Kinetics of Decomposition of Hyperoxovanadium(IV) Ions in the Presence of Vanadium(IV)

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A study of the kinetic behaviour of $[VO(O_2)]^+$ ions in 0.4M-H_2SO_4 under different conditions has led to a radical mechanism for their decomposition which is catalyzed by $[VO]^{2+}$ and retarded by $[VO_2]^+$. The rate constant for the reaction between $[VO]^{2+}$ and H_2O_2 (k_1) and the ratio of those for the reactions between $[VO(O_2)]^+$ and OH (k_4) and $[VO]^{2+}$ and OH (k_3) have been determined as 0.97 ± 0.07 l mol^{-1} s^{-1} and 33 ±1 : 1 respectively.

SINCE the irradiation of aqueous solutions can produce a range of steady-state concentrations of radicals, radiolytic studies of these solutions often give information on radical mechanisms and on the kinetics of non-radiation-induced reactions, *e.g.* for solutions of oxygen, hydrogen peroxide, and other inorganic and organic peroxides.

Our previous studies of the radiolysis of solutions of vanadium(V) (refs. 1—3) by ^{60}Co γ rays and ^{210}Po α particles led us to postulate reactions (1)—(6). It

$$[VO]^{2+} + H_2O_2 \longrightarrow [VO_2]^+ + OH + H^+ \quad (1)$$

$$[VO_2]^+ + H_2O_2 \longrightarrow [VO(O_2)]^+ + H_2O \quad (2)$$

$$[VO]^{2+} + OH \longrightarrow [VO_2]^+ + H^+ \quad (3)$$

$$[VO(O_2)]^+ + OH \longrightarrow [VO_2]^+ + HO_2 \quad (4)$$

$$[VO_2]^+ + HO_2 \longrightarrow [VO]^{2+} + O_2 + OH^- \quad (5)$$

$$[VO]^{2+} + [VO(O_2)]^+ + H_2O \longrightarrow 2[VO_2]^+ + OH + H^+ \quad (6)$$

can be seen that the free radicals OH and HO_2 are produced not only by radiolysis of water but also by reactions of vanadium ions. One can easily predict that even in the absence of radiation part of this mechanism will be initiated by reactions (1) or (6). It therefore seemed of interest to see if the results obtained after initiation by these reactions are in quantitative agreement with this mechanism and our knowledge of the rate constants.[2-6]

EXPERIMENTAL

As the radicals are produced in relatively dilute solutions the reproducibility of the results is strongly dependent on the purity of the solutions. Impurities may compete with the solute in reaction with the radicals, and organic impurities in particular can often initiate a chain reaction and produced considerable changes in the observed values. For this reason the water used was triply distilled with the last two distillations over permanganate and $Ba(OH)_2$: the conductivity of the water was 10^{-6} S cm^{-1}. The chemicals used were obtained from either Merck or Prolabo.

Stock solutions of $[VO]^{2+}$ were prepared by dissolving $[VO][SO_4]\cdot5\,OH_2$ in 0.4M-H_2SO_4.† These were standardized by oxidation with cerium(IV) sulphate at 60 °C using

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† 1M = 1 mol dm^{-3}.

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Ferroin as indicator. Solutions of $[VO_2]^+$ were prepared from $Na[VO_3]\cdot 4OH_2$. To avoid formation of polyvanadates it was necessary to first dissolve the salt in concentrated H_2SO_4 and to dilute to 0.4M-H_2SO_4 only after complete dissolution of the $Na[VO_3]\cdot 4OH_2$. The concentration of vanadium(V) was determined by reduction with Mohr's salt using barium *NN*-diphenylsulphamate as indicator.[1] Solutions of $[VO(O_2)]^+$ were prepared by adding the required amount of a standardized solution of H_2O_2 to a $[VO_2]^+$ solution. For the concentrations used here, the peroxidation is rapid and quantitative and the diperoxo-species is not formed. The results were not modified by distillation of the H_2O_2.

The solutions were thermostatted at 25 ± 0.5 °C during the measurements. To determine the concentration as a function of time, samples were taken at regular intervals following mixing of the solutions. The partition into V^V and V^{IV} ions was determined by the method described above. Under the conditions used, for a 1 : 1 mixture of vanadium solution and indicator ($H_2SO_4 : H_3PO_4 : H_2O$ = 6 : 1 : 13 v/v, three drops of saturated barium *NN*-diphenylsulphamate), the amount of Fe^{2+} required was equivalent to the sum of $[VO(O_2)]^+$ and $[VO_2]^+$.

The changes in the concentration of $[VO(O_2)]^+$ were followed by absorption spectrophotometry using a Jobin–Yvon Ultraspac spectrophotometer. The cells were thermostatted at 25 °C. The absorption maximum for $[VO(O_2)]^+$ is at 450 nm (ε 277 l mol^{-1} cm^{-1}). The Beer–Lambert law is obeyed for all the concentrations used in this work. It was necessary in some experiments to correct the optical density for the contribution of $[VO_2]^+$ (ε 3.8 l mol^{-1} cm^{-1} at 450 nm).

RESULTS

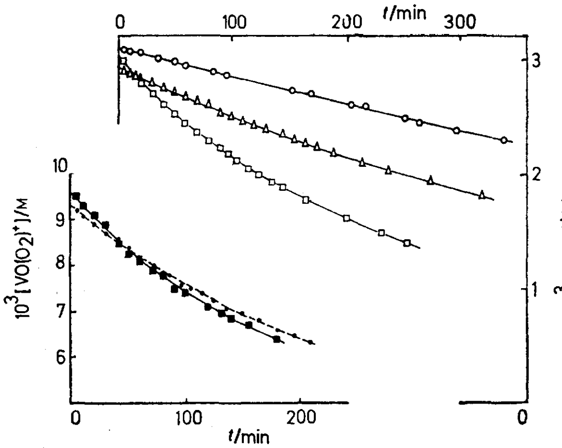

FIGURE 1 Catalytic disappearance of $[VO(O_2)]^+$ as a function of time in 0.4M-H_2SO_4. $10^3[VO(O_2)^+]_0$ = 3.09 (○), 2.92 (△), 3.03 (□), 0.93 (●), and 0.96 (■); $10^3[VO^{2+}]_0$ = 3, 3, 3, 1, and 1; and $10^3[VO_2^+]_0$ = 10.10, 5.34, 2.00, 1.11, and 1.04M

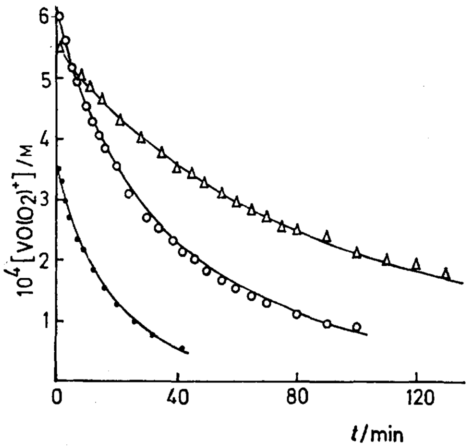

FIGURE 2 Decomposition of $[VO(O_2)]^+$ as a function of time in the presence of excess of $[VO]^{2+}$ (20—200 times at the beginning of each experiment) (0.4M-H_2SO_4). $10^4[VO(O_2)^+]_0$ = 6.15 (○), 5.54 (△), 3.64 (●); $10^2[VO^{2+}]_0$ = 3, 1, 8; $10^3[VO_2^+]_0$ = 1.98, 1.95, 2.03M; and $[VO^{2+}]_0/[VO(O_2]^+]_0 \approx 49, \approx 18, \approx 220$. (——), Calculated curves

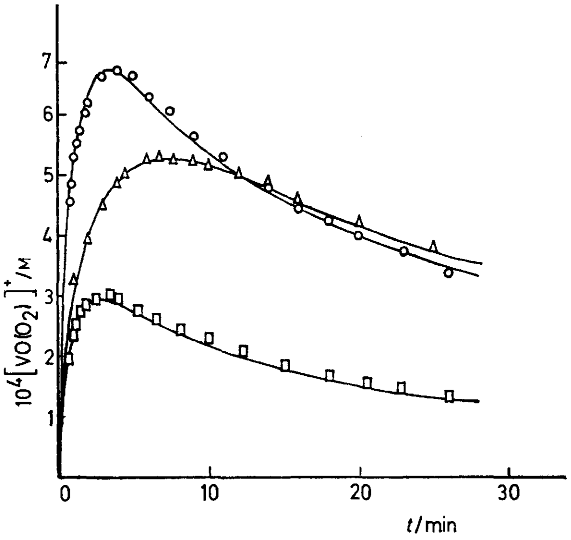

FIGURE 3 Variations in the concentration of $[VO(O_2)]^+$ as a function of time in 0.4M-H_2SO_4. $10^3[VO_2^+]_0$ = 6 (○), 3 (△), 6 (□); $10^3[H_2O_2]_0$ = 2.87, 3.12, and 0.93M. (——), Calculated curves

(a) *Decomposition of* $[VO(O_2)]^+$ *in the Presence of* $[VO]^{2+}$.—The kinetics of this reaction depend essentially on the ratio of initial concentrations $[VO(O_2)^+]_0 : [VO^{2+}]_0$. The disappearance of $[VO(O_2)]^+$ as a function of time in 0.4M-H_2SO_4 containing initially $[VO]^{2+}$ and $[VO_2]^+$ when $[VO(O_2)^+]_0 : [VO^{2+}]_0$ = *ca.* 1 : 1 is shown in Figure 1 and the initial rate is given in the Table. The sum $[VO(O_2)^+]$ + $[VO_2^+]$ remained constant during each experiment and the decomposition is therefore catalytic. On the other hand, it is evident from Figure 1 and the first three lines of the Table that there is a definite dependence on the concentration of $[VO_2]^+$, increasing $[VO_2^+]$ reducing the rate of disappearance of $[VO(O_2)]^+$.

$10^3[VO(O_2)^+]_0$/M	$10^3[VO^2]_0$/M	$10^3[VO_2^+]_0$/M	$10^6\left\{\frac{d[VO(O_2)^+]}{dt}\right\}_0$ / mol l^{-1} min^{-1}
3.09	3	10.10	2.85 ± 0.25
2.92	3	5.34	4.92 ± 0.67
3.03	3	2.00	13.0 ± 0.8
0.93	1	1.11	2.31 ± 0.19
0.96	1	1.04	2.78 ± 0.25

When the concentration of $[VO]^{2+}$ was 20—200 times that of $[VO(O_2)]^+$ at the beginning of each experiment, $[VO^{2+}]$

always increased with time. Figure 2 shows, for this case, the decomposition of $[VO(O_2)]^+$.

(b) *Oxidation of* $[VO]^{2+}$ by H_2O_2.—In order to elucidate the mechanism of the phenomena described above (see Discussion section), we studied the oxidation of $[VO]^{2+}$ by H_2O_2 leading to $[VO(O_2)]^+$ formation. Figure 3 shows the variation in concentration of $[VO(O_2)]^+$ in solutions containing initially $[VO]^{2+}$ and H_2O_2. In all cases the concentration of $[VO(O_2)]^+$ increased rapidly at first, reached a maximum, and then decreased as above.

DISCUSSION

The mechanism corresponding to these complex kinetics cannot be interpreted by simple redox reactions between $[VO(O_2)]^+$, $[VO]^{2+}$, $[VO_2]^+$, and H_2O_2. Short-lived transients must be assumed and particularly radical species arising from reduction or oxidation of H_2O_2. From this point of view, reactions (1)—(6) are very convenient for the interpretation of these experiments.

(a) *Decomposition of* $[VO(O_2)]^+$ *catalysed by* $[VO]^{2+}$ ($[VO^{2+}]_0 \leqslant [VO(O_2)^+]_0$).—Since the value of the ratio $k_4 : k_3$ is *ca.* 20,[3,4] it is expected that OH radicals formed in reaction (6) react for the most part with $[VO(O_2)]^+$ ions when these are in excess relative to $[VO]^{2+}$. The mechanism is then limited to reactions (6), (4), and (5). The net stoicheiometric reaction is (7) and assuming

$$2[VO(O_2)]^+ \longrightarrow 2[VO_2]^+ + O_2 \qquad (7)$$

steady-state conditions for OH and HO_2 leads to expression (8). It is concluded that (*i*) decomposition of

$$\frac{d[VO(O_2)^+]}{dt} = \frac{-d[VO_2^+]}{dt} = -\,2k_6[VO(O_2)^+][VO^{2+}] \quad (8)$$

$[VO(O_2)]^+$ should take place without oxidation of $[VO]^{2+}$ as the sum ($[VO(O_2)^+] + [VO_2^+]$) is constant as shown in our first series of experiments, and (*ii*) the dependence of the rate of decomposition on concentration should involve only $[VO(O_2)]^+$ and $[VO]^{2+}$. The second conclusion has not been verified by experiment (see the Table) since increasing $[VO_2]^+$ reduces the rate of disappearance of $[VO(O_2)]^+$.

In order to explain the influence of $[VO_2]^+$ it is suggested that reaction (2) is an equilibrium. Apart from the results given above there are two justifications for this hypothesis. (*i*) The reverse of reaction (2) has already been observed[7-9] and the value of the equilibrium constant has been found to be 3.5×10^4 l mol^{-1} in 1N sulphuric and perchloric acids.[7,8] Using a value of 4×10^4 l mol^{-1} for a solution of 1N-$HClO_4$, a value of $k_2' = 0.74$ s^{-1} at 25 °C (thus $k_2 = 2.96 \times 10^4$ l mol^{-1} s^{-1}) was determined[3] for the reverse reaction. (*ii*) We found that for solutions of $[VO(O_2)]^+$ with low concentrations of $[VO_2]^+$ ($<10^{-4}$M) the concentration of $[VO(O_2)]^+$ measured after dilution was smaller than predicted. This implies a displacement of the equilibrium to the left. Reaction (6) is then equivalent to the reverse of (2) followed by (1). The mechanism becomes reactions (2), (1), (4), and (5). This does not entail oxidation of $[VO]^{2+}$, but implies a dependence on the concentration of $[VO_2]^+$ so that it is now necessary to compare this dependence with the experimental results.

For this comparison stationary-state equations for the intermediates OH, HO_2, and H_2O_2 must be postulated since hydrogen peroxide remains, during the $[VO(O_2)]^+$ decomposition, in low stationary concentration. This leads to expression (9). Given the relative values of k_2

$$\frac{d[VO(O_2)^+]}{dt} = \frac{-d[VO_2^+]}{dt} = \frac{-2k_1k_2'[VO(O_2)^+][VO^{2+}]}{k_2[VO_2^+] + k_1[VO^{2+}]} \quad (9)$$

and k_1 (ref. 6) (2.96×10^4 and 5.8 l mol^{-1} s^{-1}) for the experiments where $[VO(O_2)^+]$ and $[VO^{2+}]$ are the same order of magnitude, one can neglect k_1 $[VO^{2+}]$ in relation to k_2 $[VO_2^+]$ and equation (9) becomes (10). If c_0 equals

$$\frac{d[VO(O_2)^+]}{dt} = \frac{-2k_1k_2'[VO(O_2)^+][VO^{2+}]}{k_2[VO_2^+]} \quad (10)$$

the constant sum of $[VO_2^+]$ and $[VO(O_2)^+]$, we obtain (11).

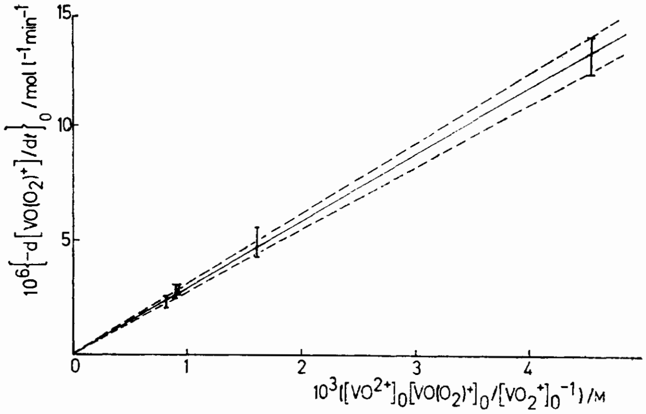

FIGURE 4 Initial rate of disappearance of $[VO(O_2)]^+$ as a function of the expression $[VO^{2+}]_0[VO(O_2)^+]_0/[VO_2^+]_0$

$$\frac{d[VO(O_2)^+]}{dt} = \frac{-2k_1k_2'[VO(O_2)^+][VO^{2+}]}{k_2(c_0 - [VO(O_2)^+])} \quad (11)$$

Since $[VO^{2+}]$ is constant equation (11) becomes (12) on integrating, where $\Delta[VO(O_2)^+] = [VO(O_2)^+]_0 - [VO(O_2)^+]_t$ is the decrease in concentration of $[VO(O_2)]^+$ at time t.

$$-\Delta[VO(O_2)^+] - c_0\ln\left(1 - \frac{\Delta[VO(O_2)^+]_t}{[VO(O_2)^+]_0}\right) = \frac{2k_1k_2'[VO^{2+}]_t}{k_2}\,t \quad (12)$$

Two methods can be used to confirm that the proposed mechanism is consistent with the experimental results. (*i*) Figure 4 shows $\{d[VO(O_2)^+]/dt\}_0$ as a function of

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$[VO(O_2)^+]_0[VO^{2+}]_0/[VO_2^+]_0$. This is a straight line passing through the origin and the value of gradient gives $k_1k_2'/k_2 = (2.4 \pm 0.2) \times 10^{-5}$ s^{-1}. The fact that this plot is a straight line supports the proposed mechanism. It is particularly significant that for the same ratio of concentrations but different individual values the same initial rate was obtained (Table). (*ii*) In Figure 5 the left-hand side of equation (12) is shown as a function of time. Whatever the initial concentrations this expression varied linearly with time. The value of k_1k_2'/k_2 obtained from the gradients of these plots at different concentrations of $[VO]^{2+}$ is $(2.35 \pm 0.3) \times 10^{-5}$ s^{-1} in agreement with the results previously obtained.

We have seen that the equilibrium constant does not vary significantly between 1N-H_2SO_4 and 1N-$HClO_4$.[7,8]

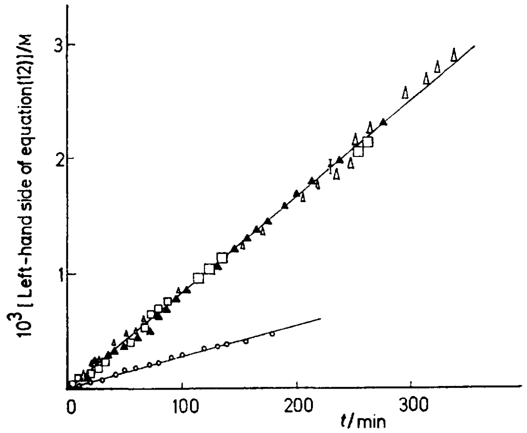

FIGURE 5 Plots of the left-hand side of equation (12) against time. $10^3[VO(O_2)^+]_0 = 3.09$ (△), 2.92 (▲), 3.03 (☐), 0.96 (○); $10^3[VO^{2+}]_0 = 3, 3, 3, 1$; $10^3[VO_2^+]_0 = 10.10, 5.34, 2.00, 1.04$M

Using the values of k_2 and k_2' as 2.96×10^4 l mol^{-1} s^{-1} and 0.74 s^{-1} (ref. 9) respectively ($k_2/k_2' = 4 \times 10^4$ l mol^{-1}), the estimation of k_1k_2'/k_2 above gives $k_1 = 0.97 \pm 0.07$ l mol^{-1} s^{-1}. This value is markedly lower than that found for 0.1N-$HClO_4$ (k_1 5.8 l mol^{-1} s^{-1}) [6] implying that $[ClO_4]^-$ or H^+ plays an important role.

(b) *Oxidation of* $[VO]^{2+}$ by H_2O_2.—The value of k_1 obtained in (a) can be verified by the experiments in which $[VO]^{2+}$ and H_2O_2 are initially present, *i.e.* where reaction (1) plays an essential part. To interpret these results it is convenient to add reaction (3) to the mechanism already established for in these experiments the $[VO]^{2+}$ ions are, at least at the beginning of each experiment, in large excess in relation to $[VO(O_2)]^+$. The mechanism is therefore as in reactions (1)—(5). Assuming stationary state conditions for OH and HO_2, this mechanism leads to the expressions (13)—(15).

$$\frac{d[VO(O_2)^+]}{dt} = \frac{k_1[VO^{2+}][H_2O_2]}{\{1 + (k_3[VO^{2+}]/k_4[VO(O_2)^+])\}} - k_2'[VO(O_2)^+] + k_2[VO_2^+][H_2O_2] \quad (13)$$

$$\frac{d[VO^{2+}]}{dt} = -\frac{2k_1[VO^{2+}][H_2O_2]}{\{1 + (k_4[VO(O_2)^+]/k_3[VO^{2+}])\}} \quad (14)$$

$$d[H_2O_2]/dt = -k_1[VO^{2+}][H_2O_2] - k_2[VO_2^+][H_2O_2] + k_2'[VO(O_2)^+] \quad (15)$$

The solution of these differential equations was found by successive iteration using a WANG 500 calculator. The values of k_1, k_2, and k_2' shown above were used. The ratio $k_4 : k_3$ was fixed by adjusting the calculated curves for formation of $[VO(O_2)]^+$ so that they coincided with the experimental results. The best agreement is observed in the curves in Figure 3, where $k_4 : k_3 = 33 \pm 1 : 1$. This value does not differ greatly from the previous results.[3,4] It is also to be noted that this value is relatively precise: an error of one unit results in a maximum variation in $[VO(O_2)^+]$ of *ca.* 3% which is the order of the experimental error. Other combinations of values of k_1 and $k_4 : k_3$ were tried, including the value of k_1 determined for 0.1N-$HClO_4$,[6] but none gave as good agreement with the experimental results. The calculated curves were not changed on dividing both the values of k_2 and k_2' used by five: only the ratio $k_2 : k_2'$ influences the kinetics of the $[VO]^{2+}$–H_2O_2 system, probably because $[VO_2]^+$ and $[VO(O_2)]^+$ are always in equilibrium (2) during these experiments. The latter therefore confirm the values of k_1 obtained in (a) and give a precise value of the ratio $k_4 : k_3$.

(c) *Decomposition of* $[VO(O_2)]^+$ *with Oxidation of* $[VO]^{2+}$ ($[VO^{2+}]_0 \gg [VO(O_2)^+]_0$).—Additional confirmation of the mechanism and values presented above is provided by experiments in which there is competition between reactions (3) and (4). As before, the mechanism includes reactions (1)—(5) and the H_2O_2 concentration is at steady state. The resulting equation for the rate of disappearance of $[VO(O_2)]^+$ is (16). Again one can neglect $k_1[VO^{2+}]$ in relation to $k_2[VO_2^+]$ so that equation (17) is obtained. With the participation of reaction (3), $[VO^{2+}]$ is no longer constant and its variation is given by (18).

$$\frac{d[VO(O_2)^+]}{dt} = -\frac{k_1k_2'[VO^{2+}][VO(O_2)^+]}{k_1[VO^{2+}] + k_2[VO_2^+]} \left\{1 + \frac{k_4[VO(O_2)^+]}{k_3[VO^{2+}] + k_4[VO(O_2)^+]}\right\} \quad (16)$$

$$\frac{d[VO(O_2)^+]}{dt} = -\frac{k_1k_2'[VO^{2+}][VO(O_2)^+]}{k_2[VO_2^+]} \left\{1 + \frac{k_4[VO(O_2)^+]}{k_3[VO^{2+}] + k_4[VO(O_2)^+]}\right\} \quad (17)$$

$$\frac{d[VO^{2+}]}{dt} = \frac{2k_1k_2'[VO^{2+}][VO(O_2)^+]}{k_2[VO_2^+]} \left\{\frac{k_3[VO^{2+}]}{k_3[VO^{2+}] + k_4[VO(O_2)^+]}\right\} \quad (18)$$

The solution of equations (17) and (18) was found by successive iteration as before and Figure 2 shows the best agreement between the calculated curves and the experimental points. The constants k_1k_2'/k_2 and $k_4 : k_3$ used to give this agreement are well within the limits previously given. These measurements thus confirm the reaction mechanism and the values of the rate constants obtained above within the experimental errors.

Conclusion.—This study of the decomposition of $[VO(O_2)]^+$ in the presence of $[VO]^{2+}$ and $[VO_2]^+$ and its formation by the oxidation of $[VO]^{2+}$ by H_2O_2 leads to the following conclusions: (*i*) the reaction mechanism is similar to that invoked to explain the radiolysis of solutions $[VO_2]^+$, $[VO]^{2+}$, and $[VO(O_2)]^+$ and implies that the free radicals OH and HO_2 are important intermediates; and (*ii*) one of the reactions previously postulated, the oxidation of $[VO]^{2+}$ by $[VO(O_2)^2]^+$, appears to be the net result of an equilibrium involving decomposition of $[VO(O_2)]^+$ into $[VO_2]^+$ and H_2O_2 followed by oxidation of $[VO]^{2+}$ by H_2O_2. The rate constants $k_1 = 0.97 \pm 0.07$ l mol^{-1} s^{-1} and $k_4 : k_3 = 33 \pm 1 : 1$ are quite consistent with the results obtained by radiolysis.

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