Kinetics of the Vanadium(v) Oxidation of Phosphorous Acid

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Kinetics of the oxidation of phosphorous acid by vanadium(v) over a temperature range of 40—55 °C have been studied. The reaction is first order with respect to vanadium(v) and phosphorous acid. The reaction is acid catalysed and is faster in sulphuric than perchloric acid. The order of the reaction with respect to mineral acid, when [Acid] $\leqslant$ 5·5M, is two. The effect of dielectric constant on the rate indicates that the reaction is of the ion–dipole type. Activation parameters have been evaluated. The reaction is initiated by formation of free radicals in the slow rate-determining step.

THE kinetics of oxidation of several inorganic[1-7] and organic[8] compounds by vanadium(v) have been studied. The kinetics of oxidation of phosphorous acid by vanadium(v) has not yet been reported, although the oxidation of the same by several inorganic ions[9-17] have already been studied. We therefore report our results on this system.

EXPERIMENTAL

The materials were of either E. Merck or AnalaR (B.D.H.) grades. Sodium perchlorate was prepared by neutralisation of perchloric acid with sodium hydroxide. Standard solutions of vanadium(v) were prepared by dissolving ammonium trioxovanadate(v) in standard solutions of perchloric and sulphuric acids. Acetic acid–water mixtures of vanadium(v) were prepared by adding the requisite amount of glacial acetic acid to a vanadium(v) solution.

Solutions of phosphorous acid (prepared from sodium phosphite) and vanadium(v) of known concentrations were thermostatted (variation ±0·1 °C). The two solutions were then mixed and aliquot portions were withdrawn at definite intervals of time and quenched in a mixture of phosphoric acid and a known excess of iron(II) ammonium sulphate solution. The unreacted iron(II) solution was immediately titrated against vanadium(v) using sodium diphenylaminosulphonate as indicator.

Formation of free radicals was tested for by addition of acrylamide to the reaction mixture. The viscosity of the resulting solution was enormously increased indicating that an intermediate free radical was formed. Viscosity measurements were carried out with an Ostwald viscometer.

RESULTS

A solution of 2·0 × 10^{-2}M-vanadium(v) and 1·2 × 10^{-1}M-phosphorous acid was allowed to react in 5M-H_2SO_4 at 35 °C for several days. When no vanadium(v) could be detected, the excess of phosphorous acid was estimated by iodometric analysis in a hydrogencarbonate–carbonic acid buffer.[18] A blank correction was made with iodine solution in hydrogencarbonate–carbonic acid buffer using the same concentration of vanadyl sulphate produced during the reaction. Phosphorous acid consumed 2·03 equivalents of vanadium(v) and the reaction may be represented stoicheiometrically by equation (1).

$$P^{III} + 2V^{V} \longrightarrow P^{V} + 2V^{IV} \qquad (1)$$

Results obtained by varying the phosphorous acid concentration in the presence of sulphuric and perchloric acids are summarised in Table 1. The reaction was followed under pseudo-first-order conditions, *viz.* phosphorous acid present in large excess. Vanadium(v) and acid concentrations were held constant in each run. First-order rate constants were determined graphically from plots of log [V^V] against time. All runs gave good first-order plots with respect to vanadium(v), the total concentration of all the vanadium(v) species, for at least 50% completion of reaction. The rate of reaction increased with increase in substrate concentration. Plots of $1/k_1$ against $1/[H_3PO_3]$ were linear and passed through the origin for runs in both

TABLE 1

Variation of the first-order rate constant with substrate concentration: (A) [V^V] = 2·23 × 10^{-2}, [H_2SO_4] = 4·0M, 45 °C; (B) [V^V] = 2·03 × 10^{-2}, [$HClO_4$] = 4·0M, 45 °C

(A)			(B)		
[H_3PO_3] / mol l^{-1}	10^5k_1 / s^{-1}	$10^4k_1/[H_3PO_3]$ / l mol^{-1} s^{-1}	[H_3PO_3] / mol l^{-1}	10^5k_1 / s^{-1}	$10^4k_1/[H_3PO_3]$ / l mol^{-1} s^{-1}
0·124	1·28	1·03	0·122	0·896	0·74
0·186	2·02	1·08	0·244	1·98	0·81
0·248	2·82	1·14	0·292	2·38	0·81
0·310	3·65	1·18	0·365	2·95	0·81
0·372	4·38	1·18	0·406	3·26	0·80
Average = 1·12 ± 0·08			Average = 0·794 ± 0·05		

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sulphuric and perchloric acids. The quotient $k_1/[H_3PO_3]$ is equal to k_2, where k_1 is the pseudo-first-order rate constant. Values of $k_1/[H_3PO_3]$ were found to be $(1.12 \pm 0.08) \times 10^{-4}$ and $(0.794 \pm 0.05) \times 10^{-4}$ l mol^{-1} s^{-1} in sulphuric and perchloric acids respectively.

The second-order rate constant k_2 was evaluated from equation (2) since $dx/dt = k_2(a - x/2)(b - x)$, where a and

$$k_2 = \frac{4.606}{t(b - 2a)} \log \frac{2a(b - x)}{b(2a - x)} \quad \text{where } b > 2a \qquad (2)$$

b are initial molar concentrations of phosphorous acid and vanadium(V) respectively and x the amount of vanadium(V) which has disappeared at time t. Values of k_2 were calculated from gradients of plots of $\log[2a(b - x)/b(2a - x)]$ against t. The oxidation reaction is, therefore, first order in each reactant at a given mineral acid concentration. Some typical second-order plots are shown in Figure 1.

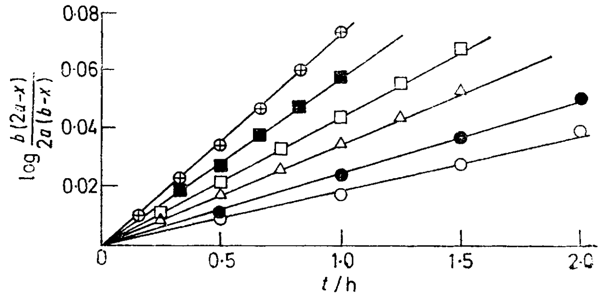

FIGURE 1 Second-order plots for the oxidation of H_3PO_3 (12.4×10^{-2}M) by vanadium(V) (2.04×10^{-2}M) in sulphuric acid medium at different temperatures: (○) 45 °C, $[H_2SO_4]$ = 4·0M; (●) 45, 4·5; (△) 50, 4·0; (□) 50, 4·5; (■) 55, 4·0; (⊕) 55, 4·5

TABLE 2

Variation of the first-order rate constant with acid concentration: $[V^V] = 2.0 \times 10^{-2}$, $[H_3PO_3] = 12.18 \times 10^{-2}$M, 45 °C

$[H_2SO_4]$/mol l^{-1}	10^5k_1/s^{-1}	$10^7k_1/[H_2SO_4]^2$/l^2 mol^{-2} s^{-1}	$[HClO_4]$/mol l^{-1}	10^5k_1/s^{-1}	$10^7k_1/[HClO_4]^2$/l^2 mol^{-2} s^{-1}
4·0	1·18	7·37	4·0	0·895	5·60
4·5	1·47	7·26	4·5	1·15	5·68
5·0	1·86	7·44	5·0	1·44	5·76
5·5	2·27	7·50	5·5	1·74	5·75
6·0	3·68	10·22	6·0	2·34	6·5
6·5	4·99	11·90			
7·0	5·63	11·49			

The rate constants obtained were always reproducible to within ±3%.

The acid dependence of the pseudo-first-order rate constant was studied at fixed substrate and oxidant concentrations in the range 4—7M-sulphuric and 4—6M-perchloric acids respectively (Table 2). The data show that the rate of reaction is faster in sulphuric than in perchloric acid for the same molar concentration of acid. Experiments were performed at constant total perchlorate concentration (I, 6·0M) in perchloric acid but ionic strength could not be maintained constant in sulphuric acid. The Hammett relations,[19] *i.e.* the plots of $\log k_1$ against $\log$ [HX] and of $\log k_1$ against $-H_0$, were linear when [HX] $\leqslant$ 5·5M. The gradient of the plot of $\log k_1$ against $\log$ [HX] was 2·05 in each acid. This indicates that the order of the reaction with respect to mineral acid is two. The gradients of the plots of $\log k_1$ against $-H_0$, 0·45 for perchloric and 0·74 for sulphuric acid, were less than the ideal slope of unity. Plots of $1/k_1h_0$ against $1/h_0$ (where $H_0 = -\log h_0$) were straight lines with an intercept, thus indicating that the data fit an expression of the form $k_1h_0 = k_ah_0/(K + h_0)$. The values of H_0 for sulphuric acid and $HClO_4$–$NaClO_4$ mixtures at different acidities were taken from the tables of Paul and Long.[20]

The constant value of the second-order rate constant in 4M-sulphuric acid was found to be 1.30×10^{-4} l mol^{-1} s^{-1} in both sodium sulphate and hydrogensulphate respectively, whereas the value of 1.01×10^{-4} l mol^{-1} s^{-1} was found in sodium perchlorate in 4M-perchloric acid. Salt concentrations were varied between the limits 0 and 0·8M at constant concentrations of vanadium(V) and phosphorous acid of 2.04×10^{-2} and 12.4×10^{-2}M respectively.

Values of the second-order rate constant at various acetic acid–water mixtures are recorded in Table 3. The values of the dielectric constants at various acetic acid–water mixtures at 50 °C were taken from the work of Radhakrishnamurty *et al.*[21] Plots of the logarithm of the second-order rate constant against the reciprocal of the dielectric constant showed straight lines up to 50% acetic acid with positive gradients. The reactive species of vanadium(V) which takes part in oxidation reactions in sulphuric acid media [5,8] is $V(OSO_3H)^{2+}$, $V(OH)_3HSO_4^+$, $(VO_2,H_2O,H_2SO_4)^+$, or $(VO_2,2H_2SO_4)^+$. On the other hand, the reactive species in perchloric acid [5,8] is $V(OH)_3^{2+}$ or $V(OH)_2^{3+}$. The second-order dependence on mineral acids can be explained assuming $(VO_2,2H_2SO_4)^+$ and $V(OH)_2^{3+}$ to be the reactive species of vanadium(V) in the respective acid; details have been discussed previously.[7]

TABLE 3

Dependence of the second-order rate constant on acetic acid–water composition: (A) $[V^V] = 2.08 \times 10^{-2}$, $[H_3PO_3] = 12.5 \times 10^{-2}$, $[H_2SO_4]$ = 3·0M; (B) $[V^V] = 2.06 \times 10^{-2}$, $[H_3PO_3] = 12.31 \times 10^{-2}$, $[HClO_4]$ = 3·06M

% Acetic acid	$10^3(1/D)$	10^4k_2/l mol^{-1} s^{-1} (A)	10^4k_2/l mol^{-1} s^{-1} (B)
20	17·39	1·40	1·19
30	19·61	1·68	1·42
40	22·38	2·30	1·59
45	24·10	2·94	1·74
50	26·04	4·11	1·90

Activation parameters for the reaction in both sulphuric and perchloric acids were determined by measuring second-order rate constants at four temperatures. From the gradient of a plot of $\log k_2$ against $1/T$ (Figure 2), the heats of activation were calculated to be 22·8 ± 0·5 and 20·4 ± 0·4 kcal mol^{-1} in sulphuric and perchloric acids respectively. Values of pZ (where p = probability or steric factor and Z = collision number) have been computed to be $(1.49 \pm 0.03) \times 10^{12}$ and $(2.6 \pm 0.3) \times 10^{10}$ l mol^{-1} s^{-1} respectively. The activation parameters, which are not widely different, indicate the similarity of the mechanism in both acids (Table 4). An attempt was also made to correlate activation parameters obtained in the cases of oxidation of phosphorous, phenylphosphonous,[7] and arsenious acids [5] by vanadium(V). A plot of $T\Delta S^\ddagger$ against $\Delta H^\ddagger$ showed two

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TABLE 4

Thermodynamic data in sulphuric and perchloric acid media: $[V^V] = 2{\cdot}04 \times 10^{-2}$; $[H_3PO_3] = 12{\cdot}40 \times 10^{-2}$M

[HX] mol l⁻¹	10^4k_2/l mol⁻¹ s⁻¹ 40	45	50	55 °C	$\Delta H^‡$ kcal mol⁻¹	$-\Delta S^‡$ cal K⁻¹ mol⁻¹	$\Delta G^‡$ kcal mol⁻¹
4·0 [a]	0·55	1·01	1·91	3·24	22·9 ± 0·5	6·9 ± 0·8	25·1 ± 0·5
4·5 [a]	0·74	1·35	2·42	4·11	22·7 ± 0·5	7·0 ± 0·5	24·9 ± 0·5
4·0 [b]	0·46	0·79	1·30	2·20	20·4 ± 0·4	15·25 ± 0·4	25·3 ± 0·5
4·5 [b]	0·58	0·99	1·70	2·82	20·4 ± 0·4	14·8 ± 0·3	25·1 ± 0·5

[a] In H_2SO_4. [b] In $HClO_4$.

lines (Figure 3) of different gradient although the reactions are all similar in character, bimolecular in each case, and were carried out under comparable conditions in the acid range 4·0—4·5M. The upper line represents the case where vanadium(V) behaves as a one-electron-transfer oxidant (ideal gradient 1·1) and the lower where it acts as a two-electron-transfer oxidant (gradient significantly less than unity). Had vanadium(V) behaved as a one-electron abstracting agent, the plots of $T\Delta S^‡$ against $\Delta H^‡$ would have been linear throughout the entire acid range.

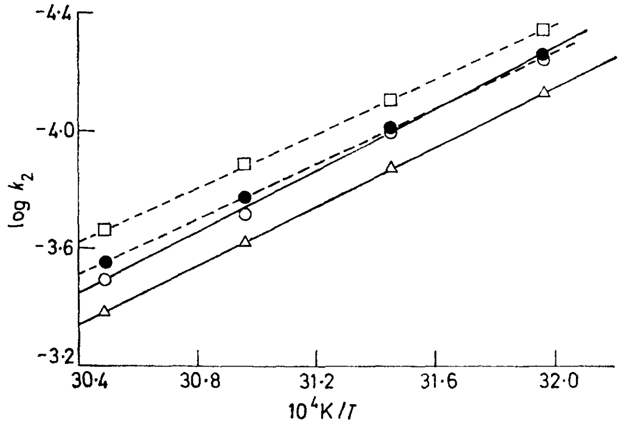


FIGURE 2 Plot of log k_2 against $1/T$ using $[V^V] = 2{\cdot}04 \times 10^{-2}$ and $[H_3PO_3] = 12{\cdot}40 \times 10^{-2}$M: (□) $[HClO_4] = 4{\cdot}0$; (○) $[H_2SO_4] = 4{\cdot}0$; (●) $[HClO_4] = 4{\cdot}5$; (△) $[H_2SO_4] = 4{\cdot}5$M

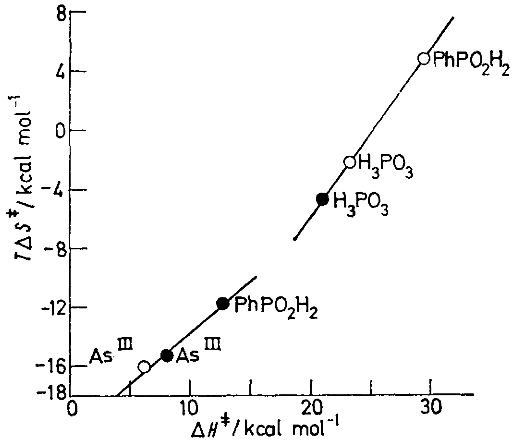


FIGURE 3 Plot of $T\Delta S^‡$ against $\Delta H^‡$ for vanadium(V) oxidations of some inorganic compounds studied under comparable conditions: (○) in H_2SO_4; (●) in $HClO_4$

DISCUSSION

Considerable space in the literature has been devoted to chemical proofs that particular phosphites are predominantly present in one or the other form. In the reactions with mercury(II) chloride and iodine, Mitchell[9] postulated that the rate-determining step is the transition between an inactive, $HPO(OH)_2$, and an active, $(HO)_3P\colon$, form of phosphorous acid. The oxidation of phosphorous acid in acid solution involves a general acid-catalysed equilibrium between the two forms of the acid.

$$H_3PO_3\ (\text{inactive}) \overset{\text{Acid}}{\rightleftharpoons} H_3PO_3\ (\text{active}) \xrightarrow{\text{Oxidant}} \text{product} \quad (3)$$

The reaction in sulphuric acid may be explained according to steps (4)—(7). A free radical of the type $(HO)_2OP^\bullet$ is formed as an intermediate by interaction of the active form of the substrate with $(VO_2,2H_2SO_4)^+$ in the slow rate-determining step (5). It then reacts further with the reactive species of vanadium(V) to give a phosphonium ion. The latter finally reacts with water to give phosphoric acid according to step (7).

$$V(OH)_4^+ + 2H_2SO_4 \xrightarrow{\text{fast}} (VO_2,2H_2SO_4)^+ + 2H_2O \quad (4)$$

$$(HO)_3P\colon + (VO_2,2H_2SO_4)^+ + H_2O \xrightarrow[\text{slow}]{k} (HO)_2OP^\bullet + V^{IV} + H_3O^+ \quad (5)$$

$$(HO)_2OP^\bullet + (VO_2,2H_2SO_4)^+ \xrightarrow{\text{fast}} (HO)_2OP^+ + V^{IV} \quad (6)$$

$$(HO)_2OP^+ + 2H_2O \xrightarrow{\text{fast}} (HO)_2OP(OH) + H_3O^+ \quad (7)$$

The slowest step in perchloric acid, on the other hand, may be explained by reaction of the active form of the substrate with the reactive species of vanadium, $V(OH)_2^{3+}$, according to step (9), terminating with step (7).

$$V(OH)_4^+ + 2H^+ \xrightarrow{\text{fast}} V(OH)_2^{3+} + 2H_2O \quad (8)$$

$$(HO)_3P\colon + V(OH)_2^{3+} + H_2O \xrightarrow{\text{slow}} (HO)_2OP^\bullet + V^{IV} + H_3O^+ \quad (9)$$

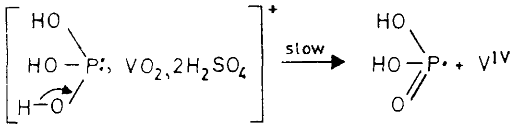
$$(HO)_2OP\cdot + V(OH)_2^{3+} \xrightarrow{\text{fast}} (HO)_2OP^+ + V^{IV} \quad (10)$$

An alternative path to steps (5) and (9) may be interaction of $H_3PO_2^-$ with vanadium(V) according to step (11), which would be followed by steps (6) and (7).

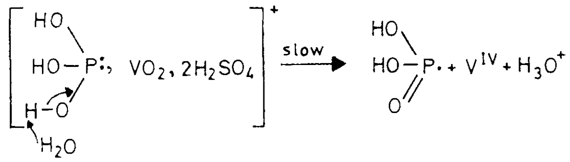
$$H_2PO_3^- + V^V \longrightarrow H_2\dot{P}O_3 + V^{IV} \quad (11)$$

The first dissociation constant of phosphorous acid is $5{\cdot}0 \times 10^{-2}$ mol l⁻¹ and hence it remains in the undissociated form in the presence of high mineral acid concentration. Moreover, Haight and his co-workers[16] have considered $H_2PO_3^-$ as an unreactive species during the oxidation by chromium(VI). Since the oxidation potential of the V^V–V^{IV} couple is 1·00 V in comparison with that for Cr^{VI}–Cr^{III} which is 1·36 V, it would be reasonable to assume $H_2PO_3^-$ as unreactive in the present study also.

The formation of free radicals by breakdown of the donor–acceptor complex, either by step (**12**) or by the solvolysis step (**13**), cannot be totally ruled out although the reaction is first order with respect to both reactants.



(12)



(13)

However, if any such complex is formed, the concentration of it would be negligible. The effect of solvent composition on the rate of reaction indicates that formation of free radicals is not possible by solvolysis step (**13**). If the reaction had depended on step (**13**), the increase in nucleophilicity would have increased the rate of reaction.

The polymerisation of acrylamide on addition to the reaction mixture indicates the formation of free radicals in solution. This also shows further that vanadium(V) behaves as a one-electron-transfer oxidant and rules out the possibility of reaction by steps (**14**)—(**16**). It is to

$$H_3PO_3 + V^V + H_2O \xrightarrow[\text{slow}]{k} H_2PO_3^+ + V^{III} + H_3O^+ \qquad (14)$$

$$H_2PO_3^+ + 2H_2O \xrightarrow{\text{fast}} H_3PO_4 + H_3O^+ \qquad (15)$$

$$V^{III} + V^V \xrightarrow{\text{fast}} 2V^{IV} \qquad (16)$$

be noted that certain reactions of phosphorous acid involve free radicals in solution. Both chromium(VI) [17] and thallium(III) [12] oxidations of phosphorous acid have been assigned two-electron-transfer mechanisms. The activation parameters calculated in the present study are widely different from those of these reactions [12,17] and confirm further that the rate-determining step is a one-electron-transfer process.

[3/096 *Received, 15th January, 1973*]