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Oxidation of Peroxovanadium(V), VO_3^+, in Acidic Aqueous Solution

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The Cl_2–VO_3^+ reaction proceeds by oxidation of trace amounts of H_2O_2 in equilibrium with VO_3^+. Preliminary results for the HOCl–VO_3^+ reaction are presented. The oxidation of VO_3^+ by $S_2O_8^{2-}$ is catalyzed by Ag^+, with the formation of the radical cation $VO_3^{2+}\cdot$ via oxidation of VO_3^+ by Ag^{2+}. The rate law for the SO_4F^-–VO_3^+ reaction is $-d(SO_4F^-)/dt = k_9(SO_4F^-)(VO_3^+)$; again, formation of the intermediate $VO_3^{2+}\cdot$ is indicated. In agreement with previous results, the decomposition of $VO_3^{2+}\cdot$ involves an internal redox reaction to produce VO^{2+} and O_2. The various pathways for the oxidation of VO_3^+ are summarized. A direct two-electron oxidation has not been observed, presumably because the formation of a peroxo complex with the oxidant prior to electron transfer is unfavorable when the peroxide moiety is complexed to vanadium(V).

Introduction

A previous study[1] of the oxidation of peroxovanadium(V), VO_3^+ (or $VO(O_2)^+$), in acidic solution indicated the formation of the $VO_3^{2+}\cdot$ radical cation intermediate, which decomposed by an internal redox reaction to form VO^{2+} and O_2. This intermediate is formed in a direct reaction with Co^{3+}. With HSO_5^-, however, the reaction can be catalyzed by VO^{2+}, with the formation of $VO_3^{2+}\cdot$ arising from oxidation of VO_3^+ by $SO_4^-\cdot$ (produced by the HSO_5^-–VO^{2+} reaction).

In extending the study, we report the results obtained with the additional oxidants Cl_2, Ag^{2+} (produced via the $S_2O_8^{2-}$–Ag^+ reaction), and fluoroxysulfate, SO_4F^-. In addition, preliminary results for HOCl and XeO_3 are summarized. In a limited sense, this study also extends our understanding of the redox behavior of hydrogen peroxide and the chemistry of the superoxide ion.

Experimental Section

Reagents. Solutions of VO_2ClO_4 were prepared by the dissolution of reagent grade V_2O_5 or $NaVO_3$ in perchloric acid. Traces of VO^{2+} were oxidized by treatment with Cl_2, followed by thorough purging with air. Solutions of $VO(ClO_4)_2$ were prepared from commercial $VOSO_4$ by ion exchange. Hydrogen peroxide (Fisher, Certified, 30%, stabilizer free) was used as supplied. Solutions containing equal amounts of OCl^- and Cl^- were prepared by passing Matheson Cl_2 first through aqueous sulfuric acid and then into cold 0.3 M NaOH. These solutions were shown to be free of chlorite or chlorate impurities and could be stored in the dark at 0 °C for several days without detectable decomposition. Solutions of Cl_2O in CCl_4 were prepared by the Cady method;[2] solutions of HOCl in perchloric acid were obtained by extraction. Samples of $CsSO_4F$ and XeO_3 were kindly furnished by Dr. Evan Appelman of the Chemistry Division, Argonne National Laboratory.

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 permanganate.

Analytical Procedures. Solutions of HOCl, OCl^- (for the Cl_2 experiments), $S_2O_8^{2-}$, and SO_4F^- were analyzed iodometrically by reaction with iodide followed by titration with thiosulfate. Silver(I) was determined gravimetrically as AgCl. Solutions of VO_3^+, VO_2^+, and VO^{2+} were analyzed spectrophotometrically, with use of extinction coefficients reported previously.[1]

Kinetic Procedures. The kinetic experiments were monitored spectrophotometrically, usually by measuring the disappearance of VO_3^+ at 455 nm and occasionally by following the loss or growth of total (V(V)) at 356 nm, an isosbestic for VO_2^+ and VO_3^+. The Cl_2–VO_3^+ reaction was initiated by injection of an aliquot of the OCl^-–Cl^- mixture in dilute base. The reaction cuvette was tightly stoppered, and the reaction solution filled the cell. This procedure avoided the loss of Cl_2 during the reaction and allowed quantitative transfer of the oxidant. No detectable consumption of VO_3^+ was observed during mixing while HOCl and Cl^- rapidly formed Cl_2.

Table I. Kinetic Results for the VO_3^+–Cl_2 System[a]

T, °C	$10^3(VO_2^+)_0$, M	$10^2[Cl^-]_0$, M	$10^3k_a/K_f$, s^{-1} [b]	k_a, M^{-1} s^{-1} [c]
20.0	13.7	3.90	2.38	109
20.0[d]	13.2	3.90	2.20	101
20.0[e]	5.19	3.84	2.29	105
20.0	5.25	3.90	2.28	105
20.0[f]	3.42	3.71	2.19	101
20.0	2.20	3.90	2.24	103
20.0	3.73	11.7	2.22	102
20.0	3.72	39.0	1.97	91
20.0	3.73	94.8	1.58	73
20.0[g]	3.73	19.5	2.81	129
20.0[g]	17.4	19.5	2.86	132
15.0	17.4	3.90	1.27	88
10.0[e]	17.2	3.84	0.646	64
5.0[e]	5.91	3.93	0.333	47

[a] Conditions: $(H^+) = 0.96$ M, $[Cl]_{T,0} = 1.06 \times 10^{-3}$ M, $(VO_3^+)_0 = 1.66 \times 10^{-3}$ M, and $I = 0.97$ M unless otherwise indicated. [b] Slope of kinetic plot (eq 1). [c] Calculated by use of K_f values and defined by eq 4. [d] VO^{2+} impurity in VO_2^+ stock solution not oxidized prior to initiation of reaction. [e] $(Cl)_{T,0} = 2.57 \times 10^{-3}$ M. [f] (VO_2^+) stock solution prepared from $NaVO_3$ instead of V_2O_5. [g] $(H^+) = 0.20$ M, $I = 0.97$ M ($LiClO_4$).

In the HOCl–VO_3^+ experiments a solution containing all reagents except H_2O_2 was thoroughly flushed with air. The large excess of HOCl used ensured very low levels of Cl_2 and Cl^- contamination. The kinetic experiments were then initiated by injection of H_2O_2.

The Ag^+-catalyzed oxidation of VO_3^+ by $S_2O_8^{2-}$ kinetic experiments was initiated by injection of Ag^+; $S_2O_8^{2-}$ is quite unreactive toward VO_3^+ in the absence of Ag^+.

Fresh solutions of SO_4F^- were prepared at 0 °C for each trial utilizing this oxidant.

Determination of the Formation Constant, K_f, for VO_3^+. Approximately equal initial concentrations of VO_2^+ and H_2O_2 over the range $(0.221-2.26) \times 10^{-3}$ M in molar perchloric acid were used. The formation of VO_5^- is negligible under these conditions. The values of K_f determined by this procedure are not highly accurate due to the relatively small extinction coefficient for VO_3^+ at 455 nm (which limits the useful concentration range) and the large value of the formation constant. The percentage of the total (H_2O_2) complexed as VO_3^+ ranged from 70 to 95% in these experiments.

Data Treatment. At least 20 data points were collected for each kinetic experiment. For the Cl_2–VO_3^+ system, the integrated form of the rate equation (4) (vide infra) was

$$([V(V)]_T/a)\ln([a + (VO_3^+)]/(VO_3^+)) + \ln[a + (VO_3^+)] + I = (k_a/K_f)t \quad (1)$$

where $[V(V)]_T = (VO_2^+) + (VO_3^+)$ and $a = (Cl_2)_0 - (VO_3^+)_0$. Values of k_a/K_f were determined from the slopes of the plots of the sum of the first two terms of eq 1 vs. time.

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(1) Thompson, R. C. *Inorg. Chem.* **1982**, *21*, 859.
(2) Cady, G. H. *Inorg. Synth.* **1957**, *5*, 156.
(3) (a) Markower, B.; Bray, W. C. *J. Am. Chem. Soc.* **1933**, *55*, 4765. (b) Markower, B. *Ibid.* **1934**, *56*, 1315. (c) Connick, R. E. *Ibid.* **1947**, *69*, 1509. (d) Morrow, J. I.; Silver, L. *Inorg. Chem.* **1972**, *11*, 231. (e) Held, A. M.; Halko, D. J.; Hurst, J. K. *J. Am. Chem. Soc.* **1978**, *101*, 5732.

Results

Oxidation of VO_3^+ by Aqueous Cl_2. Aqueous Cl_2 is known to react rather rapidly with H_2O_2 and was tested as a potential oxidant for VO_3^+. The hydrolysis of Cl_2 was suppressed by using the high acidities and added chloride ion indicated in Table I.

$$Cl_2 + H_2O = HOCl + Cl^- + H^+ \quad K_h \qquad (2)$$

The value of K_h is 4.9×10^{-4} M^2 at 25 °C and an ionic strength of 1.0 M.[4] In our experiments at least 98.7% of the total oxidant concentration was present as Cl_2.

The stoichiometric ratio $\Delta(VO_3^+)/(Cl)_{T,0} = 1.00 \pm 0.01$ was determined for the experiments with excess VO_3^+. This is in excellent agreement with the overall reaction

$$VO_3^+ + Cl_2 + H_2O = VO_2^+ + O_2 + 2Cl^- + 2H^+ \qquad (3)$$

No formation of VO^{2+} during the reaction was detected.

The kinetic experiments indicated that the reaction proceeds via the H_2O_2–Cl_2 pathway, in spite of the fact that the ratio (free H_2O_2)/(VO_3^+) ranged from 10^{-2} to 6×10^{-4} under the experimental conditions. Accordingly, the kinetic data were analyzed by use of the rate expression

$$-d(VO_3^+)/dt = k_a(Cl_2)(H_2O_2) = (k_a/K_f)(Cl_2)(VO_3^+)/(VO_2^+) \qquad (4)$$

where the uncomplexed (H_2O_2) is determined by the rapid equilibrium[5]

$$H_2O_2 + VO_2^+ = VO_3^+ + H_2O \quad K_f \qquad (5)$$

Appropriate plots of the integrated form of eq 4 were strictly linear for at least 80% of total reaction. The experimental conditions and values of k_a/K_f are summarized in Table I. It should be noted that the experiments with low (VO_2^+) were sensitive to the increasing concentration of this species as the reaction proceeded.

The values of k_a/K_f are independent of the (VO_2^+) and the reagent in excess. A small decrease in this ratio was observed as the (Cl^-) increased, while an increase was found with 0.20 M H^+ at $I = 1.0$ M.

Values of K_f equal to $(3.1 \pm 0.1) \times 10^4$, $(6.9 \pm 0.2) \times 10^4$, and $(1.4 \pm 0.1) \times 10^5$ M^{-1} were determined independently in 1.0 M $HClO_4$ at 25, 15, and 5 °C, respectively. These and interpolated values were used to estimate values of k_a; the results are summarized in Table I. It should be noted that the values determined for K_f are not very accurate (Experimental Section), but our value at 25 °C is in satisfactory agreement with the literature values.[5,6]

Oxidation of VO_3^+ by HOCl. Although our understanding of this reaction is rudimentary, we report preliminary results, since the role of HOCl relates to the Cl_2–VO_3^+ reaction.

The most straightforward results were obtained with large concentrations of HOCl and initially very low concentrations of Cl^- and Cl_2. Further, extremely low initial concentrations of VO^{2+} were present to minimize any contribution of the rapid HOCl–VO^{2+} reaction.[7] Under these conditions, plots of ln (VO_3^+) vs. time were linear for 50–60% of total reaction, with no detectable induction period. However, the rate of loss of VO_3^+ became progressively more rapid in the later stages of the reaction than could be accounted for on the basis of a pseudo-first-order process. Typical results are summarized in Table II.

Table II. Kinetic Results for the HOCl–VO_3^+ Reaction at 20.0 °C in 1.0 M $HClO_4$

$10^2[HOCl]_0$, M	$10^3[VO_3^+]_0$, M	$10^2[VO_2^+]_0$, M	$10^3 \times$ initial slope, s^{-1} [a]
6.53	1.18	1.44	3.9
6.52	1.16	0.469	4.9
13.1	1.16	1.44	8.6
6.53	1.72	1.39	4.3
6.53	0.708	1.49	3.8

[a] Obtained from plot of ln [VO_3^+] vs. time.

Table III. Kinetic Results for the Ag^+-Catalyzed Oxidation of VO_3^+ by $S_2O_8^{2-}$ [a]

$10^2 \times (S_2O_8^{2-})_0$, M	$10^2 \times (Ag^+)_0$, M	$10^3 \times (VO_2^+)_0$, M	$10^2 \times [VO^{2+}]_0$, M	$10^6 \times$ slope,[b] $M\ s^{-1}$	10^3k_4, $M^{-1}\ s^{-1}$ [c]
0.951	2.29	2.99		1.34	3.1_8
0.941	4.53	2.94		2.49	3.0_2
0.922	8.87	2.89		4.70	2.9_7
1.88	4.53	2.95		5.13	3.0_6
0.461	8.87	2.90		2.33	3.0_4
0.949	4.56	1.39		2.61	3.1_1
0.447	8.60	8.70		2.19	3.0_5
1.12	6.86	7.54		4.54	3.0_4
1.09	6.68	6.15	1.27	4.06	2.8_7
1.07	6.58	6.07	2.00	4.00	2.9_2
1.11[d]	9.05	6.28	4.65	5.63	2.8_8
1.10[e]	11.2	6.23	9.21	6.86[e] (7.20)[f]	2.7_8[e] (3.0_0)[f]

[a] Conditions: 20.0 °C, ($HClO_4$) = 0.95–1.05 M, $(VO_3^+)_0$ = (1.15–1.22) $\times 10^{-3}$ M, I = 1.05–1.11 M, and λ = 455 nm unless otherwise indicated. [b] From [VO_3^+] vs. time plot. [c] $k_4 = \text{slope}/2[Ag^+]_0[S_2O_8^{2-}]_{av}$, where $[S_2O_8^{2-}]_{av} = (S_2O_8^{2-})_0 - (VO_3^+)_0/4$. [d] I = 1.28 M. [e] I = 1.46 M. Plot linear for only 50% of total reaction. [f] Analyzed according to the integrated form of eq 20.

For the first half-life of the reaction, the empirical rate law is in fair agreement with eq 6. However, with lower concentrations of VO_2^+, a detectable rate enhancement was observed.

$$-d(VO_3^+)/dt = ((6.5 \pm 0.5) \times 10^{-2}\ M^{-1}\ s^{-1})(HOCl)(VO_3^+) \qquad (6)$$

The reaction rate is markedly enhanced by the initial presence of quite low concentrations of VO^{2+}. This rate enhancement persists far beyond the point where the HOCl–VO^{2+} reaction would be completed in the absence of VO_3^+. Unfortunately, we have been unable to determine the rate law under these conditions.

The Ag^+-Catalyzed Oxidation of VO_3^+ by $S_2O_8^{2-}$. Silver(I) has been found to be an effective catalyst for many peroxodisulfate oxidations,[8] and the VO_3^+ system proved to be no exception.

The reaction stoichiometry was found to correspond closely to eq 7. For example, values of $\Delta(VO_3^+)/(S_2O_8^{2-})_0 = 2.03$

$$S_2O_8^{2-} + 2VO_3^+ + 2H^+ \xrightarrow{Ag^+} 2HSO_4^- + 2VO^{2+} + 2O_2 \qquad (7)$$

and $(VO^{2+})_\infty/\Delta(VO_3^+) = 0.96$ were determined for a reaction mixture at 20 °C in 1.0 M $HClO_4$, with $(S_2O_8^{2-}) = 4.46 \times 10^{-4}$ M, $(VO_3^+)_0 = 1.22 \times 10^{-3}$ M, $(Ag^+)_0 = 0.823$ M, and $(VO_2^+)_0 = 1.61 \times 10^{-3}$ M.

Sufficiently high concentrations of Ag^+ and $S_2O_8^{2-}$ were usually used in the kinetic experiments to ensure pseudo-order dependences on these reagents. The reactions were monitored by measuring the disappearance of VO_3^+. Plots of $A - A_\infty$

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(4) Silverman, R. A. Thesis, University of Iowa, 1976.

(5) Orhanovic, M.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 278.

(6) (a) Dean, G. A. *Can. J. Chem.* **1961**, *39*, 1174. (b) Secco, F. *Inorg. Chem.* **1980**, *19*, 2722.

(7) Dreyer, K.; Gordon, G. *Inorg. Chem.* **1972**, *11*, 1174.

(8) Wilmarth, W. K.; Haim, A. In "Peroxide Reaction Mechanisms"; Edwards, J. O., Ed.; Interscience: New York, 1962; pp 194–200.

Table IV. Stoichiometric and Kinetic Results for the Oxidation of VO_3^+ by SO_4F^- in 1.0 M $HClO_4$

T, °C	$10^4 \times (SO_4F^-)_0$, M	$10^3 \times (VO_3^+)_0$, M	$10^3 \times (VO_2^+)_0$, M	$\Delta(VO_3^+)/(SO_4F^-)_0$[a]	$10^4 \times (VO^{2+})_\infty$, M	k_9,[b] $M^{-1}\ s^{-1}$
5.0	4.30	1.23	1.18	1.93 (1.96)	7.3	$10._0$
5.0	7.23	1.23	1.18			$10._2$
5.0	3.68	1.23	3.59	1.93 (1.97)	6.2	$10._4$
5.0[c]	3.39	1.26	1.15	1.92 (1.97)	5.8	$10._3$
10.0	3.31	1.24	1.17	1.85 (1.96)	5.6	$13._2$
10.0	3.50	1.23	3.51	1.91 (1.96)	6.1	$13._1$
15.0	3.33	1.25	1.94	1.93 (1.93)	5.7	$16._6$
15.0	3.43	1.21	3.53	1.86 (1.94)	5.6	$16._9$
20.0	3.50	1.24	1.95	1.91 (1.92)	6.0	$22._8$
20.0[d]	3.51	1.23	1.94	1.81		$21._7$
25.0	3.46	1.23	1.96	1.83 (1.89)		$27._8$
25.0[e]	3.00	1.23	1.95	1.94		$28._8$

[a] Experimental value listed first; value calculated by use of eq 27 given in parentheses. [b] Defined by eq 10. [c] $(HClO_4) = 0.25$ M; $(LiClO_4) = 0.75$ M. [d] Added $(VO^{2+})_0 = 1.04 \times 10^{-3}$ M. [e] Added $(VO^{2+})_0 = 5.20 \times 10^{-4}$ M.

vs. time were linear for at least 95% of total consumption of VO_3^+ except at the lowest $(S_2O_8^{2-})$, where the small consumption of the oxidant must be taken into account, and with very high concentrations of added VO^{2+}. The slopes of these pseudo-zero-order plots, converted to concentrations, are summarized in Table III along with the experimental conditions.

The values of the slopes divided by $2(Ag^+)_0(S_2O_8^{2-})_{av}$, where $(S_2O_8^{2-})_{av} = (S_2O_8^{2-})_0 - (VO_3^+)_0/4$, are reasonably constant. This feature, coupled with the reaction stoichiometry, establishes the empirical rate law as

$$-\tfrac{1}{2}d(VO_3^+)/dt = -d(S_2O_8^{2-})/dt = k_4(Ag^+)(S_2O_8^{2-}) \qquad (8)$$

The rates were independent of the excess (VO_2^+). No detectable effect of the VO^{2+} formed during the reaction was observed for either the kinetics or the stoichiometry. Concentrations of added VO^{2+} as great as 4.65×10^{-2} M had only a minor kinetic effect. However, at the highest (VO^{2+}) tested, the pseudo-zero-order plot deviated after approximately 50% of total reaction in the direction of a steadily decreasing slope.

The reaction rate was also monitored by measuring the loss of total (V(V)) at 356 nm, an isosbestic for VO_2^+ and VO_3^+. After complete consumption of the VO_3^+, the regrowth of VO_2^+, arising from the Ag^+-catalyzed oxidation of the VO^{2+} formed by $S_2O_8^{2-}$, was also monitored. These measurements were less precise, due both to rather small absorbance changes and to some uncertainty as to the separation of the two reactions. Nevertheless, both reactions conformed to eq 8; that is, $-d(V(V))/dt$ and subsequently, $d(V(V))/dt$ obeyed pseudo-zero-order kinetics. For example, when the sixth experiment in Table III was repeated but monitored at 356 nm, values of the rate parameter k_4 were $2.6 \times 10^{-3}\ M^{-1}\ s^{-1}$ (loss of V(V)) and $2.7 \times 10^{-3}\ M^{-1}\ s^{-1}$ (regrowth of V(V)), in fair agreement with that measured in the usual way. The kinetic profile is shown in Figure 1.

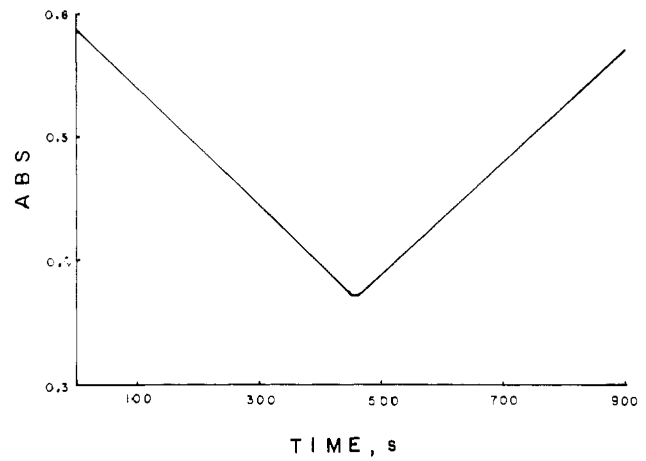

Figure 1. Kinetic plot of absorbance vs. time for the Ag^+-catalyzed oxidation of VO_3^+ by $S_2O_8^{2-}$. Conditions: $(VO_3^+)_0 = 1.22 \times 10^{-3}$ M, $(S_2O_8^{2-})_0 = 9.49 \times 10^{-3}$ M, $(Ag^+)_0 = 4.56 \times 10^{-2}$ M, $(HClO_4) = 1.0$ M, $T = 20.0$ °C, $\lambda = 356$ nm, and path length = 2.0 cm.

Oxidation of VO_3^+ by SO_4F^-. The stoichiometry in molar perchloric acid is approximately

$$SO_4F^- + 2VO_3^+ + 2H^+ = HSO_4^- + HF + 2VO^{2+} + 2O_2 \qquad (9)$$

The stoichiometric ratio $\Delta(VO_3^+)/(SO_4F^-)_0$ was determined in a number of experiments with excess (VO_3^+). The results, summarized in Table IV, indicate that the measured values are somewhat less than 2.0. The $(VO^{2+})_\infty$ formed during the reaction was estimated by the decrease in the total (V(V)). The measured values ranged from 87 to 92% of the $\Delta(VO_3^+)$. Thus, the stoichiometric results indicate that the *principal* overall reaction is eq 9.

The kinetic data were analyzed by plotting ln $((VO_3^+)/(SO_4F^-))$ vs. time, where the (SO_4F^-) was assumed to be equal to $(SO_4F^-)_0 - \Delta(VO_3^+)/2$. Such plots were linear for approximately 70% of total reaction. Values of the rate parameter k_9 appropriate to the empirical rate law

$$-d(SO_4F^-)/dt = k_9(SO_4F^-)(VO_3^+) \qquad (10)$$

are summarized in Table IV.

The kinetic results were not detectably affected by the initial presence of $(0.52–1.04) \times 10^{-3}$ M VO^{2+}, the excess (VO_2^+) over that required to complex most of the H_2O_2, or by substituting a medium of 0.25 M $HClO_4$ at $I = 1.0$ M for 1.0 M $HClO_4$. Thus we can assume that the VO^{2+} produced during the reaction, the small amounts of uncomplexed H_2O_2 present, and the trace amounts of VO_5^- are not playing a significant role in our experiments.

Activation parameters determined from the temperature dependence of k_9 are $\Delta H^\ddagger = 7._9$ kcal/mol and $\Delta S^\ddagger = -25$ cal/(deg mol).

The reaction stoichiometry is affected by the presence of substantial (VO^{2+}). The results of experiments designed to test this point are summarized in Table V.

The XeO_3–VO_3^+ System. Xenon trioxide is known to oxidize hydrogen peroxide rapidly in acid solution.[9] However, we find that the oxidation of VO_3^+ by XeO_3 is very slow, even under conditions where appreciable uncomplexed H_2O_2 is present. For example, at 20 °C with 1.18×10^{-3} M VO_3^+, 2.6×10^{-4}

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[9] (a) Haissinsky, M.; Heitz, C. *J. Chim. Phys. Physicochim. Biol.* **1973**, *70*, 737. (b) Thompson, R. C.; Appelman, E. H. *Inorg. Chem.* **1980**, *19*, 3248.

Table V. Stoichiometric Results[a] for the Oxidation of VO_3^+ by SO_4F^- in the Presence of Substantial $[VO^{2+}]$

T, °C	$10^4 \times [SO_4F^-]_0$, M	$10^3 \times [VO_3^+]_0$, M	$10^2 \times [VO^{2+}]$, M	$10^2 \times [VO^{2+}]_{av}$, M[b]	$10^4 \times [VO_3^+]_\infty$, M	$\Delta[VO_3^+]/(SO_4F^-)_0$	k_{11}/k_{10}[c]
5.0	4.65	1.58	0.761	0.798	7.43	1.81	0.034
5.0	5.92	1.24	0.759	0.799	2.52	1.67	0.039
5.0	6.19	1.58	1.71	1.75	6.07	1.57	0.045
5.0	8.66	1.57	3.78	3.81	3.66	1.39	0.037
5.0	6.71	1.26	7.59	7.60	4.54	1.21	0.043
							av 0.040 ± 0.004
20.0	4.83	1.54	0.749	0.787	6.82	1.79	0.037
20.0	5.65	1.54	1.71	1.75	6.00	1.67	0.029
20.0	9.09	1.54	3.78	3.81	3.04	1.36	0.039
							av 0.035 ± 0.004

[a] Conditions: $[HClO_4] = 0.72-0.95$ M, $[VO_2^+]_0 = (0.95-7.45) \times 10^{-3}$ M, $I = 0.97$ M. [b] $[VO^{2+}]_{av} = [VO^{2+}]_0 + \Delta[VO_3^+] - [SO_4F^-]_0$. [c] Calculated by use of eq 28.

M VO_2^+, 1.2×10^{-4} M H_2O_2, and 1.28×10^{-3} M XeO_3 in molar perchloric acid, less than 2% of the VO_3^+ is lost after 25 min. This result indicates that the oxidation of VO_3^+ by XeO_3 is very slow and that the otherwise rapid XeO_3–H_2O_2 reaction is severely inhibited by VO_3^+.

Discussion

The Cl_2–H_2O_2 reaction in acidic solution has been the subject of numerous experimental studies and mechanistic discussions.[3,10] It now appears that the mechanism first suggested by Bray and substantiated by Connick[3c] and more recently by Held, Halko, and Hurst[3e] is the most probable.

$$H_2O_2 + Cl_2 \xrightleftharpoons[k_2]{k_1} H^+ + Cl^- + HOOCl \tag{11}$$

$$HOOCl \xrightarrow{k_3} O_2 + H^+ + Cl^- \tag{12}$$

The resulting rate law is

$$-d(H_2O_2)/dt = \frac{k_1k_3(H_2O_2)(Cl_2)}{k_2(H^+)(Cl^-) + k_3} \tag{13}$$

Our kinetic analysis of the Cl_2–VO_3^+ reaction requires that the major pathway involves the oxidation of the trace amounts of uncomplexed H_2O_2. This is a remarkable observation in view of the very small ratios of $(H_2O_2)/(VO_3^+)$ present in the kinetic experiments. Apparently nucleophilic displacement of Cl^- from Cl_2 by the *complexed* peroxide moiety is quite unfavorable.

An important test of our interpretation lies in a comparison of our value of the rate constant for the bimolecular reaction between Cl_2 and H_2O_2 with those previously reported. A plot of $1/k_a$ vs. (Cl^-) is reasonably linear, as predicted by eq 13, and yields values of $k_1 = 108$ M^{-1} s^{-1} and $k_2/k_3 = 0.52$ M^{-2} in 1.0 M $HClO_4$ at 20 °C. These values are not precise particularly since the value of the formation constant for VO_3^+ is uncertain. Connick's data allow an estimate of $k_1 = 134$ M^{-1} s^{-1} at 20 °C and zero ionic strength.[3c] A value of $k_2/k_3 = 1.6$ M^{-2} has been calculated by Kustin and Davies[10] through their analysis of Markower and Bray's data[3a] at 25 °C in solutions of HCl ranging from 0.36 to 5.3 M. None of these values is accurate, and the experimental conditions varied enormously. Nevertheless, we consider the comparison in a qualitative sense as support for our interpretation of the Cl_2–VO_3^+ system.

Values of $\Delta H^\ddagger = 8$ kcal/mol and $\Delta S^\ddagger = -22$ cal/(deg mol) for the net activation process

$$Cl_2 + H_2O_2 = (HOOCl)^\ddagger + H^+ + Cl^- \tag{14}$$

were determined from the temperature dependence of the rate parameter k_a/K_f: the values have been corrected for the temperature dependence of K_f. Connick estimates $\Delta H^\ddagger = 10$ kcal/mol and $\Delta S^\ddagger = -15$ cal/(deg mol) for the same process.[3c]

The rate enhancement of the Cl_2–VO_3^+ reaction at lower acidities is puzzling. The experimental conditions maintained the same low levels of HOCl as in many of the experiments in 1.0 M $HClO_4$. Possible involvement of VO_5^- appears unlikely since the rate constant k_a was independent of (VO_2^+).

The HOCl–VO_3^+ system is clearly complex, but our preliminary results preclude significant involvement of HOCl in the Cl_2–VO_3^+ reaction. The simplest analysis of the HOCl data points to a direct reaction with VO_3^+, but in view of the rate enhancement at later stages in the reaction even this conclusion is not certain. The formation of trace amounts of VO^{2+} during the reaction is an attractive possibility, but we have been unable to devise any scheme that allows for this and is consistent with the kinetic data. Further, invoking the formation of a reactive H_2OCl_2 species[3e] via the back-reaction of Cl^- (formed during the HOCl–VO_3^+ reaction) with HOCl does not account for the observations. The HOCl–VO_3^+ reaction certainly merits further investigation, as does a possible HOCl–H_2O_2 reaction under conditions where little or no Cl_2 is initially present.

The silver(I)-catalyzed oxidation of VO_3^+ by $S_2O_8^{2-}$ is a remarkably clean reaction in view of the complex behavior reported[11] for the same catalyzed oxidation of H_2O_2. The probable mechanism for our system is shown in (15)–(18),

$$S_2O_8^{2-} + Ag^+ \xrightarrow{k_4} SO_4^{-}\cdot + SO_4^{2-} + Ag^{2+} \tag{15}$$

$$SO_4^{-}\cdot + Ag^+ \xrightarrow{k_5} SO_4^{2-} + Ag^{2+} \tag{16}$$

$$Ag^{2+} + VO_3^+ \xrightarrow{k_6} Ag^+ + VO_3^{2+}\cdot \tag{17}$$

$$VO_3^{2+}\cdot \xrightarrow{k_7} VO^{2+} + O_2 \tag{18}$$

where reaction 15 is rate determining. Consumption of the $SO_4^{-}\cdot$ radical other than by eq 16 is unlikely in view of the very large rate constant[12] and the relatively high (Ag^+), although reaction with VO_3^+ would not alter our results. We have shown previously[1] that VO_3^+ is more reactive toward

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(10) Davies, G.; Kustin, K. *Inorg. Chem.* **1973**, *12*, 961.

(11) (a) Stehlik, B.; Nechutova, E. *Acta Fac. Rerum Nat. Univ. Comenianae, Chim.* **1968**, 27 (*Chem. Abstr.* **1969**, *71*, 64684z). (b) Tsao, M.; Wilmarth, W. K. *Discuss. Faraday Soc.* **1960**, *29*, 137.

(12) Walling, C.; Camaioni, D. M. *J. Org. Chem.* **1978**, *43*, 3266.

(13) Thompson, R. C. *Inorg. Chem.* **1981**, *20*, 1005.

(14) Honig, D. S.; Kustin, K.; Martin, J. F. *Inorg. Chem.* **1972**, *11*, 1895.

(15) Thompson, R. C.; Appelman, E. H. *Inorg. Chem.* **1981**, *20*, 2114.

(16) (a) Koppenol, W. H. *Nature* (*London*) **1976**, *262*, 420. (b) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.

(17) Gordon, G. *Proc. XIII Int. Conf. Coord. Chem., 13th* **1970**, 11.

(18) Connor, J. A.; Ebsworth, E. A. V. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 279.

$SO_4^{-}\cdot$ than is VO^{2+}. Considerable support for reactions 17 and 18 comes from our previous paper[1] and the invariably rapid reactions of Ag^{2+}.[19]

The measured value of k_4 in this study is in excellent agreement with that determined in other systems.[8,13] Presumably the straightforward results reported here arise from reaction 18; with H_2O_2, the HO_2 formed is at least partially oxidized by $S_2O_8^{2-}$, triggering a complex chain reaction.[11] These considerations also point to a lack of oxidation of uncomplexed H_2O_2 by Ag^{2+} in our experiments, even though this reaction is known to be very rapid.[14]

The kinetic plots were of poorer quality for experiments with high initial concentrations of VO^{2+}. The last experiment in Table III was reanalyzed by adding reaction 19 to the mechanism.

$$Ag^{2+} + VO^{2+} + H_2O \xrightarrow{k_8} Ag^+ + VO_2^+ + 2H^+ \quad (19)$$

The resulting rate equation is

$$-d(VO_3^+)/dt = 2k_4(S_2O_8^{2-})(Ag^{2+})/(1 + k_8(VO^{2+})_0/k_6(VO_3^+)) \quad (20)$$

The appropriate plot of the integrated form of eq 20, using a best fit value of $k_8/k_6 = 5.4 \times 10^{-4}$, yields linear behavior for ca. 90% consumption of the VO_3^+. While this analysis does not give a reliable value of k_8/k_6, it is consistent with the conclusion that VO_3^+ is much more reactive toward Ag^{2+} than is VO^{2+}.

The major features of the SO_4F^-–VO_3^+ reaction are in harmony with the reaction scheme (21)–(23), where reaction

$$SO_4F^- + VO_3^+ \xrightarrow[H^+]{k_9} SO_4^{-}\cdot + VO_3^{2+}\cdot + HF \quad (21)$$

$$SO_4^{-}\cdot + VO_3^+ \xrightarrow[H^+]{k_{10}} HSO_4^- + VO_3^{2+}\cdot \quad (22)$$

$$VO_3^{2+}\cdot \xrightarrow{k_7} VO^{2+} + O_2 \quad (23)$$

21 is rate determining. The involvement of the sulfate radical anion is not established by our results but is likely in view of previous studies.[9b,15] The ratio of the rate constants for the reduction of $SO_4^{-}\cdot$ by VO_3^+ and VO^{2+} has been estimated[1] as 38. Thus it may be shown that no more than 1% of the VO^{2+} formed during the reactions without the initial presence of VO^{2+} will be competitively oxidized by the presumed $SO_4^{-}\cdot$ intermediate.

The decomposition of SO_4F^- is not entirely negligible under our experimental conditions.

$$SO_4F^- \xrightarrow{k_d} \text{products} \quad (24)$$

Kinetic data for reaction 24 are available.[9b,15] Stoichiometric data indicate that approximately equal amounts of H_2O_2 and HSO_5^- are produced.[9b] In our experiments, H_2O_2 would be rapidly complexed to re-form VO_3^+, while HSO_5^- would react[13] with VO^{2+} to result in the net loss of one VO_3^+ per HSO_5^- formed. Thus, the following consequences of reaction 24 would be anticipated:

$$-d(SO_4F^-)/dt = k_9(SO_4F^-)(VO_3^+) + k_d(SO_4F^-) \quad (25)$$

and

$$-d(VO_3^+)/dt = 2k_9(SO_4F^-)(VO_3^+) \quad (26)$$

The resulting calculated stoichiometry is

$$\Delta(VO_3^+)/(SO_4F^-)_0 = 2 - (k_d/[k_9(SO_4F^-)_0]) \ln ((VO_3^+)_0/(VO_3^+)_\infty) \quad (27)$$

for experiments with excess VO_3^+. Values of the stoichiometric ratio calculated in this manner are given in parentheses in Table IV. A comparison of the experimental and calculated values indicates that the small deviations from a limiting value of 2.00 are largely accounted for by consideration of the decomposition of SO_4F^-. This decomposition is a minor pathway that does not significantly affect the kinetic results.

The experiments with rather high concentrations of VO^{2+} allow an estimate of the ratio of rate constants for the reduction of the presumed $SO_4^{-}\cdot$ intermediate by VO^{2+} (k_{11}) and VO_3^+ (k_{10}).

$$(SO_4F^-)_0 = \frac{\Delta(VO_3^+)}{2} + \frac{k_{11}(VO^{2+})_{av}}{4k_{10}} \ln \frac{2(VO_3^+)_0 + k_{11}(VO^{2+})_{av}/k_{10}}{2(VO_3^+)_\infty + k_{11}(VO^{2+})_{av}/k_{10}} \quad (28)$$

These values are summarized in the last column of Table V and are in fair agreement with the value 0.026 reported previously[1] at 20 °C in 1 M perchloric acid.

We have found several distinct pathways for the oxidation of VO_3^+ in acidic solution. (i) A direct one-electron oxidation was found to produce the proposed $VO_3^{2+}\cdot$ radical cation, which may be viewed formally as a complex between oxovanadium(V) and the superoxide ion. To date, the only fate of this intermediate appears to be an internal redox process that produces VO^{2+} and O_2. Thermodynamic considerations[3e,16] do not preclude the formation of single oxygen, but our data are inadequate to test this point. Oxidants that exhibit this mode of reaction are Co^{3+}, SO_4F^-, Ag^{2+}, and presumably $SO_4^{-}\cdot$. All are strong oxidants, and only SO_4F^- is potentially capable of involvement in a two-electron process. Fortunately, all of these oxidants are much more reactive toward VO_3^+ than VO^{2+}. (ii) There is an indirect one-electron oxidation of VO_3^+ via reaction induced by VO^{2+}. Peroxomonosulfate, HSO_5^-, utilizes this pathway, and under most conditions the reaction is strictly catalyzed by VO^{2+}. We suspect that a number of additional multiequivalent oxidants would fall into this category. Certainly BrO_3^- gives strong indications, but our preliminary results have indicated that the reaction kinetics are quite complicated. (iii) We found indirect oxidation by reaction with the small concentrations of H_2O_2 in rapid equilibrium with VO_3^+. Aqueous Cl_2 is the only oxidant demonstrated to behave in this manner, but others such as XeO_3 may. Gordon has suggested that two-electron-transfer mechanisms are possible only in inner-sphere reactions.[17] The extension of this proposal to two-electron oxidations of hydrogen peroxide would require the involvement of peroxo complexes. This pathway may be quite unfavorable when the peroxide moiety is complexed to vanadium(V). In any event, we have not observed a fourth category involving a two-electron oxidation of VO_3^+ to form O_2 directly.

We conclude that studies of the oxidation of peroxo complexes can yield useful information. A number of additional peroxo complexes are known,[18] but vanadium(V) has the desirable redox potential that allows it to oxidize a coordinated superoxide ion rapidly but to be quite unreactive toward a coordinated peroxide ion. The use of additional experimental techniques, particularly ESR and cyclic voltammetry, may provide results that substantially broaden our understanding of these processes and the redox behavior of hydrogen peroxide itself.

Registry No. Ag, 7440-22-4; Cl, 7782-50-5; HOCl, 7790-92-3; $S_2O_8^{2-}$, 15092-81-6; FSO_4^-, 15181-47-2; VO_3^+, 12179-36-1.

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[19] Huchital, D. H.; Sutin, N.; Warnqvist, B. *Inorg. Chem.* **1967**, *6*, 838.