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Electron Transfer Reactions of Peroxydisulfate and Fluoroxysulfate Reactions with the Cyanide Complexes $M(CN)_n^{4-}$ (M=Fe(II), Ru(II), Os(II), Mo(IV), and W(IV))

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The stoichiometry and the kinetics of oxidation of the cyanide complexes $M(CN)_n^{4-}$ (M = Fe(II), Ru(II), Os(II), Mo(IV), and W(IV)) by the peroxydisulfate ion, $S_2O_8^{2-}$, and by the much more strongly oxidizing fluoroxysulfate ion, SO_4F^-, were studied in aqueous solutions containing Li^+. Reactions of $S_2O_8^{2-}$ with $M(CN)_n^{4-}$ are known to be strongly catalyzed by Li^+ and other alkali metal ions, and this applies also to the corresponding reactions of SO_4F^-. The primary reactions of $S_2O_8^{2-}$ and SO_4F^- have both been found to be one-electron processes in which the equally strong O−O and O−F bonds are broken. The primary reaction of $S_2O_8^{2-}$ consists of a single step yielding $M(CN)_n^{3-}$, SO_4^-, and SO_4^{2-}, whereas the primary reaction of SO_4F^- comprises two parallel one-electron steps, one leading to $M(CN)_n^{3-}$, SO_4^-, and F^- and the other yielding $M(CN)_{n-1}^{2-}$, CN^-, SO_4^- and F^-. The relationship between the rate constants and the standard free energies of reaction for the Li^+-catalyzed reactions of SO_4F^- and $S_2O_8^{2-}$ with $M(CN)_n^{4-}$, and for the uncatalyzed reactions of $S_2O_8^{2-}$ with bipyridyl and phenanthroline complexes ML_n^{2+} (M = Fe(II), Ru(II), and Os(II)) studied previously, suggests that the intrinsic barrier for all three sets of reactions is similar, i.e., unaffected by the Li^+ catalysis, and that the electron transfer and the breakage of the O−O and O−F bonds are concerted processes.

Introduction

Dissociative electron transfer may take place either by a stepwise mechanism in which the electron-transfer precedes the bond breakage or by a mechanism in which the bond breakage and the electron transfer is concerted. Despite the fact that concerted processes may be characterized as inner-sphere processes, both mechanisms may be represented in terms of an equation[1,2] similar to the Marcus quadratic equation which is valid for outer-sphere processes only:[3]

$$-RT \ln k = \Delta G_o^{\ddagger}(1 + \Delta G^{o\prime}/4\Delta G_o^{\ddagger})^2 + A \qquad (1)$$

where $\Delta G^{o\prime}$ is ΔG^o corrected for the electrostatic energy associated with transferring the electron from the donor to the acceptor at the reaction distance, and A stands for terms that are independent of ΔG^o. The parameter $\Delta G_o^{\ddagger}$ is called the intrinsic barrier.

For a outer-sphere stepwise mechanism $\Delta G_o^{\ddagger}$ is given by[3]

$$\Delta G_o^{\ddagger} = (\lambda_i + \lambda_o)/4 \qquad (2)$$

where λ_i and λ_o are the inner relaxation and solvent reorganization relaxation energy, respectively,[3] whereas that for a concerted process $\Delta G_o^{\ddagger}$ is given by[1,2]

$$\Delta G_o^{\ddagger} = (\Delta H_{diss} + \lambda_i + \lambda_o)/4 \qquad (3)$$

where ΔH_{diss} is the bond dissociation enthalpy. Thus, the intrinsic barrier of a concerted process is usually much larger than that of a stepwise process.

Previous studies in aqueous solution of the reductive cleavage of the O−O bond of the peroxydisulfate ion, $S_2O_8^{2-}$, by reaction with the substitution-inert, positively charged complexes ML_n^{2+} (M = Fe(II), Ru(II), and Os(II); L = bipyridyl, phenanthroline, and ammine) show that the relationship between the rate constant, k, and the standard free energy change, ΔG^o, for these reactions may be expressed by an equation which contains the same ΔG^o-dependent term as eq 1 with $\Delta G_o^{\ddagger} \sim 80 - 90$ kJ mole^{-1},[4] a range of values consistent with a concerted process.[5]

The present paper describes the relationship between rate constant and ΔG^o for fission of the O−O bond in $S_2O_8^{2-}$ and of the O−F bond in SO_4F^- by reaction with the negatively charged cyanide complexes $M(CN)_n^{4-}$ (M = Fe(II), Ru(II), Os(II), Mo(IV), and W(IV)). Under the assumption that the breaking of the O−F bond and the transfer of the electron to SO_4F^- are also concerted, the comparison of bond-breaking reactions of $S_2O_8^{2-}$ and SO_4F^- is of particular interest, since ΔG^o for these reactions differs widely, SO_4F^- being one of the strongest aqueous oxidants known,[6,7] while at the same time the values of ΔH_{diss} for the dissociation of the O−O and O−F

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bonds are similar, 150−200 kJ mol^{-1}.[8−11] Thus, despite the large difference in oxidizing power, the reactions of $S_2O_8^{2-}$ and SO_4F^- may have similar intrinsic barriers, since λ_o and λ_i cannot be expected to vary much for the reactions in question.[1,2]

In contrast to the reactions of $S_2O_8^{2-}$ with the positively charged complexes ML_n^{2+} studied previously, the reactions of $S_2O_8^{2-}$ and SO_4F^- with the negatively charged cyanide complexes described here are strongly catalyzed by alkali metal ions, as is generally observed for electron-transfer reactions among anions, whether thermal or optical.[12,13] Thus, it is found that the catalyzed path in the reaction of $S_2O_8^{2-}$ with $M(CN)_n^{4-}$ (M = Fe, Mo, W) completely overwhelms the uncatalyzed path, making the rate constant proportional to the concentration of alkali metal ion even at the lowest practical concentration.[14−16]

An adequate model for this catalysis has not yet been developed, but apparently the positively charged alkali metal ion by forming a bridge between the two reacting anions facilitates the electron transfer. The finding that the catalytic effect of the alkali metal ions increases in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ has been taken to suggest that the catalysis is governed by the polarizabilities of the ions.[12] However, recent investigations point to that the catalysis involves a partial deaquation of the catalyzing cation.[16,17]

No theoretical argument warrants the expectation that the rate constants measured for the catalyzed path should be related to ΔG^o in a manner resembling that expressed by eq 1. However, in accordance with the "bridging picture" the concept of an intrinsic barrier may also be valid for the catalyzed path of the reactions of $S_2O_8^{2-}$ and SO_4F^- with $M(CN)_n^{4-}$, in which case the observed relationship between the rate constants and ΔG^o may be interpretable in terms of a modified version of eq 1 containing the value of the parameter $\Delta G_o^{\ddagger}$ determined for the uncatalyzed reaction of $S_2O_8^{2-}$ with ML_n^{2+}. In the present investigation, we probe this possibility. However, before discussing the relation between rate constants and free energy changes for the reactions of $S_2O_8^{2-}$ and SO_4F^- with $M(CN)_n^{4-}$, we need to establish that the primary steps of the reactions are indeed one-electron processes.

Corresponding reactions of $S_2O_8^{2-}$ and SO_4F^- are in general quite similar. With simple one-electron reductants, the bond-breaking step for both ions involves either an electron transfer from the reductant, R (e.g., R = Ag^+,[18−19] ClO_2^-,[21,22] I^-,[19,20] e^-_{aq}[23,24])

$$SO_4F^- + R \rightarrow SO_4^- + F^- + R^+ \tag{4}$$

$$S_2O_8F^{2-} + R \rightarrow SO_4^- + SO_4^{2-} + R^+ \tag{5}$$

or the transfer of a fluorine atom or SO_4^- group to R (e.g., R = Cr^{2+} [19,25]):

$$SO_4F^- + R \rightarrow SO_4^- + RF \tag{6}$$

$$S_2O_8F^{2-} + R \rightarrow SO_4^- + RSO_4^- \tag{7}$$

The subsequent fast step for both types of reaction is

$$SO_4^- + R \rightarrow SO_4^{2-} + R^+ \tag{8}$$

An effect of the much stronger driving force in oxidation reactions of SO_4F^- may show up, however, in reactions with more complex reductants. Whereas measurements suggest that $S_2O_8^{2-}$ reacts with the bipyridyl complexes $Fe(bpy)_3^{2+}$, $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ according to eq 5 by dissociative electron transfer followed by a fast step equivalent to eq 8,[26,27] the stoichiometry of the reaction of SO_4F^- with excess $Ru(bpy)_3^{2+}$ was found to be one mole $Ru(bpy)_3^{2+}$ consumed per mole SO_4F^- reacted, and not two, as one would expect.[28] This stoichiometry could be taken to suggest a mechanism involving oxidative degradation of ligand bpy by transfer of two oxidation equivalents in one step. On the other hand, the fact that $Ru(bpy)_3^{3+}$ is detected as a product of the reaction,[28] points to a one-electron mechanism.

To shed further light on these questions, we have carried out a detailed study of the kinetics of the reactions of $S_2O_8^{2-}$ and SO_4F^- with the anionic cyanide complexes, $M(CN)_n^{4-}$, of Fe(II), Ru(II), Os(II), Mo(IV), and W(IV).

Experimental Section

Materials. Water was triply distilled. Cesium fluoroxysulfate (97 − 98%, by iodometric assay)[29] was prepared, isolated and stored as described previously.[29,30] $K_4Os(CN)_6 \cdot 3H_2O$ (98−99% by potentiometric titration) was prepared from KCN and K_2OsO_4.[31] K_2OsO_4 was obtained by oxidizing Os metal in a melt of KOH and KNO_3.[32] $K_4Mo(CN)_8 \cdot 2H_2O$ was prepared from MoO_3.[33] (Analysis, C calcd. 19.35%, found 19.08%; H calcd. 0.81%, found 0.86%; N calcd. 22.57%, found 22.26%; K calcd. 31.50%, found 31.63%). $K_4W(CN)_8 \cdot 2H_2O$ was prepared by reducing sodium tungstate with potassium borohydride in the presence of potassium cyanide.[34] (Analysis, C calcd. 16.44%, found 16.55%; H calcd. 0.69%, found 0.80%; N calcd. 19.17%, found 19.29%; K calcd. 26.76%, found 26.57%). $K_4Fe(CN)_6 \cdot 3H_2O$, Merck p.a., and $K_4Ru(CN)_6.3H_2O$, Alfa Reagent Grade, were used as purchased. Analysis of the batch of $K_4Ru(CN)_6 \cdot 3H_2O$ used showed C calcd. 15.41%, found 15.11%; H calcd. 1.29%, found 1.09%; N calcd.17.97%, found 17.33%; Ru calcd. 21.61%, found 21.62%. Analysis for $Ru(CN)_5H_2O^{3-}$[35] showed a content of less than 0.4% of this ion. Nitrous oxide N48 was ALFAGAZ. Other gases were N40. Materials not mentioned here were commercial products of reagent grade. Stock solutions containing 0.1 M $Li_4M(CN)_n$ and 0.6 M $LiClO_4$ were prepared from the corresponding potassium salts and lithium perchlorate by metathesis. Solutions of $M(CN)_n^{3-}$ in 1 M $LiClO_4$ were prepared from the corresponding $M(CN)_n^{4-}$ solutions by potentiostatic electrolysis.[36] All aqueous solutions were prepared in triply distilled water. Solutions containing SO_4F^- were prepared at 0 °C immediately before use.

Analytical Procedures. SO_4F^- solutions were analyzed iodometrically.[29] $M(CN)_n^{4-}$ solutions were analyzed by potentiometric titration with ammonium cerium(IV) nitrate and cerium(IV) sulfate standardized against ammonium ferrous sulfate, or with permanganate standardized against sodium oxalate. Concentrations of $M(CN)_n^{3-}$ were determined spectrophotometrically, using the values for the extinction coefficient, ϵ, given in Table 1. The extinction coefficients of $Mo(CN)_8^{4-}$, $Mo(CN)_8^{3-}$, $W(CN)_8^{4-}$, and $W(CN)_8^{3-}$ shown in Table 1 were determined by titrating solutions of $Mo(CN)_8^{4-}$ and $W(CN)_8^{3-}$ with ceric sulfate, neutralizing, filtering, and diluting to a known volume. The values thus found agree with published values.[38,39]

Measurements. UV−visible spectra were recorded on a Cary 219 spectrophotometer or a Hewlett-Packard 8452 A Diode Array Spectrophotometer. Reactions were monitored spectrophotometrically at the wavelengths listed in Table 1. The wavelengths in the third row of Table 1 are those of the band maxima of $M(CN)_n^{3-}$. The kinetics of the reaction of $W(CN)_8^{3-}$ with CN^- was monitored with the Diode Array Spectrophotometer, measurements being taken every second minute with the shutter open for 0.1 s. The kinetics of reactions of $M(CN)_n^{4-}$

TABLE 1: Extinction Coefficients ϵ/(M^{-1} cm^{-1}) at the Wavelengths λ/nm

Fe(CN)$_6^{3-}$ [a]		Ru(CN)$_6^{3-}$ [b]		Os(CN)$_6^{3-}$ [c]		Mo(CN)$_8^{3-}$ [d]		Mo(CN)$_8^{4-}$ [d]		W(CN)$_8^{3-}$ [d]		W(CN)$_8^{4-}$ [d]	
λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ
420	1040	460	1020	406	1590	388	1450	388	110	358	1760	358	250
–	–	–	–	–	–	400	1205	400	90	–	–	–	–

[a] From ref 37. [b] From ref 35. [c] From ref 36. [d] This work.

with $S_2O_8^{2-}$ was followed with the Cary spectrophotometer. Photolytic decomposition of $M(CN)_n^{3-}$ during the kinetic runs was observed for the reaction of $Mo(CN)_8^{4-}$ with $S_2O_8^{2-}$ only. However, by reducing the slit width of the spectrophotometer, the photolysis could be reduced to a negligible level. Kinetic measurements of faster reactions were made with an Aminco-Morrow or a Hi-Tech Scientific stopped-flow apparatus. All instruments were equipped with thermostatted cell compartments controlling the temperature nominally to within ±0.2 °C.

Most experiments were carried out with solutions in which the Li^+ concentration was adjusted to 1 M by addition of $LiClO_4$. A few runs were carried out at 0.5 M Li^+. The reaction of $M(CN)_n^{4-}$ with $S_2O_8^{2-}$ is strongly catalyzed by all alkali metal ions.[14−16] Preliminary results show the same catalytic effect of lithium ions on the reaction of $M(CN)_n^{4-}$ with SO_4F^-. The concentrations of Na^+, K^+, or Cs^+ were generally less than 0.02 M. Kinetic measurements of reactions of SO_4F^- are difficult, because of the ion's low stability. The extent of decomposition of SO_4F^- solutions was minimized by preparing the solutions at ice point and only just before the experiment bringing them close to the temperature of the stopped-flow instrument. This, however, impeded the temperature equalization and introduced an uncertainty estimated to be ±1 °C. Rate measurements within the same run were in general fairly reproducible, but reproducibility among different runs was much poorer. The tabulated values are means of several runs. If SO_4F^- was in large excess, its concentration was measured by taking a sample of the reactant SO_4F^- solution in the instrument after each "stopped-flow shot", adding this to a solution containing $Fe(CN)_6^{4-}$ in excess, and spectrophotometrically measuring the concentration of $Fe(CN)_6^{3-}$ formed (*vide infra*).

Measurements of electrode potentials in 1 M $LiClO_4$ were made with a Radiometer PHM 64 Research pH Meter, using a Radiometer P101 bright platinum electrode and a Radiometer K 401 saturated calomel electrode fitted with a salt bridge containing 1 M LiCl.

Computations. Rate constants and enthalpies of activation were computed by means of the least-squares program of the computer package "Easyplot"; rate constants were determined by fitting three-parameter first- or second-order rate equations to the observed optical densities; enthalpies of activation were obtained by a linear fit of the logarithm of the rate constant versus the reciprocal of the absolute temperature. Reactions with more complex kinetics were simulated using the computer package "Gepasi" equipped with the optimization module Multistart (Levenberg−Marquardt) Version 1.00.[40−42]

Results and Discussion

Reactions of $S_2O_8^{2-}$ with $M(CN)_n^{4-}$ (Table 2). Rate constants for the change of optical density in the reaction of $S_2O_8^{2-}$ with $Fe(CN)_6^{4-}$, $Os(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $W(CN)_8^{4-}$ were measured in 1 M $LiClO_4$. Reactant concentrations ranged from 3×10^{-4} M to 0.1 M for $S_2O_8^{2-}$ and from 10^{-2} M to 0.2 M for $M(CN)_n^{4-}$. No rate measurements of the reaction with $Ru(CN)_6^{4-}$ were made, because of the low stability of $Ru(CN)_6^{3-}$.[35] Most kinetic measurements were made under pseudo-first-order conditions; only a few were made with the reactants in similar concentrations. The reactions were all found to be of first order in both reactants. The rate constants in solutions containing $S_2O_8^{2-}$ in large excess were found to be twice as large as the rate constants in solutions containing $M(CN)_n^{4-}$ in large excess. A 2:1 stoichiometry, i.e., formation of two moles of $M(CN)_n^{3-}$ per mole $S_2O_8^{2-}$ consumed, has previously been established for $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $W(CN)_8^{4-}$.[14−16] In the present work, we measured the quantities

$$x = \Delta OD_{t=\infty} / (\Delta\epsilon l[S_2O_8^{2-}]_o) \qquad (9)$$

in solutions in which $Me(CN)_n^{4-}$ was in excess and

$$y = \Delta OD_{t=\infty} / (\Delta\epsilon l[M(CN)_n^{4-}]_o) \qquad (10)$$

in solutions in which $S_2O_8^{2-}$ was in excess. Here l is the length of the optical cell, $\Delta\epsilon$ is the difference between the extinction coefficients of $M(CN)_n^{3-}$ and $M(CN)_n^{4-}$ at the measuring wavelength (Table 1), $\Delta OD_{t=\infty}$ is the change of optical density at infinite time, and $[M(CN)_n^{4-}]_o$ and $[S_2O_8^{2-}]_o$ are the initial concentrations of $M(CN)_n^{4-}$ and $S_2O_8^{2-}$, respectively. Insofar as $M(CN)_n^{3-}$ and $M(CN)_n^{4-}$ are the only species that absorb light at the measuring wavelength, x is the yield of $M(CN)_n^{3-}$ per mole $S_2O_8^{2-}$ consumed, and y is the yield of $M(CN)_n^{3-}$ per mole of $M(CN)_n^{4-}$ consumed. We found $x = 2.0$ and $y = 1.0$, indicating that the stoichiometry of the reactions of $S_2O_8^{2-}$ with these species is similar to that previously observed for the reactions of $S_2O_8^{2-}$ with ML_n^{2+}.[26,27]

TABLE 2: Rate Constants (10^2k_{11}, M^{-1} s^{-1}) for the Primary Reactions (eq 11) of $S_2O_8^{2-}$ with $M(CN)_n^{4-}$ [a]

temp, °C	$Fe(CN)_6^{4-}$	$Os(CN)_6^{4-}$	$Mo(CN)_8^{4-}$	$W(CN)_8^{4-}$
15.2	1.27	0.066	0.0112	0.82
25.2	2.76	0.155	0.0268	1.91
39.6	8.0	0.54	0.110	5.15

[a] Estimated error limits for k_{10}: ±5%.

The above kinetic and stoichiometric findings fit a mechanism similar to eqs 4 and 7

$$M(CN)_n^{4-} + S_2O_8^{2-} \rightarrow M(CN)_n^{3-} + SO_4^{2-} + SO_4^{-} \quad k_{11} \qquad (11)$$

$$M(CN)_n^{4-} + SO_4^{-} \rightarrow M(CN)_n^{3-} + SO_4^{2-} \quad k_{12} \qquad (12)$$

where $k_{12} \gg k_{11}$.

The values of k_{11} were obtained from the integrated rate equation for the optical density change

$$\Delta OD(t) = \Delta OD_{t=\infty}(1 - \exp(-k_{13}t)) \qquad (13)$$

at three temperatures (Table 2). In solutions containing $M(CN)_n^{4-}$ in large excess $k_{13} = k_{11}[M(CN)_n^{4-}]$ and $k_{13} = 2k_{11}[S_2O_8^{2-}]$ in solutions containing $S_2O_8^{2-}$ in large excess. Table 6 lists the change of standard Gibbs energy, ΔG^o, and the activation energy, E_a, for the reactions of $S_2O_8^{2-}$ with $M(CN)_n^{4-}$ in 1M Li^+. Since the Li^+-catalyzed path completely overwhelms the uncatalyzed path, E_a listed in Table 6 is the activation energy

TABLE 3: The Parameters x and y for the Reactions of SO_4F^- with $M(CN)_n^{4-}$ [a]

	$Fe(CN)_6^{4-}$	$Ru(CN)_6^{4-}$	$Os(CN)_6^{4-}$	$Mo(CN)_8^{4-}$	$W(CN)_8^{4-}$
x^b	1.97	1.61	1.84	0.86	1.36
y^c	0.97	0.91	0.91	0.72	0.67

[a] Temperature range 6−25 °C. Estimated error limits ± 0.02. [b] $x = \Delta OD_{t=\infty}/(\Delta\epsilon l[SO_4F^-]_o)$, measured in solutions containing excess $M(CN)_n^{4-}$. [c] $y = \Delta OD_{t=\infty}/(\Delta\epsilon l[M(CN)_n^{4-}]_o)$, measured in solutions containing excess SO_4F^-.

for the catalyzed path. We may note that the activation energies for the uncatalyzed reactions of $S_2O_8^{2-}$ with ML_n^{2+} (50 − 60 kJ mol^{-1})[26,27] do not differ significantly from the values for E_a in Table 6. This could be taken to indicate that the catalysis does not affect the activation energy to any large extent.

Reactions of SO_4F^- with $M(CN)_n^{4-}$ (Tables 3−5). Kinetic measurements on these reactions were made under pseudo-first-order conditions in solutions containing 1 M or 0.5 M $LiClO_4$. The range of reactant concentrations was 5×10^{-5} to 2×10^{-2} M $M(CN)_n^{4-}$ and 5×10^{-5} to 5×10^{-3} M SO_4F^-. Reactions of $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Os(CN)_6^{4-}$, and $W(CN)_8^{4-}$ with SO_4F^- were found to be of first order in both reactants, whereas the reaction of $Mo(CN)_8^{4-}$ exhibited complex kinetics. Figure 1 shows the time evolution of the optical density of solutions containing $Mo(CN)_8^{4-}$ in excess. After an initial rapid increase of the optical density, a slow decrease takes over.

For reactions with $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Os(CN)_6^{4-}$, and $W(CN)_8^{4-}$, the rate constants for the change of optical density in solutions containing SO_4F^- in large excess were found to be twice as large as the rate constants in solutions containing $M(CN)_n^{4-}$ in large excess.

Table 3 shows the quantities $x = \Delta OD_{t=\infty}/(\Delta\epsilon l[SO_4F^-]_o)$ and $y = \Delta OD_{t=\infty}/(\Delta\epsilon l[M(CN)_n^{4-}]_o)$. x and y were found to be independent of the temperature. We note that x and y for $Fe(CN)_6^{4-}$ and $Os(CN)_6^{4-}$ are close to 2 and 1, respectively, suggesting that the predominant reaction for these two complexes is similar to that proposed for the reactions of $S_2O_8^{2-}$ with $M(CN)_n^{4-}$. However, the finding that $x < 2$ and $y < 1$ for the reactions with $Ru(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $W(CN)_8^{4-}$ indicates that for these complexes less than two moles of $M(CN)_n^{3-}$ are formed per mole SO_4F^- reacted, which might be interpreted in terms of a two-electron process. On the other hand, the fact that the rate constants in solutions of $M(CN)_n^{4-}$ (except $Mo(CN)_8^{4-}$) containing SO_4F^- in excess is twice the rate constant in solutions containing $M(CN)_n^{4-}$ in excess points to a one-electron mechanism similar to that of the reactions with $S_2O_8^{2-}$, with the difference, however, that the primary reaction of SO_4F^- consists of several parallel paths, all of which produce SO_4^-, but only one of which forms $M(CN)_n^{3-}$. We propose that the primary reaction of $Mo(CN)_8^{4-}$ with SO_4F^- is of the same type as those of the other cyanides, and that the complex kinetics observed in this reaction reflects a subsequent reaction of $Mo(CN)_8^{3-}$ with a product arising in one of the parallel paths.

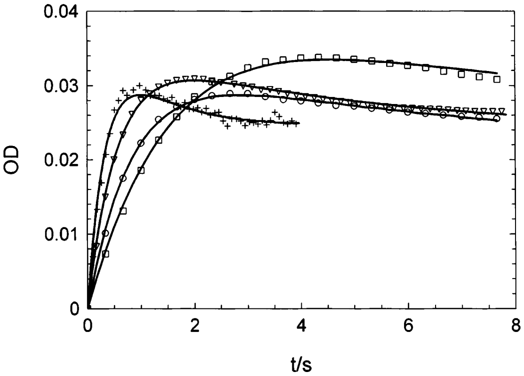

Figure 1. Time evolution of the absorbance at 400 nm in the reaction of SO_4F^- with $Mo(CN)_8^{4-}$: □, 1.16×10^{-4} M SO_4F^-, 1.00×10^{-2} M $Mo(CN)_8^{4-}$ at 5 °C; ○, 1.01×10^{-4} M SO_4F^-, 1.05×10^{-2} M $Mo(CN)_8^{4-}$ at 15 °C; +, 9.7×10^{-4} M SO_4F^-, 3.00×10^{-2} M $Mo(CN)_8^{4-}$ at 15 °C; ▽, 1.00×10^{-4} M SO_4F^-, 1.00×10^{-2} M $Mo(CN)_8^{4-}$ at 25 °C. Smooth curves are simulations calculated with the Gepasi package,[40−42] adjusting k_{14} and k_{15} and taking k_{17}, k_{18}, and ϵ_Q equal to zero.

Except for the reaction of SO_4F^- with $Ru(CN)_6^{4-}$, which exhibited an absorbance in the near-infrared at the end of the reaction suggesting the formation of a binuclear Ru(II)- Ru(III) cyanide complex,[35] no changes of absorbance other than those attributable to formation of $M(CN)_n^{3-}$ were observed. Formation of a binuclear ruthenium complex suggests the fission of a carbon - ruthenium bond with formation of CN^-, a process that may also take place in the reaction of SO_4F^- with other $M(CN)_n^{4-}$ complexes. Moreover, additional studies described below show that CN^- reduces $M(CN)_n^{3-}$. Hence, a formation of CN^- parallel to the formation of $M(CN)_n^{3-}$ in the primary process and a subsequent reduction of $M(CN)_n^{3-}$ by CN^- may explain the complex kinetics of the reaction of $Mo(CN)_n^{4-}$ with SO_4F^-.

Accordingly, the following is a possible mechanism for the reactions of SO_4F^- with $M(CN)_n^{4-}$:

$$M(CN)_n^{4-} + SO_4F^- \rightarrow M(CN)_n^{3-} + SO_4^- + F^- \quad k_{14} \tag{14}$$

$$M(CN)_n^{4-} + SO_4F^- \ (+H_2O) \rightarrow Q + CN^- + SO_4^- \quad k_{15} \tag{15}$$

$$M(CN)_n^{4-} + SO_4^- \rightarrow M(CN)_n^{3-} + SO_4^{2-} \quad k_{12} \tag{12}$$

$$CN^- + M(CN)_n^{3-} \rightarrow P + M(CN)_n^{4-} \quad k_{16} \tag{16}$$

Q represents $M(CN)_{n-1}\,H_2O^{2-} + F^-$ and/or $M(CN)_{n-1}F^{3-}$, and P represents a one-electron oxidation product of CN^-

TABLE 4: The Rate Constant k_{16} for the Reaction of $M(CN)_n^{3-}$ with CN^- in 1 M $LiClO_4$ (Temp. 25.0 °C)

$M(CN)_n^{3-}$	$[M(CN)_n^{3-}]$, M	$[M(CN)_n^{4-}]$, M	$[CN^-]$, M	k_{16}, M^{-1} s^{-1}
$Fe(CN)_6^{3-}$	$1.0 \times 10^{-3\,a}$	$1.0 \times 10^{-3\,a}$	0.1^a	$3.1 \times 10^{-4\,a}$
$Ru(CN)_6^{3-}$	4.4×10^{-4}	0	$5.0\ 10^{-5}$	$(5.1 \pm 0.5) \times 10^3$
$Os(CN)_6^{3-}$	2.7×10^{-3}	0	$1.0\ 10^{-4}$	$(2.1 \pm 0.2) \times 10^2$
	2.7×10^{-3}	1.0×10^{-2}	$1.0\ 10^{-4}$	20 ± 3
$Mo(CN)_8^{3-}$	9.9×10^{-4}	0	$9.5\ 10^{-5}$	$(1.05 \pm 0.05) \times 10^3$
	1.03×10^{-3}	0	$1.0\ 10^{-4}$	$(1.14 \pm 0.09) \times 10^3$
	1.06×10^{-3}	0	$5.0\ 10^{-5}$	$(1.24 \pm 0.13) \times 10^3$
	2.52×10^{-4}	5.0×10^{-3}	$5.0\ 10^{-5}$	$(1.21 \pm 0.12) \times 10^3$
	$(6.7\text{-}8.4) \times 10^{-5}$	0	$2.5\ 10^{-4}$	$(1.24 \pm 0.09) \times 10^3$
	5.0×10^{-3}	0	$5.0\ 10^{-4}$	$(1.23 \pm 0.04) \times 10^3$
$W(CN)_8^{3-}$	1.0×10^{-3}	1.0×10^{-2}	$1.0\ 10^{-3}$	$\sim 10^{-2}$

[a] Ref 43, $[LiClO_4] = 0$.

TABLE 5: Sum of the Rate Constants (k_{14}+ k_{15}), M^{-1} s^{-1}, for the Primary Reactions (eqs 14 and 15) of SO_4F^- with $M(CN)_n^{4-}$ [a]

temp, °C	$Fe(CN)_6^{4-}$	$Ru(CN)_6^{4-}$	$Os(CN)_6^{4-}$	$Mo(CN)_8^{4-}$	$W(CN)_8^{4-}$
6	1300 ; 600[b]	4.5	150 ; 75 b)	60	1400
15	2200	10	300	120	2500
25	4300	20	570	180	4000

[a] In 1 M $LiClO_4$ unless otherwise specified. Estimated error limits for temperature: ±1 °C; for (k_{14} + k_{15}), ±15%. [b] In 0.5 M $LiClO_4$.

TABLE 6: Standard Electrode Potential in 1 M $LiClO_4$, E^o, for $M(CN)_n^{3-}/M(CN)_n^{4-}$. The Standard Gibbs Energy Change, $\Delta G°$, and Activation Energy, E_a, for Reactions of SO_4F^- and $S_2O_8^{2-}$ with $M(CN)_n^{4-}$ (Temperature = 25.0 °C)

		ΔG^o, kJ mol^{-1} [b]		E_a, kJ mol^{-1} [c]	
$M(CN)_n^{4-}$	E^o, V[a]	SO_4F^-	$S_2O_8^{2-}$	SO_4F^-	$S_2O_8^{2-}$
$Fe(CN)_6^{4-}$	0.492	−161.9	−92.4	45	57
$W(CN)_8^{4-}$	0.549	−156.4	−86.9	41	55
$Os(CN)_6^{4-}$	0.688	−143.0	−73.5	50	65
$Mo(CN)_8^{4-}$	0.807	−131.5	−62.0	49	65
$Ru(CN)_6^{4-}$	0.971	−115.7	−46.2	56	−

Estimated error limits: [a] ±0.003 V; [b] ±0.3 kJ mol^{-1}; [c] ±3 kJ mol^{-1}.

[possibly O = CNH_2 or HC(O)NH[43,44]]. The finding that $x < 2$ and $y < 1$ (Table 3) and the absence of changes of absorbance other than those attributable to formation of $M(CN)_n^{3-}$ may be rationalized by assuming that the spectra of Q are similar to those of $M(CN)_n^{3-}$, but with a less intense absorption at the measuring wavelengths, an assumption that has proven correct in the case of $Fe(CN)_5H_2O^{2-}$.[43] $Fe(CN)_5H_2O^{2-}$ exhibits a broader spectrum with band maxima positioned at the same wavelengths as those of $Fe(CN)_6^{3-}$ (300 and 420 nm) and with band intensities that are approximately one-third of the intensities of the corresponding bands of $Fe(CN)_6^{3-}$.[43]

The occurrence of the additional primary step (eq 15) may be attributed to the higher oxidation power of SO_4F^- as follows: Kinetic measurements of the uncatalyzed reductive cleavage of the O−O bonds in dialkyl peroxides[45] and in $S_2O_8^{2-}$ by reaction with ML_n^{2+} reveal unusually low pre-exponential factors,[26,27] suggesting that the cleavage of O−O bonds in these reactions proceeds non-adiabatically, i.e., via excited states. Assuming that the reactions of $S_2O_8^{2-}$ and SO_4F^- with $M(CN)_n^{4-}$ also proceed non-adiabatically and noting that electron transfer to SO_4F^- is 70 kJ mol^{-1} more exoergic than electron transfer to $S_2O_8^{2-}$ (Table 6), we may expect the reaction with SO_4F^- to generate higher excited states of $M(CN)_n^{3-}$, for which a path of decay by breaking the C−M bond to form Q and CN^- (eq 15) is available in addition to relaxation to the ground state (eq 14). Thus, the mechanism of reaction of SO_4F^- with $M(CN)_n^{4-}$ has features in common with the mechanism operating in the photolysis of transition metal complexes in aqueous solution.[46] After optical excitation to a ligand-field state, the excited complex may either relax to the ground state or exchange a ligand CN^- with a water molecule. The values for x and y shown in Table 3 support this hypothesis. We find that x and y for $Fe(CN)_6^{4-}$ are close to two and one, respectively, while the corresponding values for $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ are significant smaller. This parallels the finding that the quantum yield (∼0.008)[46] estimated for the formation of CN^- by irradiation of $Fe(CN)_6^{3-}$ is much smaller than those estimated for the photolysis of $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$, which are ≤0.2,[47] and ∼0.1,[48] respectively.

The reactions of CN^- with $Ru(CN)_6^{3-}$ and $Fe(CN)_6^{3-}$ (eq 16) were studied previously. The reaction with $Ru(CN)_n^{4-}$ is fast,[34] whereas reaction with $Fe(CN)_6^{3-}$ is very slow and exhibits complex kinetics.[43,49] In the course of the present study, we have surveyed the reactions of CN^- with $Ru(CN)_6^{3-}$, $Os(CN)_6^{3-}$, $Mo(CN)_8^{3-}$, and $W(CN)_8^{3-}$.[50] It has been claimed that such kinetic studies could be spurious owing to catalysis by traces of copper ions.[51] However, the meticulous study of the reaction of CN^- with $Fe(CN)_6^{3-}$,[49] with and without copper ion catalysis indicates that this is not necessarily the case. Therefore, since the present measurements were found to be reproducible and coherent, we have chosen to ignore the possibility of trace catalysis.

Table 4 shows values of k_{16} for the reactions of CN^- with $M(CN)_n^{3-}$. k_{16} increases in the order M = Fe ≪ W ≪ Os ≪ Mo < Ru. Like the reactions of CN^- with $Fe(CN)_4^{3-}$,[43,49] the reactions with $Os(CN)_6^{3-}$ and $Mo(CN)_8^{3-}$ exhibit complex kinetics, which shows up when concentrations and acidity are varied. Thus, the order of the reactions changes from pseudo first order in CN^- at low CN^- concentrations to zero order at high CN^- concentration. Moreover, similar to the inhibition[43,49] of the reaction between CN^- and $Fe(CN)_6^{3-}$ by $Fe(CN)_6^{4-}$, we found that $Os(CN)_6^{4-}$ inhibits the reaction of CN^- with $Os(CN)_6^{3-}$, whereas no effect was observed on the rate of reaction between $Mo(CN)_8^{3-}$ and CN^- by addition of 5×10^{-3} M $Mo(CN)_8^{4-}$ (Table 4). The rate constant k_{16} as function of acidity passes a rather flat maximum at pH 9−10, which has the effect that k_{16} in unbuffered CN^- solutions is almost independent of the total CN^- concentration, i.e., of the extent of hydrolysis of the CN^- ion. A further indication for the complexity of the reaction 16 is that the dependence of the rate on the temperature is unusually weak (ref 49 and Table 4).

The reactions of CN^- with $M(CN)_n^{3-}$ studied are of first order in both reactants at low concentrations of CN^- and $M(CN)_n^{3-}$ in solutions of composition similar to those used to study the kinetics of the reactions of $M(CN)_n^{4-}$ with SO_4F^-. Reactions with excess $Ru(CN)_6^{3-}$, $Os(CN)_6^{3-}$, or $Mo(CN)_8^{3-}$ were found to take place in two steps. We assume the first step to be eq 16 and the second to be a reaction of P with $M(CN)_8^{3-}$. Like $Fe(CN)_6^{3-}$, $W(CN)_8^{3-}$ reacts with CN^- in one step only. The values of k_{16} shown in Table 4 fit the kinetics of the reactions of $M(CN)_n^{4-}$ with SO_4F^-. The fact that the reactions of $Fe(CN)_6^{4-}$, $Os(CN)_6^{4-}$, $W(CN)_8^{4-}$, and $Ru(CN)_6^{4-}$ with SO_4F^- are of first order is consistent with the assumption that reaction 16 either may be neglected (for M = Fe, Os, and W), or else so fast (for Ru) that CN^- may be considered an intermediate at steady-state concentration. In both cases the primary reactions are rate-determining, and the rate constants k_{13} for the change of optical density obtained from the integrated rate equation eq 13 equal $(k_{14} + k_{15})[M(CN)_n^{4-}]$ in solutions containing excess of $M(CN)_n^{4-}$, and $2(k_{14} + k_{15})[S_2O_8^{2-}]$ in solutions containing excess SO_4F^-. However, since except for $Fe(CN)_5^{2-}H_2O$ we do not know the extinction coefficients of the species $M(CN)_{n-1}H_2O^{2-}$ or $M(CN)_{n-1}F^{3-}$ which are presumably formed by reaction 15, the ratio $k_{14}/\ k_{15}$ cannot be evaluated.

In contrast, the observed kinetics of the reaction of SO_4F^- with $Mo(CN)_8^{4-}$ in excess suggests that the rate of the reaction of $Mo(CN)_8^{3-}$ with CN^- (eq 16) and the rates of the reactions of $Mo(CN)_8^{4-}$ with SO_4F^- (eqs 14 and 15) are similar. Hence, a special treatment was required in this case: the time evolution of the optical density at 400 nm was simulated by adjusting k_{14} and k_{15}, taking k_{16} and the extinction coefficients of $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$ as fixed parameters. In addition, it was necessary to take into account the reactions of CN^- with the product Q of the primary reaction (eq 17) and with SO_4F^-:

$$CN^- + Q \rightarrow \text{products } k_{17} \tag{17}$$

and

$$CN^- + SO_4F^- \rightarrow \text{products } k_{18} \tag{18}$$

However, it turned out that the values obtained for $k_{14} + k_{15}$ are rather insensitive even to large variations of the parameters k_{17}, k_{18}, and ϵ_Q, the extinction coefficient of Q. Figure 1 shows the time evolution of the absorbance at 5, 15, and 25 °C, calculated by adjusting k_{14} and k_{15} and taking the values of k_{17}, k_{18}, and ϵ_Q equal to zero.

Table 5 shows values of $k_{14} + k_{15}$ for the reactions of SO_4F^- with $Fe(CN)_6{}^{4-}$, $Os(CN)_6{}^{4-}$, $W(CN)_8{}^{4-}$, $Ru(CN)_6{}^{4-}$, and $Mo(CN)_8{}^{4-}$ in solutions containing 1M Li^+ at 6 °C, 15 °C, and 25 °C, and for the reactions of SO_4F^- with $Fe(CN)_6{}^{4-}$ and $Os(CN)_6{}^{4-}$ in solutions containing 0.5 M Li^+ at 6 °C. The values of $k_{14} + k_{15}$ for the reaction of $Mo(CN)_8{}^{4-}$ were obtained from the simulations shown in Figure 1.

Standard Gibbs Energy, ΔG^o, and Activation Energy, E_a. Table 6 lists the change of standard Gibbs energy, ΔG^o, and the activation energy, E_a, for the reactions of SO_4F^- and $S_2O_8{}^{2-}$ with $M(CN)_n{}^{4-}$ in 1 M Li^+.

The values for ΔG^o were obtained from the standard electrode potentials E^o in 1 M $LiClO_4$, for the half-cell reactions

$$M(CN)_n{}^{3-} + e- = M(CN)_n{}^{4-} \tag{19}$$

and $E^o(SO_4F^-)$ and $E^o(S_2O_8{}^{2-})$ for the half-cell reactions

$$SO_4F^- + e- = SO_4{}^- + F^- \tag{20}$$

and

$$S_2O_8{}^{2-} + e^- = SO_4{}^- + SO_4{}^{2-} \tag{21}$$

The values for $E^o(SO_4F^-)$ and $E^o(S_2O_8{}^{2-})$, 2.17 and 1.45 V, respectively, were obtained from the standard electrode potentials of the half-cell reactions $SO_4F^- + 2e- = SO_4{}^{2-} + F^-$ (2.30 V),[6,7,52] $S_2O_8{}^{2-} + 2e- = 2SO_4{}^{2-}$ (1.94 V),[52] and $SO_4{}^- + e- = SO_4{}^{2-}$ (2.43 V).[53,54]

E^o for the half-cell reactions eq 19 was calculated from electrode potentials measured against a saturated calomel electrode (standard electrode potential 0.2412 V) of solutions containing 1 M $LiClO_4$ and $Me(CN)_n{}^{3-}$ and $Me(CN)_n{}^{4-}$ in equal concentrations prepared by adding 0.5 mL 5 × 10^{-2} M ammonium cerium(IV) nitrate solution to 5 mL 10^{-2} M $M(CN)_n{}^{4-}$.

The Relationship between Rate Constants and ΔG^o. As mentioned above, the cleavage of the O−O bond in $S_2O_8{}^{2-}$ and of the O−F bond in SO_4F^- by reactions with $M(CN)_n{}^{4-}$ both appear to proceed non-adiabatically. Equation 1 is developed for adiabatic processes.[1] However, the presumably non-adiabatic cleavage of O−O bonds may be discussed advantageously in the framework of eq 1. Thus, as mentioned above, the relationship between the rate constant and ΔG^o for breakage of the O−O bond in $S_2O_8{}^{2-}$ by reaction $ML_n{}^{2+}$ may be expressed by an equation that similarly to eq 1 contains the term $\Delta G_o{}^{\ddagger}(1+ \Delta G^{o'}/4\Delta G_o{}^{\ddagger})^2$.[4] Moreover, eq 1 has been used as a starting point in a discussion of the results of a thorough investigation of the reductive cleavage of the O−O bond in dialkyl peroxides.[45] We therefore assume that eq 1 also provides a proper framework for discussing the relationship between rate constant and ΔG^o for catalyzed cleavage of the O−O bond in $S_2O_8{}^{2-}$ and of the O−F bond in SO_4F^- by reaction with $M(CN)_n{}^{4-}$.

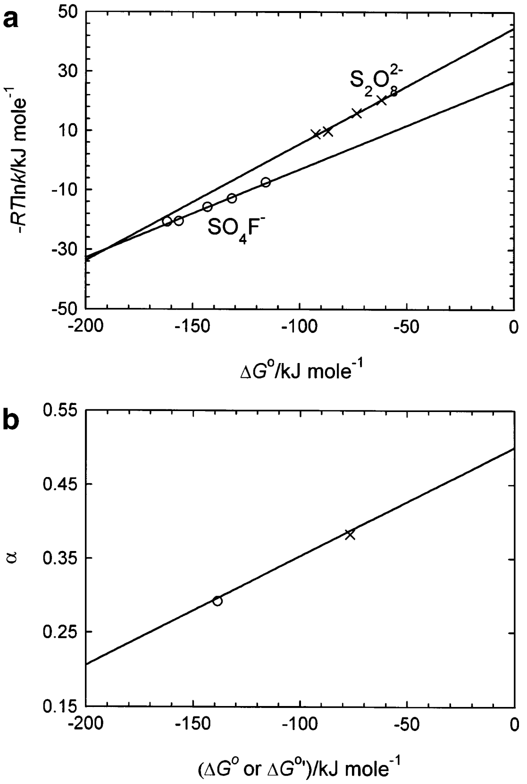

Figure 2. (a) $-RT \ln k$ plotted against ΔG^o : ×, reactions of $S_2O_8{}^{2-}$ with $M(CN)_n{}^{4-}$ in 1 M Li^+ ($k = k_{11}$); ○, reactions of SO_4F^- with $M(CN)_n{}^{4-}$ in 1 M Li^+ ($k = k_{14} + k_{15}$). The straight lines are least-square fits to the points. (b) The slope α of the lines in Figure 2a plotted against the mean of the ΔG^o values for the corresponding sets of reactions. ×, the reactions of $S_2O_8{}^{2-}$ with $M(CN)_n{}^{4-}$; ○, the reactions of SO_4F^- with $M(CN)_n{}^{4-}$. The straight line depicts eq 22 for $\Delta G_o{}^{\ddagger}$ = 85 kJ mol^{-1}.

Figure 2a shows plots of $-RT \ln k$ against ΔG^o at 25°C for reactions in 1 M Li^+ of $S_2O_8{}^{2-}$ with $M(CN)_n{}^{4-}$ ($k = k_{11}$) and of SO_4F^- with $M(CN)_n{}^{4-}$ ($k = k_{14} + k_{15}$). The plots show a linear relationship between ln$k$ and ΔG^o over the relatively small range of ΔG^o values available for the two sets of reactions. The straight lines in Figure 2a are least-squares fits to the points of the two sets. We note that the slope of the line in Figure 2a pertaining to the reactions of $S_2O_8{}^{2-}$ with $M(CN)_n{}^{4-}$ (0.39 ± 0.02) is larger than that of the line for the corresponding reactions of SO_4F^- (0.29 ± 0.02).

Figure 2b shows the slopes, α, for the two sets of reactions plotted against the mean of the values of ΔG^o at which $-RT$ ln$k$ was measured. The straight line in Figure 2b depicts the derivative of eq 1 with respect to $\Delta G^{o'}$:

$$\partial(-RT \ln k)/\partial \Delta G^{o'} = 0.5 + \Delta G^{o'}/8\Delta G_o{}^{\ddagger} \tag{22}$$

in which $\Delta G_o{}^{\ddagger}$ is set equal to 85 kJ mol^{-1}, the value estimated for the uncatalyzed reactions of $S_2O_8{}^{2-}$ with $ML_n{}^{2+}$.[4]

Using a simple "sphere-in-continuum" model,[3] we estimate the difference between $\Delta G^{o'}$ and ΔG^o for the reactions of SO_4F^- and $S_2O_8{}^{2-}$ to be quite small (<3 kJ mol^{-1}). Therefore, the finding that the two points representing α for the set of reactions of $S_2O_8{}^{2-}$ and the set of reactions of SO_4F^- both lie close to the line depicting eq 22 suggests that a relationship similar to eq 22 is valid for the catalyzed reactions of $S_2O_8{}^{2-}$ and SO_4F^- with $M(CN)_n{}^{4-}$ and indicates, moreover, that the values of the parameter $\Delta G_o{}^{\ddagger}$ for these reactions are both close to 85 kJ mol^{-1}.

This is not a mere coincidence occurring in 1 M Li^+. Rather, the fact that the rate constants for the reactions of $M(CN)_n{}^{4-}$

with $S_2O_8^{2-}$ [14−16] and SO_4F^- (Table 5) are proportional to the Li^+ concentration suggests that eq 22 may also be used to express α at other Li^+ concentrations. The observations thus indicate that the intrinsic barriers for the catalyzed and uncatalyzed paths are similar for the reactions of $S_2O_8^{2-}$ and SO_4F^-.

In a previous study of the reactions of $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $W(CN)_8^{4-}$ with $S_2O_8^{2-}$ catalyzed by Li^+, Na^+, K^+, and $(CH_3)_4N^+$, it was found that for any pair of catalytic cations the ratio between the rate constants is similar for all three cyanide complexes.[15] This, combined with the present result, may be taken to suggest that in general the intrinsic barrier $\Delta G_o^\ddagger$ for the breakage of the O−O bond in $S_2O_8^{2-}$ is unaffected by cation catalysis.

Moreover, since the bond dissociation enthalpies ΔH_{diss} of the O−O and O−F bonds are similar,[8−11] and since the parameters λ_i and λ_o (eq 3) cannot vary much for the reactions involved,[1,2] our finding that the intrinsic barriers are similar for the reactions of SO_4F^- and $S_2O_8^{2-}$ with $Me(CN)_n^{4-}$ suggests that the electron transfer and the breakage of the O−F bond in SO_4F^- are also concerted processes.

Conclusion

We conclude that the reductions of $S_2O_8^{2-}$ and SO_4F^- by the cyanide complexes, $M(CN)_n^{4-}$, of Fe(II), Ru(II), Os(II), Mo(IV), and W(IV) both proceed by dissociative one-electron transfer, and that the breakage of the O−O and O−F bonds both have the characteristics of concerted processes with similar intrinsic barriers for the catalyzed and uncatalyzed paths.

The primary reaction of $S_2O_8^{2-}$ consists of a single step yielding $M(CN)_n^{3-}$ and SO_4^-, whereas the primary reaction of SO_4F^- consists of two parallel one-electron steps, one leading to $Me(CN)_n^{3-}$ and SO_4^-, while the other yields $M(CN)_{n-1}^{2-}$, CN^-, and SO_4^-. It is proposed that the electron transfer from $M(CN)_n^{4-}$ to the strongly oxidizing SO_4F^- ion leaves $M(CN)_n^{3-}$ in states that, like excited ligand states of $M(CN)_n^{4-}$, either relax to the ground state or decay by breaking a M−CN bond to form CN^-.

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