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Oxidation of Peroxovanadium(V), VO_3^+, by HSO_5^- and Co^{3+} in Acidic Aqueous Solution. Role of the $VO_3^{2+}\cdot$ Radical Cation

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The oxidation of VO_3^+ by HSO_5^- is catalyzed by low concentrations of VO^{2+} in acidic solution. The rate law is $-d[HSO_5^-]/dt = -d[VO_3^+]/dt = k_1[HSO_5^-][VO^{2+}]_0$. The value of the rate parameter k_1 is the same as that found previously for the HSO_5^-–VO^{2+} reaction. A mechanism is proposed in which $SO_4^-\cdot$, formed in the rate determining step, oxidizes VO_3^+ to the $VO_3^{2+}\cdot$ radical cation. The $VO_3^{2+}\cdot$ cleanly undergoes an internal redox reaction to produce VO^{2+} and O_2. With relatively high concentrations of VO^{2+}, VO_3^+ and VO^{2+} competitively reduce $SO_4^-\cdot$; the ratio of the rate constants was estimated. Aqueous Co^{3+} oxidizes VO_3^+ to $VO_3^{2+}\cdot$ according to the rate expression $-d[VO_3^+]/dt = k_5[VO_3^+][Co^{3+}]$. The $VO_3^{2+}\cdot$ intermediate again undergoes an internal redox reaction; at later stages in the overall reaction, the resulting VO^{2+} competes with VO_3^+ for Co^{3+}. The ratio of the rate constants in this competition was determined. Thus, the primary mode of oxidation of VO_3^+ is a one-electron process, at least with Co^{3+} and even the potentially multiequivalent oxidant HSO_5^-. It is concluded that the use of peroxo complexes is a promising means of distinguishing between one- and two-electron oxidations of the peroxide moiety.

Introduction

The redox chemistry of molecular oxygen has been studied extensively the past decade.[1] Recent electrochemical studies indicate that a one-electron process is the principal electron-transfer step for the reduction of O_2, followed by a disproportionation reaction to yield H_2O_2 in acidic solution.[1] It would be anticipated, therefore, that oxidation of hydrogen peroxide would occur via a one-electron process to yield HO_2 as an intermediate in acidic solution. The fate of the superoxide—disproportionation, oxidation, or reduction—would depend on the particular system under investigation. This mechanistic expectation has been realized in a number of investigations that have utilized hydrogen peroxide as a reducing agent.[2] However, distinguishing between one- and two-electron oxidations in these systems often can be a challenging task for the experimentalist when a potentially multiequivalent oxidant is used. For example, the mechanism proposed for the bromate–hydrogen peroxide system invokes two-electron steps,[3] although we are not aware of any experimental evidence that rules out one-electron pathways instead.

It occurred to us that oxidations of peroxovanadium(V), VO_3^+, might have an important advantage in reaching mechanistic conclusions. Mixtures of vanadium(V) and hydrogen peroxide rapidly reach equilibrium in acidic solution, and conditions can be realized conveniently in which greater than 99% of the hydrogen peroxide is in the VO_3^+ form.[4] The rate of decomposition of VO_3^+ is sufficiently slow that oxidations by a variety of added oxidants can be studied. The key feature is that a one-electron oxidation would be expected to yield $VO_3^{2+}\cdot$ as an intermediate. Brooks and Sicilio have obtained electron spin resonance spectra that are consistent with the formation of this radical cation in the VO^{2+}–H_2O_2 system.[5] In our studies, a very useful fate of the $VO_3^{2+}\cdot$ intermediate would be an internal redox process generating VO^{2+} and O_2. In our investigations to date this sequence of reactions appears to occur quite cleanly and offers the advantage that the formation and subsequent reactions of VO^{2+} are amenable to experimental observation, albeit indirectly in some cases. In this paper we report the results of kinetic and stoichiometric studies of two reactions—the VO^{2+}-catalyzed reaction between peroxomonosulfate, HSO_5^-, and VO_3^+ and the oxidation of VO_3^+ by cobalt(III) in acidic solution. These results are somewhat complicated but taken as a whole do provide strong inferential evidence for both the formation of $VO_3^{2+}\cdot$ and its decomposition to VO^{2+} and O_2, thereby indicating one-electron oxidations of the peroxo complex at least in these systems.

Experimental Section

Reagents. The following solutions were prepared as indicated: HSO_5^-, from OXONE (Du Pont);[6] VO_2ClO_4, by dissolution of reagent grade V_2O_5 in perchloric acid; $VO(ClO_4)_2$, from commercial vanadyl sulfate by ion exchange. Hydrogen peroxide (Fisher, Certified, 30%, stabilizer free) was used as supplied. The synthesis of $LiClO_4$, $Co(ClO_4)_2$, and solutions of $Co(ClO_4)_3$ in $HClO_4$ have been described previously.[7]

All other chemicals were of reagent grade and were used without further purification. Deionized water was distilled before use, first from acid dichromate and then from alkaline dichromate.

Analytical Procedures. Solutions of HSO_5^-, Co^{3+}, and H_2O_2 were analyzed iodometrically by reaction with iodide followed by titration with thiosulfate.

Spectrophotometric assays were made for VO_3^+ (ϵ 280 M^{-1} cm^{-1} at 455 nm), VO_2^+ (ϵ 389 at 313 nm), VO^{2+} (ϵ 17.1 at 762.5 nm), and Co^{2+} (ϵ 4.79 at 510 nm). Other values of ϵ were used in this study: at 455 nm, VO_2^+ (3.2), Co^{2+} (2.57), and Co^{3+} (7.6); at 356 nm, an isosbestic for VO_2^+ and VO_3^+ (108), Co^{2+} (0.038), and VO^{2+} (0.50); at 325 nm, VO_2^+ (299), VO^{2+} (6.0), and Co^{3+} (5.5).

Kinetic and Stoichiometric Procedures. The kinetic experiments were monitored spectrophotometrically by measuring the disappearance of VO_3^+ at 455 nm or the formation of VO_2^+ at 325 nm in the case of the Co^{3+}–VO^{2+} reaction. A Zeiss PMQ 11 spectrophotometer equipped with a rapid mixing, thermostated sample compartment was used. The order of mixing the reagents was as follows: (a) VO_2^+-catalyzed reaction of HSO_5^- and VO_3^+, HSO_5^- + VO_2^+, temperature equilibration (TE), H_2O_2, and finally VO^{2+} (in a few preliminary experiments, the order was instead VO_2^+ + H_2O_2, TE, VO^{2+}, and HSO_5^-); (b) Co^{3+}–VO_3^+ reaction, VO_2^+ (VO^{2+}), TE, H_2O_2, and finally Co^{3+}.

Results

VO^{2+}-Catalyzed Oxidation of VO_3^+ by HSO_5^-. The rate of oxidation of VO_3^+ by HSO_5^- in perchloric acid solution is markedly enhanced by the presence of VO^{2+}. The stoichiometric ratio $[HSO_5^-]_0/\Delta[VO_3^+]$ is nearly unity with low concentrations of VO^{2+} and an initial $[VO_3^+] > [HSO_5^-]_0$.

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Table I. Kinetic Results for the VO^{2+}-Catalyzed Oxidation of VO_3^+ by HSO_5^- [a]

T, °C	$10^3 \times [V(V)]_0$, M	$10^4 \times [VO^{2+}]_0$, M	$10^3 \times [HSO_5^-]_0$, M	$10^3 \times k_{obsd}$, s^{-1}	k_1, M^{-1} s^{-1}
20.0	3.46	1.84	1.56	1.71	9.29
20.0	3.42	0.912	3.09	8.46	9.27
20.0	1.75	1.86	1.58	1.67	9.00
20.0	6.73	1.80	2.03	1.55	8.59
20.0	3.38	5.42	1.53	4.83	8.91
20.0	3.49	1.86	0.647	1.77	8.99
20.0[b]	3.46	20.5	1.56	19.4	9.28
					av $9.0_5 \pm 0.20$
20.0[c]	3.44	1.83	2.07	1.83	10.0
20.0[d]	3.47	1.85	2.06	2.38	12.8
20.0[e]	3.46	1.84	1.60	1.77	9.57 (8.79)[f]
20.0[e]	3.42	0.912	3.17	0.963	10.6 (8.89)[f]
20.0[e]	1.75	1.86	1.62	1.61	8.64 (8.33)[f]
25.0	3.29	1.84	1.61	2.44	13.3
15.0	3.29	1.84	1.61	1.16	6.30
10.0	3.24	1.81	3.03	0.786	4.34
5.0	3.24	1.81	3.03	0.525	2.90

[a] $[HClO_4] = 1.0$ M, $[VO_3^+]_0 =$ ca. 1.15×10^{-3} M unless otherwise indicated. [b] See text for kinetic analysis. [c] $[HClO_4] = 0.25$ M; $[LiClO_4] = 0.75$ M. [d] $[H_2SO_4] = 0.50$ M. [e] Reaction initiated by addition of HSO_5^-. [f] Calculated with the assumption that $[VO^{2+}]_0 =$ added $[VO^{2+}]_0 + 0.004 \times$ total $[V(V)]_0$.

For example, with $[VO_3^+]_0 = 1.18 \times 10^{-3}$ M, $[HSO_5^-]_0 = 6.32 \times 10^{-4}$ M, $[VO^{2+}]_0 = 1.86 \times 10^{-4}$, and an excess, uncomplexed $[VO_2^+]_0 = 2.31 \times 10^{-3}$ M in 1.0 M $HClO_4$ at 20.0 °C, the ratio was 1.06. Similar results are obtained with substantial concentrations of VO^{2+} and an initial $[HSO_5^-] > [VO_3^+]_0$ when allowance is made for the consumption of HSO_5^- by VO^{2+}. For example, with $[VO_3^+]_0 = 1.19 \times 10^{-3}$ M, $[HSO_5^-]_0 = 2.11 \times 10^{-3}$ M, $[VO_2^+]_0 = 3.05 \times 10^{-3}$ M, and an excess $[VO_2^+]_0 = 2.23 \times 10^{-3}$ M, all the VO_3^+ is consumed. However, 1.67×10^{-3} M additional VO_2^+ is formed, and with the stoichiometry of the VO^{2+}–HSO_5^- reaction taken into account,[8] the ratio $([HSO_5^-]_0 - (\text{additional } [VO_2^+]/1.92))/[VO_3^+]_0 = 1.04$.

The kinetics were monitored by following the disappearance of VO_3^+. In most of the experiments VO_2^+ and HSO_5^- in aqueous perchloric acid were allowed to reach the desired temperature. VO_3^+ was formed in situ by addition of 1 aliquot of H_2O_2 such that the $[H_2O_2]_0 = 0.17$–0.66 M $[VO_2^+]_0$. Under these conditions in moderately acidic solution, at least 95% and usually >99% of the H_2O_2 is complexed as VO_3^+. These values are based on the thoroughly studied equilibria[4] for which the value of K_1 is 3.5×10^4 M^{-1} and K_2 is 1.3 M at $I = 1.0$ M and 25 °C.

$$VO_2^+ + H_2O_2 \overset{K_1}{\rightleftharpoons} VO_3^+ + H_2O \tag{1}$$

$$VO_3^+ + H_2O_2 \overset{K_2}{\rightleftharpoons} VO_5^- + 2H^+ \tag{2}$$

It was observed that, under the conditions summarized in Table I, the rate of disappearance of VO_3^+ in the presence of HSO_5^- as outlined above was very slow. The kinetic experiments were then initiated by addition of the desired amount of VO^{2+}. Plots of ln $([HSO_5^-]_0 - \Delta[VO_3^+])$ vs. time were linear for 60–80% of total consumption of the VO_3^+. The slopes of these pseudo-first-order plots are listed in the next to last column in Table I. The values of the slope divided by $[VO^{2+}]_0$ for the first seven experiments are approximately constant, indicating the empirical rate law of eq 3. This rate

$$-d[HSO_5^-]/dt = k_1[HSO_5^-][VO^{2+}]_0 \tag{3}$$

law is remarkable in that it requires a zero-order dependence on the $[VO_3^+]$ and further requires that a constant $[VO^{2+}] = [VO^{2+}]_0$ be maintained throughout most of the reaction. This result coupled with the nearly 1:1 relationship between $\Delta[HSO_5^-]$ and $\Delta[VO_3^+]$ confirms that the net reaction is approximately

$$HSO_5^- + VO_3^+ \xrightarrow{VO^{2+}} HSO_4^- + VO_2^+ + O_2 \tag{4}$$

Table II. Stoichiometric Results for the VO^{2+}-Induced Oxidation of VO_3^+ by HSO_5^- [a]

$10^3 \times [HSO_5^-]_0$, M	$10^3 \times [VO^{2+}]_0$, M	$10^3 \times [VO^{2+}]_{av}$, M[b]	$10^3 \times [VO_3^+]_0$, M	$10^4 \times [VO_3^+]_\infty$, M	k_4/k_2[c]
1.07	5.16	5.00	1.21	3.03	0.0231
1.07	5.16	5.00	1.20	3.01	0.0246
1.53	6.03	5.59	1.18	0.85	0.0304
1.06	10.2	9.94	1.20	4.04	0.0240
1.53	15.1	14.5	1.19	2.48	0.0259
1.03	15.2	14.6	1.18	4.82	0.0252
1.55	19.9	19.2	1.13	2.95	0.0299
2.02	29.1	28.0	1.12	2.42	0.0266
					av 0.026 ± 0.002

[a] Conditions: $[HClO_4] = 1.0$ M, total $[V(V)]_0 = (3.27$–$3.47) \times 10^{-3}$ M, $T = 20.0$ °C. [b] $[VO^{2+}]_{av} = [VO^{2+}]_0 - ([HSO_5^-]_0 - \Delta[VO_3^+])$. [c] Calculated from eq 16.

At high concentrations of VO^{2+}, as in the seventh experiment in Table I, the kinetic analysis is more complicated and will be addressed later.

Other relevant observations are as follows. First, interference from a VO^{2+}–VO_3^+ reaction may be safely neglected. This was demonstrated by preparing a solution initially containing 6.89×10^{-3} M VO_2^+, 8.94×10^{-4} M H_2O_2, and 6.83×10^{-3} M VO^{2+} in 1.0 M $HClO_4$ at 20.0 °C. Only a 1.7% decrease in the $[VO_3^+]$ was found after 30 min. The rate of the VO^{2+}–H_2O_2 reaction is significantly faster[5] but may be safely neglected at the low levels of uncomplexed H_2O_2 used in this study. Peroxomonosulfate is quite unreactive toward hydrogen peroxide under our experimental conditions. Second, the excess $[VO_2^+]$ over that required to complex most of the H_2O_2 has no detectable kinetic effect. Third, the rate parameter measured in 0.25 M $HClO_4$ at $I = 1.0$ M is only ca. 10% greater than that found in 1.0 M $HClO_4$. This result indicates that trace amounts of VO_5^- are not playing a significant role in our experiments. Finally, the order of mixing the reagents has a minor effect. In the tenth through twelfth experiments in Table I, the HSO_5^- reactant was added last. The values of the rate parameter under this condition are somewhat variable and increase as more VO_2^+ or less VO^{2+} is present. However, if the assumption is made that analytically undetectable amounts of VO^{2+} are present in the VO_2^+ stock solution (ca. 0.4%), the corrected rate parameters given in parentheses are more consistent with those of the other experiments. Any VO^{2+} contaminant in the VO_2^+ would be oxidized by HSO_5^- during thermal equilibration in the usual experiments.[8]

A series of additional stoichiometric experiments were performed with substantial concentrations of VO^{2+} but under conditions where incomplete consumption of the VO_3^+ occurred. These results are summarized in Table II.

The reaction between HSO_5^- and VO_3^+ in the absence of added VO^{2+} was briefly examined. Since high concentrations of HSO_5^- were desired, the reaction was conducted in 0.50 M H_2SO_4 to facilitate dissolution of the OXONE reagent. HSO_5^- and VO_2^+ were allowed to reach temperature equilibrium before the H_2O_2 was added to initiate the reaction. The disappearance of VO_3^+ with time yielded inverted S-shaped curves but with a substantial linear region. The extent

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Table III. Stoichiometric Results for the Oxidation of VO_3^+ by Co^{3+} [a]

$10^3 \times [Co^{3+}]_0$, M	$10^3 \times [VO^{2+}]_0$, M	$10^3 \times \Delta[VO_3^+]$, M	$10^3 \times [VO^{2+}]_\infty$, M	$[Co^{3+}]_0/\Delta[VO_3^+]$	k_6/k_5 [b]	$10^3 \times [VO^{2+}]_\infty$ (calcd),[c] M
1.85		1.49	1.03	1.23	0.102	1.15
1.49		1.30	1.02	1.15	0.132	1.11
1.12		1.03	0.90	1.09	0.136	0.94
0.747		0.72	0.62	1.04	0.110	0.87
1.09[d]		1.02	0.90	1.07	0.111	0.95
1.48	1.03	1.20	1.83	1.23	0.111	1.95
1.48	2.59	1.05	3.15	1.42	0.130	3.20
1.47	6.41	0.86	6.54	1.71	0.114	6.66
2.19	6.38	1.12	6.42	1.96	0.126	6.43
					av 0.12 ± 0.01	

[a] Conditions: $[HClO_4] = 1.0$ M; total $[V(V)]_0 = 3.33 \times 10^{-3}$ M; $[VO_3^+]_0 = (1.53-1.55) \times 10^{-3}$ M; $T = 20.0$ °C (unless otherwise indicated). [b] Calculated from eq 20. [c] Calculated from eq 21. [d] Total $[V(V)]_0 = 6.54 \times 10^{-3}$ M.

Table IV. Kinetic Results for the Oxidation of VO_3^+ by Co^{3+} [a]

T, °C	$[HClO_4]$, M	$10^3 \times [Co^{3+}]_0$, M	k_5, $M^{-1}\,s^{-1}$
25.0	1.03	1.11	$18._3$
25.0[b]	1.03	1.09	$18._1$
20.0	1.03	1.33	$10._3$
20.0	1.03	1.06	$10._3$
20.0	1.03	0.799	9.9_9
20.0[b]	1.03	1.04	$11._1$
20.0	0.451	1.06	$19._4$
20.0[c]	3.0	1.06	9.2_4
15.0	1.03	1.11	6.0_3
10.0	1.03	1.14	3.3_1
10.0	0.459	1.14	6.1_7
10.0	0.268	1.14	8.9_5
10.0	0.172	1.14	$12._4$
5.0	1.03	1.14	1.8_4

[a] Conditions: $I = 1.0$ M, maintained with $LiClO_4$; total $[V(V)]_0 = 3.34 \times 10^{-3}$ M; $[VO_3^+]_0 = (1.50-1.53) \times 10^{-3}$ M (unless otherwise indicated). [b] Total $[V(V)]_0 = 6.54 \times 10^{-3}$ M. [c] $I = 3.0$ M.

Table V. Kinetic Results for the Oxidation of VO^{2+} by Co^{3+} [a]

$[HClO_4]$, M	$10^3 \times [VO^{2+}]_0$, M	k_6, $M^{-1}\,s^{-1}$	k_6/k_5 [b]
1.03	4.22	1.44	0.13_8
1.03	10.5	1.40	0.13_5
0.452	4.22	3.25	0.16_8
3.0[c]	10.5	0.923	0.10_0

[a] Conditions: $[Co^{3+}]_0 = (1.31-1.34) \times 10^{-3}$ M; $I = 3.0$ M, maintained with $LiClO_4$; $T = 20.0$ °C (unless otherwise indicated). [b] Calculated by use of k_5 values from Table IV. [c] $I = 3.0$ M.

of the linear region was ca. 12–84% and 27–86% of total reaction with 0.20 and 0.050 M HSO_5^-, respectively. Over the conditions $[HSO_5^-]_0 = 0.050-0.20$ M, $[VO_2^+]_0$ (uncomplexed) = $(2.08-5.31) \times 10^{-3}$ M, and $[VO_3^+]_0 = 1.30 \times 10^{-3}$ M in 0.50 M H_2SO_4 at 20.0 °C, the kinetics over the linear region obeyed expression 5.

$$-d[VO_3^+]/dt = ((1.5 \pm 0.2) \times 10^{-5}\ s^{-1})[HSO_5^-] \quad (5)$$

Oxidation of VO_3^+ by Co^{3+}. Some stoichiometric results for the oxidation of VO_3^+ by Co^{3+} are summarized in Table III. The extent of formation of VO^{2+} in this reaction was examined by measuring the loss of total vanadium(V) at 356 nm, an isosbestic for VO_3^+ and VO_2^+. This determination is subject to moderate error since the change is quite small in several experiments. The stoichiometric factor $[Co^{3+}]_0/\Delta[VO_3^+]$ increases with decreasing excess $[VO_3^+]$ and with increasing $[VO^{2+}]_0$. The ratio approaches unity with the largest excess $[VO_3^+]$ used and with no initially added VO^{2+}. Thus, the limiting stoichiometry is

$$Co^{3+} + VO_3^+ = Co^{2+} + VO^{2+} + O_2 \quad (6)$$

The kinetic experiments were monitored by measuring the disappearance of VO_3^+ under conditions where the limiting stoichiometry given in eq 6 was approximately obeyed. Plots of $\ln([VO_3^+]/([Co^{3+}]_0 - \Delta[VO_3^+]))$ vs. time were linear for roughly 50% of total reaction. Values of the rate parameter k_5 appropriate to the rate expression 7 are summarized in Table IV.

$$-d[VO_3^+]/dt = k_5[VO_3^+][Co^{3+}] \quad (7)$$

The results indicate that within experimental error the concentration of uncomplexed VO_2^+ is without stoichiometric or kinetic influence. The reaction between Co^{3+} and the traces of uncomplexed H_2O_2 is negligible under the experimental conditions employed.[2c,d]

The value of the rate parameter increases with decreasing $[HClO_4]$ at constant ionic strength. At 10.0 °C and $I = 1.0$ M, expression 8 correlates the $[H^+]$ dependence.

$$k_5 = 1.8\ M^{-1}\,s^{-1} + 1.9\ s^{-1}/[H^+] \quad (8)$$

Our interpretation of the Co^{3+}–VO_3^+ reaction requires the value of the rate constant for reaction 9. This reaction has

$$Co^{3+} + VO^{2+} + H_2O = Co^{2+} + VO_2^+ + 2H^+ \quad (9)$$

been studied previously, but under somewhat different conditions.[10] Therefore, we have briefly remeasured the kinetics and find that rate expression 10 is obeyed for at least 80% of

$$d[VO_2^+]/dt = k_6[Co^{3+}][VO^{2+}] \quad (10)$$

total reaction. Values of the rate parameter k_6 are summarized in Table V. The value obtained in 3.0 M $HClO_4$ at 20.0 °C is in satisfactory agreement with the previously reported value[10a] of 0.952 $M^{-1}\,s^{-1}$.

Discussion

We propose the reaction scheme of eq 11–14 for the

$$HSO_5^- + VO^{2+} \xrightarrow{k_1} SO_4^{-}\cdot + VO_2^+ + H^+ \quad (11)$$

$$SO_4^{-}\cdot + VO_3^+ \xrightarrow[k_2]{H^+} HSO_4^- + VO_3^{2+}\cdot \quad (12)$$

$$VO_3^{2+}\cdot \xrightarrow{k_3} VO^{2+} + O_2 \quad (13)$$

$$SO_4^{-}\cdot + VO^{2+} \xrightarrow[k_4]{H_2O} HSO_4^- + VO_2^+ + H^+ \quad (14)$$

HSO_5^-–VO_3^+ reaction in the presence of VO^{2+}. Equations 11 and 14 are identical with those proposed in a study of the HSO_5^-–VO^{2+} reaction.[8] Equations 12 and 13 involve the formation and decomposition of the radical cation intermediate $VO_3^{2+}\cdot$, which may be viewed formally as a complex between

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oxovanadium(V) and the superoxide ion.

According to this scheme, the rate of disappearance of HSO_5^- is eq 15. The kinetic results with low concentrations

$$-d[HSO_5^-]/dt = k_1[HSO_5^-][VO^{2+}] \qquad (15)$$

of VO^{2+} are consistent with eq 15 for most of the observed reaction (the disappearance of VO_3^+) and indicate further that $[VO^{2+}] = [VO^{2+}]_0$. That is, the overall reaction of HSO_5^- and VO_3^+ is catalyzed by VO^{2+} under these conditions. This in turn requires, in terms of the reaction scheme, a steady-state concentration of $SO_4^-\cdot$ and $VO_3^{2+}\cdot$ and the dominance of reaction 12 relative to reaction 14.

One test of this proposal is the comparison of the values of the rate parameter k_1 with the rate constant measured independently in the study of the HSO_5^-–VO^{2+} reaction.[8] The average agreement is 8%, and the maximum deviation is 14%. The activation parameters appropriate to k_1 in 1.0 M $HClO_4$ are $\Delta H^\ddagger = 12._0$ kcal/mol and $\Delta S^\ddagger = -13$ cal/(deg mol). In the previous study, $\Delta H^\ddagger = 12._8$ kcal/mol and $\Delta S^\ddagger = -11$ cal/(deg mol). The proposed reaction scheme certainly survives this test.

A second test is a comparison of k_2 and k_4 in that the kinetic results require the former to be substantially larger. The stoichiometric results in Table II allow an estimate of k_4/k_2. It may be shown[9] that under the conditions indicated

$$k_4/k_2 = ([HSO_5^-]_0 - \Delta[VO_3^+])/([VO^{2+}] \ln([VO_3^+]_0/[VO_3^+]_\infty)) \qquad (16)$$

where the minor approximation $[VO^{2+}] = [VO^{2+}]_{av} = [VO^{2+}]_0 - ([HSO_5^-]_0 - \Delta[VO_3^+])$is made. The values of k_4/k_2 calculated in this manner are listed in the last column of Table II. These results are fairly constant and indicate that $k_2 = 38k_4$.[11] Thus, in most of the kinetic experiments, reaction 14 does not begin to compete effectively with reaction 12 until most of the VO_3^+ has been consumed. With higher initial concentrations of VO^{2+}, as in the seventh experiment in Table I, this competition should occur much earlier, and the reaction is no longer strictly catalyzed by VO^{2+} but rather induced by this species. Nevertheless, the kinetic data in this experiment can be analyzed by plotting ln $[HSO_5^-]_{cor}$ vs. time, where the $[HSO_5^-]_{cor}$ is computed from the measured $[VO_3^+]$ by taking the competition for the $SO_4^-\cdot$ radical into account. This plot is linear for 83% of total consumption of VO_3^+, and the resulting value of k_1 is within the range observed with lower initial concentrations of VO^{2+}.

Our results indicate that even relatively low concentrations of VO^{2+} catalytically drive the net reaction of VO_3^+ and HSO_5^- by an indirect sequence of one-electron steps. Peroxomonosulfate is a potential two-equivalent oxidant and in a number of systems behaves in this manner via oxygen atom transfer from the terminal peroxide position following nucleophilic attack at the peroxide moiety by the substrate.[12] This mode of reaction is surely not available with VO_3^+ in view of numerous observations that the dioxygen produced by oxidation of the peroxide moiety invariably contains both peroxide oxygens.[13] Still, it is of interest to test whether a *direct* reaction between HSO_5^- and VO_3^+ can occur. Our results indicate that even trace amounts of VO^{2+} must be avoided, and accordingly high concentrations of HSO_5^- were allowed to thermally equilibrate with the VO_2^+ before the reaction was initiated. Thermodynamic and kinetic[8] considerations require an extremely low $[VO^{2+}]$ under these conditions. The observed kinetic profiles are characteristic of a chain reaction, particularly the induction period and the unusual kinetic expression (eq 5). We tentatively propose the following interpretation although it is incomplete, speculative, and would require extensive additional investigation to establish. We suggest that the reaction scheme given in eq 11–13 still holds even under these extreme conditions during the pseudo-zero-order regime of the reaction. During the induction period steady-state concentrations of $SO_4^-\cdot$, $VO_3^{2+}\cdot$, *and* VO^{2+} are established. The reaction then obeys the rate expression 3, except the $[VO^{2+}]$ is equal to the steady-state value. This value in our experiments can be estimated as ca. 1.2×10^{-6} M by use of the observed pseudo-first-order rate constant in eq 5 and the value of k_1 in 0.50 M H_2SO_4 from Table I.[14] If correct, this interpretation implies that it would be very difficult indeed to avoid VO^{2+} catalysis and instead favor the direct reaction of HSO_5^- and VO_3^+.

The reaction scheme given in eq 17–19 is adequate to

$$Co^{3+} + VO_3^+ \xrightarrow{k_5} Co^{2+} + VO_3^{2+}\cdot \qquad (17)$$

$$VO_3^{2+}\cdot \xrightarrow{k_3} VO^{2+} + O_2 \qquad (18)$$

$$Co^{3+} + VO^{2+} \xrightarrow[k_6]{H_2O} Co^{2+} + VO_2^+ + 2H^+ \qquad (19)$$

correlate our experimental results for the Co^{3+}–VO_3^+ reaction. In spite of the apparent simplicity of this scheme, it involves competitive, consecutive second-order reactions, a situation that causes serious problems in extracting rate constants.[15] We have chosen to estimate the ratio k_6/k_5 from a series of stoichiometric experiments (Table III), determine the value of k_5 under conditions where competition from reaction 19 is suppressed (Table IV), and determine the value of k_6 under our experimental conditions independently (Table V). The major test of the reaction scheme then lies in a comparison of the value of k_6/k_5 determined in the two ways.

It can be shown[9] that, under the conditions summarized in Table III, our reaction scheme leads to eq 20 and 21 where

$$\text{calcd } [Co^{3+}]_0 = \frac{2K-1}{K-1}(\Delta[VO_3^+]) + \left[[VO^+]_0 - \frac{[VO_3^+]_0}{K-1}\right]\left[1 - \left(\frac{[VO_3^+]_\infty}{[VO_3^+]_0}\right)^K\right] \qquad (20)$$

$$\text{calcd } [VO^{2+}]_\infty = \frac{[VO_3^+]_\infty}{K-1}\left(1 + \left[\frac{(K-1)[VO^{2+}]_0 - [VO_3^+]_0}{[VO_3^+]_0}\right]\left[\frac{[VO_3^+]_\infty}{[VO_3^+]_0}\right]^{K-1}\right) \qquad (21)$$

$K = k_6/k_5$. Since the experimental values of $[Co^{3+}]_0$ are more accurate than those of $[VO^{2+}]_\infty$, we have calculated the best

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(11) Previous studies have shown that the sulfate radical anion is a selective oxidant in spite of its formidable oxidizing power. For a recent compilation of rate constants, see: Ross, A. E.; Neta, P. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1979**, *NSRDS-NBS 65*.

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(14) A potential problem with this scheme is the invariant steady-state $[VO^{2+}]$ in our experiments. However, the initiation and termination reactions of the chain are unknown. An attractive possibility for the former is a direct reaction between HSO_5^- and VO_3^+ to produce $SO_4^-\cdot$ and $VO_3^{2+}\cdot$, but participation of trace impurities in the OXONE reagent must be considered also.

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value of K, from eq 20, for each experiment by an iterative procedure that minimizes the expression (experimental $[Co^{3+}]_0$ − calculated $[Co^{3+}]_0$). The results are listed in Table III, and the values of K are reasonably constant over a moderately extensive range of experimental conditions. For comparison, the values of calculated $[VO^{2+}]_\infty$ computed from eq 21 and the best value of K are listed also. The calculated values are systematically high. Much of the discrepancy can be attributed to experimental error in the determination of $[VO^{2+}]_\infty$, but also the uncertainty in the determination of K is probably larger than the indicated average uncertainty.

The kinetic results allow an independent estimate of k_6/k_5, and the results are summarized in the last column of Table V. The value of 0.13_6 obtained in 1.0 M $HClO_4$ at 20.0 °C compares favorably with the value of 0.12 obtained in the stoichiometric experiments under the same conditions.

The rate constants for the oxidation of VO_3^+ and H_2O_2[2d] by cobalt(III) are 10.3 and 11.5 M^{-1} s^{-1}, respectively, in 3.0 M $HClO_4$ at 20.0 °C. However, the H_2O_2 reaction is carried almost exclusively by $CoOH^{2+}$, whereas both Co^{3+} and $CoOH^{2+}$ appear to be reactive toward VO_3^+.[15] The composite activation parameters in 1.0 M $HClO_4$ for the VO_3^+ system are $\Delta H^* = 17._6$ kcal/mol and $\Delta S^* = 6$ cal/(deg mol).

It should be noted that the only fate of the $VO_3^{2+}\cdot$ intermediate in the proposed schemes is an internal oxidation–reduction reaction. It is important to consider the validity of this assumption since the major theme of this study is to utilize the subsequent formation of VO^{2+} as a diagnostic probe in future studies for a distinction between one- and two-electron oxidations of the complexed peroxide moiety. One alternative reaction of $VO_3^{2+}\cdot$ is dissociation to form uncomplexed $HO_2\cdot$. If this did occur, then disproportionation of the HO_2 or oxidation by HSO_5^-, Co^{3+}, or VO_2^+ would be anticipated. Our results would require effective oxidation by VO_2^+. This seems unlikely, especially in the Co^{3+} system, and further some dependence on the $[VO_2^+]$ should be seen. There is no experimental indication of this. Alternatively, oxidation of VO_3^{2+} by HSO_5^- or Co^{3+} can at least be rejected as an important process in our experiments. Finally, while we have obtained no evidence that the internal oxidation–reduction reaction of $VO_3^{2+}\cdot$ obeys first order kinetics, this is certainly the simplest assumption.

The present results thus appear to demonstrate the facile formation and clean decomposition of the intermediate $VO_3^{2+}\cdot$. The evidence is indirect in that we have relied on stoichiometric and kinetic consequences of the formation of VO^{2+}, but ESR experiments may provide more direct verification. The primary mode of oxidation of VO_3^+ is a one-electron process even with HSO_5^-. It will be interesting to see if a similar mechanism is also found with more obdurate 2-equiv oxidants. In any event, the use of peroxo complexes appears to hold promise as a means of distinguishing between one- and two-electron oxidations of the peroxide moiety.

Registry No. VO_3^+, 12179-36-1; HSO_5^-, 12188-01-1; Co, 7440-48-4; VO^{2+}, 20644-97-7.

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Carbon Monoxide Affinities of Iron(II) Octaethylporphyrin, Octaethylchlorin, and Octaethylisobacteriochlorin

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As part of continuing research directed at the elucidation of comparative structural, electronic, and reactivity properties of iron(II,III) porphyrins and hydroporphyrins, the CO binding constants for the reactions

$$\mathrm{Fe(P)} + \mathrm{CO} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{Fe(P)(CO)}$$

$$\mathrm{Fe(P)(CO)} + \mathrm{CO} \overset{K_2}{\rightleftharpoons} \mathrm{Fe(P)(CO)_2}$$

have been determined in toluene solutions at 20.0 ± 0.2 °C. For both reactions P = octaethylporphyrin (OEP), octaethylchlorin (OEC), and octaethylisobacteriochlorin (OEiBC) dianions. Iron complexes of the latter two macrocycles serve as synthetic representations of the heme *d* and siroheme prosthetic groups of nitrite and sulfite reductases. Constants were determined by least-squares analysis of visible absorbance/p_{CO} data based on a four-parameter model. The individual Fe(P)(CO) and $Fe(P)(CO)_2$ complexes were detected in dichloromethane solutions by infrared spectroscopy. Values of K_1 and K_2 exhibit the trend OEP < OEC < OEiBC, with those of K_2 (0.0022, 0.0073, 0.029 $torr^{-1}$) being more variant with macrocycle structure than those of K_1 (0.31, 0.43, 0.74 $torr^{-1}$). The greater relative stability of $Fe(OEiBC)(CO)_2$ among $Fe(P)(CO)_2$ complexes is the most prominent difference in species equilibrium distribution as dependent on P. However, for each reaction differences in ΔG as P is varied are $\lesssim 1.5$ kcal/mol, making it difficult to identify the factors responsible for trends in K_1 and K_2. Certain of these possible factors are briefly considered.

Introduction

The accelerating interest in the chemistry of hydroporphyrins derives in large measure from the detection of reduced heme prosthetic groups in a variety of enzymes. As prime examples, dissimilatory nitrite reductases contain heme *d*,[2] a Fe chlorin complex, and assimilatory forms of this enzyme and assimilatory and dissimilatory sulfite reductases incorporate as a common prosthetic group siroheme.[3-11] The latter

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(1) National Institutes of Health Postdoctoral Fellow, 1979–1980.

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