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Kinetics of oxidation of phosphinic, phenylphosphinic and phosphorous acids by ethyl N-chlorocarbamate

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The oxidation of phosphinic, phenylphosphinic and phosphorous acids by ethyl N-chlorocarbamate (ECC) in perchloric acid solution, results in the formation of corresponding phosphorous acids containing phosphorus in the higher oxidation state. The reaction is first order each in [ECC], and the oxyacid. Hydrogen ion dependence has the form: $k_{obs} = a + b[H^+]$. Oxidation of deuteriated phosphinic and phosphorous acids show the presence of a substantial primary kinetic isotope effect. The reaction does not induce polymerization of acrylonitrile. Added ethyl carbamate, one of the products of the oxidation reaction, has no effect on the reaction rate. Both ECC and $ECCH^+$ have been postulated as the reactive oxidizing species. It has been shown that the inactive tautomer of the phosphorus oxyacids, RHP(O)OH, participates in the oxidation process. A rate-determining step involving transfer of a hydride ion from the P−H bond to the oxidant has been proposed.

Oxidation of oxyacids of phosphorus (I) and (III) by various transition metal ions has been reported[1-10]. However, oxidation of phosphorus acids by halogens and their compounds has not attracted attention, except for the oxidation by iodine[11] and that by sodium N-haloarylsulphonamides[12]. We have been interested in the study of kinetics and mechanism of oxidation by N-chlorocarbamates[13] and the title investigation forms a part of our programme.

Materials and Methods

Doubly distilled, conductivity water, was used for the preparation of solutions. The oxyacids of phosphorus of commercial (Fluka) grade were used as such. The stock solutions of phosphinic acid (**1**) and phenylphosphinic acid (**2**) in water were standardized by cerimetry[14] and that of phosphorous acid (**3**) was standardized by alkalimetry. Ethyl N-chlorocarbamate (ECC) was prepared by the reported method[15] and its stock solution in water was standardized iodometrically. Perchloric acid (E. Merck, GR) was used as a source of hydrogen ions.

Deuteriation of acids **1** *and* **3**

The P−H bonds in **1** and **3** were deuteriated by repeatedly dissolving the acids in deuterium oxide (BARC, 99.4% purity), and evaporating the excess of deuterium oxide and water *in vacuo*[16]. The isotopic purity of the deuteriated **1** and **3**, as ascertained by their NMR spectra, were 91 ± 5 and 93 ± 4% respectively.

Stoichiometry

Oxidation of acids **1-3** by ECC leads to the formation of corresponding oxyacids containing phosphorus in a higher oxidation state. Reaction mixtures were prepared containing a known excess of **1** or **3**, ECC and perchloric acid. On the completion of the reaction, amount of phosphorous acid formed in the oxidation of **1** and the residual reductant in the oxidation of **3** were determined as follows[17].

The reaction mixture was partially neutralized to bring [perchloric acid] < 0.1 mol dm^{-3}. A known excess of iodine was added to it, and the *p*H adjusted to 7.3 (phosphate buffer). After 1 hr, the solution was acidified with acetic acid (6 mol dm^{-3}) and excess of iodine immediately titrated against a standardized thiosulphate solution to a starch end point.

To determine the stoichiometry of the oxidation of **2**, a known excess of ECC was treated with **2** and the residual ECC was determined iodometrically after the completion of the reaction.

Kinetic measurements

The reactions were carried out under pseudo-first order conditions, [oxyacid] ≫ [ECC] and were followed by determining unreacted [ECC] at different time intervals, iodometrically. The pseudo-first order rate constants, k_{obs}, were evaluated from the linear plots of log[ECC] against time. The reactions were followed upto almost 80% of completion. Duplicate kinetic runs indicated that the rate constants were reproducible to within ± 4%. Preliminary experiments showed that the reactions are not sensitive to changes in ionic strength (0.1-2.5 mol dm^{-3}), hence no attempt was made to keep the ionic strength constant.

Results

The results of stoichiometric runs showed that the overall reaction may be represented by Eq. (1)

$$RPO_2H_2 + EtOOCNHCl + H_2O \rightarrow RPO_3H_2 + EtCOONH_2 + HCl \quad \ldots (1)$$

(R = H, Ph or OH)

The reaction is first order in [ECC] and k_{obs} is independent of initial [ECC]. The reaction is first order in [reductant] also (Table 1).

The rate increases with increase in $[H^+]$ but not linearly. The $[H^+]$ dependence has the following form:

$$k_{obs} = a + b[H^+] \quad \ldots (2)$$

This indicated that the oxidation follows two reaction pathways—one acid-independent and another acid-dependent. The hydrogen ion dependence was studied at different temperatures (Table 2) and the values of a and b were evaluated. The specific rate constants of the acid-independent and acid-dependent reactions, k_3 and k_4, were obtained from the relations: $k_3 = a/[\text{oxyacid}]$ and $k_4 = b/[\text{oxyacid}]$.

The rate of oxidation is not affected by the addition of ethyl carbamate (EC), one of the products of the reaction.

The oxidation reaction, under nitrogen atmosphere, failed to induce polymerization of acrylonitrile. In control experiments, without the substrate, no reaction between ECC and acrylonitrile was observed.

The oxidation of deuteriated **1** and **3** indicated the presence of substantial primary kinetic isotope effect ($k_H/k_D = 4.83$ and 5.02 respectively). The rates of the deuteriated **1** and **3** were corrected for the presence of protio compounds.

The rate of oxidation was determined in solutions containing different proportions of acetic acid and water. The rate increased with increase in the amount of acetic acid in solution. For example, under the conditions [**1**] = 0.20 mol dm^{-3}, [**2**] = 0.50 mol dm^{-3}, [**3**] = 0.30 mol dm^{-3}, [ECC] = 0.005 mol dm^{-3}, $[H^+]$ = 0.5 mol dm^{-3} and temp. = 308 K, 10^5 k_{obs} increased from 33.1 to 350 s^{-1} for **1**, 39.0 to 340 s^{-1} for **2** and 6.60 to 58.7 s^{-1} for **3** when [AcOH] was increased from 0 to 60% (v/v).

The rates were determined at different temperatures and the activation parameters were evaluated (Table 3).

Table 1—Rate constants of oxidation of oxyacids of phosphorous acid by ECC at 308 K

[Oxyacid] (mol dm^{-3})	10^3 [ECC] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	10^5 k_{obs} (s^{-1})		
			1	**2**	**3**
0.10	5.0	0.5	16.5	76.8	2.17
0.14	5.0	0.5	22.8	104	2.85
0.20	5.0	0.5	33.1	153	4.35
0.24	5.0	0.5	42.3	184	5.17
0.30	5.0	0.5	50.2	235	6.60
0.40	5.0	0.5	65.2	300	8.58
0.50	5.0	0.5	82.5	387	11.0
0.70	5.0	0.5	117	—	15.0
1.00	5.0	0.5	162	—	22.2
0.40	2.5	0.5	66.0	300	8.42
0.40	10.0	0.5	63.5	292	8.75
0.40	15.0	0.5	65.7	311	8.62
0.40	20.0	0.5	64.8	304	8.51
0.40	5.0	0.5	65.6*	303*	8.62*

*contained 0.02 mol dm^{-3} acrylonitrile

Table 2—Dependence of reaction rate on hydrogen ion concentration

[oxyacid] = 0.1 mol dm^{-3}, [ECC] = 0.005 mol dm^{-3}, temp. = 308 K

$[H^+]$ (mol dm^{-3})	10^5 k_{obs} (s^{-1})		
	Phosphinic	Phenylphosphinic	Phosphorus
0.1	9.50	62.7	0.90
0.2	11.6	66.4	1.35
0.3	13.2	70.4	1.54
0.4	14.5	72.5	1.73
0.5	16.5	76.8	2.17
0.7	20.0	83.0	2.72
1.0	24.2	95.2	3.55
1.3	29.8	101	4.45
1.7	36.0	121	5.60
2.0	42.1	130	6.49
10^6 a*	80 ± 2	590 ± 10	6.66 ± 0.30
10^5 b*	16.8 ± 0.2	35.3 ± 0.8	2.91 ± 0.03
r*	0.9995	0.9978	0.9996

*a, b and r represent the intercept, slope and coefficient of correlation of the plots of k_{obs} versus $[H^+]$ respectively.

Discussion

In an acidified solution of ECC, the possible oxidizing species are HOCl, $Cl_2NCOOEt$, $EtCOONCl^-$, and ECC itself. Since added EC has no effect on the reaction rate, an equilibrium in which EC is one of the products is ruled out. This in effect rules out Cl_2COOEt and HOCl as the oxidizing species. ECC is a weak acid[13] ($pK = 8.5 \pm 0.1$)

Table 3—Rate constants and activation parameters of oxidation of oxyacids of phosphorus by ECC

Substrate	Rate constants at 298	303	308	313	318K	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})
	$10^5 k_4$ (dm^6 mol^{-2} s^{-1}): acid-dependent path							
Phosphorous acid (**3**)	12.3	19.8	29.1	46.0	71.5	66.2	−98	95.3
Phenylphosphinic acid (**2**)	176	273	353	515	747	53.0	−120	88.7
Phosphinic acid (**1**)	58.0	100	168	232	354	67.8	−80	91.4
Error: $\Delta H^\ddagger$, ±1.0 kJ mol^{-1}; $\Delta S^\ddagger$, ±3.3 J mol^{-1} K^{-1}; $\Delta G^\ddagger$, ±0.9 kJ mol^{-1}								
	$10^5 k_3$ (dm^3 mol^{-1} s^{-1}): acid-independent							
Phosphorous acid (**3**)	2.81	4.43	6.66	10.5	16.3	66.5	−110	99.0
Phenylphosphinic acid (**2**)	294	455	590	861	1250	53.0	−116	87.4
Phosphinic acid (**1**)	375	644	800	1500	2280	67.6	−65	86.9
Error: $\Delta H^\ddagger$, ±1.3 kJ mol^{-1}; $\Delta S^\ddagger$, ±4.6 J mol^{-1} K^{-1}; $\Delta G^\ddagger$, ±1.5 kJ mol^{-1}								

and even at the lowest [perchloric acid] used, almost whole of ECC exists in the undissociated form, ClNHCOOEt. Therefore, ECC is postulated as the reactive oxidizing species in the present reaction.

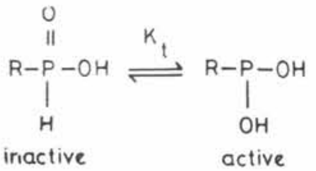
The observed [H$^+$] dependence points to protonation of ClNHCOOEt in a pre-equilibrium (Eq. 3) to give a stronger oxidant and electrophile, with both ECC and ECCH$^+$ being the reactive species.

$$\mathrm{ClNHCOOEt} + \mathrm{H_3O^+} \overset{K_p}{\rightleftharpoons} (\mathrm{ClNH_2COOEt})^+ + \mathrm{H_2O} \quad \ldots (3)$$

The value of K_p has earlier been determined to be 0.034 (ref. 13). Formation of similar protonated species has been established in structurally related chloramine-T[19].

The increase in reaction rate with a decrease in the polarity of the solvent indicates that the transition state is less polar than the reactant. This supports the postulation that in the acid-dependent reaction, ECCH$^+$ reacts with a neutral phosphorus oxyacid molecule. In the transition state, the charge is distributed over a larger area and this reduced charge density is facilitated by the reduced polarity of the solvent.

The oxyacids of phosphorus are weak acids[20], and in the presence of a strong acid like perchloric acid, they would exist almost wholly in the undissociated form. Oxyacids of phosphorus are believed to exist in two tautomeric forms[21,22] (Eq. 4).



$$\mathrm{RHP(O)OH} \overset{K_t}{\rightleftharpoons} \mathrm{RP(OH)_2} \quad \ldots (4)$$

The active form is thought to be produced as an intermediate in the exchange of phosphorus bonded hydrogen with tritium and deutarium[21,22]. The value of the equilibrium constant, K_t, is of the order of 10^{-12} (ref. 20). Two alternative broad mechanisms can be written: (i) Assuming the inactive form as the reactive species the mechanism follows the pathway shown in Scheme 1.

$$\mathrm{ECC} + \mathrm{H^+} \overset{K_p}{\rightleftharpoons} \mathrm{ECCH^+}$$

$$\mathrm{RHP(O)OH} \overset{K_t}{\rightleftharpoons} \mathrm{RP(OH)_2}$$

$$\mathrm{RHP(O)OH} + \mathrm{ECC} \xrightarrow{k_{1a}} \text{Products}$$

$$\mathrm{RHP(O)OH} + \mathrm{ECCH^+} \xrightarrow{k_{2a}} \text{Products}$$

Scheme 1

Scheme 1 leads to rate law (5)

$$\frac{-d[\mathrm{ECC}]}{dt} = \frac{[\mathrm{ECC}][\mathrm{RHP(O)OH}]_0\{k_{1a} + k_{2a}K_p[\mathrm{H^+}]\}}{1 + K_t} \quad \ldots (5)$$

where $[\mathrm{RHP(O)OH}]_0$ represents the initial [reductant]. Since $1 \gg K_t$, Eq. (5) can be written as Eq. (6),

$$-d[\mathrm{ECC}]/dt = [\mathrm{ECC}][\mathrm{RHP(O)OH}]_0\{k_{1a} + k_{2a}[\mathrm{H^+}]\} \quad \ldots (6)$$

(ii) The second mechanism involving the active form of the substrate follows the reaction pathway shown in Scheme 2. This leads to rate law (7).

$$\mathrm{ECC + H^+ \overset{K_p}{\rightleftharpoons} ECCH^+}$$

$$\mathrm{RHP(O)OH \overset{K_t}{\rightleftharpoons} RP(OH)_2}$$

$$\mathrm{RP(OH)_2 + ECC \overset{k_{1b}}{\rightarrow} Products}$$

$$\mathrm{RP(OH)_2 + ECCH^+ \overset{k_{2b}}{\rightarrow} Products}$$

Scheme 2

$$\frac{-d[\mathrm{ECC}]}{dt} = \frac{[\mathrm{ECC}][\mathrm{RHP(O)OH}]_0 K_t\{k_{1b} + k_{2b}K_p[\mathrm{H^+}]\}}{1+K_t} \quad \ldots (7)$$

which can be reduced to Eq. (8), acknowledging that $1 \gg K_t$

$$-d[\mathrm{ECC}]/dt = [\mathrm{RHP(O)OH}]_0[\mathrm{ECC}] \times K_t\{k_{1b} + k_{2b}K_p[\mathrm{H^+}]\} \quad \ldots (8)$$

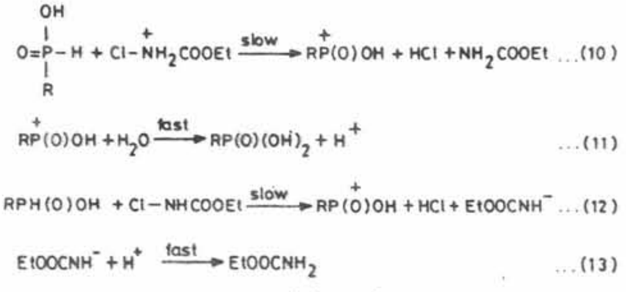
Thus the two rate equations (6) and (8) are indistinguishable and conform to the experimental rate law.

If Scheme 2 represents the mechanism of the reaction, then the experimental specific rate constants, k_3 and k_4; are given by Eq. (9).

$$k_3 = k_{1b}K_t;\ k_4 = k_{2b}K_pK_t \quad \ldots (9)$$

The value of K_t is of the order of 10^{-12}. The value of K_p is 0.034. Therefore, the value of the rate-limiting constants, k_{1b} and k_{2b}, come between 10^{11} and 10^{14} dm^3 mol^{-1} s^{-1}. These rate constants, thus, exceed/equal the rate constants of diffusion-controlled processes[23]. Therefore, one can rule out the participation of the active tautomer of the phosphorus oxyacids in the oxidation process.

The presence of a substantial kinetic isotope effect confirms the rupture of P–H bond in the rate-determining step. A one-electron oxidation, giving rise to free radicals, is ruled out in view of the failure to induce polymerization of acrylonitrile. There is no kinetic evidence for the formation of an intermediate complex. Formation of a hypochlorite ester and its subsequent decomposition can also be ruled out, in view of the nil effect of added EC on the reaction rate. The large magnitude of the observed kinetic isotope effect also militates against a non-linear transition state implied in an ester mechanism. Hence it is proposed that the rate-determining step involves a hydride ion transfer to the oxidant (Scheme 3).



$$\mathrm{O{=}\overset{\overset{OH}{|}}{\underset{\underset{R}{|}}{P}}{-}H + Cl{-}\overset{+}{N}H_2COOEt \xrightarrow{slow} R\overset{+}{P}(O)OH + HCl + NH_2COOEt} \quad \ldots (10)$$

$$\mathrm{R\overset{+}{P}(O)OH + H_2O \xrightarrow{fast} RP(O)(OH)_2 + H^+} \quad \ldots (11)$$

$$\mathrm{RPH(O)OH + Cl{-}NHCOOEt \xrightarrow{slow} RP(\overset{+}{O})OH + HCl + EtOOCNH^-} \quad \ldots (12)$$

$$\mathrm{EtOOCNH^- + H^+ \xrightarrow{fast} EtOOCNH_2} \quad \ldots (13)$$

Scheme 3

The rate of oxidation has the following order: **2** > **1** > **3**. Phenyl group is capable of stabilizing the cationic species formed in reactions (10) and (12) by resonance. This may account for the faster oxidation of **2**.

It is of interest here to compare the mode of oxidation of phosphorus oxyacids by ECC and other oxidants. The oxidations by Hg(II)[24], Ag(II)[5] and iodine[11] show a zero order dependence on the oxidant and the rate-determining step is proposed to be the conversion of inactive tautomer to the active one. The oxidation of phosphinic acid (**1**) by permaganate[7] and vanadium(V)[4] involves the inactive form. Cerium(IV) in nitric acid[3] is reported to oxidize the active form of **1**. Acid dependence of rate in the oxidation[25] of **2** by vanadium(V) has been explained on the basis of simultaneous oxidation of active form (acid-independent path) and the inactive form (acid-dependent path). Sen Gupta *et al.*[28], however, proposed that **3** is oxidized by vanadium(V) via its active form, but no evidence has been given for the same. Similarly in chromic acid oxidation also[2a], involvement of the active form has been assumed without any kinetic evidence. Recently, however, Sharma and Mehrotra[2b] reported that it was not possible, in the oxidation of **2** by chromic acid, to pinpoint the reactive form of the phosphorus compound. In view of the extremely small equilibrium constant, the concentration of the active tautomer in solution would be very small. Any reaction involving the active form only is, therefore, likely to be very slow. In most other reports, including that of oxidation by chloramine-T[12], there is no mention of the tautomerism and the predominant tautomer has been assumed as the reactive species.

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