catalyzes the oxidation process, and it is notable that under analogous conditions oxidation has not been detected in V(V) systems.

Several metal complexes of nicotinic acid *N*-oxide have been synthesized in aqueous and nonaqueous solvents.[34,49] X-ray structure analysis has been done for some,[49] showing that the ligand can coordinate in a monodentate manner via *N*-oxide oxygen or an oxygen of the carboxylato group. In addition, the ligand can be bidentate through both carboxylato oxygens or by bridging via a carboxylato oxygen and the *N*-oxide oxygen. Only an X-ray structure analysis could reveal the structure of molybdenum complexes **4**–**6**. However, the spectral and chemical data given have provided satisfactory evidence for the composition of the ligand sphere and the most likely mode of ligation to the molybdenum ion.

The ligand spheres containing the combination of coordinated peroxo groups along with nicotinic acid or its *N*-oxide represent interesting example of peroxo–heteroligand V(V) and Mo(VI) complexes, where unusual electron transfers may be facilitated and where three biochemically relevant components are combined in a compound. The structure, spectral properties, and reactivity of this type of compound are of interest and importance for biochemistry, as well as for many catalytical oxidations involving vanadium or molybdenum.

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Kinetics of Electron-Transfer Reactions between Transition-Metal Complexes and the Methyl Viologen Radical Cation

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Kinetic data for the reactions between $MV^{\bullet+}$ and eight transition-metal complexes (of cobalt, ruthenium, chromium, and iron) and the uranyl ion were determined at pH 4 in 0.1 M perchlorate medium by pulse radiolysis. All the oxidants investigated are outer-sphere reagents with known standard reduction potentials and self-exchange rate constants. The measured rate constants are in agreement with those predicted by the Marcus theory after allowances are made for the diffusion control and electrostatics.

Introduction

The reactions of the 1,1′-dimethyl-4,4′-bipyridinium ion (abbreviated methyl viologen cation or MV^{2+}) and of its radical cation, $MV^{\bullet+}$, have been of considerable recent interest. Among other considerations that motivated this study is the widespread use of this couple as an "indicator" pair in chemical and photochemical reactions, since the radical cation is so brightly colored ($\epsilon_{max} \sim 13\,000$ L mol^{-1} cm^{-1} at 600 nm).

This report concerns the kinetics of a series of nine reactions; the analysis of the data also incorporates three additional reactions from the literature. Tsukahara and Wilkins[2] have studied the reactions of several viologens with a range of cobalt(III) complexes. They noted a considerable anion effect on the rates of reaction. In the present study a constant 0.10 M perchlorate medium is used. The methyl viologen radical cation is a good outer-sphere reductant ($E° = -0.45$ V), and the series of oxidants used have known standard reduction potentials and self-exchange rate constants, making it possible to correlate the data in terms of the equations of the Marcus theory. We relied on the self-exchange rate for the $MV^{2+}/MV^{\bullet+}$ couple directly determined by NMR line broadening,[3] although other estimates[4,5] were also considered.

Experimental Section

Reagents. Methyl viologen was obtained from Aldrich and used without further purification. Most of the other chemicals were available from earlier investigations.[6]

Pulse Radiolysis. The principal reducing agent for MV^{2+} was $^{\bullet}C(CH_3)_2OH$, generated by radiolysis of O_2-free, N_2O-saturated water in the presence of 0.10 M 2-propanol.

The important reactions occurring are shown in eq 1–4.

$$H_2O \xrightarrow{e^-} e_{aq}^-, OH^\bullet, H^\bullet, H^+, H_2O_2 \qquad (1)$$

$$N_2O + e_{aq}^- \xrightarrow{H^+} OH^\bullet + N_2 \qquad (2)$$

$$OH^\bullet + (CH_3)_2CHOH \rightarrow (CH_3)_2COH^\bullet + H_2O \qquad (3)$$

$$(CH_3)_2COH^\bullet + MV^{2+} \rightarrow (CH_3)_2CO + H^+ + MV^{\bullet+} \qquad (4)$$

An acidity of 10^{-4} M was used, and an ionic strength of 0.10 M was achieved through the addition of $NaClO_4$. All solutions were prepared with triply distilled water. Pulse radiolysis was carried out with a beam of 15-MeV electrons at a 4-ns pulse length. A 2-cm reaction cell was used, and the decay of $[MV^{\bullet+}]$ was monitored at 600 nm. Pseudo-first-order rate constants were calculated from the absorbance–time data obtained by the use of a nonlinear least-squares fitting program.

Results and Discussion

Kinetic Data. The experiments were conducted so that a given oxidizing agent (an acceptor, A) was present in large stoichiometric excess over the methyl viologen radical cation. In each case the pseudo-first-order rate constant (k_{obsd}) varied linearly with the average concentration of A present in a given experiment. Typical plots are shown in Figure 1.

The slopes of the plots of k_{obsd} vs [A] give the second-order rate constants for the cross-reactions, k_{measd}, to a precision of around 5%, and are given in Table I. They range from $\sim 1 \times 10^6$ for $Co(sep)^{3+}$ to 3×10^9 M^{-1} s^{-1} for $Cr(phen)_3^{3+}$; with the literature values[2,7] for $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ included, the range ex-

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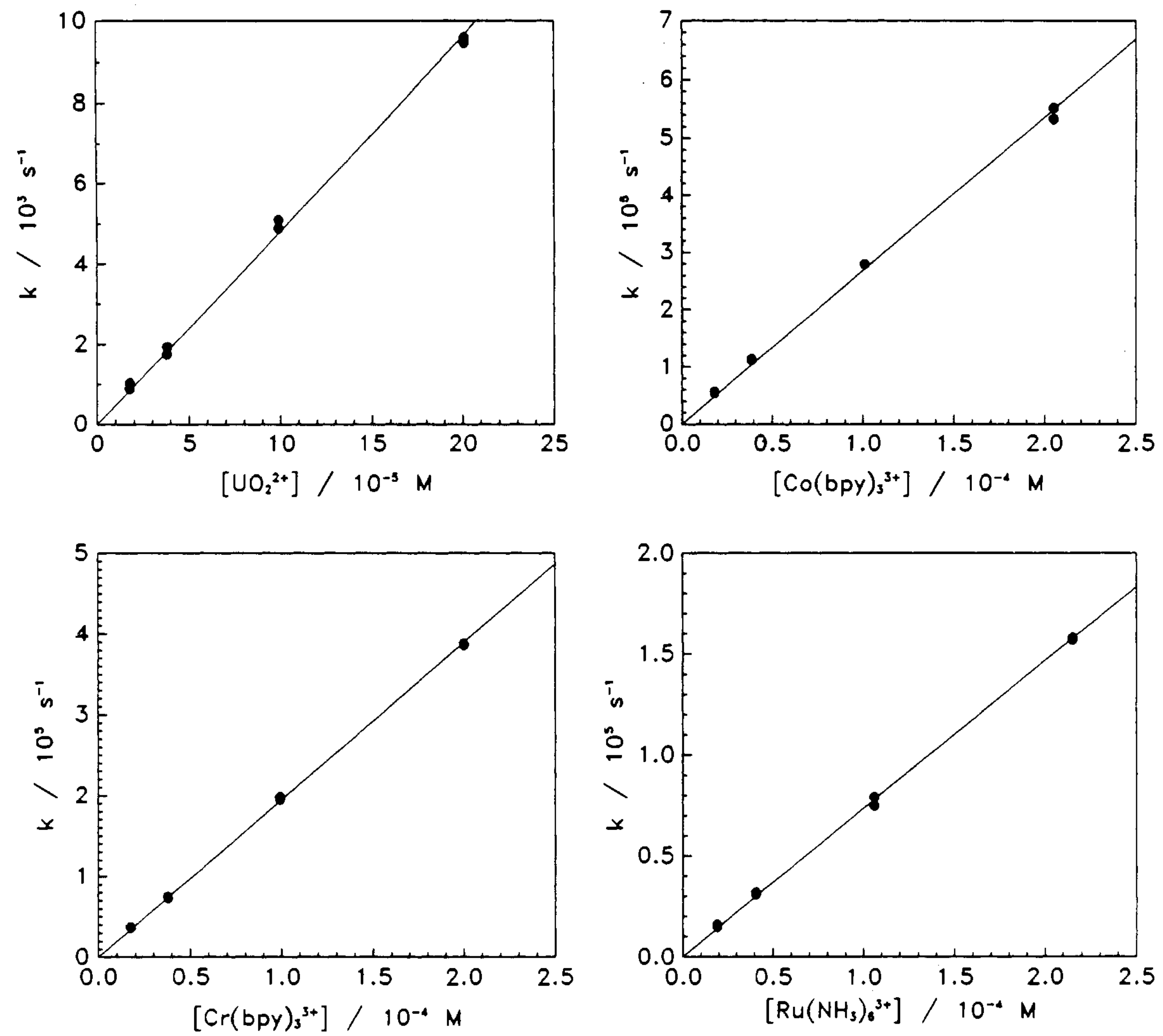

Figure 1. Four typical plots of pseudo-first-order rate constants against oxidant concentrations.

Table I. Summary of the Measured and Calculated Rate Constants for Oxidation of MV^+ by a Series of Transition-Metal Oxidants

oxidant	$\Delta E°$/V	radius^{a}/Å	k_{22}/L mol^{-1} s^{-1}	k_{measd}/L mol^{-1} s^{-1}	$k_{dif}{}^{b}$/L mol^{-1} s^{-1}	$k_{calcd}{}^{c,d}$/L mol^{-1} s^{-1}	$k_{calcd}{}^{c,e}$/L mol^{-1} s^{-1}	$k_{cor}{}^{f}$/L mol^{-1} s^{-1}
$UO_2{}^{2+}$	0.51	3.3	15^{g}	4.81×10^7	2.7×10^9	2.7×10^8	2.9×10^8	2.6×10^8
$Co(sep)^{3+}$	0.19	4.4/4.6	2.0^{h}	9.80×10^5	2.1×10^9	1.1×10^6	1.4×10^6	1.4×10^6
$Ru(NH_3)_6{}^{3+}$	0.55	3.35	820^{i}	7.33×10^8	1.3×10^9	2.7×10^9	2.6×10^9	8.7×10^8
$Cr(bpy)_3{}^{3+}$	0.19	6.8	$2 \times 10^{9\,j}$	1.95×10^9	4.2×10^9	2.0×10^{10}	1.6×10^{10}	3.3×10^9
$Co(bpy)_3{}^{3+}$	0.765	6.7/6.9	17.5^{k}	2.68×10^9	4.1×10^9	5.2×10^9	3.8×10^9	2.0×10^9
$Cr(phen)_3{}^{3+}$	0.17	7.0	$2 \times 10^{9\,j}$	2.95×10^9	4.4×10^9	1.6×10^{10}	1.3×10^{10}	3.3×10^9
$Co(tim)^{3+}$	1.014	4.5	0.05^{l}	7.70×10^8	2.2×10^9	5.9×10^9	3.7×10^9	1.4×10^9
$Fe(cp)_2{}^{+}$	0.96	3.5	$6 \times 10^{6\,m}$	2.48×10^9	5.1×10^9	6.2×10^{10}	5.3×10^{10}	4.7×10^9
$Co(phen)_3{}^{3+}$	0.82	7.0	41.7^{k}	2.28×10^9	4.4×10^9	1.1×10^{10}	7.4×10^9	2.8×10^9
$Co(en)_3{}^{3+}$	0.315	4.2	$8 \times 10^{-5\,n}$	$5.1 \times 10^{4\,p}$		6.0×10^4	6.8×10^4	
$Co(NH_3)_6{}^{3+}$	0.51	3.5/3.7	$3 \times 10^{-7\,o}$	$1.4 \times 10^{5\,q}$		8.9×10^4	1.1×10^5	

[a] Radii of oxidants. Where two numbers are given they refer to the oxidized and reduced forms of the couple. [b] Diffusion-limited rate constant corrected for ionic strength; see text. [c] Using $k_{11} = 5.4 \times 10^8$ L mol^{-1} s^{-1}; ref 3. [d] Simple Marcus theory (eq 5 and 6). [e] Electrostatics-corrected Marcus theory (eq 7–9) using a radius of 5.0 Å for methyl viologen. [f] $k_{cor} = k_{calcd}k_{dif}/(k_{dif} + k_{calcd})$ with use of electrostatics-corrected k_{calcd}. [g] Reference 6. [h] Reference 10. [i] Reference 11. [j] Reference 12. [k] Reference 13. [l] Reference 14. [m] Reference 15. [n] Reference 16. [o] Reference 17. [p] $\mu = 1.0$ M; ref 7. [q] $\mu = 2.0$ M; ref 2.

tends even further, down to 5.1×10^4.

Marcus Theory Correlations. Of the nine rate constants we have evaluated, seven are within a factor of 3 of the diffusion-controlled limit (cf. k_{measd} and k_{dif} in Table I). One might legitimately argue that further correlations involving those seven would be unwarranted, given how close they lie to the diffusion-controlled limit. Here we adopt the opposite point of view, while recognizing the limitations imposed by diffusion control.

Literature values are available for the reduction potentials and self-exchange rate constants of all of the couples whose reactions with $MV^{\bullet+}$ have been studied, as summarized in Table I. The simple Marcus cross relation is given in eq 5 and 6.

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{5}$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \tag{6}$$

As all the reactions involved charged species, it was desirable to use the Marcus theory in a form that corrects for different electrostatic work terms. The calculations were performed by use of eq 7–9.[8]

$$\Delta G^*_{12} = \frac{1}{2}(\Delta G^*_{11} + \Delta G^*_{22} + \Delta G^\circ_{12} - w_{11} - w_{22} + w_{12} + w_{21}) + \frac{(\Delta G^\circ_{12} + w_{21} - w_{12})^2}{8(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22})} \qquad (7)$$

$$w_{ij} = \frac{\alpha Z_i Z_j}{a(1 + \beta a \mu^{1/2})} \qquad (8)$$

$$k = Z \exp(-\Delta G^*/RT) \qquad (9)$$

w_{ij} is a work term, α is equal to 1.75×10^{-6} J mol^{-1} m, β is 3.285×10^9 m^{-1} L$^{1/2}$ mol$^{-1/2}$, Z_i and Z_j are the charges on the ions, and μ is the ionic strength. The distance of closest approach, a, is given by the sum of the appropriate ionic radii. The radius for methyl viologen was taken to be 5.0 Å; this is close to the 6 Å value used by others,[2] and in any event the work term corrections are so small that this causes a negligible difference. Z, the frequency of collision between two molecules within a solvent cage, is taken[10] as 10^{11} L mol^{-1} s^{-1}. Self-exchange rates are those reported in the literature.[10-17]

Since so many of the rate constants are near the diffusion-controlled limit, further adaptations were needed. The diffusion-controlled rate constant (7.4×10^9 L mol^{-1} s^{-1}) was corrected for electrostatics by the Debye equation[18]

$$k_{\mathrm{dif}} = (7.4 \times 10^9)b/(e^b - 1) \qquad (10)$$

where $b = 14Z_1Z_2/a$, a being the distance of closest approach in angstroms. This value corresponds to an ionic strength of zero and was corrected to $\mu = 0.1$ M, by using the Debye–Hückel equation[19]

$$k = 10^c k_0 \qquad (11)$$

where $c = Z_1Z_2\mu^{1/2}/(1 + \mu^{1/2})$ and k_0 is the second-order rate constant at zero ionic strength.

Finally, the correction for diffusion control was done by use of the equation[20]

$$k_{\mathrm{cor}} = k_{\mathrm{calcd}}k_{\mathrm{dif}}/(k_{\mathrm{dif}} + k_{\mathrm{calcd}}) \qquad (12)$$

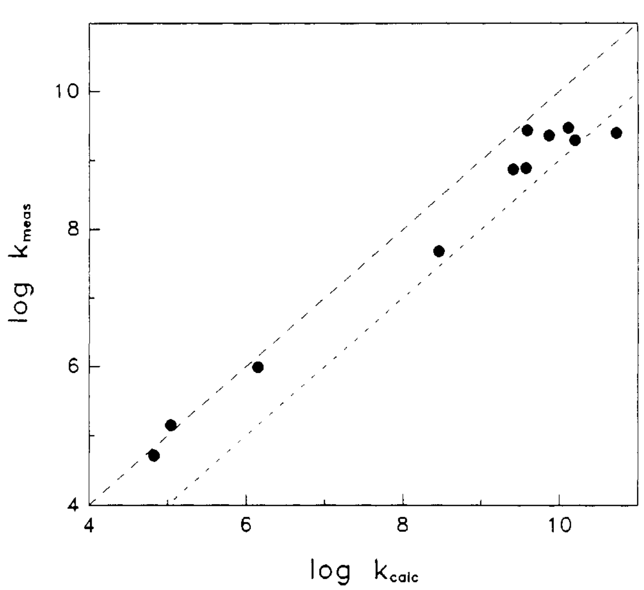

Figure 2. Comparison between the experimental rate constants (k_{measd}) and the calculated values from the Marcus theory. The latter values were corrected for diffusion limit and for electrostatic factors arising from the different charge types of the reactant ions as explained in the text. The upper dashed line has unit slope, where $k_{\mathrm{measd}} = k_{\mathrm{cor}}$. The lower dashed line represents k_{measd} 10-fold lower.

Values of k_{dif} and k_{cor} are given in Table I, which also allows comparisons for the importance of the electrostatic work terms (columns 7 and 8) and for the effect of diffusion control as expressed in eq 12 (columns 8 and 9). The calculated cross-reaction rate constants (k_{cor}) are in good agreement with the measured rate constants (k_{measd}). For assessing the agreement with the Marcus theory, a more appropriate comparison would be between k_{calcd} (electrostatics corrected) and k_{measd}. Such a comparison is illustrated in Figure 2, which shows a log–log plot of k_{measd} versus k_{calcd}. The higher measured rate constants are diffusion-controlled, with only a minor activation-controlled contribution. All the reactions, except the one with $\mathrm{Fe(cp)_2}^{2+}$, give k_{measd} values within a factor of 10 of the Marcus theory k_{calcd} values. It has been shown that the reductions of $\mathrm{Co(bpy)_3}^{3+}$ and $\mathrm{Co(phen)_3}^{3+}$ are often mildly nonadiabatic[21] (an electronic factor κ_{12} of 0.16 was quoted). In the present work, k_{measd} values for $\mathrm{Co(bpy)_3}^{3+}$ and $\mathrm{Co(phen)_3}^{3+}$ are lower than the k_{calcd} values by factors of ~2 and ~3, respectively.

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Registry No. $\mathrm{MV}^{\bullet+}$, 25239-55-8; $\mathrm{UO_2}^{2+}$, 16637-16-4; $\mathrm{Co(sep)}^{3+}$, 72496-77-6; $\mathrm{Ru(NH_3)_6}^{3+}$, 18943-33-4; $\mathrm{Cr(bpy)_3}^{3+}$, 15276-15-0; $\mathrm{Co(bpy)_3}^{3+}$, 19052-39-2; $\mathrm{Cr(phen)_3}^{3+}$, 15276-16-1; $\mathrm{Co(tim)}^{3+}$, 112506-20-4; $\mathrm{Fe(cp)_2}^{+}$, 12125-80-3; $\mathrm{Co(phen)_3}^{3+}$, 18581-79-8; $\mathrm{Co(en)_3}^{3+}$, 14878-41-2; $\mathrm{Co(NH_3)_6}^{3+}$, 14695-95-5.

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