Conclusions. The outer-sphere oxidations of SCN^- and I^- can proceed through paths first order in substrate and second order in substrate and via medium-catalyzed paths. The free energy of the first-order path usually determines its rate, while the second-order path is more often influenced by the self-exchange rates. While we cannot yet predict the rates of the medium-catalyzed paths, it should be noted that they seem to dominate for reactions of weak highly charged oxidizing agents such as $Fe(CN)_6^{3-}$ and $W(CN)_8^{3-}$.

Acknowledgment. The comments of Henry Taube and Albert Haim have been quite helpful.

Registry No. $IrCl_6^{2-}$, 16918-91-5; $IrBr_6^{2-}$, 16919-98-5; SCN^-, 302-04-5; I^-, 20461-54-5; SCN·, 15941-77-2; I·, 14362-44-8; $(SCN)_2^-$, 66555-10-0; I_2^-, 12190-71-5.

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Equilibria and Kinetics of Reduction by Iodide Ion of the Vanadium(V)–Hydrogen Peroxide System

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The equilibrium constant (K_1) for the formation of the red vanadium(V)–monoperoxo complex VO_3^+ from VO_2^+ and H_2O_2 and the equilibrium constant (K_2) for the formation of the yellow vanadium(V)–diperoxo complex VO_5^- from VO_3^+ and H_2O_2 have been determined by spectrophotometry, their values being $K_1 = (3.7 \pm 0.4) \times 10^4\ M^{-1}$ and $K_2 = 0.6 \pm 0.1$ M at 25 °C and at an ionic strength of 0.3 M ($NaClO_4$). The kinetics of reduction by iodide of acidic mixtures of H_2O_2 and VO_2^+ have been investigated at the same temperature and ionic strength of the equilibrium measurements. The results agree with the rate law $V/[I^-] = (1.2 \times 10^{-3}/[H^+] + 1.3 \times 10^{-2} + 1.8 \times 10^{-1}[H^+])[VO_3^+] + (0.73 + 154[H^+])[VO_5^-]$ and are interpreted in terms of nucleophilic attack by iodide ion on differently protonated forms of VO_3^+ and VO_5^- ions.

Introduction

The catalytic effect exerted by transition-metal derivatives on reactions involving hydrogen peroxide as an oxidant and on the decomposition of the hydrogen peroxide itself are well-known and have been extensively investigated.[1] Although the formation of peroxo compounds of transition metals has been envisaged as playing a fundamental role in the above mentioned processes, in most of the investigated systems the metal–peroxo compounds are present only as labile intermediates whose composition is seldom identified with certainty.[2] In their review on the development in redox chemistry of peroxides Jones et al.[3] stressed the importance of two-electron-equivalent processes in a field of chemistry where free-radical interpretations are perhaps superabundant.

The present study of the oxidation of iodide ion by the hydrogen peroxide–vanadium(V) system is an attempt to elucidate the mechanism of action of peroxidic species that are formed in nonnegligible amounts and whose compositions in aqueous solution are quite well established.[4,5]

Experimental Section

Materials. Stock solutions of the reactants were prepared by dissolving chemicals of analytical grade in triply distilled water, which was also used as a reaction medium. Nonstabilized hydrogen peroxide was used, and its content was frequently checked by permanganate titrations. Sodium vanadate was used as a source of vanadium(V); perchloric acid and sodium perchlorate were used to obtain the desired acidity and ionic strength.

Equilibrium Constants. These were measured by spectrophotometry using a Perkin-Elmer E 200 apparatus. The extinction coefficients of the absorbing species were measured at λ = 455 nm, their values being $\epsilon_{VO_2^+} = 3.9$, $\epsilon_{VO_3^+} = 278$, and $\epsilon_{VO_5^-} = 25\ M^{-1}\ cm^{-1}$. The ionic strength was kept constant at 0.3 M, and the temperature was 25.0 ± 0.1 °C throughout.

Kinetic Runs. Initial rates were measured by titrating with sodium thiosulfate. The iodine developed in the course of the reaction according to the procedure already described.[6,7] Care was taken to exclude the presence of oxygen by flushing the reacting mixture with a stream of purified nitrogen. The temperature and ionic strength were as in the equilibrium experiments. The reaction rates remained unaffected by changing the amount of starch added in order to reveal the developed iodine,[6,7] meaning that radical involvement is absent.

Results

Equilibrium Constants. In solutions more acidic than about 0.01 M, vanadium(V) exists mainly as the oxo cation VO_2^+ (or $H_4VO_4^+$). It forms, with hydrogen peroxide, the red monoperoxo complex VO_3^+ and the yellow diperoxo complex VO_5^- according to the reactions

$$VO_2^+ + H_2O_2 \xrightleftharpoons{K_1} VO_3^+ + H_2O \qquad (1)$$

$$VO_3^+ + H_2O_2 \xrightleftharpoons{K_2} VO_5^- + 2H^+ \qquad (2)$$

Equilibrium 2 is strongly dependent on $[H^+]$, contrary to equilibrium 1. This allows the equilibrium constants K_1 and K_2 to be determined from independent sets of measurements, by choosing the appropriate ranges of hydrogen ion and hydrogen peroxide concentrations. The two peroxo complexes are known to lose oxygen in acid solution.[8,9] However the process of decomposition is so slow, at the acid and hydrogen peroxide concentrations of this investigation, that it can be safely neglected.

The absorbancies of solutions containing equal concentrations of $NaVO_3$ and H_2O_2 ranging between 5.0 and 20 × 10^{-4}

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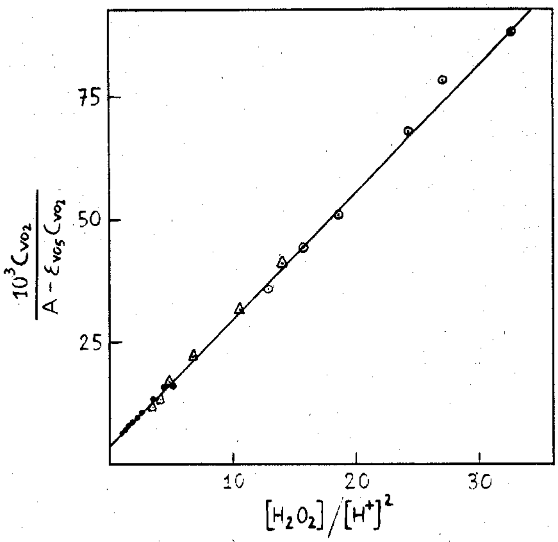

Figure 1. Plot of $C_{VO_2}/(A - \epsilon_{VO_5}C_{VO_2})$ against $[H_2O_2]/[H^+]^2$. $C_{VO_2} = 1.0 \times 10^{-3}$ M. $[H^+] = 0.025$ M (circles), 0.050 M (triangles), and 0.10 M (full circles) (25 °C, $I = 0.3$ M ($NaClO_4$)).

M were measured at $[HClO_4] = 0.10$, 0.20, and 0.30 M. Under these conditions reaction 2 is suppressed and only the species VO_2^+ and VO_3^+ are absorbing. With use of eq 1A–3A in the Appendix and the assumption that the absorbancies are additive the expression (3) for K_1 is derived where C is the

$$K_1 = \frac{A - \epsilon_{VO_2}C}{(\epsilon_{VO_3}C - A)^2}(\epsilon_{VO_3} - \epsilon_{VO_2}) \qquad (3)$$

concentration of the reactants and A is the absorbance. The value of K_1 has been found to be independent of $[H^+]$, and the mean value of 15 experiments carried out at the above concentrations of perchloric acid is $K_1 = (3.7 \pm 0.4) \times 10^4$ M^{-1}. The results obtained in 1 M perchloric acid lie within the experimental error, meaning that K_1 is also independent of the ionic strength.

In order to obtain the equilibrium constant of reaction 2, we used solutions containing lower concentrations of acid on one hand and excess of hydrogen peroxide on the other. Amounts of H_2O_2 increasing from 9.0×10^{-3} to 7.0×10^{-2} M were added to a solution of 1.0×10^{-3} M $NaVO_3$ brought to the desired acidity and ionic strength. In this way the term $[VO_2^+]$ can be neglected in eq 1A and $[VO_3^+] + 2[VO_5^-]$ in eq 2A can be equated to C_{VO_2}.

The relationship (4) is obtained under these approximations.

$$\frac{C_{VO_2}}{A - \epsilon_{VO_5}C_{VO_2}} = \frac{1}{\epsilon_{VO_3} - \epsilon_{VO_5}} + \frac{K_2}{\epsilon_{VO_3} - \epsilon_{VO_5}}\,\frac{C_{H_2O_2} - C_{VO_2}}{[H^+]^2} \qquad (4)$$

The left-hand side member of this equation, when plotted against $(C_{H_2O_2} - C_{VO_2})/[H^+]^2$, gives a straight line (Figure 1). From the ratio of slope to intercept of this line $K_2 = 0.6 \pm 0.1$ M is obtained. The linearity of the plot confirms that in the range of H_2O_2 used in the present study one can rule out the presence of species with values of the ratio (H_2O_2:V) higher than 2.

Rate Constants. The addition of excess sodium iodide to an acid solution containing a mixture of $NaVO_3$ and H_2O_2 yields vanadium(IV) as a final product. However, detectable amounts of vanadium(IV) begin to appear only when the hydrogen peroxide has been destroyed. This means that the reaction occurs in two stages. In the first, which is the only one of importance to this investigation, vanadium(V) is regenerated. In the second, much lower, stage the reduction of vanadium(V) by iodide occurs.[6] This has been ascertained by plotting the concentration of developed iodine against time for a reaction mixture of composition $[NaVO_3] = 1.0 \times 10^{-3}$ M, $[H_2O_2] = 1.0 \times 10^{-3}$ M, $[HClO_4] = 5.0 \times 10^{-2}$ M, and $[NaI] = 1.0 \times 10^{-2}$ M. At the end of the first stage the concentration of the developed iodine is 1.0×10^{-3} M, and at the end of the second stage the total iodine is 1.5×10^{-3} M.

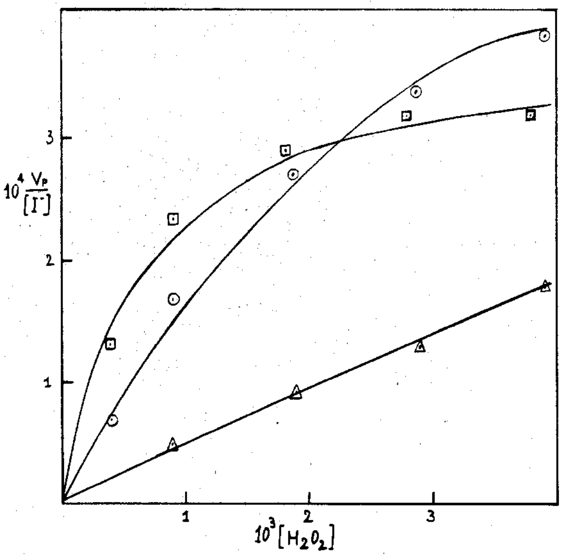

Figure 2. Plot of $V_P/[I^-]$ against $[H_2O_2]$: circles, $C_{VO_2} = 1.0 \times 10^{-4}$ M, $[H^+] = 0.020$ M; squares, $C_{VO_2} = 1.0 \times 10^{-4}$ M, $[H^+] = 0.050$ M; triangles, $C_{VO_2} = 2.0 \times 10^{-4}$ M, $[H^+] = 0.20$ M (25 °C, $I = 0.3$ M ($NaClO_4$)).

According to equilibria 1 and 2 the species H_2O_2, VO_2^+, VO_3^+, and VO_5^- are simultaneously present in solution, and since all of them oxidize iodide ion, the overall rate, V_T, can be expressed as a sum of three contributions:

$$d[I_2]/dt \equiv V_T = V_P + V_{H_2O_2} + V_{VO_2} \qquad (5)$$

where $V_{H_2O_2}$ and V_{VO_2} are initial rates for reactions of hydrogen peroxide and VO_2^+ with iodide ion, respectively, and V_P is the rate of reaction of peroxide complexes with iodide ion. $V_{H_2O_2}$ and V_{VO_2} are computed from rate data known from the literature[6,10] and from initial concentration of *free* H_2O_2 and VO_2^+ which in turn are calculated as described in the Appendix. Since in all cases $V_P > V_{H_2O_2} + V_{VO_2}$, it is inferred that the vanadium(V) peroxides are the more reactive species.

The reaction was found to be first order in iodide ion over the entire investigated range of concentrations of this reactant (2.0×10^{-4}–8.0×10^{-3} M).

More complex dependences of V_P on concentrations of hydrogen peroxide, vanadium(V), and H^+ have been observed. The plots of Figure 2 show the change of $V_P/[I^-]$ with hydrogen peroxide concentration when $C_{H_2O_2} > C_{VO_2}$. At $[H^+] = 0.2$ M the rate is proportional to $[H_2O_2]$ whereas at $[H^+] = 0.05$ M the rate tends to level off at the highest concentrations of H_2O_2. This effect is more pronounced at $[H^+] = 0.02$ M. This behavior suggests that reaction paths involving the species VO_5^- are important under these conditions (see eq 7A in the Appendix).

Figure 3 shows the dependence of $V_P/[I^-]$ on the vanadium(V) concentration. The rate increases for $C_{VO_2} < C_{H_2O_2}$ and decreases for $C_{VO_2} > C_{H_2O_2}$. This can be ascribed to the abatement of $[VO_5^-]$ with increasing C_{VO_2} (see eq 8A in the Appendix). An analogous plot is obtained for $[H^+] = 0.02$ M. The height of the maximum decreases with increasing $[H^+]$ as can be deduced from data at $[H^+] < 0.30$ M shown in Figure 4.

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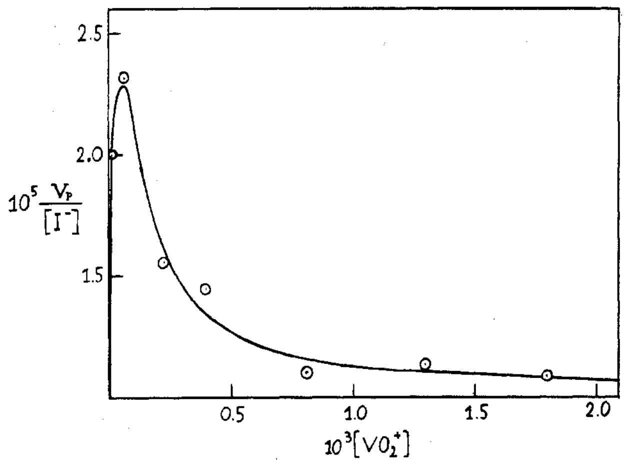


Figure 3. Plot of $V_P/[I^-]$ against $[VO_2^+]$. $C_{H_2O_2} = 2.0 \times 10^{-4}$ M, and $[H^+] = 0.050$ M (25 °C, $I = 0.3$ M ($NaClO_4$)).

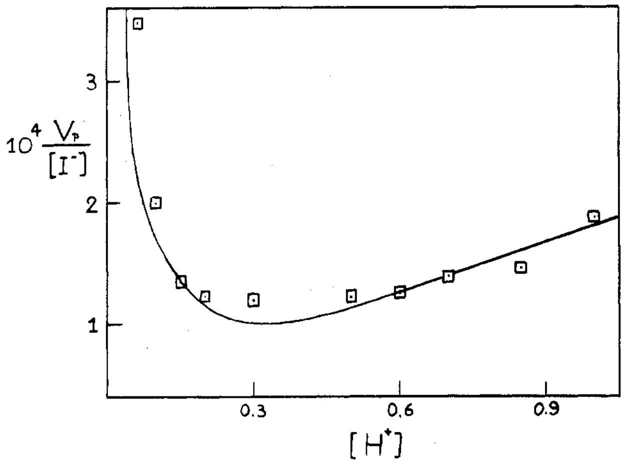


Figure 4. Plot of $V_p/[I^-]$ against $[H^+]$. $C_{VO_2} = C_{H_2O_2} = 1.0 \times 10^{-3}$ M (25 °C).

In Figure 4 $V_P/[I^-]$ is plotted against $[H^+]$. The steep increase in rate with decreasing acid concentration below 0.30 M is attributable either to the enhanced concentration of VO_5^- or to reaction paths proportional to $1/[H^+]$ whereas the modest but nevertheless well-assessed[11] increase of $V_P/[I^-]$ by increasing $[H^+]$ when the acid becomes more concentrated than 0.30 M can be ascribed to acid-catalyzed paths involving mainly the species VO_3^+.

It is reasonable to assume that the reaction proceeds via two groups of paths involving respectively VO_3^+ and VO_5^-. The rate law may be written in the form

$$V_P/[I^-] = (F(H))[VO_3^+] + (F'(H))[VO_5^-] \qquad (6)$$

where F(H) and F′(H) are functions of $[H^+]$ and of a number of kinetic parameters. The forms of these functions have been derived from least-squares treatments of 72 runs carried out over a wide range of concentrations of the reactants.

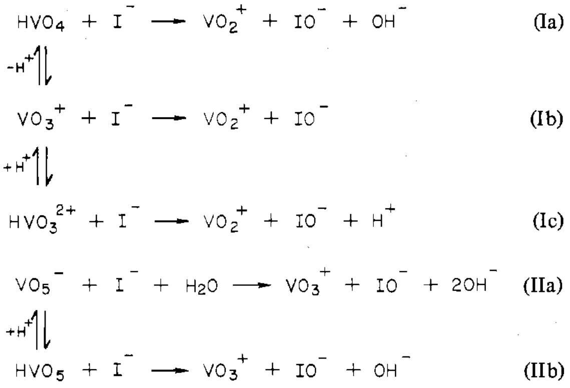
The best adjustment has been found for

$$F(H) = k_1/[H^+] + k_2 + k_3[H^+] \qquad (7)$$

$$F'(H) = k_4 + k_5[H^+] \qquad (8)$$

with $k_1 = (1.2 \pm 0.2) \times 10^{-3}$ s^{-1}, $k_2 = (1.3 \pm 0.2) \times 10^{-2}$ M^{-1} s^{-1}, $k_3 = 0.18 \pm 0.02$ M^{-2} s^{-1}, $k_4 = 0.73 \pm 0.04$ M^{-1} s^{-1}, and $k_5 = 154 \pm 6$ M^{-2} s^{-1}.

Scheme I



Scheme I is consistent with these observations. Here the hypoiodite, generated in the different paths as a result of two-electron transfers, reacts in turn with excess I^- to give I_2.

Discussion

The value of the equilibrium constant of reaction 1 is in very good agreement either with the value published by Dean[4] ($K_1 = 3.4 \times 10^4$ M^{-1} in 1 M $HClO_4$ at 22 °C) or with the value found by Orhanovic and Wilkins[5] ($K_1 = 3.5 \times 10^4$ M^{-1}, $I = 1$ M at 25 °C). The value of K_2, the equilibrium constant of reaction 2, can be compared with the value[5] of 1.3 M ($I = 1$ M, 25 °C). As expected from the ratios of activity coefficients, reaction 1 is independent of the ionic strength whereas K_2 increases with increasing ionic strength.

No direct evidence about the kinetic picture is given that rules out one-electron transfers from the peroxo complexes to I^-. However this alternative appears less reasonable since it would lead to radical routes involving formation of the peroxovanadium(IV) species VO_3, HVO_3^+, VO_5, and HVO_5^+, of which only the second has been postulated as a transient intermediate.[12] Moreover the reactions of oxo and peroxo compounds with nucleophiles seem to proceed via polar rather than radical mechanisms.[6,13]

The monoperoxide is less reactive than the diperoxide. The mechanism of reaction for the three paths involving the former species can be regarded as occurring through a nucleophilic attack by iodide on the metal center of the substrate. Equation 7 suggests that three reaction paths are operative involving, in addition to VO_3^+, a protonated and a deprotonated form of this ion. Since the equilibrium constant K_1 is independent of $[H^+]$, the species other than VO_3^+, although kinetically active, are present in very small amounts.

It is interesting to note that in the kinetics of formation of VO_3^+ from VO_2^+ and H_2O_2 (reaction 1) three reaction paths have been observed,[5] the first being dependent on $[H^+]^{-1}$, the second being independent of the acidity, and the third being proportional to $[H^+]$ as in the present case. In addition, the ratios of the rate constants

$$k_1{:}k_2{:}k_3 = 7{:}40{:}160$$

are not dissimilar from the analogous ratios of the rate constants in eq 7.

This suggests that the processes of proton transfer are preceding the formation of VO_3^+ ion and that reaction 1 occurs through the attack of H_2O_2 on differently protonated forms of vanadium(V),[14] namely, H_3VO_4, $H_4VO_4^+$, and $H_5VO_4^{2+}$,

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(11) Runs at $[H^+] = 0.3$, 0.6, 0.85, and 1 M have been performed either at ionic strengths given by the respective acidities or at $I = 1$ M ($NaClO_4$), and no remarkable differences have been observed. This allows a "medium effect" to be excluded.

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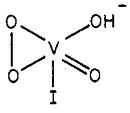
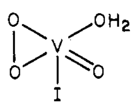
(14) The author tends to reject reaction patterns involving $H_3O_2^+$ and HO_2^- in agreement with authors of ref 5. In addition, the species $H_5VO_4^+$ has been postulated as an intermediate in the reaction of VO_2^+ with iodide ion.[6]

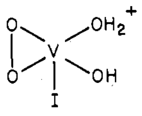
yielding three peroxidic species which can be formulated as HVO_4, $H_2VO_4^+$, and $H_3VO_4^{2+}$. These react with iodide, and the transition states for the three reaction paths can be depicted as **1**–**3**. Analogously, the transition states for reaction paths



1

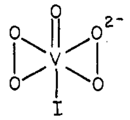


2



3

involving the diperoxide can be represented as **4** and **5**.



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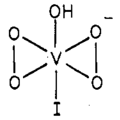

5

Although a nucleophilic attack by iodide at the peroxidic oxygen cannot be excluded "a priori" and indeed has been advanced by several authors,[13] including this author,[15,16] for a number of reactions of peroxides, it seems reasonable to discard such a mechanism for this system. The first argument against an external attack is that, since the strength of the O–O bond remains likely unaffected in changing from VO_3^+ to VO_5^-, the reactivity of the latter species should be only twice that of VO_3^+ and even less if the electrostatic effect on the respective rate constants is taken into account. The second argument is that the vanadium atom, due to its high oxidation state, is a better electrophilic center than the peroxidic oxygens. Therefore it is more reasonable to postulate a reaction of iodide at the metal center. Support to this idea comes from experimental evidence[3] for coordination of nucleophiles such as pyridine derivatives at the central vanadium of both VO_3^+ and VO_5^-.

If this picture holds, one could attempt to rationalize the different reactivities of the two peroxides. Both are hydrated but probably to a different extent. It is plausible that VO_5^- ion, due to its negative overall charge and to the presence of two O_2^{2-} groups in the coordination shell, is less hydrated than the positively charged VO_3^+ which also bears only one peroxidic group. The degree of negative charge transfer from the oxygens of hydration water molecules, to the central metal, which necessarily occurs when the solvation shell is formed, is therefore more pronounced in VO_3^+ than in VO_5^- and the electrophilic power of the vanadium in the former species is consequently depressed. Furthermore, the more abundant donation of negative charge from H_2O coordinated to the metal in VO_3^+ makes these water molecules more acidic, and this could explain the occurrence of a reaction path inversely proportional to $[H^+]$ in the reduction of the monoperoxide.

Appendix

The present system is defined by the equations

$$C_{VO_2} = [VO_2^+] + [VO_3^+] + [VO_5^-] \qquad (1A)$$

$$C_{H_2O_2} = [H_2O_2] + [VO_3^+] + 2[VO_5^-] \qquad (2A)$$

$$K_1 = [VO_3^+]/[VO_2^+][H_2O_2] \qquad (3A)$$

$$K_2 = [VO_5^-][H^+]^2/[VO_3^+][H_2O_2] \qquad (4A)$$

By appropriate combinations of these equations one obtains

$$A[H_2O_2]^3 + B[H_2O_2]^2 + C[H_2O_2] - D = 0 \qquad (5A)$$

where $A = K_2/[H^+]^2$, $B = (1 + K_2/[H^+]^2)(2C_{VO_2} - C_{H_2O_2})$, $C = 1/K_1 + C_{VO_2} - C_{H_2O_2}$, and $D = C_{H_2O_2}/K_1$. The concentrations of the peroxo species are given by the equations

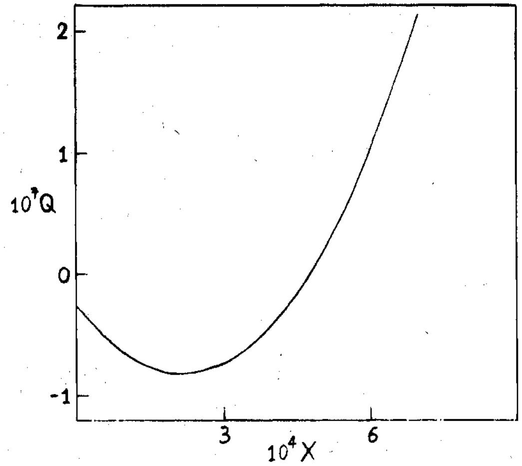

Figure 5. Dependence of the function $Q = Ax^3 + Bx^2 + Cx - D$ on the variable x. Values of parameters are $A = 2.1 \times 10^3$, $B = 0$, $C = -4.7 \times 10^{-4}$, and $D = -2.7 \times 10^{-8}$.

$$[VO_3^+] = \frac{C_M}{1 + \dfrac{1}{K_1[H_2O_2]} + \dfrac{K_2}{[H^+]^2}[H_2O_2]} \qquad (6A)$$

$$[VO_5^-] = \frac{K_2}{[H^+]^2}\,\frac{C_M[H_2O_2]}{1 + \dfrac{1}{K_1[H_2O_2]} + \dfrac{K_2}{[H^+]^2}[H_2O_2]} \qquad (7A)$$

Introduction of (6A) and (7A) into eq 6 yields the dependence of $V_P/[I^-]$ on $[H_2O_2]$ at given values of C_{VO_2} and $[H^+]$. This dependence is made simpler under the conditions of experiments of Figure 2. In these experiments $C_{H_2O_2} \gg C_{VO_2}$ and therefore the term $1/K_1C_{H_2O_2}$ in the denominator of eq 6A and 7A is negligibly small. At $[H^+] = 0.20$ M the term $(K_2/[H^+]^2)[H_2O_2]$ also becomes negligible in comparison to unity so that eq 6A is reduced to $[VO_3^+] \simeq C_{VO_2}$ and eq 7A to $[VO_5^-] \simeq (K_2/[H^+]^2)C_{VO_2}[H_2O_2]$. This leads to a linear dependence of $V_P/[I^-]$ on the hydrogen peroxide concentration.

At lower acidities ($[H^+] = 0.050$ or 0.020 M) the term $(K_2/[H^+]^2)[H_2O_2]$ is no longer negligible, and consequently $V_P/[I^-]$ tends to become independent of $[H_2O_2]$ at the highest values of hydrogen peroxide concentrations.

For $C_{VO_2} \gg C_{H_2O_2}$, $[VO_3^+] \simeq C_{H_2O_2}$ and

$$[VO_5^-] \simeq \frac{K_2}{K_1[H^+]^2}\,\frac{C_{H_2O_2}{}^2}{C_{VO_2} - C_{H_2O_2}} \qquad (8A)$$

This accounts for the decrease in rate at the highest concentrations of VO_2^+ shown in Figure 3.

Concentrations of hydrogen peroxide have been computed by making use of eq 5A. $[H_2O_2]$ coincides with the value of x for which the function Q represented by eq 9A is zero.

$$Q = Ax^3 + Bx^2 + Cx - D \qquad (9A)$$

Under the conditions of $0 \leq x \leq C_{H_2O_2}$, Q changes with the variable x as shown in Figure 5. Initially an abscissa value $x_0 = 0$ and an increment $\delta = C_0/2$ are chosen. The value of Q corresponding to an abscissa value $x = x_0 + \delta$ is calculated. If $Q > 0$, this is recalculated by setting $\delta = \delta/2$ and so on. If $Q < 0$, the calculation is repeated by setting $x_0 = x$. When δ/x becomes less than a number arbitrary small (i.e., 10^{-6}), Q is practically zero and the calculation is interrupted.

Registry No. VO_2^+, 18252-79-4; H_2O_2, 7722-84-1; VO_3^+, 12179-36-1; VO_5^-, 12179-38-3; I^-, 20461-54-5.

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