Electron Spin Resonance Kinetic Studies of the Oxidation of Vanadium(IV) by Hydrogen Peroxide

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The kinetics and stoichiometry of the oxidation of VO^{2+} by H_2O_2 has been studied over a wide range of initial concentrations, $[VO^{2+}]_i$, $[H_2O_2]_i$, and $[H^+]_i$. Continuous-flow–esr techniques were used to monitor $[VO^{2+}]$ and an intermediate $[OVOO \cdot ^{2+}]$. The proposed rate-determining steps in VO^{2+} decay are

$$VO^{2+} + H_2O_2 \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} OVOOH^+ + H^+ \tag{1}$$

$$OVOOH^+ \xrightarrow{k_2} VO_2^+ + \cdot OH \tag{2}$$
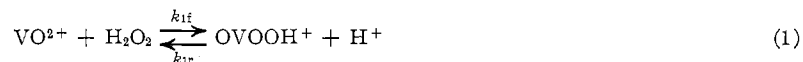
where $K_1 k_2 = 0.21$ and $k_{1f} = 52 \ M^{-1} \sec^{-1}$. Pseudo-first-order dependence on $[VO^{2+}]$ and $[H_2O_2]$ over a large range of $[H^+]$, inverse $[H^+]$ dependence below pH 1, and deviation from this $[H^+]^{-1}$ dependence at pH 4 are all consistent with the proposed mechanism. Iminodiacetic acid does not affect the rate of VO^{2+} decay, but ethylenediaminetetraacetic acid slows the rate by more than a factor of 100, supporting the inner-sphere mechanism of (1) and (2). Stoichiometry studies indicate that the intermediate is involved in a chain mechanism involving the production of O_2.

Introduction

The oxidation of titanium(III) ion by hydrogen peroxide has been studied in a continuous-flow system monitored by esr absorption.[1] In this work we have extended this technique to the oxidation of vanadium-(IV), the vanadyl ion, or VO^{2+}, by hydrogen peroxide. The esr–flow studies are especially suited for the vanadium system because both the decay of vanadium(IV) and the formation and decay of an intermediate can be observed simultaneously. The spectrum of the intermediate was reported by Setaka,[2] who observed it by treating VO^{2+} with H_2O_2. The same intermediate was also observed by Bains[3] and Czapski[4] when vanadium-(V) was present in the Fe^{2+}–H_2O_2 or Ce^{4+}–H_2O_2 system. Observed line widths are slightly different but there is agreement on the g value ($g = 2.0113$) and hyperfine splitting ($a = 4.5 \ G$).

Dean[5] reported some kinetics based on the colorimetric monitoring of the vanadium(IV) reaction. The studies were incomplete because the starting concentrations of vanadium(IV) and hydrogen peroxide were not varied. In the present study both were varied and our results are somewhat in variance with those of Dean.[5] Stoichiometric evidence and kinetic data support our mechanism for the oxidation of vanadium(IV) by hydrogen peroxide.

Experimental Procedures

Reagents.—Vanadyl dichloride, vanadyl sulfate, and sodium metavanadate were obtained from K & K Laboratories and used without purification. Since both the sulfate and dichloride gave similar results, impurities were considered unimportant. All solutions of vanadyl ion and hydrogen peroxide were standardized in acid solution with potassium permanganate which in turn had been standardized with primary standard potassium oxalate. The hydrogen peroxide solutions were prepared from Baker Analyzed reagent (30% solution).

Stoichiometry.—The consumption ratio H_2O_2:V(IV) was determined by two methods. Method A was an oxidation–reduction method in which equal volumes of hydrogen peroxide and vanadyl solutions (Table III) were mixed rapidly and allowed to equilibrate for 3 min. An excess of a standard solution of arsenious acid and 1 drop of osmium tetroxide as a catalyst were then added to the solution, reducing the H_2O_2 to H_2O. The excess arsenious acid and vanadyl ion were titrated with $KMnO_4$. Since H_2O_2 was in excess by fourfold, the reactions were assumed to go to completion. Method B was used to determine the consumption ratio H_2O_2:V(IV) when V(IV) was in excess. The two solutions were mixed in the esr–flow system as in the kinetic experiments. The flow was then shut off and the unreacted vanadyl ion was measured. The starting standardized vanadyl solution was used as a standard for the intensity measurement.

The amount of oxygen produced by the reaction was measured in a Warburg apparatus. The initial evolution of oxygen was rapid and gave a sharp end point. Determinations were made at $0.1 \ M \ H_2SO_4$, $0.05 \ M \ H_2SO_4$, and buffered $KAl(SO_4)_2$ solution at pH 4.

Kinetic Esr Procedures.—The flow system and esr apparatus has been described previously.[6] The two reactant solutions were prepared from distilled water, were adjusted to the desired pH with H_2SO_4 or $KAl(SO_4)_2$ buffer, and were deaerated by nitrogen bubbled through a glass diffusion frit for about 15 min. The concentrations of all starting solutions were determined by titration in excess acid with standardized $KMnO_4$ solution. After mixing, the initial concentrations of $VOCl_2$ were varied from 0.003 to 0.03 M ($[H_2O_2]$, 0.1 M; $[H^+]$, 0.60 M), the initial concentration of H_2O_2 was varied from 0.038 to 0.58 M ($[VO^{2+}]$, 0.005 M; $[H^+]$, 0.1 and $10^{-4} \ M$), and the hydrogen ion concentrations were varied from 10^{-4} to 0.07 M ($[VO^{2+}]$, 0.005 M; $[H_2O_2]$, 0.1 M). Immediately following preparation, the solutions were pumped into 10-l. glass reservoirs and put under a nitrogen pressure of 2 atm. The separate streams were forced through a standard Varian 4549 mixer and a Varian 4548 quartz flat cell *via* insulated polyethylene tubing. For runs at other than room temperature each solution was passed through coils immersed in a thermostated bath. The temperature was measured within 2 ft of the mixer. Only data for which the temperature was constant within $\pm 1°$ for both slow and fast flow rates were collected. The flow rate was controlled by a needle valve on the exit side of the flat cell. Total flow was measured by timing the collection of 100 ml of product solution. Flow rates of each reactant were measured separately on several runs. The "dead times," t, for the kinetic data were calculated by the relationship $t = v/r$ where v is the dead volume and r is the flow rate.

(1) F. Sicilio, R. E. Florin, and L. A. Wall, *J. Phys. Chem.*, **70**, 47 (1966).
(2) M. Setaka, Y. Kirino, T. Ozawa, and T. Kwan, *J. Catal.*, **15**, 209 (1969).
(3) M. S. Bains, J. C. Arthur, Jr., and O. Hinojosa, *J. Amer. Chem. Soc.*, **91**, 4673 (1969).
(4) A. Samuni and G. Czapski, *Isr. J. Chem.*, **8**, 563 (1970).
(5) G. A. Dean, *Can. J. Chem.*, **39**, 1174 (1961).
(6) E. L. Lewis and F. Sicilio, *J. Phys. Chem.*, **73**, 2590 (1969).

The concentration of VO^{2+} and the concentration of the intermediate were measured with a Varian 4502-15 spectrometer. The modulation amplitude was adjusted for optimum signal intensity without noticeable broadening. All kinetic runs were then made at the same modulation amplitude. Neither the vanadyl ion nor the intermediate radical saturated even at the highest power settings. Thus the power settings were maintained constant at about 120 mW. The initial vanadyl solution was used as an internal standard for measuring the concentration of both the vanadyl ion and the intermediate radical. The line width in the vanadyl spectrum, ΔH_v, was constant throughout the reaction. Thus, the concentration of vanadyl ion is related to its initial concentration by the expression $[VO^{2+}] = [VO^{2+}]_i(P/P_i)$, where P is the peak height of the sharpest peak (1 in Figure 1) at any time and P_i is the peak height of the sharp-

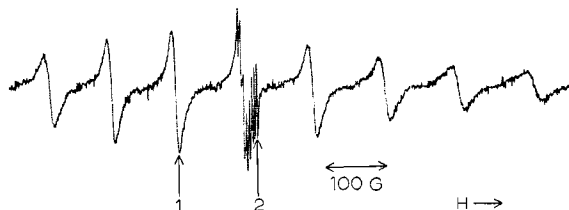Figure 1.—The esr spectra of VO^{2+} and intermediate. $[VO^{2+}]$ was monitored by (1). [Intermediate] was monitored by (2). $[VO^{2+}]_i = 6.3 \times 10^{-3}\ M;$ $[H_2O_2]_i = 0.11\ M;$ $[H^+] = 0.11\ M$.
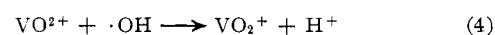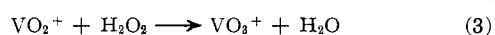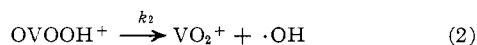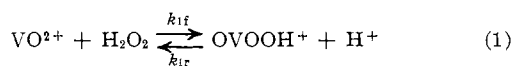
est peak in the initial solution. The area of vanadyl ion or area of intermediate I can be expressed as $A = P\Delta H^2$, in which ΔH^2 is the square of the line width. Areas from two graphical double integrations closely agreed with the relationship $A = P\Delta H^2$ for both VO^{2+} and intermediate. In addition, the VO^{2+} areas were proportional to measured VO^{2+} concentrations. By relating [I] to the initial vanadyl solution, $[I] = [VO^{2+}]_i P_I \Delta H_I{}^2 / P_i \Delta H_v{}^2$. P_I is the peak height of the intermediate (2 in Figure 1).

To measure the g values, an alkaline solution of Fremy's salt $(a = 13.0 \pm 0.1\ G,\ g = 2.00550 \pm 0.00005)^{[7]}$ was introduced into the flow cell and the low-field peak was recorded. Without interrupting the scan, the reactant streams were turned on to displace the Fremy's salt and the higher field components of the radical intermediate spectrum were recorded.

Results and Discussion

Decay of Vanadyl Ion.—In the presence of excess H_2O_2, the decay of VO^{2+} ion follows neither pseudo-first- nor second-order kinetics with respect to vanadyl ion. At short times the kinetic plots appeared to follow pseudo-second-order kinetics with respect to vanadyl ion as reported by Dean.[5] Pseudo-second-order rate constants, $k_2°$, are reported in Table I. It is seen that the values of $k_2°$ vary inversely with the initial concentration of vanadyl ion, $k_2° = k'/[VO^{2+}]_i$. Hence the initial rate law in excess $[H_2O_2]$ and $[H^+]$ is found to be $d[VO^{2+}]/dt = -k'[VO^{2+}]_i$, in contradiction to the finding of Dean.[5]

In order to explain the deviation from pseudo-first-order kinetics with respect to $[VO^{2+}]$, a consecutive competitive reaction scheme is proposed

$$VO^{2+} + H_2O_2 \underset{k_{1r}}{\overset{k_{1f}}{\rightleftarrows}} OVOOH^+ + H^+ \tag{1}$$

$$OVOOH^+ \overset{k_2}{\longrightarrow} VO_2{}^+ + \cdot OH \tag{2}$$

$$VO_2{}^+ + H_2O_2 \longrightarrow VO_3{}^+ + H_2O \tag{3}$$

$$VO^{2+} + \cdot OH \longrightarrow VO_2{}^+ + H^+ \tag{4}$$

$$VO_3{}^+ + \cdot OH \longrightarrow I + products \tag{5}$$
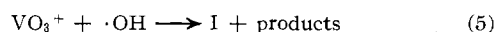
The peroxyvanadium(V) complex, $VO_3{}^+$, has been studied by Dean[5] and is the predominant product below

(7) J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966).

TABLE I
KINETIC DATA FOR VANADYL DECAY

$[H^+]$, M	$10^3[VO^{2+}]_i$, M	$[H_2O_2]_i$, M	k_{app}, sec⁻¹	$10^{-2}k_2°$, M⁻¹ sec⁻¹
0.06	2.5	0.11	0.35	5.9
0.06	3.0	0.11	0.48	4.4
0.06	2.5	0.11	0.37	
0.06	6.2	0.12	0.40	2.2
0.06	12.6	0.12	0.32	0.98
0.06	13.0	0.11	0.18	0.89
0.06	30.0	0.12	0.32	0.29
0.11	6.2	0.58	1.04	7.9
0.11	6.2	0.44	0.84	
0.11	6.5	0.22	0.42	1.9
0.11	6.3	0.11	0.22	0.95
0.11	5.8	0.056	0.059	0.27
0.11	6.3	0.027	0.054	0.21
0.51	6.3	0.12	0.044	0.30
0.11	6.3	0.11	0.22	0.94
0.06	6.2	0.12	0.40	2.2
10^{-4}	6.5ᵃ	0.12	5.9	34
10^{-4}	6.0ᵇ	0.12	5.6	30
10^{-4}	6.0ᶜ	0.47	24	
10^{-4}	6.0ᵃ	0.16	8.3	
10^{-4}	6.0ᵃ	0.12	5.9	
10^{-4}	6.0ᵃ	0.047	2.2	
0.06	6.7ᶜ	0.12	4.7	
	6.4ᵈ	0.12	0.091	

ᵃ $KAl(SO_4)_2$, 0.1 M. ᵇ IDA chelate solution. ᶜ Run at 50°. ᵈ Run at 8°. All other runs at 27°.

pH 2. At pH 4 the diperoxyvanadium(V) complex, $VO_5{}^-$, is the predominant product. Reaction 3 has been studied.[8] The rate of (3) is fast relative to (1) and (2). The intermediate, I, observed by esr spectroscopy and discussed below, is a vanadium(V) complex—possibly $OVOO \cdot {}^{2+}$. In the reaction scheme (4) and (5), both fast reactions relative to (1) and (2), compete with each other for $\cdot OH$ produced in (2).

The vanadyl decay data were calculated assuming that $k_4 = k_5$ and that $\cdot OH$ is in steady state. The kinetic expression reduces to the equation

$$\frac{d[VO^{2+}]}{dt} = -k_1[VO^{2+}][H_2O_2]\left(1 + \frac{[VO^{2+}]}{[V]_T}\right)$$

where

$$[V]_T = [VO^{2+}]_i + [VO_3{}^+]_i = [VO^{2+}] + [VO_3{}^+]$$

When no vanadium(V) is present initially, the $([VO^{2+}] + [VO_3{}^+])$ is $[VO^{2+}]_i$. The integrated expression is then

$$\ln\left(\frac{[VO^{2+}]_i}{[VO^{2+}]} + 1\right) = k_1[H_2O_2]t + \ln 2.0$$

A typical plot of $\ln\{([VO^{2+}]_i/[VO^{2+}]) + 1\}$ as a function of time is shown in Figure 2. The slopes, k_{app}, obtained from plots of this type are collected in Table I. The values obtained for k_{app} are approximately constant over a range of $[VO^{2+}]_i$ from 3×10^{-3} to $3 \times 10^{-2}\ M$, indicating good agreement with the present scheme.

The dependence of the rate on $[H_2O_2]$ was determined by varying the initial peroxide concentration, $[H_2O_2]_i$, but keeping it in excess with respect to $[VO^{2+}]_i$. The integrated rate expression is the same under these conditions, but k_{app} varies with $[H_2O_2]_i$. A plot of k_{app} as a function of $[H_2O_2]_i$ is shown in Figure 3. The plot clearly shows a pseudo-first-order dependence on $[H_2O_2]$

$$k_{app} = k_1[H_2O_2]$$

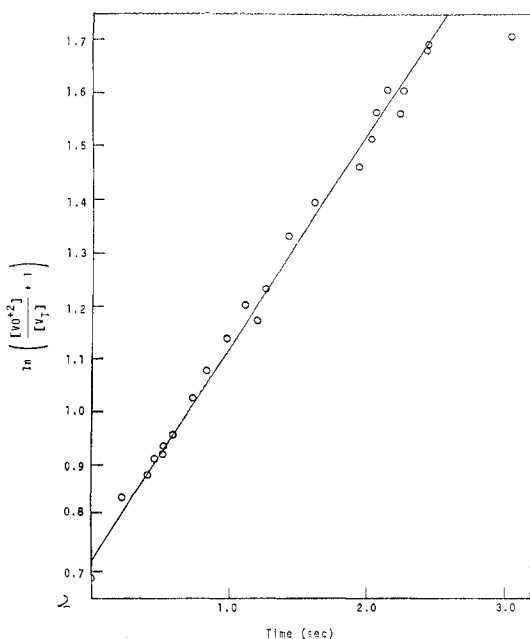(8) M. Orhanovic and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 278 (1967).

Figure 2.—Typical kinetic plot of $\ln\{([VO^{2+}]_i/[VO^{2+}]) + 1\}$ *vs.* time. Slope is k_{app}; $[VO^{2+}]_i = 6.2 \times 10^{-3}\ M$; $[H_2O_2]_i = 0.12\ M$; $[H^+] = 0.06\ M$.
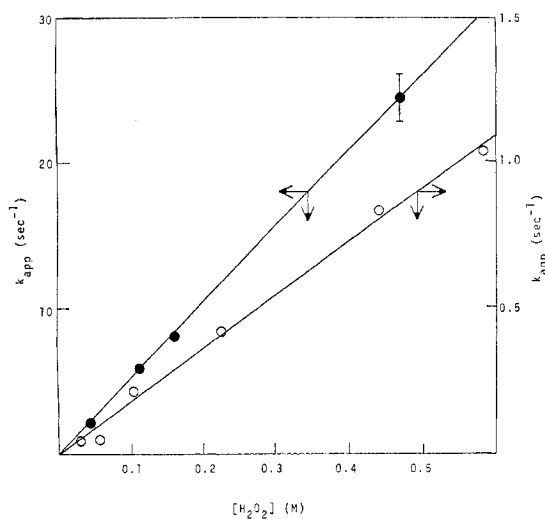

Figure 3.—Dependence of $[VO^{2+}]$ decay on $[H_2O_2]$; $[VO^{2+}]_i = 6.2 \times 10^{-3}\ M$: $\bigcirc$, $[H^+] = 0.11\ M$; $\bullet$, $[H^+] = 10^{-4}\ M$.

Methanol was used as an ·OH scavenger in one experiment. The rate data in this case approximated a pseudo-first-order plot with respect to $[VO^{2+}]$, in support of the above mechanism. In addition, as expected from the above sequence, the initial rate of reaction of vanadyl ion in the presence of methanol was half the initial rate of reaction in its absence. Also, the intermediate, I, was not observed in the presence of alcohol.

Excess vanadium(V), VO_2^+, was added to the VO^{2+} solution so that reaction 5 would predominate over reaction 4. The reaction scheme indicates that vanadyl decay should be pseudo first order under these conditions. In fact, during the first 0.1-sec period (corresponding to $<10\%$ reaction) vanadyl decay was not pseudo first order, and the intermediate I was building up to a maximum. In the derivation we have assumed that reaction 3 is very fast relative to (1) and (2). However, an induction period probably exists, since,

for our conditions, $k_3 = 1.3 \times 10^{4.8}$ (A kinetic run in which VO_2^+ was added to the H_2O_2 solution was attempted to see if VO_3^+ is the active species as indicated in (5); however, the formation of bubbles prevented the esr measurements.) Subsequent to 10% reaction the decay did follow pseudo-first-order kinetics with a pseudo-first-order rate constant that was independent of $[VO_2^+]$. The pseudo-first-order rate constant was the same as k_{app}, with $[H^+]$ and $[H_2O_2]$ constant.

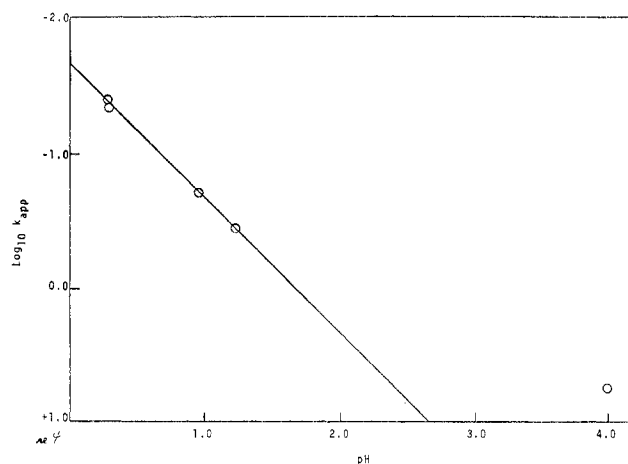Further experiments were done to determine the dependence on $[H^+]$. Figure 4 is a plot of log k_{app} as a

Figure 4.—Dependence of $[VO^{2+}]$ decay on $[H^+]$. $[VO^{2+}]_i = 6.2 \times 10^{-3}$; $[H_2O_2]_i = 0.11\ M$.

function of pH. The line has a slope of -1 showing an inverse dependence on $[H^+]$ in the high-acid region. The run at pH 4, however, deviates from this line, indicating that complications are present at this low acidity. The acid dependence can be expressed as $k_{app} = \{k_{1f}k_2/(k_2 + k_{1r}[H^+])\}[H_2O_2]$.

Equilibrium 1 and subsequent reaction 2 are proposed to account for the acid dependency. Reaction 2 is fast compared to (1f) at low concentrations of acid; then, reaction 1f is rate determining. From the slope of data at pH 4 in Figure 3, $k_{1f} = 52\ M^{-1}\sec^{-1}$. At high acid concentration, pH 1 and below, $[OVOOH^+]$ is very low so that reaction 2 is the slow step. Then K_1k_2 is determined from the slope of data at pH 1 in Figure 2, with $K_1k_2 = 0.21$. The individual values of K_1 and k_2 cannot be determined from these data, but this scheme accommodates all the data. The measurable rate of formation of $OVOOH^+$, reaction 1f, is evidence for an inner-sphere mechanism.

Some experiments with chelates were performed which also support an inner-sphere mechanism. Ethylenediaminetetraacetic acid, EDTA, was added to the vanadyl solution. The rate of reaction was slowed down by at least a factor of 100. The reaction was too slow to follow with our apparatus. In contrast, when iminodiacetic acid, IDA, was included in the VO^{2+} solution instead of EDTA, the reaction proceeded at the same rate as the system without chelate present. Two positions are available for substitution of H_2O_2 in the IDA complex where none is available in the EDTA complex. The EDTA would inhibit an inner-sphere mechanism but IDA would not. Therefore the inner-sphere mechanism of (1) and (2) is indicated by the experiment.
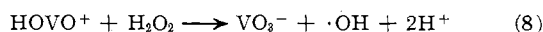
The activation energy, which was determined from values of k_{app} at temperatures of 8, 27, and 50°, with $[H^+] = 0.06$ M, was found to be 18 kcal/mol deg. If sequence (1)–(2) is correct, the sum of the enthalpy for (1) and activation energy for (2) is 18 kcal/mol deg.

A number of alternatives to this interpretation were considered, but none fits all the data. For the same scheme, if (1) were very fast compared to (2), an inverse dependence on $[H^+]$ would be expected throughout, unless both VO^{2+} and $OVOOH^+$ were indistinguishable by esr spectroscopy. Then

$$k_{app} = \frac{K_1 k_2 [H_2O_2]}{[H^+] + K_1 [H_2O_2]}$$

The equilibrium constant K_1, calculated from the dependence of k_{app} on acid, would be 3.6×10^{-2}. Hence at pH 4, k_{app} should be independent of $[H_2O_2]$. However, as shown in Figure 3, k_{app} is directly proportional to $[H_2O_2]$ at both pH 1 and pH 4, in direct contradiction to this interpretation.

Another scheme involving the hydrolysis of VO^{2+} was considered and rejected

$$VO^{2+} + H_2O \rightleftharpoons HOVO^+ + H^+ \qquad (6)$$

$$2HOVO^+ \rightleftharpoons (HOVO)_2{}^{2+} \qquad (7)$$

$$HOVO^+ + H_2O_2 \longrightarrow VO_3{}^- + \cdot OH + 2H^+ \qquad (8)$$

From Rossotti and Rossotti[9] $K_6 = 10^{-6}$ and $K_7 = 10^{5.1}$. With these values k_{app} should be inversely proportional to $[H^+]$ throughout the $[H^+]$ range examined in this work. However, the experimental results show the rate at pH 4 deviates considerably from a linear plot as shown in Figure 4. The other hydrolysis reactions listed in Martell and Sillén[10] were also considered, but none of these equilibria could explain the acid dependence of these data.

Data on Intermediate.—An eight-line spectrum ($g = 2.0113$, $a = 4.5$ G) was observed. The line width varied from 1.1 to 2.1 G. The small hyperfine splitting compared with $a = 115$ G for VO^{2+} confirms that the intermediate is a vanadium(V) complex with paramagnetic ligand[2]—possibly $OVOO \cdot {}^{2+}$. The g value greater than 2.0023 and the narrow line width also suggest a vanadium(V) complex with a paramagnetic oxygen ligand.

The concentration of intermediate, $[I]$, was monitored by esr and maximum concentrations are presented in Table II. If no vanadium(V), $VO_3{}^+$, is added to the solution initially, $[I]_{max}$ occurs at about the point when $[VO_3{}^+] = [VO^{2+}]$. The occurrence of $[I]_{max}$ at approximately half-reaction confirms the previous assumption that $k_4 = k_5$. From the above reaction sequence (1)–(5), assuming $[\cdot OH]$ is in steady state, the rate of formation of I, reaction 5, is

$$rate_{form} = \frac{k_{app}[VO^{2+}][VO_3{}^+]}{[V]_T}$$

The formation rate would then be a maximum when $[VO^{2+}] = [VO_3{}^+]$. If the decay rate of I is independent of $[VO^{2+}]$ and $[VO_3{}^+]$, $[I]_{max}$ would also occur when $[VO^{2+}] = [VO_3{}^+]$, as observed by experiments. In solutions where $VO_2{}^+$ was added to the $VO_2{}^+$ solution initially, $[I]_{max}$ occurred much earlier (before 10% VO^{2+} reacted), and $[I]_{max}$ was much greater, as shown

(9) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(10) A. E. Martell and L. G. Sillén, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1964, p 47.

TABLE II
DATA (MOLARITIES) AT MAXIMUM INTERMEDIATE CONCENTRATION

$[H^+]$	$10^3[VO^{2+}]$	$[H_2O_2]_i$	$10^3[V(V)]^a$	$10^3[VO^{2+}]^a$	$10^5[I]_{max}$
0.10	6.3	0.58	4.5	1.8	3.4
	6.0	0.44	3.5	2.5	4.9
	6.5	0.22	3.2	3.0	6.4
	6.0	0.11	2.6	3.4	6.0
	5.0	0.055	2.4	2.6	3.3
	6.3	0.026	3.0	3.4	2.9
0.06	2.5	0.11	1.4	1.1	6.0
	3.1	0.11	2.1	1.0	5.5
	6.2	0.12	3.3	2.9	8.2
	12.6	0.12	5.4	7.2	10.4
0.06	3.5	0.11	50^b	3.4	55
	3.5	0.11	33^b	3.4	62
	3.5	0.11	25^b	3.4	77
0.10	6.3	0.11	7.7^b	6.1	19
	5.8	0.11	4.1^b	6.1	10
10^{-4}	6.2	0.16	3.1	3.1	50
	6.4	0.12	3.2	3.2	55
	6.2	0.047	3.1	3.1	52

^{a} Concentrations measured at time coinciding with $[I]_{max}$. ^{b} Vanadium(V) added to solution initially. $[V(V)]_i = [V(V)]$ at $[I]_{max}$.

in Table II. $[I]_{max}$ increases with $[VO_2{}^+]$ and practically levels off at very large values of $[VO_2{}^+]$ where $[VO_2{}^+] = [V_T]$. A slight decrease in $[I]_{max}$ is noted for very large values of $[VO_2{}^+]$; this is probably due to the complexation of H_2O_2 with $VO_2{}^+$ which then tends to decrease the rate of formation of I.

Stoichiometry.—Stoichiometry results are presented in Table III. The consumption ratio for a simple oxi-

TABLE III
STOICHIOMETRY DATA

$[H^+]$, M	$10^2[VO^{2+}]_i$, M	$[H_2O_2]_i$, M	$H_2O_2:VO^{2+}$ ^{a}	$O_2:VO^{2+}$ ^{b}
Method A (Oxidation–Reduction Titrations)				
0.06	0.92	0.25	1.8	
		0.10	2.0	
		0.05	3.0	
	0.92^c	0.10	3.9	
Method B (Esr Observation of Excess VO^{2+})				
0.06	1.24	0.0151	1.8	
		0.0081	2.0	
		0.0062	2.0	
O_2 Evolution				
0.1	1.0	0.12	2.5	1.0
	1.5	0.075	2.5	1.0
	1.0	0.024	2.4	0.95
	2.0	0.024		0.39
	1.0	0.0075		0.18
	1.0	0.0045		0.11
	1.0	0.0030		0.06
	0.49^d	0.22	3.5	1.5
	0.49^d	0.054		>1.5
10^{-4}	0.49^d	0.22	1.9	0.73
	0.49^d	0.054	2.9	1.2

^{a} Moles of H_2O_2 consumed:moles of VO^{2+} consumed. ^{b} Moles of O_2 produced:moles of VO^{2+} present. ^{c} VO^{2+} dropped slowly into H_2O_2. Other runs were mixed as fast as possible. ^{d} $[VO_2{}^+]_i = 0.049$ M.

dation of VO^{2+} (reactions 1, 2, and 4) would be moles of H_2O_2:moles of $VO^{2+} = 0.5$ according to the overall reaction
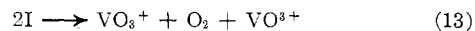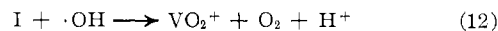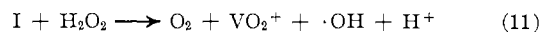
$$2VO^{2+} + H_2O_2 \longrightarrow 2VO_2{}^+ + 2H^+ \qquad (9)$$
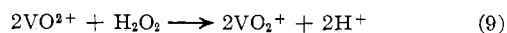
Further consumption of H_2O_2 would be explained by a net autoxidation–reduction reaction

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \qquad (10)$$
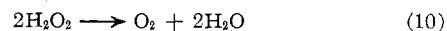
Oxidation–reduction titrations, method A, yield consumption ratios, $H_2O_2 : VO^{2+}$, of 1.8–3.9 indicating that a chain reaction mechanism which involves net reaction 10 is present. Method B and O_2 evolution studies also suggest a chain mechanism. When initial conditions are controlled so that the reaction is speeded up (high peroxide, low acid), then the ratio H_2O_2 consumed: vanadyl consumed is lowered. When VO^{2+} is added slowly to H_2O_2 so that radical concentrations are low, H_2O_2 consumed is increased relative to vanadyl consumed.

Addition of VO_2^+ to the initial solution increases the

O_2 evolution. Since increased $[VO_2^+]$ also increases the steady-state concentration of intermediate, the intermediate may be involved in a chain mechanism including reactions 11–13. For such a scheme, reaction 4 could also serve as a termination step.

$$I + H_2O_2 \longrightarrow O_2 + VO_2^+ + \cdot OH + H^+ \qquad (11)$$

$$I + \cdot OH \longrightarrow VO_2^+ + O_2 + H^+ \qquad (12)$$

$$2I \longrightarrow VO_3^+ + O_2 + VO^{3+} \qquad (13)$$

The Redox Behavior of Rhenium Halides. II. The Reactivity of β-Rhenium(IV) Chloride in Nonaqueous Media

By R. A. WALTON

The behavior of β-rhenium(IV) chloride in nonaqueous media has been studied to assess the variety of reactions this halide will undergo. Dissolution in acetonitrile is accompanied by some reduction, but cis-ReCl₄·2CH₃CN appears to be the principal reaction product. Studies on the systems β-ReCl₄–(C₆H₅)₃P–CH₃CN and β-ReCl₄–(C₆H₅)₃P–(CH₃)₂CO reveal quite markedly different reaction products, the course of the reactions depending critically upon the reaction solvent. In the former, unreduced trans-ReCl₄·2(C₆H₅)₃P and reduced [ReCl₃·(C₆H₅)₃P]₂ and ReCl₃·2(C₆H₅)₃P·CH₃CN are formed, whereas in acetone, oxygen abstraction occurs with the resulting formation of trans-ReOCl₃·2(C₆H₅)₃P. The salt (DOTP)₂Re₂Cl₉ (DOTP = 1,1-dimethyl-3-oxobutyltriphenylphosphonium) is also isolated from the latter reaction. Direct reaction of β-rhenium(IV) chloride with anhydrous pyridine also leads to the formation of unreduced cis-ReCl₄·2C₅H₅N and reduced (C₅H₅NH)₂Re₂Cl₈ species.

Introduction

Since our original report of the existence of β-rhenium(IV) chloride,[1] subsequent papers have described details of its preparation[2-4] and structure.[5] An X-ray crystallographic study[5] revealed this halide to have a polymeric structure which contains dinuclear metal–metal bonded units of the $W_2Cl_9^{3-}$ type. However, although it resembles other tetrachlorides of the heavier transition metals of the early transition series (Nb, Ta, Mo, W) in exhibiting pronounced metal–metal bonding, its other structural features are quite different.[6-8]

Reactivity differences between these halides are also apparent. Thus MCl_4 (M = Nb, Ta, Mo, W) show a marked tendency to react with a variety of donor molecules (L) to form pseudooctahedral complexes of stoichiometry $MCl_4 \cdot 2L$.[9-12] On the other hand we

found[1] that the reactions of β-ReCl₄, using acidified methanol or acetone as reaction solvents, afforded either rhenium(III) species derived from, or containing, the well-documented $Re_2Cl_8^{2-}$ anion[13] or oxorhenium(V) complexes. In no instances did we isolate rhenium(IV) complexes of the type $ReCl_4 \cdot 2L$. The apparent disproportionation of rhenium(IV) chloride into Re(III) and Re(V) appears to be quite general in solution *when the free access of air is permitted.*

When rigorously anhydrous and oxygen-free conditions are used, it has now been found that the reactions of β-rhenium(IV) chloride are sometimes quite different from those described above and rhenium(IV) complexes can indeed be isolated in certain instances.

Experimental Section

Materials.—Black crystalline β-rhenium(IV) chloride was obtained from the source described in an earlier paper.[1] All other reagents and solvents were commercially available and were used as supplied, except that solvents were dried by repeated distillation *in vacuo* from calcium hydride, phosphorus pentoxide, or anhydrous calcium sulfate.

Reaction Procedures.—To ensure the exclusion of oxygen and moisture, all reactions were carried out using an all-glass vacuum system using procedures described previously.[9,14] Once the reaction products had been isolated and dried, they could be handled in the atmosphere without fear of decomposition.

Reaction of β-Rhenium(IV) Chloride. (i) Acetonitrile.—

(1) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 223 (1967).

(2) J. H. Canterford and R. Colton, *Inorg. Nucl. Chem. Lett.*, **4**, 607 (1968).

(3) P. W. Frais, A. Guest, and C. J. L. Lock, *Can. J. Chem.*, **47**, 1069 (1969).

(4) I. R. Anderson and J. C. Sheldon, *Inorg. Chem.*, **7**, 2602 (1968).

(5) M. J. Bennett, F. A. Cotton, B. M. Foxman, and P. F. Stokley, *J. Amer. Chem. Soc.*, **89**, 2759 (1967).

(6) T. M. Brown and E. L. McCann, *Inorg. Chem.*, **7**, 1227 (1968).

(7) L. F. Dahl and D. L. Wampler, *Acta Crystallogr.*, **15**, 903 (1962).

(8) R. A. Walton, submitted for publication in *Progr. Inorg. Chem.*

(9) G. W. A. Fowles, D. J. Tidmarsh, and R. A. Walton, *Inorg. Chem.*, **8**, 631 (1969).

(10) (a) R. E. McCarley and B. A. Torp, *ibid.*, **2**, 540 (1963); (b) R. E. McCarley and J. C. Boatman, *ibid.*, **2**, 547 (1963).

(11) M. L. Larson and F. W. Moore, *ibid.*, **3**, 285 (1964).

(12) D. G. Blight and D. L. Kepert, *J. Chem. Soc. A*, 534 (1968).

(13) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

(14) G. W. A. Fowles, D. J. Tidmarsh, and R. A. Walton, *J. Chem. Soc. A*, 1546 (1969).