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Kinetics and Mechanism of Oxidation of Vanadium(2+) by Molecular Oxygen and Hydrogen Peroxide

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The reaction between hexaaquovanadium(II), $V(H_2O)_6^{2+}$, and molecular oxygen has been studied by the stopped-flow method in 0.12 M perchloric acid and in solutions containing 0.1 M sulfate ion. The kinetics and stoichiometry of the reactions are consistent with a general oxidation mechanism for divalent transition-metal ions proposed by Ochiai.[2] The following kinetic parameters have been determined: $k_2(2V^{2+} + H_2O_2) = 17.2 \pm 2.0$ M^{-1} s^{-1}; $k_3(V^{2+} + O_2) = (2.0 \pm 0.2) \times 10^3$ M^{-1} s^{-1}; $k_4((V{\cdot}O_2)^{2+}$ estimated dissociation) = 100 ± 50 s^{-1}; $k_5((V{\cdot}O_2)^{2+} + V^{2+}) = (3.7 \pm 0.5) \times 10^3$ M^{-1} s^{-1}; $k_{-5}((V{\cdot}O_2{\cdot}V)^{4+}$ dissociation) = 20 ± 5 s^{-1}; $k_6((V{\cdot}O_2{\cdot}V)^{4+}$ decomposition) = 35 ± 5 s^{-1}. At low V^{2+} concentration (<0.005 M) 2 mol of V(III) and 1 mol of oxovanadium(IV), VO^{2+}, are produced/mol of oxygen consumed. At higher $[V^{2+}]$, a limiting ratio of $\Delta[VO^{2+}]/\Delta[O_2] = 2$ is approached and a limiting rate constant for VO^{2+} formation of 40 ± 5 s^{-1} is reached in both sulfate and perchlorate solutions.

Introduction

The interaction of dioxygen with metal ion complexes is important in a wide variety of commercial and biological systems involving either oxygen transport or catalytic oxygen activation.[1,2] The autoxidation reactions of divalent metal ion complexes of the first transition series are exceptionally important because of their ubiquity and rather well-understood chemistry. The reactions of complexes of Cr(II),[3,4] Fe(II),[1,2] and Co(II)[1,2] have been widely studied as models for metal ion/dioxygen reactions. Although it is well-known that V^{2+} is a very efficient oxygen scavenger and forms as one of the reaction products the vanadyl ion, VO^{2+},[5] little is known about the intrinsic mechanism of this system. The implicit evidence that metal dioxygen complexes are involved in the overall reaction mechanism makes it an interesting example of a system in which oxidation states higher than 3+ are thermodynamically stable. The electrocatalytic reduction of oxygen without intermediate production of hydrogen peroxide is a goal for which transition-metal catalysts are being currently designed and studied. As is reported here, for certain conditions the V^{2+}/O_2 system models this behavior because of the exceptional stability of the oxygen-vanadium double bond in the vanadyl ion (V=O).[6] This study is related to our overall program that addresses the reactions of metal ion complexes with oxygen and oxyradicals.

Experimental Section

Preparation of V^{2+} Solutions. Vanadium(II) perchlorate solutions were made by dissolving $VOSO_4{\cdot}5H_2O$ in 0.12 M perchloric acid. Sulfate ion was precipitated with $Ba(ClO_4)_2$, and the concentration of VO^{2+} in this preparation was determined from its absorbance at 760 nm ($\epsilon_{760}(VO^{2+}) = 17.5$ M^{-1} cm^{-1}). Stock solutions that contained 0.12 M VO^{2+} were reduced electrolytically under nitrogen to V^{2+} over a mercury-pool cathode in an ice-cooled bath (cooling prevents reduction of perchlorate during the electrolysis).[7] The V^{3+}/V^{2+} ratio in sample preparation was checked as described by Swinehart.[5] Frozen stock solutions were stored at -60 °C. If the V^{3+} contamination in these solutions increased above 5%, new stock solutions had to be prepared because of its relatively high absorbance at the wavelength where V^{2+} was monitored. Vanadium(II) sulfate solutions were prepared in 0.1 M H_2SO_4. Experiments carried out in 0.1 M sulfate solutions were adjusted to pH 0.9 with $HClO_4$. The water used in the preparation of all solutions was distilled and passed through a Millipore ultrapurification system before use.

The oxygen and nitrogen used in the preparation of samples and as blanket gases were from Matheson (UHP grade, 99.999% purity). Hydrogen peroxide was from Apache Chemicals (Vycor distilled and stabilizer free). Perchloric acid (70%, Vycor distilled) was from GFS. Sulfuric acid was Aristar grade from BDH Chemicals. The vanadium(IV) salt used was $VOSO_4{\cdot}5H_2O$ (Baker reagent), and barium perchlorate was from Aldrich.

Table I. Pseudo-First-Order Rate Constants (k_{obsd}) for Reaction[a] between H_2O_2 and V^{2+} in Oxygen-Free 0.12 M $HClO_4$ at 21 °C

$[V^{2+}]$, M	k_{obsd}, s^{-1}	$[V^{2+}]$, M	k_{obsd}, s^{-1}
0.018 (±5%)	0.38	0.005	0.086
0.0108	0.16	0.0026	0.044

[a] $k_2 = 17.2 \pm 2.0$ M^{-1} s^{-1}.

Instrumentation. Routine UV-visible spectra were recorded on a Cary 210 spectrometer. The kinetic measurements were made on a Durrum-Gibson stopped-flow spectrophotometer at ambient temperature (21 ± 1 °C). The optical path length was either 2 cm (for most work) or 0.5 cm (necessary when high concentrations of V^{2+} were used). The photomultiplier tube was interfaced with a 4094 Nicolet digital oscilloscope. Analysis of the kinetic traces was performed either by graphic methods or on an IBM-PC microcomputer interfaced with the oscilloscope.

Simulations of the kinetic data were performed with a program using the Livermore Solver of Ordinary Differential Equations (LSODE) to integrate the differential equations. This program operated on the departmental VAX minicomputer.

Kinetic Measurements. Final solution mixtures contained either 1.3 × 10^{-4} or 6.3 × 10^{-4} M O_2 and 0.12 M $HClO_4$ or 0.1 M H_2SO_4. As reaction with excess V^{2+} was independent of $[O_2]$, conditions were chosen to optimize the signal while at least a 10:1 excess of V^{2+} was maintained. The acidity of the reaction solution was measured at the stopped-flow exhaust port with a glass electrode (calibrated with a pH 1 buffer). A measured pH of 0.9 ± 0.05 was the average for typical runs.

The formation of VO^{2+} was measured at wavelengths between 230 and 280 nm, where the absorption of V^{2+} and/or V^{3+} is low compared to that of VO^{2+}. Solutions, after dilution from stock with thoroughly deaerated 0.12 M $HClO_4$ or 0.1 M H_2SO_4, were transferred by syringe to the stopped-flow apparatus.

As was shown earlier, $(VOV)^{4+}$ can be formed by either the interaction of VO^{2+} with V^{2+}[8] or the hydrolysis of V(III),[9] shown in eq 1. The

$$VO^{2+} + V^{2+} \rightarrow (VOV)^{4+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} 2V(III) + H_2O \qquad (1)$$

spectrum (absorption maximum 435 nm) and conditions of its formation described by Newton et al.[8] provide a sensitive test for the presence of VO^{2+} in presence of an excess of V^{2+}.[5,8,10] Because the decay of $(VOV)^{4+}$ competes with its formation, the quantity ΔOD_{435nm} was determined from kinetic extrapolations to initial times. The maximum $[(VOV)^{4+}]$ is proportional to both $[V^{2+}]$ and $[VO^{2+}]$.

Results

Reaction between V^{2+} and H_2O_2. This reaction was monitored spectrophotometrically at 250 and 270 nm. Hydrogen peroxide solutions (2 × 10^{-4} M) were reacted with excess V^{2+} in 0.12 M $HClO_4$ under anaerobic conditions. The pseudo-first-order rate constants for reaction 2 as a function of $[V^{2+}]$ are listed in Table

$$\begin{gathered} 2V^{2+} + H_2O_2 \xrightarrow{H^+} 2V^{3+} + 2H_2O \\ k_2 = 17.2 \pm 2.0 \text{ M}^{-1} \text{ s}^{-1} \end{gathered} \qquad (2)$$

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(1) Neiderhoffer, E. C.; Timmon, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137 and references therein.
(2) Ochiai, E.-I. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 453.
(3) Ilan, Y. A.; Czapski, G.; Ardon, M. *Isr. J. Chem.* **1975**, *13*, 15.
(4) Sellers, R. M.; Simmic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6145.
(5) Swinehart, J. H. *Inorg. Chem.* **1965**, *4*, 1069.
(6) Selbin, J. *Chem. Rev.* **1965**, *65*, 153.
(7) King, W. R.; Garner, C. S. *J. Phys. Chem.* **1954**, *58*, 29.
(8) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1964**, *3*, 569.
(9) Pajdowski, L. *J. Inorg. Chem.* **1966**, *28*, 433.
(10) Malin, J. M.; Swinehart, J. H. *Inorg. Chem.* **1969**, *8*, 1407.

0020-1669/85/1324-4282$01.50/0

Table II. Comparison of Yields of the Dimer $(VOV)^{4+}$ (Proportional to ΔOD_{435nm}) Obtained from the Reaction of V^{2+} with 1.25×10^{-4} M O_2 and 1.25×10^{-4} M VO^{2+} (under Oxygen-Free Conditions) in 0.12 M $HClO_4$

	$\Delta OD_{435}(max)^a$		$\Delta[VO^{2+}]/\Delta[O_2]$	
$[V^{2+}]$, M	1.25×10^{-4} M O_2	1.25×10^{-4} M VO^{2+}	exptl	calcd^b
0.063	0.059	0.035	1.69	1.6
0.032	0.032	0.022	1.45	1.43
0.016	0.0165	0.012	1.38	1.3
0.008	0.0066	0.058	1.13	1.16
0.004	0.0032	0.0029	1.10	1.08

^{a}Results recorded in a $^1/_2$-cm cell at 435 nm. ^{b}For $k_4 = 100$ s^{-1} and k_3, k_5, k_{-5}, and k_6 as given in the text.

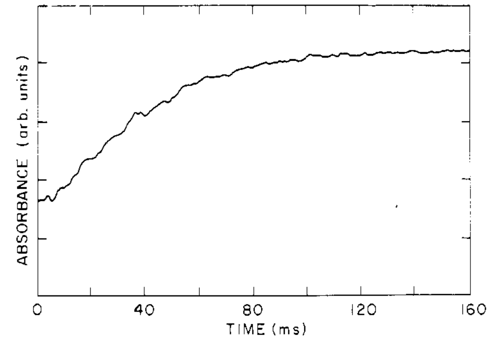

Figure 1. Oscilloscope trace of the reaction of 0.027 M V(II) with 6.5×10^{-4} M O_2 in 0.1 M sulfate (pH 0.9, perchloric acid). Wavelength = 250 nm.

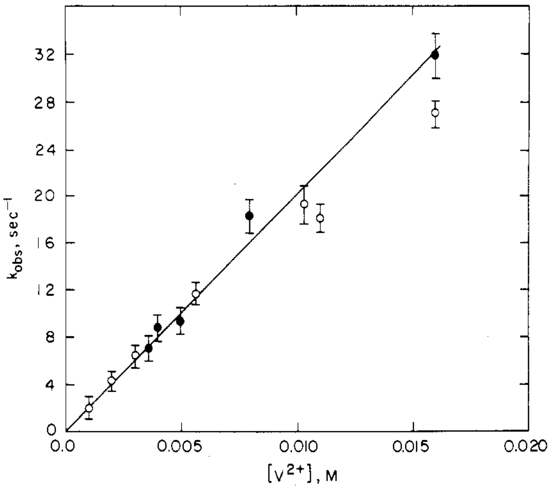

Figure 2. Dependence of k_{obsd} for VO^{2+} formation on [V(II)] at low [V(II)]: ○, 0.12 M $HClO_4$; ●, 0.1 M H_2SO_4 (pH 0.9, perchloric acid). Plotted slope = $k_3 = 2.0 \times 10^3$ M^{-1} s^{-1}.

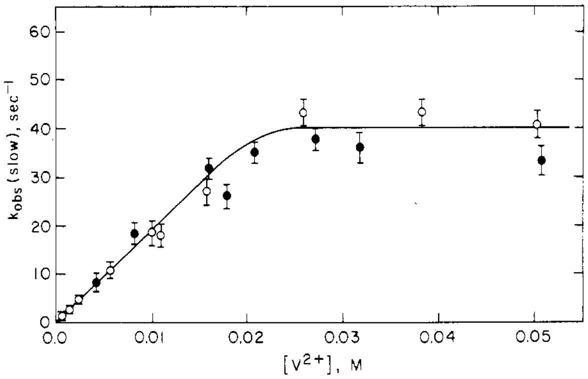

Figure 3. Dependence of k_{obsd}(slow) for VO^{2+} formation on [V(II)]: ○, 0.12 M $HClO_4$; ●, 0.1 M H_2SO_4 (pH 0.9, perchloric acid). The solid line is calculated for the rate of formation of VO^{2+} from data obtained by numerical integration of eq 3–6.

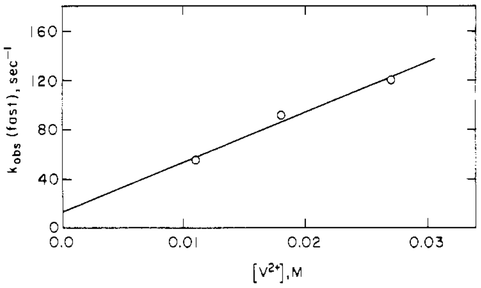

Figure 4. Dependence of k_{obsd}(fast) for formation of transient species on [V(II)] at 0.1 M H_2SO_4, pH 0.9, and $T = 21$ °C. The solid line is plotted for values of k_{obsd}(fast) obtained by integration of eq 3–6.

I. The stoichiometry indicated by eq 2 was not directly determined. However, the spectral changes, decreasing absorbance at 270 nm, are inconsistent with significant VO^{2+} formation. This was confirmed by observations at 435 nm, where no reaction between VO^{2+} and V^{2+} to form $(VOV)^{4+}$ was detected. Whether a Fenton type mechanism is operational in the overall reaction (2) has not yet been definitely established.

Reaction between V^{2+} and Oxygen. The reaction between 0.005 M V^{2+} and O_2 dissolved in sulfate or perchlorate solutions was observed directly by a rapid increase in absorbance in the wavelength range 220–280 nm. The resulting spectrum is of similar shape and intensity as that of VO^{2+} ($\lambda_{max} = 230$ nm, $\epsilon = 260$ M^{-1} cm^{-1}). The formation of VO^{2+} can also be observed at 435 nm, where it shows a slow reaction with excess V^{2+}. The quantity ΔOD_{435nm} was compared when V^{2+} was reacted with solutions containing either 1.25×10^{-4} M O_2 or 1.25×10^{-4} M deaerated VO^{2+}. The results, as a function of $[V^{2+}]$, are shown in Table II and indicate that a limiting stoichiometry of 2 mol of VO^{2+} is formed/mol of O_2 consumed as $[V^{2+}] \rightarrow 0.1$ M. At lower $[V^{2+}]$, 1 mol of VO^{2+} is formed along with 2 mol of V^{3+} in reaction 2 at a much slower rate than that of the reaction with oxygen (reaction 3).

As the reactions of V^{2+} with hydrogen peroxide and VO^{2+} are relatively slow, they do not affect the reaction of V^{2+} with dioxygen. Reactions of V^{3+} [11] and VO^{2+} [12] with dioxygen and hydrogen peroxide are also slow and do not have any bearing on the kinetics or stoichiometry of the V^{2+}/O_2 system as determined here.

Kinetics. The rate of formation of VO^{2+} from V^{2+} and O_2 was measured in the range $0.001 \text{ M} \leq [V^{2+}] \leq 0.06$ M. For runs with $[V^{2+}] \leq 0.005$ M or ≥ 0.05 M the kinetics appeared essentially first order while at intermediate concentrations in sulfate but not in perchlorate solutions they were clearly biphasic. A typical biphasic trace is shown in Figure 1. At 280 nm and $[V^{2+}] = 0.01$ M a perceptible decrease in absorbance precedes the rising signal of VO^{2+} indicating a spectrally distinct intermediate. However, because of the poor signal/noise ratio at the tail of the VO^{2+} spectrum, kinetic analysis was done at the shortest wavelength practical (240–260 nm). At $[V^{2+}] \leq 0.01$ M, the formation of VO^{2+} is first order in $[V^{2+}]$ and a plot of k_{obsd} vs. $[V^{2+}]$ is linear, as shown in Figure 2. Resolution of biphasic traces into fast (k_{obsd}(fast)) and slow (k_{obsd}(slow)) components was done graphically as for systems involving consecutive first-order reactions.[13] A plot of k_{obsd}(slow) vs. $[V^{2+}]$, $0.001 \text{ M} \leq [V^{2+}] \leq 0.06$ M, is shown in Figure 3. It should be noted that data from runs containing sulfate and perchlorate have been combined, as no systematic dependence of k_{obsd}(slow) on the anion could be observed.

Before considering the mechanism, it is useful to obtain from Figures 2–4 the various kinetic parameters needed for the analysis.

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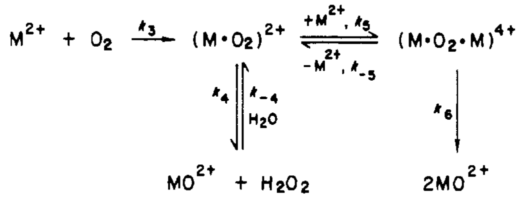
(11) V^{3+} reacts with H_2O_2 by second-order kinetics; $k = 2.3$ M^{-1} s^{-1} in 1.2 M $HClO_4$ (Rush, J., unpublished results).

(12) Brooks, H. B.; Sicilio, F. *Inorg. Chem.* **1971**, *10*, 2530.

(13) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, NY, 1961; Chapter 8.

Scheme I



The initial slope in Figure 1 yields $k_a = k_{obsd}(\text{slow})/[V^{2+}] = (2.0 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$ for $[V^{2+}] \leq 0.005$ M. Figure 3 shows that a limiting rate, $k_b \approx 40 \pm 5\ s^{-1}$, is reached when $[V^{2+}] > 0.02$ M. In Figure 4, the line drawn through the experimental points yields from the intercept and slope $k_c = 20 \pm 5\ s^{-1}$ and $k_d = 3.7 \times 10^3\ M^{-1}\ s^{-1}$, respectively.

Ochiai[2] proposed an overall oxidation mechanism for divalent transition-metal ions that he formulated as shown in Scheme I. The rate parameters, k_a–k_d, are related to the rate constants in Scheme I as follows: For the regions where $d[VO^{2+}]/dt$ is dependent on $[V^{2+}]$, $k_3 = 2 \times 10^3\ M^{-1}\ s^{-1} \approx k_a$; where it is independent of $[V^{2+}]$, $k_6 = 35\ s^{-1}$. In the range of $[V^{2+}]$ where a fast $[V^{2+}]$-dependent process precedes a slower reaction, the parameters k_d and k_c from Figure 4 have been related to $k_5 = 3.7 \times 10^3\ M^{-1}\ s^{-1}$ and $k_{-5} = 20\ s^{-1}$, respectively. The validity of these assignments was tested by numerical integration of the differential equations for VO^{2+} formation (reactions 3–6) and obtaining the time dependence of VO^{2+} formation for the entire experimental range of $[V^{2+}]$. The rate constants k_3–k_6 were used as described above. The reverse of reaction 4 in Scheme I is not significant under our conditions. However, Brooks and Sicilio[12] determined that, for VO^{2+}, $k_{-4} = 52\ M^{-1}\ s^{-1}$. In their study of VO^{2+} oxidation by H_2O_2, there was no indication of rate saturation with respect to $[H_2O_2]$ at $[H_2O_2] = 0.58$ M. From this we can conclude that $K_4 \geq 1$ M and therefore $k_4 \geq 50\ s^{-1}$. Within this constraint, the quantity k_4 was treated as an independent parameter to give the best agreement between observed and calculated stoichiometries.

The above treatment yielded curves that were evaluated in the same manner as the experimental traces. The absorbance due to $(V{\cdot}O_2{\cdot}V)^{4+}$ was neglected in our analysis of the computed traces because it is negligible compared to that of VO^{2+}. The corresponding calculated values of $k_{obsd}(\text{fast})$ and $k_{obsd}(\text{slow})$ are represented as solid lines in Figures 3 and 4. The calculated stoichiometries, $\Delta[VO^{2+}]/\Delta[O_2]$, as given in Table II, were calculated with $k_4 = 100\ s^{-1}$. We were unable to observe the formation of monomeric V(III) by reaction of H_2O_2 with excess V^{2+} owing to the large spectral changes associated with reaction 1.

The V(II) dependence of $k_{obsd}(\text{fast})$ indicates the participation of a second molecule of V^{2+}, as is required by the stoichiometry. As the fast step is difficult to resolve in perchloric acid solutions, the data in Figure 4 were obtained in the presence of sulfate ion. Reactions between VO^{2+} and sulfate cannot account for this as the spectra of VO^{2+} are virtually identical in sulfate and perchlorate solutions.[14] The absence of measurably biphasic kinetics in perchlorate media suggests that k_5 is smaller (perhaps not greater than k_3) in the absence of sulfate ion. This effect is plausible since sulfate would make an effective second bridging ligand between M(III) centers of the binuclear intermediate in Scheme I. However, the complexity of Scheme I prevents an unequivocal interpretation.

Mechanism. The kinetics and stoichiometry of O_2 reduction by V^{2+} are consistent with a mechanism that can be described by the following set of equations/equilibria.

(a) The formation of the transient V(IV) peroxy $(V{\cdot}O_2)^{2+}$ species is shown in reaction 3. Our formation of the complex

$$V^{2+} + O_2 \rightarrow (V{\cdot}O_2)^{2+}$$
$$k_3 = (2.0 + 0.2) \times 10^3\ M^{-1}\ s^{-1} \tag{3}$$

does not exclude other electronic configurations and degrees of protonation e.g., $V^{III}{\cdot}O_2H^{3+}$. However, the stability of the V(IV) and peroxide oxidation states and the known transient complex formed between these species[12] make this a reasonable assignment (see also Discussion).

(b) The dissociation of $(V{\cdot}O_2)^{2+}$ is given in reaction 4. The

$$(V{\cdot}O_2)^{2+} \underset{k_{-4}}{\overset{k_4,\ H_2O}{\rightleftharpoons}} VO^{2+} + H_2O_2$$
$$k_4(\text{estd}) \sim 100 \pm 50\ s^{-1} \tag{4}$$

characterization of the species $(V{\cdot}O_2)^{2+}$ was attempted by pulse-radiolytic reduction of the monoperoxovanadium(V) complex with hydrogen atoms.[15] Under appropriate conditions this reaction is complete within ~3 μs and yields a vanadium(IV) species. On slower time scales, no spectral changes that might be attributed to reaction 4 were observed. It is probable, however, that this is due to spectral similarities between $(V{\cdot}O_2)^{2+}$ and VO^{2+}, which is a characteristic of simple complexes of the vanadyl ion.

(c) The reaction between $(V{\cdot}O_2)^{2+}$ and excess V^{2+} leads to the reversible formation of the peroxide-bridged dimer $(V{\cdot}O_2{\cdot}V)^{4+}$ (reaction 5).

$$(V{\cdot}O_2)^{2+} + V^{2+} \rightleftharpoons (V{\cdot}O_2{\cdot}V)^{4+}$$
$$k_5 = (3.7 \pm 0.5) \times 10^3\ M^{-1}\ s^{-1} \qquad k_{-5} = 20 \pm 5\ s^{-1} \tag{5}$$

(d) The spontaneous decomposition of $(V{\cdot}O_2{\cdot}V)^{4+}$ yields two molecules of VO^{2+} (reaction 6).

$$(V{\cdot}O_2{\cdot}V)^{4+} \rightarrow 2VO^{2+} \qquad k_6 = 35 \pm 5\ s^{-1} \tag{6}$$

This reaction appears to be independent of $[H^+]$ in the pH range between 0.18 and 0.9, as k_b did not vary when V^{2+} (0.54 M) was reacted with oxygen dissolved in either 1.2 or 0.12 M $HClO_4$.

A limitation of our analysis is that a complete set of data could not be obtained in a single medium (e.g., the properties of $(VOV)^{4+}$ in sulfate solutions are unknown). The similarity of the two systems and good agreement between calculated and experimental values support the general validity of eq 3–6, although k_5 and k_{-5} in perchlorate are unknown and therefore k_4 is not well-defined for either system.

Discussion

Reactions 3–6 are analogous to those observed in the autoxidation of other M(II) complexes and are in close agreement with the mechanism proposed by Ochiai.[2] Reaction between Cr^{2+} and O_2 results in a metastable CrO_2^{2+} adduct in the absence of excess Cr^{2+}.[3,4] As in the case of CrO_2^{2+}, it is likely that $(V{\cdot}O_2)^{2+}$ is a $M^{IV}(O_2^{2-})$ species. The decomposition of $(V{\cdot}O_2)^{2+}$ to hydroxyl radicals and V(V) is slow[12] compared to its dissociation to hydrogen peroxide and VO^{2+}, and the value of k_4 (though approximate) is of the same order of magnitude as reported for the dissociation of sulfate ion from its vanadyl complex.[14]

The formation of stable peroxo-bridged dinuclear species is characteristic of Co(II) autoxidations.[16] Decomposition of the peroxide link seems to occur only when the $M^{III}O^-$ product can be stabilized by a covalent bond. This is permitted when the t_{2g} orbitals of the metal contain less than six electrons and d_π–p_π bonding between the metal and the oxo ligand is possible.[2] In the present system, reaction 6, which is postulated to be the symmetric decomposition of a peroxo-bridged V(III) dinuclear species, occurs rapidly because of the strong π-bonding in the $(V{=}O)^{2+}$ unit even though the scission of the –O–O– bond is endothermic (51 kcal/mol in H_2O_2).

The rate constant k_3 is considerably greater than other rate constants for ligand substitution on V^{2+},[17] a t_{2g}^3 ion that is considered substitutionally inert among first-row divalent transition-metal ions. A possible explanation is that one-electron redox occurs in the outer sphere, resulting in a closely associated $V^{3+}{\cdot}O_2^-$ successor. V^{3+} is expected to be susceptible to entering-ligand-

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(14) Strehlow, H.; Wendt, H. *Inorg. Chem.* **1962**, *1*, 8.

(15) Rush, J. D.; Bielski, B. H. J. *J. Phys. Chem.* **1985**, *89*, 1524.

(16) Wong, C.; Switzer, J.; Balakrishnan, K. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5511.

(17) Sutin, N. *Acc. Chem. Res.* **1968**, *1*, 225.

assisted substitution owing to the vacancy in its t_{2g} orbitals.[18]

The formation of free O_2^-/HO_2 and V(III) appears unlikely. A preliminary investigation of the reaction between V(III) and HO_2 generated by pulse radiolysis indicated that HO_2 oxidizes V(III) to VO^{2+} with a second-order rate constant $k(\mathrm{V(III)} + \mathrm{HO_2}) = 6 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$ in 0.12 M $HClO_4$. Although this rate constant increases with lowered $[H^+]$, the formation of major amounts of VO^{2+} in the V^{2+}/O_2 system would require that HO_2 react very slowly with V^{2+}, especially under those conditions where $[V^{2+}]_0$ is in large excess. This and the general kinetic complexity of the system cause us to exclude a mechanism based on simple outer-sphere electron transfer.

Reactions between V^{2+} and halogens (X_2; X = Cl, Br, I) occur at rates similar to that of reaction 3, V^{3+} however being the only product.[10] The difference in basicity of the half-reduced intermediates ($pK_{HO_2} = 4.8 \gg pK_{X_2H}$)[19] in the two systems (ligand basicity is a factor in the rates of V^{3+} substitution reactions)[20] may account for the difference in products if dissociation of a V^{3+}/X_2^- successor complex is much more rapid than ligand substitution.

Conclusion

The reaction between V^{2+} and molecular oxygen proceeds by parallel pathways, resulting in a [V(II)]-dependent stoichiometry. At low [V(II)] (<0.005 M) one molecule of VO^{2+} is produced per molecule of O_2 consumed. At [V(II)] > 0.1 M, no free peroxide is formed and two vanadyl ions VO^{2+} are the immediate reaction products. This is explained by a mechanism involving a [V(II)]-dependent equilibrium between a mononuclear Vanadium(IV) peroxide and a dinuclear vanadium(III) peroxide intermediate.

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[18] Baker, B. R.; Sutin, N.; Welch, T. J. *Inorg. Chem.* **1976**, *6*, 1948.

[19] Bielski, B. H. J. *Photochem. Photobiol.* **1978**, *28*, 645.

[20] Perlmutter-Hayman, B.; Topuhi, E. *Inorg. Chem.* **1979**, *18*, 2872.

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Evidence from the Reaction between Trioxodinitrate(II) and ^{15}NO That Trioxodinitrate(II) Decomposes into Nitrosyl Hydride and Nitrite in Neutral Aqueous Solution

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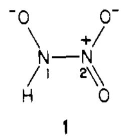
An attempt was made to trap nitrosyl hydride (nitroxyl; HNO, NO^- at pH 7) with ^{15}NO in order to decide whether trioxodinitrate(II) (Angeli's salt; oxyhyponitrite; $Na_2N_2O_3$, $HN_2O_3^-$ at pH 7) decomposes in neutral aqueous solution into nitroxyl plus nitrite or into NO plus $HONO^-$ as intermediate products. Final products are N_2O and nitrite. The reaction of ^{15}NO with nitroxyl was expected to double the yields of both N_2O and nitrite relative to those normally produced from trioxodinitrate alone and also to provide N_2O with a particular isotopic signature. The yields of N_2O and nitrite and the isotope distributions in product N_2O and the ^{15}NO pool strongly support the view that trioxodinitrate decomposes into nitroxyl and nitrite. In the trapping of nitroxyl by ^{15}NO, little exchange of ^{15}NO and $^{14}NO^-$ was observed. In addition to the trapping reaction, a fraction of the nitroxyl can partition by dimerization/dehydration to form $^{14}N_2O$. On the basis of these data and certain rate constants from the literature, a rate constant between 1.8×10^9 and $7.2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ is estimated for the dimerization/dehydration of nitroxyl at pH 7.0, 25 °C. The reaction is thus diffusion-controlled or nearly so. The calculation leading to the above rate constant is not free from kinetic ambiguity, but ambiguity could be largely removed if $N_2O_2^-$, a presumed intermediate in the trapping reaction, were asymmetrical.

Introduction



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There is some question[1] as to whether trioxodinitrate(II) ($Na_2N_2O_3$; Angeli's salt;[2] oxyhyponitrite[3]) decomposes to yield as intermediate products nitrosyl hydride (HNO/NO^-; nitroxyl) from N(1) of **1** and nitrite from N(2) in neutral aqueous solutions[4-9] (eq 1-3) or, alternatively, NO from N(1) and $HONO^-$ from N(2)[1] (eq 4-8). At pH 7, the monoanion, **1**, is the principal

$$\mathbf{1} \xrightarrow{\text{rds}} NO^- + NO_2^- + H^+ \qquad pK \text{ of HNO} = 4.7^{12} \tag{1}$$

$$NO^- + H^+ \rightarrow {}^1/_2N_2O + {}^1/_2H_2O \tag{2}$$

$$\text{net:}\quad \mathbf{1} \rightarrow {}^1/_2N_2O + NO_2^- + {}^1/_2H_2O \tag{3}$$

$$\mathbf{1} \xrightarrow{\text{rds}} NO + HONO^- \tag{4}$$

$$\mathbf{1} + HONO^- \rightarrow \mathbf{1}^- + NO_2^- + H^+ \tag{5}$$

$$\mathbf{1}^- + NO \rightarrow [ONNOHNO_2]^{2-} \tag{6}$$

$$[ONNOHNO_2]^{2-} \rightarrow N_2O + NO_2^- + OH^- \tag{7}$$

$$\text{net:}\quad 2\,\mathbf{1} \rightarrow N_2O + 2NO_2^- + H_2O \tag{8}$$

form in aqueous solution[10] ($pK_1 = 2.5$; $pK_2 = 9.7$[11]). Although nitroxyl is not involved in eq 4-8, N_2O must nevertheless arise from N(1). Thus, in the putative intermediate, $[ONNOHNO_2]^{2-}$,

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(1) Doyle, M. P.; Mahapatro, S. N. *J. Am. Chem. Soc.* **1984**, *106*, 3678-3679.

(2) Angeli, A. *Gazz. Chim. Ital.* **1903**, *33*, 245-252.

(3) Addison, C. C.; Gamlen, G. A.; Thompson, R. *J. Chem. Soc.* **1952**, 338-345.

(4) Hughes, M. N.; Wimbledon, P. E. *J. Chem. Soc., Dalton Trans.* **1977**, 1650-1653.

(5) Bonner, F. T.; Dzelzkalns, L. S.; Bonucci, J. A. *Inorg. Chem.* **1978**, *17*, 2487-2494.

(6) Bonner, F. T.; Akhtar, M. J. *Inorg. Chem.* **1981**, *20*, 3155-3160.

(7) Bonner, F. T.; Pearsall, K. A. *Inorg. Chem.* **1982**, *21*, 1973-1978.

(8) Garber, E. A. E.; Wehrli, S.; Hollocher, T. C. *J. Biol. Chem.* **1983**, *258*, 3587-3591.

(9) Bazylinski, D. A.; Hollocher, T. C. *J. Am Chem. Soc.*, in press.

(10) Bonner, F. T.; Degan, H.; Akhtar, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 3739-3742.

(11) Sturrock, P. E.; Ray, J. D.; McDowell, J.; Hunt, H. R. *Inorg. Chem.* **1963**, *2*, 649-650.

(12) Grätzel, M.; Taniguchi, S.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 1003-1010.