Dinuclear formation, oxygen atom transfer and intramolecular coordination isomerization in oxotechnetium complexes

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Dinuclear Formation, Oxygen Atom Transfer, and Intramolecular Coordination Isomerization in Oxotechnetium Complexes

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Dinuclear, asymmetric and dissymmetric, mixed-valent (III–IV), μ-oxo complexes of technetium spontaneously form in both neat pyridine and pyridine solutions in dichlorobenzene from higher valent, mononuclear species, with which they reach an equilibrium. Isolated species are *trans*-$[O_2(Py)_4Tc]^+$, $[(Py)X_3(Py)TcOTcX(Py)_3X]$, and $[X(Py)_4TcOTcX)4(Py)]$. When $[OX_4Tc^V]^-$ is used as the starting material and only the neat pyridine ligand is present, the formation of the dinuclear species is second-order in Tc^V and occurs with concomitant production of pyridine *N*-oxide, indicating that oxygen atom transfer occurs in the technetium reduction process. K_{eq} for the formation of the dinuclear species in picoline solution is 193 ± 8 M^{-1} with $k = (1.46 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1}. The asymmetric and dissymmetric dinuclear species spontaneously interconvert. In *o*-dichlorobenzene, this process is first-order in chloride ion and requires a minimum concentration (~0.1 M) of the pyridine ligand to prevent decomposition of the dinuclear starting material. With picoline as the ligand, at 140 °C the reaction proceeds with a specific rate of $(3.12 \pm 0.08) \times 10^{-3}$ M^{-1} s^{-1} to approach an equilibrium between the asymmetric and dissymmetric complexes with $K_{eq} = 2.83 \pm 0.12$. Activation parameters are $\Delta H^* = 144 \pm 2$ kJ/mol and $\Delta S^* = 53.5 \pm 1$ J/(mol K). Equilibrium thermodynamic parameters are $\Delta H = 50 \pm 1$ kJ/mol and $\Delta S = 130 \pm 4$ J/(mol K). In picoline solution the approach is also first-order in chloride with $k = (3.08 \pm 0.03) \times 10^{-3}$ M^{-1} s^{-1} and $K_{iso} = 2.89 \pm 0.11$ at 140 °C. Activation parameters at $[Cl^-] = 0.12$ M are $\Delta H^* = 147 \pm 3$ kJ/mol and $\Delta S^* = 59.7 \pm 1.5$ J/(mol K). Equilibrium thermodynamic parameters are $\Delta H = 45.5 \pm 0.9$ kJ/mol and $\Delta S = 118.5 \pm 3.5$ J/(mol K). Minor changes in the ligands generate marked differences in K_{eq} and K_{iso}.

Owing to its position in the center of the periodic table, the synthetic element technetium exhibits a wide range of chemistry in multiple oxidation states and geometries, which often appear to depend on relatively subtle changes in the ligands and reaction conditions.[1,2] However, very few careful studies of technetium reactions have been carried out. During the course of investigating the formation of complexes of the type *trans*-$[O_2(Py)_4Tc]^+$ (Py = pyridine derivative),[3] a variety of other species were also observed, including *trans*-$[O(RO)X_2(Py)_2Tc]$, where X = Cl, Br and RO = CH_3O–, CH_3CH_2O–,[4] and the unusual, asymmetric and dissymmetric, dinuclear, mixed-valent compounds $[X(Py)_3XTcO(Tc(Py)X_3(Py)]$[5] and $[X(Py)_4TcOTc(Py)X_4]$, illustrated in Figure 1.[6]

Previous work showed that the asymmetric species was the precursor to the dissymmetric one, and it was thought that this process might occur intramolecularly. Another question centers on the formation of the asymmetric dinuclear species, which must occur from different technetium(V) mononuclear complexes, and involves a three-electron reduction. Since the only reductant present is the pyridine ligand, the possibility of an oxygen atom transfer reaction[7] was raised to account for two of the electrons in the redox process. When both the kinetics and equilibria of the dinuclear formation and isomerization reactions are quantitated, oxygen atom transfer to the solvent is evident and pronounced effects of minor ligand modifications are, indeed, apparent.

Abbreviations: Py, generic pyridine derivative; py, pyridine; pic, 4-picoline; lut, 3,5-lutidine; I, $[Cl(pic)_4TcOTc(pic)Cl_4]$; III, $[Cl(pic)_3ClTcOTc(pic)Cl_3(pic)]$; II, *trans*-$[O_2(pic)_4Tc]^+$; DCB, *o*-dichlorobenzene.

Experimental Section

Synthesis. The starting material $[(n\text{-}Bu)_4N][TcOCl_4]$ was prepared from $(NH_4)TcO_4$ (Oak Ridge) by the method of Cotton.[8] Compounds of the general types $[Cl(Py)_4TcOTc(Py)Cl_4]$ and $[Cl(Py)_3ClTcOTc(Py)Cl_3(Py)]$, where Py = py, pic, lut, were prepared by previously reported methods.[5] Pyridine *N*-oxide and 4-picoline *N*-oxide (Aldrich) were purified by sublimation before use and stock solutions prepared in absolute methanol.

The new compound, *trans*-$[O(OCH_3)Cl_2(pic)_2Tc]$, was prepared in a manner similar to a recently published procedure.[9] Approximately 100 mg of $[(n\text{-}Bu)_4N][OCl_4Tc]$ and 0.5 mL of 4-picoline were dissolved in 15 mL of absolute methanol, and the mixture was stirred at room temperature. After about 10 min a greenish blue precipitate appeared, which was collected by filtration. While stable as a solid, chloroform solutions were unstable at room temperature, yielding an orange-red solution. Addition of water gave a black precipitate. Anal. Calcd for $[H_{17}C_{13}N_2O_2Cl_2Tc]$: H, 4.25; C, 38.73; N, 6.95; Cl, 17.58. Found: H, 4.21; C, 38.98; N, 6.91; Cl, 16.86. UV–visible λ_{max} in $CHCl_3$: 351, 424 (sh), 649 nm (ϵ = 7360 M^{-1} cm^{-1}). IR: 930 ($\nu_{Tc=O}$), 1612 cm^{-1} ($\nu_{C=N}$).

Caution! All syntheses were performed with ^{99}Tc, which is a β-emitting isotope with a half-life of 2.15×10^5 years. Only milligram quantities should be handled with the minimum shielding present under normal laboratory conditions. Precautions for handling this material are described elsewhere.[1,10]

Compound Characterization. All elemental analyses (except for ^{99}Tc) were performed by the Berkeley Microanalytical Laboratory, Berkeley, CA. Technetium analyses were performed by spectrophotometric or scintillation methods.[5]

Infrared spectra were taken on a Perkin-Elmer Model 599B grating spectrophotometer in CsI pellets. UV–visible spectra were obtained on a Perkin-Elmer Model 575 spectrophotometer equipped with a digital background corrector and a thermostated sample cell. HPLC separations were done on a 15-cm Waters μC_{18} column with a Gilson UV detector and IBM isocratic pump. The eluent was 70% methanol/30% water at a flow rate of 0.7 mL/min. TLC separations were performed on silica gel plates developed with a 1:1 (v:v) mixture of chloroform and benzene.

Kinetics. Reactions at high temperature (usually 140 °C) were run either in 10-mL pear-shaped flasks to which was added 3.00 mL of the reaction solvent and a stirring bar for continuous mixing before sealing with a septum cap and equilibrating in a constant-temperature bath or in reactivials thermostated in an aluminum heating block placed in a Multi-Blok (American Scientific Products) heater accurate to within ±0.5 °C and equilibrated for 1 h. Chloride concentrations were adjusted with stock solutions of $[(n\text{-}C_4H_9)_4N]Cl$ (Aldrich) dissolved in picoline and standardized by the Mohr method. A weighed amount of $[(n\text{-}C_4H_9)_4N][TcOCl_4]$ (I or III) was added and the container quickly resealed. The formation and isomerization of the μ-oxo complexes were followed until at least 80% complete by both HPLC and UV–visible spectrophotometry. In general, two runs were averaged for each graphical point. Spectrophotometric measurements were made by sampling the reaction mixtures every 1–20 min with a 100-μL syringe and trans-

(1) Clarke, M. J.; Podbielski, L. *Coord. Chem. Rev.* **1987**, *78*, 253–331.
(2) Mazzi, U.; Nicolini, M. *Technetium in Chemistry and Nuclear Medicine*; Raven Press: New York, 1983.
(3) Kastner, M. E.; Fackler, P.; Deutsch, E.; Clarke, M. J. *Inorg. Chem.* **1984**, *23*, 4683–4688.
(4) Fackler, P.; Kastner, M. E.; Clarke, M. J. *Inorg. Chem.* **1984**, *23*, 3968–3972.
(5) Clarke, M. J.; Kastner, M. E.; Podbielski, L. A.; Fackler, P. H.; Schreifels, J.; Meinken, G.; Srivastava, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 1818–1827.
(6) Kastner, M. E.; Fackler, P. H.; Podbielski, L.; Charkoudian, J.; Clarke, M. J. *Inorg. Chim. Acta* **1986**, *114*, L11–15.
(7) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401–1449.
(8) Cotton, F. A.; Davison, A.; Day, V. W.; Gage, L. D.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 3024.
(9) Pearlstein, R. M.; Lock, C. J. L.; Faggiani, R.; Costello, C. E.; Zeng, C.-H.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 2409–2413.
(10) Clarke, M. J.; Podbielski, L. In *Handbook on the Toxicity of Inorganic Compounds*; Seiler, H. G., Sigel, H., Eds.; Marcel Dekker: New York, 1988; pp 665–667.

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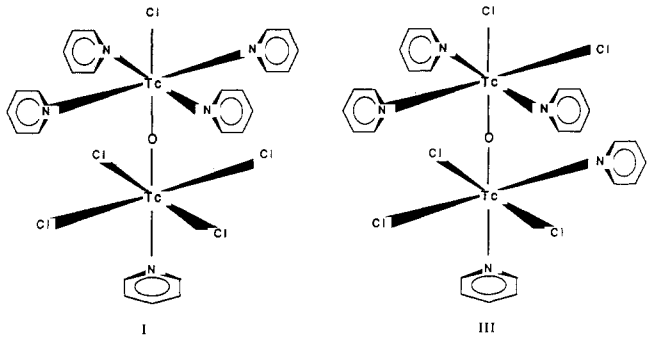


I III

Figure 1. Structures of the dissymmetric (I) and asymmetric (III) μ-oxo dinuclear complexes. Structure determinations show that the equatorial ligands adopt a staggered configuration.[5]

ferring into a UV–visible cuvette, to which was added 3.00 mL of $CHCl_3$. Absorption was measured between 400 and 500 nm against a chloroform blank. Concentrations of the two dinuclear species were determined by solving the simultaneous equations $A_{400} = (15.5 \times 10^3)[I] + (20.66 \times 10^3)[III]$ and $A_{500} = (7.34 \times 10^3)[I] + (3.65 \times 10^3)[III]$. No contributions to absorption from other products at 400 and 500 nm were observed. HPLC measurements were done by withdrawing 100 μL of the reactant solution at specified times and transferring to a sample vial, which was dried under a vacuum for several hours. The residue was dissolved in 1.00 mL of methanol before injection onto the HPLC instrument. In the case of the formation reaction, this technique introduced an artifact in that picoline *N*-oxide formed during the course of the reaction oxidized some of the Tc(V) complexes present to $[O_4Tc]^-$.

The isomerization of $[Cl(pic)_3(ClTcOTc(pic)Cl_3(pic)]$ to $[Cl(pic)_4TcOTc(pic)Cl_4]$ was additionally monitored by liquid scintillation counting.[5] The fraction of the total technetium activity in each of the products as a function of time was determined by sampling the reaction mixtures every 5–30 min with a 10-μL pipet and spotting silica gel plates, which were placed in a vacuum desiccator overnight to remove excess ligand before developing. After the plates were dried, the individual spots were scraped into separate scintillation vials, to which were added 0.5 mL of $CHCl_3$ and 5 mL of scintillation cocktail (Fischer Scintiverse) before counting. In monitoring of the isomerization reactions spectrophotometrically, isosbestic points occurred at 382 and 427 nm and only two peaks were observed by HPLC.

Second-order rate constants for the formation of the μ-oxo complexes from $[OCl_4Tc]^-$ were obtained from plots of ln $[([(\mu\text{-O})Tc] - A)/([(\mu\text{-O})Tc] - B)]$ versus time according to the relation

$$\ln\left[\frac{[(\mu\text{-O})Tc] - A}{[(\mu\text{-O})Tc] - B}\right] = 4k_2(A - B)t + \ln\left[\frac{A}{B}\right]$$

where $[(\mu\text{-O})Tc]$ is the total concentration of I and III and A and B are given by the two roots of

$$\frac{K_{eq}^{-1} + 4[Tc^V]_0 \pm [(K_{eq}^{-1} + 4[Tc^V]_0)^2 - 16[Tc^V]_0^2]^{1/2}}{8}$$

in which $K_{eq} = [(\mu\text{-O})Tc]/[Tc]_m^2$, $[Tc^V]_0$ is the initial concentration of $[OCl_4Tc]^-$, and $[Tc]_m$ is the concentration of technetium not converted to μ-oxo species as given by $[Tc^V]_0 - 2[(\mu\text{-O})Tc]$. This reaction was also followed by monitoring the concentration of the pyridine or picoline *N*-oxide formed. This was accomplished by transferring 100-μL samples from the reaction mixture to a vial to which 1 mL of water was added. The suspended solid was filtered off, and the filtrate was then passed through both cation (Sephadex CM-25) and anion (OAE Sephadex Q-25) ion-exchange columns (each eluted with 25 mL of water) to separate the *N*-oxide from oxidizable technetium species. The combined eluates were rotary evaporated, and the residue was dissolved in 1.0 mL of methanol before HPLC injection, which quantitated the *N*-oxide formation. Rate constants for the rate d[py *N*-O]/dt were determined from plots of $([Tc^V]_0 - 2[\text{py } N\text{-O}]_t)^{-1}$ versus time according to the equation $([Tc^V]_0 - 2[\text{py } N\text{-O}]_t)^{-1} - [Tc^V]_0^{-1} = 2kt$, where [py *N*-O]$_t$ is the concentration of pyridine or picoline *N*-oxide at the time of sampling and, at equilibrium, is stoichiometrically equal to $[(\mu\text{-O})Tc]$.

Rate constants for the isomerization of III to I were determined from plots of ln $[([III]_0 - [I]_t(1 + K_{iso}^{-1}))/[III]_0]$ versus time, according to the relation

$$\ln\left[\frac{[III]_0 - [I]_t(1 + K_{iso}^{-1})}{[III]_0}\right] = -(1 + K_{iso}^{-1})k_1t$$

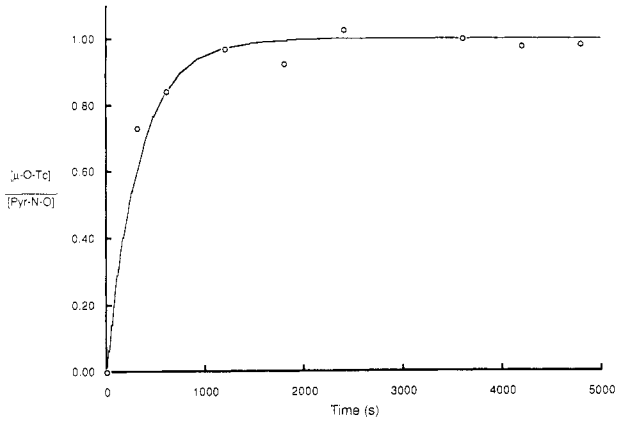


Figure 2. Plot of [py *N*-O]/$[(\mu\text{-O})Tc]_{total}$ versus reaction time in neat pyridine at 140 °C. The solid line represents a nonlinear regression fit to the equation [py N-O]/$[(\mu\text{-O})Tc]_{total} = 1 - e^{-kt}$, where $k = (2.9 \pm 0.1) \times 10^{-3}$ s^{-1}.

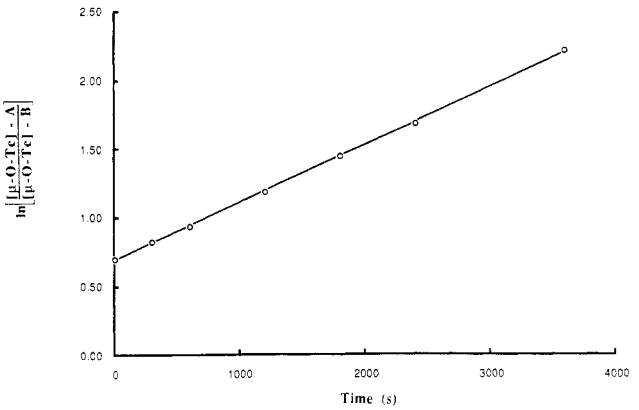


Figure 3. Plot of ln $[([(\mu\text{-O})Tc] - A)/([(\mu\text{-O})Tc] - B)]$ versus time for the reaction of $[OCl_4Tc]^-$ in picoline at 140 °C, $[(\mu\text{-O})Tc]$ being monitored.

where K_{iso} is the equilibrium constant for the reaction determined by measuring the equilibrium concentrations of I and III by both UV–visible spectrophotometry and HPLC, $[III]_0$ is the initial concentration of III, and $[I]_t$ is the concentration of I at a given time.[11]

Decomposition of III in DCB was monitored spectrophotometrically by placing the cell in a thermostated cell compartment and observing the change in absorbance at 398 nm. The temperature was monitored in situ by means of a thermistor probe. Pseudo-first-order rate constants were generated from plots of log $(A_t - A_\infty)$ versus time, where A_t is the absorbance of III at time t and A_∞ is the absorbance after completion of the reaction.

Results

Formation of μ-Oxo Complexes. The reaction of $[TcOCl_4]^-$ with hot picoline resulted in several products, which, when monitored chromatographically, yielded reaction profiles similar to that previously published.[5] These indicate that, as the starting material disappears, III and *trans*-$[O_2Tc(pic)_4]^+$ initially form, but the latter is maintained at a nearly constant concentration and is not an immediate precursor in the formation of the dinuclear complexes. The dissymmetric complex I appears at later times at the expense of its precursor isomer, III. HPLC monitoring of the reaction run in neat pyridine or picoline revealed the presence of pyridine *N*-oxide, which was absent in blank runs but formed in amounts initially greater than and finally stoichiometrically equal to $[(\mu\text{-O})Tc]$ (see Figure 2).

When studied in picoline solution at 140 °C with no added chloride, plots of ln $[([(\mu\text{-O})Tc] - A)/([(\mu\text{-O})Tc] - B)]$ versus time

(11) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley-Interscience: New York, 1981; p 304. This treatment is preferred when K is known, but the equilibrium concentrations for any given run may not be, owing to side reactions or the slowness of the reaction.

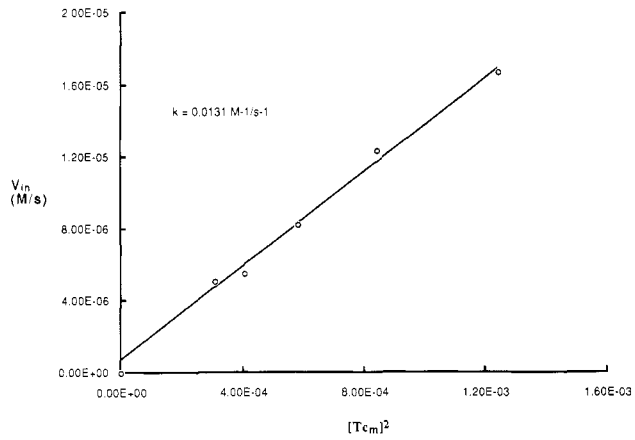


Figure 4. Plot of the initial rate of formation, V_{in}, of $[(\mu\text{-O})Tc]_{total}$ versus $[Tc]_m^2$.

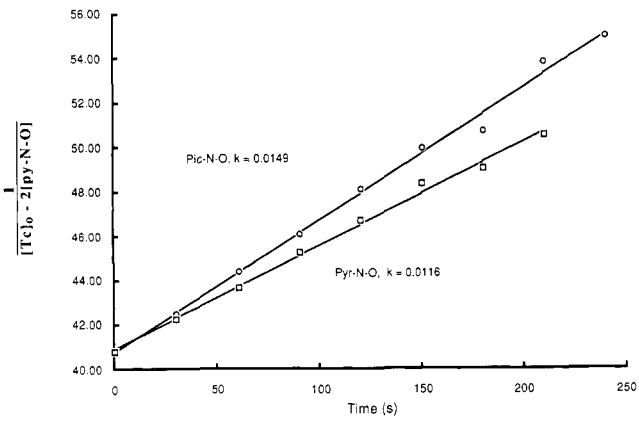


Figure 5. Plot of $1/([Tc]_0 - 2[Py\ N\text{-}O])$ versus time for the reaction of $[OCl_4Tc]^-$ in neat pyridine at 140 °C, [Py *N*-O] being monitored: (○) picoline; (□) pyridine.

(see Figure 3) and plots of the initial rate of the reaction versus $[Tc]_m^2$ (Figure 4) show that the formation of the μ-oxo technetium complexes is second-order in $[Tc]_m$. The reaction does not go to completion but approaches an equilibrium with the various monomeric technetium species that are formed. The rate law is

$$\frac{d[(\mu\text{-O})Tc]}{dt} = k_f[Tc]_m^2 - k_r[(\mu\text{-O})Tc]$$

with $k_f = (1.45 \pm 0.1) \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k_r = (3.02 \pm 0.02) \times 10^{-5}\ M^{-1}\ s^{-1}$. Slightly faster rates were obtained when picoline *N*-oxide was monitored as shown in Figure 5. Consistent with this, plots of $[(\mu\text{-O})Tc]/[Pic\ N\text{-O}]$ invariably revealed a ratio less than unity at short reaction times as indicated in Figure 2.

Values for the equilibrium constants, $K_{eq} = [(\mu\text{-O})Tc]/[Tc]_m^2$, at 140 °C varied substantially with the ligand and are $(5.3 \pm 0.2) \times 10^3\ M^{-1}$ (pyridine), $193 \pm 8\ M^{-1}$ (picoline), and $54 \pm 2\ M^{-1}$ (lutidine). Heating $[Cl(lut)_4TcOTc(lut)Cl_4]$ in boiling picoline (~140 °C) yielded I in ~20% yield along with several other products.

Decomposition and Isomerization in Dichlorobenzene. Both types of μ-oxo compounds are stable in various organic solvents at room temperature and exhibit no spectral change in common solvents over a period of hours at room temperature. As typical representatives of the asymmetric and dissymmetric dinuclear compounds, the stabilities of $[Cl(pic)_3ClTcOTc(pic)Cl_3(pic)]$ and $[Cl(pic)_4TcOTcCl_4(pic)]$ were investigated in *o*-dichlorobenzene. In this solvent, the asymmetric compound was observed to undergo transformation at temperatures over 60 °C and the dissymmetric compound was unstable at temperatures over 135 °C.

At 80 °C in DCB, $[Cl(pic)_3ClTcOTc(pic)Cl_3(pic)]$ (λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$): 253 (12 800), 398 (15 500), 498 (7340)) exhibited a decrease in the absorbance peak at 398 nm and a loss of the band at 498 nm as the solution changed from red to yellow. The

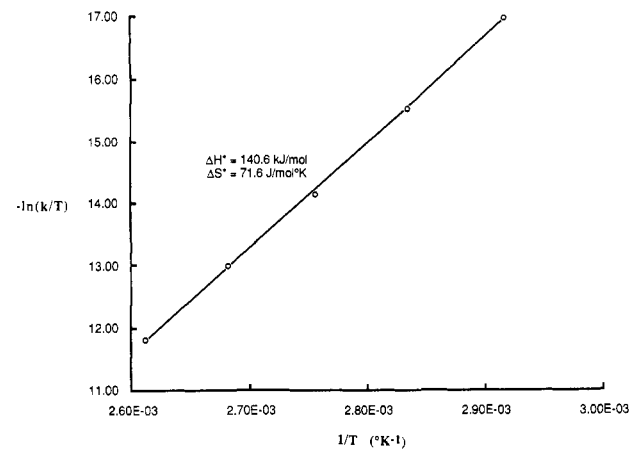


Figure 6. Eyring plot for the decomposition of III in *o*-dichlorobenzene.

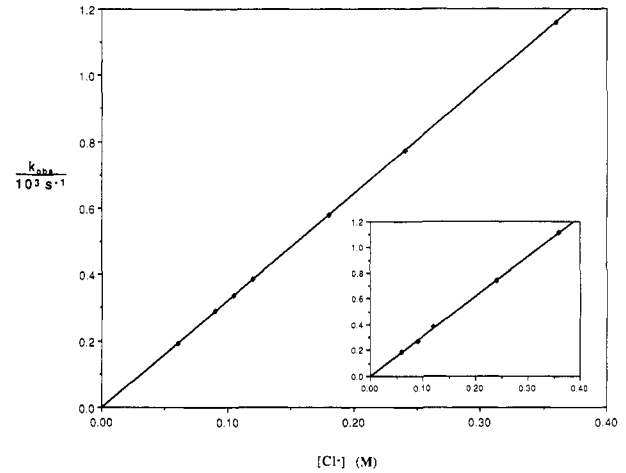


Figure 7. Plot of k_{obs} versus chloride ion concentration for III ⇄ I in neat picoline. Inset: same as main plot, but in dichlorobenzene.

decomposition exhibited first-order kinetics with activation parameters of $\Delta H^* = 140.6 \pm 3.2$ kJ/mol and $\Delta S^* = 71.6 \pm 2.7$ J/(mol K) in neat DCB (Figure 6). In this temperature range, decomposition was inhibited by picoline in concentrations greater than 0.1 M but not inhibited by chloride concentrations of 0.01–2.0 M, suggesting that the decomposition results from the dissociation of one or more pyridine ligands. Indeed, addition of picoline to fully decomposed samples regenerated 10% of the original spectrum of $[Cl(py)_3ClTcOTc(py)Cl_3(py)]$.

At 140 °C and a picoline concentration of 1.12 M, the isomerization (asymmetric to dissymmetric) approached an equilibrium between the two forms. The approach to equilibrium was observed to be linear in chloride ion concentration (Figure 7) with the rate law

$$\frac{d[I]}{dt} = [Cl^-](k_f[III] - k_r[I])$$

where $k_f = (3.12 \pm 0.08) \times 10^{-3}\ M^{-1}\ s^{-1}$. When the equilibrium constant ($K_{iso} = [I]/[III]$) of 2.83 ± 0.12 is used, the reverse rate constant is calculated to be $1.1 \times 10^{-3}\ M^{-1}\ s^{-1}$. Activation parameters from the Eyring plot in Figure 8 are $\Delta H^* = 144 \pm 2$ kJ/mol and $\Delta S^* = 53.5 \pm 1$ J/(mol K). Equilibrium thermodynamic parameters for the isomerization reaction in DCB are $\Delta H = 49.9 \pm 1.5$ kJ/mol and $\Delta S = 130 \pm 4$ J/(mol K) (see Figure 9).

Isomerizations in Neat Pyridine Solutions. Monitoring the reaction of III in neat picoline at 140–141 °C by UV–visible, HPLC, or TLC methods indicated that the concentration of I increased, while that of the starting material decreased, and that both reached a constant level after a few hours. Some of the starting compound decomposed to material that remained at the TLC origin, and is assumed to be ionic, monomeric species.

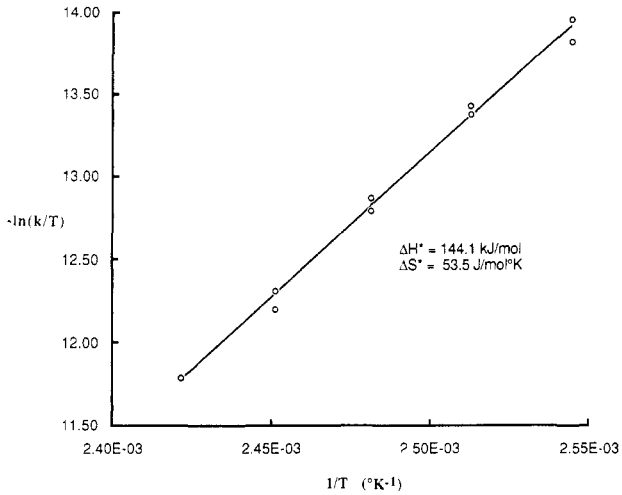


Figure 8. Eyring plot for the isomerization III ⇄ I in dichlorobenzene solution. $[Cl^-]$ = 0.12 M, [pic] = 1.12 M, and [III] = 6.23 mM.

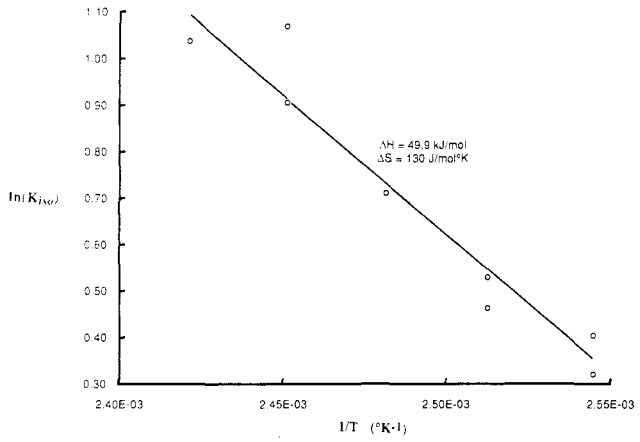


Figure 9. Plot of ln K_{iso} versus $1/T$ for the isomerization III ⇄ I in dichlorobenzene solution. $[Cl^-]$ = 0.12 M, [pic] = 1.12 M, and [III] = 6.23 mM.

Analogous experiments with I as the starting material in neat picoline at 135 °C revealed that the isomerization reaction also proceeded in the reverse direction. At 140 °C with no chloride added and $[OCl_4Tc]^-$ as the starting material, equilibrium constants (K_{iso} = [dissym]/[asym]) for the three ligands were 1.8 ± 0.3 (pyridine), 2.9 ± 0.1 (picoline), and 5 ± 1 (lutidine).

When chloride was added to solutions of III, the system approached equilibrium cleanly and isosbestic points were observed. Plots of chloride ion concentration versus the observed rate of approach to equilibrium, starting with the asymmetric compound, are linear as shown in Figure 7, yielding the same rate law as that for the isomerization in dichlorobenzene. Figure 10, showing the initial rate of the reaction as a function of [III], indicates the rate to be linearly dependent on [III]. The second-order rate constant is (3.08 ± 0.03) × 10^{-3} M^{-1} s^{-1}. K_{iso} obtained from HPLC and spectrophotometric quantitation of the two forms is 2.89 ± 0.11. For the reverse reaction, these values yield k_r = 1.18 × 10^{-3} M^{-1} s^{-1}. The Eyring plot for the isomerization of III to I in picoline solution at $[Cl^-]$ = 0.12 M is shown in Figure 11, and the activation parameters are ΔH^* = 147 ± 3 kJ/mol and ΔS^* = 59.7 ± 1.5 J/(mol K). Equilibrium thermodynamic parameters for this reaction are ΔH = 45.5 ± 0.9 kJ/mol and ΔS = 118.5 ± 3.5 J/(mol K) (Figure 12).

Discussion

μ-Oxo Complex Formation. Since the chloro ligands on the starting material, $[OCl_4Tc]^-$, are easily substituted, the array of Tc(V) species shown in Scheme I are likely to be present. Indeed, *trans*-$[O_2(pic)_4Tc]^+$ is observed and the closely related *trans*-$[O(OCH_3)Cl_2(pic)_2Tc]$ was isolated from a similar reaction mixture in methanol. Since the formation of the μ-oxo complexes

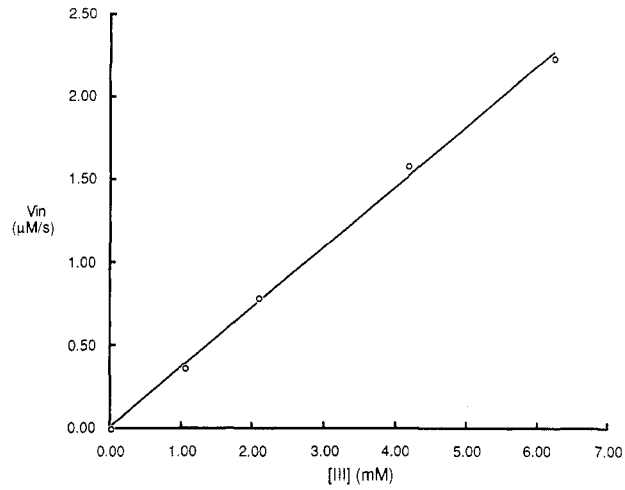


Figure 10. Plot of initial rate, V_{in}, for coordination isomerization versus [III] in picoline at $[Cl^-]$ = 0.12 M and 140 °C.

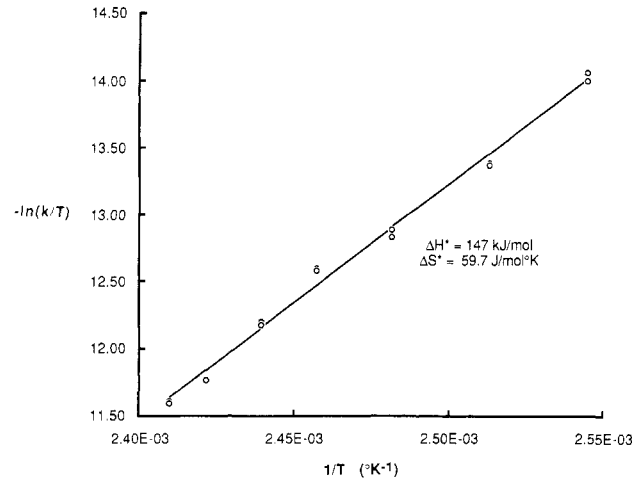
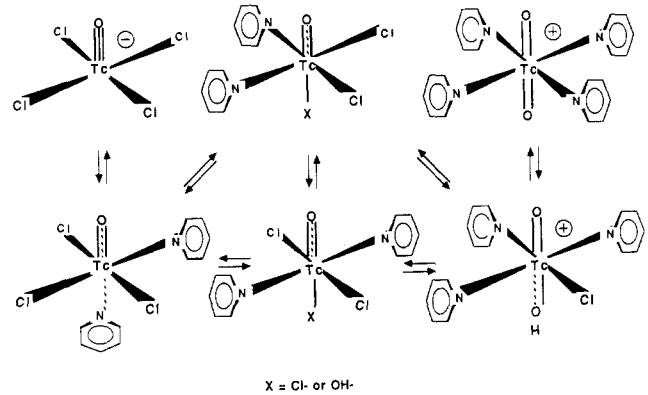


Figure 11. Eyring plot for the isomerization III ⇄ I in picoline solution. $[Cl^-]$ = 0.12 M and [III] = 6.23 and 8.35 mM.

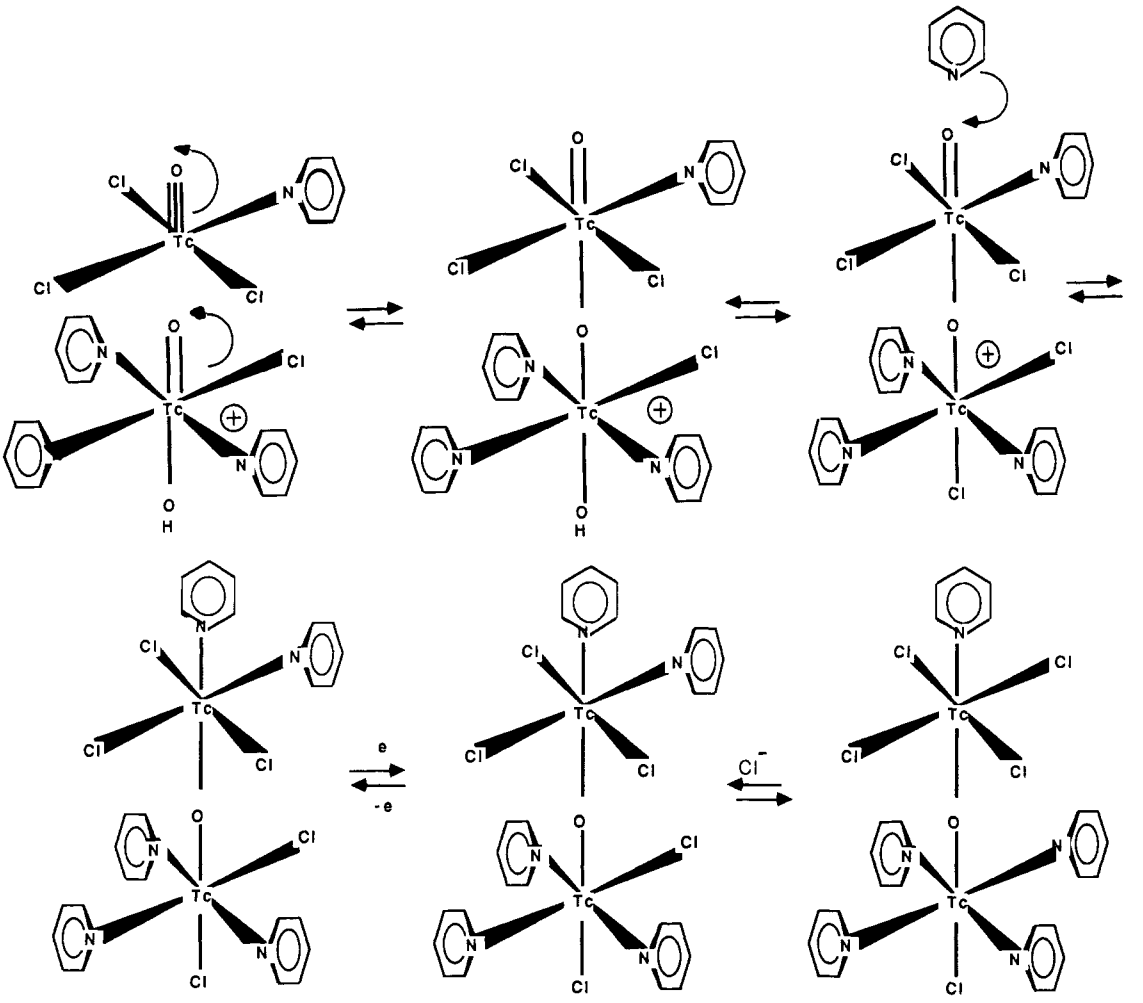
Scheme I. Equilibria Involving Oxo-Tc(V) Monomeric Complexes with Pyridine and Halide Ligands



was observed to be second-order in $[Tc]_m$ and picoline *N*-oxide is produced in a 1:1 stoichiometric ratio with [(μ-O)Tc], a likely route to the initially formed asymmetric μ-oxo complexes is illustrated in Scheme II.

The formation of picoline *N*-oxide indicates that solvent picoline reduces an oxotechnetium(V) species by oxygen atom transfer. Since the rate of picoline *N*-oxide formation is slightly faster than that of the mixed-valent, μ-oxo species, these molecules do not form simultaneously. This is not surprising, since an additional electron must be transferred to effect the full 3e reduction. While there is no direct evidence as to whether this occurs before or after dinuclear formation, complexes containing the core [O=M^V—

Scheme II. Possible Mechanism for the Formation of the Asymmetric μ-Oxo Complexes



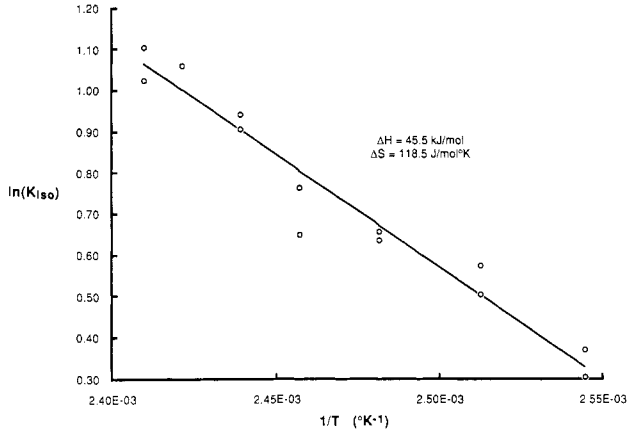


Figure 12. Plot of ln K_{iso} versus $1/T$ for the isomerization III $\rightleftarrows$ I in picoline solution. $[Cl^-]$ = 0.12 M, [pic] = 1.12 M, and [III] = 6.23 mM.

$O—M^V{=}O]^{4+}$ are known with both Tc and Re,[12,13] so that formation of the core $[O{=}Tc^V—O—Tc^V—Cl]^{5-}$ is likely before reduction. Transfer of the terminal oxygen to picoline and picoline substitution in the vacant site would then yield the necessary asymmetric core, which can be formulated as $[pic—Tc^{III}—O—Tc^V—Cl]^{5+}$ or $[pic—Tc^{IV}—O—Tc^{IV}—Cl]^{5+}$. On the other hand, as these complexes are also readily made from $[X_6Tc^{IV}]^{2-}$, X = Cl^-, Br^-, condensation involving Tc(IV) or even Tc(III) species is possible.

Since the dinuclear complexes have been shown to be in the Robin–Day class III category and the two technetium centers are in intimate electronic contact, there is a strong driving force toward the mixed-valent species. The reduction potentials of the IV–IV complexes are generally in the range 0.6–0.8 V,[5] which are probably sufficiently high to oxidize some pyridine derivatives at high temperatures.[14] Indeed, the oxidation waves of III(IV–IV) and picoline overlap at room temperature in picoline solution, and there is no other species present that could reduce the Tc in the millimolar concentrations present in syntheses. Finally, pale-colored materials that were chromatographed similar to dipicoline (4,4′-dimethyl-2,2′-bipyridine) could be isolated from reaction mixtures but not from picoline solutions heated under the same conditions without technetium.

In the course of this work it was observed that pyridine *N*-oxide rapidly oxidizes $[OCl_4Tc]^-$, *trans*-$[O_2(py)_4Tc]^+$, and *trans*-$[O_2(OR)Cl_2(py)_2Tc]$ (but not I or III) to $[TcO_4]^-$ in alcohol and halocarbon solvents at room temperature;[15] however, since these oxygen atom transfers are inhibited by pyridine, oxidation of the Tc(V) precursors was not observed in the reaction mixtures presently treated, but did cause artifacts in HPLC analyses with alcoholic solvents.

The order of magnitude variation in K_{eq} for each methyl group added to the pyridine ligand indicates that very subtle changes in the ligand can be reflected in fairly large changes in the chemistry of technetium ions. Since the methyl groups are positioned to provide a minimal steric effect, it appears that this chemistry is extraordinarily sensitive to small electronic changes. To a lesser extent, this is also evident in variations in K_{iso}.

(12) Davison, A.; Jones, A. G. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 793–99.
(13) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 860.
(14) Dryhurst, G. *Electrochemistry of Biological Molecules*; Academic Press: New York, 1977; p 490.
(15) Lu, J.; Clarke, M. J. Unpublished results, 1988.

Despite the interesting biological distributions of I and III,[5] the second-order dependence of the formation reaction of $[Tc]_m$ and the k_f value of 0.015 M^{-1} s^{-1} results in half-lives on the order of days at the submicromolar concentrations required for the synthesis of radioimaging agents in nuclear medicine, which precludes their use for this purpose. Finally, the relatively small values of K_{eq} means that these complexes can dissociate back to monomeric (probably Tc^V) species in an oxidizing environment of low technetium concentration, which may have affected their uptake by mammalian tissues.

Isomerization. The decompositon in DCB observed when sufficient picoline was not present, which was partially reversible on the addition of picoline, suggests that picoline is a good leaving group in the μ-oxo molecules, as it is in *trans*-$[O_2(pic)_4Tc^V]^+$.[3] This is confirmed by the substitution of picoline onto the dissymmetric lutidine complex to form I. Conversely, the failure of even high concentrations of chloride to have any effect on the decompostion of III in dichlorobenzene suggests that it is not an initial leaving group in the isomerization reaction. At higher temperatures, decomposition of III was evident even in the presence of high concentrations of picoline, suggesting that transformation of the species lacking one or more picoline ligands can proceed more rapidly than replacement by solvent picoline under sufficiently energetic conditions. Lack of chloride also allows for decomposition in picoline solution, suggesting that this can also serve as a reasonable leaving group.

The kinetic and equilibrium parameters are remarkably similar in either DCP or picoline, indicating a similar mechanism in both solvents. A truly dissociative mechanism involving picoline loss as the rate-limiting step would exhibit a rate law inverse in picoline concentration, while an associative mechanism dependent on picoline attack would yield a rate law first-order in picoline. The small difference in rates, when the isomerization reaction was run in 0.1-1.1 M picoline in dichlorobenzene or even in neat picoline, shows that the isomerization not only is independent of picoline in this concentration range but is also fairly independent of the solvent. It appears that excess picoline is necessary to maintain the dinuclear complexes by inhibiting their decay to species lacking this ligand; however, when it is ligated, it still serves as a good leaving group on chloride attack. Assuming that chloride addition is rate-limiting, a reasonable mechanism for the isomerization reaction is given by Scheme III.

Scheme III

$$Cl^- + III \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cl(pic)_3ClTcOTcCl_4(pic)]^- + pic$$

$$[Cl(pic)_3ClTcOTcCl_4(pic)]^- + pic \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Cl(pic)_4ClTcOTcCl_4(pic)]^-$$

$$[Cl(pic)_4ClTcOTcCl_4(pic)]^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} I + Cl^-$$

The relatively high ΔH^* and positive ΔS^* suggest that bond breaking plays some role in the rate-limiting step, and the similar activation parameters for the isomerization and decomposition reactions imply that loss of the pyridine ligand is involved. Owing to the strong electronic interaction between the two metal atoms, charge can be passed from one technetium center to the other via the metal-μ-oxo π-bonds. Consequently, addition of a chloride to one Tc may labilize bonds on the second. It is even possible that a picoline transfers from one side of the molecule to the other in concert with chloride dissociation. The reverse reaction, which has a smaller ΔH^* (94.3 kJ/mol in DCB and 105 kJ/mol in picoline) and a negative ΔS^* (-76.4 J/(mol K) in DCB and -59 J/(mol K) in picoline), may be somewhat more associative in its rate-limiting step. Assuming the first and last steps to be rate limiting in the forward and reverse directions, respectively, the net rate law and equilibrium constant for the reaction become

$$\frac{d[I]}{dt} = (k_f[III] - k_r[I])[Cl^-] \qquad K_{iso} = \frac{k_f}{k_r}$$

where $k_f = k_1k_3/(k_3 + k_{-1})$ and $k_r = k_{-3}k_3/(k_3 + k_{-1})$, which is consistent with the empirical rate law.

This mechanism, the decomposition through pyridine loss, and the substitution of one pyridine ligand for another suggest that the pyridine and chloride ligands can be sequentially replaced by other molecules, so that other heterocyclic ligands such as imidazole or purines may be incorporated into the μ-oxo complexes.

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Supplementary Material Available: Derivations of rate equations and tables giving data for all graphs in this paper (8 pages). Ordering information is given on any current masthead page.

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Kinetic Study of the Oxygen-Transfer Reactions from the Oxo Diperoxo Complexes of Molybdenum(VI) and Tungsten(VI) to (Thiolato)- and (Sulfenato)cobalt(III) Complexes

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The (thiolato)cobalt(III) complex $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ is oxidized first to $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$ and then much more slowly to $(en)_2Co(S\{O\}_2CH_2CH_2NH_2)^{2+}$ by the oxo diperoxo complexes of Mo(VI) and W(VI). Nearly quantitative oxygen atom transfer from peroxide to the coordinated sulfur acceptor accompanies these reactions. The reactions are strictly catalytic with respect to the d^0 metal ions, provided sufficient hydrogen peroxide is present to maintain them as oxo diperoxo complexes. The activation of the coordinated peroxo group is impressive; the relative reactivities for each substrate stand in the order $WO(O_2)_2$ > $WO(OH)(O_2)_2^-$ > $MoO(O_2)_2$ > $MoO(OH)(O_2)_2^-$ ≫ H_2O_2. Second-order rate constants and, with the exception of those for $WO(O_2)_2$, activation parameters for all these reactions were determined. The data are insufficient to distinguish whether nucleophilic attack by coordinated sulfur occurs directly at the peroxo ligand or after prior coordination at Mo(VI) or W(VI).

Introduction

The early transition elements in their highest oxidation states rapidly combine with hydrogen peroxide to form peroxo complexes with large formation constants.[1,2] The reactivities of these peroxo complexes toward a variety of reducing agents have been examined, both in organic solvents and in aqueous solution.[2-7] In many

(1) Connor, J. A.; Ebsworth, E. A. V. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 279.

(2) Mimoun, H. In *The Chemistry of Peroxides*; Patai, S., Ed.; Interscience: New York, 1983; pp 463-482.

(3) Sheldon, R. A.; Kochi, J. K. In *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; pp 48-97.

(4) Secco, F. *Inorg. Chem.* **1980**, *19*, 2722.

0020-1669/88/1327-4766$01.50/0