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.

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

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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 oxidation 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

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(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).

(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.

that an intermediate forms in the reaction. The spectrum of the intermediate, ΔD *vs.* wave length, where ΔD is defined in ref. 2 as the difference in absorbance between the zero time extrapolation of the decreasing portion of the absorbance *vs.* time curve minus the contribution from the initial concentrations of $V_{aq}{}^{2+}$ and $VO_{aq}{}^{2+}$, is identical with the spectrum Newton and Baker find for the intermediate in the reaction between $V_{aq}{}^{2+}$ and $VO_{aq}{}^{2+}$, $VOV_{aq}{}^{4+}$.[2] The maximum in the spectrum is at 4250 Å. Measurements at 7600 Å. show that $VO_{aq}{}^{2+}$ is an initial product in the reaction. No intermediate forms in the reaction between $V_{aq}{}^{2+}$ and $Fe_{aq}{}^{3+}$, a one-electron oxidizing agent. Spectra of the solutions recorded after completion of the reaction between $V_{aq}{}^{2+}$ and O_2 or H_2O_2 showed only $V_{aq}{}^{2+}$ and $V_{aq}{}^{3+}$ to be present. Therefore, it is concluded that one path for the oxidation of excess $V_{aq}{}^{2+}$ to $V_{aq}{}^{3+}$ by O_2 or H_2O_2 involves the *rapid* oxidation of $V_{aq}{}^{2+}$ to $VO_{aq}{}^{2+}$ followed by the reaction of $VO_{aq}{}^{2+}$ with $V_{aq}{}^{2+}$ yielding $V_{aq}{}^{3+}$. As stated in ref. 2 about 65% of the $V_{aq}{}^{2+}$–$VO_{aq}{}^{2+}$ reaction goes by the intermediate $VOV_{aq}{}^{4+}$ while the remainder proceeds by an outer-sphere mechanism. The second path, a one-electron oxidation of $V_{aq}{}^{2+}$ to $V_{aq}{}^{3+}$, must also be rapid.

The question to be answered is what fraction of the $V_{aq}{}^{3+}$ produced in the reaction of excess $V_{aq}{}^{2+}$ with O_2 or H_2O_2 proceeds by the $V_{aq}{}^{2+}$–$VO_{aq}{}^{2+}$ path? Newton and Baker have shown that for the reaction between $V_{aq}{}^{2+}$ and $VO_{aq}{}^{2+}$ the quantity $\Delta D[H^+]/[V_{aq}{}^{2+}]\cdot[VO_{aq}{}^{2+}]$, where $[V_{aq}{}^{2+}]$ and $[VO_{aq}{}^{2+}]$ are the initial concentrations of $V_{aq}{}^{2+}$ and $VO_{aq}{}^{2+}$, is a constant at a given temperature.[2] The fraction of the reaction proceeding by a $V_{aq}{}^{2+}$–$VO_{aq}{}^{2+}$ path can be estimated from the discrepancy between the quantity $\Delta D/[V_{aq}{}^{2+}][VO_{aq}{}^{2+}]$, at constant $[H^+]$, obtained for the $V_{aq}{}^{2+}$–$VO_{aq}{}^{2+}$ reaction and values obtained for the $V_{aq}{}^{2+}$–O_2 and H_2O_2 reactions assuming all of the oxidizing agent reacts rapidly with $V_{aq}{}^{2+}$ to give $VO_{aq}{}^{2+}$ ($[VO_{aq}{}^{2+}]$ equals the concentration of H_2O_2 and twice the concentration of O_2). In all cases $[V_{aq}{}^{2+}]$ was calculated using $\Delta D/[V_{aq}{}^{2+}][VO_{aq}{}^{2+}]$ from the $V_{aq}{}^{2+}$–$VO_{aq}{}^{2+}$ reaction and equations for total vanadium and total oxidizing agent.

Table I presents some typical data collected at 4250 Å. when excess $V_{aq}{}^{2+}$ was allowed to react with O_2, H_2O_2, and $VO_{aq}{}^{2+}$. The quantity $\Delta D/[V_{aq}{}^{2+}][VO_{aq}{}^{2+}]$ for the reaction of $V_{aq}{}^{2+}$ with $VO_{aq}{}^{2+}$ is approximately 13×10^3 M^{-2} at 20°, $[H^+] \approx 0.3$ M, and $\mu = 1.0$.[6] The values calculated for the H_2O_2 and O_2 reactions with $V_{aq}{}^{2+}$ are 4×10^3 and 8×10^3 M^{-2}, respectively. This means that in the $V_{aq}{}^{2+}$–H_2O_2 and $V_{aq}{}^{2+}$–O_2 reactions about 30 and 60%, respectively, of the $V_{aq}{}^{3+}$ is produced *via* the $V_{aq}{}^{2+}$–$VO_{aq}{}^{2+}$ path.

TABLE I

DATA ON THE OXIDATION OF VANADIUM(II)

Conditions: 20°, $\mu \approx 1.0$ ($HClO_4$, $NaClO_4$, and $Zn(ClO_4)_2$), $[H^+] \approx 0.3$ M

Run[a]	Oxidizing agent	10^3[oxidizing agent], M	$10^2[V_{aq}{}^{2+}]$, M	ΔD	$10^{-3}\Delta D/[V_{aq}{}^{2+}]\cdot[VO_{aq}{}^{2+}]$,[b] M^{-2}
1	H_2O_2	1.5	2.20	0.15	4.5
2	H_2O_2	3.8	1.81	0.27	3.9
3	H_2O_2	3.9	1.81	0.32	4.5
4	O_2	0.6	2.27	0.20	7.3
5	O_2	0.7	2.18	0.26	8.5
6	O_2	1.2	1.16	0.24	8.6
7	$VO_{aq}{}^{2+}$	0.3	2.26	0.09	13.3
8	$VO_{aq}{}^{2+}$	1.2	2.26	0.36	13.3
9	$VO_{aq}{}^{2+}$	3.3	2.15	0.81	11.5

[a] Each run done in duplicate. [b] $[VO_{aq}{}^{2+}] = n$[oxidizing agent], where n equals 2 for oxygen and 1 for H_2O_2 and $VO_{aq}{}^{2+}$.

The oxidation of $Cr_{aq}{}^{2+}$ by O_2 and H_2O_2 has been studied by Ardon and Plane.[7] Oxidation with H_2O_2 yields primarily $Cr_{aq}{}^{3+}$. However, a dinuclear chromium(III) species, which is believed to result from a reaction between $Cr_{aq}{}^{2+}$ and a chromium(IV) species, is the only product when O_2 is used. It is interesting to note that in both cases oxidation with O_2 proceeds primarily by the M(II)–M(IV) path, while the H_2O_2 oxidation proceeds predominantly by a one-electron path.

Lower limits can be set on the rate constants associated with the oxidation of $V_{aq}{}^{2+}$ directly to $V_{aq}{}^{3+}$ and $VO_{aq}{}^{2+}$. Assuming pseudo-first-order kinetics ($[V_{aq}{}^{2+}] = 10^{-2}$ M and a half-time less than 1 sec.) the rate constants are greater than 10^2 M^{-1} sec.$^{-1}$ at 20°.

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[6] The quantity $0.693\Delta D/[V_{aq}{}^{2+}]$ $[VO_{aq}{}^{2+}]t_{1/2}$, where $t_{1/2}$ is defined in ref. 2, is 2900 and 3000 M^{-2} sec.$^{-1}$ for runs 7 and 8, respectively. The value at 20° extrapolated from the data of Newton and Baker is 2900 M^{-2} sec.$^{-1}$.

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Proton Nuclear Magnetic Resonance Studies of the Bismuth(III) and Lead(II) Tartrate Complexes

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Metal tartrate complexes are well known and a number of stability constants have been reported.[2-5]

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