Kinetics and Mechanism of Redox Reactions in Aqueous Solution. Part 2.[1] Oxidation of Phosphorous Acid by Vanadium(v) Ion

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The redox reaction between V^V and H_3PO_3 in the presence of Ag^I has a zero-order dependence on $[V^V]$. There is a linear relation between k_0^{-1} and $[Ag^I]^{-1}$ and the plot has an intercept on the rate axis. In the absence of Ag^I the reaction exhibits a first-order dependence on $[V^V]$. Plots of k_1 against $[H_3PO_3]$ and k_1^{-1} against $[H_3PO_3]^{-1}$ are linear and pass through the origin. These plots, however, show some deviation from linearity at higher $[H_3PO_3]$. The correlations between the rate and various acidity scales are discussed. A change in the reaction medium from water to D_2O did not affect the rate; $k_D/k_H < 1$. Based on these results and other evidence reported in the literature, it is concluded that the reaction does not involve participation of the active $\ddot{P}(OH)_3$ tautomer in the initial stages of the reaction. A mechanism based on the formation of V^V–H_3PO_3 complex(es) is proposed but the question whether the complex is an intermediate remains unresolved.

THE oxidation of phosphorous acid by mercury(II) chloride[2] and iodine[3] are characterised by rate-limiting formation of the active tautomer $\ddot{P}(OH)_3$ and a zero-order dependence on the oxidant concentration. Corresponding oxidations by Cr^{VI},[4] peroxodisulphate,[5] cerium(IV) sulphate,[6] and thallium(III)[7] exhibit a first-order dependence on the oxidant concentration and the tautomer $HPO(OH)_2$ was considered to be the reactive species. The oxidation by Ag^{II} has a two-term rate law.[8] The term independent of Ag^{II} was explained on the basis of rate-limiting formation of the active tautomer $\ddot{P}(OH)_3$, and the term dependent on Ag^{II} was explained in terms of a bimolecular collision between Ag^{II} and phosphorous acid.

These results seem to be incompatible with the previous assumption[9] that the active tautomer $\ddot{P}(OH)_3$ is the reactive species in the redox reaction having a first-order dependence on vanadium(v) concentration. This reinvestigation was therefore undertaken to examine the nature of the participating tautomer of phosphorous acid and to look into some other kinetic parameters not investigated by previous workers.[9]

EXPERIMENTAL

The stock vanadium(v) solution was prepared from ammonium trioxovanadate(v) (Hopkins & Williams, G.P.R. grade) in aqueous solutions of sulphuric or perchloric acid as required. Other details are described elsewhere.[10] The stock solution of phosphorous acid was prepared from Fluka crystalline-grade product and standardised against a freshly prepared alkali solution. Stock solutions of sulphuric (Basynth, AnalaR) and perchloric acid (E. Merck, G.R.) were similarly standardised.

The P–H bond in phosphorous acid was deuteriated by repeatedly dissolving crystalline H_3PO_3 in deuterium oxide (BARC, 99.4% purity), and evaporating excess of deuterium oxide and water *in vacuo*.[4] Deuteriated phosphorous acid was dissolved in distilled water just before the start of the reaction.

Concentrated sulphuric acid was diluted with deuterium oxide and the solution was left to equilibrate for a number of months before use. Vanadium(v) solution was also prepared in D_2O as explained above. Crystalline H_3PO_3 was dissolved in D_2O just before the start of the reaction. All these solutions were used for the rate measurements in deuterium oxide. All the other chemicals were used as received. The distilled water was distilled from an all-glass unit.

Kinetic Measurements.—The progress of the reaction was followed as described elsewhere.[10] Phosphorous acid was always present in excess over V^V. Except for the variation in phosphorous acid (Table 3) and sulphuric or perchloric acid (Table 5), the ionic strength was kept constant with sodium perchlorate at a value calculated for the highest concentration of the reagent varied in a particular set of experiments. The effect of ionic strength on the reaction rate is given in Table 7.

Values of k_0 and k_1, the observed zero- and first-order rate constants respectively with respect to $[V^V]$, reported in the Tables are the average values from replicate runs. The average value agreed within 3—4% of values obtained from individual runs. Values of k_0 and k_1 were computed from the gradients of zero- and first-order plots respectively which were linear for more than two half-lives of the reaction.

Stoicheiometry.—Reaction mixtures containing excess of V^V over phosphorous acid were prepared and left in a thermostat at 50 °C. The unchanged V^V in the reaction mixture was estimated until it assumed a constant value. On average, 2.0 ± 0.04 mol of V^V were consumed per mol of phosphorous acid. The stoicheiometry of the reaction could thus be expressed as in equation (1).

$$H_3PO_3 + 2V^V + H_2O \longrightarrow H_3PO_4 + 2V^{IV} + 2H^+ \quad (1)$$

RESULTS

Dependence on $[V^V]$.—The invariance of k_0 and k_1, within experimental limits, for different initial $[V^V]$ in the presence and absence of Ag^I, respectively (Tables 1 and 2), confirmed the zero- and first-order dependence on vanadium(v) concentration.

Dependence on [Phosphorous Acid]. The values of the rate constant k_1 obtained at different $[H_3PO_3]$ are given in

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[1] A. Prakash, R. N. Mehrotra, and R. C. Kapoor, *J.C.S. Dalton*, 1976, 1578.

[2] G. A. Linehart, *Amer. J. Sci.*, 1913, **35**, 353; G. A. Linehart and E. Adams, *J. Amer. Chem. Soc.*, 1917, **39**, 948.

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[7] K. S. Gupta and Y. K. Gupta, *J. Chem. Soc. (A)*, 1971, 1180.

[8] A. Viste, D. A. Holm, P. L. Wong, and G. D. Veith, *Inorg. Chem.*, 1971, **10**, 631.

[9] K. K. Sen Gupta, B. B. Pal, and D. C. Mukherjee, *J.C.S. Dalton*, 1974, 226.

[10] A. Kumar and R. N. Mehrotra, *J. Org. Chem.*, 1975, **40**, 1248.

TABLE 1

The zero-order dependence on [V^V] in the presence of silver(I) at [$AgNO_3$] = 0.001, [$HClO_4$] = 2; [H_3PO_3] = 0.228 mol dm^{-3}, and 50 °C

[V^V]/mol dm^{-3}	0.004	0.01	0.02	0.04
10^8k_0/mol dm^{-3} s^{-1}	2.37	2.40	2.38	2.36
$10^5k_2'$/dm^3 mol^{-1} s^{-1}	10.39	10.52	10.43	10.35
[V^V]/mol dm^{-3}	0.07			
10^8k_0/mol dm^{-3} s^{-1}	2.38			
$10^5k_2'$/dm^3 mol^{-1} s^{-1}	10.43			

$k_2' = k_1/[Ag^I][H_3PO_3]$; average $10^5k_2' = 10.42 \pm 0.04$ dm^3 mol^{-1} s^{-1}.

TABLE 2

Invariance of the first-order rate constant k_1 on [V^V] in the absence of Ag^I at [H_2SO_4] = 2.75, [H_3PO_3] = 0.228 mol dm^{-3}, and 60 °C

[V^V]/mol dm^{-3}	0.004	0.01	0.02	0.04	0.07
10^5k_1/s^{-1}	7.46	7.35	7.35	7.35	7.40

Average $10^5k_1 = 7.38 \pm 0.04$ s^{-1}.

TABLE 3

Dependence of the first-order rate constant k_1 on the initial [H_3PO_3] either in the presence of sulphuric or perchloric acid at [V^V] = 0.02, [HX] = 3 mol dm^{-3}, and 50 °C

[H_3PO_3]/mol dm^{-3}	0.13	0.19	0.26	0.40
10^3k_1/s^{-1} ($HClO_4$)	1.32	1.92	2.65	4.10
(H_2SO_4)	1.70	2.51	3.40	5.26
[H_3PO_3]/mol dm^{-3}	0.59	0.83	1.1	1.25
10^3k_1/s^{-1} ($HClO_4$)	6.01	8.28	10.86	13.26
(H_2SO_4)	7.70	10.90	14.60	18.00

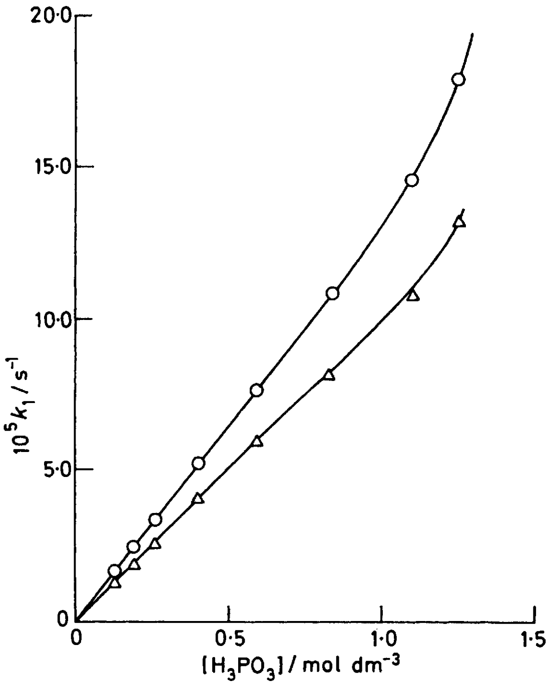

FIGURE 1 Plot of the first-order rate constant k_1 against [H_3PO_3] for 3 mol dm^{-3} perchloric (△) or sulphuric acid solution (○) at 50 °C

Table 3. A deviation in the linearity of a plot of k_1 against [H_3PO_3] (Figure 1) was noted at higher concentrations of phosphorous acid. Consistent with the observations of previous workers,[9] a plot of k_1^{-1} against [H_3PO_3]$^{-1}$ was linear and passed through the origin, but a deviation was noticeable at higher concentrations of phosphorous acid. In both cases, the deviation from linearity was in the 'wrong' direction. By analogy with the redox reaction between hypophosphorous acid and V^V,[11] it is assumed that the deviation is indicative of a higher-order dependence on [H_3PO_3] beyond the concentration where the deviation starts.

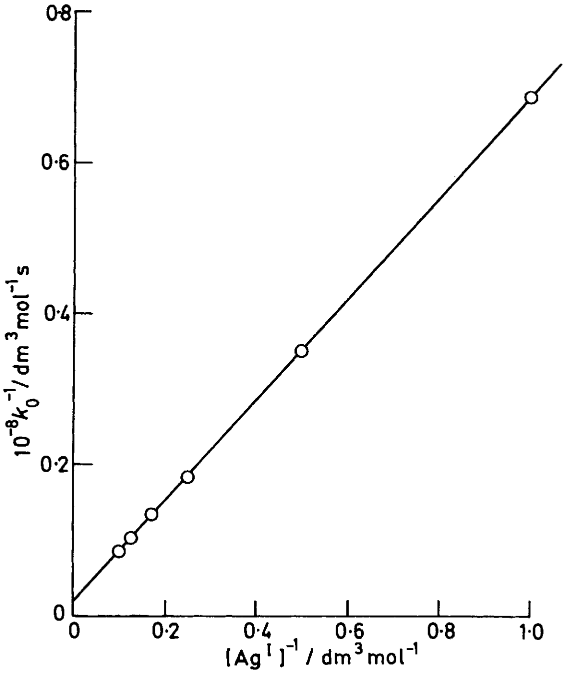

FIGURE 2 Plot of k_0^{-1} against [Ag^I]$^{-1}$ for solutions having [V^V] = 0.02, [H_3PO_3] = 0.139, [NO_3^-] = 0.01, [$HClO_4$] = 2 mol dm^{-3}, and 50 °C. The ionic strength was adjusted with sodium nitrate

Dependence on [Ag^I].—The rate data (Table 4) were consistent with a linear plot of k_0^{-1} against [Ag^I]$^{-1}$ (Figure 2) having an intercept on the rate axis.

TABLE 4

Effect of [Ag^I] on k_0, the zero-order rate constant with respect to [V^V] at [V^V] = 0.02, [H_3PO_3] = 0.139, [NO_3^-] = 0.01, [$HClO_4$] = 2 mol dm^{-3}, and 50 °C

[Ag^I]/mol dm^{-3}	0.000 4	0.001	0.002	0.004
10^8k_0/mol dm^{-3} s^{-1}	0.58	1.45	2.84	5.38
[Ag^I]/mol dm^{-3}	0.006	0.008	0.01	
10^8k_0/mol dm^{-3} s^{-1}	7.30	9.61	11.20	

Dependence on [H^+].—Rate measurements in solutions of various ionic strengths containing different concentrations of sulphuric or perchloric acid were carried out because most of the acidity scales are known for acid solutions of various ionic strengths. The rate data are given in Table 5. For a given molar concentration of sulphuric or perchloric acid, the rate was faster in the presence of H_2SO_4 as observed by previous workers.[9]

Dependence on [HSO_4^-].—The effect of [HSO_4^-] at constant [H^+] was investigated by using mixtures of

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[11] J. N. Cooper, H. L. Hoyt, C. W. Buffington, and C. A. Holmes, *J. Phys. Chem.*, 1971, **75**, 891.

sulphuric and perchloric acids with the assumption [12] that sulphuric acid, in the concentrations used here, behaved as a 1 : 1 electrolyte. The rate data are given in Table 6 and the dependence of the rate constant k_1 on $[HSO_4^-]$ was the same as observed in the oxidation of inositol (cyclohexane-1,2,3,4,5,6-hexol).[12] The correlation could be expressed by equation (2). The contradiction between the present result

$$k_1 = a + b[HSO_4^-] \qquad (2)$$

and that of Sen Gupta *et al.*[9] could be explained in terms of the not very significant variation in $[HSO_4^-]$ (0.0—0.8 mol dm^{-3}) in the presence of 4 mol dm^{-3} H_2SO_4 by previous workers.[9]

TABLE 5

Effect of [acid] on the observed first-order rate constant k_1 at $[V^V] = 0.02$, $[H_3PO_3] = 0.19$ mol dm^{-3}, and 50 °C

[acid]/mol dm^{-3}	2.0	2.5	3.0	3.5
10^5k_1/s^{-1} ($HClO_4$)	1.13	1.60	1.92	2.40
(H_2SO_4)	1.48	1.96	2.51	3.16
[acid]/mol dm^{-3}	4.0	4.5	5.0	5.5
10^5k_1/s^{-1} ($HClO_4$)	2.80	3.43	4.30	5.4
(H_2SO_4)	3.97	4.97	6.30	7.96
[acid]/mol dm^{-3}	6.0	6.5	7.0	7.5
10^5k_1/s^{-1} ($HClO_4$)	6.9	9.3	12.7	17.2
(H_2SO_4)	10.7	14.1	19.8	29.2
[acid]/mol dm^{-3}	8.0			
10^5k_1/s^{-1} ($HClO_4$)	27.5			
(H_2SO_4)	42.7			

TABLE 6

Effect of $[HSO_4^-]$ on the observed first-order rate constant k_1 at constant $[H^+] = 6$ mol dm^{-3}, $[V^V] = 0.02$, $[H_3PO_3] = 0.19$ mol dm^{-3}, and 50 °C

$[HSO_4^-]$/mol dm^{-3}	1.0	2.0	3.0	4.0
10^5k/s^{-1}	8.10	8.71	9.20	9.70
$[HSO_4^-]$/mol dm^{-3}	5.0	6.0		
10^5k_1/s^{-1}	10.2	10.7		

Dependence on Ionic Strength.—The effect of ionic strength on the reaction rate was investigated by varying the ionic strength with sodium perchlorate. The data in Table 7 indicated only a slight increase in the rate with changing ionic strength, suggesting a reaction between an ion and a molecule.

TABLE 7

Effect of variation of ionic strength on the observed first-order rate k_1 at $[V^V] = 0.02$, $[HClO_4] = 3$, $[H_3PO_3] = 0.11$ mol dm^{-3}, and 50 °C

$[NaClO_4]$/mol dm^{-3}	0.0	0.2	0.5	0.8
10^5k_1/s^{-1}	1.10	1.15	1.20	1.28
$[NaClO_4]$/mol dm^{-3}	1.2	1.6	2.0	
10^5k_1/s^{-1}	1.37	1.46	1.57	

Rate in Deuterium Oxide.—Within the experimental limits, the rate remained invariant on changing the aqueous medium to deuterium oxide, although reactions catalysed by an acid are known to proceed faster in D_2O.[13] The rate measurements on the oxidation of deuterio- and protio-phosphorous acid indicated that $k_H/k_D > 1$, where k_H and k_D are the second-order rate constants ($k = k_1/[H_3PO_3]$) corresponding to protio- and deuterio-phosphorous acid. This quotient indicates that P–H bond fission is the rate-limiting process. The absolute value of k_H/k_D is not reported because the extent of deuteriation of phosphorous acid achieved by the method, described earlier,[4] was not ascertained.

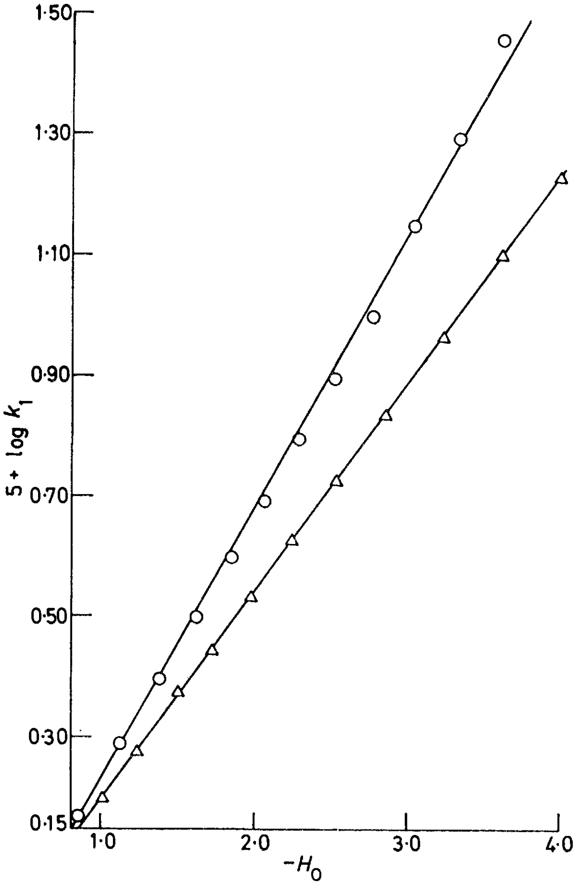

FIGURE 3 Linear correlation between log k_1 and $-H_0$, the Hammett acidity function. The data are reproduced from Table 5: (△) in sulphuric acid; (○) in perchloric acid

Thermodynamic Parameters.—The values of the energy and entropy of activation, either in 3 mol dm^{-3} sulphuric or perchloric acid (Table 8), were in agreement with those reported by previous workers [9] which referred to solutions of higher acidity. This observation is consistent with an earlier report that thermodynamic parameters are independent of the initial acid concentration.[14]

TABLE 8

Effect of temperature on the observed first-order rate constant k_1 and the values of the thermodynamic parameters in 3 mol dm^{-3} sulphuric or perchloric acid at $[V^V] = 0.02$ and $[H_3PO_3] = 0.41$ mol dm^{-3}

θ_c/°C	40	45	50	55
10^5k_1/s^{-1} ($HClO_4$)	1.34	2.42	4.20	7.45
(H_2SO_4)	1.70	3.02	5.40	9.55
θ_c/°C	60			
10^5k_1/s^{-1} ($HClO_4$)	13.4			
(H_2SO_4)	16.0			

$\Delta E(H_2SO_4) = 23.3 \pm 0.5$ kcal mol^{-1}, $\Delta S(H_2SO_4) = -6.3 \pm 1.5$ cal K^{-1} mol^{-1}, $\Delta E(HClO_4) = 23.8 \pm 0.5$ kcal mol^{-1}, and $\Delta S(HClO_4) = -5.3 \pm 1.5$ cal K^{-1} mol^{-1}.*

* 1 kcal = 4.18 kJ; ΔS was calculated at 50 °C.

Correlation of the Rate with Acidity.—Plots of k_1 against

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[12] A. Kumar and R. N. Mehrotra, *Internat. J. Chem. Kinetics*, 1974, **6**, 15.

[13] K. B. Wiberg, *Chem. Rev.*, 1955, **55**, 713.

[14] R. N. Mehrotra, *J. Chem. Soc.* (*B*), 1970, 1722.

$[HA]^2$, where HA is either sulphuric or perchloric acid, were linear for $[HA] \leqslant 5.5$ mol dm^{-3}, the inequality referring to H_2SO_4. Almost equal, but negligibly small, intercepts on the rate axis are noted in each case, and indicate a negligibly small oxidation of phosphorous acid by $[VO_2]^+$, the vanadium(v) species which exists in slightly acidic solutions.[15-17]

The correlation between log k_1 and H_0, the Hammett acidity function,[18] is illustrated in Figure 3. The plot is linear between 2 and 7 mol dm^{-3} sulphuric and 2 and 7.5 mol dm^{-3} perchloric acid. The gradients of 0.45 and 0.35 respectively are not in agreement * with the values of 0.74 and 0.45 respectively in sulphuric and perchloric acid reported by previous workers.[9] The H_0 values used were those obtained by Paul and Long.[19] Similar small gradients in such plots were recorded in these laboratories for the vanadium(v) oxidation of propane-1,3- and butane-1,4-diols [20] and citric acid.[21]

A plot of log k_1 against log $a^*(H^+)$ was also linear for a greater range of acid concentration, where $a^*(H^+)$ is the activity of the oxonium ion. This correlation was not unexpected because the H_0 scale is remarkably linear with log $a^*(H^+)$ scale.[22] The gradient of this plot is 0.25 and 0.18 in the presence of sulphuric and perchloric acid respectively. Yet another correlation, suggested by Bunnett,[23] is that between log k_1 and $-\log a(H_2O)$ at two different ranges of acid concentration. The gradients obtained were -2.3 and -1.6 respectively for sulphuric (4—8 mol dm^{-3}) and perchloric acid (5—8 mol dm^{-3}), and -4.5 and -2.5 respectively at concentrations of 2—4 and 2.5—5 mol dm^{-3} respectively.

DISCUSSION

The low value of the first dissociation constant of phosphorous acid,[24a] 0.051 mol dm^{-3}, and the knowledge that phosphite ion is unreactive to oxidation by Cr^{VI},[4] suggests that undissociated phosphorous acid is the reactive entity. The formation of V^V–H_3PO_3 complex(es) is indicated by an increase in absorbance with increasing $[H_3PO_3]$ in 6 mol dm^{-3} $HClO_4$. The colour change, on mixing the solutions of V^V and H_3PO_3, is more pronounced at higher acidity and in a perchlorate medium.† Thus the assumption of a bimolecular second-order mechanism [9] for the reaction might be considered as erroneous.

Two alternative mechanistic routes are now considered, depending on whether the complex is an intermediate or not in the reaction. These considerations are, however, restricted to the range where the order of the reaction with respect to the concentration of phosphorous acid did not exceed unity. If the reaction proceeds directly between V^V and H_3PO_3 through a path not involving a V^V–H_3PO_3 complex, *i.e.* the reaction is described by (3) and (4), rate law (6) is

$$V^V + H_3PO_3 \overset{K}{\rightleftharpoons} \text{Complex} \qquad (3)$$

$$V^V + H_3PO_3 \xrightarrow{k} V^{IV} + \text{Radical} + H^+ \qquad (4)$$

$$\text{Complex} \xrightarrow{k'} V^{IV} + \text{Radical} + H^+ \qquad (5)$$

$$\frac{-d[V^V]}{dt} = \frac{k[V^V][H_3PO_3]}{1 + K[H_3PO_3]} \qquad (6)$$

applicable. But if the reaction proceeds through (3) and (5), *i.e.* the V^V–H_3PO_3 complex is an intermediate, the rate law (7) is applicable.

$$\frac{-d[V^V]}{dt} = \frac{k'K[V^V][H_3PO_3]}{1 + K[H_3PO_3]} \qquad (7)$$

A comparison of (6) and (7) indicated that $k = k'K$, and thus the two alternate routes are indistinguishable.[25] Assuming that reactions (3) and (5) constitute the mechanism, equation (7) could be rearranged to (8).

$$\frac{1}{k_1} = \frac{1}{k'K[H_3PO_3]} + \frac{1}{k'} \qquad (8)$$

A plot of k_1^{-1} against $[H_3PO_3]^{-1}$ should be linear with an intercept on the rate axis. Should this plot pass through the origin, as it did in the present case, it simply indicates that k' is large. Since the gradient $(k'K)^{-1}$ is greater than zero, K^{-1} must be very large, *i.e.* $K \ll 1$. Hence equation (7) reduces to a simple second-order rate law (9) which is also the reduced form of (6) where $k = k'K$.

$$-d[V^V]/dt = k'K[V^V][H_3PO_3] \qquad (9)$$

The linear plot, passing through the origin, of k_1 against $[H_3PO_3]$ is illustrated in Figure 1.

Hence the only way of determining whether V^V–H_3PO_3 is an intermediate or not is to carry out careful rate studies during the time before the reaction (3) attains equilibrium.‡ Until such a study is made, it is premature to draw any definite conclusions about the participation of V^V–H_3PO_3 complex(es) in the mechanism. Nevertheless, the salient features of both alternatives can still be discussed.

The Complex is not an Intermediate.—The mechanism suggested by Sen Gupta *et al.*[9] was based on this assumption. However, certain modifications must be made in view of the present results. The present observation that $k_D/k_H < 1$ indicates that phosphorous acid is oxidised by rate-limiting P–H fission and not by

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* A re-analysis of the data in ref. 9 yielded a gradient of 0.46 in H_2SO_4; the reaction rate in $HClO_4$ of various ionic strengths was not reported. However, a gradient of 0.45 was reported by these workers for perchloric acid solution of constant ionic strength, total $[ClO_4^-] = 6$ mol dm^{-3}. This value was also found to be in error because a re-analysis of the data gave a gradient of 0.72.

† These measurements were carried out by R. R. Nagori.

‡ We thank one of the referees for this suggestion and for drawing our attention to ref. 25.

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[16] J. Meirer and G. Schwarzenbach, *Chimia* (*Switz.*), 1958, **12**, 328.

[17] N. Ingri and F. Brito, *Acta Chem. Scand.*, 1959, **13**, 1971.

[18] L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, 1940, ch. IX.

[19] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

[20] R. N. Mehrotra, *J. Chem. Soc.* (*B*), 1968, 1123.

[21] R. N. Mehrotra, *J. Chem. Soc.* (*B*), 1968, 1563.

[22] T. A. Modro, K. Yates, and J. Janata, *J. Amer. Chem. Soc.*, 1975, **97**, 1492.

[23] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

[24] A. D. F. Troy in 'Comprehensive Inorganic Chemistry,' vol. 2, ed. A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, (*a*) p. 473, (*b*) p. 531.

[25] J. Halpern, *J. Chem. Educ.*, 1968, **45**, 372.

O–H fission as suggested previously.[9] Similarly, the assumption[9] that $[VO_2{\cdot}2H_2SO_4]^+$ is the reactive vanadium(V) species in aqueous H_2SO_4 is erroneous in view of the presently observed linear relations between k_1 and $[HSO_4^-]$, and k_1 and $[H^+]^2$. Again, the assumption[9] that $[V(OH)_2]^{3+}$ is the reactive species in perchlorate medium is also erroneous because its formation by protonation of $[V(OH)_3{\cdot}H_2O]^{2+}$ is considered to be negligible.[26]

There has been considerable discussion as to whether or not the ion $[VO_2]^+$, which exists[15–17] in aqueous solutions at pH <1, should be more correctly written[27] as $[V(OH)_4]^+$. It has also been suggested[28] that $[V(OH)_4]^+$ could be represented by $[VO_2{\cdot}2H_2O]^+$.

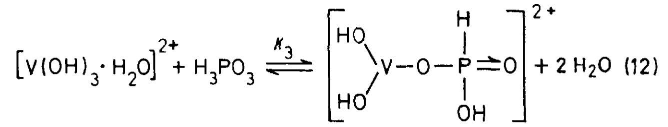
$$[VO_2{\cdot}2H_2O]^+ + [H_3O]^+ \overset{K_1}{\rightleftharpoons} [V(OH)_3{\cdot}H_2O]^{2+} + H_2O \quad (10)$$

$$[VO_2{\cdot}2H_2O]^+ + H_2SO_4 \overset{K_2}{\rightleftharpoons} [VO_2{\cdot}H_2O{\cdot}H_2SO_4]^+ + H_2O \quad (11)$$

Further discussion as to the formation of the reactive vanadium(V) species in sulphuric or perchloric acid is deferred to a later stage.

The Complex is an Intermediate.—Before the details of this mechanism are discussed it is prudent to consider the formation of reactive vanadium(V) species in sulphuric and perchloric acid.

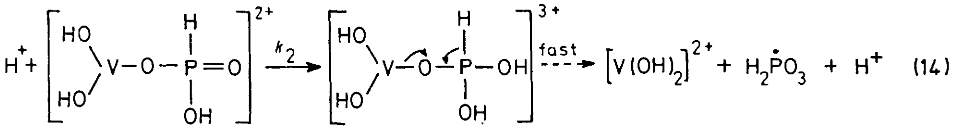
The ions $[V(OH)_3{\cdot}H_2O]^{2+}$ and $[VO_2{\cdot}H_2O{\cdot}H_2SO_4]^+$ are considered to be the reactive vanadium(V) species in the presence of sulphuric acid. In the presence of perchloric acid the reactive vanadium(V) species is $[V(OH)_3{\cdot}H_2O]^{2+}$. Any kinetic differentiation between the species $[V(OH)_3{\cdot}HSO_4]^+$ and $[VO_2{\cdot}H_2O{\cdot}H_2SO_4]^+$ is not easy. The formation of these two series could be represented by reactions (10) and (11).



$$[V(OH)_3{\cdot}H_2O]^{2+} + H_3PO_3 \overset{K_3}{\rightleftharpoons} \left[(HO)_2V{-}O{-}P(H)(OH){=}O\right]^{2+} + 2\,H_2O$$

(12)

$$[VO_2{\cdot}H_2O{\cdot}H_2SO_4]^+ + H_3PO_3 \overset{K_4}{\rightleftharpoons} [VO_2{\cdot}H_3PO_3{\cdot}H_2SO_4]^+ + H_2O \quad (13)$$



$$H^+ + \left[(HO)_2V{-}O{-}P(H)(OH){=}O\right]^{2+} \xrightarrow{k_2} \left[(HO)_2V{-}O{-}P(H)(OH){-}OH\right]^{3+} \xrightarrow{\text{fast}} [V(OH)_2]^{2+} + H_2\dot{P}O_3 + H^+$$

(14)

$$[VO_2{\cdot}H_3PO_3{\cdot}H_2SO_4]^+ \xrightarrow{k_3} VO_2{\cdot}H_2SO_4 + H_2\dot{P}O_3 + H^+ \quad (15)$$

$$V^V + H_2\dot{P}O_3 + H_2O \xrightarrow[\text{fast}]{k_4} V^{IV} + H_3PO_4 + H^+ \quad (16)$$

Mechanism in aqueous sulphuric acid. Reactions (12)—(16) are considered to be involved in the presence of sulphuric acid. The P–O–V linkage in the complex is consistent with the existence of such linkages in phosphate–vanadate copolymers.[24b] The simultaneous P–O–V bond fission together with the rate-limiting P–H fission is also supported by the reported hydrolysis of P–O–V bonds of the copolymer in water.[24b] The induced polymerisation of acrylamide, added to the reaction mixtures, is suggestive of the formation of a free radical. However, polymerisation of the monomer did not occur when it was added to separate solutions of V^V and of H_3PO_3. The second-order dependence of the reaction on $[H^+]$ is presently explained by step (14) where the rate-limiting attack of the proton on the complex gives rise to an activated state having an active phosphite group. The presence of the active phosphite group is responsible for the fast disproportionation of the activated state. This is the distinctive feature of the present mechanism, as opposed to the previously postulated involvement of the active tautomer right from the beginning of the reaction.[9]

Considering that $[V^V]$ is always much less than $[H_3PO_3]$, and assuming that all the equilibria preceding the rate-limiting steps are fast, $k_4 \gg k_2$, and $k_4 \gg k_3$, the rate of the reaction could be expressed by equation (17).

$$-\tfrac{1}{2}\frac{d[V^V]}{dt} = \frac{(k_2K_1K_3[H^+]^2 + k_3K_2K_4[H_2SO_4])[V^V][H_3PO_3]}{1 + K_1[H^+] + K_2[H_2SO_4] + (K_1K_3[H^+] + K_2K_4[H_2SO_4])[H_3PO_3]} \quad (17)$$

However, if (17) is to be identical with (9), it is easily seen that $1 \gg K_1[H^+] + K_2[H_2SO_4] + (K_1K_3[H^+] + K_2K_4[H_2SO_4])[H_3PO_3]$. The reason for $(K_1K_3[H^+] + K_2K_4[H_2SO_4])[H_3PO_3] \ll 1$ was discussed while deriving the rate law (9). Wells and Kuritsyn[29] previously maintained that $1 \gg K_1[H^+]$ and so it should not be difficult to assume that $1 \gg K_2[H_2SO_4]$ also.

The higher rate of oxidation in aqueous H_2SO_4 is now obviously because of the extra contribution to the observed rate by the additional $[V(OH)_3{\cdot}HSO_4]^+$ species

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[26] G. St. Nikolov and D. Mihailova, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2499.

[27] M. J. LaSalle and J. W. Cobble, *J. Phys. Chem.*, 1955, **59**, 519.

[28] R. N. Mehrotra, *J. Chem. Soc. (B)*, 1968, 642.

[29] C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc. (A)*, 1970, 1372.

and not because of the more reactive nature of $[VO_2{\cdot}2H_2SO_4]^+$ as had been suggested previously.[9]

Mechanism in aqueous perchloric acid. The mechanism in this medium is the same as discussed above except that reactions (11), (13), and (15) are excluded because they do not occur in this medium. The rate law (18) directly follows from (17) with the same assumption

$$-\tfrac{1}{2}\frac{d[V^V]}{dt} = k_2K_1K_3[H^+]^2[V^V][H_3PO_3] \quad (18)$$

that $1 \gg K_1K_3[H^+][H_3PO_4]$. The reactive vanadium(V) species have been discussed earlier.

Mechanism in the presence of silver(I). The observed zero-order dependence on $[V^V]$ in the presence of Ag^I indicates that Ag^I is not oxidised to Ag^{II} by V^V prior to the rate-limiting step. Thus the probability of the reaction being catalysed by Ag^{II}, a strong oxidant,[30] is completely excluded.

The reduction of Ag^I to metallic silver by H_3PO_3 is known.[24a] The linear relation between k_0^{-1} and $[Ag^I]^{-1}$ with an intercept on the rate axis (Figure 2) is suggestive of the formation of a Ag^I–H_3PO_3 complex but in no way establishes that such a complex is an intermediate in the reaction.* Hence, reactions (20) and (21) are

$$Ag^+ + H_3PO_3 \overset{K_a}{\rightleftharpoons} \text{Complex} \quad (19)$$

$$\text{Complex} \xrightarrow{k_a} Ag^0 + H_2\dot{P}O_3 + H^+ \quad (20)$$

$$\text{or} \quad Ag^+ + H_3PO_3 \xrightarrow{k_a} Ag^0 + H_2\dot{P}O_3 + H^+ \quad (21)$$

$$H_2\dot{P}O_3 + V^V + H_2O \xrightarrow{\text{fast}} H_3PO_4 + V^{IV} + H^+ \quad (22)$$

$$H_2\dot{P}O_3 + Ag^+ + H_2O \xrightarrow{\text{fast}} H_3PO_4 + Ag^0 + H^+ \quad (23)$$

$$Ag^0 + V^V \xrightarrow{\text{fast}} Ag^+ + V^{IV} \quad (24)$$

the alternative reactions depending on whether or not the complex is an intermediate in the reaction. Different rate constants have not been assigned to alternative reactions because only one of these reactions would occur. Reaction (24) is consistent with the proposal of Rao and Gowda [31] for the silver(I)-catalysed oxidation of hypophosphorous acid by V^V. The rate law in terms of disappearance of V^V, considering only reaction (20) in the mechanistic sequence, is given by (25).

$$-\tfrac{1}{2}\frac{d[V^V]}{dt} = \frac{k_aK_a[Ag^I][H_3PO_3]}{1 + K_a[Ag^I]} \quad (25)$$

Active versus *inactive tautomer*. With the acceptance of rate-limiting O–H fission in the oxidation of phosphorous acid,[9] it is difficult to visualise the resistance of phenylphosphonic acid, $PPh(O)(OH)_2$, towards oxidation by V^V despite the presence of two hydroxyl groups. The deposition of a yellow mass on mixing the two solutions of V^V and $PPh(O)(OH)_2$ has two explanations as detailed below.

(*i*) There is no reduction of V^V because of the inability of the acid to undergo transformation to the active tautomeric form. However, if this is the explanation for the non-oxidisability of $PPh(O)(OH)_2$ then it has to be established in the first place that the rate-limiting O–H fission in the oxidation of H_3PO_3 involves the hydroxyl group produced by protonation of the phosphoryl group [the chemical change that takes place when the inactive tautomer $HPO(OH)_2$ is converted into the active tautomer $\ddot{}P(OH)_3$ under the catalytic effect of H^+]. It would thus mean that one of the hydroxyl groups in the active tautomer $\ddot{}P(OH)_3$ is different from the other two. There is, however, no such mention of this in the literature available to our knowledge.

(*ii*) The non-oxidisability of $PPh(O)(OH)_2$ by V^V could also be interpreted as due to the lack of P–H bond fission in the rate-limiting step of the oxidation process. The observation that $k_D/k_H < 1$ does support this provision, and in effect means that in the oxidation of H_3PO_3 it is the inactive tautomer $HPO(OH)_2$ that is oxidised by the rate-limiting P–H fission.

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* We thank a referee for this suggestion.

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[31] G. G. Rao and H. S. Gowda, *Z. Analyt. Chem.*, 1955, **146**, 167.