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Article

Oxidation of Vanadium(III) by Hydrogen Peroxide and the Oxomonoperoxo Vanadium(V) Ion in Acidic Aqueous Solutions: A Kinetics and Simulation Study

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The reaction between vanadium(III) and hydrogen peroxide in aqueous acidic solutions was investigated. The rate law shows first-order dependences on both vanadium(III) and hydrogen peroxide concentrations, with a rate constant, defined in terms of -d[H_2O_2]/d*t*, of 2.06 ± 0.03 L mol^{-1} s^{-1} at 25 °C; the rate is independent of hydrogen ion concentration. The varying reaction stoichiometry, the appreciable evolution of dioxygen, the oxidation of 2-PrOH to acetone, and the inhibition of acetone formation by the hydroxyl radical scavengers, dimethyl sulfoxide and sodium benzoate, point to a Fenton mechanism as the predominant pathway in the reaction. Methyltrioxorhenium(VII) does not appear to catalyze this reaction. A second-order rate constant for the oxidation of V^{3+} by $OV(O_2)^+$ was determined to be 11.3 ± 0.3 L mol^{-1} s^{-1} at 25 °C. An overall reaction scheme consisting of over 20 reactions, in agreement with the experimental results and literature reports, was established by kinetic simulation studies.

Introduction

The oxidation of transition metal complexes by hydrogen peroxide has been investigated for more than a century,[1,2] with continuing efforts since that time.[3,4] Despite an extensive literature pertaining to mechanisms, no consensus has been reached; indeed, the area has been characterized by controversy.[5−8] A major issue is whether hydroxyl radicals are formed initially or not; an alternative to this is direct oxo-group transfer. The pathway that generates $HO^•$ is termed the Fenton mechanism, and the other is the oxo mechanism. These alternatives are sometimes referred to as the 1e and 2e pathways, which is stoichiometrically correct but mechanistically misleading in that both represent group-transfer reactions of OH or O, not electron transfer per se. It now seems clear that no single mechanism encompassing different metals and ligands will suffice, not even for hydrated ions, $M(H_2O)_m{}^{n+}$. Even with a single metal participant, such as iron(II), controversies are still apparent, and the issue is even less well-resolved when ligands other than water are present.

One part of this article presents the results of the previously unstudied[9] reaction between $V(H_2O)_6{}^{3+}$ and H_2O_2. This reducing agent constitutes an attractive participant because, of all the M^{n+} ions, it forms stable oxocations, $V^{IV}O^{2+}$ and $V^{V}O_2{}^+$. Therefore, either a Fenton or an oxo initial step might provide a feasible pathway. The likelihood of an oxo mechanism may, however, be greater for V^{3+} than in other cases where the oxo product lies at high Gibbs energy, such as FeO^{2+} from Fe^{2+} or CrO^{2+} from Cr^{2+}. Using V^{3+} as the example, therefore, and omitting, for the sake of simplicity, the coordinated water molecules from species that are generally six-coordinate, we write the alternative initial steps and the accompanying changes in Gibbs free energy as follows:[10]

$$\text{Fenton:}\ V^{3+} + H_2O_2 \rightarrow VO^{2+} + HO^{\bullet} + H^+ \qquad \Delta G_1^\circ = -35\ \text{kJ mol}^{-1} \quad (1)$$

$$\text{Oxo:}\ V^{3+} + H_2O_2 \rightarrow VO_2{}^+ + 2H^+ \qquad \Delta G_2^\circ = -211\ \text{kJ mol}^{-1} \quad (2)$$

Following each of these will be much faster steps that may lead to simple limiting net reactions if conditions are selected

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appropriately. In particular, if $[V^{3+}]_0 \gg [H_2O_2]$ the intermediates in eq 1 and 2 can be expected to react further with V^{3+}

$$V^{3+} + HO^{\bullet} \rightarrow VO^{2+} + H^+ \quad \Delta G_3^\circ = -240 \text{ kJ mol}^{-1} \quad (3)$$

$$V^{3+} + VO_2^{\ +} \rightarrow 2\,VO^{2+} \quad \Delta G_4^\circ = -64 \text{ kJ mol}^{-1} \quad (4)$$

Thus, *in this limit*, the net reaction would be given by eq 5, which is eq 1 + 3 and eq 2 + 4

$$2V^{3+} + H_2O_2 = 2VO^{2+} + H_2O + 2H^+ \qquad \Delta G_5^\circ = -275 \text{ kJ mol}^{-1} \quad (5)$$

Other reactions make the matter more complex, particularly when vanadium(III) is not in such a large excess. These include other reactions of $HO^{\bullet}$ and $VO_2^{\ +}$, which will lead to an overall stoichiometry that is not well represented by eq 5. These matters will be taken up subsequently as a part of the interpretation of the experimental data. Other reactions of vanadium ions with peroxides and oxy-radicals in acidic solutions have been studied previously,[9,11−20] providing data that proved to be helpful in interpreting the results obtained in this study. It has been reported that both pathways are operative in the reaction between V^{3+} and Cl_2(aq), with 1e oxidation predominating.[21]

The second part of this article examines the question of whether methyltrioxorhenium(VII), CH_3ReO_3, known as MTO, catalyzes reaction 2. This is pertinent because MTO is a catalyst for the general oxo-transfer process[22−27]

$$X + H_2O_2 = XO + H_2O \quad (6)$$

in which X is an electron-rich oxo-group-acceptor, PR_3, RSR′, alkene, etc. The active intermediate forms of MTO are the oxo-peroxo complexes $CH_3ReO_2(O_2)$ and $CH_3ReO(O_2)_2(OH_2)$. The following three possibilities occur to us: (1) reaction 2 occurs naturally and MTO increases its rate, (2) reaction 1 occurs without MTO but reaction 2 takes precedence when MTO is present, and (3) MTO has little or no effect.

The third part of this article examines a possible reaction between V^{3+} and the oxoperoxovanadium(V) ion, $OV(O_2)^+$. We have learned that a reaction does take place. A number of stoichiometric equations can be written for V^{3+} with $OV(O_2)^+$, and stoichiometry is one of the issues. Peroxo complexes of transition metal complexes have been employed as oxygen-atom-transfer reagents for many organic substrates, yet their reactions with metal complexes have been little studied.[28] In the case at hand, $OV(O_2)^+$ is in a relatively rapid equilibrium with $VO_2^{\ +}$ and hydrogen peroxide, eq 7.[17]

$$VO_2^{\ +} + H_2O_2 = OV(O_2)^+ + H_2O \qquad K_7 = 3.5 \times 10^4 \text{ L mol}^{-1} \quad (7)$$

Experimental Section

Materials. Solutions of V^{3+} in perchloric acid were prepared by the reaction of VO^{2+} and a stoichiometric amount of V^{2+} under argon, and the solutions were used the day they were prepared to avoid perchlorate reduction, which occurs quite slowly.[29,30] Solutions of vanadyl perchlorate were prepared by two methods. One method was based on the reaction in solution between vanadyl sulfate and a slight excess of barium perchlorate, followed by the removal of the barium sulfate by filtration. The other method used the reaction of V_2O_5 and excess V_2O_3 (Aldrich) in perchloric acid; the reaction was allowed to proceed until the VO^{2+} concentrations determined spectrophotometrically at 760 nm ($\epsilon = 17.5$ L mol^{-1} cm^{-1}) and 250 nm ($\epsilon = 230$ L mol^{-1} cm^{-1}) agreed. Then, the undissolved material was removed by filtration, and the concentration of VO^{2+} was determined spectrophotometrically at 760 nm. The experiments using these two methods for VO^{2+} gave the same results. Solutions of V^{2+} were prepared by reduction of VO^{2+} with zinc amalgam under argon. Solutions of hydrogen peroxide were analyzed by iodometric titration. Solutions of the oxo(monoperoxo)vanadium(V) were prepared by mixing $VO_2^{\ +}$ with a slight (ca. 5%) excess of H_2O_2 shortly before use. Ionic strength was controlled with lithium perchlorate.

Instruments. Kinetics measurements were performed with conventional UV−vis spectrophotometers (Shimadzu UV-2101/3101PC) or stopped-flow instruments (OLIS−RSM) for faster reactions. Quartz cuvettes with appropriate optical path lengths (1−5 cm) were used. The kinetics were studied at 25.0 ± 0.2 °C; the temperature was maintained by either an electronic thermostatic holder or a circulating water thermostatic system. The ^{1}H NMR measurements were conducted on Bruker DRX-400 MHz or Varian VXR-400 MHz spectrometers at 25.0 °C. The oxygen evolution experiments were carried out with an YSI Model 5300 biological oxygen monitor at 25.0 °C. The concentration of O_2 in a product solution was determined in reference to the oxygen levels in pure

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water saturated with air and O_2. The solubility of O_2 at 25 °C was taken as 1.27 mmol L^{-1}.[31]

Kinetics. The absorbance-time traces were primarily recorded at 760 nm, for the build-up of VO^{2+} for the $V^{3+}-H_2O_2$ reaction, and at 455 nm ($\epsilon = 280$ L mol^{-1} cm^{-1}), for the disappearance of $OV(O_2)^+$ in the $V^{3+}-OV(O_2)^+$ reaction. Occasionally, the consumption of V^{3+} was monitored at 398 nm ($\epsilon = 8.4$ L mol^{-1} cm^{-1}) as a check for the $V^{3+}-H_2O_2$ reaction. The absorbance-time data were fitted to pseudo-first-order kinetics using the program KaleidaGraph. The reactions of VO^{2+} and V^{3+} with the 1-hydroxy-1-methylethyl radical, $^{\bullet}CMe_2OH$, were measured by kinetic competition methods according to the literature.[32] The kinetic simulation studies were performed with the program KINSIM version 4.0.[33]

Results

General Observations. Only when the initial ratio of V^{3+} to H_2O_2 is quite large (see next section) are the data straightforward. With lower ratios of V^{3+}/H_2O_2, the reaction stoichiometry deviates from eq 5, the intermediate $OV(O_2)^+$ can be detected, appreciable amounts of O_2 are evolved, and the addition of 2-propanol suppresses O_2 evolution but leads to acetone formation, which can be inhibited by addition of other $HO^{\bullet}$ scavengers, such as Me_2SO. Taken together, these observations establish that radical intermediates are involved. Upon further experimental studies and analysis, especially by kinetics simulations of a large group of chemical reactions, all of the data are consistent with the Fenton mechanism.

Reactions Under "Simple" Conditions: A Large Excess of V^{3+}. Under such conditions, the reaction conforms to eq 5, and the only detected vanadium product was VO^{2+}. The stoichiometric ratio, $\Delta[V]/[H_2O_2]_0$, determined by measuring the absorbance change for the reactant V^{3+} at 398 nm, the product VO^{2+} at 760 nm, or both before and after the reaction, approached 2:1. The average value is 1.9 ± 0.1 in >10 determinations. The important parameter in maintaining this stoichiometry is not the absolute concentrations of V^{3+} and H_2O_2, but their initial ratio.

Kinetics experiments with a large excess of V^{3+} were carried out at 25.0 °C and 1.0 mol L^{-1} H^+ with an ionic strength of 2.0 mol L^{-1}, maintained with lithium perchlorate. The initial concentrations of V^{3+} and H_2O_2 were varied in the ranges 5−160 and 0.5−7.4 mmol L^{-1}, respectively. The initial concentration ratio, $[V^{3+}]_0/[H_2O_2]_0$ was held ≥10 to ensure pseudo-first-order kinetics and, especially, to maintain the simple 2:1 stoichiometry. The absorbance−time traces were fitted by a nonlinear least-squares program to the equation

$$\text{abs}_t = \text{abs}_\infty + (\text{abs}_0 - \text{abs}_\infty)\exp(-k_{\text{obs}}t) \qquad (8)$$

Values of k_{obs} were directly proportional to the average $[V^{3+}]$ in each experiment, as shown in Figure 1. The linearity of the plot established a first-order dependence on vanadium(III) concentration. Thus, the rate law that defines the kinetic orders and the rate constant is

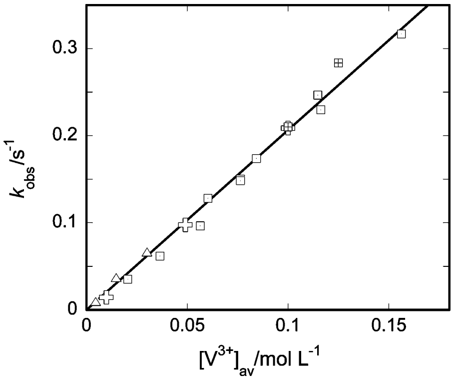

Figure 1. Pseudo-first-order rate constants, k_{obs}, for the reaction between V^{3+} and H_2O_2 on the average $[V^{3+}]$ in experiments in which V^{3+} is in large stoichiometric excess over H_2O_2. The conditions are as follows: 25 °C, 1.0 mol L^{-1} $HClO_4$, and I = 2.0 mol L^{-1} ($LiClO_4$). The initial concentrations of H_2O_2 (mmol L^{-1}) were 0.52 (triangles), 1.86 (pluses), 3.45 (squares), and 7.46 (hatched squares).

$$-\frac{d[H_2O_2]}{dt} = k[H_2O_2][V^{3+}] \qquad (9)$$

The slope of the line gives the value of the second-order rate constant as 2.06 ± 0.03 L mol^{-1} s^{-1}, independent of the hydrogen ion concentration, 0.3−1.3 mol L^{-1}, and ionic strength, 0.5−3.0 mol L^{-1}. Whereas this group of stoichiometric and kinetics determinations confirm eq 5 and provide a value for the rate constant of the initial step, eq 1 or 2, they do not, by their simplicity, address the principal issue as to which mechanism is used, Fenton or oxo. As cited in the opening section of the Results, the complications that are evident under lower concentrations define the initial mechanism as a Fenton reaction.

General Observations at Lower Vanadium(III) Concentrations. Many complications set in when a large excess of V^{3+} was not used, indicating radical intermediates and, thus, a Fenton-type mechanism with eq 1 as its initial step. With excess H_2O_2, some oxygen was released, but O_2 formation was suppressed by the addition of 2-propanol. With a large excess of H_2O_2, the final vanadium products were the red-yellow oxo-peroxo vanadium species, $OV(O_2)^+$ and $OV(O_2)_2^-$. With comparable amounts of V^{3+} and H_2O_2, the reaction stoichiometry was no longer 2:1. Other reactions consume H_2O_2 and oxidize V^{3+}. In such a scenario, the formation of small concentrations oxo-peroxo species $OV(O_2)^+$ could be observed at its absorption maximum 455 nm.

Stoichiometry and Products. When the amounts of the two reactants were comparable, the reaction stoichiometry varied depending upon the ratio of starting materials. Some selected results are given in Table 1. The calculated values from kinetic simulation, as described later, are also listed for comparison.

When H_2O_2 (usually >10 mmol L^{-1}) was in excess, the release of gaseous dioxygen from the solution was observed and the significant formation of bubbles prevented spectrophotometric measurement under these conditions, as in the

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Table 1. Stoichiometry Determinations of the $V^{3+}-H_2O_2$ Reaction[a]

entry	$[V^{3+}]_0$	$[H_2O_2]_0$	$\Delta[V]/[H_2O_2]_0$		$\Delta[V]/[H_2O_2]_0$[b]	
			observed	simulated	observed	simulated
1	119.2	3.45	1.90	1.98	0.88	1.18
2	31.97	5.62	1.56	1.62	0.70	0.60
3	12.79	5.62	1.24	1.35	0.61	0.40

[a] Reactions were carried out in 1.0 mol L^{-1} $HClO_4$ at 25.0 °C. In millimoles per liter. [b] In the presence of 0.87 mol L^{-1} 2-PrOH.

Table 2. Yields of O_2 in the $V^{3+}-H_2O_2$ Reaction[a]

entry	$[V^{3+}]_0$	$[H_2O_2]_0$	O_2 produced	O_2 calculated
1	2.44	1.04	0.17	0.17
2	4.88	1.04	0.14 (0.009[b])	0.11
3	9.75	1.04	0.095	0.054
4	10.56	5.20	0.77	0.89
5	0.81	2.60	0.62[c]	0.57[c]

[a] Reactions were carried out in 1.0 mol L^{-1} $HClO_4$ at 25.0 °C. In millimoles per liter. [b] In the presence of 0.43 mol L^{-1} 2-PrOH. [c] Yield within 40 min. It continued to grow slowly.

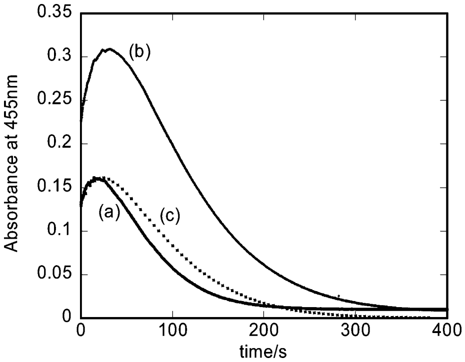

Figure 2. Absorbance−time profile of $OV(O_2)^+$ in the $V^{3+}-H_2O_2$ reaction. The conditions are as follows: 25.0 °C, 1.0 mol L^{-1} $HClO_4$, and 5 cm optical length. The profiles shown are (a) 10.2 mmol L^{-1} V^{3+} and 5.22 mmol L^{-1} H_2O_2, (b) 10.2 mmol L^{-1} V^{3+} and 10.4 mmol L^{-1} H_2O_2, and (c) a simulated profile with 10s delay with 10.2 mmol L^{-1} V^{3+} and 5.22 mmol L^{-1} H_2O_2.

Table 3. Yields of Acetone in the $V^{3+}-H_2O_2$ Reaction[a]

entry	$[V^{3+}]_0$	$[H_2O_2]_0$	acetone produced	acetone calculated
1	40.63	2.60	2.1	1.4
2	10.83	5.20	4.6	4.1
3	10.83	5.20	0.35[b] (1.1[c])	

[a] Reactions were carried out in 1.0 mol L^{-1} $HClO_4$ at 25.0 °C in the presence of 43.5 mmol L^{-1} 2-PrOH. In millimoles per liter. [b] In the presence of 157 mmol L^{-1} DMSO. [c] In the presence saturated sodium benzoate.

$Fe^{2+}-H_2O_2$ system.[34] The overall reaction was the oxidation/peroxidation of vanadium(III) to oxoperoxovanadium(V) ions and the vanadium-catalyzed decomposition of H_2O_2 to O_2 and H_2O. Even with excess V^{3+}, O_2 was still generated. The yield of dioxygen was measured with an oxygen electrode under conditions selected so that the maximum yield did not exceed the solubility of O_2 in water. A number of determinations are listed in Table 2.

It was noted previously that the formation of the monoperoxo vanadium species, $OV(O_2)^+$, occurs well before the completion of VO^{2+} oxidation, even without excess H_2O_2.[19] Two experiments were carried out accordingly, monitoring the spectral change at 455 nm, the maximum absorption of $OV(O_2)^+$, using a cell with a 5 cm optical length. The fast rise and slower fall of absorbance clearly showed the formation of $OV(O_2)^+$ during the reaction, Figure 2. The peak concentrations of $OV(O_2)^+$ were (a) 1.2×10^{-4} and (b) 2.2×10^{-4} mol L^{-1}. A simulated $OV(O_2)^+$−time profile is also shown in Figure 2c.

Reaction in the Presence of 2-PrOH. The effect of alcohol on the reaction stoichiometry and kinetics was examined. When a large amount of 2-propanol (2-PrOH), typically 0.87 mol L^{-1}, was present, the $\Delta[V]/[H_2O_2]$ value was found to be approximately half of that without an alcohol. For example, in reactions where a large excess of V^{3+} was employed, the stoichiometry determined was close to 1:1 (see Table 1). In the meantime, dioxygen release was largely inhibited (entry 2, Table 2). The organic species produced in the reaction were examined by ^1H NMR spectroscopy using deuterated water as solvent. This revealed the generation of a significant amount of acetone; no other organic product was detected. The yields of acetone were estimated by comparing the integrations of the acetone with the remaining 2-PrOH peaks, assuming mass conservation of acetone and 2-PrOH (Table 3). In the presence of another hydroxyl radical scavenger (e.g., dimethyl sulfoxide (DMSO) or sodium benzoate) the yield of acetone greatly decreased but did not disappear completely.

The kinetic measurements were then carried out in the presence of a large excess of 2-propanol (0.87 M). Again a linear relationship was found between k_{obs} and the average $[V^{3+}]$. This yielded a second-order rate constant of 2.32 ± 0.06 L mol^{-1} s^{-1}, essentially same as that without 2-propanol.

Reaction in the Presence of MTO. A series of experiments was carried out in the presence of up to 20 mol % (relative to H_2O_2, the limiting reagent) of MTO. The progress of the reaction was similar to that without MTO, except that after over 90% completion of the reaction, a much slower, yet constant increase in the absorbance at 760 nm was observed with MTO. Kinetic analysis using the data before 90% completion yielded a rate constant of 2.11 ± 0.03 L mol^{-1} s^{-1}, identical to the value obtained without MTO, indicating that the presence of MTO has little or no effect on the rate of reaction between V^{3+} and H_2O_2. The control experiment showed that MTO itself reacted slowly with V^{3+} to produce VO^{2+}, presumably via one-electron transfer, a manner analogous to the reduction of MTO by Eu^{2+} or Cr^{2+}, although the details were not further pursued.

Kinetic Simulation. Because of the complicated nature of vanadium chemistry, kinetic modeling studies were carried out to assist in the analysis of the experimental data, in an attempt at establishing the overall reaction scheme of the vanadium−hydrogen peroxide system in acidic aqueous solutions. Most known reactions involving vanadium ions and hydrogen peroxide, thoroughly studied or merely postulated, were considered in the reaction scheme. Reactions with known rate constants were generally included. When the rate constants in 1.0 mol L^{-1} $HClO_4$ were not available and could not be obtained by calculation or extrapolation from literature information, values at the closest conditions were taken or estimated via simulation.

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Table 4. Reactions between V^{3+} and H_2O_2 in Acidic Aqueous Solutions

	chemical equation	k[a,b,c]	ref
A	$V^{3+} + H_2O_2 \rightarrow VO^{2+} + {}^{\bullet}OH + H^+$	2.06	this work
B	$V^{3+} + {}^{\bullet}OH \rightarrow VO^{2+} + H^+$	(5×10^7)	−
C	$VO^{2+} + H_2O_2 \rightarrow VO_2^+ + {}^{\bullet}OH + H^+$	0.21[d]	18
D	$VO^{2+} + {}^{\bullet}OH \rightarrow VO_2^+ + H^+$	6.4×10^8	19
E	$VO_2^+ + H_2O_2 \rightarrow OV(O_2)^+ + H_2O$	$k_+ = 5.3 \times 10^3$, $k_- = 0.15$[e]	17
F	$OV(O_2)^+ + {}^{\bullet}OH \rightarrow VO_2^+ + HOO^{\bullet}$	2.1×10^{10}	39
G	$V^{3+} + HOO^{\bullet} + H_2O \rightarrow VO^{2+} + H_2O_2 + H^+$	(1×10^2)[f]	9
H	$VO^{2+} + HOO^{\bullet} \rightarrow OV(O_2)^+ + H^+$	1.1×10^4	13
I	$VO_2^+ + HOO^{\bullet} + H \rightarrow VO^{2+} + O_2 + H_2O$	2.6×10^6 [g]	13
J	$V^{3+} + VO_2^+ \rightarrow 2VO^{2+}$	243	16
K	$OV(O_2)^+ + HOO^{\bullet} + H^+ \rightarrow VO^{2+} + O_2 + H_2O_2$	2.8×10^5	13
L	$H_2O_2 + {}^{\bullet}OH \rightarrow HOO^{\bullet} + H_2O$	2.8×10^7	40
M	$2HOO^{\bullet} \rightarrow H_2O_2 + O_2$	8.3×10^5	41
N	$OV(O_2)^+ + H_2O_2 \rightarrow OV(O_2) + HOO^{\bullet} + H^+$	(2×10^{-5})	42
O	$OV(O_2)^+ + OV(O_2) + 2H^+ \rightarrow V5 + OV(O_2)^{2+\bullet} + H_2O$	(1×10^8)	42
P	$OV(O_2)^{2+\bullet} \rightarrow VO^{2+} + O_2$	(1×10^8)	42
Q	$V^{3+} + OV(O_2)^+ + H_2O \rightarrow VO^{2+} + OV(O_2) + 2H^+$	11.3	this work
R	$OV(O_2) + 2H^+ \rightarrow VO^{2+} + H_2O_2$	(1×10^7)	18
S	$CHMe_2OH + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}CMe_2OH$	1.7×10^9	40
ss[h,i]	$CHMe_2OH + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}CH_2CH(Me)OH$	2.8×10^8	40
T	${}^{\bullet}CMe_2OH + H_2O_2 \rightarrow HO^{\bullet} + Me_2CO + H_2O$	5×10^5	40
U[h]	${}^{\bullet}CMe_2OH + VO_2^+ + H^+ \rightarrow VO^{2+} + H_2O + Me_2CO$	unknown	43
V	${}^{\bullet}CMe_2OH + VO^{2+} + H^+ \rightarrow H_2O + V^{3+} + Me_2CO$	(2×10^7)	this work
W	${}^{\bullet}CMe_2OH + V^{3+} + H_2O \rightarrow H^+ + VO^{2+} + CHMe_2OH$	(5×10^5)	this work
X[h]	${}^{\bullet}CMe_2OH + V^{3+} \rightarrow V^{2+} + H^+ + Me_2CO$	unknown	12
Y[h]	${}^{\bullet}CMe_2OH + V^{2+} + H^+ \rightarrow V^{3+} + CHMe_2OH$	2.1×10^5	44
Z[i]	${}^{\bullet}CMe_2OH + O_2 \rightarrow Me_2C(OH)OO^{\bullet}$	3.9×10^9	41
zz	$Me_2C(OH)OO^{\bullet} \rightarrow Me_2CO + HOO^{\bullet}$	6.6×10^2	41
aa[h]	$V^{2+} + VO^{2+} \rightarrow 2V^{3+} + H_2O$	1.6	14,15
bb[h]	$V^{2+} + H_2O_2 + H^+ \rightarrow V^{3+} + {}^{\bullet}OH + H_2O$	15.4	9
cc[h]	$V^{2+} + VO_2^+ + 2H^+ \rightarrow V^{3+} + VO^{2+} + H_2O$	4740	11
dd[h]	$OV(O_2)^+ + H_2O_2 \rightarrow OV(O_2)_2^- + 2H^+$	$k_+ = 3.6 \times 10^3$, $k_- = 2.8 \times 10^3$	17
ee[h]	$V^{2+} + {}^{\bullet}OH + H^+ \rightarrow V^{3+} + H_2O$	unknown	12
ff[h]	$OV(O_2)^+ + {}^{\bullet}OH + H^+ \rightarrow VO^{2+} + O_2 + H_2O$	unknown	13
gg[h]	$OV(O_2)^+ + {}^{\bullet}OH + H \rightarrow OV(O_2)^{2+} + H_2O$	unknown	42
hh[h]	$OV(O_2)^+ + H_2O_2 \rightarrow VO^{2+} + O_2 + HO^- + {}^{\bullet}OH$	unknown	42

[a] At 25.0 °C in 1.0 mol L^{-1} H^+ except as noted. [b] In liters per mole second or per second. [c] Values in parentheses were estimates from this simulation study. [d] Values of 0.97 (in 0.4 M H_2SO_4)[20] and 5.8 (in 0.1 mol L^{-1} $HClO_4$)[19] were also reported. [e] Several values were reported for this reaction, see text. [f] A value of 6×10^3 L mol^{-1} s^{-1} in 0.12 mol L^{-1} $HClO_4$ was available and was reported to decrease with increasing $[H^+]$.[9] [g] pH = 0.8. [h] These reactions were not included in the simulations because they were deemed insignificant or redundant. [i] Conceivably, the $Me_2C(OH)OO^{\bullet}$ (from reaction Z) and ${}^{\bullet}CH_2CH(Me)OH$ (from reaction ss) radicals could oxidize V^{3+} and others. However, no rate constants are available and our preliminary simulation indicated that they had only minor contributions. Therefore, these reactions were not included in the final simulation scheme.

One reaction needs further comments. The equilibrium of $OV(O_2)^+$ with VO_2^+ and H_2O_2 (eq 7) was well-established,[17,35,36] yet the rate constants in 1.0 mol L^{-1} $HClO_4$ at 25 °C were not readily available. The forward reaction constant k_7 was reported to be 5.7×10^3 L mol^{-1} s^{-1} in 0.4 mol L^{-1} H_2SO_4,[37] and a value of 1.3×10^4 L mol^{-1} s^{-1} was cited[18] for 1.0 mol L^{-1} $HClO_4$. Nucci et al.[38] determined the reverse rate constant k_{-7} to be 0.74 s^{-1}, from which $k_7 = 2.96 \times 10^4$ L mol^{-1} s^{-1} was derived by Ferradini.[20] Recalculation using Nucci's experiments and Wilkins' equilibrium constant,[17] $K_7 = 3.5 \times 10^4$ L mol^{-1}, gave $k_7 = 2.27 \times 10^4$ L mol^{-1} s^{-1} and $k_{-7} = 0.67$ s^{-1}. Examination of Wilkins' experimental data suggested that $k_7 = 5.3 \times 10^3$ L mol^{-1} s^{-1} and, thus, $k_{-7} = 0.15$ s^{-1} at 25 °C. The last set of data appears to give the best overall match in the simulation. This just demonstrated the uncertainty encountered in the simulation of such a complicated system.

A number of criteria were primarily used to refine the estimated rate constants and the kinetic scheme. We tried to account for the experimental results on the reaction stoichiometry, O_2 evolution yields, the formation and disappearance profile of $OV(O_2)^+$ (Figure 2), and the effect of 2-PrOH on the reaction, as well as to accommodate some related results in the literature. One can certainly use part of the scheme to fit a particular situation sufficiently; such values obtained, however, may not agree well with valued obtained from other subsets suitable for different conditions. Thus, the overall scheme was generally used to simulate each specific experiment trying to depict a whole picture of the reaction. The resulting final scheme (Table 4) consists of reactions reported in the literature pertaining to the $V^{3+}-H_2O_2$ system, most of them with known rate constants, as well as reactions not known but required to account for the experiments (see below). Omissions were made when reactions had only minor contributions, no rate constants were available, or both. On the basis of this scheme, the calculated reaction stoichiometry, O_2 evolution yields, and acetone yields under specific experimental conditions are summarized in Tables 1−3.

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The oxidation of 2-PrOH to acetone can be rationalized by eqs 10−15.

$$\mathrm{CHMe_2OH + OH^\bullet \rightarrow H_2O + {}^\bullet CMe_2OH} \qquad (10)$$

$$\mathrm{{}^\bullet CMe_2OH + H_2O_2 \rightarrow HO^\bullet + Me_2CO + H_2O} \qquad (11)$$

$$\mathrm{{}^\bullet CMe_2OH + VO_2{}^+ + H^+ \rightarrow VO^{2+} + H_2O + Me_2CO} \qquad (12)$$

$$\mathrm{{}^\bullet CMe_2OH + VO^{2+} + H^+ \rightarrow H_2O + V^{3+} + Me_2CO} \qquad (13)$$

$$\mathrm{{}^\bullet CMe_2OH + V^{3+} \rightarrow V^{2+} + H^+ + Me_2CO} \qquad (14)$$

$$\mathrm{{}^\bullet CMe_2OH + V^{3+} + H_2O \rightarrow VO^{2+} + H^+ + CHMe_2OH} \qquad (15)$$

The hydrogen abstraction from 2-PrOH by the OH radical (eq 10) and the oxidation of $^\bullet CMe_2OH$ by H_2O_2 (eq 11) are known reactions. However, eq 11 alone could not account for all of the acetone production; other reactions have to be considered. Thermodynamically, eqs 12−14 are all feasible, with $^\bullet CMe_2OH$ being a very strong reducing agent ($E^0_{Me_2CO/^\bullet CMe_2OH} = -1.39$ V).[45] Equation 12 has been postulated on several occasions,[39,43] but no rate constants were given. Inclusion of this path seemed to be insufficient, presumably because of the very low concentration of $VO_2{}^+$ accumulated during the reaction. Consequently it was not included in the simulation studies. The reduction of VO^{2+} by $^\bullet CMe_2OH$ (eq 13) has not been reported, but the addition of it with a reasonable rate constant (2×10^7 L mol^{-1} s^{-1}) appeared to be necessary. In fact, the results here could be regarded as evidence for the occurrence of this reaction. The reduction of V^{3+} (eq 14) was possible as suggested in the literature[12] but likely to be slow; otherwise, the reaction stoichiometry $\Delta[V]/[H_2O_2]_0$ would be much less than observed when a large excess of V^{3+} was employed in the experiment. Equation 14 was, then, not included in the simulation, eliminating all reactions involving V^{2+}, to allow some simplification.

On the other hand, albeit less investigated, $^\bullet CMe_2OH$ is also a strong oxidizing agent; a reduction potential of +1.65 V could be derived from the thermodynamic data in the literature.[45,46] Such aliphatic radicals are known to oxidize a number of low valent transition metals, including Ti^{3+},[32] V^{2+},[44] Cr^{2+},[47] etc. It is thus reasonable to envision the oxidation of V^{3+} by $^\bullet CMe_2OH$ (eq 15), and this reaction is indeed required to account for the VO^{2+} generation in the simulation studies. The estimated rate constants for eqs 13 and 15 from the simulation are given in Table 4.

Attempts were made to independently determine the reaction rate constants for eqs 13 and 15 by kinetic competition methods[32] on the basis of the production of the free radical by the homolytic decomposition of an organopentaaquochromium(III) cation, $(H_2O)_5Cr(CMe_2OH)^{2+}$.[48] These experiments qualitatively confirmed the postulated reactions. Unfortunately, for the reduction of VO^{2+} (eq 13), the VO^{2+} cations seem to interfere with the thiocyanate method used to analyze the amounts of Co(II) products in the competitive reactions. As a result, only an approximate value, $k_{13} = 8.5 \times 10^6$ L mol^{-1} s^{-1}, with large deviations, was obtained at 25.0 °C and 0.1−1.0 mol L^{-1} H^+ with an ionic strength of 1.0 mol L^{-1}. The rate constant for the oxidation of V^{3+} at 25.0 °C and 0.1 mol L^{-1} H^+ with an ionic strength of 0.2 mol L^{-1} was estimated to be $k_{15} = 2 \times 10^6$ L mol^{-1} s^{-1}. However, when these values were incorporated into the simulation scheme, the agreement between the experimental results in earlier section and the simulated results was rather poor.

Edwards et al.[42] studied the decomposition of H_2O_2 catalyzed by $VO_2{}^+$ in 1.0 mol L^{-1} $HClO_4$ and found that the reaction had a slow initiation part, the rate of which was first-order dependent on both $[H_2O_2]$ and $[OV(O_2)^+]$. Reactions N, O, and P in Table 4 were thus included to account for these results, as postulated.[42] The rate constants estimated here, based on the limited data available, were very approximate, especially for the faster ones. Nevertheless, inclusion of these reactions correctly predicted the induction period as well as the effect of VO^{2+} on eliminating such induction periods. It should be noted that Edwards did not take into account the possible role of the oxodiperoxovanadium(V) anion, $OV(O_2)_2{}^-$, which might be important in the initiation of the whole radical process, as a recent photochemical study indicated.[49] The findings by Edwards did not exclude this possibility either.

Reaction between V^{3+} and $OV(O_2)^+$. This reaction was conducted with 1.0 mol L^{-1} H^+ and $I = 2.0$ mol L^{-1}. The stoichiometry of the reaction under pseudo-first-order conditions with V^{3+} in large excess was examined by measuring the absorbance change for the reactant V^{3+} at 398 nm, the product VO^{2+} at 760 nm, or both before and after the reaction. The values of $[V^{3+}]_{reacted}/[OV(O_2)^+]$ thus determined are 2.85 ± 0.10, indicating a 3:1 reaction stoichiometry. In an oxygen evolution experiment with 3.3 mmol L^{-1} V^{3+}, 3.1 mmol L^{-1} $OV(O_2)^+$, and 0.2 mmol L^{-1} H_2O_2, 1.02 mmol L^{-1} oxygen was produced. A spectrophotometric search for possible intermediates (i.e., the oxo-bridged (or hydroxo-bridged) VOV^{4+} dimetallic species, as observed in the reaction between V^{2+} and VO^{2+})[14,15] was unsuccessful.

The kinetic runs were carried out with excess V^{3+}. The initial concentrations of V^{3+} and $OV(O_2)^+$ were varied over 10−100 mmol L^{-1} and 0.5−1.0 mmol L^{-1}, respectively. The absorbance−time traces were fitted by single exponentials, although, sometimes, slight deviations could be observed.

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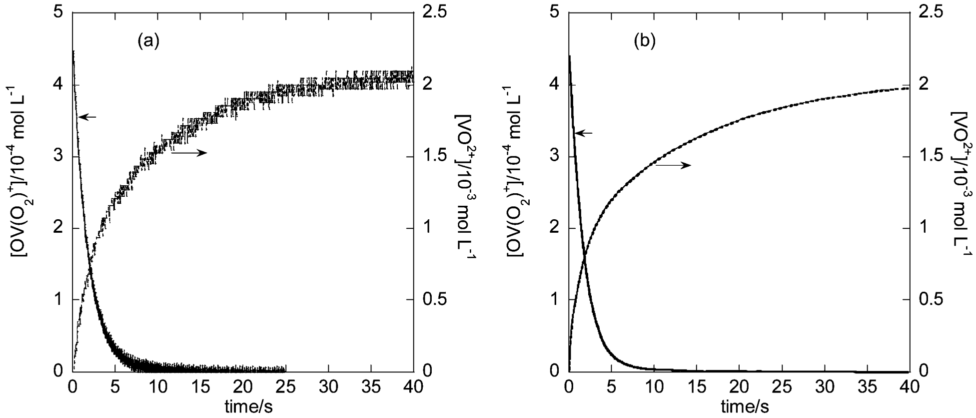

Figure 3. Comparison between the disappearance of $OV(O_2)^+$ (left axis) and the generation of VO^{2+} (right axis) in the reaction between V^{3+} (33.6 mmol L^{-1}) and a mixture of VO_2^+ (0.54 mmol L^{-1}) and H_2O_2 (0.57 mmol L^{-1}) in 1.0 mol L^{-1} $HClO_4$ with a 2.0 mol L^{-1} ionic strength at 25.0 °C. Panel a presents experimental data, and panel b shows the simulated traces.

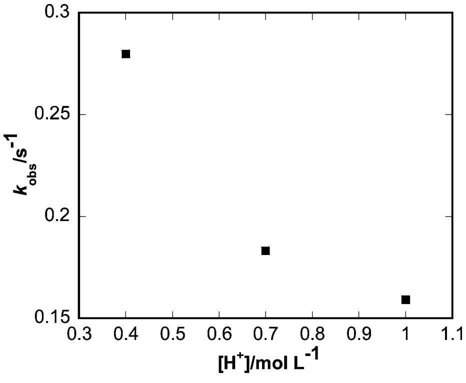

Figure 4. Plot showing the $[H^+]$ dependence of the $V^{3+}-OV(O_2)^+$ reaction under the following conditions: 25 °C, $I = 2.0$ mol L^{-1} ($LiClO_4$), 13.6 mmol L^{-1} V^{3+}, 1.1 mmol L^{-1} $OV(O_2)^+$.

The plot of the resultant rate constants k_{obs} against the average $[V^{3+}]$ yielded a straight line with a slope of 11.3 ± 0.3 L mol^{-1} s^{-1} and an intercept of 0.13 ± 0.02 s^{-1}. Notably, the generation of VO^{2+} was markedly slower than the consumption of $OV(O_2)^+$ (Figure 3a).

The rate dependence on the hydrogen ion concentration was briefly investigated in a limited range of $[H^+]$ (0.4−1.0 mol L^{-1}) with $I = 2.0$ mol L^{-1} at 25 °C. The observed pseudo-first-rate constant decreased with the increasing $[H^+]$ (Figure 4). An inverse first-order dependence on $[H^+]$ appeared to be reasonable, although accurate quantification based on these data was not carried out because of lack of information on the reaction in eq 7, as will be discussed later.

Discussion

In acidic aqueous solutions, vanadium ions are known to exist in four oxidation states from +2 to +5 as aqua or oxo ions, with vanadium(IV) being the thermodynamically most stable form. The chemistry of vanadium ions with hydrogen peroxide is exceptionally complicated, as over 20 reactions could be readily written among these species and corollary oxyradicals, even without considering the various forms in which vanadium can exist at different acidity levels.[50] Much work has been done, providing a necessary basis for the understanding of the present study, while some reactions still remain speculative.

Our study on $V^{3+}-H_2O_2$ system yielded a second-order rate constant of 2.06 ± 0.03 L mol^{-1} s^{-1}, which is in good agreement with the value (2.3 L mol^{-1} s^{-1}) in 0.12 mol L^{-1} H^+ mentioned in the literature.[9] We have further confirmed that the rate constant is independent of the hydrogen ion concentration; this behavior of V^{3+} is similar to V^{2+} [12] and contrasts that of VO^{2+},[18] where an inverse first-order dependence on $[H^+]$ was observed.

With the aid of kinetic simulation, a reaction scheme was written to accommodate all of the experimental results presented here (Table 4). The match between experiments and simulation on yields and stoichiometry, as listed in previous section, are within 30% in most situations. Given the complexity of the scheme, as evidenced by the number of reactions, and the uncertainty of several rate constants, the agreement is considered reasonably good.

It is clear that the reaction between V^{3+} and H_2O_2 proceeds via one-electron oxidation (i.e., a Fenton-like mechanism). The involvement of a radical intermediate was first inferred from the changing stoichiometry dependent on the starting conditions, which is often indicative of a radical chain process. The observation of the formation of $OV(O_2)^+$ (Figure 2) in the very early stage of the reaction apparently implied the early involvement of VO_2^+. However, this does not necessarily indicate the participation of a two-electron oxo-transfer reaction of V^{3+}. It appeared possible that VO^{2+} would effectively compete for H_2O_2 or the OH radical to generate VO_2^+ or, more directly, react with the $HOO^\bullet$ radical to yield $OV(O_2)^+$. In fact, these observations could be adequately addressed without invoking the two-electron process. On the other hand, it should be cautioned that the data presented here did not allow us completely to rule out the coexistence of a 2-electron process as a minor reaction path.

In the presence of excess 2-PrOH, the $HO^\bullet$ radical generated was intercepted and diverted to acetone production or to the secondary $^\bullet CMe_2OH$ radical, which would take up O_2 very quickly. In any event, the O_2 evolution was reduced effectively. With other hydroxyl radical scavengers, acetone

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production would be inhibited, but not completely, because of competition, as observed in the experiments. These observations provide further support for the involvement of a hydroxyl radical and a Fenton-like mechanism as the dominant pathway in the reaction.

Although the overall reaction scheme delineated here fits the experimental data and literature reports reasonably well, it should be noted that this is still a simplified view of the actual chemistry. The rate constants for some reactions were not reported in the literature; even when a rate constant is available, it may have been determined at different conditions or obtained by indirect methods. Some of reactions are not elementary steps and may have multi-term rate laws. Thus, the estimate given here should be regarded as an approximation. Furthermore, it should also be noted that this scheme does not account for the pH dependence, as various protonation–deprotonation reactions pertaining to these species were not included. Other factors, such as the photochemical reactions of vanadium ions[39,51] and the effect of ionic strength, were also neglected.

It is somewhat disappointing that MTO does not seem to catalyze the oxidation of V^{3+} by H_2O_2 because MTO is in general a good oxo-transfer catalyst. Maybe it is not so surprising as V^{3+} is a highly charged cationic species and not very likely to be a good nucleophile to attack the electrophilic peroxidic oxygen in the MTO–H_2O_2 adduct. However, it is not improbable that MTO–H_2O_2 adducts would react with V^{3+} slowly so that it was not observed under our reaction conditions.

In comparison, some important differences exist between V and Re oxoperoxo species. MTO–H_2O_2 adducts show predominantly electrophilic character in oxidations. Because of the easy reducibility of vanadium(V), $OV(O_2)^+$ may exist in a vanadyl oxide or biradical form or as a resonance hybrid, thus exhibiting nucleophilic or radical features as oxidants, analogous to the reactivity of carbonyl oxide.[52] Indeed, the ambiphilic nature of oxomonoperoxo vanadium complexes was clearly demonstrated in the competitive oxidation of sulfide and sulfoxide.[53] Also oxomonoperoxo vanadium complexes were capable of hydroxylating aromatic and aliphatic hydrocarbons under mild conditions, presumably because of the radical character.[54] We have recently shown that $OV(O_2)^+$ is a very poor oxo-transfer reagent for a variety of nucleophilic substrates such as triarylphosphines.[55]

It is known that low-valent vanadium(II or III) complexes could easily undergo oxo-transfer reactions or two-electron oxidations.[56−58] Therefore, when the reaction between V^{3+} and $OV(O_2)^+$ was considered, it seemed reasonable to postulate a direct oxo-transfer reaction from $OV(O_2)^+$ to V^{3+} producing 2 equivalents of VO_2^+ (eq 16).

$$V^{3+} + OV(O_2)^+ + H_2O \rightarrow 2VO_2^+ + 2H^+ \qquad (16)$$

However, such a reaction could hardly be incorporated into the overall reaction scheme outlined above. Specifically, the maximum concentration of $OV(O_2)^+$ in the reaction between V^{3+} (10.2 mmol L^{-1}) and H_2O_2 (5.22 mmol L^{-1}) would be significantly higher (see Figure 2), while the evolution of dioxygen would be much lower. Furthermore, if this reaction indeed occurs, the production of VO^{2+} would occur at the same approximate rate as the disappearance of $OV(O_2)^+$, which is clearly contradicted by the experimental observation (Figure 3).

On the other hand, the observed first-order dependence of the $OV(O_2)^+$ consumption rate on $[V^{3+}]$ would be difficult to explain without invoking a direction reaction between V^{3+} and $OV(O_2)^+$, although the nonzero intercept (0.13 s^{-1}) could be easily recognized as corresponding to the reverse reaction of eq 7. We thus envisioned a one-electron process (eq 17).The $OV(O_2)^+$ reduction product, $OV(O_2)$, might have an unpaired electron on oxygen and presumably a broken O–O bond, as suggested in the reduction of $OV(O_2)^+$ by H_2O_2,[42] or it could be a peroxo vanadium(IV) species, which was protonated to give $OVOOH^+$ and then VO^{2+} and H_2O_2.[18] The latter seems to fit the experiments better, especially when the oxygen evolution results were considered. Under the experimental conditions (3.3 mmol L^{-1} V^{3+}, 3.1 mmol L^{-1} $OV(O_2)^+$, and 0.2 mmol L^{-1} H_2O_2), the simulation in Figure 3 predicted that 1.0 mmol L^{-1} O_2 would be generated in 20 min, in good agreement with the observed value (1.02 mmol L^{-1} O_2). For simplicity, only these two reactions were included in simulation. Figure 3b also showed simulated concentration–time profiles for the disappearance of $OV(O_2)^+$ and the accumulation of VO^{2+}. The close match between these results provided additional support for the validity of the proposed reaction scheme.

$$V^{3+} + OV(O_2)^+ + H_2O \rightarrow VO^{2+} + OVO_2 + 2H^+ \qquad (17)$$

$$OVO_2 + 2H^+ \rightarrow \{OVOOH^+ + H^+\} \rightarrow VO^{2+} + H_2O_2 \qquad (18)$$

The detailed reaction mechanism for eq 17 can be described by following steps. The hydrolysis of V^{3+} ($K_{19} = 2.0 \times 10^{-3}$ mol L^{-1})[59] gives VOH^{2+} in a pre-equilibrium step. VOH^{2+} then undergoes an electron-transfer reaction with $OV(O_2)^+$ to generate VOH^{3+} in a rate controlling step (eq 20), followed by the deprotonation of VOH^{3+} (eq 21; $K_{21} = 4.3$ mol L^{-1}).[60] Reaction 20 should be rapid since the two reactants would only have minimal changes from the atom economy point of view. VOH^{2+} ion has been often invoked as the actual reactive species in the electron-exchange reaction of V^{3+}.[61−63] The path involving VOH^{2+} should be favored over the path in which electron-transfer

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precedes the first proton transfer (i.e., V^{3+} is oxidized to V^{4+} first, and then V^{4+} hydrolyzes to give VO^{2+}).

$$V^{3+} + H_2O \leftrightarrow VOH^{2+} + H^+ \tag{19}$$

$$VOH^{2+} + OV(O_2)^+ \rightarrow VOH^{3+} + OV(O_2) \tag{20}$$

$$VOH^{3+} \leftrightarrow VO^{2+} + H^+ \tag{21}$$

Recall that $OV(O_2)^+$ is also in fast equilibrium (eq 7) with VO_2^+, which would be consumed quickly in the presence of excess V^{3+}. Overall, the rate of disappearance of $OV(O_2)^+$ is

$$-\frac{d[OV(O_2)^+]}{dt} = k_{-7}[OV(O_2)^+] + k_{20}\frac{K_{19}}{[H^+]}[V^{3+}][OV(O_2)^+] \tag{22}$$

This leads to a straight line with a nonzero intercept at constant $[H^+]$ when k_{obs} was plotted against $[V^{3+}]$, in good agreement with the experimental result. The intercept, corresponding to the back reaction of eq 7, would not be a constant when $[H^+]$ was varied; the forward reaction has a three-term rate law,[17] while the rate dependency on $[H^+]$ for the back reaction is not clear. Under low $[H^+]$, the diperoxo species $OV(O_2)_2^-$ may also come into play. For these reasons, the limited data on rate dependence on $[H^+]$ was not quantitatively analyzed. From the slope, k_{20} was estimated to be 5.7×10^3 L mol^{-1} s^{-1}, greater than the ligand substitution rate on aqueous V^{3+} ion; a typical anation rate constant for the reaction of V^{3+} with NCS^- is 114 L mol^{-1} s^{-1},[64] while the solvent exchange rate constant for V^{3+} in aqueous solutions is 5×10^2 s^{-1}.[65] Thus, an outer-sphere electron-transfer mechanism for reaction 20 was indicated. The reaction coordinate diagram, approximated from the available thermodynamic and kinetic data with $K_{18} = 1 \times 10^2$ L mol^{-1}, a not unreasonable assumption,[18] was shown in Figure 5. The value of $\Delta G^{\ddagger}$ for the transition state was estimated from the rate constant (5.7×10^3 L mol^{-1} s^{-1}) using the Eyring equation.

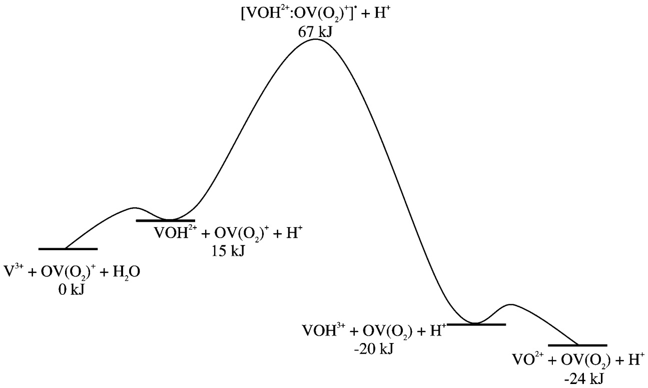

Figure 5. Reaction coordinate diagram for the rate controlling step in the $V^{3+}-OV(O_2)^+$ reaction. Note that the actual activation barriers in the first and the last steps should be minimal.

A final question concerns the rate of the $V^{3+}-H_2O_2$ reaction. The rate constants for hydrogen peroxide oxidations cover several orders of magnitude. The value for the oxidation of V^{3+}, 2.06 L mol^{-1} s^{-1}, is at the slow end of the scale. This seems to be surprising because the standard reduction potential for the VO^{2+}/V^{3+} couple is about +0.34 V, not an enormously large number. From the Gibbs free energy consideration, this reaction should be faster than the $Fe^{2+}-H_2O_2$ reaction because the Fe^{3+}/Fe^{2+} potential is +0.77 V, while in actuality, the rate constant for the $Fe^{2+}-H_2O_2$ reaction is 77 L mol^{-1} s^{-1}.

The reason, however, is not yet clear. One can certainly assume that the immediate products of M^{n+} oxidation by H_2O_2 in the rate controlling step are MOH^{n+} ions, rather than $M^{(n+1)+}$ (e.g., Fe^{3+}) or $MO^{(n-1)+}$ (e.g., VO^{2+}). VOH^{3+} ions probably have a very high unfavorable free energy. VO^{2+} is said to be practically not protonatable in aqueous solution,[66] although a protonation constant of 0.23 L mol^{-1} was reported.[60] Another obvious difference lies in how the MOH^{n+} ions evolve to the final products: $FeOH^{2+}$ takes up H^+ to give Fe^{3+} (and H_2O) (i.e., $FeOH^{3+} + H^+ \rightarrow Fe^{3+} + H_2O$), while VOH^{3+} eliminates H^+ to give VO^{2+} (i.e., $VOH^{3+} \rightarrow VO^{2+} + H^+$). However, this still offers no explanation in a quantitative sense.

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