

Kinetics of the Metal-ion Oxidation of Phenylphosphonous Acid in Solution. Part I. Oxidation by Vanadium(v)

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Kinetics of the oxidation of phenylphosphonous acid by vanadium(v) over a temperature range of 40–55 °C have been studied. The rate of oxidation increases with the increase in the concentration of hydrogen ions. The effect of acetic acid on the rate indicated the reaction to be of ion-dipole type. The thermodynamic parameters have been evaluated. The kinetic evidence does not indicate the formation of an intermediate compound between the undissociated substrate and the reactive species of vanadium(v). Possible reaction steps in two different mineral acids are suggested.

THE phosphonous acids have strong reducing properties and are oxidised in the process to phosphonic acids. The oxidant systems which have been found useful in preparative work are iodine-acetic acid,¹ mercuric chloride,² alkaline permanganate, chromic acid,³ 50% hydrogen peroxide,⁴ bromine water,² and nitric acid.⁵ Nitric acid has been found useful with aliphatic phosphonous acids because of high stability towards oxidation but aromatic phosphonous acids may suffer nitration of the ring in the process. The kinetics of the oxidation of several organic compounds by vanadium(v) have been reported by Littler and Waters.⁶ The oxidation of several inorganic compounds like hydrazine,⁷ hypophosphorous acid,⁸ tin(II),⁹ iron(II),¹⁰ thallium(I),¹¹ and arsenic(III)¹² by vanadium(v) have been investigated. Systematic kinetic studies of the metal-ion oxidation of phenylphosphonous acid have not been published. We now report on the oxidation of phenylphosphonous acid by vanadium(v).

EXPERIMENTAL

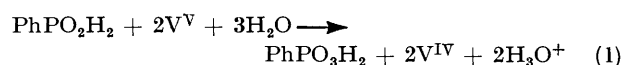
Phenylphosphonous acid was prepared¹³ by esterification of phenylphosphonous dichloride with ethanol followed by hydrolysis with water. The compound after separation was recrystallised (m.p. 84 °C) (Found: C, 50.8; H, 5.1. Calc. for C₆H₇O₂P: C, 50.7; H, 4.5%).

Inorganic materials were of either G.R. (E. Merck) or AnalaR (B.D.H.) grades. Sodium perchlorate was prepared by the neutralization of perchloric acid with sodium hydroxide. Standard solutions of vanadium(v) in perchloric and sulphuric acids were prepared by dissolving ammonium trioxovanadate in standard solutions of the respective acids. Acetic acid-water mixtures were prepared by adding requisite amounts of glacial acetic acid to vanadium(v) solution. Temperature was controlled to ±0.1 °C. The two solutions were mixed and at definite intervals aliquot parts were withdrawn and discharged into a cold mixture containing phosphoric acid and a known excess of ferrous ammonium sulphate solution. The unchanged ferrous solution was then immediately titrated

against vanadium(v) with sodium diphenylaminesulphonate as indicator.

RESULTS

Phenylphosphonous acid consumed 1.99 equivs. of vanadium(v) in 4.0M-H₂SO₄ in 48 h at 35 °C and the reaction can be represented stoichiometrically by equation (1). The



rates were studied at constant vanadium(v) but varying substrate concentrations. The acid concentration was constant in each run. The rates increased with the increase in substrate concentration. A plot of $1/k_1$ against $1/[\text{PhPO}_2\text{H}_2]$ passes through the origin (Figure 2) for both sulphuric and perchloric acid suggesting that the order with respect to substrate concentration is unity. The values of $k_1/[\text{PhPO}_2\text{H}_2]$ were found to be $1.01 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ and $0.54 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ in sulphuric and perchloric acids respectively (Table 1).

Equation (2) was used to evaluate the second-order rate

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

constant k_2 . This is the integrated form of equation (3)

$$dx/dt = k_2(a-x/2)(b-x) \quad (3)$$

where a and b are the initial molar concentrations of phenylphosphonous acid and vanadium(v) respectively and x the amount of vanadium(v) which has disappeared at time t . The values of k_2 have been calculated from the slopes of plots of $\log[2a(b-x)/b(2a-x)]$ against t . The oxidation of phenylphosphonous acid by vanadium(v) is of the first order in each reactant at a given mineral acid concentration. Some typical plots are in Figure 1. Duplicate experiments were reproducible to within ±3%.

The acid-dependence of the reaction rates were studied at a series of runs at fixed substrate and oxidant concentrations in the range 4–6.5M-sulphuric and 3.5–6.0M-perchloric acids respectively (Table 2). The data suggest that the rate is faster in sulphuric than in perchloric acid

* K. K. Sen Gupta, B. B. Pal, and D. C. Mukherjee, *Z. phys. Chem. (Frankfurt)*, 1970, **72**, 230.

⁹ D. J. Drye, W. C. E. Higginson, and P. Knowles, *J. Chem. Soc.*, 1962, 1137.

¹⁰ M. J. Nicol and D. R. Rosseinsky, *Proc. Chem. Soc.*, 1963, 116.

¹¹ A. G. Sykes, *J. Chem. Soc.*, 1961, 5549.

¹² B. B. Pal, D. C. Mukherjee, and K. K. Sen Gupta, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3433.

¹³ A. Finch, P. J. Gardner, and K. K. Sen Gupta, *J. Chem. Soc. (B)*, 1966, 1162.

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³ K. K. Sen Gupta, *Bull. Chem. Soc. Japan*, 1970, **43**, 590.

⁴ H. J. Emeleus, R. N. Haszeldine, and R. C. Paul, *J. Chem. Soc.*, 1955, 563.

⁵ H. C. Brown, *Chem. Abs.*, 1952, **46**, 9580.

⁶ W. A. Waters and J. S. Littler, 'Oxidation in Organic Chemistry,' Part I, Academic Press, New York, 1963, 196.

⁷ W. C. E. Higginson, D. Sutton, and P. Wright, *J. Chem. Soc.*, 1953, 1380.

for the same molar concentration of the acid. The ionic strengths could not be maintained fixed at higher acidities. The plots of $\log k_1$ (where k_1 is the first-order rate constant) against $\log[\text{HX}]$ gave straight lines with slopes 2.5 and 1.3 for sulphuric and perchloric acid respectively up to 5.5M-acid. The plots of $\log k_1$ against $-H_0$ were also linear

tained constant at different acidities, increases with the increase in acid concentration and therefore the activity of water would effectively alter. The values of $-H_0$ and $\log a_w$ at various acidities were taken from the tables of Paul and Long¹⁴ and Bunnett¹⁵ respectively. The addition of sodium sulphate in the presence of 5M-sulphuric

TABLE 1
Variation of rate constant with substrate concentration

A [Vanadium(v)] = $1.0 \times 10^{-2}\text{M}$, $[\text{H}_2\text{SO}_4]$ = 4M, Temp. = 45 °C
 B [Vanadium(v)] = $1.013 \times 10^{-2}\text{M}$, $[\text{HClO}_4]$ = 3.6M, Temp. = 45 °C

A			B		
$[\text{PhPO}_2\text{H}_2]$ M	$10^4 k_1$ s ⁻¹	$10^3 k_1 / [\text{PhPO}_2\text{H}_2]$ l mol ⁻¹ s ⁻¹	$[\text{PhPO}_2\text{H}_2]$ M	$10^4 k_1$ s ⁻¹	$10^3 k_1 / [\text{PhPO}_2\text{H}_2]$ l mol ⁻¹ s ⁻¹
0.06	0.6	1.00	0.05	0.269	0.537
0.10	1.01	1.01	0.10	0.550	0.550
0.15	1.536	1.02	0.15	0.810	0.537
0.20	2.046	1.02	0.20	1.07	0.537

Average $\frac{k_1}{[\text{PhPO}_2\text{H}_2]} = 1.01 \times 10^{-3}$ Average $\frac{k_1}{[\text{PhPO}_2\text{H}_2]} = 0.54 \times 10^{-3}$

TABLE 2

Dependence of rate constant on acid and salt concentrations

A [Vanadium(v)] = $2.0 \times 10^{-2}\text{M}$, $[\text{PhPO}_2\text{H}_2]$ = $1.0 \times 10^{-2}\text{M}$, Temp. = 45 °C
 B [Vanadium(v)] = $2.0 \times 10^{-2}\text{M}$, $[\text{PhPO}_2\text{H}_2]$ = $1.0 \times 10^{-2}\text{M}$, Temp. = 45 °C
 C [Vanadium(v)] = $2.35 \times 10^{-2}\text{M}$, $[\text{PhPO}_2\text{H}_2]$ = $1.02 \times 10^{-2}\text{M}$, Temp. = 50 °C

A. $[\text{H}_2\text{SO}_4]/\text{M}$		4.0	4.5	5.0	5.5	6.0	6.5
$10^5 k_1/\text{s}^{-1}$		0.90	1.19	1.52	1.95	3.45	6.14
B. $[\text{HClO}_4]/\text{M}$	3.5	4.0	4.5	5.0	5.5	6.0	
$10^5 k_1/\text{s}^{-1}$	0.59	0.70	0.83	0.96	1.23	1.76	
C. $[\text{Na}_2\text{SO}_4]/\text{M}$	0	0.4	0.6	0.8			
$10^5 k_2/\text{l mol}^{-1} \text{s}^{-1}$	3.14	3.47	3.77	3.93			

and the slopes of both the plots were less than unity in each case which were 0.51 and 0.32 for sulphuric and perchloric acids respectively. The plots of $(\log k_1 + H_0)$

acid increased the rate (Table 2) whereas a constant value of $1.54 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ was obtained when perchlorate

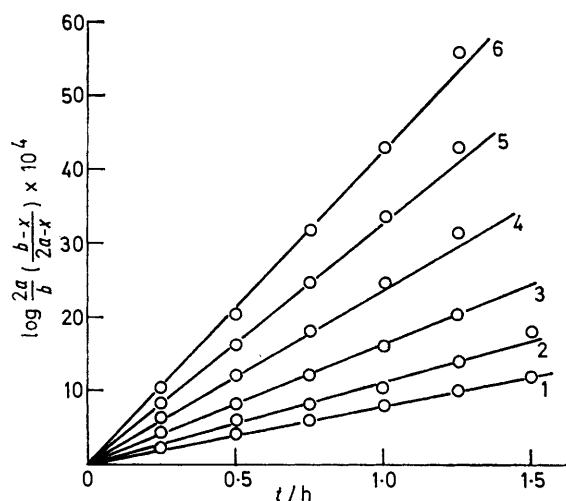


FIGURE 1 Second-order plots of the reaction between PhPO_2H_2 and vanadium(v) at different temperatures; $[\text{Vanadium}] = 2.16 \times 10^{-2}\text{M}$, $[\text{PhPO}_2\text{H}_2] = 1.0 \times 10^{-2}\text{M}$: 1, temp. = 45 °C, $[\text{H}_2\text{SO}_4] = 4.0\text{M}$; 2, 45 °C, 4.5M; 3, 50 °C, 4.0 M; 4, 50 °C, 4.5M; 5, 55 °C, 4.0M; 6, 55 °C, 4.5M

against $\log a_w$ (where $w = \text{H}_2\text{O}$) were not linear. This is expected since ionic strength, which could not be main-

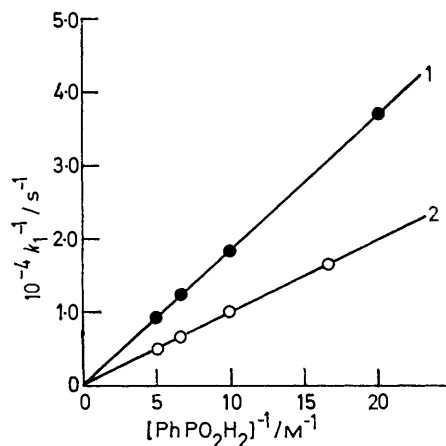


FIGURE 2 Kinetic evidence for the absence of complex formation between PhPO_2H_2 and vanadium(v). Plot of reciprocal of pseudo-first-order rate constant against the reciprocal of PhPO_2H_2 concentration; 1, $[\text{Vanadium(v)}] = 1.013 \times 10^{-2}\text{M}$, $[\text{HClO}_4] = 3.6\text{M}$; 2, $[\text{Vanadium(v)}] = 1.0 \times 10^{-2}\text{M}$, $[\text{H}_2\text{SO}_4] = 4.0\text{M}$

ion concentration was varied between the limits 0–0.8M in 4.0M- HClO_4 at reactant concentrations of vanadium(v)

¹⁴ M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

¹⁵ J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

and phenylphosphonous acid of 2.0×10^{-2} and 1.0×10^{-2} M respectively at 50 °C.

Rate constants and reciprocals of dielectric constants D are recorded in Table 3. Dielectric constants of acetic

TABLE 3

Dependence of rate constant on acetic acid-water composition

A [Vanadium(v)] = 2.26×10^{-2} M, [PhPO₂H₂] = 1.06×10^{-2} M, [H₂SO₄] = 4.0 M, Temp. = 50 °C

B [Vanadium(v)] = 2.03×10^{-2} M, [PhPO₂H₂] = 1.0×10^{-2} M, [HClO₄] = 3.31 M, Temp. = 50 °C

Acetic acid (%)	10^3	A		B	
	$\frac{1}{D}$	$10^3 k_2 / l \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_2 / l \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_2 / l \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_2 / l \text{ mol}^{-1} \text{ s}^{-1}$
20	17.39	1.76	1.05		
30	19.61	3.17	1.32		
40	22.38	7.42	1.58		
45	24.10	11.77	1.95		
50	26.04	19.91	2.33		

acid-water mixtures are from Radhakrishnamurti and Pati.¹⁶ The plot of the logarithm of second-order rate constant against reciprocal of dielectric constant¹⁶ showed a straight line up to 50% acetic acid with positive slope in each acid. The positive ions may be designated as V(OSO₃H)²⁺, V(OH)HSO₄⁺, or VO(OSO₃H)²⁺ as suggested by Littler and Waters.¹⁷ The reactive species suggested by Mehrotra,¹⁸ on the other hand, for solutions in sulphuric

DISCUSSION

Phenylphosphonous acid is known to exist in two forms in solution, *e.g.*, active and inactive forms. The active form PhP(OH)₂ is expected to predominate in acid solutions like hypophosphorous and phosphorous acids rather than the normal form PhPHO(OH). Phenylphosphonous acid is a weak monobasic acid and has a dissociation constant in the neighbourhood of 10⁻³. It would be in the undissociated form in the presence of high mineral acid concentration at *ca.* 4.0 M. Consequently the reactive species of vanadium(v), *e.g.*, V(OH)₃²⁺ or V(OH)₃HSO₄⁺ would attack PhPO₂H₂ and not PhPO₂H⁻. The results do not support the mechanism of the formation of an intermediate compound. The simple absence of the Michaelis-Menten type of kinetics does not rule out the possibility of the formation of an intermediate complex. It is not unlikely, however, that a small concentration of an intermediate compound is formed proceeding to the formation of reaction products.

In explaining the reaction steps in sulphuric acid medium it may be suggested that a free radical of the type PhṖO₂H is formed as an intermediate in the slow rate-determining step. The free radical would then be

TABLE 4

Thermodynamic data in sulphuric and perchloric acid media

[Vanadium(v)] = 2.155×10^{-2} M, [PhPO₂H₂] = 1.0×10^{-2} M

[HX] M	$10^3 k_2 / l \text{ mol}^{-1} \text{ s}^{-1}$				ΔH^\ddagger kcal mol ⁻¹	ΔS^\ddagger cal mol ⁻¹ K ⁻¹	ΔG^\ddagger at 318 K kcal mol ⁻¹
	40 °C	45 °C	50 °C	55 °C			
4.0 ^a	0.309	0.660	1.34	2.72	28.8 ± 0.5	15.3 ± 1.5	23.9 ± 1.0
4.5 ^a	0.426	0.908	1.94	3.51	28.8 ± 0.5	15.9 ± 1.5	23.7 ± 1.0
4.0 ^b	0.457	0.660	0.908	1.26	12.2 ± 0.4	-36.9 ± 1.3	23.9 ± 0.8
4.5 ^b	0.525	0.743	1.03	1.44	12.2 ± 0.4	-36.6 ± 1.3	23.8 ± 0.8

^a H₂SO₄ medium. ^b HClO₄ medium.

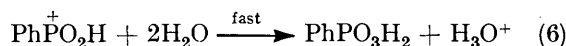
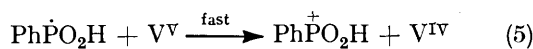
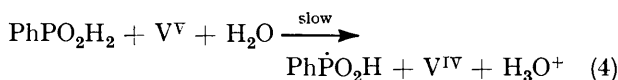
and perchloric acids at lower acidities are (VO₂,H₂O,H₂SO₄)⁺ and V(OH)₃²⁺ and those at higher acidities are (VO₂,2H₂SO₄)⁺ and V(OH)₂³⁺ respectively. However, the species (VO₂,H₂O,H₂SO₄)⁺ or V(OH)₃²⁺ and (VO₂,2H₂SO₄)⁺ or V(OH)₂³⁺ do not participate in the present reaction since we have not observed any retardation with increase in sulphate ion concentration at higher acidities, unlike the vanadium(v) oxidation of some hydroxy-compounds.¹⁹ Since V(OH)₃²⁺ is a better oxidant than VO₂⁺ in perchloric acid, we can assume V(OH)₃²⁺ and V(OH)₃HSO₄⁺ to be the active oxidising species in the respective acid-catalysed reaction by vanadium(v).

The energy of activation was calculated from the slope of the plot of log k_2 against $1/T$. The heat, entropy, and free energy of activation were then evaluated. The results indicate that about 2.5 times as much activation energy is needed to oxidise phenylphosphonous acid in sulphuric as in perchloric acid and the activation parameters in sulphuric acid are widely different from those with the value in perchloric acid. This is possibly because the rate-determining steps are different in the two different mineral acids.

¹⁶ P. S. Radhakrishnamurti and S. C. Pati, *Indian J. Chem.*, 1969, **7**, 687.

¹⁷ J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 1959, 3014, 4046.

converted into phosphonium ion which subsequently by reacting with water would form the stable product phenylphosphonic acid. The steps are (4)–(6).

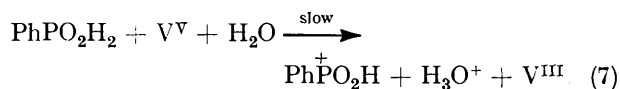


The polymerisation of acrylamide added to the reaction mixture had been observed indicating that a free radical of the type PhṖO₂H intervenes in the oxidation reaction. This suggests further that vanadium(v) behaves as a one-electron transfer oxidant. A similar free-radical mechanism has been suggested for vanadium(v) oxidation of hypophosphorous acid. Free radicals involving phosphorus in the +3 oxidation

¹⁸ R. N. Mehrotra, *J. Chem. Soc. (B)*, 1968, 642.

¹⁹ R. Shanker and S. S. Joshi, *Indian J. Chem.*, 1963, **1**, 289.

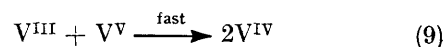
state^{20,21} are well known and the evidence for the formation of radical intermediate of the type $\text{H}_2\dot{\text{P}}\text{O}_2$ during the oxidation of hypophosphorous acid by diazonium chlorides has been given. Since we have been unable to adduce any experimental evidence for the formation of free radicals in solution in perchloric acid medium, the formation of phosphonium ion $\text{Ph}\overset{+}{\text{P}}\text{O}_2\text{H}$ in the rate-determining step is suggested. Step (7) will then be followed by step (6). The two-electron



transition in the case of vanadium(v), *i.e.*, reaction (8) followed by reaction (9), have been suggested during

²⁰ N. Kornblum, G. D. Cooper, and J. E. Taylor, *J. Amer. Chem. Soc.*, 1950, **72**, 3013.

the oxidation of benzyl alcohol by vanadium(v).^{19,22} The similar pattern in the activation parameters as obtained in the oxidation of benzyl alcohol by vanadium(v) is also observed indicating further that vanadium(v) behaves as a two-electron-transfer oxidant in perchloric acid.



We thank Professor M. N. Das, Head of the Physical Chemistry Section, Jadavpur University, and Professor S. Basu of Calcutta University for laboratory facilities.

[2/1175 Received, 22nd May, 1972]

²¹ N. Kornblum, A. F. Kelley, and G. D. Cooper, *J. Amer. Chem. Soc.*, 1952, **74**, 3074.

²² G. V. Bakore and R. Shanker, *Canad. J. Chem.*, 1966, **44**, 1717.