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Properties of the Reaction Intermediate Formed during Oxidation of Vanadium(IV) by Permanganate Ion

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While studying the kinetics of the oxidation of the vanadium(IV) ion, VO^{2+}, by the permanganate ion, MnO_4^-, in perchlorate media by spectrophotometric stopped-flow techniques, the formation of a reaction intermediate absorbing near 410 nm with an absorption coefficient of about 160 M^{-1} cm^{-1} was observed.[1] In an attempt to learn more about this intermediate, the kinetics of its reaction with VO^{2+} were studied in detail.

Experimental Section

The preparation of the reactants and experimental methods of determining the kinetics have been previously described.[1] The kinetics were studied at 410 nm, the absorption maximum of the intermediate. The pseudo-first-order rate constants were determined graphically from plots of log (absorbance) vs. time.

Results and Discussion

The stopped-flow traces obtained at 410 nm show a rapid increase in absorbance followed by a slow decay to an absorbance characteristic of products (Figure 1). The absorbance reaches a maximum value at a reaction time labeled t_{max}. Using initial rate data from λ 410 nm, it was shown that the rate of formation of the intermediate (reaction I, Figure 2) is about equal to the rate of disappearance of MnO_4^- obtained at 526 nm ($k_1 = 105$ M^{-1} s^{-1}, $[H^+] = \mu = 1.00$ M, $T = 25.0$ °C). No attempt was made to study the formation reaction in detail at 410 nm because of the low quality of the traces at the beginning of the reaction. Under pseudo-first-order reaction conditions, plots of log $(A_t - A_\infty)$ vs. time indicated that the decay of the intermediate consisted of two simultaneous reactions; a faster reaction, reaction II, and a slower process, reaction III, Figure 2. The kinetics of reaction II were determined from log (absorbance $(A_t - A_\infty)$) values vs. time plots by extrapolating the straight-line portion of reaction III back to t_{max} and subtracting the absorbance value from the experimental $(A_t - A_\infty)$ absorbance values at each time interval. The rate constants obtained for reactions II and III are shown in Table I.

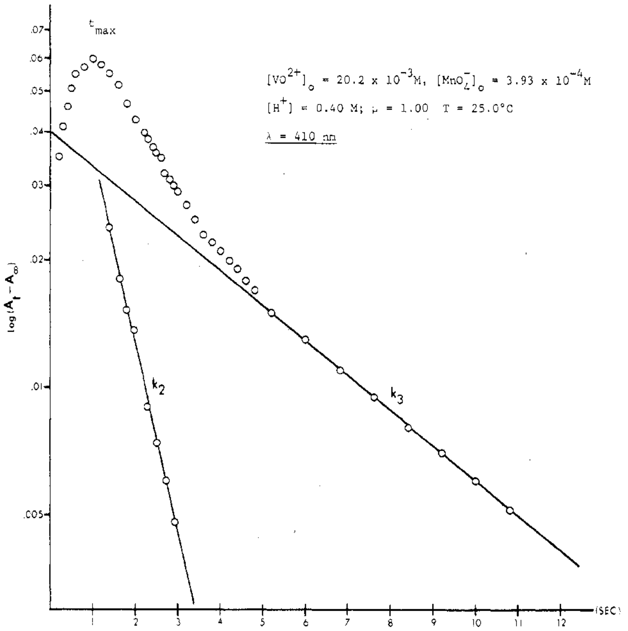

Figure 1. Plot of log $(A_t - A_\infty)$ vs. time at λ 410 nm.

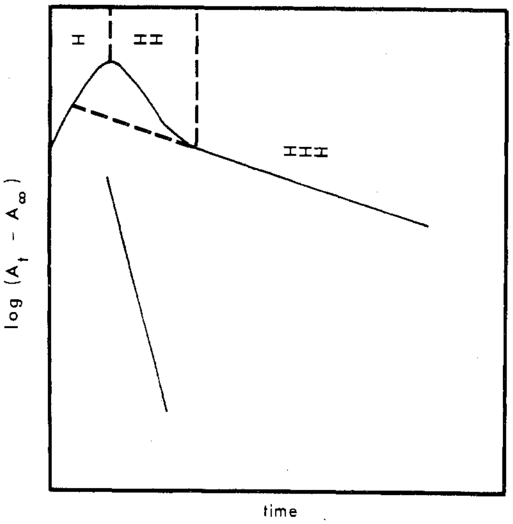

Figure 2. Representative diagrams of kinetic processes at 410 nm.

The near constancy of the second-order rate constant for the more rapid process indicates that this reaction is first order in each reactant. The second-order rate constants for reaction II were found to be independent of H^+ concentration (Table II) and were unaffected by addition of vanadium(V), VO_2^+.

The rate constant of reaction III was determined from the straight-line portion of a log (absorbance) vs. time plot at long reaction times and the data obtained are summarized in Table I. This process was found to be a third-order reaction with a second-order dependence on VO^{2+} and the rate was independent of added VO_2^+. Over a hydrogen ion concentration range of 0.10–1.00 M, the reaction was found to be inversely dependent on the H^+ concentration (Table II). This relationship is of the form $k_3 = k_{30} + k_{3H}(1/[H^+])$ and a least-squares treatment of these data yields a value of 223 M^{-2} s^{-1} for k_{30} and 150 M^{-1} s^{-1} for k_{3H}.

Although previous studies of the oxidation of VO^{2+} by MnO_4^- in $HClO_4$ with excess MnO_4^{2-} or in H_2SO_4[3] were

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Table I. Rate Constants for Reactions of Intermediate with VO^{2+} ($[H^+] = 1.00$ M, $\mu = 1.00$ M, $T = 23.5$ °C)

		Reaction II		Reaction II	
10^3-$[VO^{2+}]_0$, M	10^4-$[MnO_4^-]_0$, M	k^2_{obsd}, s^{-1}	k_2, $M^{-1}\,s^{-1}$	k^3_{obsd}, s^{-1}	k_3, $M^{-2}\,s^{-1}$
20.2	1.48	0.66	32.4	0.180	441
	1.97	0.74	36.7	0.164	402
	1.97[a]	0.70	34.6	0.171	419
	1.97[b]	0.68	33.7	0.156	382
	2.95	0.60	29.5	0.146	359
	3.93	0.73	36.0	0.156	382
40.3	1.48	1.41	35.2	0.587	361
	1.97	1.22	30.2	0.524	323
	2.95	1.39	34.4	0.627	386
	3.93	1.27	31.2	0.559	344
			Av 33.4 ± 2.3		Av 380 ± 33

[a] $[VO_2^+]_0 = 0.20 \times 10^{-3}$ M. [b] $[VO_2^+]_0 = 1.00 \times 10^{-3}$ M.

postulated to proceed by means of an intermediate containing Mn(III), it is believed that the intermediate observed in the present study contains Mn(V). Under the reaction conditions of this study, the reaction of VO^{2+} with Mn(III) would take place much more rapidly with a complex H^+ dependency[4] and Mn(III) has an absorption maximum at 460 nm, with an extinction coefficient of 187 $M^{-1}\,cm^{-1}$.[5] Intermediates believed to contain Mn(V) were observed in the MnO_4^- oxidations of cinnamic acid[6] and crotonic acid[7] and these species absorbed at 410–415 nm. Thus, it appears that the Mn(VI) product formed by the initial reduction of MnO_4^- by VO^{2+} must react rapidly with additional VO^{2+} to yield the Mn(V)-containing intermediate. (ESR experiments might be helpful in indicating the presence of Mn(V)). It was proposed by Sutter et al., in the study of the $HClO_4$ decomposition of MnO_4^{2-}, that $H_2MnO_4^-$ may be formed.[8] It is possible that a rapid reaction of the type $HMnO_4^- + VO^{2+} + H_2O \rightarrow H_3MnO_4 + VO_2^+$ may occur; this process is similar to the reaction believed to occur in the oxidation of VO^{2+} by $HCrO_4^-$.[9]

The disappearance of the intermediate occurs by two distinct processes. The faster process (reaction II) is first order in $[VO^{2+}]$ and is independent of $[H^+]$. If the intermediate is written as Mn(V), this reaction sequence appears to be

$$\mathrm{Mn(V)} + VO^{2+} \xrightarrow{k_2} \mathrm{Mn(IV)} \xrightarrow{2VO^{2+}} \text{products}$$

Although, it is difficult to speculate on the types of Mn(IV) and Mn(V) species present since so little is known about them in acidic solutions,[10] the Mn(V) species in reaction II is most likely $H_2MnO_4^-$ and the Mn(IV) is probably $H_2MnO_4^{2-}$. This latter species has been postulated as being present in acidic Mn(IV) solutions.[11] The reduction of $H_2MnO_4^-$ to $H_2MnO_4^{2-}$ would require no change in coordination number and would be independent of H^+ concentration.

The slower reaction of the Mn(V) intermediate with VO^{2+} (reaction III) is more complex with a second-order dependence on VO^{2+} and takes place by both a hydrogen ion independent and an inverse H^+ dependent pathway. A mechanism for reaction III can be written as

$$\begin{array}{ll}
\mathrm{HMn^{V}} + 2VO^{2+} \rightarrow \mathrm{HMn^{III}} + 2VO_2^+ & k_{30} \\
\mathrm{HMn^{V}} \leftrightharpoons H^+ + \mathrm{Mn^{V}} & K_{3H} \\
\mathrm{Mn^{V}} + 2VO^{2+} \rightarrow \mathrm{Mn^{III}} + 2VO_2^+ & k'_{3H} \\
\mathrm{Mn^{III}} + VO^{2+} \rightarrow \mathrm{Mn^{II}} + VO_2^+ & \text{fast}
\end{array}$$

The inverse hydrogen ion dependence appears to implicate $H_2MnO_4^-$ as the Mn(V) species in this step. The value of $K_a(OMn(OH)_3)$ can be approximated as 10^{-2} M in keeping with the rule of Pauling[15] and k'_{3H} would be 1.5×10^4 $M^{-2}\,s^{-1}$.

Table II. Hydrogen Ion Dependency of the Rates of Reactions II and III (λ 410 nm, $[VO^{2+}]_0 = 20.2 \times 10^{-3}$ M, $[MnO_4^-]_0 = 3.93 \times 10^{-4}$ M, $\mu = 1.00$ M, $T = 23.5$ °C)

$[H^+]$, M	k^2_{obsd}, s^{-1}	k_2, $M^{-1}\,s^{-1}$	k^3_{obsd}, s^{-1}	k_3, $M^{-1}\,s^{-1}$
0.10	0.66	32.5	0.693	1686
0.20	0.52	25.6	0.390	965
0.40	0.71	35.2	0.255	625
0.50	0.66	32.5	0.213	521
0.60	0.61	30.4	0.166	408
0.80	0.65	32.5	0.171	419
1.00	0.73	36.0	0.156	382
		Av 32.1 ± 3.2		

Other reaction schemes are also possible depending upon the nature of the initial Mn(V) species and upon whether or not the reaction proceeds by a single two-electron step or by two one-electron-transfer steps with the formation of a transient Mn(IV) species. The final reduction of Mn(III) would be expected to be rapid.[4]

Although the oxidation potentials for the Mn(III)/Mn(IV) and Mn(IV)/Mn(V) couples have not been measured in acidic media, Rosseinsky and Nicol have estimated the potential of the $Mn(III)/MnO^{2+}$ couple as −1.53 V and that of the MnO^{2+}/MnO_4^{3-} system as −3.66 V.[12] This latter value is probably too negative, since MnO_4^{3-} would readily oxidize water, so the potential of this system is probably closer to the value of −0.9 V found for the MnO^{2+}/MnO_4^{3-} couple in basic solution.[7] It would appear that both MnO_4^{3-} and MnO^{2+} are capable of oxidizing VO^{2+} if these potentials are nearly correct. The starting Mn(V) species could be $H_2MnO_4^-$ or H_3MnO_4 and the final Mn(III) species are Mn^{3+} and $MnOH^{2+}$. A change in coordination number from 4 to 6 must occur which partially explains the slowness of this reaction. The rate-determining step in most chromium(VI) oxidations is believed to be due to a change in coordination number from 4 to 6 ($HCrO_4^-$ to Cr^{3+}).[13,14]

Registry No. VO^{2+}, 18252-79-4; MnO_4^-, 14333-13-2; Mn(V), 20574-97-4.

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Preparation and Fluxional Properties of *cis*-Dichloro(sulfoxide)(olefin)platinum(II) Complexes

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During the course of an investigation of the interaction of chiral sulfoxide ligands with prochiral olefins coordinated to platinum(II), we had occasion to develop a direct, efficient