A Kinetic Study of the Reaction between Vanadium(V) and Iodide Ions

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The kinetics of the reaction between vanadium(V) and iodide ions have been studied in the absence of oxygen and in a range of acidity such that all quinquevalent vanadium is converted into hydroxovanadium(V) ion. The rate equation, obtained by a statistical treatment of the results is (i) where $k_{1,5} = (1{\cdot}20 \pm 0{\cdot}04) \times 10^{-2}$ l^2 mol^{-2} s^{-1},

$$-d[H_4VO_4^+]/dt = k_{1,5}[H_4VO_4^+][I^-][H^+] + k_{2,5}[H_4VO_4^+][I^-][H^+]^2 + k_{4,5}[H_4VO_4^+][I^-]^2[H^+]^2 \qquad (i)$$

$k_{2,5} = (5{\cdot}9 \pm 0{\cdot}4) \times 10^{-2}$ l^3 mol^{-3} s^{-1}, and $k_{4,5} = (4{\cdot}7 \pm 0{\cdot}4) \times 10^{-1}$ l^4 mol^{-4} s^{-1} at 25 °C and at ionic strength 0·4M ($NaClO_4$). Equation (i) is found to fit the results of previous workers as well. A mechanism for the reaction is suggested, which is based on replacement in the co-ordination shell of the vanadium(V) atom before the redox process takes place.

THE oxidation of iodide ions by quinquevalent vanadium has been studied by several authors [1-4] but, probably owing to the different experimental conditions, they found different rate laws and suggested different mechanisms. Within the framework of investigations of the oxidation of iodide ion by oxo-compounds [5-8] we have performed a kinetic study of this reaction. In the range of $[H^+]$ between 0·05 and 2·9M, VO_3^- ion is completely converted into tetrahydroxovanadium(V) ion $H_4VO_4^+$ [or dioxovanadium(V) ion VO_2^+] [9] and the overall reaction may therefore be written as (1).

$$2H_4VO_4^+ + 2I^- + 4H^+ \longrightarrow 2VO^{2+} + I_2 + 6H_2O \qquad (1)$$

EXPERIMENTAL

Conductivity water was used to prepare and recrystallize the reactants and as reaction medium. Sodium metavanadate, iodide, and perchlorate were AnalaR; perchloric acid and potassium and tetraethylammonium perchlorates were Erba RP reagents. Barium perchlorate was prepared from the corresponding carbonate and recrystallized twice from water. Stock solutions of the reactants were prepared, deaerated, and stored under nitrogen pressure, and standardized by the usual analytical procedures.[10] The reaction vessel was a double-walled glass vessel thermostatted at 25 °C with circulating water and the measurements were carried out with constant stirring. The rates of the reaction were conveniently measured by determining the times of reappearance of iodine in the reacting mixture after the injection of successive small quantities of sodium thiosulphate solution with an Agla microsyringe.[11] To avoid any possible reaction between thiosulphate and hydroxovanadium(V) ions, the additions were performed in such a way that the amounts of thiosulphate exceeded the quantity of developed iodine just for a short time before the end-point. Starch was used to indicate the time of reappearance of iodine. A small amount of edta (2×10^{-5}M) was present in all runs to eliminate the possibility of catalysis by traces of heavy-metal ions. The reaction rate was unaffected by a change of edta concentration from 10^{-3} to 10^{-4}M. Since reaction (1) is very sensitive to the presence of oxygen, which induces the oxidation of iodide by vanadium(V) ion,[12] a stream of purified nitrogen was flushed through the reacting mixture during the experiments.

RESULTS

The measurements were performed over a small initial extent of the reaction (within 5%), and the initial rates, $-d[H_4VO_4^+]/dt$, were measured from the slopes of straight lines obtained by plotting the concentrations of added thiosulphate against time.[8,13] The agreement between repeated runs was within 5%. Some preliminary experiments showed that the reaction is not sensitive to light, nor to increasing amounts of vanadium(IV) or starch. The results in Table 1 were obtained at 25 °C and at ionic strength 0·4M ($NaClO_4$) and show that the reaction is of the first order in $H_4VO_4^+$ (runs 26—30) whereas the order is higher than unity for H^+ (runs 2, 14, 25, 34, 36, 40, 41) and for I^- (runs 4, 10, 16—24). The orders measured from slopes of dilogarithmic plots appear not to be constant, and plotting $V_{\text{exptl}}/[H^+]$ against $[H^+]$, and $V_{\text{exptl}}/[I^-]$ against $[I^-]$ at constant concentrations of the other reactants, straight lines of positive slope and intercept are obtained. This is evidence for several reaction paths some of which are of more than first order with respect to $[H^+]$ and $[I^-]$. In the investigated range of H^+ concentrations it is assumed that all the vanadium(V) is present in the form $H_4VO_4^+$, and the hydrogen-ion concentrations were thus obtained by subtracting twice the sodium vanadate concentrations from the concentrations of added $HClO_4$.[2] This procedure is justified by the fact that potentiometric and absorptiometric studies [9] indicated that in the range of acidity $2{\cdot}9 > [H^+] > 0{\cdot}05$M the cation $H_4VO_4^+$ (or VO_2^+) is the sole species in aqueous solution.

Since the initial rates are measured directly and are

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therefore independent of any preliminary hypothesis about the order of the reaction, a statistical treatment of the results is made in order to find the function of the concentrations which, among those tested, gives the best fit.

TABLE 1

Observed and calculated initial rates at different concentrations of reactants at 25 °C

Run	$10^2[H_4VO_4^+]$ (mol l^{-1})	$10^2[I^-]$ (mol l^{-1})	$10^2[H^+]$ (mol l^{-1})	$10^7 V_{exptl}$ (mol l^{-1} s^{-1})	$10^7 V_{calc}$ (mol l^{-1} s^{-1})
1	0·5	10·0	4·0	3·47	3·25
2	1·0	1·5	5·0	1·15	1·15
3	5·0	2·0	5·0	7·19	7·71
4	0·5	5·0	5·0	2·10	2·02
5	0·5	7·5	5·0	3·22	3·14
6	0·5	10·0	5·0	4·38	4·33
7	0·5	15·0	5·0	6·80	6·94
8	0·5	20·0	5·0	9·72	9·84
9	0·5	25·0	5·0	12·1	13·0
10	0·5	30·0	5·0	17·1	16·5
11	2·0	1·0	6·0	1·80	1·90
12	2·0	2·0	6·0	3·76	3·87
13	2·0	2·5	6·0	4·43	4·87
14	1·0	1·5	7·5	1·88	1·91
15	1·0	5·0	8·0	7·01	7·44
16	3·0	0·15	9·0	0·700	0·703
17	3·0	0·25	9·0	1·20	1·18
18	3·0	0·50	9·0	2·42	2·37
19	3·0	0·75	9·0	3·40	3·57
20	3·0	1·00	9·0	5·00	4·79
21	3·0	1·50	9·0	7·50	7·27
22	3·0	2·00	9·0	11·4	9·80
23	3·0	2·50	9·0	14·8	12·4
24	3·0	3·05	9·0	15·7	15·3
25	1·0	1·5	10·0	2·78	2·79
26	0·3	5·0	10·0	3·21	3·04
27	0·5	5·0	10·0	5·15	5·06
28	1·0	5·0	10·0	9·89	10·1
29	2·0	5·0	10·0	21·4	20·3
30	3·0	5·0	10·0	29·3	30·4
31	0·25	10·0	10·0	5·80	5·66
32	1·0	2·0	13·0	5·45	5·43
33	0·5	2·0	14·0	3·28	3·02
34	1·0	1·5	15·0	4·49	4·93
35	1·0	5·0	18·0	24·1	24·2
36	1·0	1·5	20·0	8·01	7·56
37 *	0·25	20·0	20·0	42·8	42·7
38	1·5	1·0	25·0	9·61	10·7
39 *	0·25	25·0	25·0	87·8	88·0
40	1·0	1·5	30·0	12·8	14·3
41	1·0	1·5	35·0	20·0	18·4
42 *	1·5	1·0	40·0	24·6	23·0

All the measurements were done at ionic strength 0·4M ($NaClO_4$) except runs marked with asterisk.

The parameters and the standard deviations of equations (2)—(6) are obtained by a least-squares treatment[8] of 42 runs by use of a CTC 6400 computer. The per cent

$$V = k_{2,2}[H_4VO_4^+][I^-][H^+]^2 \qquad (2)$$

$$V = \{k_{1,3}[I^-][H^+] + k_{2,3}[I^-][H^+]^2\}[H_4VO_4^+] \qquad (3)$$

$$V = \{k_{1,4}[I^-][H^+] + k_{4,4}[I^-]^2[H^+]^2\}[H_4VO_4^+] \qquad (4)$$

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

$$V = \{k_{1,6}[I^-][H^+] + k_{2,6}[I^-][H^+]^2 + k_{3,6}[I^-]^2[H^+]\}[H_4VO_4^+] \qquad (6)$$

standard deviations (s.d.) of equations (2)—(6) are respectively: (2) 37·8, (3) 14·1, (4) 17·7, (5) 6·3, and (6) 9·9%. Equation (5) fits the experimental data better than the others. However, in order to test whether the remaining equations [in particular equation (6)], despite their higher standard deviations, had a significant probability of also fitting the results the 'chi square' test was used[8,14,15] in the form (7) where $d = 1 - (V_{calc}/V_{exptl})$, and S_{opt} is the

$$\chi^2 = \Sigma d^2/S_{opt}^2 \qquad (7)$$

standard deviation of equation (5) which gives the best fit. The values of χ^2 for the above equations are respectively: (2) 1485; (3) 200; (4) 318; and (6) 97·5. For **41**, **40**, and **39** degrees of freedom the values of χ^2 corresponding to the probability of 99·5% are respectively 68·1, 66·8, and 65·5. This means that equations (2)—(4) and (6) can be ruled out with a probability greater than 99·5%. The four-parameter equation (8) was also tested. This is expected

$$V = \{k_{1,8}[I^-][H^+] + k_{2,8}[I^-][H^+]^2 + k_{3,8}[I^-]^2[H^+] + k_{4,8}[I^-]^2[H^+]^2\}[H_4VO_4^+] \qquad (8)$$

to give the best fit if a path of the first order with respect to H^+ and second order with respect to I^- does contribute appreciably to the overall rate. Despite the slightly lower value of Σd^2, the standard deviation of equation (8) (6·9%) is slightly higher than that of equation (5) because the degrees of freedom change from 39 in the latter to 38 in the former. Moreover the value of $k_{3,8}$ is negative ($-1{\cdot}00 \times 10^{-3}$ l^3 mol^{-3} s^{-1}). Such a path is therefore meaningless. It is possible to conclude thus that equation (5) represents the rate law with the higher probability. Table 1 reports the experimental rates for given concentrations of the reactants and the rates calculated according to equation (5) whose parameters at 25 °C and at ionic strength 0·4M ($NaClO_4$) are: $k_{1,5} = (1{\cdot}20 \pm 0{\cdot}04) \times 10^{-2}$ l^2 mol^{-2} s^{-1}, $k_{2,5} = (5{\cdot}89 \pm 0{\cdot}35) \times 10^{-2}$ l^3 mol^{-3} s^{-1}, $k_{4,5} = (4{\cdot}73 \pm 0{\cdot}37) \times 10^{-1}$ l^4 mol^{-4} s^{-1}. At $[H^+] < 0{\cdot}04$M the experimental rates are higher than predicted by equation (5), and the deviations do increase as the hydrogen-ion concentration decreases. This is evidence for a reaction path of order lower than unity with respect to hydrogen ion, which becomes important at low acidities. Rossotti and Rossotti[9] found that at pH > 1·3 a series of pH-dependent equilibria involving polyvanadate ions, the first of which is represented by equation (9), is established.

$$10H_4VO_4^+ \rightleftharpoons H_2V_{10}O_{28}^{4-} + 14H^+ + 12H_2O \qquad (9)$$

The same analysis was applied to the data of Ramsey *et al.*[2] who reported for the reaction a rate law corresponding to equation (2). Run no. 20 of these authors was excluded, because it was done at very high acidity and shows a large error. The initial rates were obtained from the equation $V_{exptl} = (2{\cdot}303/60 \times S)[NaVO_3]$, where S is the slope of first-order plots of log $\Sigma[V^V]$ against time in minutes.[2] In this case too equation (5) fits the data with the lowest standard deviation (7·4%), and the parameters are: $k_{1,5} = (1{\cdot}1 \pm 0{\cdot}2) \times 10^{-2}$ l^2 mol^{-2} s^{-1}, $k_{2,5} = (8{\cdot}0 \pm 0{\cdot}6) \times 10^{-2}$ l^3 mol^{-3} s^{-1}, $k_{4,5} = (4{\cdot}0 \pm 1{\cdot}1) \times 10^{-1}$ l^4 mol^{-4} s^{-1}. According to equation (2) the value of the rate constant is $k_{2,2} = 1{\cdot}22 \times 10^{-1}$ l^3 mol^{-1} s^{-1} with a standard deviation of 16·5%.

Table 2 reports the rates measured in the presence of different added salts. The salts exert a retarding effect.

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TABLE 2

Effects of added electrolytes: $[NaVO_3] = 5 \times 10^{-3}$M, $[NaI] = 5 \times 10^{-2}$M, and $[H^+] = 5 \times 10^{-3}$M at 25 °C

$[NaClO_4]$/M	0·05	0·1	0·2	0·4
$10^7 V$/mol l^{-1} s^{-1}	2·50	2·32	2·25	2·10
$[KClO_4]$/M	0·025	0·05		
$10^7 V$/mol l^{-1} s^{-1}	2·73	2·65		
$[(Et_4N)ClO_4]$/M		0·05	0·1	
$10^7 V$/mol l^{-1} s^{-1}		2·05	1·96	
$[Ba(ClO_4)_2]$/M	0·01667	0·0333	0·0667	
$10^7 V$/mol l^{-1} s^{-1}	2·32	2·10	1·98	

DISCUSSION

The rate law found, equation (5), includes a term not contained in either of the previously reported rate expressions, equations (2)[2] and (3).[4] The importance of the $k_{4,5}$ pathway is shown by a comparison of the percentage of the reaction proceeding *via* the three paths in two runs respectively at low and high iodide concentration. In run 4 of Table 1 the extents of reaction corresponding to the $k_{1,5}$, $k_{2,5}$, and $k_{4,5}$ are respectively 74·3, 18·2, and 7·5%, and in run 10 they are respectively 54·4, 13·3, and 32·3%.

The agreement between our results and those calculated by applying equation (5) to the data of Ramsey *et al.*[2] is satisfactory in view of the different experimental conditions. The contribution of paths $k_{1,5}$ and $k_{4,5}$ represents, in most of the experiments of the latter authors, *ca.* 40% of the overall reaction rate. The one-parameter equation (2) is therefore not appropriate to represent the kinetic pathway.

The rate law is the same for this reaction as for the iodide–arsenate reaction, and it contains terms which are common to the rate laws for oxidations of iodide ion by halogen oxyanions [16,17a] and $HCrO_4^-$ ion.[17] All these reactions are explicable on the basis of the concept of replacement before the redox process. Rapid protonation equilibria followed by attack by iodide ion might reasonably depict the reaction mechanism.

The path corresponding to $k_{1,5}$ is consistent with reactions (10) and (11). The role of the proton is to weaken the strong bond between the negative oxygen atom and the positive central atom. The hydroxide group is converted into a water molecule which can easily be lost,[16] and the increased positive charge on the substrate facilitates the attack by iodide ion. The redox process does occur subsequently and it probably consists in the transfer of an OH group to the iodine atom. The products V^{III} and HIO are immediately converted into vanadium(IV) [18] and I_2 by the reactants, as in equations (12) and (13). When the acidity is increased, a diprotonated form of hydroxovanadium(V) ion competes with $V(OH)_3^{2+}$ for the iodide ions according to equations (14) and (15), which yield the rate law for the path $k_{2,5}$.

$$H_4VO_4^+ + H^+ \rightleftharpoons V(OH)_3^{2+} + H_2O \text{ (fast equilibrium)} \tag{10}$$

$$V(OH)_3^{2+} + I^- \rightleftharpoons V(OH)_3I^+ \longrightarrow V(OH)_2^{2+} + OH^- + HIO \tag{11}$$

$$V^{III} + V^{V} \longrightarrow 2V^{IV} \tag{12}$$

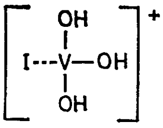
$$HIO + I^- + H^+ \longrightarrow I_2 + H_2O \tag{13}$$

$$V(OH)_3^{2+} + H^+ \rightleftharpoons V(OH)_2^{3+} + H_2O \text{ (fast equilibrium)} \tag{14}$$

$$V(OH)_2^{3+} + I^- \rightleftharpoons V(OH)_2I^{2+} \longrightarrow V(OH)^{2+} + HIO \tag{15}$$

It should be noted that stable solid sulphates of vanadium(V) were precipitated from concentrated sulphuric acid solutions,[19] and they were formulated as follows: $V(OH)_3SO_4,2{\cdot}5H_2O$, $V(OH)_3SO_4$, and $[V(OH)_2]_2(SO_4)_3,(H_3O)(HSO_4)$. The vanadium cation of each of the first two salts is thus conceived as a product of the addition of one proton to the hydroxovanadium(V) ion, and the cation of the last to the addition of two protons.[2] At high concentrations of iodide ions a second I^- does react with the intermediate $V(OH)_2I^{2+}$ formed in reaction (15) as shown by equation (16). In this case the iodide ion is supposed to attack the iodine atom bonded to the substrate. The same explanation was advanced to interpret kinetic paths of the second order in iodide ion in the reactions of this ion with arsenic acid [8] and with iodate [20] and chromate [17] ions. It should be made clear that from the kinetic results it is not possible to discriminate between attack by iodide at the central vanadium or at an oxygen centre. By analogy with vanadium(V) oxychloride [21] it seems reasonable to suppose that the polarizable nucleophile I^- does react at the V^V centre. Transition states for the three reaction paths $k_{1,5}$, $k_{2,5}$, and $k_{4,5}$ could be pictured as (I), (II), and (III) respectively. Structure (III) might explain, on the ground of leaving group basicity, why the path of second order in both H^+ and I^- is more effective than a path of the first order in H^+ and second order in I^- [equations (6) and (8)]. In the former case the leaving group is the $V(OH)_2^+$ ion, and in the latter should be the $V(OH)_3$ species. Because an inverse

$$V(OH)_2I^{2+} + I^- \longrightarrow V(OH)_2^+ + I_2 \tag{16}$$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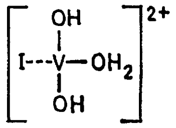
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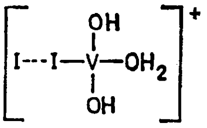
(III)

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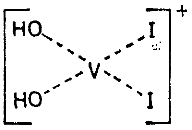
correlation between rates of oxidation and leaving-group basicity has been observed,[16] the releasing of the more acidic $V(OH)_2^+$ ion is expected to be favoured. About the $k_{4,5}$ path it should be noted that if the fast equilibrium represented by equation (10) is postulated, a similar rapid replacement of a water molecule in $(HO)_2VI(H_2O)^{2+}$ might be operative. The transition state would then be (IV), the leaving group being unaffected. The redox process might also be explained by a one-electron transfer from iodide to vanadium(V), through intermediate formation, yielding V^{IV} and iodine radicals, and this has been suggested[4] for the first two paths of the reaction. The path $k_{4,5}$, if interpreted on the same basis, should involve production of I_2^- radical ions. The salt effect is negative. In fact at the concentrations of the reactants quoted in Table 2 the path $k_{1,5}$ prevails. On the basis of equations (10) and (11) the activity coefficient ratio is[22] $f_{H_4VO_4^+} \times f_{H^+} \times f_{I^-}/f_{C\ddagger}$ which is equivalent to the ratio corresponding to a reaction between two ions of unlike sign. However the effect is smaller than that predicted by the Brønsted theory[22] and the specificity is very low. The same behaviour is common to the oxidation reactions of iodide by arsenic acid[8] and $HCrO_4^-$ ions,[17] for which mechanisms involving nucleophilic attack by the reductant on the substrate have been suggested. On the contrary, reactions in which a straightforward electron transfer is operative are known to be very sensitive to specific salt effects.[23]



(IV)

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