Kinetics of Reaction between Vanadium(V) and Iodide Ions in the Presence of Oxygen

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The kinetics of reduction of vanadium(V) by iodide ions in aqueous solution have been investigated in the presence of oxygen at 25 °C and ionic strength 0·4M ($NaClO_4$). The results show that the reaction occurs through two parallel paths (i), the first being oxygen-independent, the second involving a molecule of O_2. The term b (s^{-1})

$$v = a + b[O_2] \qquad (i)$$

is given by equation (ii). The mechanism of the oxygen-dependent path involves formation of a peroxovanadium(V) intermediate, $[VO(O_2)]^+$, which, rapidly reacting with iodide ions, regenerates vanadium(V), VO_2^+, ions.

$$b = (3{\cdot}3 \pm 0{\cdot}5) \times 10^3[H_4VO_4^+][I^-]^2[H^+]^2 \qquad (ii)$$

A KINETIC study of the reduction of vanadium(V) by iodide ions in aqueous acidic solutions has been recently reported.[1] Care was taken to exclude air from the reaction mixtures because the rates were enhanced by the presence of oxygen. This effect was also observed by previous workers [2-4] who explained it in different ways. First [3] a mechanism involving reaction between vanadium(III) (which is assumed to be the first product of the reduction) and oxygen to give a peroxovanadium(V) ion, $[(H_2O)_2V(OH)O_2]^{2+}$, was suggested as in equations (1) and (2). This peroxo-complex rapidly reacts with I^- ions and vanadium(V) is reproduced. Subsequently by measuring the induction factor at high acidity and at very low vanadium(V) concentrations Boyer and Ramsey [4] proposed a chain mechanism in which I_2^- ion is assumed to be the species responsible for the induced reaction.

$$H_3O^+ + [(HO)_3V(H_2O)]^{2+} + I^- \longrightarrow H_2O + [(H_2O)_2V(OH)]^{2+} + HIO \qquad (1)$$

$$[(H_2O)_2V(OH)]^{2+} + O_2 \rightleftharpoons [(H_2O)_2V(OH)O_2]^{2+} \qquad (2)$$

Our preliminary experiments showed that the induction period is strongly decreased by increasing the vanadium(V) and decreasing the hydrogen-ion concentration, and in the ranges $2{\cdot}5 \times 10^{-3} \leqslant [NaVO_3] \leqslant 3 \times 10^{-2}$M and $0{\cdot}05 \leqslant [H^+] \leqslant 0{\cdot}3$M the induction period is practically zero. Nevertheless the rates measured in these conditions are definitely higher than in deaerated solutions suggesting that, even when the induced reaction is suppressed, a dependence on oxygen is operative. We have now investigated the influence of oxygen on the reaction between vanadium(V) and iodide ions under conditions where the induction period is negligible.

EXPERIMENTAL

Stock solutions of the reactants were prepared by dissolving chemicals of analytical grade in conductivity water, which was also used as a reaction medium. Rates of reaction were measured by the iodometric method already described.[1] A small amount of EDTA (2×10^{-5}M) was added to the reactant mixtures in order to avoid possible catalysis by traces of heavy-metal ions. The reacting solutions were flushed with mixtures of purified nitrogen and oxygen during the experiments.

Determination of dissolved oxygen was carried out by a polarographic technique which makes use of a platinum electrode with periodic renewal of the diffusion layer [5] (DLPRE). Suitable oxygen–nitrogen mixtures were passed through the polarographic cell containing 0·2M-$HClO_4$–0·2M-$NaClO_4$ as supporting electrolyte and the limiting current due to O_2 electroreduction, measured at constant potential (0·0 V against s.c.e.), was recorded with a Polarecord E 261 Metrohm. The gaseous stream from the polarographic cell was directly passed through the reaction vessel. The limiting current of oxygen was recorded during the course of each experiment and its constant value provided a check for the constancy of the oxygen concentration during each kinetic run. The percentage of O_2 was obtained as the ratio of the limiting current of oxygen present in a given mixture to the limiting current of an O_2-saturated solution. The concentration in the latter was measured by the Winkler procedure [6] and we obtained $[O_2]_{sat.} = 9{\cdot}92 \times 10^{-4}$M at 25 °C and ionic strength 0·4M. The concentration of oxygen present in the different O_2–N_2 mixtures is given by the product $(\%O_2)[O_2]_{sat}$.

RESULTS

If in a solution saturated with oxygen the concentrations of iodide and H^+ ions were sufficiently high, *i.e.* [NaI] and $[HClO_4] = 0{\cdot}5$M, iodine was formed much more rapidly than in a corresponding deaerated solution or one in which the tetrahydroxovanadium(V) ion was absent, and the iodine is thus produced by reaction between I^- and O_2. In a deaerated solution containing the above concentrations of I^- and H^+ ions and $[NaVO_3] = 2{\cdot}2 \times 10^{-3}$M, the concentration of iodine formed was $1{\cdot}12 \times 10^{-3}$M in agreement with equation (3). In an oxygen-saturated solution the

$$2[H_4VO_4]^+ + 2I^- + 4H^+ \longrightarrow 2VO^{2+} + I_2 + 6H_2O \qquad (3)$$

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[1] F. Secco, S. Celsi, and C. Grati, *J.C.S. Dalton*, 1972, 1675.

[2] W. C. Bray and J. B. Ramsey, *J. Amer. Chem. Soc.*, 1933, **55**, 2279.

[3] J. B. Ramsey, E. L. Colichman, and L. C. Pack, *J. Amer. Chem. Soc.*, 1946, **68**, 1695.

[4] M. H. Boyer and J. B. Ramsey, *J. Amer. Chem. Soc.*, 1953, **75**, 3802.

[5] D. Cozzi, R. Raspi, and L. Nucci, *J. Electroanalyt. Chem.*, 1966, **12**, 36; G. Raspi and L. Nucci, *Ricerca sci.*, 1967, **37**, 509; M. Venturini and F. Secco, *J.C.S. Perkin II*, 1973, 491.

[6] N. H. Furman, 'Standard Methods of Chemical Analysis,' ed. N. H. Furman, D. Van Nostrand Company, Inc., Princeton, New Jersey, 1963, p. 784.

concentration of iodine produced from the same concentrations of the reactants was $3\cdot25 \times 10^{-3}$M. The reaction in these conditions may thus be represented by equation (4).

$$2[H_4VO_4]^+ + O_2 + 6I^- + 8H^+ \longrightarrow 2VO^{2+} + 3I_2 + 8H_2O \quad (4)$$

If the same concentration of vanadium(v) was allowed to react with low concentrations of iodide and hydrogen ions, *i.e.* 0·01 and 0·04M respectively in a O_2 saturated solution, the resulting concentration of iodine was only $1\cdot25 \times 10^{-3}$M, implying that in these conditions the reaction is almost independent of oxygen.

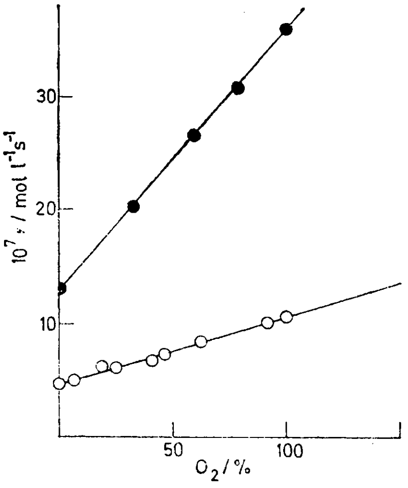
Initial rates of reaction, v, were measured as previously reported[1] and the agreement between repeated runs was 5%. The dependence of the rates on the amount of dissolved oxygen was tested for different constant concentrations of the reactants. The plots in the Figure show that the overall rate is split into two terms, the first being independent of the concentration of dissolved oxygen and the second being first order in $[O_2]$ according to equation (5).

$$v = a + b[O_2] \quad (5)$$

The term a corresponds to the rate of reaction in the absence of oxygen which is given[1] by equation (6). At

$$a = (k_{1,5}[I^-][H^+] + k_{2,5}[I^-][H^+]^2 + k_{4,5}[I^-]^2[H^+]^2)[H_4VO_4^+] \quad (6)$$

25 °C and ionic strength 0·4M $k_{1,5} = 1\cdot2 \times 10^{-2}$ l^2 mol^{-2} s^{-1}, $k_{2,5} = 5\cdot9 \times 10^{-2}$ l^3 mol^{-3} s^{-1}, and $k_{4,5} = 4\cdot7 \times 10^{-1}$ l^4 mol^{-4} s^{-1}.



Dependence of initial rates of the reaction between vanadium(v) and iodide ions on oxygen concentration at 25 °C and ionic strength 0·4M ($NaClO_4$). 100% O_2 corresponds to $[O_2] = 9\cdot92 \times 10^{-4}$M. (○), $[H_4VO_4^+] = 2\cdot5 \times 10^{-3}$, $[NaI] = 8\cdot5 \times 10^{-3}$, $[HClO_4] = 0\cdot1$; (●), $[H_4VO_4^+] = 2\cdot5 \times 10^{-3}$, $[NaI] = 8\cdot5 \times 10^{-2}$, $[HClO_4] = 0\cdot2$M

Initial rates for the reaction between vanadium(v) and iodide ions in oxygen-saturated solutions, v, and in deaerated solutions, a*

$10^2[H_4VO_4^+]$ / mol l^{-1}	$10[I^-]$ / mol l^{-1}	$10[H^+]$ / mol l^{-1}	$10^7 v$ / mol l^{-1} s^{-1}	$10^7 v_{calc.}$ † / mol l^{-1} s^{-1}	$10^7 a$ / mol l^{-1} s^{-1}
0·5	0·25	0·5	1·22	1·23	0·97
0·5	0·50	0·5	3·20	3·05	2·02
0·5	0·75	0·5	5·87	5·45	3·13
0·5	1·00	0·5	8·30	8·46	4·33
1·0	1·00	0·5	16·6	16·9	8·65
0·5	1·50	0·5	18·5	16·2	6·93
0·5	2·50	0·5	42·6	38·8	13·0
0·5	3·00	0·5	57·3	53·6	16·5
0·25	0·475	1·0	4·00	4·25	2·39
0·48	0·475	1·0	7·54	8·16	4·59
0·96	0·475	1·0	15·3	16·3	9·18
1·92	0·475	1·0	31·2	32·7	18·4
2·5	0·475	1·0	40·1	42·5	23·9
3·00	0·475	1·0	50·1	51·0	28·7
0·5	0·50	1·0	7·98	9·18	5·06
1·0	1·50	1·0	113	112	37·4
1·0	0·15	1·5	5·14	6·60	4·93
1·0	0·50	1·5	34·1	36·9	18·3
0·5	1·50	1·5	120	119	35·4
0·5	2·00	1·5	216	201	52·4
1·0	0·25	2·0	19·5	21·4	13·1
0·5	1·50	2·0	221	205	56·9
0·5	2·00	2·0	372	349	85·2
1·0	0·15	2·5	11·3	11·2	10·7
0·5	0·50	2·5	45·9	43·6	20·4
0·98	0·147	3·43	18·1	17·9	17·1

* All the runs were carried out at 25 °C and ionic strength 0·4M ($NaClO_4$). † Obtained from equation (5).

In order to obtain the dependence of the term b on the concentrations of the reactants a set of runs in oxygen-saturated solutions was carried out at different initial concentrations of tetrahydroxovanadium(v), iodide, and hydrogen ions (Table). According to the procedure described in ref. 7 a statistical analysis based on the least-squares method was undertaken with an IBM computer on several equations of the form (7), where $(v - a)$ is the rate

$$v - a = \Sigma_n k_n [H_4VO_4^+]^p [I^-]^q [H^+]^r \quad (7)$$

of the oxygen-dependent path. The equation which gave the best fit is (8), where $k_{obs} = k[O_2] = 3\cdot3 \pm 0\cdot5$ l^4 mol^{-4} s^{-1}

$$v - a = k_{obs}[H_4VO_4^+][I^-]^2[H^+]^2 \quad (8)$$

at 25 °C and $I = 0\cdot4$M ($NaClO_4$). The ratio $k_{obs} : [O_2]_{sat.}$ yields the rate constant $k = (3\cdot3 \pm 0\cdot5) \times 10^3$ l^5 mol^{-5} s^{-1}.

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[7] F. Secco, A. Indelli, and P. L. Bonora, *Inorg. Chem.*, 1970, **9**, 337.

The dependence of b on reactant concentrations is as in (9).

$$b = k[H_4VO_4^+][I^-]^2[H^+]^2 \qquad (9)$$

It should be noted that, from gradients of the plots in the Figure, a k value in agreement with that given by statistical treatment of the runs in the Table was obtained, and the a values derived from the intercepts agreed with those calculated by using rate constants previously reported.[1]

DISCUSSION

The rate equation found, (5), shows that reduction of vanadium(V) in the presence of oxygen occurs through an oxygen-independent set of reactions (6) and a reaction (8) which involves a molecule of O_2. The features of paths (6) have been explained in ref. 1 and therefore only the oxygen-dependent path will be discussed here.

The insensitivity of the reaction to light and starch, and the form of the rate law, which displays integral orders in substrate and in oxygen, are suggestive of a polar mechanism.[8-10] An examination of the data in the Table shows that the contribution of path (8) to the overall rate of reaction becomes predominant at high hydrogen- and iodide-ion concentrations. Under these conditions formation of an intermediate involving one $[H_4VO_4^+]$, two H^+, and two I^- ions is favoured. The mechanism we suggest is as in equations (10)—(12).

$$[H_4VO_4]^+ + 2H^+ \rightleftharpoons [V(OH)_2]^{3+} + 2H_2O \qquad (10)$$

(fast equilibrium)

$$[V(OH)_2]^{3+} + I^- \rightleftharpoons [V(OH)_2I]^{2+} \qquad (11)$$

$$[V(OH)_2I]^{2+} + I^- \rightleftharpoons [V(OH)_2I_2]^+ \qquad (12)$$

The two highly polarizable iodine atoms can easily increase the negative charge on the central vanadium atom facilitating attack by $[V(OH)_2I_2]^+$ on the relatively electrophilic oxygen molecule as in reaction (13).

$$O_2 + [(HO)_2VI_2]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [O_2V(OH)_2I_2]^+ \xrightarrow{k_2} [O_2VO]^+ + I_2 + H_2O \qquad (13)$$

This mechanism reflects the observed kinetics if the stability constant for the peroxo-complex is very small. Oxoperoxovanadium(V) ion is unstable under our experimental conditions and rapidly reacts with excess of I^- ions according to equation (14), regenerating

$$[VO(O_2)]^+ + 2I^- + 2H^+ \longrightarrow VO_2^+ + I_2 + H_2O \qquad (14)$$

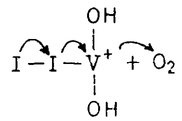
dioxovanadium(V) ion, VO_2^+ (or $[H_4VO_4]^+$), which is in turn reduced to VO^{2+}. From equations (10)—(14) and (3) the overall equation (4) is obtained. Reaction (14) may be regarded as occurring by a mechanism analogous to that for reduction of organic and inorganic peroxides[8,11] by nucleophilic reducing agents, and its stoicheiometry was checked by iodometric titration of mixtures of $NaVO_3$ and H_2O_2 (2 : 1) in acidic solutions where formation of $[VO(O_2)]^+$ ion is practically quantitative.[12,13] We reject the mechanism proposed by Ramsey *et al.*,[3] based on formation of a peroxovanadium(V) intermediate [equations (1) and (2)], because, in this case, all paths included in term a [which yields vanadium(III) as the first product of reduction (1)] would be oxygen dependent.

The possibility of peroxovanadium(V) ion formation according to equation (15) may also be considered.

$$2VO_2^+ + O_2 \rightleftharpoons 2[VO(O_2)]^+ \qquad (15)$$

However, if this reaction occurred as a rapid equilibrium preceding slow reduction by iodide ion the order with respect to oxygen would be one half, contrary to experiment. In addition it should be noted that equilibrium (15) is strongly disfavoured. From the reaction[12] $VO_2^+ + H_2O_2 \rightleftharpoons [VO(O_2)]^+$ ($K = 3{\cdot}5 \times 10^4$ l mol^{-1} at 25 °C) and from the standard potential[14] of the couple H_2O_2–H_2O (E^0 1·77 V) one obtains $E^0[VO(O_2)^+–VO_2^+]$ 1·636 V. Since[14] $E^0(O_2–H_2O)$ 1·23 V, the value $K = 10^{-27}$ atm^{-1} is in fact obtained for equation (15).

In our opinion the ability of vanadium(V) complexes to take up oxygen depends on the electron-donating capacity of the groups co-ordinated to the vanadium atom. Hydroxide or water ligands bonded to vanadium(V) are not sufficiently good electron donors to cause the metal to react with oxygen. However, two large, polarizable iodide ions can push electrons on to the vanadium atom, facilitating attack by the electrophilic oxygen molecule. The first step of equation (13) might thus be depicted as below.



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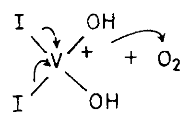

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[8] E. J. Behrman and J. O. Edwards, *Progr. Phys. Org. Chem.*, 1967, **4**, 93.

[9] W. K. Wilmarth and A. Haim, 'Peroxide Reaction Mechanisms,' ed. J. O. Edwards, Interscience Publishers, New York, London, 1962, p. 175.

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[13] L. Nucci, R. Guidelli, and G. Raspi, *J.C.S. Faraday I*, 1973, **69**, 82.

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