13446-74-7; CsF, 13400-13-0; $(LiF)_2$, 12265-82-6; $(NaF)_2$, 12285-64-2; $(KF)_2$, 12285-62-0; $(RbF)_2$, 37279-33-7; $(CsF)_2$, 12285-54-0.

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Mechanism of the Permanganate Ion Oxidation of Vanadium(IV)

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The reduction of the permanganate ion by oxovanadium(IV) in perchloric acid solutions was determined using stopped-flow spectrophotometric techniques. The rate expression $-d[MnO_4^-]/dt = (k_0 + k_1[H^+])[MnO_4^-][VO^{2+}]$, where $k_0 = 72.9 \pm 1.6\ M^{-1}\ sec^{-1}$ and $k_1' = 28.8 \pm 1.7\ M^{-2}\ sec^{-1}$, was found to represent the reaction at 526 nm at 25.0°, $[H^+] = \mu = 1.00$. The form of the rate expression, the observation of a transient intermediate (λ_{max} ~410 nm), and thermodynamic parameters $\Delta H^\ddagger = 10.8 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -12.9 \pm 1.9$ eu give indication for a mechanism in which there is complex formation.

The reaction between the permanganate ion, MnO_4^-, and the vanadium(IV) ion, VO^{2+}, in acid media was investigated as part of a series of permanganate ion oxidations of inorganic ions in an effort to elucidate the conditions necessary for the occurrence of the two-electron reduction pathway for the MnO_4^- ion.[1] The reaction between the permanganate ion, MnO_4^-, and various metal ions, $Fe(phen)_3^{2+}$,[2] $Fe(CN)_6^{4-}$,[3] and $Mo(CN)_8^{4-}$,[1] have been shown to occur *via* an outer-sphere, one-electron-transfer process. The reactions are classified as outer sphere from their observed rate laws and the reasonable agreement with rate constants obtained from the Marcus theory.[4] The reaction between VO^{2+} and MnO_4^- is also of interest in that protons are produced in the overall reaction

$$MnO_4^- + 5VO^{2+} + H_2O \rightarrow Mn(II) + 5VO_2^+ + 2H^+$$

whereas in the majority of reactions involving the reduction of the permanganate ion, protons are consumed. It has been observed that when the oxidation half-cell reaction of the reductant is less than +0.56 V, the value for the MnO_4^-–MnO_4^{2-} couple, the reaction proceeds without the aid of a proton. However, when the oxidation half-cell reaction is more negative than −0.56 V, the reaction proceeds with a direct proton dependence.[5]

A two-electron-transfer step accompanied by the formation of a transient intermediate has been observed for several MnO_4^-–organic systems[6–8] with the reduced manganese species characterized as Mn(V). This pathway was shown to be operative in the reaction of the bromide ion, Br^-, with MnO_4^-.

Kriss and Yatsimirskii reported experiments performed in sulfuric acid involving the VO^{2+}–MnO_4^- reaction in which they observed an induction period in the disappearance of the permanganate ion and postulated the presence of Mn(III) as a stable reaction product.[9] Rosseinsky and Nicol also reported a study of this reaction performed in $HClO_4$ in which they found the stoichiometry to vary from 2.5 to 4.7 depending upon the reaction conditions.[10] We report herein experiments which provide a somewhat different interpretation.

Experimental Section

A stock solution of potassium permanganate was prepared by dissolving Baker Analyzed reagent grade $KMnO_4$ in distilled water, boiling the solution, and standardizing against As_2O_3 after a fine glass frit filtration to remove MnO_2. The solution was stored in a dark bottle away from light and restandardized periodically. Perchloric acid solutions were prepared by dilution of concentrated $HClO_4$ with permanganate-distilled, ion-exchanged water and were standardized against NaOH solutions. Stock solutions of $NaClO_4$ were prepared by the addition of recrystallized reagent grade Na_2CO_3 to $HClO_4$ solutions of known concentration. The remaining hydrogen ion concentration was determined by titration against NaOH. Vanadium(IV) perchlorate stock solutions were prepared by two methods: (1) by the addition of a stoichiometric amount of $Ba(ClO_4)_2$ to a solution of $VOSO_4$ dissolved in 0.1 *M* $HClO_4$; $BaSO_4$ was removed by centrifugation; (2) by the electrolytic reduction of a slurry of V_2O_5 at platinum electrodes in 0.1 *M* $HClO_4$. Both solutions gave similar kinetic results. Total vanadium content was determined spectrophotometrically as the V^V–H_2O_2 complex[11] and [V(IV)] was determined spectrophotometrically at its maximum absorbance (λ_{max} 760 nm, ϵ 17.1 M^{-1} cm^{-1}).[12]

Kinetic Studies. The kinetics of the reaction were determined using an Aminco-Morrow stopped-flow apparatus attached to a Beckman DU monochromator. The progress of the reaction was observed at 526 nm, where MnO_4^- is the only absorbing species, and at 410 nm. The output from the photomultiplier was monitored by a Tektronic Model 564 storage-type oscilloscope and the stored trace recorded with a Polaroid camera. Apparent pseudo-first-order ($[VO^{2+}]_0 \gtrsim 25[MnO_4^-]_0$) and second-order rate constants were calculated from absorbance–time data using both a linear least-squares program and graphical techniques.

Ionic strength was maintained at 1.00 *M* in most experiments by

Table I. Stoichiometry of the MnO_4^--VO^{2+} Reaction ($[H^+] = 1.00\ M$, $\mu = 1.00$)

$10^3[MnO_4^-]_0$, M	$10^3[VO^{2+}]_0$, M	$[VO^{2+}]_{consumed}/[MnO_4^-]_0$
2.95	96.2	5.00
4.12	96.2	5.03
5.30	48.1	5.00
7.67	48.1	5.03
1.77	10.18	5.00
1.33	11.45	5.15
		Av 5.04 ± 0.05

the addition of $NaClO_4$ when needed and the reaction cell was attached to a thermostated stage for accurate temperature control (±0.05°).

Results

Stoichiometry. The stoichiometry of the overall reaction of MnO_4^- with excess VO^{2+} in 1.00 *M* $HClO_4$ was determined by the use of batch-mixing experiments and data from spectro–titrimetric plots of the absorbance due to VO^{2+} at 760 nm *vs.* $[MnO_4]$, Table I. A stoichiometric ratio of 5.04 ± 0.05 ($[VO^{2+}]_{consumed}/[MnO_4^-]_0$) was obtained for several different initial concentrations of VO^{2+}. Similar values for the stoichiometry were also obtained from experiments at 0.1 and 0.5 *M* $HClO_4$. The decrease in absorbance at 760 nm was accompanied by the corresponding stoichiometric increase in absorbance at 350 nm due to the formation of V(V) and the overall reaction can be represented by the equation

$$MnO_4^- + 5VO^{2+} + H_2O \rightarrow Mn(II) + 5VO_2^+ + 2H^+$$

Repetitive scans of the 400–500-nm spectral region were taken with a Beckman DK-2A spectrophotometer to detect the presence of Mn(III) as a reaction product. There was no indication from the shape of the spectral envelope that Mn(III) (λ_{max} 470 nm, $\epsilon \simeq 220\ M^{-1}\ cm^{-1}$)[13] was present as a long-time product.

Kinetics. The disappearance of MnO_4^- was monitored at 526 nm. All of the kinetic data were obtained using excess VO^{2+} to minimize possible further reaction of the Mn(II) produced with the excess MnO_4^-. Plots of ln ($A_t - A_\infty$) where A_t and A_∞ represent the absorbance at time *t* and infinite time, respectively, were linear for over 4 half-lives for reactions at $[H^+] = 1.00\ M$. The values of the pseudo-first-order rate constant, k_{obsd}, and the second-order ($k_1 = k_{obsd}/[VO^{2+}]_0$) rate constant, where $-d[MnO_4^-]/dt = k_{obsd}[MnO_4^-]$, are presented in Table II. The presence of VO_2^+ and Mn(II) initially in the reaction mixtures appeared to have no effect on k_1 and all of the experimental data could be represented by the expression $-d[MnO_4^-]/dt = k_1[VO^{2+}][MnO_4^-]$. Support for this rate expression is drawn from kinetic experiments in which the stoichiometric ratio $[VO^{2+}]_0/5[MnO_4^-]_0$ was ~2. These reaction plots showed second-order behavior for >3 half-lives and gave comparable values of k_1.

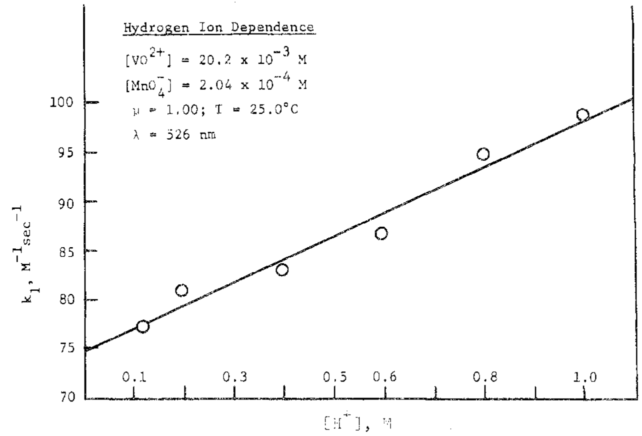

Figure 1. Dependence of k_1 on the hydrogen ion concentration.

Pseudo-first-order plots from experiments in which the hydrogen ion concentration was varied from 1.00 to 0.12 *M* at constant concentrations of permanganate and vanadyl ion showed significant deviation from linearity at long time for $[H^+] < 0.5\ M$. Using values for k_1 (Table III) taken from the initial linear portion of the reaction plot (~2 half-lives), plots of k_1 *vs.* $[H^+]$ (Figure 1) for several MnO_4^- and VO^{2+} concentrations show a linear dependence of k_1 on $[H^+]$ with a nonzero intercept. The behavior is described by the equation $k_1 = k_0 + k_1'[H^+]$, where $k_0 = 72.9 \pm 1.6\ M^{-1}\ sec^{-1}$ and $k_1' = 28.8 \pm 1.7\ M^{-2}\ sec^{-1}$. A variation in the ionic strength ($[H^+] = 0.50\ M$, $\mu = 0.50$–1.50) was found to have no effect on k_1.

The activation parameters $\Delta H^\ddagger = 10.8 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -12.9 \pm 1.9$ eu were obtained from values of $k_1 \times 10^{-2}\ M^{-1}\ sec^{-1}$ (0.80 ± 0.04, 1.05 ± 0.06, 1.60 ± .07, 2.04 ± 0.09, 2.75 ± 0.14) at 20.5, 25.0, 30.0, 35.0 and 40.1°, respectively, using a least-squares fit of ln (k_1/T) *vs.* $1/T$.

Intermediate Formation. Stopped-flow kinetic traces obtained in the wavelength region 390–450 nm showed a rapid absorbance increase followed by a slow decay to an absorbance value characteristic of only products. The molar absorption coefficients of both reactants and products are small in this spectral region and the initial and final absorbance due to reactants and products is negligible at the concentrations being used.

A comparison of data taken at 526 and 410 nm ($[MnO_4^-]_0 = 3.06 \times 10^{-4}\ M$, $[VO^{2+}]_0 = 40.3 \times 10^{-3}\ M$) indicated that greater than 85% of the $[MnO_4^-]_0$ has been consumed when the absorbance maximum seen at 410 nm was obtained ($\tau_{max} \simeq 0.45$ sec) and that the kinetic process observable at 526 nm was completed while the process observable at 410 nm was still in progress. A stopped-flow spectrophotometric scan between 370 and 470 nm showed an absorbance maximum for the intermediate at λ 410 nm (Figure 2), and an "effective" absorption coefficient ($\epsilon \simeq 160 \pm 20\ M^{-1}\ cm^{-1}$) of the in-

Table II. Rate Constants for the MnO_4^--VO^{2+} Reaction (25.0°, $[H^+] = 1.00\ M$, $\mu = 1.00$, λ 526 nm)

$10^3[VO^{2+}]_0$, M	$10^4[MnO_4^-]_0$, M	k_{obsd}, sec^{-1}	k_1, $M^{-1}\ sec^{-1}$
43.2	1.16	4.87	112
40.3	1.02	4.07	101
	2.04	4.15	103
	3.06	4.63	115
	4.08	4.43	110
20.7	0.56	2.23	108
20.2	1.02	2.14	105
	2.04	2.00	99.0
	2.04	2.20	109 ± 1[a]
	2.04	2.08	103 ± 4[b]
	3.06	1.86	99.0
	4.08	1.99	98.7
17.3	0.56	1.73	100 ± 5
13.8	0.56	1.37	100
10.8	0.56	1.13	104
10.1	0.51	1.21	112
	1.02	1.04	103
	2.04	1.05	104
6.05	0.51	0.689	114
	1.02	0.646	107
	2.04	0.657	108
		Av	105 ± 6

[a] $[Mn(II)]_0 = (0–18.6) \times 10^{-5}\ M$. [b] $[VO_2^+]_0 = (0–10.0) \times 10^{-4}\ M$.

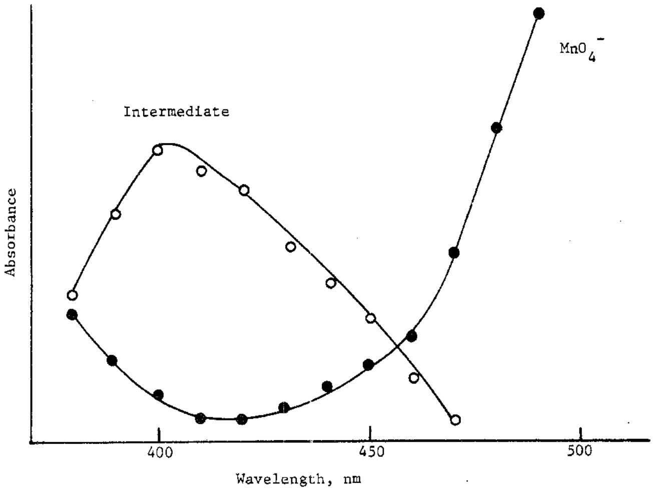

Figure 2. Absorption spectra of permanganate and of the intermediate as obtained at the time of maximum absorbance ($\tau_{max} = 0.45$ sec). The absorbance values for the intermediate have been corrected for the contribution due to products and reactants at that time.

Table III. Hydrogen Ion Dependence at λ 526 nm, $\mu = 1.00$, and 25.0° [a]

	$10^3[VO^{2+}]$, *M*		
	40.3	40.3	20.2
		$10^4[MnO_4^-]$, *M*	
	1.02	4.08	2.04
$[H^+]$, *M*	k_1, M^{-1} sec^{-1}	k_1, M^{-1} sec^{-1}	k_1, M^{-1} sec^{-1}
0.12	75.0		77.4
0.20			80.9
0.40	82.4		84.0
0.50	85.3	86.7	81.3
0.60	89.3	91.8	86.8
0.80	96.2	100	94.7
1.00	101	103	98.9

[a] $k_1 = 72.9 \pm 1.6\ M^{-1}\ \text{sec}^{-1} + (28.8 \pm 1.7\ M^{-2}\ \text{sec}^{-1})[H^+]$.

termediate at λ 410 nm was obtained from plots of A_{max} *vs.* $[MnO_4^-]_0$ at several initial V(IV) concentrations. Beer's law was observed and the absorbance values at $[MnO_4^-]_0 = 0$ corresponded to the $[VO^{2+}]_0$ being used. A value of 92 M^{-1} sec^{-1} ($[H^+] = 1.0\ M$) was calculated using initial rates for the formation of the intermediate.

Several reaction mixtures of MnO_4^- and VO^{2+}, at both high and low hydrogen ion concentrations, were mixed with acrylonitrile. There was no indication of polymerization due to the possible presence of free radicals.

Discussion

The observed reduction of the permanganate ion by the vanadyl ion in 1.0 *M* $HClO_4$ at λ 526 nm appears to be a process that is first order in both VO^{2+} and MnO_4^- when VO^{2+} is in excess. Experiments at λ 526 nm, in which the hydrogen ion concentration was varied at constant $[VO^{2+}]_0$ and $[MnO_4^-]_0$, indicate that the disappearance of MnO_4^- occurs *via* two pathways, where $k_1 = k_0 + k_HK[H^+]$ and $k_H = 9.63 \times 10^3\ M^{-1}$ sec^{-1}. The observed proton-assisted pathway is in keeping with reactions in which the oxidation potential for the reductant is more negative than that of the MnO_4^-–MnO_4^{2-} couple.[5] The protonation of MnO_4^- ($H^+ + MnO_4^- \rightleftharpoons HMnO_4$, $K = 2.99 \times 10^{-3}$)[14] changes the Mn(VII)–Mn(VI) couple to a much more positive value ($E° \approx 1.3$ V) and the Mn(VII) species becomes a stronger oxidizing agent than V(V).

The MnO_4^-–VO^{2+} reaction has previously been examined by Kriss and Yatsimirski and later by Rosseinsky and Nicol with different mechanistic interpretations being presented by the authors. The latter authors characterized the reaction as being one of variable stoichiometry depending upon the reaction conditions but did conclude that the reaction was most probably simple second order with a nearly first-order dependence upon $[H^+]$. Mn(III) was reported to be a reaction product and the rate constants vary significantly from those of this study. The study by Kriss and Yatsimirski (excess VO^{2+}, low $[H^+]$, sulfate media) is characterized by (1) an induction period, (2) the lack of $[H^+]$ effect on the postinduction process, and (3) a rate constant, $1 \times 10^2\ M^{-1}$ sec^{-1} ($[H_2SO_4] = 0.021\ M$, $\mu \approx 0.062$, $T = 25°$), that is more in agreement with values extrapolated from data of the Mn^{III}–VO^{2+} reaction[15] ($k \approx 92\ M^{-1}$ sec^{-1}) than the reactants of interest. The low $[H^+]$ and the presence of sulfate ions, which can help to stabilize the presence of Mn(III), may provide somewhat different kinetic results than a reaction studied in noncomplexing perchlorate media.

Support for the idea that the absorbing species observed in this study is not Mn(III) under the conditions of excess VO^{2+} comes from batch-mixing experiments in which the stoichiometric ratio $[VO^{2+}]_0/5[MnO_4^-]_0$ was 1.2 and 0.83. Only those spectrophotometric scans of reaction solutions in which the ratio was 0.83 or less, indicating excess MnO_4^-, showed excess absorbance in the 450–480-nm region. Despite the fact that reproducible spectral scans were difficult to obtain due to the deposition of MnO_2 over a period of time, the presence of Mn(III) was evident. The ratio of 0.83 or less represents the conditions under which Rosseinsky and Nicol[9] observed a changing stoichiometry in their study of the MnO_4^-–VO^{2+} reaction and the presence of some residual absorbance after several minutes of reaction. This absorbance was ascribed to Mn(III). Under these conditions of excess MnO_4^-, the reaction stoichiometry may well be changing due to the possible reaction of Mn(IV) and/or Mn(III) with either of the initial reactants.

Although the occurrence of the absorbance maximum of the intermediate of the MnO_4^-–VO^{2+} reaction in the 400-nm spectral region might tend to indicate the presence of Mn(III), as a kinetic intermediate, the position of λ_{max} ~410 nm, the "effective" molar absorption coefficient of the intermediate, the rate of disappearance of the intermediate, and the batch-mixing experiments rule against the presence of Mn(III). Under the reaction conditions of this study, a reaction between VO^{2+} and Mn(III) would have a half-life of approximately 0.07–0.12 sec.[15] Lee and Brownridge[6] and Wiberg and Deutsch[7] have observed the presence of an absorbing intermediate in the 400-nm region in reaction of MnO_4^- with cinnamic acid (λ ≃415 nm) and crotonic acid (λ ≃420 nm), respectively. The intermediate is described by both investigators in terms of a manganese(V) species.

The observed rate expression for the reduction of the permanganate ion by vanadyl ion in 1.0 *M* $HClO_4$ and the characterization of the observed intermediate as a manganese(V) species suggests that the reaction sequence can be described as a series of consecutive pseudo-first-order reactions

$$\text{Mn(VII)} \xrightarrow{1} \text{Mn(VI)} \xrightarrow{2} \text{Mn(V)} \xrightarrow{3} \text{products}$$

in which the disappearance of the permanganate ion (1) is sufficiently more rapid than the reaction between Mn(VI) and VO^{2+} that it can be studied independently, with process 2 giving rise to the Mn(V) species detected. One possible, but by no means unique, mechanism can be represented by the equations

$$\text{Mn(VII)} + VO^{2+} \rightarrow [\text{Mn}^{VII}\text{–}VO^{2+}] \quad k_1, \text{rate determining}$$

$$[\text{Mn}^{VII}\text{–}VO^{2+}] \rightarrow \text{Mn(VI)} + VO_2^+ \quad \text{rapid}$$

$$\text{Mn(VI)} + VO^{2+} \rightarrow \text{Mn(V)} + VO_2^+ \quad \text{rapid}$$

$$\text{Mn(V)} + 3VO^{2+} \rightarrow \text{products}$$

The characterization of the interaction between the MnO_4^- and VO^{2+} ions in terms of a complex ion is in keeping with arguments advanced by Carrington and Symons and Stewart and van der Linden in the MnO_4^-–CN^- reaction.[8] The

Table IV. Thermodynamic Values for Some Permanganate Reactions

Reagent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Remarks[a]
HCO_2H	16.4	−19	Complex formation[8]
CO	13	−17	Complex formation[8]
CN^-	8.7	−27	Complex formation[8]
H_2	14.7	−13	Two-electron process[8]
Br^-	6.2	−29.7	Complex formation[5]
VO^{2+}	10.8	−12.9	This work
VO^{2+}	7.1	−25.6	Complex formation[9]
$W(CN)_8{}^{4-}$	13.1	+6.2	Outer-sphere[b]
$Mo(CN)_8{}^{4-}$	10.8	−5.6	Outer-sphere[1]
$Fe(phen)_3{}^{2+}$	15.5	+16.3	Outer-sphere[2]
$KFe(CN)_6{}^{3-}$	21.5	+36.5	Outer-sphere[3]

[a] Complex formation was observed or postulated by the authors.
[b] K. W. Hicks, manuscript in preparation.

$[Mn^{VII}–VO^{2+}]$ complex can be considered a precursor to the Mn(VI) and $VO_2{}^+$ ions. This idea also finds support from consideration of the activation parameters discussed below.

It is often possible to discuss electron-transfer reactions in terms of either an outer-sphere or an inner-sphere type mechanism on the basis of thermodynamic values observed for a series of common reactions.[16,17] In Table IV are listed the thermodynamic parameters observed for some permanganate ion reactions with both organic and inorganic substrata and the characterization of the reaction by the authors. The activation parameters calculated from the data presented by Kriss and Yatsimirskii are also presented.

It is of interest to note that the entropy of activation, $\Delta S^{\ddagger}$, is rather negative, for the group of $MnO_4{}^-$ reactions for which the investigators either present direct evidence or describe in their mechanism a complex composed of Mn(VII) and the reductant species, while the values of $\Delta S^{\ddagger}$ for the reactions of $MnO_4{}^-$ with a few outer-sphere compounds that have been studied tend to be more positive. Arguments have also been presented in several cases of the inner-sphere type reaction for a two-electron process. Although VO^{2+} is a d^1 system and is not thought to undergo a two-electron transfer with $MnO_4{}^-$, its mode of reaction may well resemble those compounds for which complex formation is the suggested pathway on the basis of the similarity of the $\Delta S^{\ddagger}$ values. The lability of the equatorial water molecules on VO^{2+} and the ability of VO^{2+} to associate with a variety of ions are seen as indications of conditions that render it suitable for an inner-sphere reaction with $MnO_4{}^-$.[18] While the reaction could still be inner-sphere without the postulation of the $[Mn^{VII}–VO^{2+}]$ species and an alternative rate-determining step written $Mn(VII) + VO^{2+} \rightarrow Mn(VI) + VO_2{}^+$ (k_1), the description of the reaction of VO^{2+} with $HCrO_4{}^-$, another multiequivalent oxidant, in terms of an inner-sphere reaction[19] and the formation of a binuclear complex in the $MnO_4{}^-$–Ti(III) reaction[20] is seen as further indication of an inner-sphere reaction process involving $MnO_4{}^-$ and VO^{2+} giving rise to the $[Mn^{VII}–VO^{2+}]$ complex.

No evidence for a two-electron process was observed in this study. Despite the fact that this pathway for the reduction of the permanganate ion is favored thermodynamically, the pathway is not a prominent one kinetically. It appears, however, that the reduction of the permanganate ion can occur *via* complex formation, an inner-sphere type pathway. This inner-sphere process may be characterized by a negative $\Delta S^{\ddagger}$ value, whereas outer-sphere processes involving $MnO_4{}^-$ show more positive values of $\Delta S^{\ddagger}$. The reduction of $MnO_4{}^-$ can occur *via* an inner-sphere process when the reductant is substitution labile or when ligand transfer is to occur whereas the oxidation of substitution-inert complexes by $MnO_4{}^-$ appears to be an outer-sphere process and to occur *via* the transfer of a single electron. The difference in $\Delta S^{\ddagger}$ for the $MnO_4{}^-$–VO^{2+} and $MnO_4{}^-$–CO reactions, both of whose oxidized products gain an oxygen, may reflect a different number of water molecules being involved in the activated complex due to the differences in the net charge of the activated complex. A comment is also in order with regard to the sign of the entropy of activation for the $MnO_4{}^-$–$Mo(CN)_8{}^{4-}$ reaction. Although $\Delta S^{\ddagger}$ is negative, −5.6 eu, its mode of reaction is felt to approximate more closely that of an outer-sphere process on the basis of (1) the agreement of the experimental and calculated rate constants, (2) the fact that the one-electron reduction of the permanganate ion by the outer-sphere complexes in Table IV follows a linear free energy relationship and (3) the fact that most inner-sphere reactions of $MnO_4{}^-$ are slow [k_1, M^{-1} sec^{-1}: $Mo(CN)_8{}^{4-}$, 6.18×10^3; VO^{2+}, 75.0 ($[H^+] = 0.12\ M$)].

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Registry No. $MnO_4{}^-$, 14333-13-2; VO^{2+}, 20644-97-7.

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