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Temperature Dependence of the Rate Constants for Reaction of Dihalide and Azide Radicals with Inorganic Reductants

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Rate constants for several reactions of inorganic radicals with inorganic reductants in aqueous solutions have been measured by pulse radiolysis as a function of temperature, generally between 5 and 75 °C. The reactions studied were of the dihalide radicals, $Cl_2^{\bullet-}$, $Br_2^{\bullet-}$, and $I_2^{\bullet-}$, the $(SCN)_2^{\bullet-}$ radical, and the neutral radical $N_3^{\bullet}$, reacting with the substitution-inert metal complexes, $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $W(CN)_8^{4-}$, and with the anions SO_3^{2-}, HSO_3^-, NO_2^-, and ClO_2^-. The rate constants measured were in the range of 10^6 to 5×10^9 M^{-1} s^{-1} and the calculated Arrhenius activation energies ranged from 5 to 35 kJ mol^{-1}. The preexponential factors also varied considerably, with log A ranging from 8.9 to 13.1. The temperature dependence of the reaction rate constant is correlated to the reaction exothermicity for the metal complexes, which apparently react by outer-sphere electron transfer. The simple anions, however, have lower activation energies, which do not correlate well with the exothermicities, suggesting that these anions probably react by an inner-sphere mechanism.
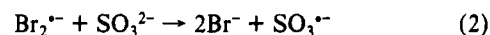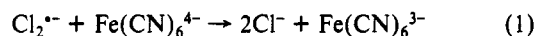
Introduction

Rate constants have been measured at room temperture for a large number of reactions of inorganic free radicals,[3] but few results have been reported on the variation of these rate constants with temperature. In recent work, we have determined the temperature dependence for the reactions of several inorganic radicals with organic reductants[4] and for several reactions of $SO_4^{\bullet-}$, with organic and inorganic anions.[5] In general, we have found that, while the rate constant for these reactions increased with the exothermicity of the reaction, this change in the rate constant seemed to be related more to an increase in the Arrhenius preexponential factor than to a decrease in the activation energy. The interpretation of the reactivity patterns of small inorganic free radicals reacting with many organic reductants is complicated by the possibility that there may be addition of the radical to some part of these unsaturated organic compounds prior to electron transfer, particularly when an aromatic reductant is involved. In the present work, we have measured rate constants as a function of temperature for a number of reactions of inorganic free radicals with several inorganic reductants. The radicals investigated are $Cl_2^{\bullet-}$, $Br_2^{\bullet-}$, $I_2^{\bullet-}$, $(SCN)_2^{\bullet-}$, and $N_3^{\bullet}$.

The azide radical, $N_3^{\bullet}$, has a one-electron reduction potential of about 1.35 V[6,7] and is known to react more rapidly, in many cases, than radicals with higher reduction potentials. A self-exchange rate of $\approx 4 \times 10^4$ M^{-1} s^{-1} was estimated for the $N_3^{\bullet}/N_3^-$ couple.[7] The $X_2^{\bullet-}$ radicals have one-electron reduction potentials of 2.09 V ($Cl_2^{\bullet-}/2Cl^-$), 1.62 V ($Br_2^{\bullet-}/2Br^-$), 1.03 V ($I_2^{\bullet-}/2I^-$), and 1.32 V ($(SCN)_2^{\bullet-}/2SCN^-$).[8] These radicals react by reductive cleavage, in which there is dissociation of the product, probably concerted with the electron transfer. Spectrophotometric studies on the reactions of $I_2^{\bullet-}$ and $(SCN)_2^{\bullet-}$ with $Os(2,2'$-bipyridyl$)_3^{2+}$ did not detect any intermediate adducts.[9]

We have studied the reactions of the radicals with the metal complexes $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $W(CN)_8^{4-}$, and with the simple inorganic anions SO_3^{2-}, HSO_3^-, ClO_2^-, and NO_2^-. These reactions are expected to involve an overall one-electron transfer, leading to either the oxidized metal complex or to an inorganic radical; for example,

$$Cl_2^{\bullet-} + Fe(CN)_6^{4-} \rightarrow 2Cl^- + Fe(CN)_6^{3-} \qquad (1)$$

$$Br_2^{\bullet-} + SO_3^{2-} \rightarrow 2Br^- + SO_3^{\bullet-} \qquad (2)$$

The metal complexes were chosen to be substitution-inert and to span a range of reduction potentials.[10] The inorganic anions chosen consist of one pair, HSO_3^- and SO_3^{2-}, which differ only in degree of protonation, and the pair ClO_2^- and NO_2^-, bent triatomics, which undergo either large (NO_2^-) or small (ClO_2^-) geometry changes upon oxidation.[11]

There have been previous studies[12] on the temperature dependence of the reactions of the dihalide radical anions $Cl_2^{\bullet-}$ and $Br_2^{\bullet-}$ with Fe^{2+}, Co^{2+}, and Mn^{2+}. These reactions can proceed by either outer-sphere electron transfer, an inner-sphere substitution-controlled reaction, or an inner-sphere electron-transfer-controlled reaction. Only the reaction of $Cl_2^{\bullet-}$ with Fe^{2+}, which is the most exothermic of those studied, was found to have an outer-sphere path.[12] Even in this case, the inner-sphere path was also important. The rates of the inner-sphere oxidation reactions of Fe^{2+} and Co^{2+} by $Br_2^{\bullet-}$ and $Cl_2^{\bullet-}$ were found to be the same as the rates of substitution on the metal ions, while the rates of oxidation of Mn^{2+} by $Cl_2^{\bullet-}$ and $Br_2^{\bullet-}$ were found to be only about 2% of the substitution rate. The former reactions were assigned an inner-sphere substitution path, while the latter reactions were assumed to proceed by a path in which inner-sphere electron transfer was the rate-determining step. In the present study, we have chosen to investigate the reactions of substitution-inert metal complexes, where the inner-sphere path should be suppressed completely, and compare them with reactions of simple inorganic anions, where the inner-sphere path is more likely.

Experimental Section

The rate constants were determined by kinetic spectrophotometric pulse radiolysis. The inorganic radicals were produced by reaction of the corresponding anions with $^{\bullet}OH$ radicals in N_2O-saturated aqueous solutions as described before.[4] The ionic strength was established mainly by the precursor salt ($NaCl$, $NaBr$, NaI, $KSCN$, NaN_3, $NaNO_2$, and $NaClO_2$) and was not otherwise adjusted. The pH was adjusted by the addition of KOH

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TABLE I: Rate Constants for Oxidation of the Metal Complexes at Different Temperatures

reaction	pH	μ	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹
$Fe(CN)_6^{4-} + Cl_2^{•-}$	2.6	0.1	10	1.3×10^8	26	1.9×10^8	48	2.7×10^8	69	3.4×10^8	90	3.7×10^8
$Fe(CN)_6^{4-} + Br_2^{•-}$	6.4	0.1	3	1.4×10^7	16	2.5×10^7	37	4.1×10^7	57	5.7×10^7	77	8.8×10^7
$Fe(CN)_6^{4-} + I_2^{•-}$	6.9	0.1	5	1.1×10^6	16	1.8×10^6	34	4.6×10^6	54	8.4×10^6	79	2.1×10^7
$Fe(CN)_2^{4-} + (SCN)_2^{•-}$	6.9	0.1	7	1.2×10^7	17	1.8×10^7	35	3.6×10^7	53	6.1×10^7	72	1.2×10^8
		0.7	2	1.6×10^7	20	3.8×10^7	46	9.8×10^7			77	2.1×10^8
$Fe(CN)_6^{4-} + N_3^{•}$	9.0	0.1	7	2.8×10^9	18	2.2×10^9	36	2.2×10^9	58	3.6×10^9	79	1.9×10^9
$Mo(CN)_8^{4-} + Cl_2^{•-}$	2.7	0.1			19	5.0×10^7	36	6.6×10^7	57	1.2×10^8	83	1.3×10^8
$Mo(CN)_8^{4-} + Br_2^{•-}$	9.0	0.1	50	6.2×10^6	58	1.0×10^7	71	1.4×10^7	83	1.5×10^7	96	2.0×10^7
$Mo(CN)_8^{4-} + (SCN)_2^{•-}$	9.0	0.7	8	2.1×10^6	19	3.3×10^6	38	5.2×10^6	59	1.3×10^7	82	2.1×10^7
$Mo(CN)_8^{4-} + N_3^{•}$	9.0	0.1	8	1.4×10^9	18	1.5×10^9	38	3.2×10^9	58	3.1×10^9	83	5.8×10^9
$W(CN)_8^{4-} + Cl_2^{•-}$	2.6	0.1	9	2.1×10^8	26	3.3×10^8	47	3.7×10^8	68	6.1×10^8	89	6.8×10^8
$W(CN)_8^{4-} + Br^{•-}$	9.0	0.2	11	3.7×10^7	28	6.5×10^7			50	9.3×10^7	92	2.0×10^8
$W(CN)_8^{4-} + I_2^{•-}$	9.2	0.5			29	3.7×10^6	49	8.5×10^6	69	1.5×10^7	91	2.4×10^7
$W(CN)_8^{4-} + (SCN)_2^{•-}$	6.7	0.7	10	4.9×10^7	26	7.9×10^7	46	1.1×10^8	68	1.9×10^8	90	2.9×10^8
$W(CN)_8^{4-} + N_3^{•}$	8.2	0.1	5	2.5×10^9	14	3.4×10^9	30	5.5×10^9	49	8.5×10^9	68	8.8×10^9

TABLE II: Rate Constants for Oxidation of the Anions at Different Temperatures

reaction	pH	μ	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹
$HSO_3^- + Cl_2^{•-}$	3.2	0.1	5	3.1×10^8	16	3.5×10^8	37	5.4×10^8	59	5.6×10^8	80	6.4×10^8
$HSO_3^- + Br_2^{•-}$	3.0	0.1	5	5.2×10^7	19	6.3×10^7	37	6.4×10^7	59	8.3×10^7	75	1.1×10^8
$HSO_3^- + I_2^{•-}$	3.7	0.1	5	8.2×10^5	18	9.8×10^5	36	1.4×10^6	56	3.5×10^6	79	5.4×10^6
$HSO_3^- + (SCN)_2^{•-}$	3.0	0.1	5	1.4×10^6	20	3.0×10^6	37	4.9×10^6	60	8.8×10^6	79	1.6×10^7
$SO_3^{2-} + Br_2^{•-}$	11.7	0.1	1	1.7×10^8	16	2.4×10^8	37	2.8×10^8	56	2.3×10^8	76	3.0×10^8
$SO_3^{2-} + I_2^{•-}$	11.8	0.1	4	1.1×10^8	18	1.6×10^8	34	1.9×10^8	54	2.6×10^8	79	3.5×10^8
$SO_3^{2-} + (SCN)_2^{•-}$	11.7	0.1	1	1.2×10^8	16	1.7×10^8	37	2.4×10^8	57	3.3×10^8	76	3.6×10^8
$NO_2^- + Br_2^{•-}$	6.7	0.1	5	1.1×10^7	15	1.4×10^7	34	2.1×10^7	54	2.8×10^7	79	4.4×10^7
$NO_2^- + (SCN)_2^{•-}$	6.7	0.5	4	1.0×10^6	16	1.8×10^6	34	3.8×10^6	54	1.1×10^7	79	2.2×10^7
$ClO_2^- + Br_2^{•-}$	6.8	0.1	5	9.2×10^6	17	1.5×10^7	34	1.9×10^7	54	4.3×10^7	79	6.2×10^7
$ClO_2^- + N_3^{•}$	6.8	0.1	7	1.9×10^9	17	3.2×10^9	33	3.5×10^9	50	4.7×10^9	71	5.2×10^9

or $HClO_4$ or by the use of phosphate buffer. The rate of reaction for radicals which exhibit intense absorptions ($Cl_2^{•-}$ at 350 nm, $Br_2^{•-}$ at 360 nm, $I_2^{•-}$ at 380 nm, and $(SCN)_2^{•-}$ at 480 nm) was determined by following the decay of the inorganic radical as a function of substrate concentration. The reaction of $N_3^{•}$, however, was followed by monitoring the buildup of products: $ClO_2^{•}$, $Fe(CN)_6^{3-}$, $W(CN)_8^{3-}$, and $Mo(CN)_8^{3-}$ at 360, 420, 385, and 360 nm, respectively. The second-order rate constants were determined from plots of k_{obs} vs concentration employing three substrate concentrations that differed by a factor of 4. The whole experiment was repeated at five temperatures, generally between 5 and 75 °C. The temperature was achieved in a flow system by passing the solution through a thin coiled quartz tubing immersed in a thermostated fluid immediately before entering the irradiation cell and the temperature was read by a thermocouple immersed in the solution at the point of its exit from the cell. Other details of the experimental procedures were as described before.[4]

Potassium octacyanotungstate(IV) and octacyanomolybdate (IV) were prepared by literature methods.[13] In the course of these preparations, we found that, whereas the potassium salts formed good crystalline precipitates, the sodium salts formed ill-behaved pastes. The other materials used were commercial analytical reagents as in our previous studies.[4,6,14]

Results

The second-order rate constants determined for the various reactions at the different temperatures are summarized in Tables I and II. For each reaction, the pH is specified in order to define the acid–base form of the reacting species. The ionic strength due to the precursor salt is also specified but no correction to zero ionic strength was made. For some of the reactions involving the metal complexes, the ionic strength did increase significantly due to the increase in the reactant concentration. The effect of ionic strength was examined by varying the concentration of the precursor salt in the reactions of $(SCN)_2^{•-}$ with $W(CN)_8^{4-}$ and $Fe(CN)_6^{4-}$. The results (Table III) show that the rate constants increase with added KSCN, but only by less than a factor of 2

TABLE III: Effect of KSCN Concentration on the Rate Constants of the Complexes

	k, M⁻¹ s⁻¹	
[KSCN], M	$Fe(CN)_6^{4-}$	$W(CN)_8^{4-}$
0.1	2.2×10^7	3.5×10^7
0.2	2.3×10^7	4.5×10^7
0.4	2.8×10^7	5.8×10^7
0.7	3.6×10^7	6.5×10^7
0.8	3.3×10^7	

for an increase in salt from 0.1 to 0.8 M. This result is the combined effect of the association of $Fe(CN)_6^{4-}$ and $W(CN)_8^{4-}$ with K^+,[15] to form anions with lower charge, and the effect of ionic strength on the reactivity of charged species. No attempt was made to operate at lower precursor salt concentration since the reaction of OH with the reductant would begin to compete with its reaction with the precursor. Our results for the metal complexes are in general agreement with the reported room temperature rate constants,[16] with some variations due to pH and ionic strength.

The second-order rate constants were fit to the Arrhenius expression, $k = Ae^{-E_a/RT}$, by a weighted least-squares routine; the weights were taken as the reciprocal of the squares of the standard errors derived from the second-order fits. The Arrhenius parameters are presented in Tables IV and V, along with the calculated value of the rate constant at 298 K. The error limits reported for the activation energy are the standard errors from the least-squares fit. Due to the long extrapolation involved, we have chosen not to report the calculated statistical error limits for the preexponential factors. We estimate that, over the temperature range of these studies, the errors in the rate constants calculated from the Arrhenius expressions are ±20%. Tables IV and V also include the driving force of each reaction, calculated as the difference between the one-electron-reduction potential of the radical, $E°_R$, and the reduction potential of the substrate, $E°_S$.[8,10]

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TABLE IV: Arrhenius Parameters and Room Temperature Rate Constants for Oxidation of the Metal Complexes by the Inorganic Radicals

reaction	pH	μ	$E°_R - E°_a$, V	E_a, kJ mol^{-1}	log A	k_{298}
Fe(CN)$_6$$^{4-}$ + Cl$_2$$^{•-}$	2.6	0.1	1.63	12.9 ± 0.8	10.5	1.8 × 10^8
Fe(CN)$_6$$^{4-}$ + Br$_2$$^{•-}$	6.4	0.1	1.16	19.8 ± 0.6	10.9	2.7 × 10^7
Fe(CN)$_6$$^{4-}$ + I$_2$$^{•-}$	6.9	0.1	0.57	34.7 ± 1.4	12.5	2.4 × 10^6
Fe(CN)$_6$$^{4-}$ + (SCN)$_2$$^{•-}$	6.9	0.1	0.86	27.8 ± 0.3	12.3	2.4 × 10^7
		0.7		29.3 ± 1.1	12.8	4.3 × 10^7
Fe(CN)$_6$$^{4-}$ + N$_3$$^•$	9.0	0.1	0.89	~0	~9	2.5 × 10^9
Mo(CN)$_8$$^{4-}$ + Cl$_2$$^{•-}$	2.7	0.1	1.25	14.0 ± 1.2	10.2	5.6 × 10^7
Mo(CN)$_8$$^{4-}$ + Br$_2$$^{•-}$	9.0	0.1	0.78	18.8 ± 3.7	9.9	4.5 × 10^6
Mo(CN)$_8$$^{4-}$ + (SCN)$_2$$^{•-}$	9.0	0.7	0.48	24.1 ± 3.0	10.8	3.5 × 10^6
Mo(CN)$_8$$^{4-}$ + N$_2$$^•$	9.0	0.1	0.51	~12	~11	2.2 × 10^9
W(CN)$_8$$^{4-}$ + Cl$_2$$^{•-}$	2.6	0.1	1.52	12.3 ● 2.0	10.7	3.0 × 10^8
W(CN)$_8$$^{4-}$ + Br$_2$$^{•-}$	9.0	0.2	1.05	15.4 ± 0.7	10.5	5.8 × 10^7
W(CN)$_8$$^{4-}$ + I$_2$$^{•-}$	9.2	0.5	0.46	27.1 ± 1.7	11.1	3.7 × 10^6
W(CN)$_8$$^{4-}$ + (SCN)$_2$$^{•-}$	6.7	0.7	0.75	18.5 ± 0.7	11.1	7.1 × 10^7
W(CN)$_8$$^{4-}$ + N$_3$$^•$	9.0	0.1	0.78	~20	~13	4.7 × 10^9

TABLE V: Arrhenius Parameters and Room Temperature Rate Constants for Oxidation of the Anions by Inorganic Radicals

reaction	pH	μ	$E°_R - E°_a$, V	E_a, kJ mol^{-1}	log A	k_{298}
HSO$_3$$^-$ + Cl$_2$$^{•-}$	3.2	0.1	1.13	9.0 ± 0.3	10.3	4.7 × 10^8
HSO$_3$$^-$ + Br$_2$$^{•-}$	3.0	0.1	0.66	6.5 ± 0.8	8.9	6.3 × 10^7
HSO$_3$$^-$ + I$_2$$^{•-}$	3.7	0.1	0.10	19.3 ± 2.1	9.5	1.4 × 10^6
HSO$_3$$^-$ + (SCN)$_2$$^{•-}$	3.0	0.1	0.34	24.8 ± 1.1	10.9	3.4 × 10^6
SO$_3$$^{2-}$ + Br$_2$$^{•-}$	11.7	0.1	0.87	5.4 ± 1.0	9.3	2.2 × 10^8
SO$_3$$^{2-}$ + I$_2$$^{•-}$	11.8	0.1	0.27	11.8 ± 0.4	10.3	1.7 × 10^8
SO$_3$$^{2-}$ + (SCN)$_2$$^{•-}$	11.7	0.1	0.55	12.5 ± 1.0	10.5	2.0 × 10^8
NO$_2$$^-$ + Br$_2$$^{•-}$	6.7	0.1	0.62	14.3 ± 0.4	9.7	1.7 × 10^7
NO$_2$$^-$ + (SCN)$_2$$^{•-}$	6.7	0.5	0.27	32.9 ● 1.5	12.2	3.0 × 10^6
ClO$_2$$^-$ + Br$_2$$^{•-}$	6.8	0.1	0.72	20.0 ± 2.7	10.8	1.9 × 10^7
ClO$_2$$^-$ + N$_3$$^•$	6.8	0.1	0.39	~13	~12	3.1 × 10^9

The results from the tables are plotted in Arrhenius form (log k vs $1/T$) and presented separately for each radical (Figure 1). The results for the azide radical are not shown in the figure and are considered to be much less accurate than those for the other radicals due to experimental limitations. These limitations arose from the low molar absorptivities of the species monitored, which necessitated the use of higher radiation doses, thus introducing complications due to radical–radical reactions and to partial depletion of the stable reactant. The measured rate constants are given in Tables I and II but the activation parameters in Tables IV and V for N$_3$$^•$ are given as approximate values only.

Discussion

The calculated Arrhenius activation energies range from 5 to 35 kJ mol^{-1} (Tables IV and V). In most cases, the activation energy is very low, much below the activation energy for diffusion ($\sim$17.5 kJ mol^{-1}).[5] Except for some of the N$_3$$^•$ reactions, the rate constants are much below the diffusion limit and therefore not influenced by the diffusion rate constant. Thus the temperature dependence of the rate constant is not affected by the temperature dependence of the diffusion rate. The general trends in Tables IV and V appear to indicate that the slower reactions are slow in certain cases because of low preexponential factors and in other cases because of high activation energies. This is in contrast with the situation in hydrogen-abstraction reactions, where the acti-
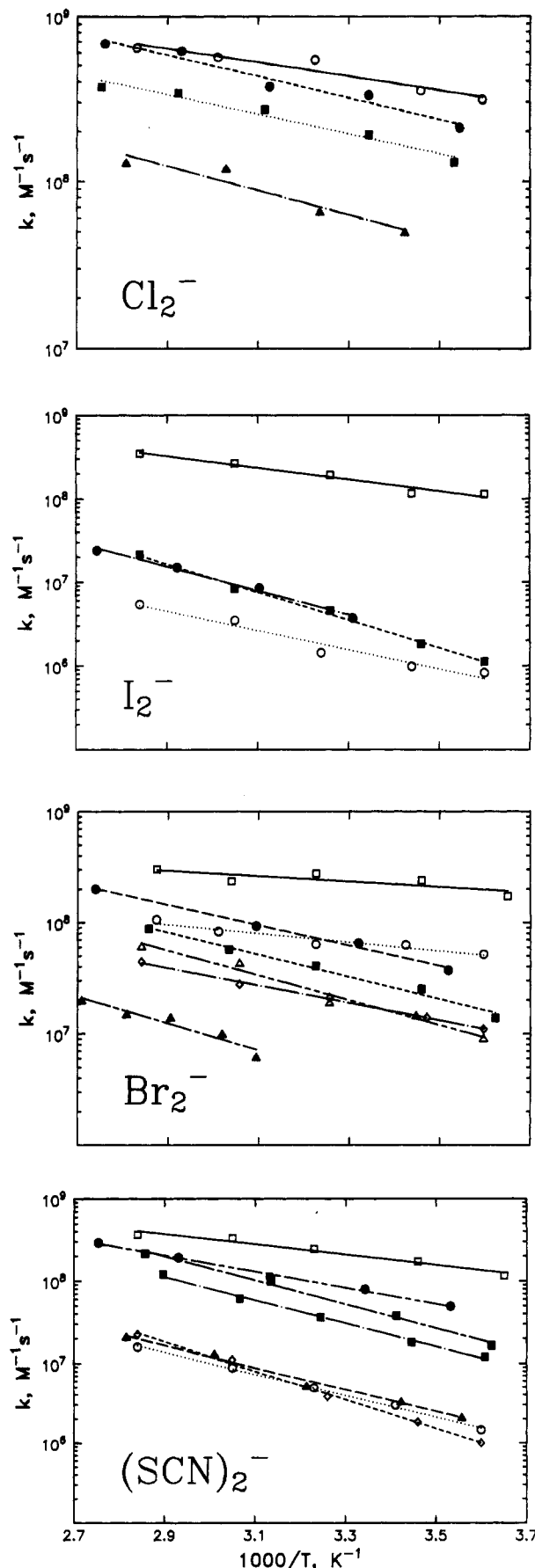

Figure 1. Arrhenius plots for the reactions of several inorganic radicals with the various reductants. In each plot the symbols for the reductants are as follows: Fe(CN)$_6$$^{4-}$ (■), Mo(CN)$_8$$^{4-}$ (▲), W(CN)$_8$$^{4-}$ (●), HSO$_3$$^-$ (○), SO$_3$$^{2-}$ (□), NO$_2$$^-$ (◇), ClO$_2$$^-$ (△). In the plot for (SCN)$_2$$^{•-}$, two lines are given for Fe(CN)$_6$$^{4-}$, the upper is for 0.7 M, and the lower is for 0.1 M KSCN.

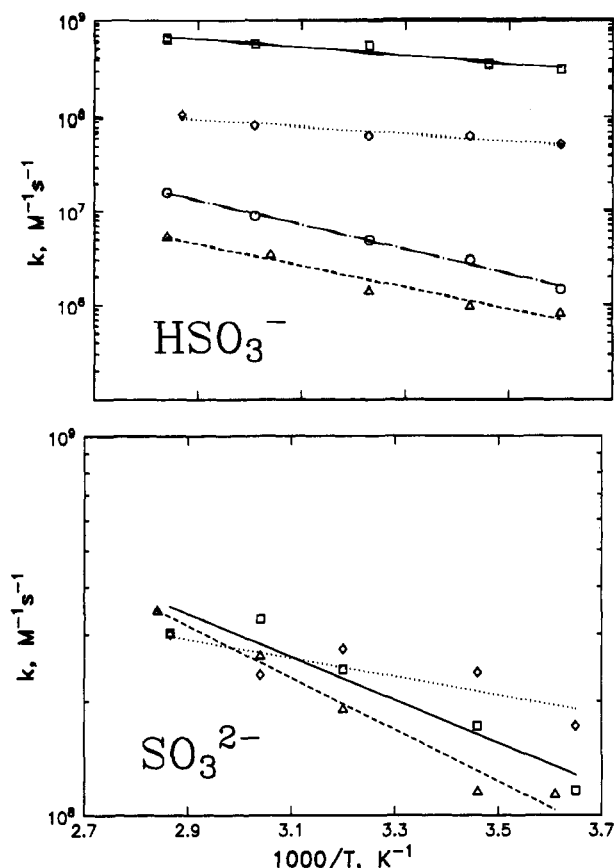**Figure 2.** Arrhenius plots for the reactions of sulfite and bisulfite with various radicals: $Cl_2^{\cdot-}$ ($\square$), $Br_2^{\cdot-}$ ($\Diamond$), $I_2^{\cdot-}$ ($\triangle$), $(SCN)_2^{\cdot-}$ (O).

vation energy and the rate constants correlate with the bond dissociation energy.

The results for the various radicals (Figure 1) show that the order of reactivity for the three metal complexes is $Mo(CN)_8^{4-}$ < $Fe(CN)_6^{4-}$ < $W(CN)_8^{4-}$. The reduction potentials for these complexes depend strongly on cation concentration and, particularly for $Fe(CN)_6^{4-}$, on the pH.[10] For our experimental conditions, the best values of the reduction potentials are 0.84 V for $Mo(CN)_8^{4-}$, 0.46 V for $Fe(CN)_6^{4-}$, and 0.57 V for $W(CN)_8^{4-}$, all vs NHE.[10] The difference in the order of reactivities and the order of reduction potentials is probably due to the lower self-exchange rate for $Fe(CN)_6^{4-}$ compared to $W(CN)_8^{4-}$ or $Mo(CN)_8^{4-}$.[17] The heterogeneous electron-transfer rate constant for $Fe(CN)_6^{4-}$ has also been found to be much lower than for the other complexes.[18] For the reaction of $(SCN)_2^{\cdot-}$ with $Fe(CN)_6^{4-}$ we also have examined the temperature effect at different ionic strengths. As is apparent from Figure 1 and Table IV, an increase in ionic strength raises the preexponential factor but has little effect on the activation energy.

The redox potential for the $SO_3^{\cdot-}/SO_3^{2-}$ couple is 0.72–0.76 V vs NHE,[19,20] less than that for $Mo(CN)_8^{3-/4-}$ but higher than those for $W(CN)_8^{3-/4-}$ or $Fe(CN)_6^{3-/4-}$. Yet SO_3^{2-} is oxidized much more rapidly than the metal complexes or any of the other reductants. HSO_3^-, with a considerably higher reduction potential (0.97 V) than any of the metal complexes, is oxidized more rapidly than the metal complexes by $Cl_2^{\cdot-}$ at all temperatures studied and by $Br_2^{\cdot-}$ at low temperatures, although it is oxidized less rapidly by $I_2^{\cdot-}$ or $(SCN)_2^{\cdot-}$.

The rate constants for the reactions of SO_3^{2-} and HSO_3^- with the various radicals are plotted in Arrhenius form in Figure 2. For bisulfite, the reactivity of the radical is clearly related to its
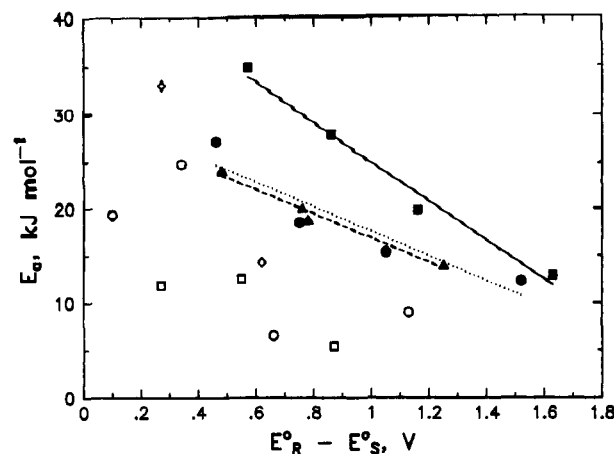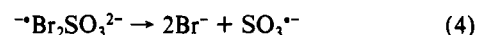

Figure 3. Dependence of activation energy, E_a, on the reaction driving force, $E^\circ_R - E^\circ_S$. The symbols for each anion are the same as in Figure 1. The lines show the linear fits for the metal complexes: $Fe(CN)_6^{4-}$ (solid line), $Mo(CN)_8^{4-}$ (dashed line), and $W(CN)_8^{4-}$ (dotted line).

reduction potential over the entire temperature range covered. For sulfite, however, both $(SCN)_2^{\cdot-}$ and $I_2^{\cdot-}$ increase in reactivity more rapidly than $Br_2^{\cdot-}$, sufficiently so that they are more reactive than $Br_2^{\cdot-}$ at the upper end of the temperature range. For all radicals, the activation energy for the HSO_3^- reaction is greater than that for SO_3^{2-}.

The observation that the reaction of $Br_2^{\cdot-}$ with ClO_2^- has a higher activation energy than the reaction of this radical with NO_2^- is quite surprising. Although the activation energy difference is in line with the difference in the reaction exothermicity, the large geometry change that NO_2^- undergoes upon oxidation[11] would have been expected to lead to a large reorganization energy term compared to the ClO_2^- reaction.

Since the product of the one-electron reduction of the dihalide radicals is dissociative, the actual value of the driving force for the electron-transfer reaction of a dihalide radical and a reductant cannot be defined precisely.[21] In Figure 3 we have plotted the activation energies for the various reactions against the difference between the reduction potential for the one-electron oxidation of the anion and the reduction potential for the $X_2^{\cdot-}/2X^-$ couple, which is a useful surrogate for the actual driving force.[22] The activation energy for the oxidation of $Fe(CN)_6^{4-}$ by the various radicals shows a clear linear relationship with this term. The reactions of $Mo(CN)_8^{4-}$ also appear to have a linear decrease in activation energy with increasing difference in reduction potential, but with a lower slope than for $Fe(CN)_6^{4-}$. The activation energy for the $W(CN)_8^{4-}$ reaction also decreases with about the same slope as found for $Mo(CN)_8^{4-}$. The fit of the straight line to the data for $W(CN)_8^{4-}$ is not as good as for the other complexes. Straight lines, however, have been drawn only for convenience; a curve may be a better representation.[21,23] By contrast with these results for the complexes, the points for the reactions of the simple anions scatter considerably and are generally below the lines for the metal complexes. These results suggest that whereas the metal complexes react by an outer-sphere electron-transfer mechanism, the simple anions probably react by an inner-sphere mechanism involving the reversible formation of a transient intermediate. For example

$$Br_2^{\cdot-} + SO_3^{2-} \rightleftharpoons {}^{-\cdot}Br_2SO_3^{2-} \tag{3}$$

$${}^{-\cdot}Br_2SO_3^{2-} \rightarrow 2Br^- + SO_3^{\cdot-} \tag{4}$$

with the intermediate possibly releasing the Br^- ions sequentially. As discussed before,[5] if a steady state in the intermediate is assumed, the observed rate constant will be given by

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$$-d \ln [Br_2^{\bullet-}]/dt = k_{obs} = k_3 k_4 [SO_3^{2-}]/(k_{-3} + k_4)$$

If $k_4 \gg k_{-3}$, the reaction will behave as a simple bimolecular reaction. If, however, k_{-3} is important, it can dramatically affect the kinetics and, particularly, decrease the activation energy. The more general case, in which the initial intermediate complex is in equilibrium with a secondary complex resulting from electron transfer, and in which the entire reaction is reversible, has been discussed before.[24] In that study, in which electron-transfer reactions between oppositely charged transition-metal complexes were investigated, activation energies less than that for diffusion were measured, even though the rate constants for the reactions were close to the diffusion-controlled limit.

There have been room temperature measurements of the rate constants for several of these reactions,[3] which generally agree with our k_{298} values.[25] There have been a few studies of the temperature dependence for other radicals that we can discuss in light of the present results. The reaction of the stable free radical ClO_2 with the substitution-inert metal complex Co(ter-py)$_2^{2+}$, which has a driving force of 0.67 V, was studied over the temperature range 5–30 °C and gives an activation energy of 18.6 kJ mol^{-1}.[11] This would lie slightly below the line we find for the oxidation of $W(CN)_8^{4-}$ and $Mo(CN)_8^{4-}$. The reaction of O_3 with $IrCl_6^{3-}$, studied from 4 to 34 °C, has an activation energy of 46.8 kJ mol^{-1}.[26] With a driving force of 0.12 V, this reaction lies

slightly above the line extrapolated from the Fe(CN)$_6^{4-}$ results. In our earlier work,[4] we reported activation energies for a number of reactions of inorganic radicals with organic compounds. For reactions with driving forces above 0.4 V, the activation energies scatter below the lines presented here for the metal complexes. At lower driving force, the measured activation energies appear to increase sharply. The exception to this pattern is for the reactions of NO_2. This radical undergoes a large geometry change upon reduction,[11] possibly contributing to the higher activation energies for its reactions. The endothermic reaction of ClO_2 with NO_2^-, which has a driving force of −0.11 V, has an activation energy of 57.7 kJ mol^{-1}.[27] The reactions of NO_2 are probably not outer-sphere electron-transfer reactions. Indeed, the kinetic results on the reaction of NO_2 with SO_3^{2-} were interpreted to suggest that NO_2 adds to SO_3^{2-} to form a long-lived complex.[28]

In conclusion, the activation energies for the oxidation of the metal complexes by the various radicals are found to decrease with increasing exothermicity of the reaction. This is in line with an outer-sphere electron-transfer mechanism. On the other hand, we find little correlation of the activation energy with the driving force for the oxidation of the simple inorganic anions. Rather, variations in rate constants for these reactions are found to be, in some cases, more strongly dependent on changes in preexponential factors, which suggests that these reactions take place by an inner-sphere mechanism involving an intermediate adduct.

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(25) An exception is the recent work of: DeFelippis, M. R.; Murthy, C. P.; Faraggi, M.; Klapper, M. H. *Biochemistry* 1989, *28*, 4847. They reported rate constants at room temperature for the oxidation of ClO_2^- by $N_3^{\bullet}$ and $Br_2^{\bullet-}$ almost 40 times lower than we found by a similar technique and under similar conditions. They also reported a rate constant for the reaction of $(SCN)_2^{\bullet-}$ with ClO_2^-, whereas we found that SCN^- reacted with ClO_2, so that we could not study this reaction. Our results, both here and in our earlier work (ref 12), are in line with the reactivity of ClO_2^- toward other oxidants and its reactivity relative to the reactivity of NO_2^-.

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Photoinduced and Redox-Induced Transmembrane Processes with Vesicle-Stabilized Colloidal Cadmium Sulfide and Multicharged Viologen Derivatives

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Colloidal cadmium sulfide (CdS) and methylviologen (MV^{2+}) or new viologen derivatives carrying more positive charges were placed at specific sites of dihexadecyl phosphate (DHP) vesicles. Benzyl alcohol was used as a sacrificial electron donor to promote reduction of the viologens by photoexcited CdS colloid majority carriers. Transmission electron microscopy, ^{13}C nuclear magnetic resonance, and differential scanning calorimetry were used for physical characterization. Photochemical events were followed by in situ optical and electrochemical monitoring. Redox-induced transmembrane diffusion, which had been found with MV^{2+}, could be reduced by a factor 18 by using a triply charged viologen derivative and by a further factor of 30 in a configuration involving transmembrane electron transfer. In that case the quantum yield was ca. 0.05 at 410 nm, while virtually no reduced viologen leaking could be observed during at least 10 min. Physical evidence was found for a partial penetration of the CdS colloids into the DHP membrane.

Introduction

Photochemical solar energy storage is a popular candidate as a possible source of alternative energy.[1] Despite substantial progress, its practical use is still restricted by energy-wasting back reactions. In natural photosynthesis, these reactions are avoided by use of lipid membranes carrying selectively located electron

donors and acceptors. Attempts to re-create this scheme have been performed with various synthetic organized media. The models that most closely mimic biological membranes are planar bilayer lipid membranes (BLMs) and closed, unilamellar vesicles.[2,3]

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