °C in water, a value of $I_{\text{out}} = 16.4 \text{ kcal mol}^{-1}$ and a total reorganization energy of $I = I_{\text{in}} + I_{\text{out}} = 22.3 \text{ kcal mol}^{-1}$ were calculated.

Classically, the bimolecular rate constant of an outer-sphere electron-transfer reaction is sometimes written as shown in eq 40, where Z is again the universal frequency factor, and K is a factor that is unity for adiabatic electron transfers and less than unity for nonadiabatic ones:¹³

$$k_{\text{os}} = \kappa Z \exp(-\Delta G^\ddagger/RT) \quad (40)$$

The commonly used value of Z (usually taken to be $\sim 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ in solution) is based on a colliding-sphere model in which reaction does not occur until the reactants “touch” one another (i.e., reach an internuclear distance of $r_{12} = r_1 + r_2$). However, adiabatic electron transfer can occur at internuclear distances greater than r . Using a radial distribution function to modify Z accordingly, Marcus showed that for exothermic adiabatic reactions between reactants with radii of 3 Å, a value of $Z = \sim 10^{12}$ might be more appropriate.¹³ Larger Z values were predicted for exothermic adiabatic electron transfer between reactants with larger radii.

A classical approach to the calculation of the rate constant at infinite dilution, k_0 , for the α -[PW₁₂O₄₀]^{3–}/ α -[PW₁₂O₄₀]^{4–} system (i.e., eq 1, using $Z = 10^{11}$, $I = 22.3 \text{ kcal mol}^{-1}$, and $r = 11.2 \text{ Å}$ gives $k_{0\text{calc}} = 3.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, substantially lower than that obtained by Kozik and Baker using the most current level of theory ($k_{0\text{calc}} = 3.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).²³ Although derived

for exothermic reactions, modified classical treatment,¹³ using a theoretically predicted value of $Z = 3.5 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ ($r = 11.2 \text{ \AA}$), gives $k_{0\text{calc}} = 1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, which is within experimental error of the observed value of $(1.1 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

The excellent agreement between theory and experiment lends support to the validity of the assumptions made by Kozik and Baker. In particular, in combination with the unexpectedly high degree of fit of their data to the Debye-Hückel equation at higher than anticipated ionic strengths, the observed agreement between theory and experiment suggests that their assignment of $I = 22.3 \text{ kcal mol}^{-1}$ is correct or very close. In addition, their application of semiclassical theory of outer-sphere electron transfer sets a standard for future work in this area. The large difference between the classically calculated value ($Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$) and the results obtained using mathematical models that allow for electron transfer over distances greater than the sum of ionic radii further suggests the possibility that conclusions reached using less-comprehensive treatments might be inadequate.

An additional conclusion reached was that "electron delocalization of itself does not significantly contribute to the activation energy" of electron transfer.²³ This phenomenon is not without precedent. The rate of self-exchange between $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{3+}$ ($r = 13.6 \text{ \AA}$, compared to 11.2 \AA for exchange between Keggin anions) is consistent with an adiabatic (i.e., outer-sphere) electron-transfer mechanism. However, based on direct 4d-4d overlap between the two metal centers, ab initio calculations showed that the reaction should be highly nonadiabatic.⁵³ On this basis it was concluded that electron exchange between the metalloorganic cations occurred predominantly via ligand-ligand overlap. The observed adiabaticity was the result of p^*-p^* interactions between the two reactants, which arose from delocalization of the metal dp electron density onto the p^* orbitals of the bipyridine ligands.⁵³

Theoretically predicted rate constants for exchange between the 1- and 2-e⁻-reduced anions $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{4-}$ and $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{5-}$ were $k_0 = 2.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{(\mu=0.125\text{M})} = 3.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Experimentally determined values were $k_0 = (1.6 \pm 0.3) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ (by extrapolation) and $k_{(\mu=0.125\text{M})} = 2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (the apparent ionic-strength limit for reasonable fit to the Debye-Hückel equation).

The smaller-than-predicted experimental rate constants were attributed to the additional energy needed to decouple the paired electrons in diamagnetic 2-e⁻-reduced $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{5-}$. The Coulombic repulsion commonly associated with the formation of localized electron pairs is essentially absent in this system and not expected to contribute to the free energy of activation. The magnitude of the energy likely required to decouple the paired electrons in $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{5-}$ was not evaluated. However, from the difference between experimental and theoretical values of k_0 , electron coupling would appear, from eq 41, to have contributed an additional 1.45-1.76 kcal mol⁻¹ to ΔG^\ddagger .

$$\Delta G^\ddagger_{\text{experimental}} - \Delta G^\ddagger_{\text{theory}} = RT \ln (k_{0,\text{experimental}}/k_{0,\text{theoretical}}) \quad (41)$$

For the $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}/\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{7-}$ system, observed rate constants, $k_{(\mu=0.59\text{M})} = 1.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{(\mu=1.49\text{M})} = 1.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, were approximately 3 orders of magnitude smaller than those predicted, $k_{(\mu=0.59\text{M})} = 9.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{(\mu=1.49\text{M})} = 5.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. (Rates at lower ionic strengths were too slow to be determined from ³¹P NMR line widths.)

The small rate constants could not be attributed to ion pairing (eq 37). By effectively decreasing the charge product, $z_1 z_2$, of the reacting pair (eq 1), ion pairing would have exponentially increased observed reaction rates (eq 42, $(z_1 z_2)_{\text{ip}} < z_1 z_2$):

$$k_{\text{ip}}/k = \exp[(z_1 z_2) - (z_1 z_2)_{\text{ip}}] \quad (42)$$

Rather, the small rate constants were attributed to nonuniformity in the distribution of electron density over the reduced Wells-Dawson anion, $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{7-}$. Not only is the anion ellipsoidal rather than spherical, but the blue electron is delocalized only over the 12 belt tungsten atoms at the midsection of the anion. Both factors might be expected to add a geometrical constraint on orientation of the anions during electron transfer. Although not evaluated further from a theoretical point of view, this hypothesis was supported by previously obtained experimental data. The rate of self-exchange between the potentially more "orientationally challenged" anions $\alpha\text{-}[\text{P}_2\text{Mo}_3\text{W}_{15}\text{P}_{62}]^{6-}$ and $\alpha\text{-}[\text{P}_2\text{Mo}_3\text{W}_{15}\text{P}_{62}]^{7-}$, in which the blue electron is localized in the trimolybdenum cap, was ~25 times slower than that in the $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}/\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{7-}$ system.^{25,26}

In view of these arguments, the rate of electron self-exchange between Ru(III) and Ru(II) in the Ru-substituted tungstophosphate anions $[\text{PRu}^{\text{III}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{4-}$ and $[\text{PRu}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{5-}$ was one of several lines of evidence used by Rong and Pope to argue that n -electron density from the d orbitals of the Ru(II) (d^6) ion was partially delocalized onto the polytungstate ligand.⁷⁵ A self-exchanging system was prepared by dissolving cesium salts of the anions (1.3 and 0.06-0.26 mM for the Ru(III) and Ru(II) anions, respectively) in water at high ionic strength ($\mu = 1.5 \text{ M}$, Na_2SO_4 buffer) at pH 3. A preliminary value of the rate constant for electron self-exchange, $k_{(\mu=1.5\text{M})} = 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, was determined by analysis of line broadening in ³¹P NMR spectra of the mixed POM system. This value is close to that measured by Kozik and Baker for the similarly charged 1- and 2-e⁻-reduced anions $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{4-}/\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{5-}$ where $k_{(\mu=1.025\text{M})} = 2.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

Although a provocative preliminary result, the value of this comparison is limited by (1) the high ionic strength used in the Ru system (Kozik and Baker observed deviation from Debye-Hückel ionic-strength dependence at μ values near 1.0 M);²³ (2) the apparent use of Na^+ cations in the sulfate buffer (Kozik used Li^+ cations); and (3) the use of cesium salts of the Ru complexes as opposed to the free-acid salts used by Kozik (thermodynamic constants for the

formation of cation-POM ion pairs increase in the order $\text{H}^+ < \text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{C8}^+$).⁵²

C. Reevaluation of the Reorganization Energy of the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}/[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ Couple

Over the past several decades, Rasmussen and Brubaker's published data⁵ have been used to calculate the reorganization energy for electron self-exchange between $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$. Calculated reorganization energies vary widely, from $l = 23$ to 61 kcal mol^{-1} .^{59,76-78} During this time, $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ has been used repeatedly as a well-defined probe of outer-sphere electron-transfer reactions (more than 50 published studies). In those cases in which kinetic data are compared to the results of theoretical analyses (Marcus), use of a correct value for the reorganization energy of the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}/[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ system is critical.

In particular, rates of cross-reactions between $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and organic or inorganic substrates have frequently been used to "measure" the reorganization energies associated with oxidation of the substrate under investigation (eqs 43 and 44):

$$\lambda_{12} = (1/2)(\lambda_{11} + \lambda_{22}) \quad (43)$$

or

$$\lambda_{22} = 2\lambda_{12} - \lambda_{11} \quad (44)$$

where I_{12} is the experimentally determined reorganization energy of the cross-reaction between species 1 and 2, while I_{11} and I_{22} are the reorganization energies corresponding to self-exchange reactions between oxidized and reduced forms of 1 and between oxidized and reduced forms of 2. When $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ is used as a probe to determine the reorganization energy, I_{22} , of a substrate, the result is linearly proportional to the value of the self-exchange reorganization energy, λ_{11} , of the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}/[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ system (eq 44). Without reliable "calibration" (i.e., accurate measurement of I_{11} , the value of the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ "probe" is compromised. Past efforts to derive I_{11} from the data published by Rasmussen and Brubaker can now be evaluated in light of the detailed studies of Kozik, Hammer, and Baker.

Disagreement regarding the value of I_{11} for the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}/[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ couple appears to stem from an anomalous dependence of the self-exchange rate constant on ionic strength. The plot of $\ln k$ vs $\exp(-\chi r_{12})$, reported by Rasmussen and Brubaker, was linear and thus appeared meaningful and useful (Figure 1). At the same time, the slope of this plot gave a charge product of $z_1 z_2 = 7.8$. The Debye correction term, $\exp(-\chi r_{12})$ was derived for very dilute solutions of ionic strengths less than 0.001 M . At higher ionic strengths, the Debye-Hückel relation (eq 36), which was derived for ionic strengths of up to 0.01 M , often gives better results. In Figure 2, Rasmussen and Brubaker's data are plotted using the Debye-Hückel equation.

Linear regression analysis of these data (dotted line) gives a coefficient of correlation almost identical with that obtained in Rasmussen and Brubaker's plot

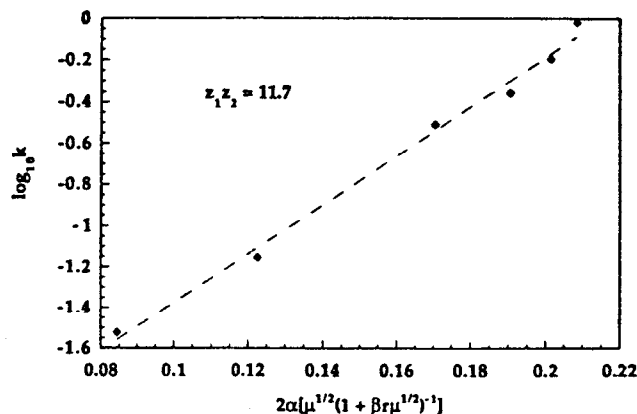


Figure 2. Plot of $\log k$ vs $2\alpha[\mu^{1/2}/(1 + \beta r\mu^{1/2})]$ (eq 36) for the electron self-exchange reaction between $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$, using data (k and μ values) reported by Rasmussen and Brubaker.⁵

of $\ln k$ vs $\exp(-\chi r_{12})$ (Figure 1). The slope of the line shown in Figure 2 gives a charge product of $z_1 z_2 = 11.7$. Extrapolation to $\mu = 0 \text{ M}$ gives $k_0 = 2.75 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, very similar to the value obtained from the plot in Figure 1. Both functions, $\exp(-\chi r_{12})$ and the Debye-Hückel equation, were derived for solutions much more dilute than those actually used. Hence, failure to obtain expected charge-product values need not of itself be viewed as evidence of ion-pair formation.

Rasmussen and Brubaker also measured the effect of the dielectric constant of the reaction medium on k at a constant ionic strength of 0.6 M . The plot of $\ln k$ vs $1/D$, where D is the dielectric constant of the reaction medium, is expected to give a slope directly proportional to the charge product of the reacting species (eqs 45 and 46, from eq 15):

$$k = Z \exp\{-(z_1 z_2 e^2 / Dr) \exp(-\chi r_{12}) + \lambda/4 / RT\} \quad (45)$$

from which

$$\ln k = -(z_1 z_2 e^2 / Dr) \exp(-\chi r_{12}) / RT - \lambda/4 / RT + \ln Z \quad (46)$$

The slope of the plot of $\ln k$ vs $1/D$ is equal to $-(z_1 z_2 e^2 / r) \exp(-\chi r_{12}) / RT$, from which the charge product, $z_1 z_2$, can be calculated. Rasmussen and Brubaker's data are plotted in Figure 3.

The slope of the line obtained by linear regression of the data plotted in Figure 3 gives a charge product of $z_1 z_2 = 32$. This result might be viewed as empirical evidence for a lack of significant ion pairing with Li^+ cations, even at relatively high ionic strength ($\mu = 0.60 \text{ M}$). Within error, the activation energy for the self-exchange reaction varied with the dielectric constant of the reaction medium as expected for a precursor complex possessing a charge product of 30.

This result may not necessarily contradict that obtained from the plot of $\ln k$ vs $\exp(-\chi r_{12})$ (Figure 1). Careful inspection reveals that the ionic strengths reported by Rasmussen and Brubaker were calculated incorrectly: Some of the ionic-strength values reported are smaller than those dictated by the concentrations of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$.

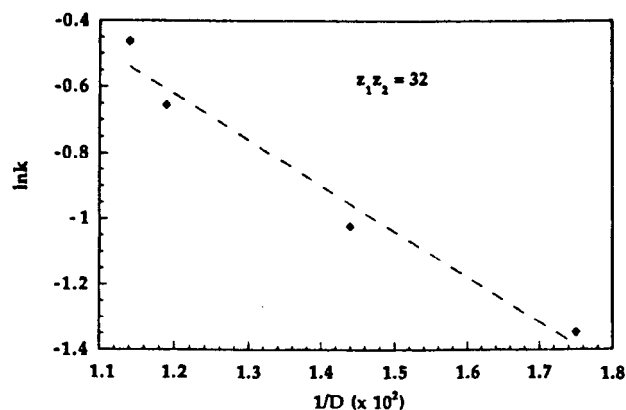


Figure 3. Plot of $\ln k$ vs $1/D$ (eq 46) for the electron self-exchange reaction between $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$, using data (k and D values) reported by Rasmussen and Brubaker.⁵

Table 1. Dependence of Rate Constant on Temperature and Ionic Strength

ionic strength (M)	rate constant k ($\text{M}^{-1} \text{s}^{-1}$)	T ($^{\circ}\text{C}$)	Arrhenius activation energy E_a (kcal mol^{-1})
0.21	0.31	00.0	5.0 ± 0.5
0.21	0.48	12.7	
0.21	0.72	25.0	
0.05	0.07	00.0	8.0 ± 1
0.05	0.13	12.7	
0.05	0.34	25.0	
0.015	0.03	00.0	12.8 ± 2
0.015	0.08	12.7	
0.015	0.24	25.0	

used in the experiments.⁷⁹ This error raises a serious question regarding the reliability of their data for use in the calculation of fundamental theoretical parameters.

In addition, there is some suggestion from the work of Kozik and Baker that ion pairing with Li^+ cations in the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}/[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ system would not occur to a significant extent at moderate ionic-strength values. The evidence is from a study of the $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}/\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{7-}$ self-exchange reaction.²³ Experimental rate-constant values for this reaction were 3 orders of magnitude smaller than calculated ones, even at fairly high ionic strengths ($\mu = 1.49 \text{ M}$, LiCl). Localization of the blue electron notwithstanding, if ion pairing were occurring, one would expect observed rate constants to have exceeded, rather than to have fallen short of, calculated values.

Finally, Rasmussen and Brubaker measured the temperature dependence of k as a function of ionic strength (Table 1).

These data were used to extrapolate to infinite dilution, which gave $E_a(\mu=0\text{M}) = \sim 18 \text{ kcal mol}^{-1}$. Using a preexponential factor of $Z = 10^{11} \text{ M}^{-1} \text{s}^{-1}$, this value of E_a would give (using eq 4) $k_0 = 10^{11} \exp(-E_a/RT) = 3.9 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1}$ at 0°C .

Unfortunately, a conceptual error was made in Rasmussen and Brubaker's extrapolation $\mu = 0 \text{ M}$. To determine $E_a(\mu=0\text{M})$ from data of this kind, it is necessary to determine k_0 , by extrapolation to $\mu = 0 \text{ M}$, at each temperature studied.¹⁹ (Note that the Arrhenius preexponential factors indicated by the

rate constants and E_a values in Table 1 are small and vary with ionic strength.)

Irrespective of the explanation for the low charge product calculated from Figure 1, the Coulombic work term at infinite dilution should reflect the ideal (no ion pairing) charge product of $z_1 z_2 = 30$. Hence, the slope of the plot of $\ln k$ vs $\exp(-\chi r_{12})$ should have steepened as the ionic strength approached 0 M . However, there is no way of knowing at what ionic strength this might have occurred. This uncertainty makes extrapolation of k to infinite dilution problematic. The value of $k = 4.5 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$ reported by Rasmussen and Brubaker was obtained by extrapolating to $\mu = 0 \text{ M}$, using the slope of $\ln k$ vs $\exp(-\chi r_{12})$ shown in Figure 1 (slope = $z_1 z_2 = 7.8$).

Values of k obtained from the data of Rasmussen and Brubaker have been used to determine the self-exchange reorganization energy, I_{11} , using eq 47 (from section II.B.3):

$$k = Z \exp\{-(W(r) + I/4)RT\} \quad (47)$$

where $W(r)$ is given by

$$W(r) = (z_1 z_2 e^2 / Dr) \exp(-\chi r_{12}) \quad (48)$$

At $\mu = 0$, $\exp(-\chi r_{12}) = 1$ and eq 48 becomes

$$W(r) = (z_1 z_2 e^2 / Dr) \quad (49)$$

The k_0 value reported by Rasmussen and Brubaker was obtained by extrapolation of the line plotted in Figure 1 to infinite dilution ($\exp(-\chi r_{12}) = 1$). Thus, the k_0 value they reported could only have been correct if the slope of the plot shown in Figure 1 ($z_1 z_2 = 7.8$) had been constant to $\mu = 0 \text{ M}$. Thus, in choosing Rasmussen and Brubaker's value of k_0 as a basis for calculating I_{11} , one is forced to use a charge product of 7.8 for calculation of the Coulombic term, $W(r)$, in eq 49. Doing so ($r = 11.2 \text{ \AA}$, $T = 273 \text{ K}$), one obtains, from eq 47, $I = 61.2 \text{ kcal mol}^{-1}$ ($Z = 10^{11} \text{ M}^{-1} \text{s}^{-1}$) or $I = 56.2 \text{ kcal mol}^{-1}$ ($Z = 10^{12} \text{ M}^{-1} \text{s}^{-1}$).

A formally analogous method was used by Amjad, Brodovitch, and McAuley in 1977.⁷⁶ Returning again to Figure 1, Amjad et al. extrapolated to an ionic strength of $\mu = 1.0 \text{ M}$, which was pertinent to their study of the oxidation of organic acids and phenolic compounds by $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$. At $\mu = 1.0 \text{ M}$, $\exp(-\chi r_{12}) = 0.037$; the contribution of Coulombic work to ΔG^\ddagger was less than 4% of that at $\mu = 0$ (eq 1). Hence, the contribution of $W(r) \exp(-\chi r_{12})$ to ΔG^\ddagger was ignored. The free energy of activation, ΔG^\ddagger , calculated from the rate constant obtained by extrapolation to $\mu = 1.0 \text{ M}$ ($k_{(\mu=1.0\text{M})} = 1.7 \text{ M}^{-1} \text{s}^{-1}$), was set equal to $I/4$ (eq 14). A value of $I = 4(15.36 \text{ kcal mol}^{-1}) = 61.4 \text{ kcal mol}^{-1}$ was obtained.

Fair agreement between theory and experiment was found when the extrapolated self-exchange rate-constant value ($k_{(\mu=1.0\text{M})} = 1.7 \text{ M}^{-1} \text{s}^{-1}$) was used to predict the rate constant, k_{12} , for cross-reaction between $\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}^{5-}$ and ascorbate anion.^{76,80} In addition, $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ was reacted with $[\text{Ru}(\text{CN})_6]^{3-}$ and the Marcus cross-relation (eq 17) used to calculate the self-exchange rate constant, $k_{\text{Ru-Ru}}$, for the $\text{Ru}(\text{CN})_6^{3-/4-}$ couple. Notably, the $k_{\text{Ru-Ru}}$ value cal-

Table 2. Kinetic and Thermodynamic Parameters of Redox Reactions Involving POM Anions in Water at 298 K; 0.5 M HClO₄, $\mu = 1.0$ M (NaClO₄)^a

entry	reaction	rate constant, k (M ⁻¹ s ⁻¹)	$\ln k$	$W(r)$ (kcal mol ⁻¹)	ΔG° (kcal mol ⁻¹)	λ^b (kcal mol ⁻¹)
1	SiW ₁₂ ⁵⁻ + Co ^{III} W ₁₂ ⁵⁻ → SiW ₁₂ ⁴⁻ + Co ^{II} W ₁₂ ⁶⁻	7×10^6	3.8	9.49	-23.7	53.8
2	PW ₁₂ ⁴⁻ + Co ^{III} W ₁₂ ⁵⁻ → PW ₁₂ ³⁻ + Co ^{II} W ₁₂ ⁶⁻	2.9×10^6	5.3	7.60	-18.8	51.6
3	PW ₁₂ ⁴⁻ + Fe ³⁺ → PW ₁₂ ³⁻ + Fe ²⁺	6×10^6	24.9	-5.69	-9.89	45.2
4	Fe ²⁺ + Co ^{III} W ₁₂ ⁵⁻ → Fe ³⁺ + Co ^{II} W ₁₂ ⁶⁻	6×10^6	23.4	-4.59	-9.39	43.5
5	SiW ₁₂ ⁵⁻ + Fe ^{III} (CN) ₆ ³⁻ → SiW ₁₂ ⁴⁻ + Fe ^{II} (CN) ₆ ⁴⁻	3.3×10^5	5.5	6.31	-8.20	40.3
6	PW ₁₂ ⁴⁻ + Fe ^{III} (CN) ₆ ³⁻ → PW ₁₂ ³⁻ + Fe ^{II} (CN) ₆ ⁴⁻	2.2×10^5	6.6	4.99	-3.30	34.5
7	SiW ₁₂ ⁵⁻ + Cu ²⁺ → SiW ₁₂ ⁴⁻ + Cu ⁺	9.1×10^4	19.2	-4.59	-1.10	38.8
8	PW ₁₂ ⁴⁻ + Cu ²⁺ → PW ₁₂ ³⁻ + Cu ⁺	3.5×10^2	12	-3.70	3.80	42.3
9	PV ₂ W ₁₀ ⁶⁻ + PV ₂ Mo ₁₀ ⁶⁻ → PV ₂ W ₁₀ ⁵⁻ + PV ₂ Mo ₁₀ ⁵⁻	5.7	-11.9	11.4	1.60	43.1
10	PV ₂ W ₁₀ ⁶⁻ + PV ₂ Mo ₁₀ ⁶⁻ → PV ₂ W ₁₀ ⁵⁻ + PV ₂ Mo ₁₀ ⁵⁻	80	-9.2	11.4	-1.60	43.1
11	Co ^{II} W ₁₂ ⁵⁻ + Co ^{III} W ₁₂ ⁵⁻ → Co ^{II} W ₁₂ ⁶⁻ + Co ^{III} W ₁₂ ⁵⁻	0.24	-12.2	11.4	0.00	47.1
12 ^c	HA ⁻ + Co ^{III} W ₁₂ ⁵⁻ → HA ⁻ + Co ^{II} W ₁₂ ⁶⁻	2.4×10^5	8.6	2.01	-4.09	43.2
13 ^d	H ₂ A + Co ^{III} W ₁₂ ⁵⁻ → H ₂ A ⁺ + Co ^{II} W ₁₂ ⁶⁻	1.4×10^4	9.6	0.00	1.41	38.2
14 ^e	H ₂ Cat + Co ^{III} W ₁₂ ⁵⁻ → H ₂ Cat ⁺ + Co ^{II} W ₁₂ ⁶⁻	9.5×10^2	6.9	0.00	3.49	40.2
15 ^f	H ₂ Q + Co ^{III} W ₁₂ ⁵⁻ → H ₂ Q ⁺ + Co ^{II} W ₁₂ ⁶⁻	77	4.3	0.00	6.60	39.3
16	SiW ₁₂ ⁵⁻ + O ₂ → SiW ₁₂ ⁴⁻ + O ₂ ⁻	127	4.8	0.00	3.11	46.0
17	PW ₁₂ ⁴⁻ + O ₂ → PW ₁₂ ³⁻ + O ₂ ⁻	2.9	1.1	0.00	8.39	42.8

^a The rate constant listed in entry 11 was determined by Rasmussen and Brubaker;⁵ all other rate constants were determined by Kozhevnikov.⁷⁸ ^b Calculated by solving eq 50 for each reaction using $Z = 5 \times 10^{11}$ M⁻¹ s⁻¹. ^c HA⁻ is ascorbate anion. ^d H₂A is ascorbic acid. ^e H₂Cat is catechol. ^f H₂Q is hydroquinone.

culated using the extrapolated rate-constant value (1.7 M⁻¹ s⁻¹) was consistent with $k_{\text{Ru-Ru}}$ values determined by other cross-reactions of the Ru complex.⁸¹ These results might suggest that the reorganization energy of the Co^{III}W₁₂⁵⁻/Co^{II}W₁₂⁶⁻ electron self-exchange reaction is near 60 kcal mol⁻¹.

In 1987 Kozhevnikov⁷⁸ revisited the data reported by Rasmussen and Brubaker and pointed out (footnote to reaction 11 from Table 1, p 481 in the English translation of the cited article) that the experimental k_0 value originally reported was likely in error (too large) by several orders of magnitude. Rather than use the slope of the data shown in Figure 1, he extrapolated to $\mu = 0$ using a charge product of $Z_1 Z_2 = 30$ (no other details were provided). This gave an experimental value of $k_0 = 5.03 \times 10^{-6}$ M⁻¹ s⁻¹, from which I_{11} values of 46.1 ($Z = 10^{12}$ M⁻¹ s⁻¹, $T = 273$ K) or 41.1 ($Z = 10^{11}$ M⁻¹ s⁻¹) are obtained using eqs 47 and 49.

In addition, Kozhevnikov reported rate constants, activation parameters, and thermodynamic data for cross-reactions between POM anions and between POM anions and organic substrates or other inorganic complexes (Table 2). From eq 6

$$RT \ln k_0 + W(r) = -(\lambda/4)(1 + \Delta G^\circ/\lambda)^2 - RT \ln Z \quad (50)$$

Reorganization energies, calculated by solving eq 50 for each reaction, are included in the rightmost column of Table 2.

Values of $RT \ln k_0 + W(r)$, as a function of ΔG° , are plotted as shaded diamonds in Figure 4. A nonlinear regression of the data (solid line, $Z = 10^{11}$ M⁻¹ s⁻¹) was performed using the Solver program in Microsoft Excel by minimizing the sum-of-error-squared with respect to the reorganization energy, λ . Using a preexponential factor of $Z = 10^{11}$ M⁻¹ s⁻¹, the best fit was found for $I = 38.6$ kcal mol⁻¹ ($I = 42.6$ kcal mol⁻¹ for $Z = 5 \times 10^{11}$ M⁻¹ s⁻¹ and 44.4 kcal mol⁻¹ for $Z = 10^{12}$ M⁻¹ s⁻¹). These values differ substantially from that reported by Kozhevnikov⁷⁸ for

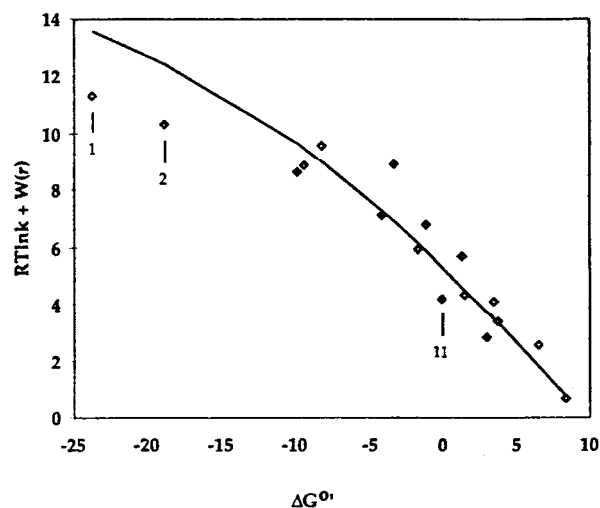


Figure 4. Calculated values of $RT \ln k_0 + W(r)$, as a function of ΔG° (Table 2) (shaded diamonds). The solid line was obtained by nonlinear regression of the data ($Z = 10^{11}$ M⁻¹ s⁻¹), in which the sum-of-error-squared was minimized using the reorganization energy, λ , as an adjustable parameter. Data points labeled 1, 2, and 11 correspond to entries 1, 2, and 11 in Table 2.

the same set of reactions, $I = 78.9$ kcal mol⁻¹, which appears to be in error by a constant factor (calculation of I from eq 7, as it appears on page 482 of the English edition of the cited article,⁷⁸ gives a value of 81 kcal mol⁻¹).

Attributing the scatter in Figure 4 to uncertainty in k_0 values, Kozhevnikov argued that the POM anions used in reactions 1-17 possessed a common inner-sphere reorganization energy. On this basis, it was concluded that the barrier to reduction of the Co(III) ion in [Co^{III}W₁₂O₄₀]⁵⁻ entailed no additional energy over that involved in reduction of the addendum atoms-V(V), Mo(VI), or W(VI)-of Keggin anions possessing PO or Si(IV) heteroatoms. Furthermore, the absence of an additional energy barrier was taken as evidence that contrary to the hypothesis of Varga, Papaconstantinou, and Pope (summarized above), the central atom in [Co^{III}W₁₂O₄₀]⁵⁻ was not

“electronically isolated” from the tungsten framework. Some of the data used in reaching this conclusion warrant further scrutiny.

The reactions between $[\text{SiW}_{12}\text{O}_{40}]^{5-}$ and $[\text{PW}_{12}\text{O}_{40}]^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ (reactions 5 and 6 in Table 2) were carried out at pH 1 in 0.1 M HClO_4 (vs 0.5 M HClO_4 used for other reactions). Kozhevnikov calculated the standard free energy of the reactions using the commonly published value of the standard reduction potential for the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ couple, 0.36 V vs the normal hydrogen electrode (NHE). However, this reduction potential value applies only to neutral or basic $[\text{Fe}(\text{CN})_6]^{3-}$ solutions; at pH values between 3 and 4, $[\text{HFe}(\text{CN})_6]^{3-}$ rather than $[\text{Fe}(\text{CN})_6]^{4-}$ is the dominant species in solution, and at pH 2, $[\text{H}_2\text{Fe}(\text{CN})_6]^{2-}$ predominates.^{82–84} Hence, at pH 1 in 0.1 M HClO_4 , the reduction potential of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ couple is actually ~ 200 mV (~ 4.6 kcal mol⁻¹) more positive than that at neutral pH. In entries 9 and 10 (Table 2), $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ anions were reacted with $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ anions. Although attempts were made to evaluate the extent of vanadium dissociation from the more labile vanadomolybdophosphate anion and the impact this dissociation might have had on the rate of electron transfer,⁸⁵ the kinetic data reported for these reactions must be viewed with caution. Additionally complicating these reactions is the tendency of $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ anions to exist in solution not only as mixtures of positional isomers, but as equilibrium mixtures^{86,87} of anions: $[\text{PVMo}_{11}\text{O}_{40}]^{4-}$, $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$, and $[\text{PV}_3\text{Mo}_9\text{O}_{40}]^{6-}$. In reactions 16 and 17, reduced POM anions were reacted with O_2 . Complications inherent in evaluating the reorganization energy associated with the reduction of O_2 to $\text{O}_2^{\bullet -}$ are discussed in section VIII.

Calculated reorganization energies (Table 2, $Z = 5 \times 10^{11}$) for the reactions of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ with well-defined POM anions (entries 1 and 2 in Table 2 and labeled 1 and 2 in Figure 4) and with $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ (self-exchange; entry 11 in Table 2 and labeled 11 in Figure 4) were 54, 52, and 47 kcal mol⁻¹, respectively. The value of 47 kcal mol⁻¹ for self-exchange of the $[\text{Co}^{\text{III/II}}\text{W}_{12}\text{O}_{40}]^{5-/6-}$ couple followed from the k_0 value Kozhevnikov obtained by extrapolation from the data of Rasmussen and Brubaker, using $z_1 z_2 = 30$, as noted above. Significantly, the reorganization energy values for the cross-reactions between $\alpha\text{-}[\text{SiW}_{12}\text{O}_{40}]^{5-}$, or $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{4-}$, and $\alpha\text{-}[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ (reactions 1 and 2) are quite high (54 and 52 kcal mol⁻¹). Using the reorganization energy calculated by Kozik and Baker for the $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{3-/4-}$ self-exchange reaction (23 kcal mol⁻¹), these data give reorganization energies for the $[\text{Co}^{\text{III/II}}\text{W}_{12}\text{O}_{40}]^{5-/6-}$ self-exchange reaction of 85 or 81 kcal mol⁻¹, which seem a bit high and may reflect errors arising from extrapolations to k_0 .

In summary, Kozhevnikov's suggestion that the POM anions listed in Table 2 might possess similar reorganization energies is unwarranted. This suggestion was reached by attributing the scatter in Figure 4 to experimental uncertainties. However, in light of the more recent work of Kozik and Baker, it is now clear that the scatter in Figure 4 can be attributed to real differences between the reorganiza-

tion energies of the POM anions. In addition, observing no additional energy barriers to electron transfer, Kozhevnikov was led to suggest that CoO_4 moieties present at the center of $\alpha\text{-}[\text{CoW}_{12}\text{O}_{40}]^{5-/6-}$ anions are not electronically isolated from the $\text{W}_{12}\text{O}_{36}$ shell. However, convincing data obtained from ESR and NMR spectroscopies, measurements of magnetic properties, and X-ray crystallography^{30,64,88} suggest otherwise.

Eberson used the k_0 value that Rasmussen and Brubaker calculated based upon a charge product of $z_1 z_2 = 7.8$ (Figure 1). At the same time, however, Eberson chose the more intuitively compelling, yet internally inconsistent, charge product of $z_1 z_2 = 30$ for calculation of the work term at infinite dilution (i.e., in eq 1 with $\exp(-\chi r_{12}) = 1$).^{59,77} Taking $Z = 10^{11}$, Eberson calculated $I = 23$ kcal mol⁻¹ at 0 °C. This reorganization energy value, which is very close to that determined for the $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{3-}/\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{4-}$ system ($I_{\text{theoretical}} = I_{\text{in}} + I_{\text{out}} = 16.4 + 6.1 = 22.5$ kcal mol⁻¹ at 25 °C), appears to be too small.

Furthermore, in 1992 Eberson⁷⁷ used Kozhevnikov's data to recalculate a common reorganization energy of ~ 28 kcal mol⁻¹ for electron-transfer reactions involving the anions $[\text{PW}_{12}\text{O}_{40}]^{3-/4-}$, $[\text{SiW}_{12}\text{O}_{40}]^{4-/5-}$, and $[\text{CoW}_{12}\text{O}_{40}]^{5-/6-}$ (entries 1, 2, and 11, Table 2). The calculation was based on the thermodynamic and kinetic parameters compiled by Kozhevnikov.⁷⁸ However, recent recalculation by Professor Eberson⁸⁹ gives values of $I_{11} = 49, 48$, and 43 kcal mol⁻¹, respectively, for these reactions (1, 2, and 11). Moreover, it is likely that the reorganization energy of the $[\text{CoW}_{12}\text{O}_{40}]^{5-/6-}$ self-exchange reaction is considerably larger than that for $[\text{PW}_{12}\text{O}_{40}]^{3-/4-}$ or $[\text{SiW}_{12}\text{O}_{40}]^{4-/5-}$ (see section III.C, above). If so, the reorganization energy for the $[\text{CoW}_{12}\text{O}_{40}]^{5-/6-}$ couple could be significantly greater than 43 kcal mol⁻¹ ($I_1 = \frac{1}{2}(I_{11} + I_{22})$, eq 43).

In summary, it appears that the reorganization energy for the $\text{CoW}_{12}^{5-/6-}$ self-exchange reaction may be substantially higher than that of the $\alpha\text{-}(\text{PW}_{12})^{3-/4-}$ couple or related heteropolyanion/heteropoly blue pairs. One way to see this directly is to compare the rate constant for the $\text{CoW}_{12}^{5-/6-}$ self-exchange reaction with that of the Wells-Dawson anions ($\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{7-}$). The rate constant observed for self-exchange between the Wells-Dawson anions at $\mu = 0.59$ M was 1.1×10^3 M⁻¹ s⁻¹ compared to 0.64 M⁻¹ s⁻¹ for the $\text{CoW}_{12}^{5-/6-}$ couple at a similar ionic strength of 0.61 M. Even though the Wells-Dawson anion has a higher charge and thus a larger value of $W(r)$ at a given ionic strength, electron self-exchange is much faster than for CoW_{12} . The difference in rates is likely attributable to a higher value for the inner-sphere reorganization of the Co ion.

In their original paper, Rasmussen and Brubaker⁵ calculated a $I_{\text{theoretical}}$ value for the $\text{CoW}_{12}^{5-/6-}$ couple of $I_{\text{in}} + I_{\text{out}} = 11.1 + 18.4 = 29.5$ kcal mol⁻¹ at 0 °C. The outer-sphere reorganization energy is very similar to that calculated by Kozik and Baker,²³ the discrepancy likely due to differences in temperature and in accepted ionic radii for the Keggin anion. The larger value of I_{in} calculated for the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$

$[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ system (Kozik and Baker estimated $I_{1n} = 6.1 \text{ kcal mol}^{-1}$ for the $\alpha\text{-(PW}_{12})^{3-/4-}$ couple) arose from consideration of the difference in Co-O bond lengths between tetrahedral $\text{Co}^{\text{III}}\text{O}_4$ and $\text{Co}^{\text{II}}\text{O}_4$. However, their calculation did not account for distortion seen in the X-ray crystal structure⁹⁰ of the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ anion, which was subsequently confirmed by accurate magnetic measurements^{63,64} and by variable-temperature ^{183}W NMR spectroscopy⁹¹ to be Jahn-Teller distorted. The $\text{Co}^{\text{II}}\text{O}_4$ moiety in $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$, on the other hand, was found to describe a near-perfect tetrahedron.^{64,91} Hence, one explanation for the slow rate of self-exchange in the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}/[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ system is that a large inner-sphere reorganization energy is associated with reduction of the CoO_4 moiety. Kozik, Hammer, and Baker point out that the much slower rate is "not surprising because...of the considerable energy barrier involved in interconversion of the small Jahn-Teller distorted $\text{Co}^{\text{III}}\text{O}_4$ tetrahedron and larger regular $\text{Co}^{\text{II}}\text{O}_4$ tetrahedron".²⁵

In light of the well-established electronic isolation of the central Co(II) ion in $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$, poor electronic overlap between the d orbitals of the Co(II) and Co(III) ions may also result in low values for v_{el} (i.e., transmission coefficients less than unity). Poor electronic overlap has been suggested as an explanation for slow rates of electron transfer observed for a number of $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ reactions.^{53,92} In octahedral Co(III) complexes, spin-multiplicity restrictions have also been suggested as an explanation for slow rates of exchange. However, analysis has shown that coupling of the vibrational modes of the ground electronic states is sufficient to lift the spin-state restrictions, such that when vibronic coupling is considered, the reduction of Co(III) is in fact allowed.⁹² Although no spin-state restrictions would apply to the reduction of tetrahedrally coordinated Co(III), the situation with respect to Jahn-Teller distorted $\text{Co}^{\text{III}}\text{O}_4$ in $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ may be different.

Finally, much of the above discussion has assumed that, despite flaws in their published data, the low rates of electron self-exchange between $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ measured by Rasmussen and Brubaker were reliable. If so, it would be untenable to argue that the reorganization energy of the $\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}^{5-/6-}$ couple is not significantly larger than that of the $\text{PW}_{12}^{4-/3-}$ couple. Unfortunately, in light of the flawed nature of some of their data, the k_{obs} value published by Rasmussen and Brubaker may not be reliable.

D. One-Electron Oxidation of $[\text{Cu}^{\text{I}}\text{W}_{12}\text{O}_{40}]^{7-}$ to $[\text{Cu}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$

Slow rates were also observed for electron transfer at tetrahedral copper in the room-temperature reaction between $[\text{Cu}^{\text{I}}\text{W}_{12}\text{O}_{40}]^{7-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ at pH 4.5 in acetate buffer (ionic strength adjusted to 0.1 M using NaClO_4).⁹³ The reaction is first order in $[\text{Cu}^{\text{I}}\text{W}_{12}\text{O}_{40}]^{7-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, and a second-order rate constant of $k_{12} = 4.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ was measured. The Marcus cross-relation (eqs 17 and 18, $Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$) was used to calculate the rate constant for the $[\text{Cu}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}/[\text{Cu}^{\text{I}}\text{W}_{12}\text{O}_{40}]^{7-}$ self-exchange reaction.

Using 0.41 V vs NHS for the reduction potential of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ couple at pH 4.5 and -0.02 V for the $[\text{Cu}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}/[\text{Cu}^{\text{I}}\text{W}_{12}\text{O}_{40}]^{7-}$ couple at the pH and ionic strength of the cross-reaction, a rate constant of $k_{11} = 2.61 \text{ M}^{-1} \text{ s}^{-1}$ was calculated for self-exchange between the copper complexes. The purpose of this study was to investigate the nature of electron transfer in blue copper proteins, such as plastocyanine and azurin, in which both Cu(I) and Cu(II) oxidation states share a common distorted tetrahedral geometry. The self-exchange rate constant, which had been calculated for the plastocyanin system, was ca. $10^5 \text{ M}^{-1} \text{ s}^{-1}$; it was thought that a similar rate might be observed in the $[\text{Cu}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ system, the central Cu ions similarly residing in pseudotetrahedral environments. The surprisingly small self-exchange rate constant found for the $[\text{Cu}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ system was attributed to the need for the transferring electron to pass through the $\text{W}_{12}\text{O}_{36}$ shell, a proposal originally set forth by Rasmussen and Brubaker to explain the slow rate of electron exchange in the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{5-/6-}$ system.⁵

However, unlike in the electronic spectra of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$, some intervalence charge transfer (i.e., $\text{Cu}(\text{I}) \leftrightarrow \text{W}(\text{VI}) \equiv \text{Cu}(\text{II}) \leftrightarrow \text{W}(\text{V})$) has been observed in $[\text{Cu}^{\text{I}}\text{W}_{12}\text{O}_{40}]^{7-}$.⁷⁻⁹⁴ Thus, as observed in the self-exchange of $[\text{Ru}(\text{bpy})_3]^{2+/3+}$,⁵³ it might be argued that electron delocalization of this type would allow for greater electronic overlap between the Cu(I) and Cu(II) d orbitals in the $[\text{Cu}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ system, thus minimizing the insulating effect of the $\text{W}_{12}\text{O}_{36}$ shell. At the same time, by analogy with the considerable distortion seen for the $\text{Co}^{\text{III}}\text{O}_4$ moiety in $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$, more energy might be required for the Cu ions to obtain their favored geometries (square planar for Cu(II) and tetrahedral for Cu(I)) in the $[\text{Cu}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ anions than in the enzymatic system. Hence, the low value for self-exchange between $[\text{Cu}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ anions might also be attributed to large inner-sphere reorganization energies and not to "electronic isolation", as the literature might lead one to conclude.

IV. Oxidation of Organic Electron Donors by POM Anions

A. Alkylaromatic Compounds

In 1970 Chester recognized the potential utility of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ ($\text{Co}^{\text{III}}\text{W}_{12}^{3+}$) as a well-defined probe for determining the nature of outer-sphere oxidations of alkylaromatic hydrocarbons.⁷ Neat toluene and *o*-, *m*-, and *p*-xylene were reacted with $\text{K}_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}] \cdot 1\text{H}_2\text{O}$ under heterogeneous conditions at 96 °C. Analogous reactions were carried out in refluxing aqueous acetic acid (15 mL each of water and the organic substrate and 75 mL of acetic acid). The products of the heterogeneous oxidations were dominated by isomeric diphenylmethane derivatives, which implicated the intermediacy of benzylic cations. Oxidation of toluene in the presence of excess benzene gave diphenylmethane, which is consistent with electrophilic aromatic substitution of benzene by benzyl cation intermediates. In aqueous acetic acid, benzyl cation intermediates gave rise to benzyl acetates.

Because $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ was a known outer-sphere oxidant, oxidation of the alkylaromatic compounds to benzyl radical cations, followed by expulsion of a proton, was seen as a more likely route to intermediate benzylic radicals than was direct abstraction of a hydrogen atom, H^\cdot . The absence of dibenzyl products, which form rapidly via coupling of benzylic radicals, suggested that the benzyl radical intermediates were preferentially oxidized to cationic species by an additional equivalent of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$. No kinetic studies were performed. However, it was proposed that under heterogeneous conditions, oxidation occurred via overlap of the aromatic π system with the tungstate framework "conduction bands". Electron transfer to the $\text{W}_{12}\text{O}_{36}$ framework was followed by rapid reduction of the $\text{Co}(\text{III})$ ion. An analogous mechanism was proposed for the homogeneous oxidation of alkylaromatics by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ in aqueous acetic acid.⁷ Despite the potential intermediacy of a charge-transfer complex between substrate and the $[\text{CoW}_{12}\text{O}_{40}]^{5-}$ complex, the $\text{Co}(\text{III})$ ion, buried in the center of the $[\text{W}_{12}\text{O}_{40}]^{8-}$ framework, was entirely inaccessible by the substrate. It was thus concluded that direct coordination of alkyl aromatics to metal cation oxidants, in this case $\text{Co}(\text{III})$, was not a necessary prerequisite to homogeneous oxidation.

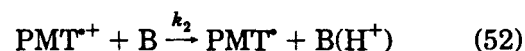
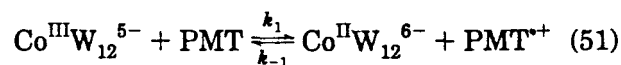
In 1980 Eberson published the first in a series of papers that characterized the homogeneous oxidations of alkylaromatic compounds by POM anions.^{8,59,77,95} A preliminary study of the oxidation of *p*-methoxy toluene (PMT) and of its deuterated derivative, 4-methoxy(α,α,α - $^2\text{H}_3$)toluene, revealed a kinetic-isotope effect of $k_{\text{H}}/k_{\text{D}} = \sim 6$ —clear evidence for proton transfer in the rate-determining step. The oxidations of toluene, xylenes, and mesitylene were also studied, although kinetic-isotope data were not obtained. Because $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ was considered an outer-sphere oxidant, the observation of rate-limiting proton transfer led Eberson to propose that electron-transfer oxidations of C-H bonds might involve a "wide spectrum of electron transfer/proton-transfer mechanisms, ranging from 'pure' outer-sphere...to an inner-sphere mechanism in which an H atom is transferred from the C-H bond to a ligand atom of a metal complex".⁸ Shortly thereafter, the notion of simultaneous electron and proton transfer was described theoretically by Perrin.⁹⁶ A similar range of mechanisms were observed independently by Meyer in oxidations of C-H bonds by polypyridyl complexes of ruthenium and osmium.⁹⁷

Jönsson⁹⁸ studied the oxidation of alkylaromatic hydrocarbons by $[\text{Ni}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ and $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-99}$ in aqueous acetic acid. The ratio of acetoxylated (4-methoxybenzyl acetate) to hydroxylated (4-methoxybenzyl alcohol) products increased with increase in the acetic acid-to-water ratio of the solvent. By analogy with the reactions of these substrates with $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$, the reactions were assumed to proceed via solvolysis of benzylic cation intermediates. Notably, kinetic isotope effects of $k_{\text{H}}/k_{\text{D}} = 4.2$ and 2.7 were observed in the oxidations of toluene and 4-methoxytoluene by $[\text{Ni}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$. Unlike $\text{Co}(\text{III})$ in $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$, the $\text{Ni}(\text{IV})$ and $\text{Mn}(\text{IV})$ heteroatoms in $[\text{Ni}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ and $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ are readily reduced by two

electrons, probably irreversibly; the 2- e^- -reduced anions $[\text{Ni}^{\text{II}}\text{Mo}_9\text{O}_{32}]^{8-}$ and $[\text{Mn}^{\text{II}}\text{Mo}_9\text{O}_{32}]^{8-}$ have not been reported. These complications mitigated against use of the nonamolybdometalate complexes for further mechanistic study of the alkylbenzene oxidation reactions.

Following the observation of a kinetic-isotope effect in the oxidation of PMT by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$, Eberson carried out a detailed investigation that clarified the role of proton and electron transfer in this reaction and laid the groundwork for the subsequent use of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ as a probe for the study of outer-sphere electron-transfer processes.⁵⁹ $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ was reacted with PMT in 55:45 (w/w) acetic acid to water. The water was included to keep the dielectric constant of the system as high as possible in order to avoid ion pairing. The reaction was followed at 50 °C by monitoring the absorbance of the $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ anion ($I_{\text{max}} = 390 \text{ nm}$) in the presence of large (100-fold) excesses of PMT. A nonlinear regression method was used to determine the fit of proposed rate expressions to absorbance vs time data. In addition to kinetic isotope effects, the effects of added base (AcO^-); of alkali-metal, alkaline-earth, and tetraalkylammonium cations; and of the dielectric constant of the medium were also determined under conditions of constant ionic strength. Prior to theoretical analysis of the data (Marcus), the reduction potential of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ was determined in the reaction medium (including added electrolytes) used for the acquisition of kinetic data.

After failure to fit the experimental data to expressions of absorbance vs time derived by integration of simple rate laws, an excellent fit was found for an expression derived by integration of a rate law that described the elementary steps shown in eqs 51 and 52 (B is either H_2O or AcO^-).



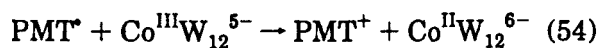
A steady-state approximation ($d[\text{PMT}^{\bullet+}]/dt = 0$) was used to derive a rate expression for the disappearance of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ (eq 53).

$$-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt = \frac{(k_1 k_2 / k_{-1} [\text{PMT}][\text{B}]) [\text{Co}^{\text{III}}\text{W}_{12}^{5-}]}{(k_2 / k_{-1}) [\text{B}] + [\text{Co}^{\text{II}}\text{W}_{12}^{6-}]} \quad (53)$$

Substitution of $[\text{Co}^{\text{II}}\text{W}_{12}^{6-}] = A_0 - A$, where A_0 is the initial absorbance of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and A its absorbance at time t , into eq 53, followed by integration, gave an expression for absorbance vs time, which by nonlinear regression, provided an excellent fit to experimental data. The proposed rate expression was further verified by systematic variation of key variables, $[\text{PMT}]$, $[\text{B}]$, and $[\text{Co}^{\text{II}}\text{W}_{12}^{6-}]$, in eq 53.

The data were consistent with a mechanism in which a rapid and reversible electron-transfer step (eq 51) was followed by rate-limiting reaction of $\text{PMT}^{\bullet+}$ with base to give PMT^\bullet . The benzylic radical,

PMT[•] was rapidly oxidized by a second equivalent of Co^{III}W₁₂⁵⁻ to give a cation that reacted with acetic acid (eqs 54 and 55).



Additional evidence for rate-limiting proton transfer was provided by the observation of a kinetic isotope effect of -6 when the reaction was carried out using 4-methoxy(a,a,a-²H₃)toluene. At low concentrations of acetate ion, such that B = H₂O (the concentration of water being ~25 M), *k*₂ was found to be 80 M⁻¹ s⁻¹, while when [AcO⁻] was increased to 0.5 M, such that B = AcO⁻, *k*₂ increased to 3.6 × 10⁶ M⁻¹ s⁻¹.

Values for *k*₁ and *k*₋₁ were calculated (eqs 1 and 4) using values for the reorganization energy of the Co^{III}W₁₂⁵⁻/Co^{II}W₁₂⁶⁻ self-exchange obtained from the data of Rasmussen and Brubaker (*I*₁₁₁ = 16–23 kcal mol⁻¹ at 50 °C), and *I*₂₂ = 9.0 kcal mol⁻¹ for the PMT/PMT^{•+} self-exchange reaction. The reorganization energy, *I*₁₂, for reaction of Co^{III}W₁₂⁵⁻ with PMT was then calculated: *I*₁₂ = (½)(*I*₁₁ + *I*₂₂) = 16 kcal mol⁻¹. As discussed above (section III.C), the reorganization energy for the Co^{III}W₁₂⁵⁻/Co^{II}W₁₂⁶⁻ couple is probably somewhat higher, and the *I* value used for the PMT/PMT^{•+} self-exchange reaction may also have been underestimated.⁷⁷ However, analysis by the author showed that error in estimation of reorganization energies did not greatly affect the calculated ratio, *k*₋₁/*k*₁, which for a reorganization energy of 16 kcal mol⁻¹, was found to be ~10¹⁰. Greater uncertainty was attributed to the effects of ion pairing on the forward reaction rate constant, *k*₁.

A specific-cation effect was observed by replacing Na⁺ by a series of alkali-metal, alkaline-earth, and tetrabutylammonium cations at constant ionic strength. The observed rate constant decreased in the order Sr²⁺ > Cs⁺ > Ca²⁺ > Rb⁺ > K⁺ > Li⁺ > Na⁺ > Me₄N⁺ > Pr₄N⁺ > Hex₄N⁺ > Dec₄N⁺. Catalysis by H⁺ was also noted. These results suggested that significant ion pairing was occurring. The charge products *z*₁*z*₂, used to calculate Coulombic terms and to correct the standard free energy of reaction (eq 1, with *z*₁ = -5 for Co^{III}W₁₂⁵⁻ and *z*₂ = -6 for Co^{II}W₁₂⁶⁻), were probably representative of limiting rather than prevalent values. Although the data did not allow for strict quantification of the effects of ion pairing on observed rate constants, approximate equilibrium constants for ion pairing of Co^{III}W₁₂⁵⁻ with Na⁺ (*K*₁ = ~10¹ M⁻¹) and with Bu₄N⁺ (*K*₂ = 10³ M⁻¹) were estimated (the above trend in specific-cation effects may reflect greater extents of ion pairing with Co^{II}W₁₂⁶⁻, vs with Co^{III}W₁₂⁵⁻, which would decrease the ratio *k*₁/*k*₋₁ in eq 51).

The results of this study suggested that if the rate of proton abstraction from the cation-radical intermediate (*k*₂ in eq 52) could be increased, outer-sphere electron transfer might become rate limiting and the forward rate constant for electron transfer (*k*₁ in eq 51) observed directly.⁹⁵ It was known that rates of C-H bond cleavage in cation radicals increased with

reduction potential (i.e., with less easily oxidized neutral substrates). Hence, one way to observe rate-limiting electron transfer, it was argued, might be to use alkylaromatic substrates less easily oxidized than PMT. To oxidize these compounds, POM anions with reduction potentials more positive than that of Co^{III}W₁₂⁵⁻ would be required. Investigation in this direction led not to more direct measurement of the rate of outer-sphere electron transfer (*k*₁), but to the observation of synchronous proton and electron transfer.

p-Xylene (irreversible anodic potential, *E*_{anodic} = 2.18 V vs NHE in acetonitrile, compared with 1.82 V for PMT) was reacted with (NH₄)₆H₂[Ce^{IV}Mo₁₂O₄₂] in aqueous acetic acid.⁹⁵ In 3:1 water to acetic acid, five anodic waves were observed in the cyclic voltammogram of (NH₄)₆H₂[Ce^{IV}Mo₁₂O₄₂] (graphite electrode, no added electrolyte). The most positive of these, an irreversible anodic wave observed at -1.42 V (NHE), was assigned to the oxidation of Ce(III) to Ce(IV). The next most positive wave was observed at ~1.2 V. Ebersson assigned the couples observed at 1.2 V and at more negative potentials to the reduction of Mo(VI) ions in [Ce^{IV}Mo₁₂O₄₂]⁸⁻. These redox couples were reported to be quasi-reversible or nearly so (*E*_{anodic} - *E*_{cathodic} = 100, 55, 120, and 65 mV at sweep rate of 50 mV s⁻¹). No distinct cathodic peak, which would have corresponded to the reduction of Ce(IV) to Ce(III), was seen. The absence of this peak was attributed to the "reduction" of water. It is unclear how water could be reduced at such positive electrode potentials (>+1.3 V).

In polarographic analysis of the [Ce^{IV}Mo₁₂O₄₂]⁸⁻ anion in 1.0 M sulfuric acid, Pope¹⁰⁰ observed reversible reduction of Ce(IV) to Ce(III) (+0.68 V). The discrepancy between this value and that reported by Ebersson appears to exceed the range of values defined by study of medium (solvent and electrolyte) effects on the reduction potential of the Co^{III/II}W₁₂^{5-/6-} couple.⁵² No further reduction was seen by Pope until the electrode potential reached -0.1 V, at which a complex multielectron process was observed. The absence of an anodic peak after multielectron reduction of [Ce^{IV}Mo₁₂O₄₂]⁸⁻ was consistent with irreversible reduction of the anion. (Irreversible reduction of addendum atoms is typical of "type II" polyanions, such as [Ce^{IV}Mo₁₂O₄₂]⁸⁻, in which MO₆ octahedra-where M is an addendum atom, usually Mo(VI) or W(VI)-possess two cis terminal oxygens.)¹⁰¹ However, apart from Ebersson's seemingly high reduction potential value for the 1-e- reduction of [Ce^{IV}Mo₁₂O₄₂]⁸⁻, which when used to calculate the standard free energy of reaction with substrate, would have a significant impact on theoretical analysis, the use of this polyanion as a reversible-potentially outer-sphere-single electron oxidant appears sound.

The products of oxidation of *p*-xylene by [Ce^{IV}Mo₁₂O₄₂]⁸⁻ (Ce^{IV}Mo₁₂⁸⁻) were the ones (4-methylbenzyl acetate and 4-methylbenzyl alcohol) expected to result from the formation of benzyl cation intermediates under the prevailing reaction conditions. Progress of reaction was followed by observation of the absorbance of the [Ce^{III}Mo₁₂O₄₂]⁹⁻ anion at 410 nm. At 50 °C under pseudo-first-order condi-

tions ($[\text{ArCH}_3]_0/[\text{Ce}^{\text{IV}}\text{Mo}] > 37.5$), absorbance vs time data were fitted to an expression derived by integration of the second-order rate law shown in eq 56.

$$-d[\text{Ce}^{\text{IV}}\text{Mo}_{12}^{8-}]/dt = k_1[\text{ArCH}_3][\text{Ce}^{\text{IV}}\text{Mo}_{12}^{8-}] \quad (56)$$

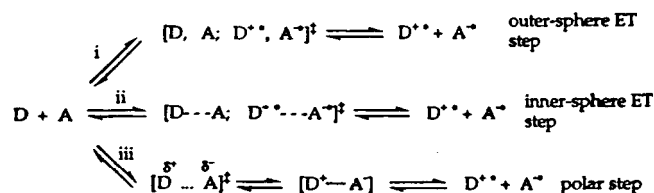
A value for k_1 of $9.4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ was determined, and a kinetic isotope effect of 1.5 was observed. In contrast to the reaction between $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and PMT, the present reaction was zero order in $[(\text{Ce}^{\text{III}}\text{Mo}_{12}\text{O}_{42})^{9-}]$ and in $[\text{AcO}^-]$. Despite the high value assigned to the reduction potential of $\text{Ce}(\text{IV})$ in $[\text{Ce}^{\text{IV}}\text{Mo}_{12}\text{O}_{42}]^{8-}$, theoretical analysis of the reaction, assuming a rate-limiting outer-sphere electron-transfer step, gave rate constants 5–6 orders of magnitude smaller than observed values. Uncertainties with regard to the reorganization energy of the $[(\text{Ce}^{\text{IV}}\text{Mo}_{12}\text{O}_{42})^{8-}/(\text{Ce}^{\text{III}}\text{Mo}_{12}\text{O}_{42})^{9-}]$ system, the extent of ion pairing present, the $\text{p}K_a$ of the $[\text{Ce}^{\text{III}}\text{Mo}_{12}\text{O}_{42}]^{9-}$ anion, and related issues were acknowledged and systematically discussed. After careful consideration, it was concluded that agreement with Marcus theory could not be obtained without unreasonable assumptions. Finally, it was suggested that the reaction might not proceed by simple outer-sphere electron transfer and that an alternative mechanism, one involving synchronous electron-proton transfer, should be seriously considered.

All the same, the authors argued that the relatively Weak kinetic isotope effect ($k_H/k_D = 1.5$) did not unequivocally exclude a rate-limiting outer-sphere electron-transfer step. The k_H/k_D value of 1.5 might have been due to secondary kinetic isotope effects, including the effect of deuterium substitution on inner-sphere reorganization energies.^{77,95,102}

Nonetheless, the possibility of concerted electron-proton transfer was strongly supported by the unexpectedly rapid rate observed for the oxidation of *p*-nitrotoluene ($E^\circ > 3 \text{ V}$) by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$.^{8,59} Given the high endergonicity associated with oxidation of *p*-nitrotoluene to its radical cation, the rapid oxidation of *p*-nitrotoluene by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ argued against an outer-sphere electron-transfer mechanism. Concerted electron-proton transfer was suggested.

In 1992 Eberson⁷⁷ used POM anions and other outer-sphere oxidants to clarify fundamental issues concerning the mechanisms of reactions involving the formation of radical cations from organic substrates. Three pathways for electron transfer between organic donor, D, and acceptor, A, each involving greater degrees of electronic coupling in the transition state, were considered (Scheme 3).

Scheme 3



Case 1, outer-sphere electron transfer, is defined by the criterion that electronic coupling in the transition state is less than $\sim 1 \text{ kcal mol}^{-1}$ (but still large

Table 3. Summary of Self-Exchange Reorganization Energies Calculated from Cross-Reactions with Inorganic and Organic Oxidants

entry	ArH (no. of compounds)	oxidant	λ_{calc} (kcal mol ⁻¹) ArH ^{•+} /ArH
1	4-methoxytoluene (1)	$[\text{Co}^{\text{III}}\text{W}_{12}]^{5-}$	55
2	alkylbenzenes (7)	$[\text{Ce}^{\text{IV}}\text{Mo}_{12}]^{8-}$	35
3	methylbenzenes (5)	$[\text{Fe}^{\text{III}}\text{phen}_3]^{3+}$	48
4	methylbenzenes (8)	$[\text{Ru}^{\text{III}}\text{L}_3]^{3+}$	39
5	4-methoxytoluene (1)	$[\text{Os}^{\text{V}}\text{Cl}_6]^-$	50
6	naphthalene (1)	$[\text{Os}^{\text{V}}\text{Cl}_6]^-$	30
7	HetArh (5) ^a	HetArH ^{•+}	5.4–8.8
8	9,10-Ph ₂ -anthracene ^b	ArH ^{•+} ^c	3.4
9	tris- <i>p</i> -tolylamine	ArH ^{•+} ^d	11.8
10	1,4-Me ₂ NC ₆ H ₄ NMe ₂	ArH ^{•+} ^e	10.5

^a Dibenzo-*p*-dioxin, phenoxazine, phenoxathiin, phenothiazine, and 10-methylphenothiazine. ^b In dichloromethane. ^c 9,10-Ph₂-anthracene^{•+}. ^d Tris-*p*-tolylamine^{•+}. ^e 1,4-Me₂NC₆H₄NMe₂^{•+}.

enough to keep the probability of electron transfer occurring, once Franck-Condon requirements have been satisfied, equal to unity). The inner-sphere step, case 2, can be assumed to embody an electronic interaction of near 5 kcal mol^{-1} or greater, while case 3, a polar pathway, is likely associated with an electronic interaction of $15\text{--}20 \text{ kcal mol}^{-1}$. (Charge-transfer complexes, often associated with electronic interactions of $1\text{--}2 \text{ kcal mol}^{-1}$, may be viewed as forming en route to an inner-sphere electron-transfer step, case 2.)

In previous work, Eberson, in collaboration with Shaik,¹⁰³ had performed a theoretical and experimental analysis of the organic electron-transfer reactions of organic radical anions. The authors concluded that in reactions of radical anions, $\text{RH}^{\bullet-}$, with neutral organic molecules, RH, sizable electronic interactions ($\sim 3\text{--}8 \text{ kcal mol}^{-1}$) were involved in the relevant transition states. Similar interactions were predicted for reactions of radical cations, $\text{RH}^{\bullet+}$.

Cross-reactions between POM anions and neutral organic compounds, RH, were used to estimate reorganization energies, I , associated with electron self-exchange between RH and 1-e⁻-oxidized derivatives, $\text{RH}^{\bullet+}$. The estimated reorganization energies were then used to calculate (Marcus) the rate constants expected for outer-sphere electron transfer between RH and $\text{RH}^{\bullet+}$. Differences between theoretically and experimentally determined rate constants indicated that electronic interactions in the transition state were greater than those allowed for by an outer-sphere mechanism.

In addition to POM anions, data obtained using a number of other inorganic outer-sphere oxidants were reviewed (entries 1–6, Table 3). The reorganization energies listed for entries 7–10 were obtained by Marcus treatment of kinetic data obtained from the indicated self-exchange reactions.¹⁰⁴

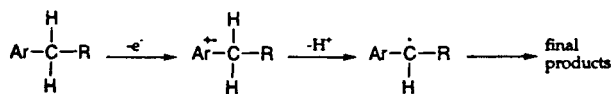
The reorganization energies calculated from rate data for the self-exchange reactions (entries 7–10, Table 3) were consistently lower than those calculated from rate data obtained from the cross-reactions with inorganic outer-sphere oxidants. Although no rate data for self-exchange of alkylaromatic compounds, such as those referred to in entries 1–5, were available, the difference between the I values calculated for the reaction of naphthalene with OsCl_6^- and

the I values calculated for the self-exchange reactions between the polycyclic aromatic compounds listed in entries 7 and 8, suggested that the I values obtained by Marcus treatment of the self-exchange reactions were low by ~ 20 kcal mol $^{-1}$. Because I values contribute $1/4$ kcal mol $^{-1}$ to the activation energies of outer-sphere electron-transfer reactions (eq 11, the 20 kcal mol $^{-1}$ error would correspond to an electronic interaction of ca. 5 kcal mol $^{-1}$ in the transition states of the ArH/ArH $^{+}$ self-exchange reactions (case 2, Scheme 3). This result, consistent with those obtained in analysis of self-exchange between ArH and radical anions, ArH $^{\cdot-}$,¹⁰³ led to the conclusion that outer-sphere mechanisms may be less kinetically facile than inner-sphere pathways in electron-transfer reactions between neutral organic compounds and cationic or anionic organic radicals.

The reorganization energy determined for the ArH/ArH $^{+}$ self-exchange reaction reported in entry 1 (Table 3, $I = 55$ kcal mol $^{-1}$) was calculated using a reorganization energy (I_{11}) for the Co $^{III/II}$ W $_{12}^{5-/6-}$ couple of 23 kcal mol $^{-1}$.⁷⁷ Cause for concern regarding the accuracy of this I_{11} value, which was calculated from the data of Rasmussen and Brubaker,^{5,59} was discussed above (section IIIC). Possible use of an artificially low value for the reorganization energy of the [CoW $_{12}$ O $_{40}$] $^{5-/6-}$ couple might have contributed to the high value, 55 kcal mol $^{-1}$, reported in entry 1. Because roughly similar results were obtained in only two cases (entries 3 and 5, Table 3), reliable determination of I_{11} for the Co $^{III/II}$ W $_{12}^{5-/6-}$ couple would place Ebersson's conclusions⁷⁷ on more solid footing.

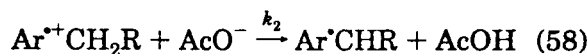
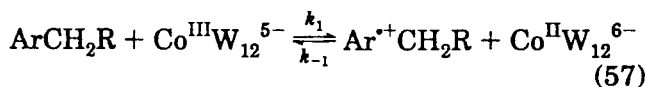
In 1993 Baciocchi¹⁰⁵ and co-workers studied the oxidation of *a*-substituted 4-methoxytoluenes (4-MeOPhCH $_2$ R; R = H, Me, OH, OMe, OAc, and CN) by Co III W $_{12}^{5-}$ in AcOH/H $_2$ O (55:45) in order to further explore the formation and deprotonation of intermediate cation radicals (Scheme 4).

Scheme 4



Ar = 4-MeOPh; R = H, Me, OH, OMe, OAc, and CN

The mechanism of oxidation of 4-methoxytoluene (*p*-methoxytoluene, PMT), as described by Ebersson,⁵⁹ involved two potentially rate-limiting steps (see also eqs 51 and 52)



followed by rapid formation of products (X = OH or OAc; see also eqs 54 and 55):

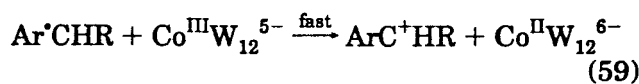


Table 4. Kinetic Data for the Oxidation of ArCH $_2$ R by [Co III W $_{12}$ O $_{40}$] $^{5-}$

R	k_1 (M $^{-1}$ s $^{-1}$)	k_{-1}/k_2	$t_{1/2}$ (min) ^a	E° (V vs NHE) ^b
Me	1.8×10^{-1}	8.2×10^3	3	1.75
H	9.7×10^{-2}	7.2×10^3	4	1.77
OH	2.1×10^{-2}	1.2×10^3	6.5	1.89
OMe	7.0×10^{-3}	1.1×10^3	20	1.91
OAc	9.8×10^{-4}	2.0×10^3	165	1.93
CN	3.5×10^{-4}	2.7×10^2	240	2.00

^a Time needed to halve the initial concentrations of Co III W $_{12}^{5-}$ (9.4×10^{-4} M) in the presence of 100-fold excesses of substrate.

^b Standard reduction potentials for ArCH $_2$ R $^{+}/$ ArCH $_2$ R couples.¹⁰⁶

It was anticipated that careful kinetic analysis would provide information regarding the role of the *a*-substituents, R, in the two kinetically pertinent steps of the oxidation process (eqs 57 and 58).

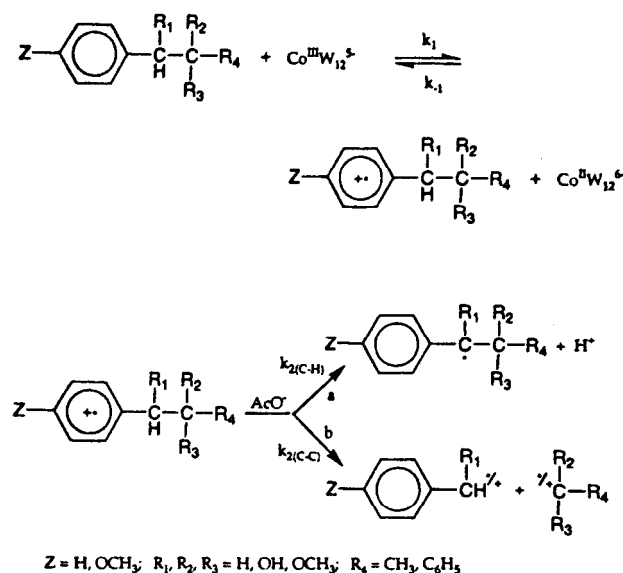
Reactions of Co III W $_{12}^{5-}$ with ArCH $_2$ R were carried out at 50 °C in the presence of 0.47 M KOAc. Under these conditions, side-chain-substituted α -hydroxy and α -acetoxy products (ArCXHR, X = OH and OAc) were formed when R = H or Me. With R = OH, OMe, or OAc, however, the first-formed α -hydroxy or acetoxy derivatives were hydrolyzed to 4-methoxybenzaldehyde. In the case of R = CN, both the α -acetoxy derivative and 4-methoxybenzaldehyde were observed.

Kinetic studies were carried out spectrophotometrically using Co III W $_{12}^{5-}$ concentrations of 2.5 – 9.4×10^{-4} M and 100-fold excesses of substrate. A mathematical solution of the integrated rate expression derived for eqs 57 and 58, in terms of absorbance as a function of time, was fitted to the experimental data; values for k_1 and the ratio k_{-1}/k_2 (Table 4) were obtained by nonlinear regression analysis. A plot of $\log k_1$ vs ΔG° values¹⁰⁶ for the reactions was fitted to the Marcus equation (eq 1) using the reorganization energy, I , as an adjustable parameter. A good fit of the experimental data was obtained for a reorganization energy of $I = 41$ kcal mol $^{-1}$.

Because the forward electron-transfer steps (eq 57, k_1) were considerably endergonic, the rate constants for back electron transfer, k_{-1} , were all in the diffusion-controlled range and could be assumed constant. Hence, the data in Table 4 indicated that as the reduction potentials, E° , of the ArCHR $^{+}/$ ArCH $_2$ R couples became more positive, the rate of forward electron transfer (k_1) decreased, while that of the deprotonation step (k_2) increased. The former trend was consistent with the effect of larger positive ΔG° values on k_1 , the latter with decreasing stabilities of intermediate cation radicals. However, although cation-radical intermediates derived from less easily oxidized substrates were more rapidly deprotonated, k_1 values were considerably more sensitive to changes in E° than were k_2 values. As a result, overall oxidation rates ($t_{1/2}$ values, Table 4) decreased as the reduction potentials of the ArCHR $^{+}/$ ArCH $_2$ R couples became more positive.

Finally, using a value of $I = 25$ kcal mol $^{-1}$ for the reorganization energy associated with the Co $^{III/II}$ W $_{12}^{5-/6-}$ electron self-exchange reaction,^{59,77} a reorganization energy for the ArCH $_2$ R $^{+}/$ ArCH $_2$ R couple of 57 kcal mol $^{-1}$ was calculated. The authors noted that although high, the reorganization energy

Scheme 5



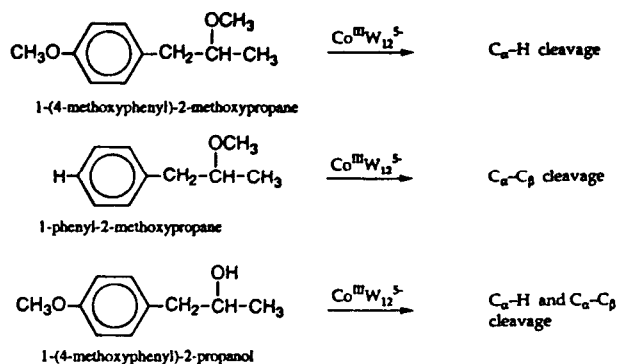
assigned to the $\text{ArCH}_2\text{R}^+ \text{ArCH}_2\text{R}$ couple agreed with that obtained by Eberson⁷⁷ (55 kcal mol⁻¹; cross-reaction of *p*-methoxytoluene with $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$). Such high reorganization energies have been justified on the basis of the strong hyperconjugative effect of the α -CHa group, a phenomenon confirmed by ESR measurements. However, Baciocchi pointed out that theoretical calculations did not show any substantial differences in molecular geometry between toluene and the toluene radical cation.¹⁰⁷ Underestimation of the reorganization energy of the $\text{Co}^{\text{III}}\text{W}_{12}^{5-/6-}$ couple might also have contributed to the high reorganization energy calculated for the $\text{ArCH}_2\text{R}^+/\text{ArCH}_2\text{R}$ couples.

An additional manifestation of the kinetic significance of k_1 (electron transfer) and k_2 (deprotonation by reaction with base) was demonstrated by Baciocchi, Galli, and co-workers.¹⁰⁸ They noted that in H-atom-transfer reactions, the order of C-H bond selectivities was tertiary > secondary > primary. However, in outer-sphere electron-transfer reactions, compounds possessing secondary C-H bonds were oxidized most rapidly.

Overall reaction rates depend on the values of both k_1 and k_2 . Moreover, changes in the structures of alkyl side chains (e.g., methyl, ethyl, or isopropyl) present in a homologous series of alkylaromatic compounds have only small effects on oxidation potentials. Thus, in the outer-sphere oxidation of such a homologous set of compounds, k_2 values carry significant kinetic weight. In addition, it was argued that steric and electronic factors favored the abstraction of secondary (over primary or tertiary) protons in cation-radical intermediates. When $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ was reacted with 4-methoxyalkylbenzene derivatives possessing methyl (primary C_α -H bonds), ethyl (secondary C_α -H bonds), and isopropyl (tertiary C_α -H bond) side chains, the following relative reaction rates were observed: Et (2.1) > *i*-Pr (1.8) > Me (1).

Baciocchi, Steenken, and co-workers used $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ to study C_α -C_b vs C_α -H bond cleavage and the role of α - and *b*-OH and -OCH₃ groups in the side-chain fragmentation of arylalkanol radical cations.¹⁰⁹ They

Scheme 6



performed a detailed kinetic and product study of the reactions of 1-arylpropanols, 1-aryl-1,2-propanediols, and their corresponding methyl ethers, and 1,2-diarylethanols, with $\text{Co}^{\text{III}}\text{W}_{12}^{6-}$ in aqueous acetic acid in the presence and absence of base (AcO^-). The compounds studied possessed the generalized structures shown in Scheme 5, and the fragmentation of intermediate cation radicals was expected to occur via either C-H or C-C bond cleavage (pathways a or b). The 12-tungstocobalt(III)ate ion was used to reliably oxidize the parent compounds to cation-radical intermediates.

Ten compounds of the form shown in Scheme 5 were studied in detail, and both C_α -H and C_α -C_b bond cleavage were observed. The reactions of three of these compounds—1-(4-methoxyphenyl)-2-methoxypropane, 1-phenyl-2-methoxypropane, and 1-(4-methoxyphenyl)-2-propanol—were exemplary (Scheme 6).

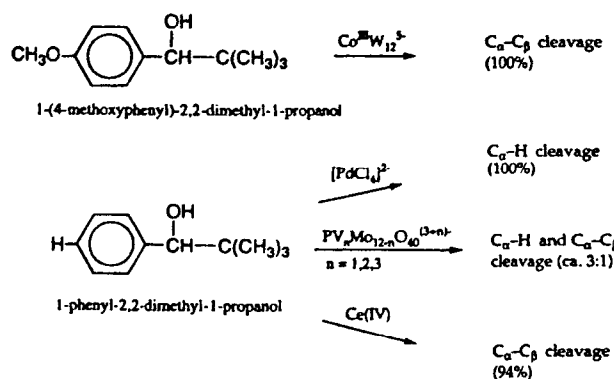
Reaction of the α -methoxy derivative 1-(4-methoxyphenyl)-2-methoxypropane with $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ gave only products of C_α -H bond cleavage (pathway a, Scheme 5). Removal of the 4-methoxy group (1-phenyl-2-methoxypropane) resulted in a dramatic change in reactivity: Only products of C_α -C_b bond cleavage (pathway b) were observed. Oxidation of the *b*-hydroxy derivative 1-(4-methoxyphenyl)-2-propanol gave products of both C_α -H and C_α -C_b bond cleavage.

It was reasoned that the 4-methoxy group in the ring favored C_α -H bond cleavage by opposing the accumulation of positive charge on the scissile C_α -C_b bond. In addition, while the presence of both OH and OCH₃ groups in the alkyl side chain enhanced C_α -C_b bond cleavage rates, the effect of OH was larger than that of OCH₃. Kinetic data, including solvent isotope effects, suggested that hydrogen bonding or specific solvation played a key role in the enhancement of C_α -C_b bond cleavage by α - or *b*-OH substituents.

The reactivity of one α -OH-substituted arylpropanol studied by Baciocchi, 1-(4-methoxyphenyl)-2,2-dimethyl-1-propanol (Scheme 7),¹⁰⁹ is notable in view of earlier work by Kozhevnikov.¹¹⁰ Kozhevnikov studied the oxidation of 1-phenyl-2,2-dimethyl-1-propanol (Scheme 7) by several inorganic oxidants ($[\text{PdCl}_4]^{2+}$, Ce(IV), $\text{S}_2\text{O}_8^{2-}$, and $[\text{VO}(\text{H}_2\text{O})_x]^{2+}$) and by a series of phosphomolybdovanadate complexes ($[\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}]^{(3-n)-}$).

The difference in product distributions observed for oxidation by Pd(II) (100% C_α -H bond cleavage) vs

Scheme 7



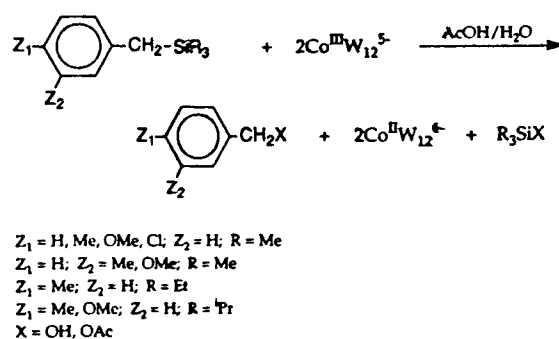
for oxidation by Ce(IV) (primarily $\text{C}_\alpha\text{-C}_\beta$ bond cleavage) was attributed to the nature of the electron-transfer step. Hydride abstraction by Pd(II) gave 100% $\text{C}_\alpha\text{-H}$ bond cleavage products, while oxidation by Ce(IV) , a single-electron oxidant, occurred via the formation by either inner- or outer-sphere mechanisms of intermediate arylpropanol radical cations. Fragmentation of these radicals appeared to occur primarily via $\text{C}_\alpha\text{-C}_\beta$ cleavage.

For oxidation by aqueous V(V) and by phosphomolybdovanadate complexes in water, the following $\text{C}_\alpha\text{-H}/\text{C}_\alpha\text{-C}_\beta$ product distribution ratios were observed: $[\text{VO}(\text{H}_2\text{O})_x]^{2+}$ (0.17), $[\text{PVMo}_{11}\text{O}_{40}]^{4-}$ (3.9), $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ (3.1), and $[\text{PV}_3\text{Mo}_9\text{O}_{40}]^{6-}$ (2.0). Because the phosphomolybdovanadate complexes are labile with respect to loss of V(V) ions to solution, Kozhevnikov proposed that the $\text{C}_\alpha\text{-C}_\beta$ cleavage products resulted from single-electron oxidations by dissociated V(V) ions, while the dominant pathway ($\text{C}_\alpha\text{-H}$ bond cleavage) was indicative of multielectron oxidation by the phosphomolybdovanadate complexes. On the basis of this reasoning, however, it is not obvious how to explain the result obtained using $[\text{PVMo}_{11}\text{O}_{40}]^{4-}$: Either V(V) was reduced by two electrons to V(III) or the V(V) ion and a Mo(VI) ion were each reduced by one electron.

In oxidations by $[\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}]^{(3+n)-}$, an inner-sphere mechanism, involving coordination of the alcohol to a V(V) ion in a fragment of the labile vanadium-containing polyanion, was suggested. The formation of vanadate esters, $[\text{ROV}^{\text{VO}}]^{2+}$, prior to the oxidation of alcohols by V(V) was cited as a supporting precedent.¹¹¹ Because polyanions can be reduced by more than one electron, it was proposed that the reaction proceeded via inner-sphere transfer of two electrons from the alcohol to the polyanion. This proposal is somewhat puzzling. While 2- e^- oxidations of alcohols by high-valent-metal cations are well-known, these reactions occur via hydride-transfer mechanisms (the reactions are associated with large kinetic isotope effects). Also, the unimolecular decomposition of vanadate esters is known to occur in a homolytic fashion, resulting in 1- e^- reduction of V(V) to V(IV) .¹¹¹

In the oxidation of 1-(4-methoxyphenyl)-2,2-dimethyl-1-propanol by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ (Scheme 7), Baciocchi's observed 100% $\text{C}_\alpha\text{-C}_\beta$ bond cleavage, despite the presence of the 4-methoxy group, which would have been expected to suppress the rate of $\text{C}_\alpha\text{-C}_\beta$ cleavage of the radical-cation intermediate. Thus, Baciocchi's

Scheme 8

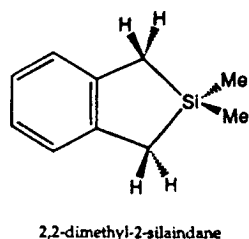


results support Kozhevnikov's reasoning that the products of $\text{C}_\alpha\text{-H}$ cleavage observed in the oxidation of 1-phenyl-2,2-dimethyl-1-propanol (no 4-methoxy group in the ring, Scheme 7) probably arose via mechanistic pathways that did not involve cation-radical intermediates. One reviewer has also pointed out that deprotonation from 1-aryl-2,2-dimethyl-1-propanol radical cations—whether a *p*-methoxy group is present or not—is unlikely due to stereoelectronic effects. Hence, where C-H bond cleavage is observed, a different mechanism (probably H-atom transfer) is probably involved.

Baciocchi and co-workers also used the $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ anion to study the electron-transfer-initiated carbon-silicon bond cleavage reactions of ring-substituted benzyltrialkylsilanes (Scheme 8).¹⁰⁷

In all but one case ((*p*-methoxybenzyl)triisopropylsilane), the reactions were strictly first order in $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and in benzylsilane. Added salts (NaClO_4 or NaOAc) decreased the reaction rate, while addition of $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ had no retarding effect. By contrast, in the oxidation of (*p*-methoxybenzyl)triisopropylsilane, the rate was no longer first order in substrate, and added $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ had a retarding effect. These data were interpreted in terms of an electron-transfer mechanism in which benzyltrialkylsilane cation radical intermediates underwent $\text{C}_\alpha\text{-Si}$ bond cleavage to give benzyl radicals that were further oxidized to benzyl cations by a second equivalent of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$. The final step was reaction of the benzyl cations with solvent (H_2O or HOAc). In most cases, initial electron transfer from the substrate to $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ was the rate-determining step; in the case of (*p*-methoxybenzyl)triisopropylsilane, cleavage of the $\text{C}_\alpha\text{-Si}$ bond in the cation-radical intermediate was rate limiting. The changeover in mechanism, indicative of a much lower rate of $\text{C}_\alpha\text{-Si}$ bond cleavage in the (*p*-methoxybenzyl)triisopropylsilane cation radical, was attributed to the presence of the bulky isopropyl groups on the silicon atom. These groups decreased the rate of $\text{C}_\alpha\text{-Si}$ bond cleavage by stabilizing the silicon atom in the radical cation toward nucleophilic attack by solvent.

On the other hand, orientation of the $\text{C}_\alpha\text{-Si}$ bond with respect to the aromatic ring (stereoelectronic effect) did not appear to influence the rate of $\text{C}_\alpha\text{-Si}$ bond cleavage.¹¹² Oxidation of 2,2-dimethyl-2-silindan (Chart 1) by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ was first order in both oxidant and substrate, and the value of the bimolecular rate constant ($1.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) was unaffected by addition of $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$.

Chart 1. Structure of 2,2-Dimethyl-2-silaindane

Despite the unfavorable stereoelectronic situation (the C_α -Si bond could not align itself with the aromatic π system), almost 100% yields of C_α -Si bond-cleavage products were found. No products of C_α -H bond cleavage, the stereoelectronically favored pathway, were detected.

Bimolecular rate constants, k_1 , were measured for the oxidations of ring-substituted benzyltrimethylsilanes by $Co^{III}W^{125-187}$. By using nonlinear least-squares regression, the Marcus equation (eq 1) was fit to kinetic (k_1) and thermodynamic (ΔG°) data, with reorganization energy, I , as an adjustable parameter. The best fit gave a reorganization energy of $I = 43 \text{ kcal mol}^{-1}$. Introduction of the frequently accepted value of I for the $Co^{III/II}W_{12}^{5-6-}$ electron self-exchange reaction (25 kcal mol^{-1}) gave a reorganization energy of 61 kcal mol^{-1} for the $ArCH_2SiMe_3^+ / ArCH_2SiMe_3$ couple. This value was smaller than that calculated for the $SiEt_4^+ / SiEt_4$ couple (70 kcal mol^{-1} from the cross-reactions of $SiEt_4$ with $Fe(III)$ complexes.¹⁰⁴ The authors proposed that the larger value found for $SiEt_4$ was plausible considering the difference in inner-sphere reorganization energies associated with removal of an electron from a C-Si σ orbital ($SiEt_4$) vs from the aromatic π system of $ArCH_2SiMe_3$.

The I value found for the $ArCH_2SiMe_3^+ / ArCH_2SiMe_3$ couple was also larger than those determined for $ArCH_3^+ / ArCH_3$ (~ 40 – 55 kcal mol^{-1} by cross-reaction with $Co^{III}W_{12}^{5-}$ (55 kcal mol^{-1}) and other inorganic oxidants.^{77,121} This suggested that replacement of a hydrogen atom by a trimethylsilyl group in the α carbon of the side chain influenced the reorganization energy associated with removal of an electron from the aromatic system.

More generally, the relatively higher I values of substituted ($ArCH_3^+ / ArCH_3$) vs unsubstituted (Ar^+ / Ar) aromatics ($\sim 10 \text{ kcal mol}^{-1}$) had been attributed to strong hyperconjugative effects of the CH_3 group in the radical cation, which might have led to redistribution of C-H bond electron densities.⁹⁵ Thus, Baciocchi reasoned, one might expect an even larger I value for the $ArCH_2SiMe_3^+ / ArCH_2SiMe_3$ couple because σ - π conjugation in a β C-Si bond is more effective than like conjugation in a β C-H bond. However, although ESR measurements have provided evidence for the hyperconjugative effects of side-chain C_α -H and C_α -Si bonds, ab initio calculations have indicated only very slight changes in bond lengths and angles upon formation of radical cations from toluene and benzylsilanes. As a result, Baciocchi concluded that clarification of the factors responsible for the reorganization energies associated with the formation of alkylaromatic radical cations

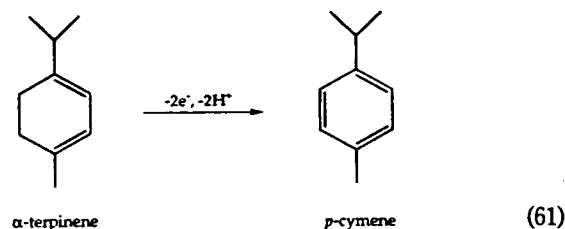
would require further study. To this remark should be added Ebersson's suggestion (above in this section) that direct electron exchange between $ArCH_3^{\bullet+}$ and $ArCH_3$ (i.e., oxidation of $ArCH_3$ by $ArCH_3^{\bullet+}$) might not occur via an outer-sphere mechanism.⁷⁷

8. Cyclohexadienes

The Keggin structural class of vanadomolybdophosphates are versatile and selective catalysts for homogeneous O_2 oxidations of numerous organic and inorganic substrates.^{113,114} Thus, despite the complexity of their solution and redox chemistry, which make detailed kinetic analysis extremely difficult, efforts to elucidate the mechanisms of the reactions particular to these systems¹¹⁴ are to be welcomed (see also sections VIII.A and F).

In 1989 Neumann and Lissel reported the catalytic aromatization (dehydrogenation) of cyclic dienes by the mixed-addenda vanadomolybdophosphate complex $H_5[PV_2Mo_{10}O_{40}]$ in the presence of tetraethylene glycol dimethyl ether (tetraglyme) and O_2 in methylene chloride.¹¹⁵

In a more detailed investigation, Neumann and Levin¹¹⁶ provided evidence that stable organic radical-POM association complexes formed during the homogeneous dehydrogenation of α -terpinene to p -cymene by $H_5[PV_2Mo_{10}O_{40}] \cdot (H_2O)_n$ in acetonitrile (eq 61).



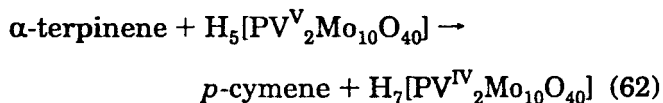
One of the difficulties encountered in interpreting kinetic data obtained from homogeneous reactions of vanadomolybdophosphate anions is that in aqueous solution, mixtures of heteropolyanions are usually present. For example, when dissolved in D_2O , samples of $H_5[PV_2Mo_{10}O_{40}] \cdot (H_2O)_n$, prepared and isolated according to the method cited¹¹⁷ by Neumann and Levin, give rise to ^{31}P and ^{51}V NMR signals attributable to a mixture of compounds: $H_{3+n}[PV_nMo_{12-n}O_{40}]$, where $n = 1, 2$, and 3 and in which the $n = 2$ species dominate.^{86,118-120} Positional isomers of the polyvanadium anions $[PV_2Mo_{10}O_{40}]^{5-}$ and $[PV_3Mo_9O_{40}]^{6-}$ are also apparent in NMR spectra.¹²¹ The speciation chemistry of this labile class of compounds (vanadomolybdophosphates of the Keggin structural type) in acetonitrile, however, has not been well-characterized. Notably, in ^{31}P NMR spectra of acetonitrile solutions of $H_5[PV_2Mo_{10}O_{40}] \cdot (H_2O)_n$, Neumann¹¹⁶ and Levin observed signals corresponding to only one heteropolyanion, $H_5[PV_2Mo_{10}O_{40}]$ (mixture of positional isomers).

Another complication inherent in the study of multielectron oxidations by polyvanadium-containing anions is the capacity of these oxidants to be reduced by one or more electrons (reduction of each V(V) ion

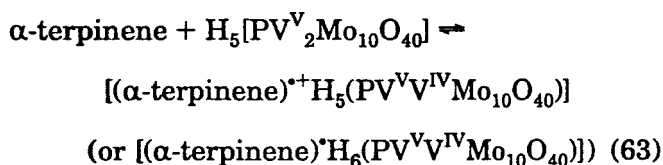
to V(IV)).^{110,115} In the 2-e⁻ oxidation of α -terpinene, either 1 or 2 equiv of $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ might be reduced.

In an attempt to determine the stoichiometry of the reaction, increasing amounts of α -terpinene (0–7 equiv) were allowed to react with acetonitrile solutions of $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}] \cdot (\text{H}_2\text{O})_n$ (8 mM). After each reaction, the final absorbance of the heteropoly blue product (750 nm) was recorded. Irreversible reduction of $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ by α -terpinene would have resulted in a linear increase in absorption until a maximum was reached at the required [substrate] to [POM] ratio. However, as the number of equivalents of α -terpinene increased, asymptotic behavior, indicative of a reversible reaction between POM and substrate, was observed.

Free-energy calculations indicated that the reverse of 2-e⁻ oxidation of α -terpinene by a single equivalent of $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ (i.e., the reverse of eq 62) was highly endergonic ($\Delta G^\circ \approx +44 \text{ kcal mol}^{-1}$).

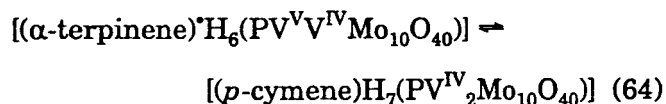


This fact forced the authors to contemplate reversible formation of a higher-energy intermediate:

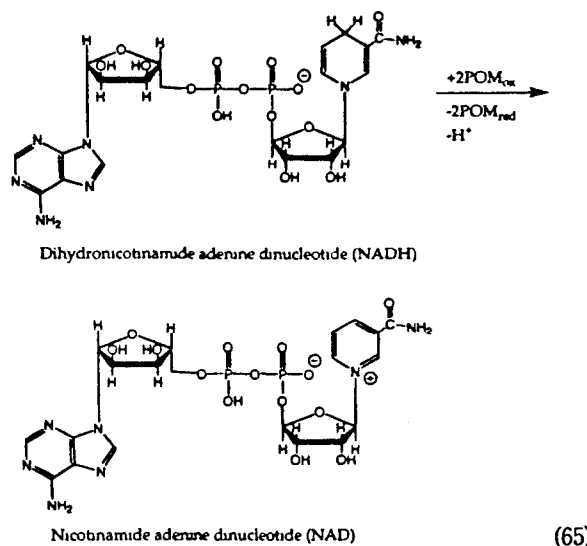


The suspected intermediate was observed by ESR spectroscopy. The intermediate was stable for several hours at room temperature: ESR spectra, which confirmed that the POM anion was reduced by only one electron, remained unchanged after 6 h. Support for the formation of an organic radical was provided by the observation of new lines in the ESR spectrum upon addition of the spin trap 2-methyl-2-nitroso-propane.

Possible mechanisms for conversion of the radical intermediate to *p*-cymene were discussed. The absence of oxygenation products observed after catalytic oxidation of α -terpinene by $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ in the presence of O_2 argued against diffusion of organic radical intermediates into solution. Although no conclusion was reached, the authors considered further unimolecular decay of the association complex (electron transfer followed rapidly by proton transfer or perhaps H-atom transfer; eq 64) an attractive possibility.

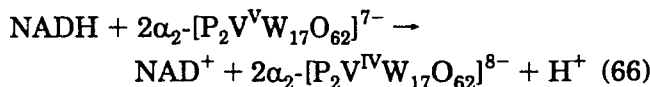


Keita, Nadjo, and co-workers studied the 2-e⁻ oxidation of dihydronicotinamide adenosine dinucleotide (NADH) to nicotinamide adenosine dinucleotide (NAD) and H⁺ by Wells-Dawson heteropolytungstates (POM_{ox} , eq 65). In the biological oxidation of



NADH to NAD^+ , aromatization of the heterocyclic diene (dihydronicotinamide) ring to the aromatic cation (*N*-alkylnicotinamide substituent) occurs via the loss of two electrons and one proton.^{122–124}

Using electrochemical and spectroscopic techniques, Nadjo demonstrated that in aqueous solution at pH 7 (phosphate buffer), 2 equiv of $\alpha_2 - [\text{P}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ were rapidly reduced by each equivalent of NADH:



The nature of the oxidation product and analogy of eq 65 to biological oxidation were confirmed by biochemical reduction (addition of alcohol dehydrogenase and ethanol) of the product, NAD^+ , back to NADH.

In an elegant study, Nadjo used both stopped-flow¹²³ and electrochemical (double potential step chronocoulometry, DPSC)¹²⁴ methods to explore the kinetics of oxidation of NADH by a series of mixed-addenda Wells-Dawson anions. The reduction potentials of the heteropolyanions studied spanned a range of $\sim 250 \text{ mV}$: $\alpha_2 - [\text{P}_2\text{Mo}^{\text{VI}}\text{W}_{17}\text{O}_{62}]^{6-}$ ($E^\circ = +466 \text{ mV}$ vs NHE), $[\text{P}_2\text{V}_2\text{W}_{16}\text{O}_{62}]^{8-}$ ($+519 \text{ mV}$), $\alpha_2 - [\text{P}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ ($+634 \text{ mV}$), $\alpha_1 - [\text{P}_2\text{Mo}^{\text{VI}}\text{W}_{17}\text{O}_{62}]^{6-}$ ($+637 \text{ mV}$), and $\alpha_1 - [\text{P}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ ($+719 \text{ mV}$). In both studies, 1-e⁻ reduction of the Wells-Dawson anions was observed and the stoichiometry shown in eq 66 obeyed. The reactions were first order in POM and in NADH.

For the set of reactions studied, the straight line ($R = 0.999\,987$) obtained by plotting $\log k$ (k = bimolecular rate constant) vs E° (reduction potential of each POM anion) had a slope of $+16.4 \text{ V}^{-1}$ (Figure 5; see section II.D).

In theory, for a series of endergonic electron-transfer reactions in which electron transfer within encounter complexes is reversible and where the rates of back-electron transfer compete effectively with dissociation of the successor complexes, the plot of $\log k$ vs E° (E° = anodic potential or reduction potential of an oxidant) should give a straight line with a slope equal to $+16.6 \text{ V}^{-1}$ (see eq 34 in section

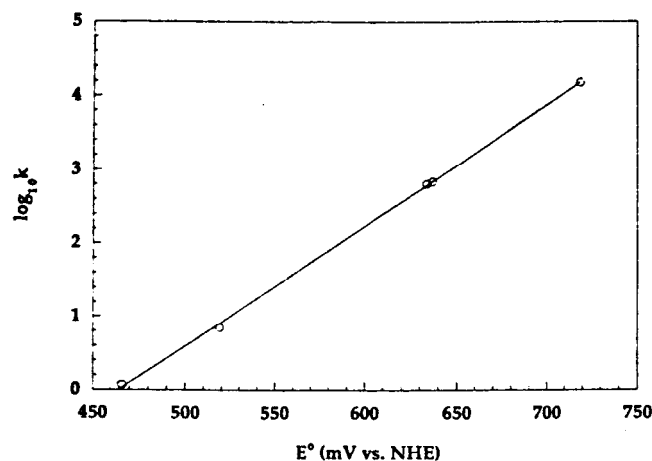
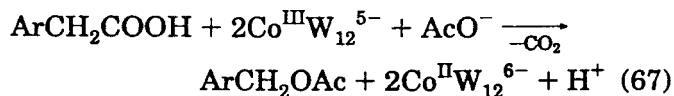


Figure 5. Plot of $\log k$ vs E° (reduction potential vs NHE of each POM anion) for the oxidation of NADH by mixed-addenda (V(V)- and Mo(VI)-substituted) Wells-Dawson tungstophosphate anions.

II.D). As described in section II.D, the bimolecular rate constant, k , can be described as the product $k = K_1 K_{et} k_3$, where K_1 = the equilibrium constant for formation of the encounter complex, K_{et} = equilibrium constant for electron transfer within the encounter complex, and k_3 is the rate of dissociation of the successor complex. Therefore, the observed slope (16.4 V^{-1}) provided strong evidence that separation of the radical ion pair was the rate-determining step; that the reaction was thus under thermodynamic control (i.e., dictated by K_{et} , which is equal to k_{fet}/k_{ret}), and that oxidation step (k_{fet}) involved 1-e- oxidation of NADH to the radical cation $\text{NADH}^{+\cdot}$. By extrapolation to an estimated diffusion-rate-limited value of $\ln k$ (from the plot of $\log k$ vs E° , Figure 5), the potential of the $\text{NADH}^{+\cdot}/\text{NADH}$ couple was calculated. Close agreement between their experimental value, $E^\circ = 1.05 \text{ V}$ (NHE), and one literature value (1.00 V) provided satisfying closure to this study.

C. Organic Acids, Esters, Aldehydes, and

The oxidation of arylacetic acids by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and $[\text{Ni}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ ($\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$) was reported by Jönsson in 1983.⁹⁸ The reaction between $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ or $\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$ and arylacetic acids in refluxing acetic acid, in the presence of 0.5 M KOAc and acetic anhydride, resulted in the formation of benzyl acetates in greater than 80% yields:



Arylacetic acids studied and relative rates of oxidation by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and $\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$ are shown in Table 5.

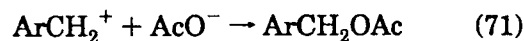
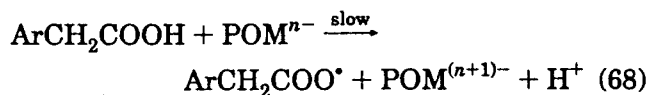
log-log plot of the rate data in Table 5 gave a linear correlation of 0.97, indicative of similar rate-limiting steps when oxidized by either anion. This was significant considering that $\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$ is rapidly and irreversibly reduced by two electrons, while multiple-electron reductions of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ are reversible, and 1-e- reduction of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ to $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$

Table 5. Relative Rates of Oxidation of Substituted Arylacetic Acids by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and $\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$ in Acetic Acid/KOAc

substituent	relative rate	
	$\text{Co}^{\text{III}}\text{W}_{12}^{5-}$	$\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$
<i>p</i> -OCH ₃	2200 ± 500	44.6 ± 1
<i>m</i> -OCH ₃	69.4 ± 4	7.1 ± 0.2
<i>p</i> -Ph	14.8 ± 3	2.6 ± 0.1
<i>p</i> -CH ₃	2.00 ± 0.08	1.95 ± 0.02
<i>m</i> -CH ₃	1.28 ± 0.05	1.15 ± 0.02
H	1.00	1.00
<i>p</i> -Cl	0.36 ± 0.05	1.00 ± 0.02
<i>m</i> -Cl	0.25 ± 0.04	0.55 ± 0.05

occurs at a substantially more positive potential than those associated with the reduction of $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ to $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}$ or $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{8-}$.^{52,88,99} In addition, good Hammett correlations were found for all but the methoxy-substituted compounds, which reacted more rapidly. For oxidations by $\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$, and excluding the methoxy-substituted derivatives, a Hammett r value of -1.71 was calculated, and for $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$, a r of -0.77 . Both values were reported to be in range for a process involving rate-limiting formation of a benzyl radical ($r = -1.5$ to -0.31).

In addition, good correlations (log-log plots) of the rates of oxidation by $\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$ (again excluding the methoxy-substituted derivatives) with the relative rates of decarboxylation of the same set of substrates by three other oxidants— $\text{Co}^{\text{III}}(\text{OAc})_3$, $\text{Cu}(\text{III})$, and $\text{Ce}(\text{IV})$ —suggested similar mechanisms. In oxidations by $\text{Ce}(\text{IV})$, rate-limiting decomposition of metalorganic intermediates $[\text{ArCH}_2\text{CO}_2\text{Ce}^{2\text{IV}}]^{3+}$ were proposed.¹²⁵ Jönsson, however, on the assumption that $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and $\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$ acted exclusively as outer-sphere oxidants, proposed that both POM-oxidation reactions proceeded via outer-sphere oxidation of the carboxylic acid group (eqs 68–71).

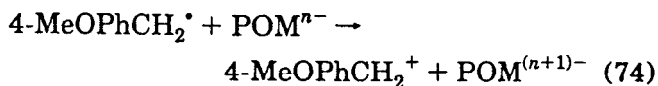
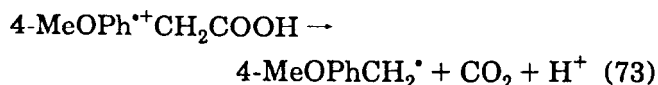
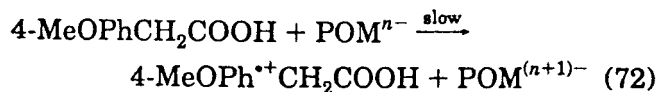


This mechanism is analogous to that seen in the anodic oxidation of carboxylic acids (Kolbe mechanism): Electron transfer from the carboxylic acid group is followed, after loss of CO_2 , by oxidation of the benzylic radical.

The assumption that oxidation by $\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$ occurred via an outer-sphere mechanism may have been incorrect. In related work,¹²⁶ Jönsson observed very similar behavior to that of $\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$ ($r = -1.71$) when a series of arylacetic acids were oxidized by $\text{Cu}(\text{III})$ in refluxing acetic acid (a r value of -1.4 for arylacetic acids with less electron-donating substituents and unusually rapid rates of oxidation of methoxy-substituted derivatives). An inner-sphere mechanism involving intermediate $[\text{ArCH}_2\text{CO}_2\text{Cu}^{\text{III}}]^{2+}$ complexes was proposed. The results obtained using

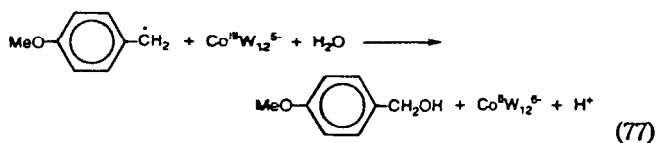
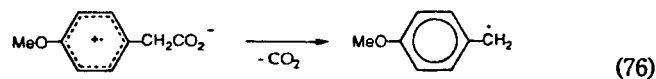
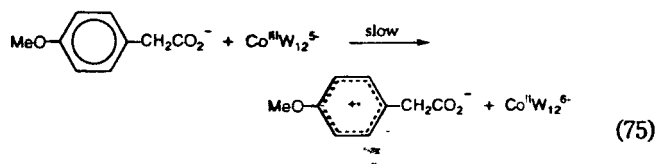
$\text{Ni}^{\text{IV}}\text{Mo}_9^{6-}$ did not clearly exclude rate-limiting decomposition of related inner-sphere complexes.

The unusually rapid rate of oxidation of the *r*-methoxy-substituted derivative was attributed to an alternative mechanism: direct oxidation of the electron-rich aromatic moiety to a radical cation, followed by loss of carbon dioxide and a proton, giving a benzylic radical that was further oxidized to the cation (eqs 72–74).



Trahanovsky¹²⁵ had previously attributed unusually rapid rates of oxidation of methoxy-substituted arylacetic acids by $\text{Ce}(\text{IV})$ to a like mechanism.¹²⁶

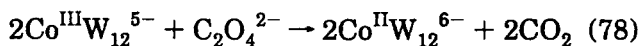
In 1996, Bietti, Baciocchi, and Engberts returned to the oxidation of *r*-methoxyphenyl acetate by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ to study the effects of solvent composition on reaction rate.¹²⁷ On the basis of a theoretical model developed by Engberts for the quantitative analysis of medium effects on reaction rates in highly aqueous binary solvents,¹²⁸ the rate of oxidation of the *r*-methoxyphenyl acetate anion ($\text{KH}_2\text{PO}_4/\text{KNaHPO}_4$ buffer at pH 7.4 in water) was measured as a function of added alcohol (0–3 mol % ROH; R = Me, Et, *n*-Pr, *n*-Bu, *t*-Bu, or CF_3H_2) concentration. Kinetic data were consistent with the mechanism shown in eqs 75–77 and even at low concentrations, all of the alcohols induced large decreases in reaction rates. For example, the rate constant in 1.5 molal (*m*) 1-propanol (91.5 g of 1-propanol per kilogram of solvent mixture or ~3 mol % ROH) was ~27% of that in water.



As predicted, plots of $-\ln(k_m/k_w)$ vs *m* of added alcohol (k_m = rate constant in the presence of *m* molal alcohol; k_w = rate constant in buffered water alone) were linear. According to Engbert's model, the slope of each line was proportional to the difference between the pairwise Gibbs energies associated with the 1:1 interaction of added alcohol with initial vs

transition states of the reaction. The results demonstrated that the rate of the outer-sphere electron-transfer step (eq 75) was highly sensitive to low concentrations of added solutes (in this case alcohols) capable of forming 1:1 encounter complexes. In addition, greater rate retardation was observed as the number of methylene groups in the alkyl side chain of the added alcohol increased. This was interpreted as indicating a loss of hydrophobicity in the transition state, relative to that of the initial state, of the reaction.

Banejee and colleagues, in a carefully executed study, provided clear evidence for the formation of stable ternary (donor- M^+ -acceptor, M = alkali-metal cation) complexes prior to electron transfer in the oxidative decarboxylation of aliphatic organic acids by aqueous $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ in solutions of very high ionic strengths ($\mu = 1\text{--}2$ M added electrolyte). (Electron-exchange and electron-transfer reactions of heteropolyanions were reviewed by Saha, Ali, and Banerjee in 1993.)¹²⁹ Oxidations of oxalate,¹³⁰ formate,¹³¹ citric acid,¹³² and a variety of amine-*N*-carboxylates (iminodiacetate, nitrilotriacetate, and ethylenediaminetetraacetic acid, H_4edta)¹³³ and histidine¹³⁴ were studied. In each case, due attention was paid to the effects of pH, ionic strength, and added alkali-metal cations (K^+ , Na^+ , and Li^+) or anions (ClO_4^- , SO_4^{2-} , and NO_3^-). Indicative of the care exercised in these studies was the measurement of rate constants for both uncatalyzed and alkali-metal cation catalyzed oxidations of H_4edta as a function of pH (i.e., rate constants for oxidations of H_4edta , H_3edta^- , $\text{H}_2\text{edta}^{2-}$, and Hedta^{3-}).¹³³ Progress of reaction was measured spectrophotometrically by observation of $\text{Co}(\text{III})$ ($I_{\text{max}} = 388$ nm) and/or $\text{Co}(\text{II})$ ($I_{\text{max}} = 625$ nm), and 2:1 reaction stoichiometries (i.e., $2\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ per equivalent of organic acid) were observed in each case (cf., oxidation of oxalate, eq 78).



Well-defined isosbestic points in the time-dependent visible spectra of reaction mixtures argued against the accumulation of appreciable amounts of reaction intermediates. The intermediacy of organic radicals in the multistep reactions was demonstrated by the polymerization of acrylonitrile, which occurred only when all components of the reaction were present. Reactions were carried out under pseudo-first-order conditions using submillimolar concentrations of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and 100- to 500-fold excesses of organic acids.

The oxidation of oxalate was studied at ~1 M ionic strength. First-order dependence of reaction rates on $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and oxalate concentrations (pH = 5) suggested a rate law of the form

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt}{2} = k[\text{Co}^{\text{III}}\text{W}_{12}^{5-}][\text{C}_2\text{O}_4^{2-}] \quad (79)$$

Setting $k_1 = k[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$ gave

$$-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt = 2k_1[\text{C}_2\text{O}_4^{2-}] \quad (80)$$

Measurement of reaction rate, $-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt$, as a function of added K^+ revealed a linear dependence of k_1 on $[\text{K}^+]$:

$$-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt = 2(k_0 + k'[\text{K}^+])[\text{C}_2\text{O}_4^{2-}] \quad (81)$$

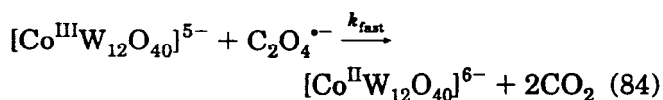
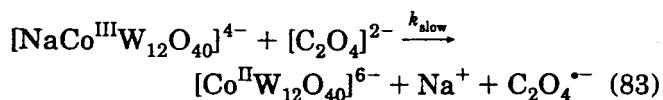
At 30 °C, values of $k_0 = 12.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ and $k' = 10.2 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ were obtained. These values were typical (within a few orders of magnitude) of those found for catalyzed and uncatalyzed oxidations of a variety of acids and their conjugate bases.^{130–134} Similar results were obtained for HC_2O_4^- at pH 1.32. Catalysis by alkali-metal cations followed the order $\text{K}^+ > \text{Na}^+ > \text{Li}^+$, while neither the nature of the anions present (ClO_4^- , SO_4^{2-} , or NO_3^-) nor changes in ionic strength at constant alkali-metal cation concentrations, had significant effects on reaction rates. In catalysis of the oxidation of HC_2O_4^- by Na^+ , a second-order dependence on $[\text{Na}^+]$ was observed:

$$-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt = 2(k_0 + k'[\text{Na}^+]^2)[\text{HC}_2\text{O}_4^{2-}] \quad (82)$$

Inverse relationships between reaction rates and $[\text{H}^+]$ were quantitatively correlated with the pK_a values for acid dissociation of oxalic acid and qualitatively rationalized in term of the effect of protonation state on the oxidation potential of $\text{C}_2\text{O}_4^{2-}$.

A lack of dependence of reaction rate on ionic strength ruled out an effect of ionic strength on Coulombic work terms (eqs 1 and 36) as a source of the rate enhancement. Moreover, the strictly linear or second-order dependencies of reaction rates on alkali-metal cation concentrations suggested that ternary complex formation (section II.D), rather than ion pairing alone (i.e., $[(\text{M}^+)(\text{POM}^{n-})]^{(n-1)-}$, M = alkali metal; section II.C), was responsible for the observed rate enhancements. Additional evidence for ternary complex formation was provided by variable temperature studies of the uncatalyzed and Na^+ -catalyzed oxidations of formate anion.¹³¹ Reductions in ΔH^\ddagger values associated with Na^+ catalysis (from $\Delta H^\ddagger = 35$ to $\Delta H^\ddagger = 24 \text{ kcal mol}^{-1}$) were too large to be accounted for by M^+ -POM ion pairing alone (i.e., by changes in effective charge products, $z_1 z_2$ (eq 1)).

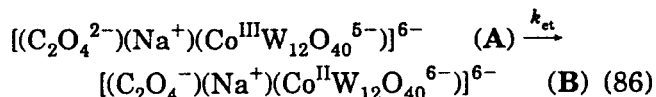
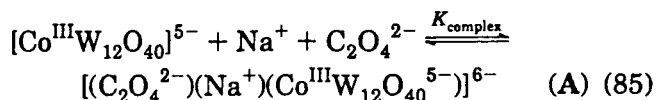
In the case of Na^+ -catalysis of oxalate ($\text{C}_2\text{O}_4^{2-}$) oxidation, the following reaction mechanism was suggested:



An activated complex of the form $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-} \cdots \text{Na}^+ \cdots \text{C}_2\text{O}_4^{2-}]$, in which the Na^+ cation acted as a bridge, was proposed for the rate-limiting step (eq 83). More conservatively, the kinetic data suggested that ternary complexes, of indeterminate structure

and probably held together by electrostatic forces, formed prior to electron transfer.

Alternatively, the elementary steps leading to reduction of the first equivalent of $\text{Co}(\text{III})$ might have been depicted more explicitly in terms of an equilibrium constant for ternary complex formation, K_{complex} (M^{-2}), and a unimolecular rate constant for intramolecular electron transfer, k_{et} (s^{-1}) (waters of hydration have been ignored):

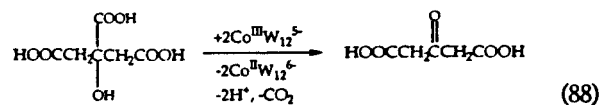


Spontaneous self-assembly of the ternary complex anion, A, which exists in solution at concentrations dictated by the formation constant, K_{complex} , is followed by intramolecular electron-transfer associated with the unimolecular rate constant, k_{et} (see section II.D). First-order dependence of absorbance on $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$ suggests that dissociation of the $\text{Co}(\text{II})$ complex, B, occurred prior to rapid oxidation of the oxalate radical anion, $\text{C}_2\text{O}_4^{\bullet -}$, by a second equivalent of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$. (This was not the case in the Na^+ -catalyzed oxidation of formate,¹³¹ in which second-order dependence of absorbance on the concentration of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ suggested that formate-radical anions in complexes analogous to B might have been oxidized by a second equivalent of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ prior to dissociation into component species.) The rate expression for oxidation of oxalate by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ might thus have been expressed as the product:

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt}{2} = K_{\text{complex}} k_{\text{et}} [\text{Co}^{\text{III}}\text{W}_{12}^{5-}] [\text{C}_2\text{O}_4^{2-}] [\text{Na}^+] \quad (87)$$

Although this expression has the same form as those used by Sutin to describe outer-sphere electron-transfer processes (section II.B.2, eq 10), the equilibrium constant, K_{complex} , in eq 87 refers to the formation of a stable ternary complex (section II.D).

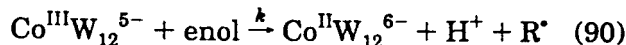
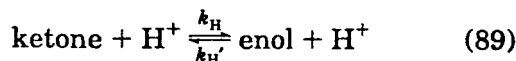
Linear or second-order dependences of rates on alkali-metal cation concentrations ($\text{K}^+ > \text{Na}^+ > \text{Li}^+$) were also observed in the oxidation of citrate,¹³² iminodiacetate, nitrilotriacetate, ethylenediamine-tetraacetic acid (H_4edta),^{133,135,136} *N*-(2-hydroxyethyl)-ethylenediamine triacetate,¹³⁷ α -hydroxyacids (mandelic, lactic, and glycolic),¹³⁸ and histidine¹³⁴ at high ionic strengths. In the 2- e^- oxidation of citric acid at high ionic strengths (eq 88), limiting dependences



of rates on citrate anion (H_2A^- , HA^{2-} , and A^{3-}) concentrations at very high citrate anion to $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ ratios (i.e., saturation kinetics) provided additional

evidence for the formation of donor-acceptor complexes prior to electron transfer.

In the oxidation of cyclohexanone, 2-butanone, and 1,3-dihydroxy-2-propanone by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ at high ionic strengths (0.5–1.0 M Na^+), the reaction was first-order in oxidant at high $[\text{H}^+]$ (0.30–0.40 M HClO_4) and low $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$ (0.1–0.2 mM) but zeroth-order in oxidant at low $[\text{H}^+]$ (0.02–0.0006 M) and high $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$ (5.0 mM).¹³⁹ These data were consistent with a mechanism in which acid-catalyzed enolization occurred prior to oxidation by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ (eqs 89 and 90; R^{\bullet} is an enolyl radical).



Assuming $-d[\text{enol}]/dt = 0$ (steady state in $[\text{enol}]$) and that the enolyl radical formed in eq 90 was oxidized rapidly by a second equivalent of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$, the following rate expression was derived:

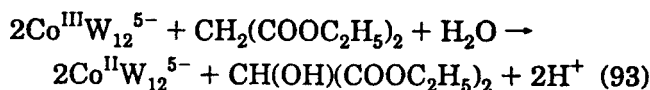
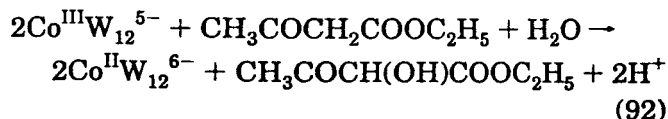
$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt}{2} = \frac{k_{\text{H}}k[\text{ketone}][\text{Co}^{\text{III}}\text{W}_{12}^{5-}][\text{H}^+]}{k_{\text{H}}'[\text{H}^+] + k[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]} \quad (91)$$

Under conditions at which enolization was rate limiting (zeroth order in $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$), reaction rates were independent of $[\text{Na}^+]$. Catalysis by alkali-metal cations was not investigated under conditions at which reaction rates exhibited a pseudo-first-order dependence on $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$.

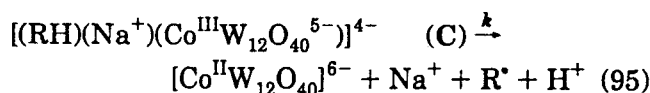
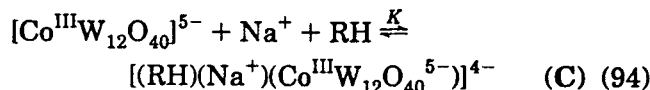
Unable to correlate reaction rates with those predicted by Marcus theory, it was proposed that "since the central $[\text{Co}]$ ions are surrounded by WO_4 octahedra rather than by oxygen atoms, the transfer of electrons across the octahedra may not be equivalent to transfer in simple oxo-anions". This proposal was originally set forth by Rasmussen and Brubaker to account for lower-than-theoretical rates of electron self-exchange between $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ (see section III.C).⁵

However, in calculating the thermodynamic driving force (ΔG° or E°) for the reaction, Banerjee and coauthors chose a value for the reduction potential of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ (1.0 V vs NHE) that was not applicable⁵² at the ionic strengths used. More generally, failure to observe correlations between Marcus theory and rates of oxidation of ketones by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ were likely due to ion pairing, complex formation, and related phenomena (see sections II.C and D), rather than to a unique property of the $[\text{W}_{12}\text{O}_{40}]^{8-}$ ligand.

In the oxidation of simple esters (ethyl acetate, eq 92; diethyl malonate, eq 93) by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ under acidic conditions at high ionic strengths, no evidence was found for rate-limiting keto-enol tautomerization.¹⁴⁰

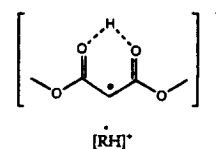


The reaction was first order in $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$ over a range of pH values, throughout which an inverse dependence on $[\text{H}^+]$ was observed. Specific alkali-metal cation catalysis was observed as well, but in an unexpected order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. For the Na^+ -catalyzed reaction, the following elementary steps and rate expression were proposed (RH = ethyl ester):



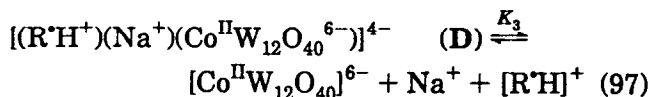
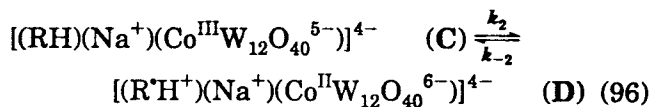
Inverse dependence on $[\text{H}^+]$ was tentatively attributed to stabilization of the free radicals, R^{\bullet} (Chart 2). It was proposed that stabilization of these intermediates increased the rate of the reverse path of the rate-determining step (eq 95).

Chart 2. H^+ -Stabilized Ethyl Ester Radical Intermediates

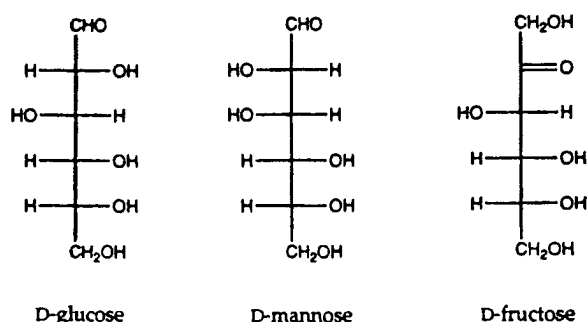
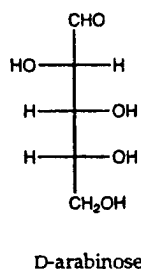


The unusual order of the alkali-metal cation dependence was tentatively attributed to ion-induced dipole interactions exerted by the alkali-metal cation on the neutral ester (RH in the ternary complex, **C**, eq 95). Thus, the poorer the cation at inducing positive charge in the neutral ester ($\text{Li}^+ < \text{Na}^+ < \text{K}^+$), the more easily and rapidly the neutral ester was oxidized.

However, the order of tetraalkylammonium and alkali-metal cation catalysis in the reduction of organic substrates by $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ is opposite¹⁴¹ to that observed in oxidations by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$. Hence, if the oxidation of RH to $[\text{R}^{\bullet}\text{H}]^+$ was in fact reversible, the observed order of alkali-metal cation catalysis might simply have reflected the effect of ion pairing on the rate of reduction of $[\text{R}^{\bullet}\text{H}]^+$ by $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ in **D** (k_{-2} and the ratio k_2/k_{-2} , eq 96; eq 97 is added for completeness, although other elementary steps are possible).



Catalysis by alkali-metal cations, rate-limiting acid-catalyzed enolization, and second-order depen-

Chart 3. Structures of D-Glucose, D-Mannose, and D-Fructose**Chart 4. Structure of D-Arabinose**

dence of reaction rates on $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$ were observed in the oxidation of D-glucose (Glu), D-mannose (Man), and D-fructose (Fru) (Chart 3).¹⁴²

Reactions were carried out under pseudo-first-order conditions ($[\text{Co}^{\text{III}}\text{W}_{12}^{5-}] = 0.2 \text{ mM}$ and $[\text{sugar}] = 800 \text{ mM}$) at low pH values ($[\text{H}^+] = 0.05\text{--}1.00 \text{ M}$, HClO_4 or HNO_3) and at high ionic strengths ($\mu = \sim 1.0 \text{ M}$, NaClO_4). At 60°C , 2 equiv of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ were reduced by each equivalent of sugar, and the oxidations of Glu and Man gave arabinose (Chart 4). The oxidation of Fru gave a mixture of products, including arabinose.

Kinetic data were summarized by the following experimental rate laws ($M = \text{alkali-metal cation}$):

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt}{2} = k[\text{H}^+][\text{Fru}] \quad (98)$$

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt}{2} = (k + k'[\text{M}^+])[\text{sugar}][\text{Co}^{\text{III}}\text{W}_{12}^{5-}]^2 \quad (99)$$

For Glu, n was equal to 1 for K^+ and 2 for Na^+ and Li^+ ; for Man, n was equal to 1 for K^+ and Na^+ and 2 for Li^+ . Rate constants for the uncatalyzed reactions ranged from $\sim 10^{-1}$ to 10^1 (variable units) with values of k' in the same range and generally somewhat smaller than corresponding values of k . With characteristic attention to detail, the authors noted that the rate of mutarotation between α and β anomeric forms of Glu was fast relative to the rate of oxidation by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$.

The rate laws determined by Banerjee suggested extensive ion pairing and the formation of donor-acceptor complexes, the latter involving both unoxidized sugars and radical intermediates. Given the care and attention to detail obvious in Banerjee's work, his evidence for the presence of these phenomena must be regarded as highly reliable. It is hoped that he and his colleagues might be provided with

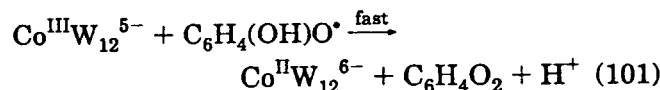
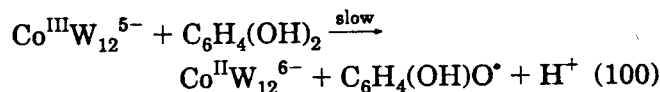
the opportunity and facilities needed to obtain further information, such as would be required to better define the extent of ion pairing, the nature of the donor-acceptor complexes, the rate of intramolecular electron transfer within these and related complexes, and the possible role of atom (H^\bullet) transfer in rate-determining oxidation steps (kinetic isotope effects).¹⁴³

D. Aromatic and Aliphatic Alcohols

The large and growing number of examples of homogeneous oxidations of phenols and related compounds by vanadium-containing mixed-addenda heteropolymolybdate anions, mostly of the Keggin-structural type $(\text{H}_{3+n}[\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}])$, $n = 1\text{--}6$ have been adequately reviewed.

Limited evidence for both outer-sphere¹⁴⁶ and multiple-electron-transfer mechanisms^{114,145} has been reported. In the oxidation of a series of alkylated phenols by $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$, Lissel et al.¹⁴⁶ observed a strong dependence of percent conversions on E° values of the phenolic substrates. On this basis, an electron-transfer mechanism was proposed. In the oxidation of phenols by mixed-addenda vanadomolybdophosphate complexes, $\text{H}_{3+n}[\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}]$, products of 1- and 2- e^- oxidations were observed and complex mechanisms, involving dissociation of V(V) ions, proposed.¹⁴⁷⁻¹⁴⁹

In 1977 Amjad, Brodovitch, and McAuley⁷⁶ studied the oxidation of L-ascorbic acid, hydroquinone, and catechol ($0.7\text{--}1.5 \text{ mM}$) by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ ($0.1\text{--}0.45 \text{ mM}$) at low pH values ($[\text{HClO}_4] = 0.04\text{--}1.0 \text{ M}$) and high ionic strength ($\mu = 1.0 \text{ M}$, LiClO_4) using a stopped-flow apparatus. Under pseudo-first-order conditions, the reactions were first order in $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$ and in $[\text{alcohol}]$, and reaction stoichiometries of 2:1 $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ to alcohol suggested the formation of quinonoid products. For hydroquinone and catechol, no $[\text{H}^+]$ dependence was observed over the pH range used, and the proposed mechanism involved rate-limiting oxidation followed by loss of a proton:



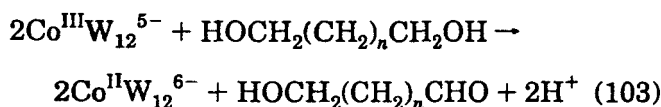
In the oxidation of L-ascorbic acid (H_2A), an inverse dependence of rate on $[\text{H}^+]$ gave an experimental rate expression that included the parallel oxidation of both diprotic (H_2A) and monoprotic (HA^-) forms of the acid:

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt}{2} = \frac{(k + k'K_a[\text{H}^+]^{-1})[\text{Co}^{\text{III}}\text{W}_{12}^{5-}][\text{H}_2\text{A}]}{(1 + K_a[\text{H}^+]^{-1})} \quad (102)$$

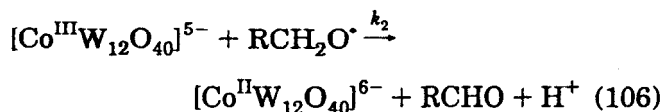
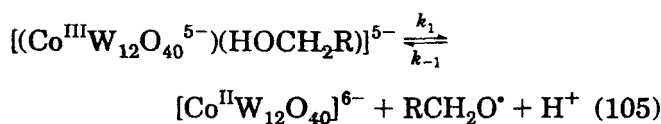
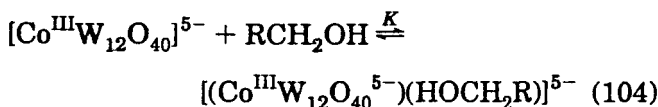
Comparison of experimental rate constants with those predicted by Marcus gave only qualitative agreement. (A value of 1 for the $\text{Co}^{\text{III}}\text{W}_{12}^{5-}/\text{Co}^{\text{II}}\text{W}_{12}^{6-}$

self-exchange reaction of $61.4 \text{ kcal mol}^{-1}$ was used. This value was obtained by extrapolating to $\mu = 1.0 \text{ M}$, using data published by Rasmussen and Brubaker;⁵ see section III.C.) More fundamentally, kinetic isotope effects, which might have clarified the nature of the e^-/H^+ -transfer step, were not performed. In addition, neither the dependence of reaction rate on ionic strength nor on the nature of the alkali-metal cation present were investigated. Hence, the proposed mechanism (eqs 100 and 101), while consistent with the experimental rate law, may be overly simple.

The oxidation of aliphatic alcohols (butane-1,3-diol, butane-1,4-diol, and pentane-1,5-diol; $0.3\text{--}1.5 \text{ M}$ in each) by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ (0.0002 M , pseudo-first-order in diol) at very high ionic strength ($\mu = 2.0 \text{ M}$, NaClO_4) was investigated by Olatunji and Ayoko over a $[\text{H}^+]$ range of from 0.75 to 1.75 M , using an initial rate method.¹⁵⁰ Reaction of butane-1,3-diol was immeasurably slow. The 1,4- and 1,5-diols, however, were oxidized by two electrons to 4- and 5-hydroxy aldehydes (eq 103; $n = 2$ or 3):



The rate of oxidation of butane-1,4-diol was independent of $[\text{H}^+]$ and first order in both oxidant and diol. The proposed mechanism included equilibrium formation of a donor-acceptor complex, followed by reversible, rate-limiting electron transfer:



Assuming a steady-state concentration of the donor-acceptor complex (eq 104) and that $k_2[\text{Co}^{\text{III}}\text{W}_{12}^{5-}] \gg k_{-1}[\text{Co}^{\text{III}}\text{W}_{12}^{5-}][\text{H}^+]$, the rate expression derived from the proposed mechanism gave the experimentally observed rate law

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt}{2} = k[\text{Co}^{\text{III}}\text{W}_{12}^{5-}][\text{RCH}_2\text{OH}] \quad (107)$$

Although the proposed mechanism (eqs 104–106) reasonably suggested complexity beyond that needed to account for the experimentally observed rate law, no evidence for ion-pair formation or for association (donor-acceptor) complex formation was provided. In addition, one reviewer has pointed out that, because aliphatic alcohols have very high oxidation potentials

(> 3 V), outer-sphere oxidation to the corresponding alkoxy radical (eq 105) is unlikely to occur.

The oxidation of pentane-1,5-diol exhibited a first-order dependence on $[\text{H}^+]$ and second-order dependence on $[\text{HOCH}_2(\text{CH}_2)_3\text{CH}_2\text{OH}]$. A set of elementary steps, which included donor-acceptor complex formation and which was consistent with the observed participation of water in the rate-limiting step, was proposed. Appropriate approximations gave a rate expression consistent with the kinetic data:

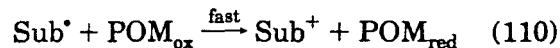
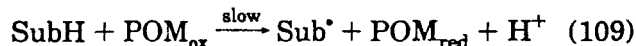
$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt}{2} = k'K[\text{Co}^{\text{III}}\text{W}_{12}^{5-}][\text{R}'\text{CH}_2\text{OH}]^2[\text{H}^+] \quad (108)$$

The lack of reactivity of the butane-1,3-diol and mechanistic divergence between the 1,4- and 1,5-diols, were rationalized by a suggestion that the “1,3 and 1,4 diols may...involve a chelate type complex in the transition state in which the two hydroxyl groups are closely associated with the oxidant through one of the tungsten atoms” and that such a transition state was less likely for the larger 1,5-diol. Considering the kinetic stability of the tungsten-oxygen bonds in heteropolytungstates and the lack of an available coordination site on octahedral W(VI) , hydrogen bonding between two hydroxyl hydrogen of the diol and two $\mu\text{-}2 \text{ W-O-W}$ oxygens of $[\text{CoW}_{12}\text{O}_{40}]^{5-}$ is a more reasonable proposal.

Banerjee¹²⁹ has pointed out that the specifics of Olatunji's proposal were unsupported by experimental data. Nonetheless, the experimental rate law determined for the oxidation of pentane-1,5-diol did suggest a complex, multistep reaction mechanism that may have differed in some fundamental way from that operative in the oxidation of butane-1,4-diol. Comparison of kinetic results obtained in the oxidation of the 1,3-, 1,4, and 1,5-diols suggested that the bifunctional nature of these substrates had mechanistic consequences.

E. Carbon-Centered Organic Radicals

In the (overall) 2-e^- oxidation of organic substrates (subH) by 2 equiv of oxidized POM anions (POM_{ox} , eqs 109 and 110) the second electron-transfer step (oxidation of radical intermediates, eq 110) is usually assumed to occur very rapidly.



In a series of detailed studies involving POM oxidations of a variety of organic radicals generated by continuous and pulse radiolysis, Papaconstantinou,^{151–155} working in Athens, Greece, single-handedly proved this assumption correct.

In an initial study, Papaconstantinou investigated the rate of reduction of aqueous Keggin and Wells-Dawson heteropolytungstate and molybdate anions ($[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, and $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$) under conditions of continuous exposure to ^{60}Co γ -radiation.¹⁵¹ The irradiation reactions were carried out

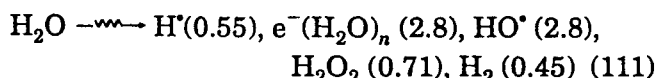
Table 6. Second-Order Rate Constants for the 1-e⁻ Reductions of Heteropolytungstate Anions by Hydroxyalkyl and Carboxyl Radicals

radical	$k/10^9 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$			
	$[\text{PW}_{12}\text{O}_{40}]^{3-}$ (+0.218 V) ^a	$[\text{SiW}_{12}\text{O}_{40}]^{4-}$ (+0.054 V)	$[\text{FeW}_{12}\text{O}_{40}]^{5-}$ (-0.108 V)	$[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ (-0.340 V)
•CO ₂ H	2.96	0.64	0.40	0.12
•CO ₂ ^{-b}	c	0.84	0.17	0.011
•CH ₂ OH	2.2	0.91	0.22	≤0.013
CH ₃ C•HOH	5.9	3.8	2.0	0.35
(CH ₃) ₂ C•OH	7.6	5.3	4.5	1.3

^a One-electron reduction potentials vs NHE; converted from SCE values by addition of 0.2412 V. ^b All reactions carried out at pH values of 5–6, well above the pK_a (1.4) of •CO₂H. ^c No data obtained; the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion is unstable at pH values greater than ~1.2.

in the presence of O₂, Ar, N₂O, several alcohols, and formic acid and over a pH range of ~1–4.

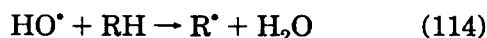
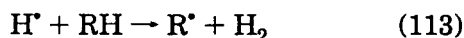
The radiolysis of water gives a number of products (eq 111); numbers in parentheses (*G* values) indicate the number of species, of the indicated type, produced for each 100 eV of radiation energy absorbed by water.



In solutions deaerated with Ar at pH ≈ 1, solvated electrons, e⁻(H₂O)_n, react rapidly with H⁺ ions to give hydrogen atoms, H[•]. At pH values of ~3–4 in solutions deaerated using N₂O, the aqueous-solvated electrons are rapidly consumed in the stoichiometric production of HO[•] radicals:



In the presence of excess organic alcohols or formic acid—MeOH, EtOH, *n*-PrOH, *i*-PrOH, or HCOOH (RH, eqs 113 and 114)—either set of reaction conditions gives the corresponding carbon-centered radicals (R[•], where R = CH₂OH, etc.).¹⁵¹ However,



oxidation of RH by HO[•] (eq 114, $k = 10^8\text{--}10^9 \text{ M}^{-1} \text{ s}^{-1}$) is ~100 times more rapid than oxidation by H[•] (eq 113).

Plots of absorbance of the reduced (heteropoly blue) anions vs time, from spectroscopic data obtained during conditions of continuous ⁶⁰Co-*I*-irradiation of aqueous solutions of POM anions and alcohols or formic acid (15 POM:RH combinations in total), were consistently linear. While the tungstophosphates were each reduced by one electron, only 2-e⁻-reduced $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{8-}$ was observed. This result was attributed to rapid disproportionation of 1-e⁻-reduced $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{7-}$ anions (see below). On the basis of dosimetric analysis; the sum of the *G* values associated with the radiolytic formation of e⁻, H[•], and HO[•]; and the extinction coefficients of the heteropoly blue species, it was calculated that the reactions (from radiolysis to POM reduction) were 100% efficient. The zero-order kinetics (linear plots of absorbance, measured at 2-min intervals, vs time) were attributed to

the near-diffusion-controlled rates and 100% efficiencies of the electron-transfer reactions leading from radiolysis to POM reduction.

The potentials associated with successive stepwise reductions of many POM anions are easily measured by electrochemical methods. Making use of this thermodynamic data, Papaconstantinou used heteropolytungstates and heteropolymolybdates to determine the apparent reduction potentials of several radiolytically generated hydroxyalkyl and carboxyl radicals.¹⁵² For each type of radical generated by continuous ⁶⁰Co-*I*-irradiation, reduction of the heteropoly blue continued until the potential of its next reduction step was more negative than the reduction potential of the radical. Hence, the reduction potential of each radical was estimated by measuring the degree-of-reduction of the heteropoly blue formed in its presence.

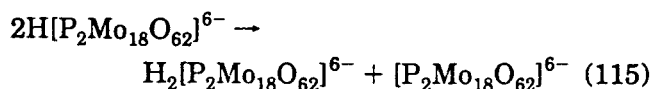
To obtain kinetic data pertaining to the near-diffusion-controlled rate constants for reduction of POM anions by alkyl radicals, a rapid pulse-radiolysis technique was required. With the use of 30 ns pulses of a 2.3 MeV electron beam to irradiate aqueous solutions containing POM anions and simple alcohols, formic acid, or formate, second-order rate constants were determined from oscilloscope traces of the absorbance-formation kinetics of the 1-e⁻-reduced POM anions (Table 6).¹⁵⁶

Although the rates of most of the reactions were substantially diffusion controlled, clear trends were evident: For each POM anion, rates of reduction by the hydroxyalkyl radicals increased in the order of their electron-donating abilities, •CH₂OH < CH₃C•HOH < (CH₃)₂C•OH; rates of reaction decreased as the reduction potentials of the POM anions moved to more negative (less thermodynamically favorable) values.

Additional factors were evident in the carboxyl radical reactions.¹⁵⁵ As in reduction of the POM anions by the hydroxyalkyl radicals, reaction rates decreased as the reduction potentials of the POM anions became more negative, and reduction of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ by •CO₂H was slower than reduction by the more electron donating alkyl radical, •CO₂⁻. However, as the negative charge of the POM_{ox} anion increased, the rates of 1-e⁻ reduction by •CO₂⁻ dropped more rapidly than did those observed for 1-e⁻ reduction by •CO₂H. In fact, when generated in the presence of the highly negatively charged anions $[\text{FeW}_{12}\text{O}_{40}]^{5-}$ and $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$, the more electron-

donating radical $\bullet\text{CO}_2^-$ reacted more slowly than did $\bullet\text{CO}_2\text{H}$. This effect, attributed to repulsion between the negatively charged radical, $\bullet\text{CO}_2^-$, and the POM anions, was consistent with the likely outer-sphere nature of these electron-transfer reactions.

Whereas 1-e^- reductions of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and other tungstates are well resolved by electrochemical methods, only 2-e^- reduction steps are observed for $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$. Using pulse radiolysis, Papaconstantinou¹³⁷ determined the bimolecular rate constant ($3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) for 1-e^- reduction of $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ to $\text{H}[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ (pH 2) by $(\text{CH}_3)_2\text{C}\bullet\text{OH}$ radicals and recorded the absorbance spectrum of $\text{H}[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$. From subsequent changes in the absorption spectrum (the $\text{H}[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anion was stable Only in the subsecond time frame), the bimolecular rate constant for disproportionation ($1.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) was measured:



Building on this work, Papaconstantinou used the $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anion to investigate the redox chemistry of fat-soluble α -tocopherol (vitamin E)¹⁵⁸ and water-soluble ascorbic acid (vitamin C)¹⁵⁹ in micellar media (aqueous aggregates of nonionic surfactants) designed to model biological membranes. Relative to rates observed in isotropic media, the rate of reduction of $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ by vitamin E decreased by 3 orders of magnitude, while the rate of polyanion reduction by vitamin C decreased by only a factor of 10.

After Papaconstantinou's studies, Lerat et al. evaluated the rate constants for reduction of metatungstate, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$, by hydrated electrons, by H atoms, and by $\text{CH}_3\text{C}\bullet\text{HOH}$ radicals generated by pulse radiolysis.¹⁶⁰ Notably, the rate of reduction of metatungstate by hydrated electrons was observed to depend on the ionic strength of the medium according to the Brönsted equation (i.e., the Debye-Hückel relation; eq 36). Extrapolation to zero ionic strength gave a bimolecular rate constant of $k_0 = (2.5 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The rate constant measured for reduction of metatungstate by $\text{CH}_3\text{C}\bullet\text{HOH}$, $k = (2.2 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, was similar to that measured by Papaconstantinou (see Table 6).

In Rome, Baciocchi¹⁶¹ and co-workers later used several pulse-radiolysis methods to measure the rates of reduction of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ ($E^\circ = 1.01 \text{ V}$ vs NHE) by a variety of acyclic and cyclic carbon-centered radicals (alkyl, α -hydroxyalkyl, α -alkoxyalkyl, α -amidoxyalkyl, and benzyl), which, instructively, included those previously studied by Papaconstantinou.

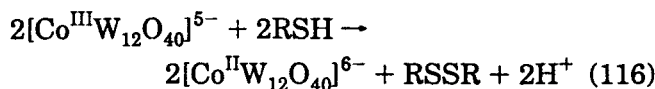
Considering the high positive reduction potential of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$, rates of reduction of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ by hydroxyalkyl and carboxyl radicals were in line with those reported by Papaconstantinou (above).¹⁵²⁻¹⁵⁵⁻¹⁵⁷ In particular, Baciocchi found that the rates of reduction of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ to $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ by simple α -hydroxyalkyl radicals were all near the diffusion-controlled limit; $\bullet\text{CH}_2\text{OH} < \text{CH}_3\text{C}\bullet\text{HOH} < (\text{CH}_3)_2\text{C}\bullet\text{OH}$ and rate constants ranged from 2.4 to $4.0 \times 10^9 \text{ M}^{-1}$

s^{-1} . In addition, the rate-retarding effect of the negative charge of the carboxyl radical ($\bullet\text{CO}_2^-$) was noted.

However, very different results were observed in the reduction of $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ by increasingly branched acyclic alkyl radicals. In this case, rates of reduction covered 4 orders of magnitude, from less than $10^5 \text{ M}^{-1} \text{ s}^{-1}$ to the diffusion-controlled limit: $\text{CH}_3\bullet (< 10^5 \text{ M}^{-1} \text{ s}^{-1}) \ll \text{CH}_3\text{CH}_2\bullet (2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}) \ll (\text{CH}_3)_2\text{CH}\bullet (1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}) < (\text{CH}_3)_3\text{C}\bullet (3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$, probably diffusion limited). The Taft plot (Hammett linear free-energy relationship extended to aliphatic systems) gave a slope (r^* value) of -28 , indicative of high sensitivity of the reaction rate to the nature of the alkyl substituent at C_α . By contrast, the Hammett r^* value measured for reaction of the same set of radicals with $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ was -13 , indicative of a substantially different mechanism. The $\text{Fe}(\text{III})$ complex, it was pointed out, could react via ligand transfer to give alkyl nitrile products (for example, reaction of $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ with $\text{CH}_3\bullet$ gives CH_3CN in 20% yield). In addition, Baciocchi found that the rates of reaction of the same set of alkyl radicals with $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ were all near the diffusion-controlled limit ($(1.2\text{--}3.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and noted that reaction of $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ with $\text{CH}_3\bullet$ gave CH_3Cl in 100% yield. Taken together, these data indicated that oxidation of the alkyl radicals by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ occurred via an electron-transfer mechanism.

F. Thiols and Organic Sulfides

Ayoko and Olatunji investigated the oxidative dimerization of biologically relevant thiols (glutathione,¹⁶² L-cysteine, mercaptoacetic acid, and *b*-mercaptoethylamine¹⁶³ ($2.0\text{--}40 \text{ mM}$)) by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ (0.2 mM) at high ionic strength ($\mu = 1.0 \text{ M}$, NaClO_4) over a range of $[\text{H}^+]$ ($0\text{--}1.0 \text{ M}$). Although direct evidence for the proposed oxidation products was not obtained, reaction stoichiometries were consistent with the formation of disulfide derivatives:



The oxidation of glutathione was first order in $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$ and $[\text{RSH}]$ and inverse order in $[\text{H}^+]$. A rate expression consistent with these observations was derived for a mechanism involving acid dissociation of RSH and rate-limiting oxidation of RS^- by $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$. The oxidations of L-cysteine and mercaptoacetic acid were first order in $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]$, second order in $[\text{RSH}]$, and inverse second order in $[\text{H}^+]$. In the oxidation of *b*-mercaptoethylamine, parallel paths, first and second order in thiol, and an inverse dependence on $[\text{H}^+]$ were observed. Proposed mechanisms accounted for the $[\text{H}^+]$ dependencies by including the acid dissociation of RSH and for the dependencies on $[\text{RSH}]$ by including reactions of RS^- (L-cysteine and mercaptoacetic acid), or of RS^- or RSH (*b*-mercaptoethylamine), with association complexes between $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ and RS^- (i.e., reaction of RS^- or RSH with $[(\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40})^{5-}(\text{RS}^-)]^6$). Evidence for the inclusion of alkali-metal cations in these association complexes was reported.

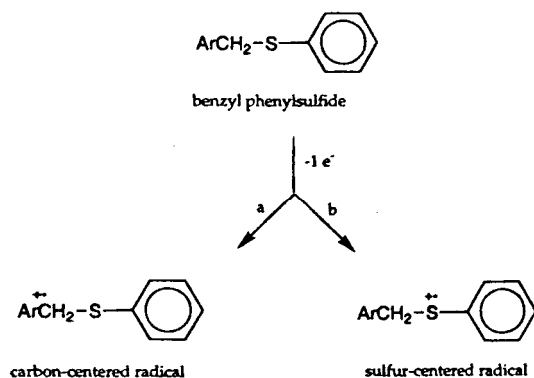
The catalytic oxidation of organic sulfides (R_2S , $R = \text{Me, Et, and } n\text{-Bu}$) by vanadomolybdophosphates ($H_{3+n}[PV_nMo_{12-n}O_{40}](^{3+n-})$, $n = 1-6$) and oxygen was reported by Kozhevnikov, Matveev, and co-workers in 1979.¹⁶⁴ Highly selective oxidations of R_2S to mixtures of R_2SO and R_2SO_2 (but no other products) were obtained with conversions of 100%. In stoichiometric reactions between several different POM anions and sulfides in water, the following order of reactivity was found: $\text{Me}_2S \gg \text{Et}_2S > n\text{-Bu}_2S$. The monovanadium anion $[PVMo_{11}O_{40}]^{4-}$ was inactive in water but quite effective in acetone, a result that may have been due to the degree of protonation, and hence reduction potential of the anion in the two solvents, or to solvent-dependent differences in the kinetics of speciation or in the stabilities (formation constants) of potentially active speciation products. The authors argued that the absence of products of R-S bond rupture implied that freely diffusing R_2S^{++} radicals were not formed during the multielectron oxidation process.

The utility of the $\text{Co}^{\text{III}}\text{W}_{12}^{6-}$ anion as a probe in the study of electron-transfer reactions is highlighted by the use of this anion by Baciocchi to elucidate the mechanisms of chemical and biochemical oxidations of a range of aryl sulfide compounds.¹⁶⁵⁻¹⁷⁰ In addition to its fundamental value, study of the reactivity of the free-radical and radical ion intermediates generated by oxidation of these sulfur-containing compounds is pertinent to processes ranging from the industrial to the purely biological.¹⁶⁵

The reactivity of simple alkyl sulfide radical cations is complicated by the propensity of these ions to react with their neutral parent compounds to form relatively stable two-center-three-electron sulfur-sulfur bonds.¹⁶⁹ Radical cations derived by 1-e- oxidation of aromatic sulfides, however, have a much lower tendency to "dimerize" via the formation of sulfur-sulfur bonds. Thus, data pertaining to the reactivity of aryl sulfide radical cations is more easily interpreted than that obtained from reactions of alkyl sulfides. For this reason, and because of the lack of previous attention paid to aryl sulfide oxidation reactions, Baciocchi studied the oxidations of a variety of benzyl phenyl sulfide compounds.

Depending on the nature of the substituents on the benzylic phenyl ring (Ar in Scheme 9), however, 1-e-oxidation of these compounds gave either carbon-centered cation radicals (Scheme 9, path a) or sulfur-centered radicals (Scheme 9, path b).

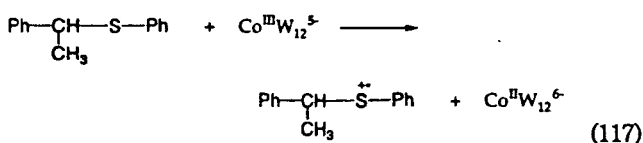
Scheme 9



The nature of the radical-cation intermediates formed upon reaction of the phenyl sulfides with $\text{Co}^{\text{III}}\text{W}_{12}^{6-}$ was central to interpretation of reactivity data.¹⁷⁰ Thus, in addition to studying the reactivity of the sulfur-centered radicals, some of the factors responsible for the formation of either carbon- or sulfur-centered radicals were also clarified.^{169,170}

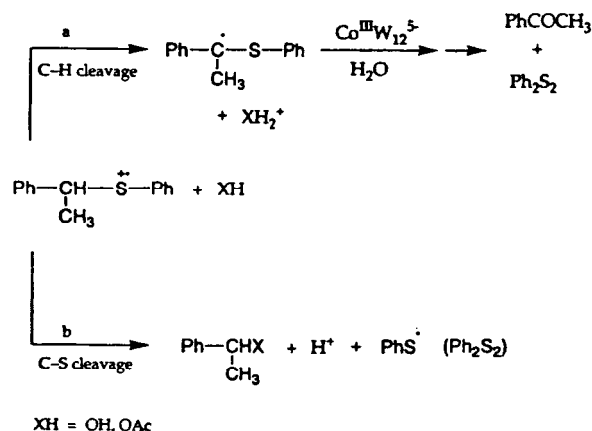
In an initial reactivity study, the mechanism of C-S bond cleavage in 1-phenylethyl phenyl sulfide radical cation (eq 117) was investigated by determining the stereochemistry of the products of the reaction of the parent sulfide with $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$. In question was whether the C-S bond cleavage occurred via unimolecular (S_N1) or bimolecular (S_N2) mechanisms.

Initially, reaction of 1-phenylethyl phenyl sulfide with $\text{Co}^{\text{III}}\text{W}_{12}^{5-}$ in $\text{AcOH}/\text{H}_2\text{O}$ (70:30) at 50 °C gave the corresponding sulfur-centered radical:



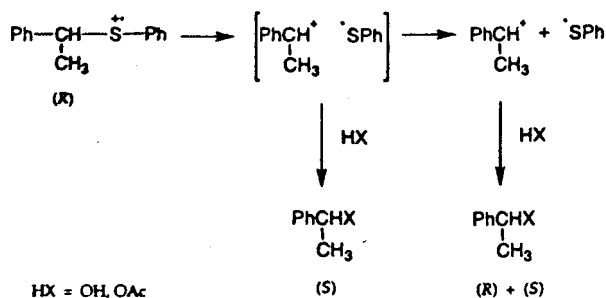
After completion of the reaction, products resulting from both C-H bond cleavage (Scheme 10, path a) and C-S bond cleavage (Scheme 10, path b) were found. As expected, the deprotonation pathway (path a) became more important when base (KOAc) was added.

Scheme 10



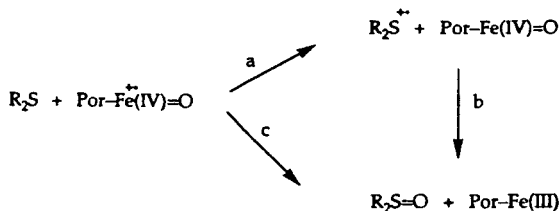
More significantly, when the reaction was carried out using enantiomerically pure (*R*)-(+)-1-phenylethyl phenyl sulfide, racemization was observed, along with modest (16%) inversion of configuration. These results indicated that the C-S cleavage reaction took place by two pathways. The simplest possibility was that racemization occurred via a unimolecular pathway and inversion via a competing bimolecular route. However, several lines of evidence suggested that unassisted cleavage of the C-S bond led first to a contact radical-cation pair and then to a solvent-separated radical-cation pair. Inversion of configuration was attributed to nucleophilic attack by solvent on the contact radical-cation pair; racemization resulted when the contact radical-cation pair separated prior to reaction of the benzylic cation with solvent (Scheme 11).

Scheme 11



Reactions of phenyl sulfides with Co^{III}W₁₂⁵⁻ were also used to help clarify a long-standing question regarding the mechanism of oxidation of sulfides by enzymatic oxidation catalysts such as peroxidases (horseradish peroxidase, HRP)¹⁶⁸ and microsomal cytochrome P 450^{167,170} and by biomimetic catalysts such as *meso*-(tetraphenylporphyrinato)iron(III) chloride (TPPFe^{III}Cl).^{167,170} It had been generally accepted that oxidation of sulfides (R₂S) to sulfoxides (R₂S=O) by hemoproteins was initiated via transfer of an electron from the sulfide to the Fe(IV) oxo porphyrin radical cation (Por^{•+}-Fe^{IV}=O) (path a, Scheme 12). According to this mechanism, the resultant sulfur-centered radical cation, R₂S^{•+}, was oxidized to the sulfoxide by reaction with the neutral Fe(IV) oxo porphyrin (Por-Fe^{IV}=O; oxygen-rebound mechanism) (path b, Scheme 12). Alternatively, however, the sulfide might be oxidized to the sulfoxide by direct oxo transfer from Por^{•+}-Fe^{IV}=O (path c, Scheme 12).

Scheme 12

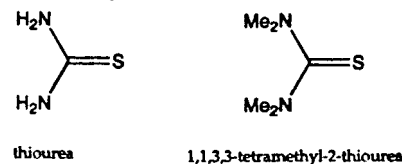


Where reaction of sulfide with Co^{III}W₁₂⁵⁻ gave sulfoxide, an additional mechanism, hydrolysis of the first-formed radical cation, R₂S^{•+}, to give R₂S•(OH) followed by 1-e- oxidation by a second equivalent of Co^{III}W₁₂⁵⁻, was proposed.¹⁷⁰

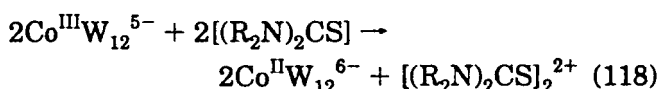
By comparing the reactivities of phenyl sulfides with Co^{III}W₁₂⁵⁻ and HRP, Baciocchi confirmed that reactions with HRP occurred via an oxygen-rebound mechanism and measured the rate of the oxygen-rebound step.¹⁶⁸ In addition, the products obtained by reactions of phenyl sulfides with Co^{III}W₁₂⁵⁻, with enzymes, and with biomimetic oxidants were interpreted as evidence that reactions with microsomal cytochrome P 450 and (TPPFe^{III}Cl) most likely occurred via oxo transfer.^{167,170} However, recent kinetic studies have shown that apparent rate constants for oxygen rebound by cytochrome P 450 can be incredibly fast and that nonsynchronous concerted mechanisms are possible.¹⁷¹⁻¹⁷³ Given this apparent continuum between oxygen-rebound and oxo-transfer mechanisms, conclusions arrived at through product analysis studies, however elegantly conceived, must be viewed with a degree of circumspection.

Olatunji and Ayoko¹⁷⁴ observed that the rates of oxidations of thiourea, (H₂N)₂CS, and 1,1,3,3-tetramethyl-2-thiourea, (Me₂N)₂CS (2.0–20 mM), were independent of [H⁺] at pH values well below the pK_b values of the substrates (Chart 5).

Chart 5. Structures of Thiourea and 1,1,3,3-Tetramethyl-2-Uourea

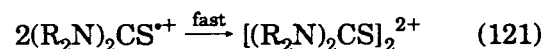
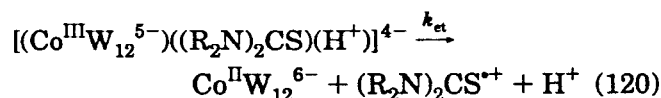
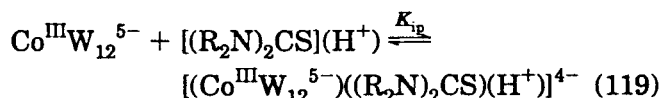


The reactions were carried out at high ionic strength ($\mu = 1.0$ M, NaClO₄) and at pH values sufficiently low ([H⁺] = 0.2–0.8 M) that the substrates were assumed to be monoprotonated. On the basis of reaction stoichiometries and UV-vis spectroscopic analysis of independently synthesized disulfide standards, the reaction with Co^{III}W₁₂⁵⁻ was represented as



At 25 °C under pseudo-first-order conditions ([Co^{III}W₁₂⁵⁻] = 0.2 mM), the oxidation of monoprotonated thiourea was first order in oxidant and substrate ($k_{\text{obs}} = 12.50 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$), while monoprotonated (Me₂N)₂CS was oxidized by two parallel pathways, first and second order in substrate.

One mechanism proposed for the oxidation of monoprotonated thiourea included the formation of an association complex, followed by electron transfer and rapid radical coupling:



Assuming $1 \gg K_{\text{ip}}[(\text{R}_2\text{N})_2\text{CS}](\text{H}^+)$, these elementary steps gave the rate expression

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]/dt}{2} = \frac{K_{\text{ip}}k_{\text{et}}[(\text{R}_2\text{N})_2\text{CS}(\text{H}^+)][\text{Co}^{\text{III}}\text{W}_{12}^{5-}]_{\text{T}}}{2} \quad (122)$$

where $[\text{Co}^{\text{III}}\text{W}_{12}^{5-}]_{\text{T}} = [\text{Co}^{\text{III}}\text{W}_{12}^{5-}] + [(\text{Co}^{\text{III}}\text{W}_{12}^{5-})(\text{R}_2\text{N})_2\text{CS}(\text{H}^+)]^{4-}$ and $K_{\text{ip}}k_{\text{et}} = 12.50 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$. In an effort to determine whether the reaction occurred via an outer-sphere electron-transfer mechanism, evidence for the existence of a linear free-energy relationship between $\log k_{\text{obs}}$ and E° for this and a set of similar reactions of Co^{III}W₁₂⁵⁻ with organic and inorganic substrates (glutathione,^{162,163} N₂H₅⁺,¹⁷⁵ and HNO₂¹⁷⁶) was sought. Although a

reasonably good correlation was found (linear regression coefficient = 0.98), the authors claimed that the slope of the line (-8.6 V^{-1}) was inconsistent with either classical adiabatic outer-sphere electron transfer within donor-acceptor "precursor" complexes (expected slope = $+8.5 \text{ V}^{-1}$; i.e., a positive value)³ or reversible, endergonic outer-sphere electron transfer within ion-paired association complexes (slope = -16.9 V^{-1}).⁵⁴ Confronted with this discrepancy, the authors concluded that although the reaction did not comply with Marcus's theory, the substitutionally inert nature of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ argued in favor of an outer-sphere mechanism.

It appears, however, that the experimental data are entirely in line with theoretical expectations; based on accepted convention, the sign of the slope of the plot of $\log k_{\text{obs}}$ vs E° , where E° values are reduction potentials of electron donors (i.e., the reduction potentials of the $1e^-$ -oxidized forms of the donors) should be negative (see section II.D). Because Ayoko and Olatunji, the authors of the data used in this analysis, appear to be first-rate experimentalists, their data should be regarded as highly reliable. It is gratifying that an elegant conclusion might be drawn from it.

In 1994, Hill studied POM ($\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}] \cdot (\text{H}_2\text{O})_n$) catalyzed oxidations of thioethers, RSR' (including the mustard gas analogue 2-chloroethyl ethyl sulfide, $\text{CH}_2(\text{Cl})\text{CH}_2\text{SCH}_2\text{CH}_3$ by *tert*-butyl hydroperoxide (TBHP) in acetonitrile.¹⁷⁷ The larger context for the detailed mechanistic studies reported was the use of POMs as catalysts for rapid destruction of toxic agents.

Reactions of thioethers with TBHP in the presence of $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}] \cdot (\text{H}_2\text{O})_n$ at room temperature gave sulfoxides, $\text{RS}(\text{O})\text{R}'$, in remarkably high yields ($>99.9\%$) with no evidence of overoxidation to sulfones, $\text{RS}(\text{O}_2)\text{R}'$. The high selectivity was traced to the mode of catalysis: The thioethers were directly oxidized by $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$. The role of TBHP in the catalytic cycle was simply to reoxidize the reduced POM anions, $\text{H}_6[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$. Kinetic and mechanistic studies thus focused on the stoichiometric oxidation of a model thioether compound, tetrahydrothiophene (THT), by solutions of $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}] \cdot (\text{H}_2\text{O})_n$ in acetonitrile (the nature of acetonitrile solutions of $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}] \cdot (\text{H}_2\text{O})_n$ was discussed in section IV.B).

In the course of these studies, an inverse dependence of reaction rate on the concentration of H_2O was observed. When water was present at concentrations of $2.2 \times 10^{-1} \text{ M}$ ($\sim 0.4 \text{ vol } \%$) or greater, the rate law, $\text{rate} = k_{\text{obs}}[\text{THT}] [\text{POM}_{\text{tot}}] [\text{H}_2\text{O}]^{-1}$ ($[\text{POM}_{\text{tot}}]$ is the total concentration of catalyst, $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}] \cdot (\text{H}_2\text{O})_n$, where n is zero or greater) was observed. However, as $[\text{H}_2\text{O}]$ was decreased from 0.4% to the experimental limit of $1.5 \times 10^{-2} \text{ M}$ (a limit imposed by hydration of $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ and the hygroscopic nature of the solvent), the order of reaction with respect to $[\text{THT}]$ decreased to near 0.5.

Inhibition by water (the inverse dependence on $[\text{H}_2\text{O}]$) was attributed to unimolecular loss of water from $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}] \cdot (\text{H}_2\text{O})_n$. In the proposed mechanism, loss of water occurred prior to bimolecular

reaction of the dehydrated intermediate, $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$, with THT. Subsequent reaction of THT with water and a second equivalent of POM was assumed to occur rapidly. Assuming that the concentration of the dehydrated intermediate, $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$, remained constant, a general rate expression was derived using a steady-state approximation. At high $[\text{H}_2\text{O}]$ the general rate expression gave the observed rate law, $\text{rate} = k_{\text{obs}}[\text{THT}] [\text{POM}_{\text{tot}}] [\text{H}_2\text{O}]^{-1}$. The steady-state rate expression was also consistent with the fractional order of reaction with respect to $[\text{THT}]$ observed at low $[\text{H}_2\text{O}]$.

It is well-established that water present within the crystalline lattices of solid POM acids and salts plays an important role in the heterogeneous-phase catalysis of reactions of organic substrates in nonaqueous media.¹⁴⁴ It is also well-known that the reactivity of organic-soluble d-electron-containing transition-metal-substituted POM anions in nonaqueous media is strongly influenced by the presence of water or of other oxygen- or nitrogen-donor ligands.^{178,179} In the latter cases, the donor ligands compete with substrates for occupation of the sixth coordination site on the d-electron-containing transition-metal cation. However, as the present report demonstrates, small concentrations of water can also influence the nonaqueous chemistry of organic-soluble POMs that do not appear to possess open addendum-atom coordination sites. As such, the results of Hill's study could have broad technological implications for the use of organic-soluble POM catalysts in nonaqueous solvents.

V. Oxidation of Inorganic Electron Donors by POM Anions

A. Introduction

Experimental rate laws have been determined for reactions of $\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}^{5-}$ and other POMs with a wide variety of inorganic electron donors. These studies are summarized in tabular form in Table 7.

In addition to the reactions summarized in Table 7, numerous examples of homogeneous oxidations catalyzed by multicomponent systems consisting of $\text{Pd}(\text{II})$ salts, vanadomolybdophosphate complexes ($\text{H}_{3+n}[\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}]^{(3+n)-}$), substrate, and oxygen have been reported.^{86,87,113,114,145,180-190} Generally, the POM anions play a role analogous to that of Cu salts in the Wacker process. During the catalytic cycle, $\text{Pd}(\text{II})$ is reduced by the substrate (SubH_2 , eq 123), and the POM anion catalyzes reoxidation of the reduced-Pd species. After electron transfer from the reduced-Pd species to the POM anion (eq 124), the resultant heteropoly blue is oxidized by O_2 (eq 125).

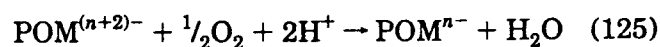
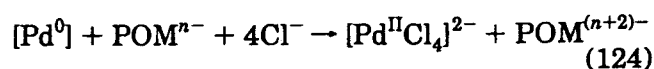
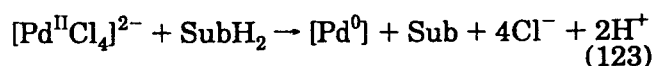


Table 7. Experimental Rate Laws for Oxidations of Inorganic Electron Donors by $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ ($\text{Co}^{\text{III}}\text{W}$) and by Other POM Anions

entry	stoichiometric reaction	electrolyte and ionic strength (M)	$[\text{H}^+]$ (M)	experimental rate law ($= -d[\text{Co}^{\text{III}}\text{W}]/dt$)	ref
1	$2\text{Co}^{\text{III}}\text{W} + 2\text{NH}_3\text{OH}^+ \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{N}_2 + 4\text{H}^+ + 2\text{H}_2\text{O}$	NaCl (2.0)	0.1–1.0	$= 2k[\text{Co}^{\text{III}}\text{W}][\text{NH}_3\text{OH}^+]^a$	191
2	$2\text{Co}^{\text{III}}\text{W} + 2\text{N}_2\text{H}_5^+ \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{N}_2 + 2\text{NH}_4^+ + 2\text{H}^+$	NaCl (2.0)	0.1–1.5	$= 2k[\text{Co}^{\text{III}}\text{W}][\text{N}_2\text{H}_5^+]^b$	175
3	$(\text{PV}_n\text{W}_{12-n}\text{O}_{40})^{(3+n)-} + \text{NO} + \text{H}_2\text{O} \xrightarrow{k} (\text{PV}_n\text{W}_{12-n}\text{O}_{40})^{(4+n)-} + \text{HNO}_2 + \text{H}^+$; $n = 1-3$	H_2SO_4 , NaCl (intrinsic)	0.6–3.0	not determined ^c	192
4	$2\text{Co}^{\text{III}}\text{W} + \text{HNO}_2 + \text{H}_2\text{O} \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{NO}_3^- + 3\text{H}^+$	LiClO_4 (1.0)	0.1–1.0	$= 2k[\text{Co}^{\text{III}}\text{W}][\text{HNO}_2]$	176
5	$2\text{Co}^{\text{III}}\text{W} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{H}_3\text{PO}_3 + 2\text{H}^+$	NaCl (2.0)	0.1–1.5	$= 2k[\text{Co}^{\text{III}}\text{W}][\text{H}_3\text{PO}_2]$	193
6	$9(\text{PV}_6\text{Mo}_6\text{O}_{40})^{9-} + \text{AsH}_3 \rightarrow \gamma^d$	variable	variable	$= 2k[(\text{PV}_6\text{Mo}_6\text{O}_{40})^{9-}][\text{AsH}_3]$, catalyzed by halide ions	194
7	$2\text{Co}^{\text{III}}\text{W} + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{H}_3\text{AsO}_4 + 2\text{H}^+$	NaCl (2.0)	0.1–1.5	$= 2k[\text{Co}^{\text{III}}\text{W}][\text{H}_3\text{AsO}_3]$	193
8 ^e	$2\text{Co}^{\text{III}}\text{W} + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{H}_3\text{AsO}_4 + 2\text{H}^+$	LiClO_4 (1.0)	0.4–1.4	$= 2(k_0 + k_1[\text{M}^+] + k_2K_a[\text{H}^+]^{-1})[\text{Co}^{\text{III}}\text{W}][\text{H}_3\text{AsO}_3]$, $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$; K_a = first acid dissociation constant of H_3AsO_3	195
9	$2\text{Co}^{\text{III}}\text{W} + 2\text{SCN}^- \rightarrow 2\text{Co}^{\text{II}}\text{W} + (\text{SCN})_2$	LiClO_4 (1.0)	0.1–0.5	$= 2k[\text{Co}^{\text{III}}\text{W}][\text{SCN}^-]$	196
10	$2\text{Co}^{\text{III}}\text{W} + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{S}_4\text{O}_6^{2-}$	NaClO_4 (1.0)	4.2–5.2	$= 2(k_0 + k_1[\text{M}^+])[\text{Co}^{\text{III}}\text{W}][\text{S}_2\text{O}_3^{2-}]$, $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$	197
11	$2\text{Co}^{\text{III}}\text{W} + 2\text{HSO}_3^- \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{S}_2\text{O}_6^{2-} + 2\text{H}^+$	NaClO_4 (0.5)	1.5–3.5	$= 2(k_0 + k_1[\text{H}^+]^{-1} + k_2[\text{HSO}_3^-])[\text{Co}^{\text{III}}\text{W}][\text{HSO}_3^-]$	198
12	$2\text{Co}^{\text{III}}\text{W} + 3\text{I}^- \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{I}_3^-$	(intrinsic)	f	$2(k_0 + k_1[\text{I}^-])[\text{Co}^{\text{III}}\text{W}][\text{I}^-]$	128
13	$2\text{Co}^{\text{III}}\text{W} + 3\text{I}^- \rightarrow 2\text{Co}^{\text{II}}\text{W} + \text{I}_3^-$	LiClO_4 (1.0)	0.1–1.0	$= 2k[\text{Co}^{\text{III}}\text{W}][\text{I}^-]$	196
14	$\text{Co}^{\text{III}}\text{W} + \text{VO}^{2+} + \text{H}_2\text{O} \rightarrow \text{Co}^{\text{II}}\text{W} + \text{VO}_2^+ + 2\text{H}^+$	NaClO_4 (1.0)	0.1–1.0	$= k[\text{Co}^{\text{III}}\text{W}][\text{VO}^{2+}]$	199
15	$(\text{PV}_n\text{W}_{12-n}\text{O}_{40})^{(3+n)-} + \text{VO}^{2+} + \text{H}_2\text{O} \rightarrow (\text{PV}_n\text{W}_{12-n}\text{O}_{40})^{(4+n)-} + \text{VO}_2^+ + 2\text{H}^+$; $n = 1-4$	Na_2SO_4 , Na_3PO_4 , NaCl (intrinsic) ^g	0.95–2.0	$= k[(\text{PV}_n\text{W}_{12-n}\text{O}_{40})^{(3+n)-}][\text{VO}^{2+}]$, $n^h = 1, 2$;	200, 201
16	$2(\text{PV}_n\text{W}_{12-n}\text{O}_{40})^{(3+n)-} + \text{Fe(II)} \rightarrow 2(\text{PV}_n\text{W}_{12-n}\text{O}_{40})^{(4+n)-} + \text{Fe(III)}$; $n = 1-4$	Na_2SO_4 , (intrinsic)	1.0–1.5	$= 2[(\text{PV}_n\text{W}_{12-n}\text{O}_{40})^{(3+n)-}][\text{Fe(II)}]$	201, 202
17	$\text{Co}^{\text{III}}\text{W} + \text{Fe(CN)}_6^{4-} \rightarrow \text{Co}^{\text{II}}\text{W} + \text{Fe(CN)}_6^{3-}$	LiClO_4 (0.25)	0.01–0.1	$= (k_0 + k_1[\text{H}^+]^{-1} + k_2[\text{M}^+])[\text{Co}^{\text{III}}\text{W}][\text{Fe(CN)}_6^{4-}]$, $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$	203
18	$\text{Co}^{\text{III}}\text{W} + \text{Mo}^{\text{IV}}(\text{CN})_6^{4-} \rightarrow \text{Co}^{\text{II}}\text{W} + \text{Mo}^{\text{V}}(\text{CN})_6^{3-}$	NaClO_4 (0.25)	0.05–0.6	$= (k_0 + k_1[\text{H}^+]^{-1} + k_2[\text{M}^+])[\text{Co}^{\text{III}}\text{W}][\text{Mo}^{\text{IV}}(\text{CN})_6^{4-}]$, $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$	204
19	$\text{Co}^{\text{III}}\text{W} + \text{W}^{\text{IV}}(\text{CN})_6^{4-} \rightarrow \text{Co}^{\text{II}}\text{W} + \text{W}^{\text{V}}(\text{CN})_6^{3-}$	NaClO_4 (0.01)	0.005–0.06	$= (k_0 + k_1[\text{H}^+]^{-1} + k_2[\text{M}^+])[\text{Co}^{\text{III}}\text{W}][\text{W}^{\text{IV}}(\text{CN})_6^{4-}]$, $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$	204
20	$\text{Co}^{\text{III}}\text{W} + \text{Ru}^{\text{II}}(\text{CN})_6^{4-} \rightarrow \text{Co}^{\text{II}}\text{W} + \text{Ru}^{\text{III}}(\text{CN})_6^{3-}$	NaClO_4 (0.10)	6.3	$= k[\text{Co}^{\text{III}}\text{W}][\text{Ru}^{\text{II}}(\text{CN})_6^{4-}]$	81

^a Ren observed an inverse dependence of k_{obs} on $[\text{H}^+]$ in acetate buffer²⁰⁵ and, when added as catalyst, a first-order dependence on $[\text{Fe}^{3+}]$.^{206,207} ^b An inverse dependence of k_{obs} on $[\text{H}^+]$ was observed in acetate buffer.²⁰⁵ ^c Mixtures of products (HNO_2 and NO_3^-) and complex mass-transfer kinetics ($\text{NO}_g \rightarrow \text{NO}_{\text{aq}}$) prevented detailed kinetic analysis. ^d The published stoichiometric eq $9\text{H}_9[\text{PV}_6\text{Mo}_6\text{O}_{40}] + \text{AsH}_3 + 3\text{H}_3\text{O}^+ \rightarrow \text{H}_3\text{AsO}_3 + 9\text{H}_{10}[\text{PV}_6\text{Mo}_6\text{O}_{40}]$ is unbalanced, and no other product information was reported. ^e Spectroscopic evidence for the rapid formation of $[(\text{M}^+)(\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40})]^{4-}$ ion pairs was reported. ^f Binary aqueous-solvent mixtures were used to investigate initial and transition-state solvation effects. ^g Specific anion effects were noted. ^h For $n = 3$ and 4, complex kinetics were observed.

These reactions sum to the net oxidation of the substrate by O₂:



The global kinetics of these multicomponent systems and the effects of specific variables on overall reaction rates have been studied in detail.⁸⁶ However, little if any detailed information concerning oxidation of the reduced-Pd species by POM anions is available. One reason is that the reduced-Pd species formed during catalyst-turnover conditions (usually written as Pd(0)) are unstable and poorly defined.⁸⁶

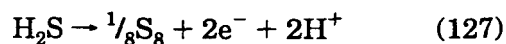
The potentially commercially useful POM-catalyzed oxidation of hydrogen sulfide to elemental sulfur was first explored using vanadomolybdophosphate complexes, H_{3+n}[PV_nMo_{12-n}O₄₀]⁽³⁺ⁿ⁾⁻, where *n* = 1–6. In later studies, oxidations of hydrogen sulfide by well-defined heteropolytungstate anions were investigated. Available information concerning the mechanisms of oxidation of hydrogen sulfide by heteropolymolybdate and tungstate anions is summarized below. In addition, due to its theoretical importance and because of its value in illustrating intellectually substantive issues pertinent to the role of donor-acceptor ion pairing in outer-sphere electron-transfer reactions (see section II.D), the luminescence quenching of Ru(II) complexes by well-defined and kinetically inert heteropolytungstates is presented in detail.

B. Inorganic Electron Donors

Balanced equations and experimentally determined rate laws for oxidations of inorganic electron donors by Co^{III}W₁₂⁵⁻, and by other POMs, are listed in Table 7. With few exceptions, the studies were carried out under conditions of high ionic strength. In general, the phenomena noted in the oxidation of organic substrates (section IV, above), such as acid-base equilibria, ion pairing, the formation of donor-acceptor complexes, and catalysis by alkali-metal cations, were observed in the studies reported here as well.

C. Hydrogen Sulfide

In 1975 Matveev disclosed²⁰⁸ the catalytic oxidation of hydrogen sulfide (H₂S) to elemental sulfur (S₈) by vanadomolybdophosphate anions, H_{3+n}[PV_nMo_{12-n}O₄₀]⁽³⁺ⁿ⁾⁻:



The kinetics of the stoichiometric oxidations of aqueous solutions of H₂S by [PV_nM_{12-n}O₄₀]⁽³⁺ⁿ⁾⁻ (M = Mo, *n* = 0–6; M = W, *n* = 0, 2, and 3) were later investigated by Kozhevnikov and Kholdeeva.²⁰⁹ The p*K*_a of the first acid dissociation of H₂S is 7.0, and the kinetic studies were carried out at pH 3 ([H₂S]/[HS⁻] = ~10⁴) in Na₂SO₄/NaHSO₄ buffer (μ = 2.0 M) using a stopped-flow apparatus.

At 25 °C the heteropolytungstates were inactive on the stopped-flow-experiment time scale, while the

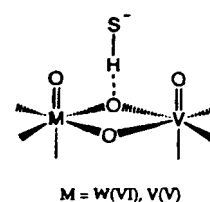
reactivity of the molybdate complexes followed the order (with respect to the number of vanadium(V) ions, *n*) *n* = 0 ≫ *n* = 1 > *n* = 2 > *n* = 3 > *n* = 6. Notably, the order of the reduction potentials of the anions at pH 3 (M = W > M = Mo and *n* = 1 > *n* = 2 > *n* = 0) did not correlate with their reactivities. Pseudo-unimolecular kinetics plots (ln of absorbance vs time) were obtained for the molybdates with *n* = 0, 1, and 2. However, the dependence of rate on [POM] demonstrated saturation kinetics or some other equilibrium-based phenomenon. Namely, solutions of Na₂MoO₄, adjusted to pH 3 (i.e., solutions of isopolymolybdates), exhibited kinetic behavior identical with that of [PMo₁₂O₄₀]³⁻ solutions. The authors suggested that the kinetically active oxidants were actually isopolymolybdates, products of speciation (i.e., reaction with water and electrolyte) of the vanadium-free and vanadium-substituted heteropoly-molybdate precursors.

In 1989 Kuznetsova, Chernyshova, and Maksimovskaya²¹⁰ studied the oxidation of H₂S at 20 °C by the heteropolytungstates earlier examined by Kozhevnikov.²⁰⁹ One intellectually compelling goal of the study was to determine the effects of positional isomerism on rate. Reactions of the anions [PV_nW_{12-n}O₄₀]⁽³⁺ⁿ⁾⁻, where *n* = 1, 2 (neighboring V atoms and mixture of positional isomers), 3 (α-1,2,3 isomer and mixture of isomers), and 4 (mixture of positional isomers), were carried out over a range of pH values (pH 1.5–3 for *n* = 1 or 2 and 2–5 for *n* = 3 or 4) under pseudo-first-order conditions of excess POM. Critically, both ³¹P and ⁵¹V NMR were used to confirm that the heteropolytungstates (and their isomeric forms) remained intact during the reaction.

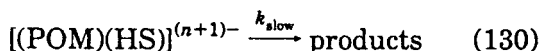
Although most of the kinetic data was obtained at high ionic strengths (μ = 0.25–0.5 M, Na₂SO₄), no dependence of rate on ionic strength was observed over a dramatic range of electrolyte concentrations (0–2.0 M Na₂SO₄). At pH 2.6 the reaction was zeroth order in the *n* = 1 or 2 anions and, provided the [POM] was not excessively large, first order in the *n* = 3 and 4 anions. At higher pH values (4.5–5.0) and sufficiently high POM concentrations, the reactions were zeroth order in the *n* = 3 and 4 anions, as well. At low pH values (1.3–3.0), an inverse dependence of rate on [H⁺] was observed for the *n* = 1 and 2 anions. More complex dependencies on [H⁺] were observed at higher pH values.

On the basis of analysis of the kinetic data, the authors proposed that the rate-limiting step in the reactions involved the unimolecular decomposition of hydrogen-bonded structures of the form shown in Chart 6.

Chart 6. Hydrogen-Bonded Intermediate in the Oxidation of HS⁻



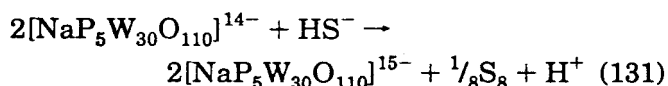
Given that the anions studied were stable over different pH ranges, a suitable rate expression for the calculation of constants for a potentially common rate-limiting elementary-reaction step might have required a rate expression that included (1) the pK_a of H_2S , (2) the formation of donor-acceptor ion pairs, and (3) the pK_a of H_2S within the donor-acceptor ion pairs. However, the entire pH range over which all the reaction were studied (~1.5–5) was sufficiently below the pK_a of H_2S ($pK_a = 7.0$), such that acid dissociation of H_2S was not included in the proposed reaction sequence:



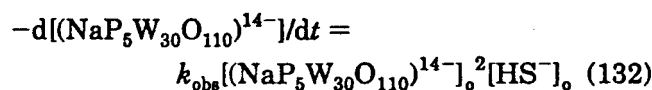
From a rate expression based on eqs 128–130, values of k_{slow} were calculated for the anions ($n = 1$ –4) studied. One significant result was clear: For $n = 3$, k_{slow} for oxidation by the α -1,2,3 isomer was greater (1.3 min^{-1} at pH 4.5) than k_{slow} for oxidation by the mixture of $n = 3$ isomers (0.6 min^{-1} at pH 5.3). This result was rationalized in terms of the greater basicity of the μ -2 oxygen atoms coordinated to neighboring V(V) ions in the α -1,2,3 isomer (Chart 6, $M = V(V)$). It should be noted that very few such investigations of the effects of polarization (i.e., loci of higher electron density) within soluble POM anions have been reported.

In separate work aimed at the development of catalytic processes for the oxidation of hydrogen sulfide by oxygen, Kuznetsova²¹¹ reported that the end products of the reaction of $[PFe^{III}(OH_2)W_{14}O_{39}]^{4-}$ with H_2S at pH 4–5 were $[PFe^{II}(OH_2)W_{11}O_{39}]^{3-}$ and elemental sulfur.

Harrup and Hill later reported the catalytic oxidation of H_2S to S_8 by a variety of transition-metal-substituted and mixed-addenda heteropolytungstates and oxygen.^{212,213} In conjunction they studied the stoichiometric oxidation of HS^- in aqueous solutions of the potassium salt of the remarkably alkali-stable²¹⁴ Pope–Jeannin–Preyssler anion, $K_{14}[NaP_5W_{30}O_{110}]$,²¹⁵ at pH 8.5, (0.025 M Borax buffer, $\mu = 0.310 \text{ M}$)²¹³ (eq 131).



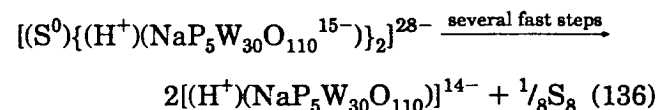
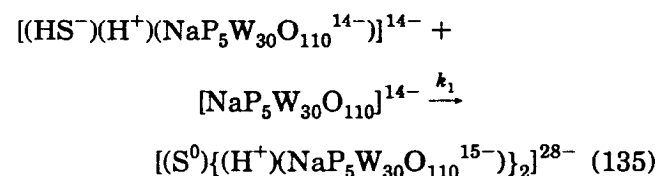
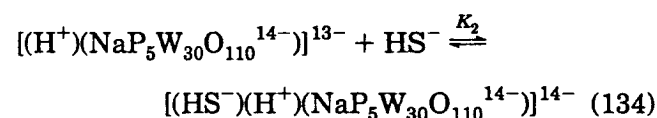
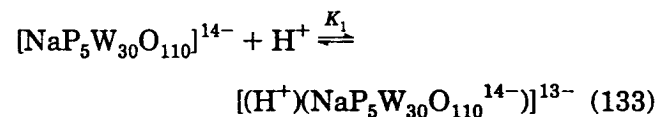
The rates of oxidation of the sulfur-redox intermediates (polysulfide (S_n^{2-}), $S_2O_6^{2-}$, $S_2O_3^{2-}$, and S_8) were also examined. Relative rates of reaction were HS^- (0.96), S_n^{2-} (22.2), $S_2O_6^{2-}$ (159), $S_2O_3^{2-}$ (0), and S_8 (0). To avoid the oxidation of sulfur-redox intermediates, some of which were oxidized more rapidly than HS^- itself, conversions of HS^- were kept to low values. Reactant concentrations were also kept low (1.0–3.0 and 0.7–10.0 mM, respectively, for $[NaP_5W_{30}O_{110}]^{14-}$ and HS^-). Based on log-log plots of initial rates, the reaction was first order in $[HS^-]$ and second order in $[NaP_5W_{30}O_{110}]^{14-}$:



The value of k_{obs} found using the initial rate method was $k_{obs} = 79.3 \pm 7.1 \text{ M}^{-2} \text{ s}^{-1}$. However, nonlinear least-squares fit of absorbance vs time data to the appropriate integrated third-order kinetic expression gave $k_{obs} = 96 \pm 43 \text{ M}^{-2} \text{ s}^{-1}$, and as the reaction progressed, systematic deviations in k_{obs} increased. The large experimental error and systematic deviation with reaction time were attributed to the complex chemistry of the aqueous sulfide solutions and to disparate reactivities of partially oxidized sulfur intermediates.

The $[H^+]$ dependence of the initial rate, investigated over a pH range of 7.5 to 9.5 at constant ionic strength, was complex. Initial rates rose slightly from pH 7.5 to ~8 and dropped by a factor of 5 from pH 8 to 9.5. Deprotonation of the POM anion was one explanation tentatively proposed to account for the $[H^+]$ dependence. Although repeated acid-base titrations of solutions of $K_{14}[NaP_5W_{30}O_{110}]$ failed to exhibit a clear endpoint, the POM anion appeared to undergo deprotonation somewhere in the 7.4–9.5 pH range.

On the basis of the experimental rate law and the $[H^+]$ dependence of initial rates, the following elementary reaction steps were proposed:



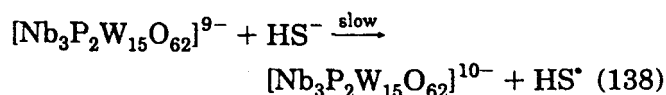
Ion pairing between $[NaP_5W_{30}O_{110}]^{14-}$ and the alkali-metal cations present, although not addressed experimentally, was mentioned as a likely possibility.

Harrup and Hill²¹² observed a different rate law in the oxidation of HS^- by the tetramethylammonium (TMA) salt of the Nb_2O_{13} -capped Wells–Dawson anion $[Nb_3P_2W_{15}O_{62}]^{9-}$.²¹⁶ As with $[NaP_5W_{30}O_{110}]^{14-}$, the reaction was carried out in Borax-buffered aqueous solutions with low reactant concentrations and low conversion rates. As before, the stoichiometry shown in eq 131 was verified. Unlike in the previous study, however, log-log plots of initial rates revealed

that the reaction was first order in both $[\text{HS}^-]$ and $[\text{Nb}_3\text{P}_2\text{W}_{15}\text{O}_{62}]^{9-}$:

$$-d[(\text{Nb}_3\text{P}_2\text{W}_{15}\text{O}_{62})^{9-}]/dt = k_{\text{obs}}[(\text{Nb}_3\text{P}_2\text{W}_{15}\text{O}_{62})^{9-}]_0[\text{HS}^-]_0 \quad (137)$$

The possibility of 2-e⁻ reduction of the $[\text{Nb}_3\text{W}_{15}\text{O}_{62}]^{9-}$ anions was discounted on the basis of thermodynamic considerations. In addition, log-log plots of the dependence of rate on $[\text{H}^+]$ (pH range of ~7–9) were linear, but a slope of 0.4 indicated that the role of protons in the reaction was complex. Acknowledging oversimplification, the following rate-limiting electron-transfer step was proposed:



D. Luminescence Quenching of Electronically Excited $[\text{Ru}(\text{bpy})_3]^{2+}$ Cations

Luminescence from photochemically generated electronically excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ cations (bpy = 2,2'-bipyridine) can be quenched by a number of mechanisms and pathways.^{217–222} One luminescence-quenching process, energy transfer to quencher A, where D^* represents the photoexcited Ru(II) complex $[\text{Ru}(\text{bpy})_3]^{2+*}$ (eq 139), is instructive of the principles involved.



The luminescence emission of $[\text{Ru}(\text{bpy})_3]^{2+*}$ can be quenched by both static and dynamic energy-transfer mechanisms (Figure 6).²¹⁸ Static quenching is associated with the quenching of luminescence intensity within $(\text{D}:\text{A})^*$ ion pairs (K_{ip} and k_5 in Figure 6), while dynamic quenching of both emission lifetime and intensity occurs during the collision encounter between D^* and A (k_1 or k_4). Static quenching of luminescence intensity is observed at the wavelength of the light emitted during stationary irradiation; lifetime measurements require rapid-time-scale monitoring of the decay in luminescence emission after photoexcitation.

In the absence of static or dynamic quenching, the lifetime (τ°) of the luminescence emission induced by photoexcitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ is determined by k_3 . In the presence of A, dynamic quenching of either the initially generated singlet-excited-state complex, $1[\text{Ru}(\text{bpy})_3]^{2+*}$ (k_1), or of the lower energy triplet-excited-state complex, $3[\text{Ru}(\text{bpy})_3]^{2+*}$ (k_4), can occur. However, under certain conditions,²¹⁸ $k_1[\text{A}] \ll k_2$, so that dynamic quenching is described by k_4 . Under these conditions, the lifetime of the emission is shortened to an extent dictated by the product $k_4[\text{A}]$. Plot of the ratio τ°/τ vs $[\text{A}]$, τ being the emission lifetime in the presence of A, gives a straight line (Stern–Volmer plot of emission lifetime) whose slope is proportional to k_4 :

$$\tau^\circ/\tau = (1 + k_4\tau^\circ[\text{A}]) \quad (140)$$

In the absence of static quenching, dynamic quenching decreases the intensity of the luminescence

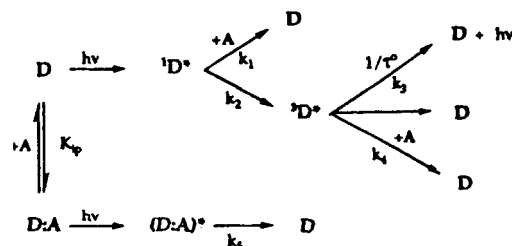


Figure 6. Static and dynamic energy-transfer quenching of the luminescence emission of $[\text{Ru}(\text{bpy})_3]^{2+}$. D , ${}^1\text{D}^*$, and ${}^3\text{D}^*$ represent the ground, lowest-excited singlet, and lowest-excited triplet states of $[\text{Ru}(\text{bpy})_3]^{2+}$, and τ° is the lifetime of the luminescence emission in the absence of the quencher, A. K_{ip} is an ion-pair association constant.

emission at the same rate at which it shortens the emission lifetime:

$$I^\circ/I = (1 + k_4\tau^\circ[\text{A}]) \quad (141)$$

As a result, plots of τ°/τ or I°/I vs $[\text{A}]$ are linear and coincident; either can be used to determine k_4 .

Static quenching, if present, does not alter the ratio of k_4/k_3 . Hence, the lifetime of the luminescence emission remains unchanged; eq 140 still applies. Static quenching does, however, attenuate the steady-state intensity of the luminescence emission. In this case (provided that the dynamics of photoexcitation of D in $\text{D}:\text{A}$ parallel that of D and k_5 is fast), the emission intensity decreases at a rate determined by both k_4 and K_{ip} :

$$I^\circ/I = (1 + k_4\tau^\circ[\text{A}])(1 + K_{\text{ip}}[\text{A}]) \quad (142)$$

When both static and dynamic quenching are present, the plot of I°/I vs $[\text{A}]$ (Stern–Volmer plot of emission intensity) is curved and deviates from the line described by eq 140. Mathematical comparison of the plot of I°/I vs $[\text{A}]$ (eq 142) to the plot of τ°/τ vs $[\text{A}]$ (eq 140) provides K_{ip} .

In the luminescence quenching of photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ cations by $[\text{PMn}^{\text{II}}(\text{OH})\text{W}_{11}\text{O}_{40}]^{6-}$ and $[\text{SiCo}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{40}]^{6-}$,⁶⁰ a much more complex situation pertained.^{61,223} Namely, the $[\text{Ru}(\text{bpy})_3]^{2+}$ and POM anions were highly ion paired (K_{ip} values ranged from $\sim 10^3$ to nearly 10^5 M^{-1} , depending on ionic strength of the solution).⁶¹ Both static and dynamic oxidative electron-transfer quenching were observed and in both cases, occurred within ion pairs (Figure 7).

One of the challenges encountered in studying electron transfer between reactants that form stable donor-acceptor ion pairs is to accurately determine rate constants for the “intramolecular” electron-transfer step (e.g., k_{fet} in Figure 7). In these cases, values for k_{fet} must usually be extracted from k_{obs} values, which are often composites of a number of rate and equilibrium constants (see discussion of Scheme 2 in section II.D). In addition, if the reaction is diffusion controlled (i.e., k_{fet} (in units of s^{-1}) $> k_{\text{d}}[\text{Donor}][\text{Acceptor}]$; Scheme 2 and Figure 7), k_{obs} values might provide only a lower limit on k_{fet} . Ballardini, Gandolfi, and Balzani, however, devised a strategy for direct determination of the rate constant for intramolecular electron transfer between

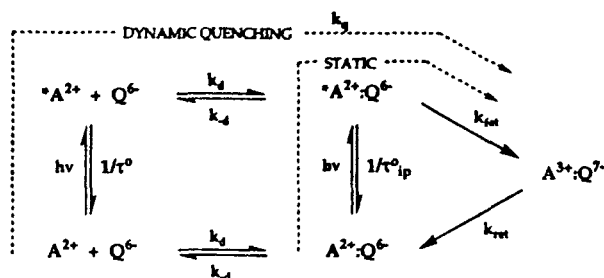


Figure 7. Static and dynamic luminescence quenching of photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ (A^{2+}) cations by POM anions, Q^{6-} ($\text{Q}^{6-} = [\text{PMn}^{\text{II}}(\text{OH})\text{W}_{11}\text{O}_{40}]^-$ or $[\text{SiCo}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{40}]^{6-}$), via oxidative electron transfer within $\text{A}^{2+} \cdots \text{Q}^{6-}$ ion pairs. The reduced POM anions, Q^{7-} , are heteropoly blues, formed by 1-e^- reduction of the tungsten oxide frameworks of Q^{6-} . Static and dynamic pathways are indicated by dotted lines.

$\text{Ru}(\text{II})$ and $\text{W}(\text{VI})$ in $[(\text{Ru}^{\text{II}}(\text{bpy})_3)^*(\text{SiCo}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{40})]^{4-}$ ion pairs (k_{fet} in Figure 7).⁶⁰

As part of a larger study,⁶¹ Ballardini and co-workers discovered that in solutions of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{SiCo}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{40}]^{6-}$, at moderate ionic strength ($\mu = 0.01 \text{ M}$, LiCl), rates of static quenching were much larger than those of dynamic quenching (see caption to Figure 7). Rather than a single composite curve, the exponential decay in luminescence intensity observed after pulse excitation was bimodal, each mode corresponding to one of the two quenching pathways. Thus, the decay constant associated with static quenching could be individually discerned. In addition, thermodynamic arguments dictated that static energy-transfer quenching ($1/\tau^0_{\text{ip}}$, Figure 7) was ineffective relative to the static electron-transfer pathway, k_{fet} . As a result, the k_{obs} values associated with static quenching depended only upon k_{fet} , k_{d} , and k_{q} .

By using the decay in luminescence intensity attributed solely to static quenching as the experimentally observable, solution of the integrated rate expression for static quenching gave $k_{\text{fet}} = 8.5 \times 10^7 \text{ s}^{-1}$, $k_{\text{d}} = (3.5 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{q}} = (1.6 \pm 0.5) \times 10^6 \text{ s}^{-1}$, and $K = k_{\text{d}}/k_{\text{q}} = \sim 2 \times 10^4 \text{ M}^{-1}$. Notably, k_{fet} values were independent of the concentration of the quencher, $[\text{SiCo}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{40}]^{6-}$.

More generally, information regarding the detailed structure of the $[(\text{Ru}^{\text{II}}(\text{bpy})_3)^*(\text{SiCo}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{40})]^{4-}$ and $[(\text{Ru}^{\text{II}}(\text{bpy})_3)^*(\text{PMn}^{\text{II}}(\text{OH})\text{W}_{11}\text{O}_{40})]^{4-}$ ion pairs was inferred from theoretical evaluation of the observed effects of ionic strength on the constants ($K = k_{\text{d}}/k_{\text{q}}$, Figure 7) associated with their formation.²²³ The observed rate constant for dynamic quenching, k_{q} (Figure 7), is equal to the product, Kk_{fet} , where $K = k_{\text{d}}/k_{\text{q}}$. Values of k_{q} were obtained from Stern–Volmer plots of τ^0/τ vs $[\text{A}]$, while association constants, K , were derived from combined lifetime and intensity-quenching experiments. Both k_{q} and K were determined at several ionic strengths ($\mu = 4 \times 10^{-3}$ to 0.5 M), using the $\text{Co}(\text{II})$ - and $\text{Mn}(\text{II})$ -substituted heteropolytungstates and $\text{Ru}(\text{II})$ complexes containing several ligand types (bpy , $4,4'\text{-Cl}_2\text{bpy}$, etc.).

At constant ionic strengths, k_{q} values were independent of ΔG° , a strong indication the process was diffusion controlled ($k_{\text{q}} \approx k_{\text{d}}$; see section II.D). Herein

lay the key to what followed. Able to determine K , and recognizing that $k_{\text{q}} \approx k_{\text{d}}$, Ballardini and co-workers sought to determine whether the ionic-strength dependence of k_{q} obeyed the Debye–Smoluchowski (DS) equations³⁷ (see discussion of the derivation of eq 1 in section IIA). The DS equation provides k_{d} as a function of ionic strength for spherical reactants of specific size and charge freely diffusing in a dielectric medium. Ballardini et al. found that for ionic radii of 7.0 and 5.5 Å for the $\text{Ru}(\text{II})$ complex and POM, respectively, k_{q} did in fact obey the DS equation. Because the DS equation was obeyed, it followed that the Eigen–Fuoss (EF) equation, used to calculate $K_{\text{EF}} (= k_{\text{d}}/k_{\text{q}})$ and based on the same theoretical model as the DS equation, should provide an accurate estimate of the K_{exp} values obtained from Stern–Volmer plots. This, however, was not the case.

Throughout the ionic-strength range over which the DS equation was obeyed by k_{q} , values of K_{EF} were smaller than K_{exp} by a constant factor. This result suggested that the effective encounter distance might be smaller than the sum of the radii of the reactants. However, decreasing the encounter distance in the Eigen–Fuoss calculation did not bring K_{EF} values in line with experimental observation. A good fit to experimental data was obtained, however, by multiplying K_{EF} (calculated using an encounter distance of 12.5 Å) by a constant.

To understand how the authors rationalized this result, it is essential to note that K_{exp} values, derived from analysis of Stern–Volmer plots, represented the equilibrium constants for formation of the ion pairs involved in static quenching. The k_{q} values, on the other hand, were derived from the emission-lifetime measurements associated with dynamic quenching. Hence, the authors proposed that the k_{q} ($\approx k_{\text{d}}$) values, which obeyed the DS equation, represented the rate of formation of “regular” encounter complexes with encounter distances of $\sim 12.5 \text{ Å}$. The K_{exp} values, however, associated with intensity quenching within preexisting ion pairs (Figure 7), were larger than those predicted by the Eigen–Fuoss equation because of penetration of the POM anion into a pocket of the cation structure.

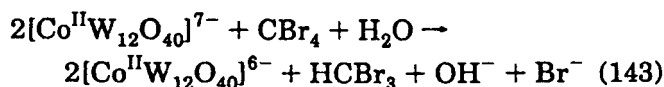
On the basis of ab initio calculations, similar interpenetration of coordination spheres within intimate ion pairs was once proposed for the $\text{Fe}^{\text{III/II}}(\text{H}_2\text{O})_6]^{3+/2+}$ electron self-exchange reaction.⁵³

VI. Reduction of Halogenated Alkanes by Reduced POM Anions

A. Carbon Tetrabromide

Carbon tetrabromide (CBr_4) was reduced by the one-electron heteropoly blue $\text{K}_7[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]$ ($\sim 0.2 \text{ mM}$) at pH 7 (buffered by tris(hydroxymethyl)aminomethane, TRIS) in mixtures of MeCN and H_2O containing low concentrations of added electrolyte ($1\text{--}200 \text{ mM Li}^+$, Na^+ , K^+ , Cs^+ , Me_4N^+ , and Bu_4N^+).²²⁴ The only products found were CHBr_3 (77%) and C_2Br_6 (1%). Yields were based on consumption of

$[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}$, and control experiments confirmed that the dimer C_2Br_6 did not result from uncontrolled photochemical processes. The stoichiometric reaction is shown in eq 143.



The potentials of the 1- and 2- e^- reductions of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ as a function of pH were measured by cyclic voltammetry. Due to protonation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}$ (or of both $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}$ in the mixed-solvent system), addition of H^+ increased the electrochemical potential of the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ couple. (In water, no protonation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ occurs even at pH 0.)⁶³ At low pH values, positive shifts in the potential of the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ couple led to decreases in rates of reduction of CBr_4 .

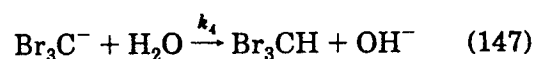
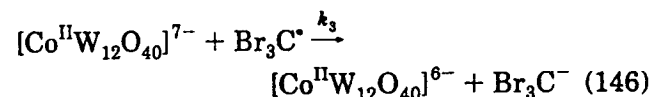
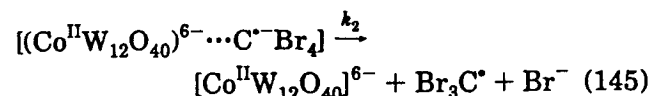
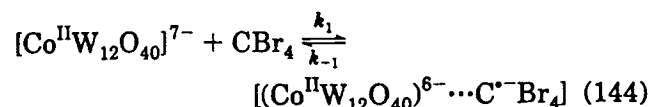
Similarly, comparison of the relative rates of reactions run using 10 mM concentrations of added electrolyte suggested that ion pairing slowed the rate of reduction of CBr_4 (numbers in parentheses are relative rates): Me_4N^+ (3.0) > Bu_4N^+ (2.2) > Li^+ (1.0) \approx Na^+ (1.0) > K^+ (0.7) > Cs^+ (0.5). Moreover, saturation kinetics was observed in the deceleration of reaction rates upon incremental addition of $\text{Na}^+\text{ClO}_4^-$ (1.0–200 mM) to 0.2 mM solutions of $\text{K}_7[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]$ (1.4 mM in K^+). This behavior was consistent with formation of ion-paired species, $\text{M}^+_x\text{M}'^+_y[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{(7-x-y)-}$, where $\text{M} = \text{K}$, $\text{M}' = \text{Na}$, and $x + y$ was probably = 2,²³ which shifted the potential of the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ couple to more positive values.

Saturation kinetics was also observed in the acceleration of reaction rates upon incremental addition of $\text{Me}_4\text{N}^+\text{ClO}_4^-$ (0–100 mM) to 0.2 mM solutions of $\text{K}_7[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]$. The electrochemical potential of the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ couple (0.5–2.0 mM $\text{K}_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]$) was measured by cyclic voltammetry, $E^\circ = (E_{\text{anodic}} - E_{\text{cathodic}})/2$, in 100 mM solutions of NaClO_4 or $\text{Me}_4\text{N}^+\text{ClO}_4^-$ buffered at pH 7 in 64% MeCN. E° values (vs NHE) of –439 mV (NaClO_4) and –485 mV ($\text{Me}_4\text{N}^+\text{ClO}_4^-$) were observed. These values were consistent with the acceleration in rate observed upon addition of Me_4N^+ cations: Shift in the potential of the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-/7-}$ couple to more negative values by addition of Me_4N^+ resulted in an increase in ΔG° for reduction of CBr_4 .

In a related study, Carloni and Eberson measured the effects of added cations on the chemical potential of the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}/[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ couple.⁵² The addition of Me_4N^+ shifted the potential of the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-/6-}$ couple to more negative values, while addition of Na^+ shifted the potential in the positive direction. In electron transfer between $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}$ and neutral CBr_4 , the kinetic impact of added cations is due primarily to the effect of ion pairing between M^+ and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}$ on ΔG° for the electron-transfer step. However, Carloni and Eberson noted that in other reactions, notably electron transfer between two charged species, the thermodynamic (and hence kinetic) effects of ion pairing on ΔG° could be counterbalanced by the

relative abilities of specific cations to participate in the formation of donor– M^+ –acceptor association complexes.⁵²

On the basis of product analyses, kinetic data, and pertinent control experiments, a mechanism for the reduction of CBr_4 by $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}$ was proposed:



Implied in this reaction sequence was the assumption that in contrast to aliphatic monohalides, the polyhalogenated compounds could form relatively long-lived anion radicals (experimental data in support of this assumption is discussed in section VI.B, immediately below). Spin-trapping studies (ESR spectroscopy of reactions run in the presence of the spin trap *N*-tert-butyl- α -phenylnitrone, PBN) provided evidence for Br_3C^* radicals.²²⁵ Ion pairing, although discussed, was not explicitly represented in the elementary steps of the proposed reaction mechanism.

An expression, identical in form to the experimental rate law (eq 148), was derived by setting $d[\text{Br}_3\text{C}^-]/dt = 0$ (steady-state approximation) and by assuming that $k_2 \gg k_1 = k_{\text{obs}} = 1.1 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1} \gg k_{-1}$ and that k_3 was fast:

$$\frac{-d[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}/dt}{2} = k_1[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}[\text{CBr}_4] \quad (148)$$

The rate of reduction of CBr_4 by the two-electron heteropoly blue $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{8-}$ was also studied. The observed rate constant, $k_1([\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{8-})$, was compared to $k_1([\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-})$ from eq 144 on the basis of two assumptions: (1) electron transfer from $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{8-}$ to CBr_4 was rate limiting, and (2) reduction of Br_3C^* by $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{8-}$ was fast relative to its reduction by $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}$. The ratio of experimental rate constants, $k_1([\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{8-})/k_1([\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-})$, was equal to 4, while the ratio predicted using Marcus theory was 3. The relatively good agreement suggested that the rates of both reduction reactions were controlled by activation energies associated with parallel outer-sphere electron-transfer processes.

B. Halomethanes

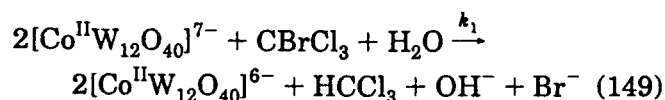
Eberson and Ekström²²⁵ also measured the rates of reduction of a series of polyhalogenated alkanes. The following order of reactivity toward $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{7-}$

Table 8. Product Distributions and Yields for the Reductive Dehalogenation of Halocarbons by Reduced Polytungstates^a

entry	POM anion	RX	conversion (%) ^b	products (yield %) ^c
1	[H ₂ W ₁₀ O ₃₂] ⁴⁻	CCl ₄	26.0	CHCl ₃ (82), C ₂ Cl ₆ (2.0)
2	[H ₂ W ₁₀ O ₃₂] ⁴⁻	CBrCl ₂	66.0	CHCl ₃ (77), C ₂ Cl ₆ (1.9)
3	[H ₂ W ₁₀ O ₃₂] ⁴⁻	1-C ₁₀ H ₂₁ Br ^d	6.0	C ₁₀ H ₂₂ (18), 1-C ₁₀ H ₂₀ (13), (C ₁₀ H ₂₁) ₂ (5.0)
4	[H ₂ W ₁₀ O ₃₂] ⁴⁻	C ₆ H ₁₁ Br	8.0	C ₆ H ₁₂ (39), C ₆ H ₁₀ (42), (C ₆ H ₁₁) ₂ (8.0)
5	[H ₂ W ₁₀ O ₃₂] ⁴⁻	<i>t</i> -C ₄ H ₉ Br	40.0	C ₄ H ₁₀ (18), C ₄ H ₈ , ^e <i>t</i> -C ₄ H ₉ NHC(O)CH ₃ (43)
6	[HW ₁₂ O ₄₀] ³⁻	CCl ₄	14.0	CHCl ₃ (5.0), C ₂ Cl ₆ (trace)

^a All reactions run for 24 h at 60 °C. ^b Based on initial concentration of RX. ^c Based on moles of RX consumed. ^d Reaction run at 80 °C. ^e Uncertain due to decomposition of unreacted *t*-C₄H₉Br in the hot injector port of the gas chromatograph.

was found: CBr₄ > (CBrCl₂)₂ > CBr₂Cl₂ > C₂Cl₆ > CBrCl₃ > CF₃HCIBr > CHBr₃ > CCl₄. Spin-trap studies (PBN) provided evidence for the formation of intermediate radicals during reduction of the most- and least-reactive substrates, CBr₄ and CCl₄. Reduction of CBrCl₃ by [Co^{II}W₁₂O₄₀]⁷⁻ (eq 149) obeyed the same rate law as that found for the reduction of CBr₄ (eq 148, above).



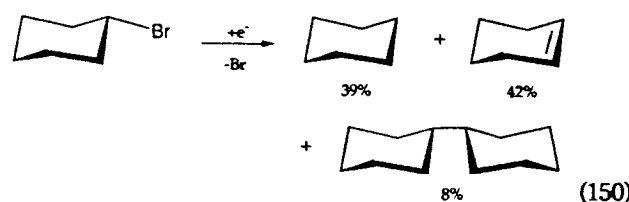
Comparison of the rate constants for the two reactions gave $k_1(\text{CBr}_4)/k_1(\text{CBrCl}_3) = 80$. The authors argued that if the mechanism of the electron-transfer reactions was dissociative (i.e., dissociation of a halide anion upon reduction and no radical-anion intermediates in eqs 144 and 145), both CBr₄ and CBrCl₃ would have reacted at the same rate. On the basis of published thermodynamic data (enthalpies and entropies of dissociation), the difference between the reduction potentials of the two haloalkanes was calculated to be small: $E^\circ(\text{CBr}_4) - E^\circ(\text{CBrCl}_3) = +0.01$ V. In addition, good linear relationships were known to exist between the energies of dissociation and (concomitant) reorganization, λ , of simple aliphatic halides. On the basis of Marcus analysis, it was reasoned that if the electron-transfer step was dissociative, rates of reduction of the two substrates would be very similar. Hence, the relatively large value observed for the $k_1(\text{CBr}_4)/k_1(\text{CBrCl}_3)$ ratio was seen as evidence for relatively long-lived radical-anion intermediates.

C. Carbon Tetrachloride, Halomethanes, and Haloalkanes

The reductive dehalogenation of the haloalkanes CCl₄, CBrCl₃, 1-C₁₀H₂₁Br (bromodecane), C₆H₁₁Br (bromocyclohexane), and *t*-C₄H₉Br by reduced (heteropoly blue) forms of the decatungstate anion [W₁₀O₃₂]⁴⁻²²⁶⁻²³⁰ and of CCl₄ by the reduced form of the Keggin anion α -[PW₁₂O₄₀]³⁻^{231,232} (fully oxidized forms shown) was investigated by Sattari and Hill.^{233,234} The "Q" salts (Q = tetra-*n*-butylammonium cation) of the decatungstate and undecatungstophosphate anions (i.e., Q₄[W₁₀O₃₂] and α -Q₃-[PW₁₂O₄₀]), dissolved in dry degassed acetonitrile, were reduced photochemically by irradiation in the presence of 2-butanol (sacrificial reductant) under an inert atmosphere.²³⁵ Oxidative titration of the reduced anions with Ce(IV) gave 1.0 ± 0.05 electrons

([PW₁₂O₄₀]⁴⁻) and 1.6 ± 0.05 electrons (3:2 [W₁₀O₃₂]⁶⁻/[W₁₀O₃₂]⁵⁻ mixture). Potentiometric titration with hydroxide (introduced as *n*-Bu⁴NOH) showed that the reduced species, [HPW₁₂O₄₀]³⁻ and [H₂W₁₀O₃₂]⁴⁻, were protonated. However, the endpoint for titration of the reduced decatungstate solution was less distinct due to the presence of the 1-e⁻ heteropoly blue [W₁₀O₃₂]⁵⁻. In kinetic studies of the haloalkane reduction reactions, the progress of the reaction was followed spectrophotometrically. Quantification of the oxidation of [HPW₁₂O₄₀]³⁻ was straightforward; oxidation of mixtures of [H₂W₁₀O₃₂]⁴⁻ and [HW₁₀O₃₂]⁴⁻ to fully oxidized [W₁₀O₃₂]⁴⁻ was accomplished by simultaneous observation of the spectral characteristics of all three species. Product distributions and yields are shown in Table 8.

The products were dominated by those typically derived from disproportionation, coupling, or 1-e⁻ reduction of free-organic-radical intermediates. Clear evidence for disproportionation and coupling was seen in the 1:1 ratio of cyclohexane to cyclohexene and in the formation of dimeric (C₆H₁₁)₂ upon reduction of cyclohexyl bromide (Table 8, entry 4 and eq 150). The distribution of products obtained upon

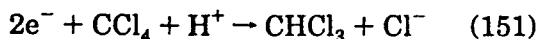


reduction of CBrCl₃ (Table 8, entry 2) was almost identical with that observed by Ebersson and Ekström²²⁵ after its reduction by the 1-e⁻ heteropoly blue [Co^{II}W₁₂O₄₀]⁷⁻: CHCl₃ (72%), C₂Cl₆ (2%), and CBrCl₂ (< 1%).

Initial rates of reduction of CCl₄ (0.2–3.500 M) at 60 °C by 3:2 mixtures of [H₂W₁₀O₃₂]⁴⁻ and [HW₁₀O₃₂]⁴⁻ (3.9–33 mM) were studied in detail under pseudo-first-order conditions (excess CCl₄). The precise stoichiometry of the reaction was complicated by the presence of two reducing agents.

Detailed study of the reduction reaction could easily have been simplified by use of [HPW₁₂O₄₀]³⁻, a well-defined 1-e⁻ heteropoly blue. Nonetheless, the decatungstate mixture was chosen deliberately. Use of the reduced decatungstate mixture, prepared photochemically, better represented a key thermal step in the catalytic photochemical reduction of haloalkanes by [W₁₀O₃₂]⁴⁻, a much more versatile²³⁶⁻²⁴⁰ and active photocatalyst than [PW₁₂O₄₀]³⁻.

Although products of both 1- and 2-e⁻ reductions of haloalkanes were observed (Table 8), the relatively high and exclusive yield of CHCl₃ (entry 1, Table 8) was indicative of a 2-e⁻-reduction stoichiometry (eq 151).



By monitoring the rate of formation of fully oxidized [W₁₀O₃₂]⁴⁻ the following rate law was determined:

$$d[W_{10}O_{32}^{4-}]/dt = k_{obs}[H_2W_{10}O_{32}^{4-} + HW_{10}O_{32}^{4-}][CCl_4] \quad (152)$$

log-log plots of rate vs [CCl₄] and vs [(H₂W₁₀O₃₂)⁴⁻ + (HW₁₀O₃₂)⁴⁻] had slopes of 1.02 (*R* = 0.99) and 0.93 (*R* = 0.97), respectively. The observed rate law, product distributions, and relative reaction rates argued for the existence of at least short-lived radical intermediates in the reactions listed in Table 8.

Comparison with other studies of reductive dehalogenation reactions argued that rate-limiting electron transfer was more likely than halogen atom abstraction. The remaining question was whether the electron-transfer step was dissociative (i.e., whether addition of an electron to the σ* antibonding LUMO of the alkyl halide occurred with concerted carbon-halogen bond rupture) or whether short-lived but discrete anion radicals were the first products of electron transfer. It was concluded that while adequate experimental evidence could be cited in support of the existence of anion radicals resulting from the reduction of aromatic halides and from the reduction of polyhalogenated halides, such as CBr₄ or CCl₄,²²⁵ the situation was not simple in the case of common aliphatic halocarbons.

VII. Reduction of Inorganic Oxidants by Reduced POM Anions

A. Introduction

The use of inorganic electron acceptors, such as Br₂,²⁴¹ permanganate,^{242,243} and inorganic peroxides,²⁴⁴⁻²⁴⁷ is often encountered in POM synthesis. Taking advantage of the oxidative stability of many POM anions, researchers have also used ozone.¹²⁰ Though some reactions, such as the reduction of H⁺²⁴⁸ and nitrite,²⁴⁹ have been studied in the context of photo- and electrocatalysis, relatively few kinetic studies concerning POM reductions of common inorganic oxidants have been reported.

Because of its complexity, and its important role in POM-catalyzed oxidations of organic and other substrates, the reduction of dioxygen (O₂) by reduced POM anions will be discussed separately (section VIII).

B. Hydrogen Cations

In 1981 Papaconstantinou submitted a communication to the Royal Society of Chemistry outlining the photocatalytic oxidation of organic compounds by POM anions and oxygen.^{250,251} At the same time,

Savinov²⁵² and co-workers published a full paper on the reduction of H⁺ to H₂ by stoichiometrically reduced heteropolytungstates. Shortly thereafter, Darwent noted that when the photocatalytic chemistry described by Papaconstantinou was carried out in the absence of O₂, H⁺ was reduced to H₂ by reduced POM anion intermediates.²⁵³ Under standard conditions, the electrochemical potential for reduction of O₂ to H₂O by reduced POM anions is +1.23 V more exergonic than that for reduction of H⁺ to H₂. Nonetheless, in many cases the latter reaction is spontaneous.

More thorough investigations of the chemical processes outlined in the above-mentioned reports were published by Papaconstantinou²⁵⁴ and Darwent²⁵⁵ in 1985. In the same year, Hill²³⁶ outlined the broad scope of POM-catalyzed photooxidations and photodehydrogenations of organic compounds. In a 1993 review,²⁴⁸ Hill and Prosser-McCarthy commented that "most of the scope and mechanistic details in polyoxometalate photochemistry have been clarified since 1985 and thirty research groups have now published nearly two hundred papers in this area". Despite this activity, and the use of both aerobic and anaerobic reaction conditions, little detailed kinetic data pertaining specifically to the homogeneous (no colloidal Pt catalyst^{236,253,254} present) reduction of H⁺ by reduced POM anions has been published.

Savinov²⁵² deoxygenated aqueous solutions of [SiW₁₂O₄₀]⁴⁻ and used zinc amalgams to produce mixtures of the protonated 1- and 2-e⁻-reduced heteropoly blues, H[SiW₁₂O₄₀]⁴⁻ and H₂[SiW₁₂O₄₀]⁴⁻, respectively, at low pH (0.1 N H₂SO₄). After separating the heteropoly blue solutions from the amalgams, progress of reaction was followed using three techniques: UV-vis and ESR spectroscopy and determination of evolved H₂. At 22 °C the 2-e⁻-reduced anions reduced H⁺ to H₂ according to the overall stoichiometry:

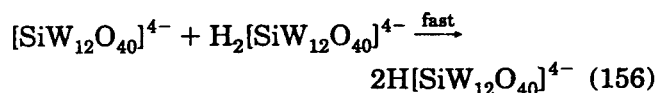


The reaction rate was constant over a dramatic range of H⁺ concentrations (0.0001–6 N H₂SO₄). Also, rather than second order in [H₂(SiW₁₂O₄₀)⁴⁻], as the reaction stoichiometry might have implied, the process obeyed first-order kinetics (eq 154, *k*_{obs} = 1.2 ± 10⁻³ s⁻¹). Analogous results were obtained by UV-

$$d[H_2]/dt = k_{obs}[H_2(SiW_{12}O_{40})^{4-}] \quad (154)$$

vis spectroscopy and by ESR observation of the accumulation of paramagnetic H[SiW₁₂O₄₀]⁴⁻.

These observations suggested that the reaction might occur via slow unimolecular decay of H₂[SiW₁₂O₄₀]⁴⁻, followed by rapid comproportionation:



This hypothesis was confirmed by adding fully oxi-

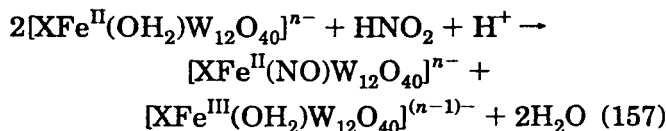
dized $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ to the reaction: Although less H_2 was produced, k_{obs} remained unchanged.

Like Savinov, Papaconstantinou²⁵⁴ observed that decreases in optical density of acidic (pH 1) solutions of mixtures of 1- and 2- e^- photochemically reduced $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anions obeyed pseudo-first-order kinetics.

Although reduction of H^+ by $\text{H}[\text{SiW}_{12}\text{O}_{40}]^{4-}$ was not observed by Savinov, Darwent²⁵³ noted that at high $[\text{H}^+]$, the reaction was thermodynamically favorable and in the presence of colloidal Pt, kinetically facile. Darwent later studied the rate of evolution of H_2 during irradiation ($\lambda > 300 \text{ nm}$) of acidic (0.5 M H_2SO_4) solutions containing $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, CH_3OH , and colloidal Pt²⁵⁴. Discussion of these and related²⁴⁸ heterogeneous photocatalytic reactions is beyond the scope of this review.

C. Nitrite

The reduction of nitrite ($\text{N}^{\text{III}}\text{O}_2^-$) to nitric oxide ($\text{N}^{\text{II}}\text{O}$) by aqueous $[\text{XFe}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{n-}$ anions ($\text{X} = \text{Si}$ or Ge , $n = 6$; $\text{X} = \text{P}$ or As , $n = 5$) was examined in the context of a larger effort to develop efficient catalysts for multielectron electrochemical reduction of nitrite to ammonia.²⁶⁹ Kinetic runs were carried out at constant ionic strength ($\mu = 0.1 \text{ M}$) under pseudo-first-order conditions of excess nitrite. The reaction was first-order with respect to the total nitrite concentration and with respect to $[\text{XFe}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{n-}$. Observed second-order rate constants were proportional to $[\text{H}^+]$ at pH values above the pK_a of nitrous acid (HNO_2 , $\text{pK}_a = 3.3$) and independent of $[\text{H}^+]$ at lower pH values. The largest rate constant was observed below the pK_a of nitrous acid, indicating that HNO_2 was the active form of the oxidant. The initially observed nitrogen-containing product of the reaction was the nitrosyl adduct $[\text{XFe}^{\text{II}}(\text{NO})\text{W}_{11}\text{O}_{39}]^{n-}$, and 2 equiv of $[\text{XFe}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{n-}$ were consumed in its formation:



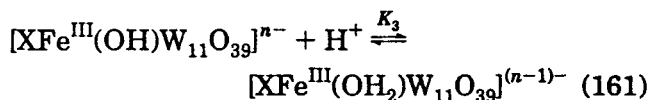
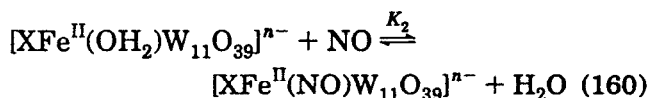
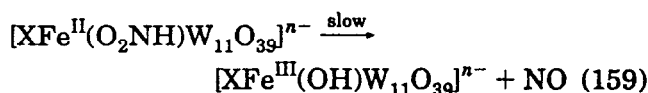
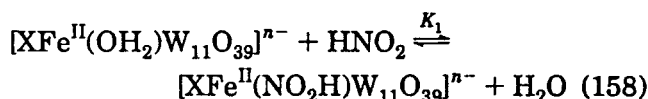
The identity of the adduct was confirmed by independent synthesis from $[\text{XFe}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{n-}$ and NO . In addition, at pH 5 the authors observed a correlation between the formal potentials of the $[\text{XFe}^{\text{III}}\text{W}_{11}\text{O}_{39}]^{(n-1)-}/[\text{XFe}^{\text{II}}\text{W}_{11}\text{O}_{39}]^{(n-1)-}$ couples ($\text{X} = \text{Si}$, Ge , P , and As) and the rate constants for nitrosyl complex, $[\text{XFe}^{\text{II}}(\text{NO})\text{W}_{11}\text{O}_{39}]^{n-}$, formation (Table 9).

Table 9. Correlation of Formal Potentials (E^f) for $[\text{XFe}^{\text{III}}\text{W}_{11}\text{O}_{39}]^{(n-1)-}/[\text{XFe}^{\text{II}}\text{W}_{11}\text{O}_{39}]^{(n-1)-}$ Couples with Their Kinetic Properties

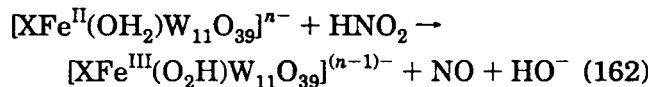
X	E^f (mV vs NHE) ^a	k_{obs} ($\text{M}^{-1} \text{s}^{-1}$)
Si	26	1.3 ± 0.1
Ge	98	1.0 ± 0.1
P	216	0.6 ± 0.1
As	294	0.4 ± 0.1

^a Formal potential measured at pH 5 and $\mu = 0.1 \text{ M}$.

Despite the difference in charge between the $\text{X} = \text{Si}$ or Ge and the $\text{X} = \text{P}$ or As anions, the insensitivity of k_{obs} to their formal reduction potentials (Table 9) is strong evidence that the reaction with NO_2^- (pH 5) occurred via an inner-sphere mechanism (cf. Figure 5). While still acknowledging that at lower pH values outer-sphere 1- e^- reduction of HNO_2 by $[\text{XFe}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{n-}$ was plausible, the authors favored an inner-sphere pathway involving coordination of HNO_2 to $\text{Fe}(\text{II})$ (eqs 158–161). This reaction scheme is consistent with the labile nature of octahedral $\text{Fe}(\text{II})$ aquo complexes (cf. reduction of O_2 by less labile $\text{Ru}(\text{II})$ aquo complexes; section VIII.E).



Three lines of electrochemical evidence were presented in support of this reaction scheme: (1) At pH 5 in acetate buffer, the reduced anions formed by electrochemical reduction of the lacunary anions, $[\text{XW}_{11}\text{O}_{39}]^{(n-3)-}$, which although strongly reducing, lacked a suitable coordination site for NO_2^- , did not reduce nitrite at an appreciable rate. (2) Because of the affinity of $\text{Fe}(\text{III})$ for hydroxide anion, the outer-sphere reduction of HNO_2 to give NO and uncoordinated HO^- (eq 162) would possess a significantly smaller driving force than the inner-sphere electron-transfer step shown in eq 159. This argument



assumes that an outer-sphere electron-transfer step would generate free hydroxyl anion (eq 162). Although outer-sphere electron transfer to HNO_2 might be expected to give HNO_2^- , the latter is a high energy molecule whose generation would likely require a greater driving force than that provided by the $\text{Fe}^{\text{III/II}}$ -heteropolyanion couple.²⁵⁶ (3) At pH 5 no reduction of NO_2^- was observed upon electrochemical reduction of $[\text{XFe}^{\text{III}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{(n-1)-}$ to $[\text{XFe}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{n-}$. Yet at more negative potentials (reduction of the tungsten oxide framework), catalytic currents corresponding to the reduction of coordinated NO to NH_3 were observed. No reduction of NO was observed upon reduction of the iron-free lacunary anions at pH 5. These observations implied the accessibility, at the more negative electrode potentials, of an alternate route for the formation of $[\text{XFe}^{\text{II}}(\text{NO})\text{W}_{11}\text{O}_{39}]^{n-}$. It was proposed that coordi-

nated HNO_2 , in $[\text{XFe}^{\text{II}}(\text{O}_2\text{NH})\text{W}_{11}\text{O}_{39}]^{n-}$, was reduced not by electrons originating in $\text{Fe}(\text{II})$, but rather by more energetic electrons available at the more negative electrode potentials.

The third argument is less straightforward than the first two lines of evidence. The observation of electrocatalytic reduction of NO to NH_3 exclusively in the presence of iron implies a role for $\text{Fe}(\text{II})$ coordination of NO . However, the lack of electrocatalytic NO reduction in the absence of iron does not rule out the possibility that electrostatic factors might have been responsible for the lack of reactivity of NO_2^- with reduced lacunary anions, which are more highly negatively charged than reduced $\text{Fe}(\text{II})$ -substituted analogues.

Finally, it should be noted that any electron-transfer reaction that proceeds along an outer-sphere pathway does not require (and cannot benefit from) a redox catalyst that operates via an outer-sphere pathway. The reason is that the same outer-sphere electron-transfer reaction should be just as facile at an electrode surface held at the potential of the $(\text{catalyst})_{\text{ox}}/(\text{catalyst})_{\text{red}}$ couple.²⁵⁶ While true for elementary electron-transfer steps, this reasoning need not preclude the occurrence of intermediate outer-sphere electron-transfer reactions in multistep reduction pathways.

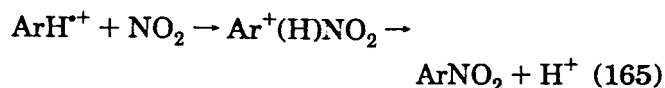
In the electrocatalytic reduction of NO_2^- to NH_3 , $[\text{XFe}^{\text{II}}(\text{NO})\text{W}_{11}\text{O}_{39}]^{n-}$ was further reduced at the cathode. The authors provided strong circumstantial evidence that the electrons accepted by the NO ligand coordinated to $\text{Fe}(\text{II})$ were delivered via the tungsten oxide framework of the polyanion rather than directly from the electrode surface to the bound NO ligand.²⁴⁹

D. Nitronium Ion

It is generally accepted that electrophilic aromatic nitration by the nitronium ion (eq 163) proceeds via bond formation between N^+O_2 and ArH to give a nitrocyclohexadienyl cation followed by loss of a proton.²⁵⁷

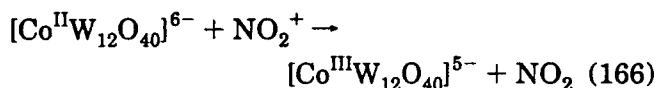


A possible alternative mechanism, outer-sphere electron transfer from ArH to NO_2^+ (eq 164) followed by the reactions shown in eq 165, has been ruled out on the basis of theoretical and experimental evidence-



A primary theoretical difficulty with the outer-sphere mechanism is that the reorganization energy of the $\text{NO}_2^+/\text{NO}_2$ couple, which would have a large influence on the reaction rate, is probably prohibitively large. The large reorganization energy is a consequence of the change in geometry, from linear NO_2^+ to bent NO_2 , in the transition state. The actual value of the reorganization energy, however, has been controversial.

At issue is the value of the inner-sphere reorganization energy, I_{in} . Theoretically calculated values have ranged from $I_{\text{in}} = 78$ to $I_{\text{in}} = 108 \text{ kcal mol}^{-1}$. Combined with an estimated outer-sphere reorganization value of $I_{\text{out}} = 36 \text{ kcal mol}^{-1}$, total reorganization energies of $I_{\text{tot}} = 114\text{--}144 \text{ kcal mol}^{-1}$ are obtained. At the same time, from the rate of heterogeneous electron transfer to NO_2 from a Pt electrode, a value of $I_{\text{in}} = 79 \text{ kcal mol}^{-1}$ was calculated. To obtain an accurate value of the reorganization energy of the $\text{NO}_2^+/\text{NO}_2$ couple, Lund and Ebersson (1997) measured the rate of homogeneous-phase outer-sphere electron transfer from $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to NO_2^+ (eq 166).²⁵⁷



The reactions of Bu_4N^+ and mixed $\text{Bu}_4\text{N}^+\text{--K}^+$ salts of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ with $\text{NO}_2^+\text{BF}_4^-$ were studied in acetonitrile and in nitromethane at 26°C . Although due consideration was paid to the extent of ion pairing in solution and to the reduction potentials of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and NO_2^+ under reaction conditions, considerable uncertainty in these parameters was acknowledged. For the Bu_4N^+ salts, bimolecular rate constants of $k_{\text{obs}} = 0.097 \pm 0.013 \text{ M}^{-1} \text{ s}^{-1}$ and $12.5 \pm 1.5 \text{ M}^{-1} \text{ s}^{-1}$ were measured in acetonitrile and nitromethane, respectively. In acetonitrile, a rate constant of $k_{\text{obs}} = 0.073 \text{ M}^{-1} \text{ s}^{-1}$ was measured for the K^+ salt.

Although confronted with large uncertainties in key parameters, Marcus theory (eqs 1 and 4) was used to calculate reorganization energies for the reaction (eq 166) from the experimentally determined rate constants. Analysis of the data obtained in nitromethane was complicated by unacceptably large uncertainty in the reduction potential of NO_2^+ in this solvent. From the rate constant for reaction of the Bu_4N^+ salt of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ in acetonitrile ($k_{\text{obs}} = 0.097 \pm 0.013 \text{ M}^{-1} \text{ s}^{-1}$), a total reorganization energy (I_{tot}) of from 80 to 85 kcal mol^{-1} was calculated.

The reorganization energy associated with the $\text{NO}_2^+/\text{NO}_2$ couple was then calculated using $I_{\text{tot}} = (I_{11} + I_{22})$ (eq 43) where I_{11} and I_{22} are total reorganization energies associated with the $\text{Co}^{\text{III/II}}\text{W}_{12}^{5-/6-}$ and $\text{NO}_2^+/\text{NO}_2$ couples, respectively (section II.B.4). Taking I_{22} equal to $140 \text{ kcal mol}^{-1}$, a reorganization energy of $I_{11} = 25 \text{ kcal mol}^{-1}$ for the $\text{Co}^{\text{III}}\text{W}_{12}^{5-/6-}$ couple gave a total reorganization energy, $I_{\text{tot}} = (25 + 140)/2 = 82.5 \text{ kcal mol}^{-1}$. This value was consistent with the I_{tot} value of between 80 and 85 kcal mol^{-1} obtained from k_{obs} using eqs 1 and 4. This agreement was presented as evidence in support of a high value ($\sim 140 \text{ kcal mol}^{-1}$) for the reorganization energy of the $\text{NO}_2^+/\text{NO}_2$ couple.

At the same time, assuming a I_{22} value of $140 \text{ kcal mol}^{-1}$ for the $\text{NO}_2^+/\text{NO}_2$ couple, good fit of the k_{obs} value ($k_{\text{obs}} = 0.073 \text{ M}^{-1} \text{ s}^{-1}$) obtained for reaction of the mixed $\text{Bu}_4\text{N}^+\text{--K}^+$ salt of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ in acetonitrile with eqs 1 and 4 required that a value of $I_{11} = \sim 40 \text{ kcal mol}^{-1}$ be assigned to the $\text{Co}^{\text{III/II}}\text{W}_{12}^{5-/6-}$ couple. This higher value for I_{11} —a consequence of the somewhat lower k_{obs} value obtained for the mixed

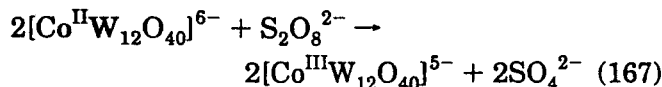
Bu₄N⁺-K⁺ salt vs that obtained using the Bu₄N⁺ salt—was tentatively attributed to a greater degree of ion pairing between K⁺ and [Co^{II}W₁₂O₄₀]⁶⁻.

In light of the uncertainty that appears to exist in the value of *I*₁₁ (section III.C), these conclusions must be regarded, at least for the present, as tentative. In particular, assignment of a high reorganization energy to the NO₂⁺/NO₂ couple requires that the reorganization energy associated with the Co^{III/II}W₁₂O₄₀^{5-/6-} couple (*I*₁₁) be small (i.e., ~25 kcal mol⁻¹). In section III.C, a concern was raised that this value for *I*₁₁ might be considerably underestimated. To the extent that the true value for *I*₁₁ might be greater than 25 kcal mol⁻¹, the conclusions reached here by Lund and Eberson would be compromised.

At the time of this writing, Professor Eberson has indicated his intention of cross-checking the NO₂⁺/NO₂ reorganization energy by using other substrates.⁸⁹ More generally, however, given the continued and frequent use of the cobaltotungstate anions as quantitative probes for investigating outer-sphere electron-transfer reactions—the present recently published work of Lund and Eberson being a case in point—accurate redetermination of the reorganization energy of the Co^{III/II}W₁₂O₄₀^{5-/6-} couple appears justified.

E. Peroxodisulfate

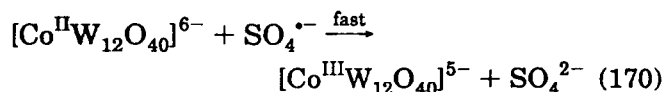
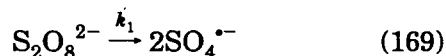
Banerjee investigated the 2-e⁻ reduction of peroxodisulfate by [Co^{II}W₁₂O₄₀]⁶⁻ under pseudo-first-order conditions (excess [S₂O₈]²⁻):^{258,259}



At 50 °C the reaction was first order in [S₂O₈²⁻] (10–80 mM) but zeroth order in [(Co^{II}W₁₂O₄₀)]⁶⁻ (0.1–0.2 mM), and the rate was independent of [H⁺] (0.001–0.50 M; ionic strength kept constant by the addition of Na₂SO₄) and ionic strength (*μ* = 1.56–2.06 M, KNO₃). The experimental rate law (eq 168) was

$$\frac{-d[(\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40})^{6-}]/dt}{2} = k_1[\text{S}_2\text{O}_8^{2-}] \quad (168)$$

consistent with rate-limiting unimolecular dissociation of S₂O₈²⁻ (eqs 169 and 170).



Banerjee noted that previous investigators had observed an [H⁺] dependence that was not evident here. However, Banerjee's value of *k*₁ ((0.73 ± 0.03) × 10⁻⁶ s⁻¹) agreed with the literature value (1.0 × 10⁻⁶ s⁻¹), as did the observed activation parameters (Δ*H*[‡] = 30 kcal mol⁻¹ and Δ*S*[‡] = 6.9 cal K⁻¹ mol⁻¹).

Investigating the same reaction, Mehrotra²⁶⁰ made an interesting observation regarding the absence of

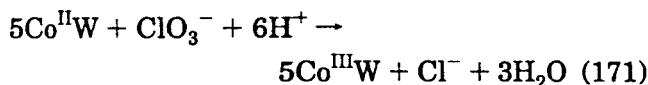
any [H⁺] dependence reported by Banerjee: By using Na₂SO₄ to (conscientiously) maintain a constant ionic strength while varying [H₂SO₄], Banerjee had inadvertently buffered the reaction solutions at the p*K*_a of bisulfate. After controlling for the pH-leveling effect of SO₄²⁻, Mehrotra observed the [H⁺] dependence Banerjee had apparently anticipated.

Recognizing that lacunary POM anions could be used to stabilize high oxidation states of coordinated metal ions, Shilov^{261,262} used S₂O₈²⁻ to oxidize lanthanide- (M = Pr and Tb) and actinide- (M = Am) substituted heteropolytungstates, [M^{III}P₂W₁₇O₆₁]⁷⁻ to [MIVP₂W₁₇O₆₁]⁶⁻. The oxidation of [Am^{III}P₂W₁₇O₆₁]⁷⁻ to [Am^{IV}P₂W₁₇O₆₁]⁶⁻ was first order in S₂O₈²⁻ and zeroth order in polyanion. More recently You and Gu²⁶³ reproduced Shilov's results using [Tb^{III}(PW₁₁O₃₉)₂]¹¹⁻ complexes.

Using a similar synthetic strategy, Pope²⁴⁷ recently prepared Mn(IV)-substituted heteropolytungstates, [Mn^{IV}(OH)XW₁₁O₃₉]ⁿ⁻ (X = Zn, B, and Si), by reaction of the corresponding Mn(II) complexes with S₂O₈²⁻. This result might help explain some puzzling kinetic data, reported several years earlier by Mumtaz and Zubairi.²⁶⁴ They found that the 1-e⁻ oxidation of [Mn^{II}SiW₁₁O]⁶⁻ by S₂O₈²⁻ was one-half order in S₂O₈²⁻, and although details of the data analysis are sketchy, they appear to have observed a first-order dependence of reaction rate on [(Mn^{II}SiW₁₁O₃₉)⁶⁻]. They proposed a mechanism involving rapid and reversible homolytic dissociation of S₂O₈²⁻ followed by slow oxidation of Mn(II) to Mn(III) by SO₄^{•-}. This proposal should be reevaluated.

F. Chlorate and Periodate

Ayoko, Iyun, and co-workers²⁶⁵ investigated the reduction of ClO₃⁻ to Cl⁻ by [Co^{II}W₁₂O₄₀]⁶⁻ in aqueous HClO₄ solution at an ionic strength of *μ* = 1.0 M (NaClO₄) (eq 171).



Uncatalyzed, the reaction was very slow even at 60 °C. In the presence of Ag⁺, however, more rapid rates were seen and the following rate law (eq 172) observed. Even in the presence of Ag⁺, however, the

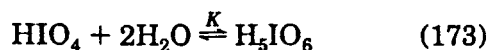
$$-d[\text{Co}^{\text{III}}\text{W}]/dt = 5(k_o + k_1[\text{H}^+]^2)[\text{Ag}^+][\text{Co}^{\text{II}}\text{W}][\text{ClO}_3^-] \quad (172)$$

reaction was not particularly fast: At 60 °C *k*_o and *k*₁ were reported to be (1.28 ± 0.10) × 10⁻⁴ M⁻¹ s⁻¹ and (2.22 ± 0.20) × 10⁻⁴ M⁻³ s⁻¹, respectively.

Ayoko also used [Co^{II}W₁₂O₄₀]⁶⁻ to investigate the reductions of BrO₃⁻²⁶⁵ and IO₄⁻.²⁵⁹

Banerjee²⁵⁸ investigated the rate of 2-e⁻ reduction of periodate, I^VO₄⁻ (1.0–60.0 mM total [I(VII)]), to iodate, I^VO₃⁻, by [Co^{II}W₁₂O₄₀]⁶⁻. The reaction was studied over a pH range of 0.7 to 3.0 ([H⁺] = 1.0–200 mM, HNO₃) at *μ* = 0.10 M (KNO₃). In aqueous-acid solution, periodic acid exists in equilibrium with its hydrated form, orthoperiodic acid, H₅I^VO₆ (eq

173). At 25 °C periodic acid dominates ($K = 3.4 \times 10^{-2}$). The acid mixture has an apparent pK_a of 1.6.



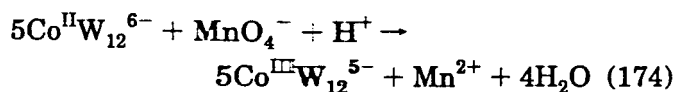
At 60 °C the reaction stoichiometry was dependent upon the $[\text{Co}^{\text{II}}\text{W}_{12}^{6-}]/[\text{I(VII)}]_{\text{T}}$ ratio, where $[\text{I(VII)}]_{\text{T}}$ is the total concentration of I(VII). When the $[\text{Co}^{\text{II}}\text{W}_{12}^{6-}]/[\text{I(VII)}]_{\text{T}}$ ratio was 1:10 (excess I(VII)), the stoichiometry was $0.9 \pm 0.02 \text{ Co}^{\text{II}}\text{W}_{12}^{6-}:\text{I(VII)}$; at a ratio of 6:1 (excess $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$), the stoichiometry was 2.01 ± 0.03 .

At pH 1 under pseudo-first-order conditions (excess I(VI), 60 °C), the reaction was first order in $[\text{Co}^{\text{II}}\text{W}_{12}^{6-}]$. At constant $[\text{Co}^{\text{II}}\text{W}_{12}^{6-}]$ (0.2 mM), the reaction was first order in $[\text{I(VI)}]_{\text{T}}$ at low $[\text{I(VI)}]_{\text{T}}$ (~1–3 mM) and gradually became independent of $[\text{I(VI)}]_{\text{T}}$ at higher concentrations (>15 mM I(VI); i.e., saturation kinetics). A plot of k_{obs} vs $[\text{H}^+]$ (0.001–0.200 M, pH 3–0.7) possessed a nearly zero intercept and increased asymptotically to a limiting value at high $[\text{H}^+]$. This suggested that the acids, HIO_4 and H_5IO_6 , rather than their conjugate bases, were the reactive species. At constant $[\text{Na}^+]$ at pH 1, increase in the ionic strength had no effect on rate. However, increases in Na^+ or K^+ concentrations decreased the reaction rate, and the inhibitory effect of Na^+ was slightly greater than that of K^+ .

Proposed mechanistic schemes included the acid dissociation of H_5IO_6 and association between $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ and H_5IO_6 prior to electron transfer (relative reactivities of HIO_4 , vs HIO_6 were not explicitly addressed). The observation of both association-complex formation and inhibition by specific cations, M^+ (as opposed to the specific-cation catalysis observed in oxidations by $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$), led the authors to propose an “inner-sphere” mechanism involving an intermediate complex, formed by “bonding of a periodate oxygen to a surface tungsten atom”. (The inhibitory effect of alkali-metal cation was attributed to competition with H_5IO_6 for association with $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$.) It is puzzling why the observation of association-complex formation and inhibition by alkali-metal cations should require recourse to such a mechanism. The observations are adequately accounted for by ion pairing between $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ and alkali-metal cations, M^+ (section II.C),⁵² and the formation of donor- M^+ -acceptor association complexes prior to electron transfer (section II.D).

G. Permanganate

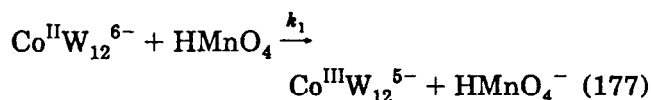
Ayoko recently studied the reduction of permanganate by $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ at 25 °C (eq 174) by moni-



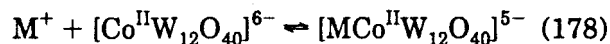
toring the decrease in absorbance of MnO_4^- (525 nm) under pseudo-first-order conditions (10-fold excess of $\text{Co}^{\text{II}}\text{W}_{12}^{6-}$) at high ionic strength ($\mu = 1.0 \text{ M}$, NaClO_4) over a range of H^+ concentrations (0.01–0.50 M, HClO_4).²⁶⁷ The following rate law was observed:

$$\frac{-d[\text{Co}^{\text{II}}\text{W}_{12}^{6-}]/dt}{5} = \frac{k_0 + k'[\text{M}^+][\text{H}^+][\text{Co}^{\text{II}}\text{W}_{12}^{6-}][\text{MnO}_4^-]}{(k_0 + k'[\text{M}^+])[\text{H}^+][\text{Co}^{\text{II}}\text{W}_{12}^{6-}][\text{MnO}_4^-]} \quad (175)$$

where $\text{M} = \text{Li}, \text{Na}, \text{or K}$. Values for k' , determined at low $[\text{H}^+]$ (0.01 M) (i.e., higher $[\text{MnO}_4^-]$), followed the order $k'_{\text{Li}} < k'_{\text{Na}} < k'_{\text{K}}$. The following elementary reaction steps were proposed (subsequent reduction steps were assumed to occur rapidly):



It was noted that the order of rate enhancement by the alkali-metal cations was in keeping with the greater degrees of ion pairing frequently observed for the larger cations. The authors recognized, however, that ion pairing (eq 178) shifted the potential of the $\text{Co}^{\text{III}}\text{W}_{12}^{5-}/\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ couple to more positive values.⁵²



Thus, ion pairing (eq 178) alone would have been expected to decrease the reaction rate, with $k_{\text{Li}} > k_{\text{Na}} > k_{\text{K}}$, opposite to the order actually observed. Faced with these enigmatic results, the authors proposed that the greater polarizability of the larger cations might make them more kinetically facile “bridges” for electron transfer. Recent data⁵⁰ appear to argue against this proposal (see section II.C).

An alternative explanation is that the larger cations better facilitated the formation of ternary complexes, $[(\text{MnO}_4^-)(\text{M}^+)(\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}^{6-})]^{6-}$ (i.e., larger formation constants for the ternary aggregates). Analogous considerations pertain to the effects of alkali-metal cation pairing (eq 178) on the electrochemical potential⁵² of the $\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}^{5-}/\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}^{6-}$ couple.

The Marcus cross-relation (eq 17) was used to evaluate the reduction of protonated HMnO_4 by setting the $[\text{H}^+]$ -dependent rate constant, k_0 (eq 175), equal to Kk_1 . Division of k_0 ($6.0 \text{ M}^{-2} \text{ s}^{-1}$) by the literature value for K ($2.99 \times 10^{-3} \text{ M}^{-1}$) gave $k_1 = 2.01 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. Application of the Marcus cross-relation to the evaluation of k_1 assumed the absence of association-complex formation prior to electron transfer. This appears justified: Values of k' (eq 175) were small relative to k_1 (eq 177) (i.e., ternary complex formation did not appear to be important in the reactions of $[\text{M}_n\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{(6-n)-}$ ion pairs with neutral HMnO_4).

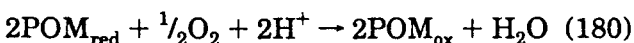
In the Marcus calculation, a literature value of $k_{2,2}$ for the $\text{HMnO}_4/\text{HMnO}_4^-$ self-exchange reaction (measured at $\mu = 1.0 \text{ M}$, NaClO_4) was used. For the $\text{Co}^{\text{III}}\text{W}_{12}^{5-}/\text{Co}^{\text{II}}\text{W}_{12}^{6-}$ self-exchange reaction, the published k_{11} value³ determined at $\mu = 0.1 \text{ M}$ (LiCl) was used without extrapolation to prevalent ionic strength (see section III.A above). Nevertheless, the Marcus cross-relation gave a value of k_1^{cal} ($5.37 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) in relatively good agreement with experimental observation, $k_{1, \text{exp}} = 2.01 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

In light of section III.C, it should be noted that although use of the Marcus cross-relation (eq 17) requires knowledge of self-exchange rate constants, in this case k_{11} for the $\text{Co}^{\text{III/II}}/\text{W}_5^{5-/6-}$ couple, no assumptions regarding the reorganization energy inherent in k_{11} need be made.

VIII. Reduction of Dioxygen by Reduced POM Anions

A. introduction

POM anions can serve as electron-transfer agents in the selective homogeneous thermal or photochemical oxidations of organic or other substrates by dioxygen.^{113,144} The catalytic cycle is often represented by two steps: (1) selective oxidation of a substrate (SubH_2 , eq 179) by the oxidized form of a POM anion (POM_{ox}) and (2) reoxidation of the reduced POM anion (POM_{red}) by dioxygen (eq 180).



The two steps can occur consecutively, as shown, or simultaneously; the POM anions can be reduced by one electron each, as shown, or by more than one electron. The selective oxidation of substrate (eq 179) may be either thermal or photochemical (i.e., utilizing photoexcited POM_{ox}^*). However, the reduction of dioxygen by POM_{red} anions, the topic of this section, is generally a thermal process. (The kinetics and mechanisms of a number of homogeneous POM-catalyzed oxidations by O_2 are discussed by Kozhevnikov¹¹⁴ in this issue of *Chemical Reviews*.)

B. Single-Electron Reduction of O_2

Reduced POM anions reduce dioxygen by both inner- and outer-sphere mechanisms. In the outer-sphere reduction of dioxygen, the first step is electron transfer to O_2 :



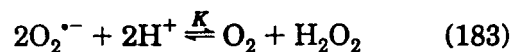
In water at low pH values, the reduction is accompanied by protonation of the superoxide anion to the superoxide radical ($\text{HO}_2^{\bullet -}$; eq 182), which has a pK_a of 4.69.²⁶⁸



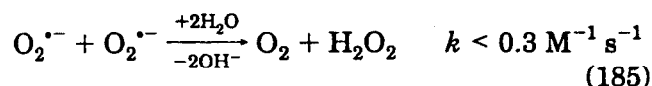
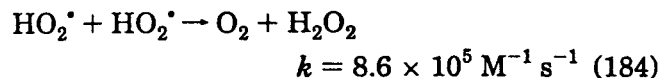
At pH 0 in water, the single-electron-reduction potential, E° , of O_2 is +0.12 V vs NHE. This value is based on unit concentrations of O_2 and its reduction products in water. If unit pressure is taken as the standard state of O_2 , the more often quoted value of -0.05 V vs NHE applies.²⁶⁹ The standard reduction potential of O_2 decreases with pH. At pH values substantially above the pK_a of $\text{HOO}^{\bullet -}$ (e.g., above ~pH 7), $E^\circ = -0.16$ V for unit concentrations of O_2 in water (-0.33 V for 1 atm O_2).

Also pertinent to discussion of O_2 reduction reactions is the disproportionation (or in biology, dismu-

tation) of superoxide to hydrogen peroxide and dioxygen. The reaction (eq 183) is spontaneous over the entire pH range in water and goes to completion even at pH 14.²⁶⁸ At neutral pH, $K_{\text{pH } 7} = 4 \times 10^{20}$.



The bimolecular disproportionation reaction is promoted by protons; it is relatively rapid at pH values well below 4.69 (the pK_a of superoxide radical, $\text{HO}_2^{\bullet -}$) and quite slow at pH values above 4.69 (eqs 184 and 185).²⁶⁹ (The pK_a of H_2O_2 is 11.75, well above that of $\text{HO}_2^{\bullet -}$.)²⁷⁰



The pH dependences of the reduction potentials of additional reactions involved in the stepwise 4- e^- reduction of O_2 to water or hydroxide anions have been reviewed.²⁷¹

C. The $\text{O}_2/\text{O}_2^{\bullet -}$ Self-Exchange Reaction

The value of the self-exchange rate constant, k_{11} (and implicitly, reorganization energy, I , for reduction of O_2 to $\text{O}_2^{\bullet -}$ is central to theoretical evaluation of rate constants for reactions that involve outer-sphere reductions of O_2 . However, as recently as a decade ago, a great deal of uncertainty surrounded experimentally determined rate constants for the $\text{O}_2/\text{O}_2^{\bullet -}$ self-exchange reaction.²⁷² The reason for this uncertainty was that estimated k_{11} values, obtained by Marcus treatment of rate constants measured for cross-reactions of O_2 or $\text{O}_2^{\bullet -}$ with inorganic electron-donor or electron-acceptor complexes, ranged from 10^{-7} to $10^7 \text{ M}^{-1} \text{ s}^{-1}$. Questions pertinent to explanation of this variation included²⁷³ (1) was the Marcus-Hush theory applicable to systems involving small molecules in which the size, charge, and extent of solvation of the oxidized and reduced species (e.g., O_2 and $[\text{O}_2^{\bullet -}(\text{H}_2\text{O})_n]$) differed greatly from one another, and (2) were some of the reactions used to determine k_{11} values truly adiabatic outer-sphere electron-transfer processes?

In 1988 Zahir, Espenson, and Bakac²⁷³ found that the relationship between kinetic and thermodynamic data for single-electron reductions of O_2 by a series of Cr(II) complexes obeyed that predicted by Marcus. Moreover, examination of published data showed that the highly scattered k_{11} values previously reported had *all* been derived from cross-reactions involving reduction by $\text{O}_2^{\bullet -}$ anions (the italics are the authors'), while k_{11} values determined from reductions of O_2 were in good agreement with one another. They suggested that some complicated interactions were likely involved in the reductions of oxidants by $\text{O}_2^{\bullet -}$ anions. From their and others' rate data for reductions of O_2 by substitution-inert inorganic complexes, k_{11} was determined to lie in the range $1\text{--}10 \text{ M}^{-1} \text{ s}^{-1}$.

Table 10. Polyanion Reduction Potentials, Relative Quantum Yields for the Photochemical Formation of Reduced Polyanion, and Rate Constants for Electron Transfer from the Reduced Polyanion to O₂

POM _{ox}	POM _{red}	E (V vs NHE)	ΔG° ^a (kcal mol ⁻¹)	Φ _{rel} [POM _{red}]	k ^b (M ⁻² s ⁻¹)
[P ^V W ₁₂ O ₄₀] ³⁻	[P ^V W ₁₂ O ₄₀] ⁴⁻	+0.218	+2.26	1.00	7.5 × 10 ²
[P ^V W ₁₂ O ₄₀] ³⁻	[P ^V W ₁₂ O ₄₀] ⁴⁻	+0.218	+2.26	not reported	8.8 × 10 ² ^c
[Si ^{IV} W ₁₂ O ₄₀] ⁴⁻	[Si ^{IV} W ₁₂ O ₄₀] ⁵⁻	+0.054	-1.52	0.70	6.5 × 10 ⁴
[Fe ^{III} W ₁₂ O ₄₀] ⁵⁻	[Fe ^{III} W ₁₂ O ₄₀] ^{7-d}	-0.169 ^d	-6.66	0.09	2.8 × 10 ⁶
[H ₂ W ₁₂ O ₄₀] ⁶⁻	[H ₂ W ₁₂ O ₄₀] ⁷⁻	-0.162	-6.50	0.13	1.7 × 10 ⁶

^a Calculated using E°(O₂/HO₂) = +0.12 V vs NHE at pH 0. ^b Calculated from reported k_{obs}, using [O₂] = 2 × 10⁻⁴ M and [H⁺] = 0.1 M. ^c Calculated from the reported pseudo-first-order rate constant, k = 2.2 × 10⁻² s⁻¹,²⁵⁰ using [O₂] = 2.5 × 10⁻⁴ M and [H⁺] = 0.1 M. ^d The doubly reduced anion was formed.

In a 1989 study by Lind, Shen, Merényi, and Jonsson,²⁷⁴ the rate constant for the O₂O₂^{•-} self-exchange reaction in water was measured directly under alkaline conditions (pH > pK_a of HOO[•]) by means of ¹⁸O/¹⁶O isotope marking. A second-order rate constant of k₁₁ = 450 ± 160 M⁻¹ s⁻¹ was found. From this value, a reorganization energy of I = I_{in} + I_{out} = 45.5 ± 0.7 kcal mol⁻¹ was calculated from the Marcus relationship (eq 1). The authors pointed out that in outer-sphere reactions in which the effective radii of the reacting partners differ substantially, I_{out} values are not strictly additive. Consequently, k₁₁ values calculated from cross-reaction rate data (such as those determined by Zahir, Espenson, and Bakac) might easily be a few orders of magnitude smaller than 450 M⁻¹ s⁻¹, the directly determined value.

In 1993 Merényi, Lind, and Jonsson²⁷⁵ demonstrated that application of the Marcus equation (eq 1, using I as an adjustable parameter) to kinetic and thermodynamic data for the oxidations of 25 closed-shell (singlet ground-electronic-state) organic compounds by ³O₂ gave an excellent fit. The best fit gave I = 37.4 ± 2.5 kcal mol⁻¹ which corresponded to an apparent k₁₁ of 2 M⁻¹ s⁻¹. Notably, the closed-shell organic compounds studied were similar in size to the substitution-inert Cr(II) and Ru(II) complexes (atomic radii ranging from 3.4 to 6.8 Å) evaluated by Zahir, Espenson, and Bakac.²⁷³ The atomic radii of most POM anions also fall within this range.

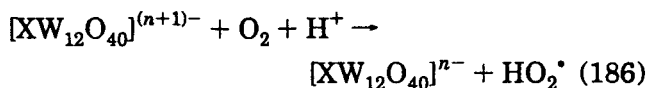
Reductions of O₂ by three general categories of POM anions have been reported: (1) isopoly- and heteropolytungstates, (2) d-electron-containing first-row transition-metal- (and ruthenium-) substituted heteropolytungstates, and (3) mixed-addenda vanadomolybdophosphates.

D. Reduction of O₂ by Reduced Isopoly- and Heteropolytungstates

In 1980 Papaconstantinou²⁷⁶ and co-workers reported that various isopoly- and heteropolyanions, when irradiated in the presence of organic compounds, were reduced to the corresponding blues, and the organic compounds present were oxidized. Two years later he reported²⁵⁰ that when coupled with reoxidation of the reduced POM anions by O₂, the photochemical reactions could provide the basis for photocatalytic oxidations of organic substrates by dioxygen (eqs 179 and 180). As part of a preliminary survey of POM reactivity, he used microsecond flash photolysis of [PW₁₂O₄₀]³⁻, in the presence of 2-propanol, to generate the 1-e⁻-reduced heteropoly blue anion [PW₁₂O₄₀]⁴⁻ in oxygen-saturated ([O₂] = ~2.5

× 10⁻⁴ M) water at pH 1 (HClO₄). The pseudo-first-order rate constant for reoxidation of [PW₁₂O₄₀]⁴⁻ by O₂ (k = 2.2 × 10⁻² s⁻¹, excess O₂) was measured by monitoring the rate of decrease of the absorption band (751 nm) attributed to the reduced polyanion.

The same technique was used by Akid and Darwent²⁵⁵ several years later to determine the rates of oxidation of a series of reduced Keggin anions by O₂. Microsecond flash photolysis of aqueous solutions containing the Keggin heteropolytungstate anions [XW₁₂O₄₀]ⁿ⁻ (POM_{ox} X = P(V), Si(IV), Fe(III), 2H⁺, and Co(II); 2 × 10⁻⁶ M) and *i*-PrOH (1.7 M) in oxygenated water ([O₂] = 2 × 10⁻⁴ M) at pH 1 (H₂SO₄) gave the 1-e⁻-reduced anions, [XW₁₂O₄₀]⁽ⁿ⁺¹⁾⁻ ((5–8) × 10⁻⁷ M). The rate of reduction of O₂ to HOO[•] was measured by monitoring the rate of decay of the absorbance attributed to the heteropoly blue anion [XW₁₂O₄₀]⁽ⁿ⁺¹⁾⁻ (eq 186). The reaction was first order



in [POM_{red}], [O₂], and [H⁺], which suggested a rate expression of the form

$$\frac{-d[\text{XW}_{12}\text{O}_{40}]^{(n+1)-}}{dt} = k[\text{XW}_{12}\text{O}_{40}]^{(n+1)-}[\text{H}^+][\text{O}_2] \quad (187)$$

The first-order dependence of rate on [H⁺] suggested that HOO[•], rather than OO^{•-}, was involved in the rate-determining step. More direct evidence for the formation of HOO[•], which at low pH values disproportionates rapidly to O₂ and H₂O₂ (eq 184), or of H₂O₂, was not reported. Although the rate of oxidation of the reduced Keggin anions by H₂O₂ was also not discussed, it has been shown²⁷⁷ that the rate of reaction of a closely related heteropolytungstate, the 1-e⁻-reduced Wells-Dawson anion [P₂W₁₈O₆₂]⁶⁻ (POM_{ox}, shown) with hydrogen peroxide is an order of magnitude slower than the rate of oxidation of the reduced anion by O₂.

POM reduction potentials and termolecular rate constants for the reduction of O₂ measured at constant O₂ and H⁺ concentrations ([O₂] = 2 × 10⁻⁴ M, pH = 1) are shown in Table 10.

Plot of ln k vs -ΔG°/RT (eq 8 and Figure 8) gave a slope of 0.52, very close to the value of 0.5 predicted by Marcus (eq 1; |ΔG°| < I). In keeping with the first-order dependence of rate on [H⁺] noted above, the [H⁺]-dependent value for the reduction potential of O₂ was used to calculate ΔG° (see footnote in Table

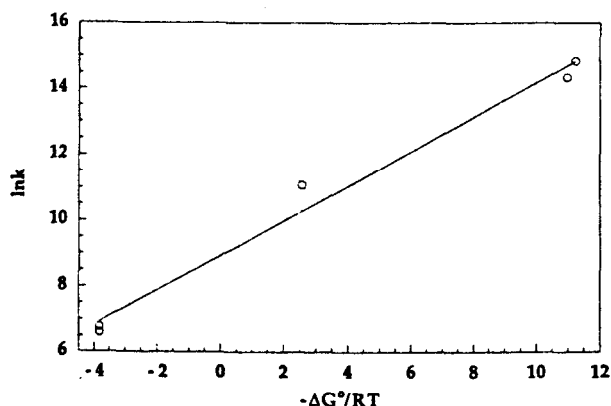


Figure 8. Plot of $\ln k$ vs $-\Delta G^\circ/RT$ for the reduction of O_2 by reduced heteropolytungstate anions.

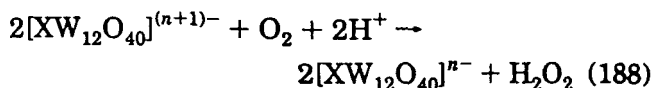
10). The y intercept of the plot in Figure 8 ($\ln Z - I/4RT$) is 8.9, from which a collision frequency of $Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ gives $I = 38.9 \text{ kcal mol}^{-1}$.

If the reorganization energies for the O_2/O_2^- (I_{11}) and $POM^{n/(n+1)-}$ (I_{22}) self-exchange reactions were strictly additive (i.e., $I = 0.5(I_{11} + I_{22})$), a value of $I = 0.5(45.5 + 22.3) = 33.9 \text{ kcal mol}^{-1}$ would have been expected on the basis of published data for I_{11} ²⁷⁴ and I_{22} .²³ However, large differences in size and shape between O_2 (linear) and spherical electron donors have been shown to cause deviations from strict additivity. For example, radius ratios, r_{22}/r_{11} (effective radius of O_2 , $r_{11} = \sim 2.5\text{--}3.0 \text{ \AA}$), of ~ 2.5 are expected to give experimental cross-reaction I values that are $\sim 6 \text{ kcal mol}^{-1}$ greater than those predicted on the basis of strict additivity.²⁷⁵ Due to the discrepancy in size and shape between O_2 and the Keggin anion (relatively spherical, $r = 5.6 \text{ \AA}$), similar deviation from strict additivity should be anticipated. The result obtained from the combined data of Papaconstantinou²⁵⁰ and Akid and Darwent,²⁵⁵ ($I_{e \times p} - I_{calc}$) = $38.7\text{--}33.9 = 5.0 \text{ kcal mol}^{-1}$, is in line with this expectation.

The rate of oxidation of tetra- n -propylammonium (Pr_4N^+) salts of a mixture of 2- and 4-e⁻-reduced $[PW_{12}O_{40}]^{3-}$ anions in air-saturated acetonitrile was followed by visible absorption spectroscopy at 25°C .²⁷⁸ In acetonitrile-containing tetrabutylammonium perchlorate (0.1 M) supporting electrolyte, the half-wave potential for the first reduction of $(Pr_4N)_3[PW_{12}O_{40}]$ was -0.1 V vs NHE compared to $+0.218 \text{ V}$ at pH 1 in water. Plot of $\ln(\text{absorbance})$ vs time for reoxidation of the reduced POM anion mixture gave a straight line, which implied nearly identical rate constants for the reactions of O_2 with the different reduced POM species present. Using the known solubility of O_2 in acetonitrile, an aggregate pseudo-unimolecular rate constant of $3.7 \times 10^{-2} \text{ s}^{-1}$ was calculated for the reoxidation reactions. Analogous pseudo-unimolecular rate constants for reoxidation of $[PW_{12}O_{40}]^{4-}$ in water at pH 1 were $2.2 \times 10^{-2} \text{ s}^{-1}$ ²⁵⁰ and $15 \times 10^{-3} \text{ s}^{-1}$.²²⁵

Hiska and Papaconstantinou studied the rate of reoxidation of 1-e⁻-reduced heteropolyanions ($P_2W_{18}O_{62}]^{7-}$, $[SiW_{12}O_{40}]^{5-}$, and $[H_2W_{12}O_{40}]^{7-}$) as a function of $[H^+]$ by adjusting the ratio of $[H^+]$ to $[Na^+]$ at high ionic strength (0.5 M, ClO_4^-).^{277,279} As anticipated the magnitudes of pseudo-first-order rate

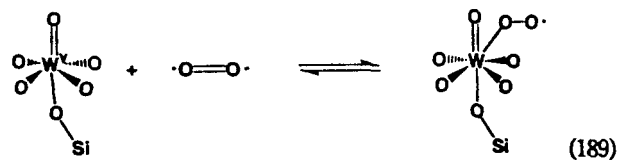
constants followed the reduction potentials of the anions, the more thermodynamically favored reoxidation reactions occurring more rapidly: $[P_2W_{18}O_{62}]^{7-} < [SiW_{12}O_{40}]^{5-} < [H_2W_{12}O_{40}]^{7-}$. Although the anticipated reduction product, H_2O_2 , was not observed (hypothetical concentrations were too low in any event), the expected stoichiometry, 2 equiv of 1-e⁻-reduced POM anion per equivalent of O_2 , was established by following the consumption of dioxygen (eq 188).



At pH 1 the rate of reaction of $[P_2W_{18}O_{62}]^{7-}$ with O_2 ($k_{obs}/[O_2] = 4.8 \text{ M}^{-1} \text{ s}^{-1}$) was 24 times faster than its rate of reaction with H_2O_2 ($k_{obs}/[H_2O_2] = 0.2 \text{ M}^{-1} \text{ s}^{-1}$). In addition, in contrast to results reported for the reduction of O_2 by 2- and 4-e⁻-reduced $(Pr_4N)^{3-}[PW_{12}O_{40}]$ salts in acetonitrile,²⁷⁸ Hiskia and Papaconstantinou found that the rates of reoxidation of 2-e⁻-reduced anions in water were greater than those of 1-e⁻-reduced anions.

At constant pH and ionic strength, the reoxidations of 1-e⁻-reduced heteropolyanions were first order in $[POM_{red}]$ and in $[O_2]$. However, in plots of k_{obs} vs pH, some reactions (reoxidation of $[P_2W_{18}O_{62}]^{7-}$ and $[SiW_{12}O_{40}]^{5-}$) appeared independent of $[H^+]$ at low and high $[H^+]$ values and first order in $[H^+]$ at intermediate $[H^+]$ values. At low pH values of ~ 1 , pseudo-first-order rate constants of $k_{obs} = 3.8 \times 10^{-3}$, 1.0, and $> 5.5 \text{ s}^{-1}$ were observed, and at high pH values (> 3), k_{obs} values of 0.0, 2.7×10^{-2} , and 0.15 s^{-1} were observed for the reactions of O_2 with $[P_2W_{18}O_{62}]^{7-}$, $[SiW_{12}O_{40}]^{5-}$, and $[H_2W_{12}O_{40}]^{7-}$, respectively. (The k_{obs} values observed at pH 1 are comparable to those reported in Table 10.) The reduced anions $[P_2W_{18}O_{62}]^{7-}$ and $[SiW_{12}O_{40}]^{5-}$ remained unprotonated over the pH range studied. By contrast, k_{obs} values for reoxidation of $[H_2W_{12}O_{40}]^{7-}$, which is protonated at pH values below 4.9, increased to a maximum as the pH was increased from near 0 to 1 and then decreased, reaching a near-constant value at pH values greater than 3.

Because two of the anions were known to remain unprotonated over the pH range studied, ion pairing between the POM and H^+ ions was excluded as an explanation for the pH dependence of k_{obs} . One alternative possibility considered was that the pH dependence resulted from protonation of a dioxygen molecule coordinated to the reduced POM anion. The formation of an adduct between the 3O_2 diradical and an unpaired electron in the $b_2(d_{xy})$ orbital of a tungsten atom in the 1-e⁻-reduced POM anion was suggested. Given the kinetic stability of the W-O-W bonds in most heteropolytungstates, a 7-coordinate tungsten complex (eq 189), although sterically con-



gested, was deemed more likely than an intermediate

Table 11. Standard One-Electron-Reduction Potentials of Mn(III)-Substituted α -Keggin Heteropolytungstate Anions

redox pair $E^\circ(\text{V vs NHE})$	$\text{BMnW}_{11}^{6-/7-}$ +0.43	$\text{ZnMnW}_{11}^{7-/8-}$ +0.53	$\text{SiMnW}_{11}^{6-/5-}$ +0.65	$\text{GeMnW}_{11}^{6-/5-}$ +0.81	$\text{PMnW}_{11}^{5-/4-}$ +0.88
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involving coordination of O_2 to either a terminal ($\text{M}=\text{O}$) or bridging ($\text{M}-\text{O}-\text{M}$) oxide (O^{2-}) anion of the reduced polyoxoanion.

On the basis of this reasoning, the inflection points seen in the plots of k_{obs} vs pH might have corresponded to the $\text{p}K_{\text{a}}$ value of the coordinated dioxygen molecule and/or might have signified a mechanism involving rate-limiting electrophilic attack of H^+ on coordinated dioxygen. Attempts to observe O_2 -bound intermediates by ESR, as had been observed in the reactions of Mn(II)-substituted heteropolyanions with O_2 in anhydrous apolar organic solvents,^{178,179} were unsuccessful, and the issue was left unresolved.

In retrospect, however, these data need not be interpreted as evidence of an inner-sphere mechanism. The effects of pH on k_{obs} might be attributed not to $[\text{H}^+]$, but rather to the changes in Na^+ concentrations required to maintain the high ionic strength ($\mu = 0.5 \text{ M}$) as H^+ concentrations were varied. At pH values near 0, Na^+ concentrations would be very small ($\sim 0.003 \text{ M}$), while at pH values greater than 3, Na^+ concentrations would exceed 0.499 M . At these high Na^+ concentrations, significant ion pairing can be expected. The effect of ion pairing is to shift the reduction potentials of the POM anions to more positive values, making ΔG° for electron transfer to O_2 less favorable. Hence, the inflection points observed in the plots of pH vs k_{obs} might reflect $\text{p}K_{\text{f}}$ values for Na^+ -ion pairing (K_{f} = formation constant for ion pairing) rather than $\text{p}K_{\text{a}}$ values for protonation of coordinated dioxygen. At the same time, the pH dependence of the reduction potential of the O_2/O_2^- couple (i.e., the effect of this potential on ΔG°) must still be considered.

A general correlation between POM anion reduction potentials and rates of reoxidation by O_2 was also observed by Kuznetsova and co-workers,^{280,281} who studied the oxidation of 0.05 M solutions of reduced mixed-addenda vanadotungstophosphate anions, $[\text{PV}_n\text{W}_{12-n}\text{O}_{40}]^{(3+n)-}$ (POM_{ox} forms indicated), in 40% acetic acid. They found that at moderate temperatures neither $[\text{PV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{5-}$ nor $[\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{6-}$ reacted with O_2 . However, at pH 3 reduced $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$ anions (POM_{ox} shown) reacted slowly, while $[\text{PV}_4\text{W}_8\text{O}_{40}]^{7-}$ anions reacted to the same extent reacted rapidly. Although the degrees of ion (H^+ or Na^+) pairing present in each case were not evaluated, more negatively charged anions generally possess more negative reduction potentials.³²

Duncan and Hill²⁸² provided additional support for an outer-sphere mechanism in the reactions of reduced isopoly- and heteropolytungstates with O_2 . They used ^{17}O NMR to investigate the temporal evolution of ^{17}O in products resulting from the reactions of reduced POM anions with $^{17}\text{O}_2$.^{283,284} Upon reduction of $^{17}\text{O}_2$ by POM_{red} , the ^{17}O label was initially observed in solution as $\text{H}_2^{17}\text{O}_2$ and H_2^{17}O . From a series of control experiments, it was deter-

mined that the rates of formation of labeled H_2O_2 and water were much greater than the rates of exchange of these products with oxygen atoms in the polyoxometalate ($[\text{W}_{10}\text{O}_{32}]^{4-}$ and $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$) frameworks. Hence, it was unequivocally established that no oxygen incorporation into the polyoxoanions occurred during, or immediately after, electron transfer to O_2 .

Duncan and Hill argued that if inner-sphere complexes, such as that shown in eq 189, were involved, at least some of the ^{17}O -labeled oxygen would have been incorporated into the polyanion frameworks. At the same time, the authors acknowledged that because the oxygen-exchange chemistry of hypothetical $\text{POM}-\text{O}_2$ adducts could not be assessed, the absence of O_2 incorporation did not entirely rule out an inner-sphere mechanism. However, these ^{17}O -labeling studies, combined with the close correlation with Marcus theory reported by Akid and Darwent,²⁵⁵ point strongly to an outer-sphere mechanism for the reduction of O_2 by aqueous solutions of reduced isopoly and heteropolytungstate anions.

E. Reduction of O_2 by d-Electron-Containing, Transition-Metal-Substituted Heteropolytungstates

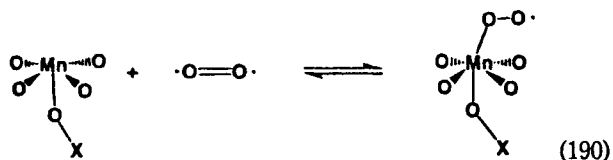
In 1970, building on the work of Baker et al.²⁸⁵ and Malik and Weakley,^{244,246} Tourné and Weakley²⁴² prepared a series of isostructural Mn(II)-substituted α -Keggin heteropolytungstate anions, $[\text{X}^{\text{Mn}}\text{Mn}^{\text{II}}(\text{OH}_2)_n\text{W}_{11}\text{O}_{39}]^{(10-x)-}$, where $\text{X} = \text{Zn(II), B(III), Si(IV), Ge(IV), and P(V)}$. In addition, Mn(III) analogues were prepared by chemical oxidation of Mn(II), and the reduction potentials of the $[\text{X}^{\text{Mn}}\text{Mn}^{\text{III/II}}(\text{OH}_2)_n\text{W}_{11}\text{O}_{39}]^{(9-x)-(10-x)-}$ couples were determined (Table 11).

In only one case, $\text{X} = \text{B}$, was the reduction potential of the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ couple sufficiently negative that oxidation of Mn(II) by molecular oxygen was kinetically, as well as thermodynamically, feasible. Thus $[\text{BMn}^{\text{III}}(\text{OH}_2)_n\text{W}_{11}\text{O}_{39}]^{6-}$ was prepared by exposing slightly acidic aqueous solutions of $[\text{BMn}^{\text{II}}(\text{OH}_2)_n\text{W}_{11}\text{O}_{39}]^{7-}$ to air for several days at room temperature.

Inner-sphere oxidation of Mn(II) to Mn(III) in coordinatively unsaturated Mn(II)-substituted heteropolytungstates in dry apolar solvents was first reported by Katsoulis and Pope in 1984.^{178,179} The organic-soluble polyanions were prepared via exchange of alkali-metal counteranions by organic-soluble quaternary alkylammonium cations, such as tetra-*n*-heptylammonium bromide.²⁸⁶ The heteropolyanions $[\text{XMn}^{\text{II}}(\text{OH}_2)_n\text{W}_{11}\text{O}_{39}]^{n-}$ ($\text{X} = \text{P(V), Si(IV), Ge(IV), and B(III)}$) and $\alpha_2\text{-}[\text{P}_2\text{Mn}^{\text{II}}(\text{OH}_2)_n\text{W}_{17}\text{O}_{61}]^{8-}$ were transferred into nonpolar solvents (benzene and toluene) by shaking aqueous solutions of the POM anions with equal volumes of organic-solvent solutions of the quaternary ammonium salts.

Following separation and drying of the POM anion solutions, coordinatively unsaturated Mn(II) complexes (e.g., $[\text{SiMn}^{\text{II}}\text{W}_{11}\text{O}_{39}]^{6-}$) were observed by ESR spectroscopy. These coordinatively unsaturated com-

plexes formed adducts with a variety of donors, such as alcohols, pyridine, and halides, and in several cases, reversible formation of O₂ adducts was observed at low temperatures. (Even at -70 °C, however, exposure of solutions of [BMn^{II}W₁₁O₃₉]⁷⁻ to O₂ resulted in instantaneous formation of [BMn^{III}-W₁₁O₃₉]⁶⁻. Formation of the O₂ adducts (eq 190) was reversed by bubbling N₂ through the solution; warming the oxygenated solutions to ambient temperature resulted in irreversible oxidation of Mn(II) to Mn(III). (By contrast, even at 150 °C and 100 psig O₂, oxidation of K₆[SiMn^{II}(OH₂)W₁₁O₃₉] in water is slow.)¹²⁰



In the presence of polar substances, such as water, pyridine, methanol, acetone, acetonitrile, or chloride ions, no reaction was observed upon oxygenation. This behavior was attributed to competition of the donor molecules for the available (sixth) coordination site on Mn(II) and was interpreted as evidence that the reaction with oxygen occurred via direct inner-sphere coordination of O₂ to Mn(II).

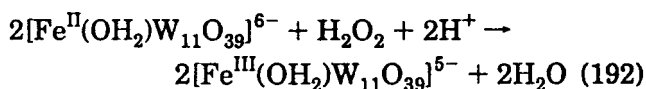
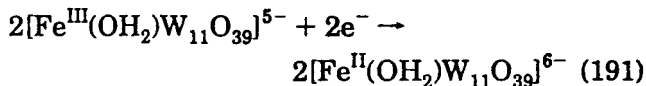
Paradoxically, however, no reaction was observed when the phase-transfer-derived POM anion solutions were scrupulously dehydrated; it was suggested that the oxygen adducts might be stabilized by hydrogen bonding to a water molecule. Efforts to fully characterize an O₂ adduct were only partially successful: Addition of the spin trap 5,5-dimethyl-1-pyrroline N-oxide (dmpo) resulted in solutions that had ESR spectra consistent with the formation of Mn-O₂-dmpo adducts and that over time gave rise to ESR signals tentatively interpreted as resulting from the oxidation of dmpo by superoxide. In addition, in solutions of oxygenated [SiMn^{II}W₁₁O₃₉]⁶⁻, hindered phenols were oxidized to cyclohexadienyl radicals. However, no oxidation was observed when the phenols were added to oxygen-free solutions of [SiMn^{III}W₁₁O₃₉]⁷⁻. It was thus suggested that attack by a 'Mn(III)O₂•' moiety or related polyanion-O₂ species was responsible for single-electron oxidation of the phenols.

Analogous reversible O₂-adduct formation and inner-sphere oxidation of Mn(II) to Mn(III) and of Co(II) to Co(III) was observed upon bubbling of O₂ into anhydrous toluene solutions of tetraalkylammonium salts of Mn(II)- and Co(H)-substituted Keggin and Wells-Dawson anions.²⁸⁷

Reactions of oxygen, superoxide anions, hydrogen peroxide, and hydroxyl radicals with aqueous solutions of Fe(II)-substituted heteropolytungstate anions were studied in connection with the catalytic oxidation of H₂S to S⁰ by [PFe^{II}(OH₂)W₁₁O₃₉]⁵⁻ and O₂ (eq 172, SubH₂ = H₂S)^{211,288-290} and the electrocatalytic reduction of H₂O₂ by [SiFe^{III}(OH₂)W₁₁O₃₉]⁵⁻.^{291,292} At 20 °C aqueous [PFe^{II}(OH₂)W₁₁O₃₉]⁵⁻ was oxidized slowly to [PFe^{III}(OH₂)W₁₁O₃₉]⁵⁻ by O₂. The reaction rate ($k = 3.3 \times 10^{-4} \text{ M min}^{-1} \text{ L}^{-1}$)²⁸⁹ was independent of [H⁺] over a pH range of 2 to 5. The reaction was

autocatalytic: Order of reaction with respect to [PFe^{II}(OH₂)W₁₁O₃₉]⁵⁻ was ~1.6–1.8. The high, nonintegral concentration dependence suggested that additional equivalents of [PFe^{II}(OH₂)W₁₁O₃₉]⁵⁻ were being oxidized by products resulting from the reductive activation of O₂.

A closely related and analogously complex system was the topic of a detailed kinetic study performed by Toth and co-workers.²⁹¹ They found that the rate constant governing the electrocatalytic reduction of H₂O₂ by aqueous solutions of [SiFe^{III}(OH₂)W₁₁O₃₉]⁵⁻ was $9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. At high [SiFe^{III}(OH₂)W₁₁O₃₉]⁵⁻ concentrations, the expected stoichiometry for the reduction of H₂O₂ to water (two electrons per equivalent of H₂O₂, eqs 191 and 192) was observed. How-



ever, under catalytic conditions (substrate-to-catalyst ratios greater than unity), fewer than two electrons were consumed for each H₂O₂ molecule consumed. A catalytic mechanism involving an Fe(IV) intermediate (or an HO• adduct of the Fe(III) complex) produced by reaction of [SiFe^{III}(OH₂)W₁₁O₃₉]⁵⁻ with hydroxyl radicals (HO•) was proposed. The nonintegral stoichiometry observed in the electrocatalytic reduction of H₂O₂ was attributed to competition between two pathways, each involving further reaction of the Fe(IV) intermediate: reaction of the Fe(IV) intermediate with itself to give [SiFe^{III}(OH₂)W₁₁O₃₉]⁵⁻ and an equivalent of H₂O₂ (overall stoichiometry two electrons per equivalent of H₂O₂ consumed) or reduction of the Fe(IV) intermediate by H₂O₂ to give [SiFe^{III}(OH₂)W₁₁O₃₉]⁵⁻ and HOO•, and via disproportionation of HOO•, O₂ and H₂O₂ (0.67e⁻ per equivalent of H₂O₂ consumed). The mechanistic proposal was supported by detailed kinetic analysis of proposed elementary reactions: [SiFe^{II}(OH₂)W₁₁O₃₉]⁵⁻ + H₂O₂, [SiFe^{III}(OH₂)W₁₁O₃₉]⁵⁻ + HO•, and [SiFe^{III}(OH₂)W₁₁O₃₉]⁵⁻ + O₂•⁻.

Significantly, the rate constant for the reaction between [SiFe^{II}(OH₂)W₁₁O₃₉]⁵⁻ and H₂O₂ ($9 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$) was only 1 order of magnitude greater than the value reported for the reaction of H₂O₂ with [Fe(H₂O)₆]²⁺, even though the reaction with [SiFe^{II}(OH₂)W₁₁O₃₉]⁵⁻ was more favorable by 680 mV. It was noted that this insensitivity to thermodynamic driving force argued against an outer-sphere mechanism.

In related work Bart and Anson studied the 1e-oxidation of the second-transition-series cogener, [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻,^{755,293,294} by O₂ in water.^{295,296} Rong and Pope,⁷³ who observed clean metalation of the [PW₁₁O₃₉]⁷⁻ "lacunary" ligand upon addition of [Ru^{II}(H₂O)₆]²⁺, found that warm aqueous solutions of the resultant product, K₅[PRu^{III}(OH₂)W₁₁O₃₉] (~5 mM), were oxidized to K₄[PRu^{III}(OH₂)W₁₁O₃₉] in 0.5 h by bubbling with O₂.

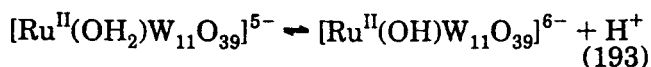
The reduction potential of the [PRu^{III/II}(OH₂-W₁₁O₃₉)]^{4-/5-} couple (+0.21 V vs Standard Hydrogen

Table 12. Reaction Conditions and Rate Constants (Measured and Calculated) for the Reduction of O₂ by Cs₅[PRu^{II}(OH₂)W₁₁O₃₉] and Other POM Salts in Water

entry	pH; μ (M), salt	POM _{red}	E° (V vs NHE)	ΔG° (kcal mol ⁻¹)	k_{exp} (M ⁻¹ s ⁻¹)	k_{calc} (M ⁻¹ s ⁻¹)
1	2.0; 1.0, Na ₂ SO ₄	Cs ₅ [PRu ^{II} (OH ₂)W ₁₁ O ₃₉]	+0.221	+2.3 ^b	2.0	10
2	5.4; 1.0, LiOAc	Cs ₅ [PRu ^{II} (OH ₂)W ₁₁ O ₃₉]	+0.156	+7.3 ^c	2.9	10
3	5.75; 0.1, LiOAc	Cs ₅ [PRu ^{II} (OH ₂)W ₁₁ O ₃₉]	+0.141	+6.9 ^c	2.9	10
4	5.4; 1.0, LiOAc	K ₆ [PFe ^{II} (OH ₂)W ₁₁ O ₃₉]	+0.275 ^d	+10.0 ^c	0.67	
5	0; 1.0, H ₂ SO ₄ ^e	[PW ₁₂ O ₄₀] ⁴⁻	+0.203	+1.9 ^b	2.1	

^a Converted from reported values, which were referenced to the standard sodium chloride electrode (SSCE), by addition of 0.2360 V. ^b From $\Delta G^\circ = -nFE^\circ$; approximated using $E^\circ(\text{O}_2/\text{HO}_2) = +0.12$ V vs NHE at pH 0. ^c Approximated using $E^\circ(\text{O}_2/\text{O}_2^-) = -0.16$ V vs NHE at pH 7. ^d Measured at pH 2 in 0.1 M NaClO₄²⁹²; the value of -0.033 V vs SSCE (0.203 V vs NHE) reported by Bart and Anson²⁹⁵ appears to be in error. ^e The ionic strength of 1.0 M was provided by H₂SO₄; no LiOAc was present.²⁵⁶

Electrode, SHE) was similar to that of the Fe^{III}/Fe^{II} couple of [PFe^{III}(OH₂)W₁₁O₃₉]⁶⁻ (+0.28 vs SHE).⁷⁵ By contrast, oxidation of aqueous solutions of [PMn^{II}(OH₂)W₁₁O₃₉]⁶⁻ by O₂ (the potential of the [PMn^{III/II}(OH₂)W₁₁O₃₉]^{4-/5-} couple is +1.12 V vs SHE) has not been reported. In addition, the pK_a associated with deprotonation of the aquo ligand coordinated to Ru(II) in [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ (eq 193) was 5.1. The potential of the [PRu^{III/II}(OH₂)W₁₁O₃₉]^{4-/5-}



couple was independent of [H⁺] between pH 0 and 4 and decreased by ~80 mV (to ~+0.13 V) as the pH was increased from 4 to 6.

Rong and Pope presented several lines of evidence that suggested that n-electron density from the d orbitals of the Ru(II) (d⁶) ion was partially delocalized onto the polytungstate ligand.⁷⁵ This previously unobserved phenomenon, which could influence electron-transfer reactions of Ru-substituted polytungstate complexes, was attributed to the more extended d-orbital structures of the second- and third-row transition-metal cations.

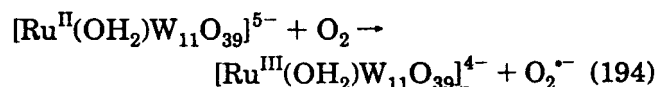
Bart and Anson used spectroscopic and electrochemical methods to measure the rate of room-temperature oxidation of cesium salts of [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ by O₂ at several ionic strengths and over a range of pH values that encompassed the pK_a of the Ru-coordinated aquo ligand (Table 12).^{295, 296} In all cases changes in absorption attributed to the [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ anion corresponded to the 2-e⁻ reduction of O₂ to H₂O₂; no nonintegral stoichiometries were observed. In addition, the reaction was first order in [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ and in O₂. No dependence of rate on pH (between pH 2 and 5.4) was observed.

Using the Marcus cross-relation (eq 17), $k_{22} = 1 \times 10^7$ M⁻¹ s⁻¹ for electron self-exchange between [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ and [PRu^{III}(OH₂)W₁₁O₃₉]⁴⁻, and $k_{11} = 450$ M⁻¹ s⁻¹ for the O₂/O₂⁻ self-exchange reaction,²⁷⁴ the authors calculated a single theoretical rate constant of 10 M⁻¹ s⁻¹ for all three reaction conditions (Table 12). The relatively good agreement with k_{exp} values was regarded as evidence for outer-sphere electron transfer.

The inapplicability of the k_{11} value determined directly from the ¹⁸O₂/¹⁶O₂ self-exchange reaction (450 M⁻¹ s⁻¹) to reactions of O₂ with much larger electron donors has been noted^{274, 275} and was dis-

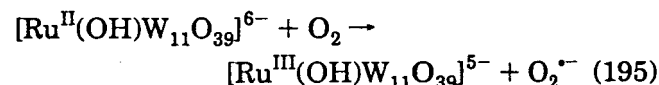
cussed in section VII.C. This error may have contributed to overestimation of k_{calc} (Table 12).

Closer examination of the data in Table 12 points out a problem rarely discussed in applications of Marcus theory, that is, how to deal with pH-dependent driving forces. The ΔG° values listed in Table 12 were estimated by the author of the present review using the pH-dependent chemical potentials associated with the 1-e⁻ oxidations of the POM anions and the 1-e⁻ reduction of O₂. However, in calculating k_{calc} values, Bart and Anson assumed that electron transfer from [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ to O₂ occurred as shown in eq 194, that is, prior to pH-dependent deprotonation of [PRu^{III}(OH₂)W₁₁O₃₉]⁵⁻ or protonation of O₂⁻.²⁵⁶ Thus, despite the large varia-



tions in ΔG° values associated with the overall reactions, a single theoretical k_{calc} value (10 kcal mol⁻¹) was obtained. The validity of Bart and Anson's approach is suggested by the near constancy in reported k_{exp} values and is consistent with the above-noted lack of a dependence of rate on pH.

At the same time, the pK_a for deprotonation of [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ to [PRu^{II}(OH)W₁₁O₃₉]⁶⁻ is 5.1 (eq 193). Thus, determination of k_{calc} for the reaction carried out at pH 5.75 (entry 3 in Table 12) would appear to have required more explicit consideration of the 80 mV larger driving force associated with the elementary reaction step shown in eq 195. Curiously, however, the rate constant observed at pH 2 (entry 1, Table 12) was not substantially smaller than those measured above the pK_a of [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ (entries 2 and 3, Table 12).



An additional line of experimental evidence in support of an outer-sphere mechanism was also presented.^{75, 295} When polar *s*-donor and *p*-acid ligands were added to aqueous solutions of [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ the rates of exchange of the aqua ligand on Ru(II) were several orders of magnitude smaller than the rates of oxidation of [PRu^{II}(OH₂)W₁₁O₃₉]⁵⁻ by O₂.

F. Reduction of O₂ by Reduced Vanadomolybdophosphates

Reductions of O₂ by solutions of reduced (heteropoly blue) vanadomolybdophosphate anions are reviewed

by Kozhevnikov in this issue of *Chemical Reviews*.¹¹⁴

In general a number of factors have made full characterization of the mechanisms of reoxidation of reduced vanadomolybdophosphate anions by O₂ an extraordinarily difficult task. First, POM anions consisting largely of molybdenum addendum atoms are more labile than their tungsten analogues. As a result, equilibrium mixtures of polyanions of varying composition are often rapidly established in aqueous solution. For example, the most widely cited preparation of H₅[PV₂Mo₁₀O₄₀]¹¹⁷ yields a product whose elemental analysis is consistent with the proposed formula. However, ⁵¹V and ³¹P NMR spectra of aqueous solutions of the product reveal an equilibrium mixture of acids, H_{3+n}[PV_nMo_{12-n}O₄₀] (*n* = 1, 2, and 3), in which H₅[PV₂Mo₁₀O₄₀] is the major product.^{86,119,120} Also, when more than one vanadium atom is present (e.g., [PV_nMo_{12-n}O₄₀]⁽³⁺ⁿ⁾⁻, *n* > 1), mixtures of positional isomers are present.¹²¹ Third, dissociation of V(V) and V(IV) from both fully oxidized and reduced (V(IV)-containing) anions, respectively, has been observed. The extent of dissociation varies with the number of vanadium addendum atoms in the POM structure, pH, the extent of reduction of the POM anion, and more than likely (although rarely mentioned), concentration.^{188,189,297-300} Despite considerable effort, these complications have hindered detailed characterization of the mechanisms of O₂ reduction by heteropoly blue vanadomolybdophosphate complexes.

Nonetheless, Matveev, Kozhevnikov, Kuznetsova, Neumann, and their co-workers, who have studied these reactions in the greatest detail, propose inner-sphere mechanisms involving intermediate complexes between O₂ and V(IV) addendum atoms of the POM anion.^{85,116,145,301-306} In only one report have data, which might be regarded as evidence for an outer-sphere mechanism, been presented²⁸² (see discussion of this report by Kozhevnikov).¹¹⁴

According to the prevalent view, an open coordination site on the V(IV) ion is provided by the breaking of a V(IV)-O bond between the reduced (d¹) vanadium ion and a bridging p-oxygen atom (i.e., within a V-O-Mo linkage) of the parent heteropoly blue, a process consistent with the labile nature of the vanadomolybdophosphate anions.

IX. Acknowledgments

The topic of this review, written while the author was a visiting scientist in the laboratory of Professor Craig L. Hill at Emory University, arose from questions encountered over the course of a long-standing collaboration between the USDA Forest Service, Forest Products Laboratory, Madison, WI (the author's home institution), and the Emory University Department of Chemistry. The hospitality, encouragement, and intellectual vision of Professor Hill are warmly acknowledged, as are the hospitality and assistance of co-workers at Emory, in particular, Marc Theune, Dr. Qin Chen, Dr. Michael Wemple, Jeff Rhule, Jennifer Cowan, and Kun Liu. Acknowledgment is also due the author's colleagues at the USDA Forest Service, Forest Products Laboratory:

Dr. Rajai H. Atalla, Dr. Carl J. Houtman, Dr. Cindy E. Sullivan, Richard S. Reiner, and Matthew J. Birchmeier; their probing and intellectually demanding questions, over the course of an ongoing effort to develop POM-based catalyst systems for the selective oxidation of agricultural products by oxygen, led the author to address the issues covered in this article. The topic of this article was also influenced by the work of Dr. P. Banejee and co-workers, who published a similarly titled article in 1993. In addition, warm thanks are extended to Professor L. C. W. Baker for sharing his thoughts regarding the structure and reactivity of Keggin dodecatungstocobaltate anions, which he originally prepared almost 50 years ago, and for his insight regarding the work of Rasmussen and Brubaker, who measured the rate of electron self-exchange between these complexes over 30 years ago. In addition, thoughtful feedback on draft copies of the manuscript by Professors Ivan V. Kozhevnikov, Fred C. Anson, Craig L. Hill, and Lennart Eberson is gratefully noted, while special thanks are due to Professor Eberson for his gracious assistance in the critical reevaluation of published values for key theoretical parameters. Finally, the editorial assistance of Janel Showalter of the Forest Products Laboratory is warmly acknowledged. The cover art was created by Jennifer Cowan.

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