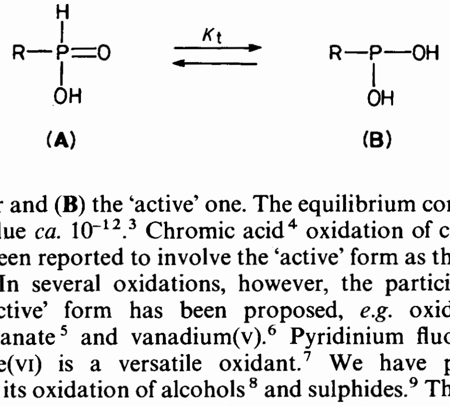
Kinetics and Mechanism of the Oxidation of Phosphinic, Phenylphosphinic, and Phosphorous Acids by Pyridinium Fluorotrioxochromate(VI)

Anu Moondra, Abha Mathur, and Kalyan K. Banerji *
Department of Chemistry, University of Jodhpur, Jodhpur 342 001, India

Oxidation of the lower phosphorus oxyacids by $[C_5H_5NH][CrO_3F]$ results in the formation of corresponding oxyacids in the higher valence states. The reaction is first order with respect to the oxidant concentration. A Michaelis–Menten type kinetics was observed with respect to the substrate, indicating the formation of a complex in a pre-equilibrium. The formation constants and the rates of disproportionation of the complexes have been evaluated at different temperatures. The reaction exhibits a substantial primary kinetic isotope effect. The rates in 19 different organic solvents have been analysed using Kamlet-Taft and Swain equations. It has been found that the cation-solvating power of the solvents plays an important role. It is proposed that the 'inactive' tautomer of the phosphorus oxyacids is the reactive reductant, and that transfer of a hydride ion from the P–H bond to the oxidant in the rate-determining step occurs.

The three lower oxyacids of phosphorus, *viz.* phosphinic (hypophosphorus) (**1**; R = H), phenylphosphinic (**2**; R = Ph), and phosphorous (**3**; R = OH), are known to exhibit tautomerism [reaction (1)].[1,2] Generally, tautomer (**A**) is called the 'inactive'



$$\mathrm{R{-}P(H)(=O)OH} \;\underset{}{\overset{K_t}{\rightleftharpoons}}\; \mathrm{R{-}P(OH){-}OH} \qquad (1)$$

(**A**) (**B**)

tautomer and (**B**) the 'active' one. The equilibrium constant, K_t, has a value *ca.* 10^{-12}.[3] Chromic acid[4] oxidation of compound (**2**) has been reported to involve the 'active' form as the reactive species. In several oxidations, however, the participation of the 'inactive' form has been proposed, *e.g.* oxidation by permanganate[5] and vanadium(V).[6] Pyridinium fluorotrioxochromate(VI) is a versatile oxidant.[7] We have previously reported its oxidation of alcohols[8] and sulphides.[9] There seems to be no report on the oxidation of phosphorus compounds except on the synthetic aspects of oxidation of triphenylphosphine.[10] In this paper we report the kinetics of oxidation of the three lower oxyacids of phosphorus by $[C_5H_5NH][CrO_3F]$ in dimethyl sulphoxide (dmso) as solvent. The mechanistic aspects are discussed.

Experimental

Materials.—The oxyacids were commercial products (Fluka) and used as such. Their solutions in dmso were standardized, after dilution with water, by alkalimetry. The salt $[C_5H_5NH][CrO_3F]$ was prepared and purified as reported.[7] Organic solvents were purified by the usual methods.[11]

The P–H bonds in compounds (**1**) and (**3**) were deuteriated by dissolving the acid in deuterium oxide (BARC, 99.4% purity) and evaporating the excess of deuterium oxide and water *in vacuo*.[12] The isotopic purity, as determined by n.m.r. spectroscopy, was 91 ± 5 and 93 ± 4% respectively.

Stoicheiometry.—The oxidation of phosphorus-(I) and -(III) oxyacids by $[C_5N_5NH][CrO_3F]$ leads to the formation of the corresponding phosphorus-(III) and -(V) oxyacids. Reaction mixtures, containing a known excess of compound (**2**) were prepared. Upon completion of the reaction the phenylphosphonic acid formed was determined by the reported method.[13] Several determinations indicated that $\Delta(\mathbf{2})/\Delta[\text{chromate}] = 1.04 \pm 0.07:1$. To determine the stoicheiometry of the oxidation of compounds (**1**) and (**3**), reaction mixtures containing a known excess of the chromate were prepared and after completion of the reaction the residual oxidant was determined. The observed stoicheiometry is 1.88 ± 0.18 and 0.96 ± 0.05:1 respectively. It seems that (**1**) is finally oxidized to phosphoric acid through (**3**). Rates of oxidation of (**1**) and (**3**) are of the same order, but (**1**) was always kept in large excess over the oxidant and, therefore, the amount of (**3**) formed would be relatively small and is not likely to affect significantly the kinetics of oxidation of (**1**).

Kinetic Measurements.—Pseudo-first-order conditions were attained by keeping a large excess of the phosphorus compound over the oxidant. The solvent was dmso, unless specified otherwise. The reactions were followed at constant temperature (±0.1 K), by monitoring the decrease in the oxidant concentration at 356 nm. Pseudo-first order rate constants, $k_{obs.}$, were evaluated from least-squares plots of log [chromate] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. Corrections were applied to the rate constants of the deuteriated compounds for the hydrogen-1 content.

Results and Discussion

The oxidation exhibited a 1:1 stoicheiometry and the overall reaction may be written as in equation (2). The oxidation is first

$$RH_2PO_2 + [C_5H_5NH][CrO_3F] \longrightarrow RH_2PO_3 + [C_5H_5NH][CrO_2F] \quad (2)$$

order with respect to the oxidant concentration and follows Michaelis–Menten type kinetics with respect to the oxyacid (Tables 1—3). This indicated the formation of an intermediate complex in the pre-equilibrium and its decomposition in the rate-determining step. An overall mechanism as in equations (3) and (4) and an experimental rate law (5) are proposed

Table 1. Rate constants for the oxidation of phosphinic acid by $[C_5H_5NH][CrO_3F]$ at 308 K

[Phosphinic acid]/mol dm^{-3}	10^3[Oxidant]/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
0.01	1.0	1.51
0.02	1.0	3.02
0.04	1.0	5.21
0.06	1.0	7.52
0.08	1.0	9.55
0.12	1.0	12.0
0.16	1.0	14.5
0.20	1.0	16.5
0.16	2.0	15.1
0.16	4.0	14.7
0.16	6.0	14.5
0.16	8.0	14.0
0.16	10.0	14.5
0.16	12.0	14.2

Table 2. Rate constants for the oxidation of phenylphosphinic acid by $[C_5H_5NH][CrO_3F]$ at 298 K

$[PhH_2PO_2]$/mol dm^{-3}	10^3[Oxidant]/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
0.01	1.0	1.70
0.02	1.0	3.30
0.04	1.0	5.54
0.06	1.0	7.90
0.08	1.0	9.64
0.12	1.0	13.0
0.16	1.0	15.0
0.20	1.0	16.2
0.12	2.0	13.2
0.12	4.0	13.1
0.12	6.0	12.7
0.12	8.0	13.0
0.12	10.0	12.7

Table 3. Rate constants for the oxidation of phosphorous acid by $[C_5H_5NH][CrO_3F]$ at 303 K

$[H_3PO_3]$/mol dm^{-3}	10^3[Oxidant]/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
0.01	1.0	1.31
0.02	1.0	2.44
0.04	1.0	4.54
0.06	1.0	6.30
0.08	1.0	8.05
0.12	1.0	10.0
0.16	1.0	13.3
0.20	1.0	14.9
0.16	2.0	13.0
0.16	4.0	13.3
0.16	6.0	13.1
0.16	8.0	13.6
0.16	10.0	13.5

$$\text{Oxyacid} + \text{Oxidant} \xrightleftharpoons[k_{-1}]{k_1} \text{Complex} \qquad (3)$$

$$\text{Complex} \xrightarrow{k_2} \text{Products} \qquad (4)$$

$$\frac{-\text{d[Oxidant]}}{\text{d}t} = \frac{Kk_2\text{[Oxidant][Oxyacid]}}{1 + K\text{[Oxyacid]}} \qquad (5)$$

where K is the equilibrium constant of reaction (3) and is equal to k_1/k_{-1}.

The dependences of the reaction rate on the concentrations of compounds (**1**)—(**3**) were determined at different temperatures and the values of the equilibrium constants, K, and the rates of disproportionation, k_2, were evaluated from plots of $1/k_{obs.}$ *versus* 1/[Oxyacid]. From the values of k_2 at different temperatures the activation parameters for the decomposition of the complexes were also calculated (Tables 4—6).

The data in Table 4 showed that the formation constants of the oxyacid–oxidant complexes are almost constant over the experimental temperature range. Similar observations were recorded for alcohol oxidations with $[C_5H_5NH][CrO_3F]$.[8] This may be due to either the formation constant (experimental) being a composite term of two equilibrium constants with opposing temperature coefficients, or the temperature coefficient being so small that it is masked by the experimental errors.

The oxidation of deuteriated acids (**1**) and (**3**) indicated the presence of a substantial primary kinetic isotope effect (k_H/k_D = 6.55 and 5.80 respectively, at 298 K) indicating the rupture of a P–H bond in the rate-determining step.

The oxidation of compound (**2**) was studied in 19 different organic solvents. The choice of solvent was limited by the solubility of the oxidant and its reaction with primary and secondary alcohols. There was no noticeable reaction with the solvents used. The kinetics is similar in all the solvents. The values of K and k_2 at 303 K are recorded in Table 7. The equilibrium constant is not very sensitive to a change in solvent, but k_2 varies considerably with the solvents.

The rate of disproportionation of the complex, k_2, in 17 solvents (CS_2 and acetic acid were not considered as the complete range of solvent parameters was not available) was correlated by the linear solvation energy relationship (l.s.e.r.) of Kamlet *et al.*[14] [equation (6)], where π^* represents the solvent

$$\log k_2 = A_0 + p\pi^* + a\alpha + b\beta \qquad (6)$$

polarity for a solvent–solute interaction of non-specific type, β is a scale of solvent hydrogen-bond acceptor basicity, while α represents the solvent hydrogen-bond donor acidity of the solvent; A_0 is the intercept term. It may be mentioned here that, out of the 17 solvents, for 12 solvents α has a value of zero. The analyses in terms of the three parameter l.s.e.r. [equation (6)], a two-parameter equation involving π^* and β, and separately with π^* and β gave the results in equations (7)—(10).

$$\log k_2 = -0.05 + 2.28\pi^* + 0.53\alpha + 0.18\beta \qquad (7)$$

$$R^2 = 0.8932, \text{s.d.} = 0.22, n = 17, \psi = 0.36$$

$$\log k_2 = 0.04 + 2.18\pi^* + 0.27\beta \qquad (8)$$

$$R^2 = 0.8664, \text{s.d.} = 0.23, n = 17, \psi = 0.40$$

$$\log k_2 = (0.09 \pm 0.02) + (2.25 \pm 0.24)\pi^* \qquad (9)$$

$$r^2 = 0.8464, \text{s.d.} = 0.24, n = 17, \psi = 0.42$$

$$\log k_2 = (1.31 \pm 0.23) + (0.67 \pm 0.49)\beta \qquad (10)$$

$$r^2 = 0.1102, \text{s.d.} = 0.58, n = 17, \psi = 1.04$$

Here n is the number of data points, s.d. is the standard deviation, ψ is Exner's statistical parameter,[5] R is the coefficient of multiple correlation, and r is the coefficient of simple regression.

The results show that *ca.* 90% of the data on the solvent effect is explained by equation (7). According to Exner's criterion,[15] however, the correlation is poor. The major contribution is from the solvent-polarity term π^* [*cf.* equation (9)], both α and β playing relatively insignificant roles.

Table 4. Formation constants of phosphorus oxyacid complexes with $[C_5H_5NH][CrO_3F]$

	K/dm^3 mol^{-1}				
Acid	298	303	308	313	318 K
Phosphinic	4.01 ± 0.2	3.52 ± 0.2	4.53 ± 0.3	3.12 ± 0.1	3.49 ± 0.3
Phenylphosphinic	6.12 ± 0.3	5.61 ± 0.3	4.62 ± 0.2	4.78 ± 0.2	4.76 ± 0.1
Phosphorous	4.44 ± 0.1	4.75 ± 0.2	3.25 ± 0.3	4.11 ± 0.1	3.31 ± 0.2
Deuteriated phosphinic	3.72 ± 0.2	3.49 ± 0.2	4.20 ± 0.2	3.35 ± 0.2	4.30 ± 0.3
Deuteriated phosphorous	4.73 ± 0.2	4.37 ± 0.2	3.92 ± 0.2	4.80 ± 0.3	4.15 ± 0.3

Table 5. Rate constants of decomposition of phosphorus oxyacid complexes with $[C_5H_5NH][CrO_3F]$

	10^6k_2/s^{-1}				
Acid	298	303	308	313	318 K
Phosphinic	1.31 ± 0.06	2.81 ± 0.20	3.54 ± 0.25	6.75 ± 0.32	9.56 ± 0.96
Phenylphosphinic	2.97 ± 0.14	4.75 ± 0.23	7.66 ± 0.39	11.0 ± 0.38	17.3 ± 0.52
Phosphorous	1.74 ± 0.05	2.89 ± 0.15	5.74 ± 0.51	7.22 ± 0.20	12.9 ± 0.05
Deuteriated phosphinic	0.20 ± 0.01	0.47 ± 0.03	0.63 ± 0.02	1.30 ± 0.07	1.99 ± 0.10
Deuteriated phosphorous	0.30 ± 0.01	0.54 ± 0.04	1.13 ± 0.06	1.53 ± 0.06	3.07 ± 0.12

Table 6. Activation parameters for the decomposition of phosphorus oxyacid complexes with $[C_5H_5NH][CrO_3F]$

Acid	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	$\Delta G^‡$/ kJ mol^{-1}
Phosphinic	73.9 ± 4.4	−71 ± 14	94.9 ± 3.4
Phenylphosphinic	66.3 ± 0.9	−91 ± 3	93.1 ± 0.7
Phosphorous	75.1 ± 3.6	−63 + 11	94.4 ± 2.8

Table 7. Effect of solvent on the oxidation of phenylphosphinic acid by $[C_5H_5NH][CrO_3F]$ at 303 K

Solvent	K/dm^3 mol^{-1}	10^6k_2/s^{-1}
Chloroform	4.95 ± 0.5	63.4
Carbon disulphide	5.35 ± 0.4	33.0
1,2-Dichloroethane	5.50 ± 0.4	70.5
Dichloromethane	5.10 ± 0.4	81.6
Dimethyl sulphoxide	5.61 ± 0.3	475
Acetone	5.34 ± 0.5	60.4
Dimethylformamide	6.13 ± 0.5	210
Butanone	5.44 ± 0.4	31.4
Nitrobenzene	4.93 ± 0.3	126
Benzene	4.98 ± 0.5	14.2
Cyclohexane	5.50 ± 0.4	1.52
Toluene	5.34 ± 0.3	8.97
Acetophenone	5.85 ± 0.6	100
Tetrahydrofuran	6.10 ± 0.6	28.3
t-Butyl alcohol	5.37 ± 0.7	18.5
Dioxane	4.70 ± 0.2	31.7
1,2-Dimethoxyethane	6.00 ± 0.4	10.5
Acetic acid	5.81 ± 0.7	26.5
Ethyl acetate	5.94 ± 0.5	12.5

The data on solvent effect were also analysed in terms of Swain's equation[16] (11) where A represents the anion-solvating

$$\log k_2 = aA + bB + C \qquad (11)$$

power of the solvent and B the cation-solvating power; C is the intercept term, and $(A + B)$ is postulated to represent the solvent polarity.[16] The results of the correlation analysis in terms of equation (11), individually with A and B, and with $(A + B)$ are given in equations (12)—(15).

$$\log k_2 = 0.52A + 2.51B + 0.32 \qquad (12)$$

$$R^2 = 0.9635, \text{s.d.} = 0.13, n = 19, \psi = 0.20$$

$$\log k_2 = 1.85(A + B) + 0.26 \qquad (13)$$

$$r^2 = 0.7295, \text{s.d.} = 0.35, n = 19, \psi = 0.55$$

$$\log k_2 = 0.16A + 1.41 \qquad (14)$$

$$r^2 = 0.0022, \text{s.d.} = 0.68, n = 19, \psi = 1.03$$

$$\log k_2 = 2.47B - 0.15 \qquad (15)$$

$$r^2 = 0.9413, \text{s.d.} = 0.17, n = 19, \psi = 0.18$$

The analysis in terms of Swain's equation[16] indicated that *ca.* 96% of the data is explained. A comparison of equations (12) and (15) indicates that the cation-solvating power of the solvents plays the major role; B alone accounts for *ca.* 94% of the data. The value of Exner's ψ points to a fair correlation with both equations (11) and (15).

The non-specific solvent polarity, π^*, as defined by Kamlet *et al.*[14] is able to account for *ca.* 85% of the data [*cf.* equation (9)] whereas the solvent polarity $(A + B)$ of Swain's treatment[16] accounts for only 73% of the data [*cf.* equation (13)]. Thus it seems that π^* and $(A + B)$ do not represent the same property of the solvents, though there is some collinearity between $(A + B)$ and π^* for the 17 solvents (r^2 = 0.8050).

Mechanism.—Compounds (1)—(3) exist in two tautomeric forms.[1,2] A mechanism can be written assuming the 'inactive' form to be the reactive species (Scheme 1). The reaction

$$\text{RHP(O)OH} \xrightleftharpoons{K_t} \text{RP(OH)}_2 \qquad (1)$$

$$\text{RHP(O)OH} + \text{Oxidant} \xrightleftharpoons{K_a} \text{Complex} \qquad (16)$$

$$\text{Complex} \xrightarrow{k_{2a}} \text{Products} \qquad (17)$$

Scheme 1.

sequence leads to the rate equation (18) where $[\text{RHP(O)OH}]_0$

$$\frac{-d[\text{Oxidant}]}{dt} = \frac{k_{2a}K_a[\text{Oxidant}][\text{RHP(O)OH}]_0}{1 + K_t + K_a[\text{RHP(O)OH}]_0} \quad (18)$$

represents the initial concentration of the phosphorus oxyacid. Since $1 \gg K_t$, equation (18) is reduced to (19), which is identical to the rate law (5).

$$\frac{-d[\text{Oxidant}]}{dt} = \frac{k_{2a}K_a[\text{Oxidant}][\text{RHP(O)OH}]_0}{1 + K_a[\text{RHP(O)OH}]_0} \quad (19)$$

Scheme 2 represents an alternative mechanism involving the 'active' tautomer. The corresponding rate law is given by equation (22). In view of the relation $1 \gg K_t$, equation (22) is reduced to (23).

$$\text{RHP(O)OH} \overset{K_t}{\rightleftharpoons} \text{RP(OH)}_2 \quad (1)$$

$$\text{Oxidant} + \text{RP(OH)}_2 \overset{K_b}{\rightleftharpoons} \text{Complex} \quad (20)$$

$$\text{Complex} \xrightarrow{k_{2b}} \text{Products} \quad (21)$$

Scheme 2.

$$\frac{-d[\text{Oxidant}]}{dt} = \frac{k_{2b}K_tK_b[\text{RHP(O)OH}]_0}{1 + K_t + K_tK_b[\text{RHP(O)OH}]_0} \quad (22)$$

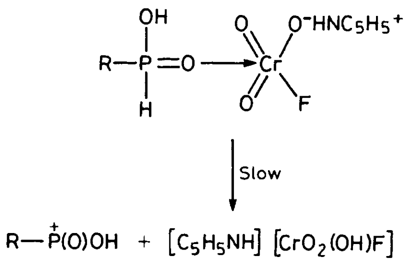
$$\frac{-d[\text{Oxidant}]}{dt} = \frac{k_{2b}K_tK_b[\text{RHP(O)OH}]_0}{1 + K_tK_b[\text{RHP(O)OH}]_0} \quad (23)$$

Therefore in the plots of $1/k_{obs.}$ *versus* 1/[substrate], the slope and intercept are equivalent to the values given in equation (24).

$$\text{Slope} = (k_{2b}K_tK_b)^{-1}, \text{ intercept} = 1/k_{2b}, \quad \text{intercept/slope} = K_tK_b \quad (24)$$

It is thus seen that $k_2 = k_{2a} = k_{2b}$, which means that the rate constant for the disproportion of the complex is not affected by the reactive form of the phosphorus oxyacid. However, $K = K_tk_b$, so that $K_b = 10^{-12}K$ or K_b for compound (**1**) at 298 K should have a value of *ca.* 4×10^{12} dm^3 mol^{-1}. Generally Cr^{VI} does not give rise to extensive and highly stable series of complexes.[17] Further, the values of the formation constant for the chromic acid–phenylphosphinic acid complex are 11 ± 2 and 19 ± 4 dm^3 mol^{-1} (refs. 4 and 18). Similarly, the formation constant of a complex[19] between triethylamine and a chromium(VI) diperoxide derivative is 0.0014 dm^3 mol^{-1}. Thus the very high value of the formation constant of the present oxidant–phosphorus oxyacid complex is improbable, and it is highly unlikely that the 'active' form is involved in the oxidation process.

The presence of a substantial primary kinetic isotope effect in the oxidation of compounds (**1**) and (**3**) confirms the rupture of the P–H bond in the rate-determining step. A one-electron oxidation, giving rise to free radicals, is not likely, in view of the failure to induce polymerization of acrylonitrile. The analysis of the solvent effect indicated the importance of the cation-solvating power of the solvent. Therefore, it is proposed that the rate-determining disproportionation of the complex involves transfer of a hydride ion from the substrate to the oxidant [equation (25)]. The phosphenium cation may react with traces of water present in the solvent.



$$R-\overset{+}{P}(O)OH + [C_5H_5NH][CrO_2(OH)F] \quad (25)$$

$$R-\overset{+}{P}(O)OH + H_2O \xrightarrow{\text{Fast}} R-P(O)(OH)_2 + H^+ \quad (26)$$

It has been shown that both $[C_5H_5NH][CrO_3F]$[10] and $[C_5H_5NH][CrO_3Cl]$[20] act as two-electron oxidants and are reduced to a chromium(IV) species by determining the oxidation state of chromium by magnetic susceptibility, e.s.r., and i.r. studies.

In the chromic acid oxidation of phosphinic acid, Sen Gupta and Chakaldar[4] postulated the participation of the 'active' tautomer. However, no evidence has been presented and the authors did not take into consideration the small value of K_t. However, recently Sharma and Mehrota[18] reported that in chromic acid oxidation it is not possible to pinpoint the reactive form of compound (**2**). Formation of a phosphenium ion in the rate-determining step has been postulated by earlier workers.[4,18]

The faster rate of oxidation of phenylphosphinic acid can be attributed to the stabilization of the phosphenium ion by the phenyl group through conjugation.

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