Kinetics of the Metal-ion Oxidation of Phenylphosphonous Acid.   Part II.[1] Oxidation by Chromium(VI)

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Phenylphosphonous acid and chromium(VI) react in aqueous perchloric acid as follows: $3 P^{III} + 2 Cr^{VI} \longrightarrow 3 P^V + 2 Cr^{III}$. The oxidation is effected by the $HCrO_4^-$ ion. Complex formation between phenylphosphonous acid and chromium(VI) is suggested and the empirical rate law is as shown (i). The rate is proportional to the

$$-d[Cr^{VI}]/dt = k_3 K[Cr^{VI}][PhPO_2H_2]/(1 + K[PhPO_2H_2]) \qquad (i)$$

first power of hydrogen-ion concentration. The effect of solvent composition on the reaction rate indicates the reaction to be of ion–dipole type. Chloride, sulphate, and phosphate ions decreased the rate considerably whereas an increase in rate in the presence of perchlorate ion has been observed. The activation parameters have been evaluated.

THE kinetics of the oxidation of several inorganic ions e.g., iron(II),[2] vanadyl(II),[3] $Ta^{II}_6Br_{12}$,[4] arsenic(III),[5] and some phosphorus compounds, by chromium(VI) have been reported.[6,7] We now report the results of the oxidation of phenylphosphonous acid by chromium(VI).

EXPERIMENTAL

Potassium dichromate, sodium chloride, sodium sulphate, disodium hydrogen phosphate, and manganous chloride were G. R. (Merck) products. Pyridine was purified twice by distillation. Other reagents have been described.[1]

Kinetic Measurements.—A Beckman DU spectrophotometer had its cell compartment kept at constant temperature by circulating water from a thermostat. The reactants previously equilibriated to bath temperature were mixed and the mixture was then transferred to a cell of path length 0·1 cm. The rate of decrease of chromium(VI) up to 50% conversion of initial chromium(VI) was determined from the measurement of optical densities at

different time intervals at 355 nm. Neither phenylphosphonous nor phenylphosphonic acid has any absorption at this wavelength. The pseudo-first-order rate constants were then calculated. Duplicate experiments were reproducible to within $\pm 2\%$.

RESULTS

The reaction product in excess of substrate concentration was phenylphosphonic acid. The substrate was quantitatively oxidised to the same product at 30 °C when it was mixed with a large excess of dichromate ions and stored for 24 h according to equation (1). The rate at which

$$3P^{III} + 2Cr^{VI} \longrightarrow 3P^V + 2Cr^{III} \qquad (1)$$

chromium(VI) disappeared follows a first-order law and is not independent of initial gross chromium(VI) concentration. The result indicates that $HCrO_4^-$ is the reacting species.[8] The constancy of $k_1[Cr^{VI}]/[HCrO_4^-]$ was checked

[1] Part I, K. K. Sen Gupta, B. B. Pal, J. K. Chakladar, and D. C. Mukherjee, preceding paper.
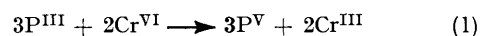[2] J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, 1963, **85**, 3328.
[3] J. H. Espenson, *J. Amer. Chem. Soc.*, 1964, **86**, 5101.
[4] J. H. Espenson, *J. Amer. Chem. Soc.*, 1964, **86**, 1883.
[5] J. G. Mason and A. D. Kowalak, *J. Inorg. Chem.*, 1964, **3**, 1248.
[6] N. R. Dhar, *Ann. Chim. (Italy)*, 1919, **11**, 130; *J. Chem. Soc.*, 1917, 707.
[7] K. K. Sen Gupta, *Bull. Chem. Soc. Japan*, 1970, **43**, 590.
[8] K. B. Wiberg, ' Oxidation in Organic Chemistry,' Part A, Academic Press, New York, 1965, 71.

at various chromium(VI) concentrations (Table 1); Cr^{VI} and HCrO$_4^-$ denote gross and reacting species of chromium-(VI) respectively. Each experiment was performed at constant ionic strength, $\mu = 1\cdot0M$, maintained by the

TABLE 1

Effect of oxidant on the reaction rate

[PhPO$_2$H$_2$] = 1·366 × 10^{-1}M, [H$^+$] = 0·924M, $\mu = 1\cdot0M$, Temp. = 35 °C

10^3[Cr^{VI}]/M	10^2[HCrO$_4^-$]/M	$10^2 k_1$/min^{-1}	k_{cor}/min^{-1}
6·66	0·66	0·76	0·76
3·33	0·42	1·11	0·88
1·66	0·24	1·44	0·98
0·83	0·14	1·53	0·92

$$k_{cor} = 10^2 k_1[\text{Cr}^{VI}]/[\text{HCrO}_4^-]$$

addition of sodium perchlorate. The concentrations of HCrO$_4^-$ were calculated from the relation (2) the dimer

$$1/k_d = [\text{HCrO}_4^-]^2/[\text{Cr}^{VI}] - [\text{HCrO}_4^-]/2 \qquad (2)$$

being assumed to be the initial reacting species. The value for the dissociation constant K_d of reaction (3) at

$$2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \qquad (3)$$
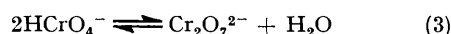
35 °C has been reported [9] to be 76 at $\mu = 1\cdot0M$. This has been used to evaluate HCrO$_4^-$ concentrations from the relation (2).

The rate of oxidation increased with the increase in the concentration of the substrate. The empirical rate law is (4) where k_3 and K denote the specific reaction rate for

$$-\text{d}[\text{Cr}^{VI}]/\text{d}t = k_3K[\text{Cr}^{VI}][\text{PhPO}_2\text{H}_2]/$$
$$(1 + K[\text{PhPO}_2\text{H}_2]) \qquad (4)$$

the decomposition and the equilibrium constant of the 1 : 1 complex. The plot of $1/k_1$ against $1/[\text{PhPO}_2\text{H}_2]$ gave a
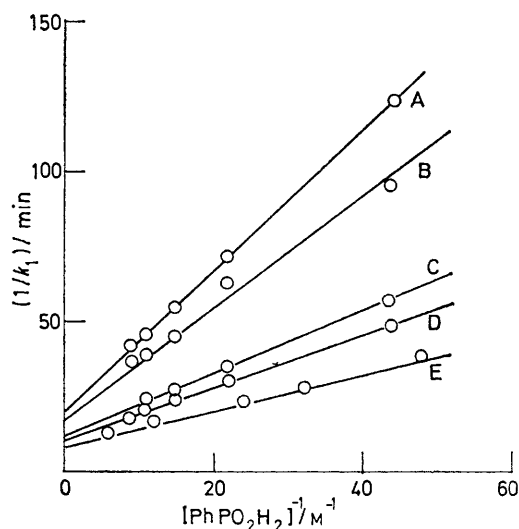

FIGURE 1 Kinetic evidence for intermediate complex formation between PhPO$_2$H$_2$ and chromium(VI). Plots of $1/k_1$ against $1/[\text{PhPO}_2\text{H}_2]$ at different temperatures: [Cr^{VI}] = 3·3 × 10^{-3}M, [H$^+$] = 0·935M; temp., A, 26 °C; B, 30·4 °C; C, 36 °C; D, 39·5 °C; E, 46 °C

straight line (Figure 1). From the slope and intercept of each line the equilibrium constants were calculated to be 8·46, 9·24, 11·1, 11·9, and 13·3 at 26, 30·4, 36, 39·4, and 46 °C respectively. The decrease in free energy of

formation of the complex was calculated from the relation $-\Delta G = RT \ln K$. The enthalpy change ΔH associated with the equilibrium constant K was calculated to be $5\cdot2 \pm 0\cdot8$ kcal mol^{-1} from the slope of the plot of log K against $1/T$ (Figure 2) which was used to evaluate the entropy change from the relation $\Delta G = \Delta H - T\Delta S$. The thermodynamic parameters are in Table 5.
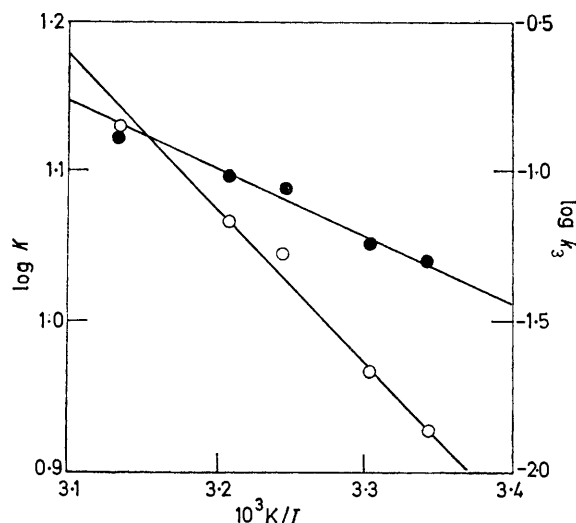

FIGURE 2 Plot of log K against $1/T$ (open circles) and plot of log k_3 against $1/T$ (filled circles): [Cr^{VI}] = 3·3 × 10^{-3}M, [H$^+$] = 0·936M

The reaction was studied at various hydrogen-ion concentrations. The acidity was varied by the addition of perchloric acid. The ionic strength of each solution was adjusted to 1·6M by the addition of sodium perchlorate. The rate increased with the first power of hydrogen-ion concentration when [H$^+$] $\leqslant$ 1·40M. The values of k_1/[H$^+$] at different acidities were calculated (Table 2).

TABLE 2

Dependence of reaction rate on [H$^+$]

[PhPO$_2$H$_2$] = 4·3 × 10^{-2}M, [Cr^{VI}] = 0·33 × 10^{-2}M, $\mu = 1\cdot68M$, Temp. = 35 °C

[H$^+$]/M	$10k_1$/min^{-1}	$10^2 k_1$/[H$^+$] 1 mol^{-1} min^{-1}
0·468	0·48	1·03
0·612	0·78	1·27
0·702	0·89	1·27
0·833	1·03	1·24
0·936	1·20	1·28
1·078	1·49	1·38
1·170	1·60	1·37
1·404	1·93	1·37

The effect of addition of sodium perchlorate, chloride sulphate, and hydrogen phosphate on the rate was studied. In all cases except perchlorate ion, the rate decreased considerably with the increase in salt concentration (Figure 3). The observed rate constants at 1·5 × 10^{-1}M concentration of the salts are found to be 0·23 × 10^{-2}, 0·65 × 10^{-2}, 0·85 × 10^{-2}, and 1·16 × 10^{-2} min^{-1} for hydrogen phosphate, chloride, sulphate, and perchlorate, and the rate decrease followed the order hydrogen phosphate > chloride > sulphate > perchlorate. This is probably due to the

[9] J. H. Espenson and R. J. Kinney, *J. Inorg. Chem.*, 1971, **10**, 1376.

tendency of the anions to react with the acid chromate ion to form complexes of different stabilities,[10–13] the oxidising ability of which increases in the order, $H_3CrPO_7 <$ $HCrClO_3 < H_2CrSO_7 < HCrClO_7$ for a given acid concentration.[11] The present results are in agreement with the observation of Lee and Stewart.[11] A good linear relationship has, however, been observed in sodium perchlorate when log k_1 was plotted against μ according to equation [14]

$$\log k_1 = \log k_0 + (b_0 + b_A - b\ddagger)\mu \qquad (5)$$

(5) indicating the reaction between an ion and an uncharged molecule. This is expected since perchlorate ion is the least complex-forming anion and the calculated and actual ionic strength in solution would not differ appreciably. On the other hand, deviations from linearity have been observed in the other cases possibly because of the complexing tendencies of the anions with $HCrO_4^-$.

The rate of oxidation decreased with the increase in manganous ion concentration and a limiting value is reached at higher manganous ion concentration. The pseudo-first-order rate constants in the absence and presence of $Mn^{2+} \geqslant$ $5.0 \times 10^{-3}M$ are 1.99×10^{-2} and 0.96×10^{-2} min^{-1} respectively. Chloride ion does not have any influence at
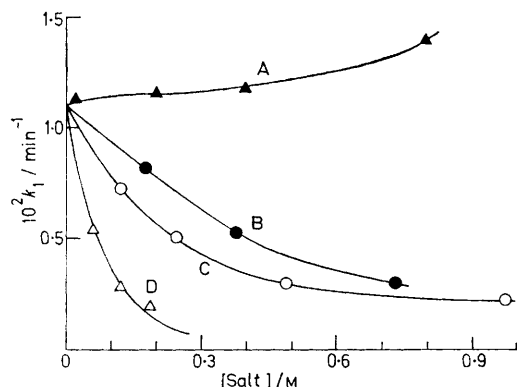

FIGURE 3 Effect of A, perchlorate; B, sulphate; C, chloride; and D, hydrogen phosphate ions on $[Cr^{VI}] = 3.3 \times 10^{-3}M$, $[PhPO_2H_2] = 4.36 \times 10^{-2}M$, $[H^+] = 0.936M$, temp. $= 35$ °C

this low concentration of the manganous salt. The rate of oxidation, however, decreased to half of that in the absence of Mn^{2+} ions. This is in accordance with what has been observed by Watanabe and Westheimer.[15] This is possibly due to the involvement of intermediate valence states of oxidant, e.g., chromium(IV), which may catalyse the disproportion of intermediate valency [12,16] and indicates further that the rate-determining step is possibly a two-electron transfer process.

The enhancement of rate at higher percentages of acetic acid may be explained as due to the formation of a stronger electrophile produced on replacement of a hydroxy-hydrogen atom by an acetyl group. Cohen and West-heimer [13] suggested that an increase in acetic acid concentration would decrease the dielectric constant of the solvent and consequently would lead to the increased rate of oxida-

tion. The present studies at different chromium(VI) concentrations indicate that the species is negatively charged, e.g., $HCrO_4^-$ and not $HCrO_3^+$, $H_3CrO_4^+$, or a highly polar molecule like $Cr^{\delta+}O_3^{\delta-}$ as suggested by Rocek and Krupica.[17] Waters [18] has suggested that in acetic acid medium, acetylchromic acid $AcCrO_2OH$ or its conjugate acid $AcCrO_2OH_2^+$ is responsible for the enhancement of rate.

TABLE 3

Effect of dielectric constant on the reaction rate

$[Cr^{VI}] = 3.33 \times 10^{-3}M$, $[PhPO_2H_2] = 4.43 \times 10^{-2}M$, $[H^+] =$ $0.936M$, Temp. $= 35$ °C

Acetic acid (%)	0	10	20	30	40
$10^2 k_1/min^{-1}$	0.97	1.26	1.49	2.24	3.29

The influence of pyridine on the rate has been studied at different pyridine concentrations but at constant hydrogen-ion concentration of $1.4M$. However, at this high concentration of the acid most pyridine would remain as pyridinium ion and hence the concentrations of the different species involved in the reaction were calculated by assuming the equilibrium (6).

$$PyH^+ \xrightleftharpoons{K_d'} Py + H^+ \qquad (6)$$
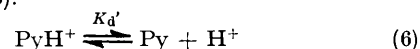
The dissociation constant of pyridinium ion [19] is of the order of 4×10^{-6} at 35 °C. The results indicate that pyridine does not catalyse the reaction, since $k_1/[H^+] -$ $[Py]_{free}$ decreased with the increase in base (Table 4).

TABLE 4

Influence of pyridine on the reaction rate

$[PhPO_2H_2] = 4.43 \times 10^{-2}M$, $[Cr^{VI}] = 3.3 \times 10^{-3}M$, $[H^+] =$ $1.40M$, Temp. $= 35$ °C

$[Py]_0/M$	$[PyH^+]/M$	$\dfrac{[Py]_{free}}{M}$	$\dfrac{10^2 k_1}{min^{-1}}$	$\dfrac{10^2 k_1/([H^+] - [Py]_{free})}{1\ mol^{-1}\ min^{-1}}$
0	0	0	1.93	1.37
0.017	0.0166	0.004	1.88	1.34
0.034	0.0255	0.0085	1.77	1.27
0.068	0.0557	0.0123	1.70	1.22

This is in contrast with the observation made earlier [12] that pyridine catalysed the oxidation of some organic compounds.

TABLE 5

Thermodynamic data of the complex and the activation parameters

$t/°C$	$\dfrac{\Delta G \pm 0.01}{kcal\ mol^{-1}}$	$\dfrac{\Delta S \pm 2.6}{cal\ mol^{-1}\ K^{-1}}$	$\dfrac{\Delta G\ddagger \pm 2.4}{kcal\ mol^{-1}}$	$\dfrac{-\Delta S\ddagger \pm 3.9}{cal\ mol^{-1}\ K^{-1}}$
26.0	1.27	21.6	22.3	40.2
30.4	1.34	21.5	22.6	40.4
36.0	1.48	21.6	22.7	40.3
39.4	1.54	21.5	22.9	40.4
46.0	1.64	21.4	23.2	40.7

The values of k_3 calculated from the intercepts of Figure 1 were found to be 5.0×10^{-2}, 5.7×10^{-2}, 8.62×10^{-2}, 9.52×10^{-2}, and 12.50×10^{-2} min^{-1} at 26, 30.4, 36, 39.4, and 46 °C respectively. The plot of log k_3 against $1/T$

[10] P. Holloway, J. Amer. Chem. Soc., 1952, **74**, 224.
[11] D. G. Lee and R. Stewart, J. Amer. Chem. Soc., 1964, **86**, 3051.
[12] F. H. Westheimer, Chem. Rev., 1949, **49**, 419.
[13] M. Cohen and F. H. Westheimer, J. Amer. Chem. Soc., 1952, **74**, 4387.
[14] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1953, p. 140.
[15] W. Watanabe and F. H. Westheimer, J. Chem. Phys., 1949, **17**, 61.
[16] K. B. Wiberg and T. J. Mill, J. Amer. Chem. Soc., 1958, **80**, 3022.
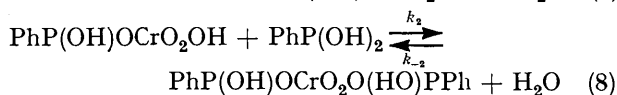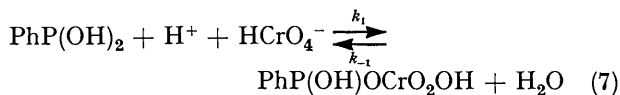[17] J. Rocek and J. Krupica, Coll. Czech. Chem. Comm., 1958, **23**, 2068.
[18] W. A. Waters, ' Mechanism of Oxidation of Organic Compounds,' Methuen, London, 1964, p. 60.
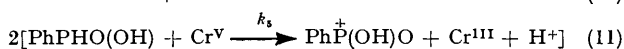[19] R. Bruehlman and F. Verhoek, J. Amer. Chem. Soc., 1948, **70**, 1401.

gave a straight line (Figure 2) from the slope of which the energy of activation for the slow step (9) was calculated to be $10 \cdot 3 \pm 1 \cdot 2$ kcal/mol. The entropy of activation and the free energy of activation were finally evaluated (Table 5).
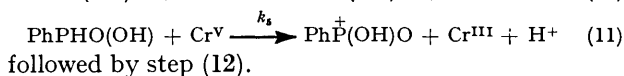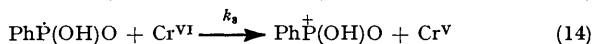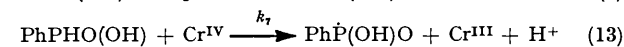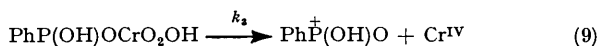
DISCUSSION

The kinetic evidence indicated the formation of a 1 : 1 intermediate complex which is formed by the condensation of the active form of the substrate with $HCrO_4^-$ according to equation (7). The formation of a 1 : 2 complex in the presence of a higher substrate concentration according to (8) is unlikely since the order with respect to substrate is 0·8. The phosphonium ion

$$PhP(OH)_2 + H^+ + HCrO_4^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$
$$PhP(OH)OCrO_2OH + H_2O \quad (7)$$

$$PhP(OH)OCrO_2OH + PhP(OH)_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$
$$PhP(OH)OCrO_2O(HO)PPh + H_2O \quad (8)$$

which is formed slowly by the breakdown of the 1 : 1 complex is converted into the stable product phenylphosphonic acid by reacting rapidly with water according to equation (12). Three mechanisms (1)—(3) can
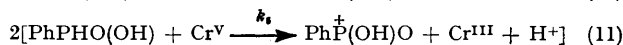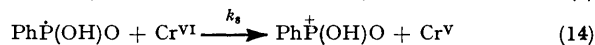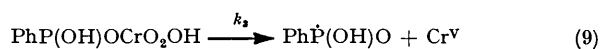
$$PhP(OH)OCrO_2OH \overset{k_3}{\longrightarrow} Ph\overset{+}{P}(OH)O + Cr^{IV} \quad (9)$$

$$Cr^{IV} + Cr^{VI} \overset{k_4}{\longrightarrow} 2Cr^V \quad (10)$$

$$2[PhPHO(OH) + Cr^V \overset{k_5}{\longrightarrow} Ph\overset{+}{P}(OH)O + Cr^{III} + H^+] \quad (11)$$

$$3[Ph\overset{+}{P}(OH)O + H_2O \overset{k_6}{\longrightarrow} PhPO_3H_2 + H^+] \quad (12)$$

SCHEME 1

$$PhP(OH)OCrO_2OH \overset{k_3}{\longrightarrow} Ph\overset{+}{P}(OH)O + Cr^{IV} \quad (9)$$

$$PhPHO(OH) + Cr^{IV} \overset{k_7}{\longrightarrow} Ph\overset{+}{P}(OH)O + Cr^{III} + H^+ \quad (13)$$

$$Ph\overset{+}{P}(OH)O + Cr^{VI} \overset{k_8}{\longrightarrow} Ph\overset{+}{P}(OH)O + Cr^V \quad (14)$$

$$PhPHO(OH) + Cr^V \overset{k_5}{\longrightarrow} Ph\overset{+}{P}(OH)O + Cr^{III} + H^+ \quad (11)$$

followed by step (12).

SCHEME 2

[20] J. Rocek and A. E. Radkowsky, J. Amer. Chem. Soc., 1968, 90, 2986.
[21] J. Rocek and A. Riehl, Tetrahedron Letters, 1966, 1437.

$$PhP(OH)OCrO_2OH \overset{k_3}{\longrightarrow} Ph\overset{+}{P}(OH)O + Cr^V \quad (9)$$

$$Ph\overset{+}{P}(OH)O + Cr^{VI} \overset{k_8}{\longrightarrow} Ph\overset{+}{P}(OH)O + Cr^V \quad (14)$$

$$2[PhPHO(OH) + Cr^V \overset{k_5}{\longrightarrow} Ph\overset{+}{P}(OH)O + Cr^{III} + H^+] \quad (11)$$

followed by step (12).

SCHEME 3

therefore be suggested for the reaction. The slowest step is represented by k_3 and all other steps are fast.

Acrylamide added to the reaction mixture failed to polymerise indicating that no free radical of the type $PhPO_2H$ intervenes in the oxidation and therefore chromium(VI) does not behave as a one-electron-transfer oxidant. Consequently Scheme 1 appears to be favoured. The absence of a free radical from the solution further indicates that chromium(IV) does not participate in the reaction as an oxidising species as in Scheme 2; rather it would react with chromium(VI) to give chromium(V) as Scheme 1. Regardless of which Scheme is correct, the participation of chromium(V) as an oxidant cannot be ruled out, although conflicting views have been put forward [20-22] regarding the reactivity of chromium(V). The standard oxidation potential of the chromium(VI)–chromium(III) couple is 1·36 V, as compared with that for chromium(V)–chromium(III) couple which is 1·75 V. This indicates further that chromium(V) would behave as a highly reactive species and its reaction with the inactive variety of the substrate molecule would be very fast. Thus only one-third of the total oxidation is effected by chromium(VI) and two-thirds is effected by chromium(V). The activation parameters obtained in the present study are widely different from those of Part I,[1] indicating that chromium(VI) behaves as a two-electron and not a one-electron transfer oxidant.

[22] K. B. Wiberg and H. Schafer, J. Amer. Chem. Soc., 1969, 91, 927, 933.