$$trans\text{-}[Co(NH_3)_4(NO_2)_2]^+ \longrightarrow trans\text{-}[Co(NH_3)_4(NO_2)H_2O]^{2+}$$
$$\downarrow$$
$$cis\text{-}[Co(NH_3)_4(HSO_4)_2]^- \longleftarrow cis\text{-}[Co(NH_3)_4(HSO_4)H_2O]^{2+}$$

The identification of the intermediates in these reactions is based not only on the number and relative intensities of the n.m.r. peaks, but also on the chemical shifts, which are discussed below. It is noteworthy that when a solution of $cis\text{-}[Co(NH_3)_4(HSO_4)_2]^+$ in 97% $H_2SO_4$ was diluted with water to make the solvent 75% $H_2SO_4$, the resulting solution contained both $cis\text{-}[Co(NH_3)_4(HSO_4)_2]^+$ and $cis\text{-}[Co(NH_3)_4(HSO_4)H_2O]^{2+}$.

We have calculated the chemical shifts relative to that for the hexaamminecobalt(III) ion. (The peak for this ion lies 3.12 p.p.m. to low field of tetramethyl-

TABLE I

CHEMICAL SHIFTS, RELATIVE TO THE HEXAAMMINECOBALT(III) ION, FOR SEVERAL PENTAAMMINECOBALT(III) IONS IN CONCENTRATED $H_2SO_4$

| Acido ligand | Chemical shift, p.p.m. |
|---|---|
| $cis\text{-}HSO_4^-$ | $-0.65$ |
| $trans\text{-}HSO_4^-$ | $0.84$ |
| $cis\text{-}H_2O$ | $-0.57$ |
| $trans\text{-}H_2O$ | $0.67$ |
| $cis\text{-}Cl^-$ | $-0.17$ |
| $trans\text{-}Cl^-$ | $0.49$ |
| $cis\text{-}Br^-$ | $-0.06$ |
| $trans\text{-}Br^-$ | $0.42$ |
| $cis\text{-}$ and $trans\text{-}NO_2^-$ | $0.00$ |

TABLE II

CHEMICAL SHIFTS, RELATIVE TO THE HEXAAMMINECOBALT(III) ION, FOR SEVERAL TETRAAMMINECOBALT(III) IONS IN CONCENTRATED $H_2SO_4$

| Acido ligands | Chemical shift, p.p.m. Observed | Estimated |
|---|---|---|
| $cis\text{-}HSO_4^-$, $cis\text{-}HSO_4^-$ | $-1.30^a$ | $-1.30$ |
| $cis\text{-}HSO_4^-$, $trans\text{-}HSO_4^-$ | $0.22$ | $0.19$ |
| $cis\text{-}HSO_4^-$, $cis\text{-}H_2O$ | $-1.10^a$ | $-1.22$ |
| $cis\text{-}HSO_4^-$, $trans\text{-}H_2O$ | $-0.07$ | $-0.02$ |
| $trans\text{-}HSO_4^-$, $cis\text{-}H_2O$ | $0.24$ | $0.27$ |
| $cis\text{-}HSO_4^-$, $cis\text{-}Cl^-$ | $-0.91,^a -1.16^b$ | $-0.82$ |
| $cis\text{-}HSO_4^-$, $trans\text{-}Cl^-$ | $-0.29$ | $-0.16$ |
| $trans\text{-}HSO_4^-$, $cis\text{-}Cl^-$ | $0.66$ | $0.67$ |
| $cis\text{-}H_2O$, $cis\text{-}NO_2^-$ | $-0.52^b$ | $-0.57$ |

$^a$ *cis* complex. $^b$ *trans* complex.

silane.) The chemical shifts for the two kinds of ammonia molecules in the pentaammine complexes are given in Table I, and the chemical shifts for the various kinds of ammonia molecules in the tetraammine complexes are given in Table II. If we assume that the chemical shift for a coordinated ammonia molecule is the sum of five terms characteristic of the other five ligands and their positions, then it is possible, using the data of Table I, to estimate the chemical shift values for ammonia molecules in tetraammine complexes.[6] These estimated chemical shifts are presented

(6) For example, we take the chemical shift contributions of *cis*-NH₃, *trans*-NH₃, *cis*-HSO₄⁻, and *trans*-HSO₄⁻ as 0, 0, −0.65, and 0.84 p.p.m., respectively. Thus in the complex *cis*-[Co(NH₃)₄(HSO₄)₂]⁺ we calculate a chemical shift of 2(−0.65) = −1.30 p.p.m. for the ammonia molecules which are *cis* to two HSO₄⁻ ions and a chemical shift of 0.84 − 0.65 = 0.19 p.p.m. for the ammonia molecules which are *cis* to one HSO₄⁻ ion and *trans* to the other.

alongside the experimental values in Table II. The close agreement of the experimental and estimated values gives us confidence in our structural assignments.
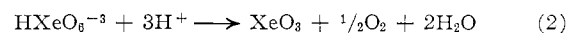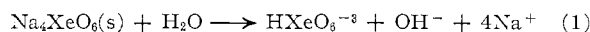
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CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

## Intermediates in the Oxidation of Water by Perxenate[1]

BY E. H. APPELMAN AND M. ANBAR[2]

Octavalent xenon in acid solution is one of the few substances that rapidly oxidize water to molecular oxygen.[3] We may write the reactions that take place when we dissolve solid sodium perxenate in water and subsequently acidify the solution

$$Na_4XeO_6(s) + H_2O \longrightarrow HXeO_6^{-3} + OH^- + 4Na^+ \quad (1)$$
$$HXeO_6^{-3} + 3H^+ \longrightarrow XeO_3 + \tfrac{1}{2}O_2 + 2H_2O \quad (2)$$

The product is a stable solution of hexavalent xenon.[3]

The xenon(VI)–xenon(VIII) electrode potential is about 3 v.,[3] making a number of mechanisms possible for reaction 2. Among these are processes involving the direct transfer of one or more electrons to the xenon(VIII) from one of its ligand oxygens or from a solvent water molecule. Transfer of a single electron leads to the formation of an OH radical and a transient Xe(VII) intermediate, while a double electron transfer from a single donor results in an oxygen atom and Xe(VI).

In the gas phase, atomic oxygen is known to bring about isotopic "scrambling" of the atoms in $O_2$ molecules by means of the chain reaction[4]

$$O^{16} + O^{18}O^{18} \rightleftharpoons O^{16}O^{18} + O^{18} \quad (3)$$
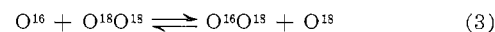
In aqueous solution the situation may be more complicated, but it still seems likely that by one mechanism or another atomic oxygen will bring about "scrambling" of the atoms of dissolved $O_2$. If this is true, we may look for the formation of oxygen atoms by allowing reaction 2 to proceed in a solution that is saturated with oxygen containing $O^{16}O^{16}$ and $O^{18}O^{18}$, but containing very little $O^{16}O^{18}$. If oxygen atoms are formed, we should observe the production of $O^{16}O^{18}$ molecules.

We may check our method by using ozone instead of perxenate. In the gas phase, ozone forms atomic oxygen by dissociation, and the O atoms then participate in reaction 3.[4] Thus we would expect appreciable "scrambling" to occur in a solution containing $O^{16}O^{16}$, $O^{18}O^{18}$, and ozone. However, even if we find that

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) On Sabbatical leave from the Weizmann Institute of Science, Rehovoth, Israel.

(3) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

(4) R. A. Ogg and W. T. Sutphen, *Discussions Faraday Soc.*, **17**, 47 (1954).

aqueous ozone itself does not cause "scrambling" of $O_2$, atomic oxygen in solution should still bring about some "scrambling" by reacting with $O_2$ to form $O_3$, which then decomposes.

If the perxenate–water reaction does not produce oxygen atoms, but forms OH radicals instead, perxenate in acid should rapidly oxidize substances that are known to be oxidized by these radicals. Chlorate ion appears to be oxidized to perchlorate by OH radicals,[5] but by very few other oxidants. If we find that perxenate rapidly oxidizes chlorate to perchlorate, we may suspect that OH radicals are indeed being formed, particularly if the reaction is suppressed by such OH scavengers as methanol and toluenesulfonic acid, and if the efficiency of these scavengers is proportional to the rate at which they react with OH radicals.

However, even if we can show that OH radicals are formed during the oxidation of water by perxenate, it is still possible that they are being produced in a side reaction. If the production of OH radicals constitutes the principal path through which reaction 2 proceeds, then the presence of OH scavengers should substantially inhibit the formation of oxygen, and again the extent of inhibition should depend on the rate at which the scavenger reacts with OH radicals.

Making use of these considerations, we have sought to determine whether the oxidation of water by perxenate takes place *via* one of these electron-transfer mechanisms.

### Experimental

**Reagents.**—Solutions of $RbClO_3$ tagged with $Cl^{36}$ were prepared in the following manner: Technical $Rb_2CO_3$ was recrystallized from a water–methanol solution and then dissolved in concentrated $HCl^{36}$ obtained from Oak Ridge National Laboratory. The concentrated RbCl solution was electrolyzed between platinum electrodes at a current density of about 10 amp./cm.[2]. Rubidium chlorate precipitated as soon as it was formed and the electrolysis was stopped after passing through a number of coulombs equivalent to 90% conversion of $Cl^-$ to $ClO_3^-$. The radioactive $RbClO_3$ was twice recrystallized from a RbCl solution and then dissolved in a minimum of water. A small amount of $RbClO_4$ was added and then recrystallized, carrying with it radioactive perchlorate contamination. The $RbClO_4$ procedure was repeated three times. Finally, after evaporation of most of the water, the radioactive $RbClO_3$ was recrystallized. The final yield of $RbCl^{36}O_3$ was about 40% of the initial $RbCl^{36}$, and its specific activity was 0.3 curie/mole.

Oxygen gas 99% in $O^{18}$ was obtained from Yeda Research and Development Co., Rehovoth, Israel. Ozonized oxygen was made with a Welzbach Model T-18 ozone generator and analyzed iodometrically. Sodium perxenate was prepared and analyzed as described elsewhere.[3] Formic acid, methanol, ethanol, and *p*-toluenesulfonic acid were Fluka Purissimum grade, and dioxane was Eastman White Label. Other chemicals were commercial products of reagent grade. Ordinary distilled water was redistilled from alkaline permanganate, then from dilute sulfuric acid, and once more without additive before being used.

**Oxygen "Scrambling" Experiments.**—The oxygen gas that was 99% in $O^{18}$ was mixed with an approximately equal volume of normal oxygen and a sample of the mixture was analyzed in the mass spectrometer. Portions of deaerated water were equilibrated with this mixture in syringes and the excess gas was

expelled. Appropriate amounts of acid were injected, and an equal volume of deaerated 0.0025 $M$ sodium perxenate solution was added from another syringe. This resulted in the solution being saturated with oxygen after reaction had occurred. In reference experiments a small volume of 0.01 $M$ $HClO_4$ saturated with oxygen and $3 \times 10^{-4}$ $M$ in $O_3$ was substituted for the perxenate solution. After all the perxenate or ozone had decomposed, the solution was transferred to a Van Slyke apparatus, and the dissolved gases were evolved by agitation under vacuum and were analyzed by mass spectrometry.

**Chlorate Oxidation Experiments.**—Sodium perxenate was dissolved in the radioactive rubidium chlorate solution and any desired organic reductant was added. The solution was stirred vigorously while the appropriate amount of perchloric acid was rapidly injected to bring about reaction 2. The solution was then neutralized with LiOH and evaporated to dryness. The residue was dissolved in 50% HBr and again evaporated to dryness. The residue was taken up in concentrated HCl and once more evaporated to dryness. The residue was then dissolved in a small amount of water, transferred to a platinum plate, dried, and counted in an end-window proportional $\beta$ counter. Any activity found was assumed to be due to perchlorate formed by oxidation of the chlorate, since in the absence of perxenate the platinum plate retained less than 0.005% of the initial chlorate activity. Experiments in which radioactive perchlorate was introduced demonstrated that the perchlorate is quantitatively carried through this procedure.

**Oxygen Evolution Experiments.**—Most of the experiments were carried out by the following method: A deaerated solution containing perxenate and reducing agent was placed in a syringe and the appropriate amount of acid was injected rapidly into it. The mixture was then transferred to a Van Slyke apparatus and agitated under vacuum in the presence of mercury. The mercury reduced the $XeO_3$ formed in reaction 2 to xenon, and the resulting gas mixture was analyzed by mass spectrometry for xenon and oxygen.

For a few experiments a different technique was used that permitted more rapid mixing of the reagents. A gas-conversion Y tube of the type described by Sprinson and Rittenberg[6] was used. A perxenate solution was placed in one leg, and acid and reducing agent in an equal volume were placed in the other. The solutions were frozen and the tube was evacuated. The solutions were deaerated by successive thawing and freezing, and reaction 2 was initiated by rapidly mixing the contents of the two arms. Afterward a small amount of mercury was sucked into the tube and agitated with the solution to reduce the $XeO_3$ and liberate the xenon. The gas mixture was again analyzed for xenon and oxygen by mass spectrometry.

We found that chloride ion inhibited the reaction of $XeO_3$ with mercury. Hence in the chloride experiments, which were carried out in the Y tubes, no mercury was added, but instead the gas was pumped with a Toepler pump through a liquid nitrogen trap into a standard volume. The pressure of the gas, which was assumed to be pure oxygen produced by reaction 2, was then measured with a Bourdon gauge.

### Results

The results of the "scrambling" experiments appear in Table I. Table II shows the results of the chlorate-

TABLE I

OZONE AND PERXENATE INDUCED "SCRAMBLING" OF $O_2$
DISSOLVED IN 0.2 $M$ $HClO_4$

| | Ozone | Perxenate |
|---|---|---|
| Reagent concn., m$M$ | 0.03 | 1.2 |
| $O^{16}O^{18}/O^{18}O^{18} \times 100$ | | |
|   Obsd. | 5.0 | 9.0 |
|   Calcd. if no "scrambling" | 2.1 | 2.8 |
| Moles of $O^{16}O^{18}$ formed per mole of reagent | 0.6 | 0.017 |

(5) Radiolysis of a chlorate solution produces perchlorate in low yield. The reaction can be suppressed by the addition of methanol: M. Anbar, unpublished results.

(6) D. B. Sprinson and D. Rittenberg, *J. Biol. Chem.*, **180**, 707 (1949).

TABLE II

OXIDATION OF CHLORATE BY PERXENATE[a]

| | ——% of chlorate oxidized—— | |
|---|---|---|
| Additive | $[H^+] = 1.0 M$ | $[H^+] = 0.1 M$ |
| None | 5.4 | 2.1 |
| Formic acid | 3.7 | 2.0 |
| Methanol | 2.7 | 1.6 |
| Ethanol | 1.0 | |
| p-Toluenesulfonic acid | 0.07 | 1.25[c] |
| None | 1.0[b] | |

[a] Unless otherwise specified, $[Na_4XeO_6] = 0.0184$–$0.0196 M$, $[RbClO_3] = 0.0154$–$0.016 M$, and the added reductant was equal in concentration to the $RbClO_3$. Perchloric acid concentrations are corrected for neutralization of the perxenate. [b] $[Na_4XeO_6] = 0.0148 M$, $[RbClO_3] = 0.34 M$. [c] $[C_7H_8SO_3H] = 7.7 \times 10^{-4} M$.

oxidation experiments, and Table III shows the oxygen-evolution results.

TABLE III

EVOLUTION OF OXYGEN IN THE OXIDATION OF
WATER BY PERXENATE[a]

| Added reductant | $[Na_4XeO_6]$, mM | [reductant], mM | $2[O_2]/[Na_4XeO_6]$ |
|---|---|---|---|
| None | 8 | ... | 1.0 |
| Methanol | 8 | 8 | 0.31 |
| Methanol | 8 | 80 | <0.01 |
| Methanol | 4 | 4 | 0.57[b] |
| Methanol | 4 | 8 | 0.12[b] |
| Methanol | 4 | 4 | 0.33[b,c] |
| Methanol | 4 | 16 | 0.01[b,c] |
| Dioxane | 3.8 | 3.3 | 0.07 |
| Dioxane | 3.8 | 17.4 | 0.03 |
| p-Toluenesulfonic acid | 8 | 8 | 0.06 |
| p-Toluenesulfonic acid | 8 | 18 | 0.01 |
| Cl⁻ | 2 | 4 | <0.05[b] |
| Cl⁻ | 2 | 4 | 0.05[b,d] |

[a] Unless otherwise specified, $[HClO_4] = 1 M$. [b] In Y tubes. [c] $[HClO_4] = 0.045 M$ after reaction. [d] $[HClO_4] = 0.022 M$ after reaction.

## Discussion

From Table I we see that reaction 2 causes very little isotopic "scrambling" of the atoms of molecular oxygen, whereas ozone is a fairly efficient "scrambler." Hence the formation of atomic oxygen by transfer of two electrons from a water molecule to Xe(VIII) can be only a very minor path. This leaves us to see if there is any evidence for a single-electron transfer to form OH radicals.

Table II indicates that perxenate does indeed oxidize chlorate to perchlorate in acid, and that the reaction is inhibited by OH scavengers. Furthermore, we see by comparison with Table IV that the efficiency of inhibition corresponds closely to the relative rates at which the scavengers react with OH radicals.[7] Comparison of Table III with Table IV shows that the OH scavengers act in this same order of efficiency to suppress the evolution of oxygen from reaction 2, although chloride ion at low acidity appears to be a little more efficient than we would have predicted. If all these substances were being oxidized directly by the perxenate, we would expect dioxane and toluenesulfonic acid to be the least

(7) The rate constant for the oxidation of chlorate ion by hydroxyl radicals has not been determined, but from the data in Tables II and IV we can estimate it to be about $5 \times 10^3$ l./mole sec. in 1 $M$ acid.
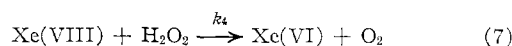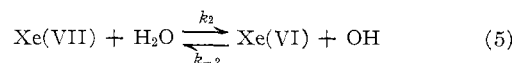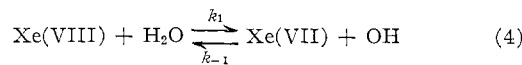
efficient instead of the most, since they are both relatively inert to anionic oxidants like permanganate and dichromate,[8] which ought to react in a manner roughly analogous to perxenate. Therefore, it seems likely that dioxane and toluenesulfonic acid do not react directly with perxenate, but instead react with hydroxyl radicals formed in the reaction of perxenate with water. Furthermore, the fact that these substances can suppress oxygen evolution essentially completely implies that reaction 2 proceeds almost entirely through the formation of OH radicals.

TABLE IV

REACTIONS OF HYDROXYL RADICALS AT ROOM TEMPERATURE

| Reagent | $10^{-9}k$, l./mole sec. | Ref. |
|---|---|---|
| OH | 8 | c |
| p-Toluenesulfonic acid | 4.5 | d |
| Cl⁻[a] | 4 | e |
| Cl⁻[b] | 0.45 | e |
| Dioxane | 2.4 | c |
| Ethanol | 0.7 | c |
| Methanol | 0.5 | c |
| Formic acid | 0.14 | c |

[a] 1 $M$ $HClO_4$. [b] 0.025 $M$ $HClO_4$. [c] J. K. Thomas, *Trans. Faraday Soc.*, **61**, 702 (1965). [d] M. Anbar and D. Meyerstein, to be published. [e] M. Anbar and J. K. Thomas, *J. Phys. Chem.*, **68**, 3829 (1964).

A mechanism for the oxidation of water by perxenate that is consistent with these observations is the following.

$$Xe(VIII) + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Xe(VII) + OH \qquad (4)$$

$$Xe(VII) + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Xe(VI) + OH \qquad (5)$$

$$2OH \overset{k_3}{\longrightarrow} H_2O_2 \qquad (6)$$

$$Xe(VIII) + H_2O_2 \overset{k_4}{\longrightarrow} Xe(VI) + O_2 \qquad (7)$$

Hexavalent xenon is also reduced by $H_2O_2$, but this reaction is probably much slower than reaction 7. Although solvent water is shown as the reductant in reactions 4 and 5, these reactions may instead take place entirely within the coordination spheres of the Xe(VIII) and Xe(VII). In that case the reductant would be oxygen bound to the xenon, and the reaction would be unimolecular.

Although the data in this paper are largely qualitative, on the basis of Tables III and IV we can set a lower limit of about $10^5$ sec.$^{-1}$ to the unimolecular rate constant $k_1$ in 1 $M$ $HClO_4$. In addition to making the usual steady-state assumptions regarding OH and Xe(VII), we are assuming that $k_{-1}[Xe(VII)] + k_{-2}[Xe(VI)] \ll k_3[OH]$ and that there is no direct reaction between methanol and perxenate. Failure of either of the latter two assumptions will make $k_1$ larger. If these assumptions are valid, the steady-state OH concentration is about $3 \times 10^{-4} M$ during the reaction of $4 \times 10^{-3} M$ perxenate in the absence of scavengers.

(8) R. Stewart "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964.

It is likely, but not essential to the argument, that reaction 4 is rate-determining in the over-all oxidation of water.

If direct reaction of the additives with the perxenate were predominant in our experiments, these reactions would have to have bimolecular rate constants exceeding $10^8$ l./mole sec. Although it is possible that chloride might react with perxenate at such a rate, it seems very unlikely that any of the organic materials would do so, particularly when we consider that under these conditions dichromate oxidizes such materials with rate constants of $10^{-2}$ or less.[8] Thus it seems highly probable that at the concentrations employed in this study, all of the organic additives react primarily with the OH radicals formed by reactions 4 and 5.

**Acknowledgments.**—We wish to thank Mr. Lloyd Krout for carrying out the mass spectrometric analyses, and we are greatly indebted to Professor Henry Taube for valuable criticism.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA

## On the Oxidation of Vanadium(II) by Oxygen and Hydrogen Peroxide

BY JAMES H. SWINEHART

The mechanism by which aqueous solutions of first-row transition metal ions in the $+2$ oxidation state, M(II), are oxidized to the $+3$ oxidation state, M(III), has received considerable attention. The problem becomes especially interesting with oxygen and hydrogen peroxide which can act as one- or two-electron oxidizing agents.[1] Two possible mechanisms for the oxidation process are: (i) a one-electron oxidation and (ii) a two-electron oxidation of M(II) to M(IV) followed by a reaction between M(IV) and M(II) yielding M(III). The question is how much of the reaction proceeds by each mechanism?

Recently an intermediate in the reaction between $V_{aq}^{2+}$ and $VO_{aq}^{2+}$, $VOV_{aq}^{4+}$, was characterized.[2] This intermediate, which has a high intensity absorption band centered at 4250 Å., forms slowly from the reactants. The extent to which the intermediate forms will depend on its rate of decomposition, which to a first approximation in acid solution is proportional to the product of the intermediate and hydrogen ion concentrations. At moderate hydrogen ion concentrations the intermediate is a sensitive probe of the mechanism by which $V_{aq}^{2+}$ is oxidized to $V_{aq}^{3+}$ by $O_2$ and $H_2O_2$. Detection of the intermediate means that the oxida-

(1) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, Chapter 4.

(2) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).

tion has yielded $VO_{aq}^{2+}$ by a process which is rapid compared with the rate of formation of the intermediate. If the intermediate is not observed either a one-electron oxidation of $V_{aq}^{2+}$ and $V_{aq}^{3+}$ occurs or the formation of $VO_{aq}^{2+}$ is very slow compared to the formation of the intermediate.

This note describes a study of the reaction of excess $V_{aq}^{2+}$ with $O_2$ and $H_2O_2$ in acid solution.

### Experimental

**Materials.**—The chemicals used were: $VOSO_4 \cdot 2H_2O$ (purified, Fisher Scientific Co.); $HClO_4$, 70.9% by specific gravity measurement (reagent, Baker and Adamson); $Ba(ClO_4)_2 \cdot 3H_2O$ (G. F. Smith Chemical Co.); $Na_2CO_3$ (reagent, J. T. Baker Chemical Co.); $H_2O_2$, 30% solution (reagent, J. T. Baker Chemical Co.); and $Fe(ClO_4)_3 \cdot 6H_2O$ (G. F. Smith Chemical Co.).

Vanadium(II) perchlorate solutions were prepared by reduction of $VO(ClO_4)_2$ solutions containing $HClO_4$ and $NaClO_4$ with Zn amalgam. Vanadium(IV) perchlorate solutions were prepared from $VOSO_4$ solutions by adding $Ba(ClO_4)_2$ to precipitate $BaSO_4$. Constant ionic strength solutions of $HClO_4$ and $NaClO_4$ were prepared by adding the appropriate amount of $HClO_4$ (70.9% by weight) to weighed amounts of $Na_2CO_3$. Iron(III) and vanadium(IV) solutions were prepared by adding weighed amounts of $Fe(ClO_4)_3 \cdot 6H_2O$ or $VOSO_4 \cdot 3H_2O$ to the proper $NaClO_4$–$HClO_4$ solution.

**Measurements.**—All absorbancy measurements were made with a Cary Model 14 recording spectrophotometer using 1-cm. cells. An appropriate volume of the solution of the oxidizing agent ($O_2$, $H_2O_2$, $Fe_{aq}^{3+}$, or $VO_{aq}^{2+}$) at a total ionic strength of approximately 1.0 in $NaClO_4$, $HClO_4$, and $Zn(ClO_4)_2$ was prepared in a 1-cm. capped spectrophotometer cell. Iron(III) and vanadium(IV) solutions were outgassed with $N_2$ which had passed through bubblers containing chromium(II) to remove $O_2$. Oxygen-containing solutions were prepared by bubbling the gas into $NaClO_4$–$HClO_4$ solutions contained in capped cells. Hydrogen peroxide solutions were prepared by adding the appropriate volume of 30% $H_2O_2$ to $N_2$-outgassed $NaClO_4$–$HClO_4$ solutions.

The $V_{aq}^{2+}$ solution was added to the capped 1-cm. cell with a syringe while the cell was in the spectrophotometer. The solution was mixed by pulling the contents of the cell back into the syringe and then forcing it back into the cell. The order of mixing did not affect the results. Blanks were run by adding vanadium(II) solutions to $N_2$-outgassed solutions containing no oxidizing agent. The resulting solutions were spectrophotometrically pure $V_{aq}^{2+}$ as determined from knowledge of the visible spectrum of $V_{aq}^{2+}$.[3] The concentration of oxidizing agent present in the original solution was determined from the amount of $V_{aq}^{3+}$ produced in the reaction. The total vanadium content of each solution, $[V_{aq}^{2+} + V_{aq}^{3+}]$, was determined spectrophotometrically using the absorbance at 5700 Å. At this wave length the extinction coefficient of $V_{aq}^{2+}$ equals that of $V_{aq}^{3+}$ (5.25 cm.$^{-1}$ $M^{-1}$).[3,4] The $V_{aq}^{3+}$ produced in the oxidation was determined from the absorbance at 4000 Å. which was corrected for the excess $V_{aq}^{2+}$ present. At 4000 Å. $\epsilon_{V_{aq}^{3+}}$ equals 8.30 cm.$^{-1}$ $M^{-1}$,[3-5] and $\epsilon_{V_{aq}^{2+}}$ equals 1.16 cm.$^{-1}$ $M^{-1}$.[5] The concentration of oxidizing agent in the original solution was the final concentration of $V_{aq}^{3+}$ divided by 4 for oxygen and 2 for $VO_{aq}^{2+}$ and $H_2O_2$.

### Results and Discussion

When excess $V_{aq}^{2+}$ reacts with $O_2$ or $H_2O_2$, curves of the absorbance at wave lengths between 3500 and 5500 Å. recorded as a function of time increase to a maximum and then decrease to a final value indicating

(3) W. R. King, Jr., and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

(4) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).

(5) As determined by the author.