Kinetics and mechanism of oxidation of lower oxyacids of phosphorus by tetrabutylammonium tribromide

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Oxidation of lower oxyacids of phosphorus by tetrabutylammonium tribromide (TBATB) in aqueous acetic acid leads to the formation of corresponding oxyacids with phosphorus in a higher oxidation state. The reaction exhibits 1:1 stoichiometry. The reaction is first order each in [TBATB] and [oxyacids]. The reaction does not induce polymerization of acrylonitrile. There is no effect of tetrabutylammonium chloride on the reaction rate. The proposed oxidative species is tribromide ion. It has been shown that the pentacoordinated tautomer of the phosphorus oxyacid is the reactive oxidant. The oxidation of deuteriated oxyacids exhibits a substantial primary kinetic isotope effect. The effect of solvent composition indicates that the rate increases with an increase in the polarity of the solvent. A mechanism involving transfer of a hydride ion in the rate-determining step has been proposed.

Tetralkylammonium polyhalides are widely used as halogenating reagents in synthetic organic chemistry\(^1\). These compounds are more suitable than molecular halogens because of their solid nature, ease of handling, stability, selectivity and excellent product yields. Recently, tetrabutylammonium tribromide (TBATB) has been used for the bromination of some selected organic substrates\(^2\). We have been interested in the kinetic and mechanistic studies of the reactions of polyhalides and a few reports including that of TBATB, have already been emanated from our laboratory\(^3\). There seems to be no report on the oxidation of oxyacids of phosphorus by TBATB. We report here the kinetics of oxidation of three oxyacids of phosphorus namely, phosphinic acid (PA), phenylphosphinic acid (PPA) and phosphorus acid (POA) by TBATB in aqueous acetic acid solution. A suitable mechanism has also been proposed.

Experimental

The phosphorus oxyacids were commercial products (Fluka) and were used as supplied. TBATB was prepared by the reported method\(^1\) and its purity was checked by an iodometric method and melting point determination. Deuteriated phosphinic (DPA) and phosphorus acids (DPOA) were prepared by repeatedly dissolving the acid in deuterium oxide (BARC, 99.4%) and evaporating water and the excess of deuterium oxide in vacuo\(^9\). The isotopic purity of the deuterated PA and POA, as determined from their NMR spectra, was 93±5% and 92±5% respectively. Acetic acid was refluxed with chromium trioxide and acetic anhydride for 6 h and then distilled\(^10\).

Stoichiometry

The oxidation of lower oxyacids of phosphorus leads to the formation of corresponding oxyacids containing phosphorus in a higher oxidation state. Reaction mixtures were prepared containing a known excess of phosphinic or phosphorous acids. On completion of the reaction, the amount of phosphorous formed in the oxidation of phosphinic acid and the residual reductant in the oxidation of phosphorus acids were determined by reported method\(^11\). To determine the stoichiometry of the oxidation of PPA, a known excess of TBATB was treated with PPA and the residual TBATB was determined spectrophotometrically at 394 nm after the completion of the reaction.

Kinetic measurements

The reactions were studied under pseudo-first order conditions by keeping an excess (× 15 or greater) of the [oxyacid] over [TBATB]. The solvent was 1:1 (v/v) acetic acid-water, unless specified otherwise. Tribromide ion is known to dissociate to a large extent to bromine and bromide ion. The value\(^12\) of the dissociation constant in 1:1 (v/v) acetic acid-water is ca. 0.02 mol dm\(^{-3}\). To suppress the dissociation, all kinetic runs were carried out in the presence of an excess (0.2 mol dm\(^{-3}\)) of potassium bromide. The reactions were studied at constant temperature (±0.1 K) and were followed by monitoring the decrease in the [TBATB] spectrophotometrically at 394 nm for up to 80% reaction. Pseudo-first-order rate constants, \(k_{obs}\), were evaluated from linear plots (r>0.9990) of log[TBATB] against time. Duplicate kinetic runs
showed that the rates were reproducible to within ±3%. The second order rate constants, $k_2$ were determined from the relation: $k_2 = k_{obs}/[\text{oxyacid}]$.

**Results and discussion**

The oxidation exhibited a 1:1 stoichiometry and the overall reaction may therefore, be represented as Eq. (1).

$$\text{RPH (O) OH} + (C_4H_9)_{4}N^+Br^- + H_2O \rightarrow \text{RP (O) (OH)} + (C_4H_9)_{4}N^+ + 3 Br^- + 2H^+$$  \hspace{1cm} (1)

(R=H, Ph or OH)

The reactions are of first order with respect to TBATB. Further, the pseudo-first order rate constant, $k_{obs}$ are independent of the initial [TBATB]. The reaction rate increases linearly with an increase in [oxyacids] (Table 1). The oxidation of oxyacids, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on rate of oxidation (Table 1).

To ascertain importance of the cleavage of the P-H bond in the rate-determining step, oxidation of deuteriated PA and POA was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table 2). Addition of tetrabutylammonium chloride (TBACI) had no effect on the rates of oxidation.

The rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It was observed that the rate increased with an increase in the amount of water in the solvent mixture. For example, under the conditions [TBATB]=0.001 mol dm$^{-3}$, [PA]=1.011 mol dm$^{-3}$ and at temp. 303 K, $10^3 k_2$ values decrease from 42.2 to 2.81 s$^{-1}$ when the % of acetic acid was increased from 25 to 72.

The rates of oxidation of oxyacids were determined at different temperatures and the activation parameters were calculated at 298 K (Table 2).

As reported earlier, TBATB can be considered as an ionic compound, which exists, in aqueous acetic acid solutions, as tetrabutylammonium and tribromide ions as shown in Eq. (2). Absence effect of added tetrabutylammonium ion also indicates that the equilibrium (2) lies far towards the right.

$$(C_4H_9)_4NBr^- \leftrightarrow (C_4H_9)_4N^+ + Br^-$$  \hspace{1cm} (2)

The oxidation of alcohols by bromine is reported to be much faster as compared to this reaction. This also supports the view that bromine is not the reactive species in this oxidation. Thus in the present reaction the reactive oxidizing species is the tribromide ion.

The increase in the rate constant with an increase in the polarity of the medium suggests that the transition state is more polar than the reactants. The solvent effect was analysed using Grunwald- Winstein equation$^{14}$.

Log $k_2$=log $k_0$ + My 

The plot of log $k_2$ versus Y is linear ($r^2=0.9935$) with $m=0.65\pm0.03$. The value of $m$ suggests a transition state, which is more polar than the reactants. Thus considerable charge separation takes place in the transition state of the reaction.

Lower oxyacids of phosphorus are reported to exist in two tautomeric forms$^{15,16}$. The predominant species is the pentacoordinated form (A). The value$^{17}$ of the equilibrium constant, $K_1$ in aqueous solutions, is of the order of $10^{12}$. Though in acetic acid solution, the value of $K_1$ might be different, the order is likely to be the same.

$$\text{RPH(OH)} \rightleftharpoons \text{R-P}-(\text{OH})_2$$  \hspace{1cm} (4)

Hence two alternative broad mechanisms can be formulated. Assuming in the first instance pentacoordinated tautomer (A) as the reactive reducing species, the following mechanism may be proposed which leads to the rate law (7).

| Table 1—Rate constants for the oxidation of oxyacids of phosphorus by TBATB at 303 K |
|-------------------|-----------------|------------------|
| $10^3[\text{TBATB}]$ | [oxyacid] | $10^4 k_{ob}/(\text{s} \cdot \text{dm}^{-3})$ |
| (mol dm$^{-3}$) | (mol dm$^{-3}$) | (mol dm$^{-3}$) |
| 1.00 | 0.10 | 9.95 |
| 1.00 | 0.20 | 20.1 |
| 1.00 | 0.40 | 39.6 |
| 1.00 | 0.60 | 59.2 |
| 1.00 | 0.80 | 79.5 |
| 1.00 | 1.00 | 102 |
| 2.00 | 0.40 | 40.8 |
| 4.00 | 0.40 | 39.2 |
| 6.00 | 0.40 | 40.4 |
| 8.00 | 0.40 | 39.5 |
| 1.00 | 0.20 | 20.3 |

* contained 0.005 mol dm$^{-3}$ acrylonitrile.
Table 2—Rate constants and activation parameters of the oxidation of phosphorus oxyacids by TBATB

<table>
<thead>
<tr>
<th>Acid</th>
<th>$10^3 k_2$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^*$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G^*$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293 K</td>
<td>303 K</td>
<td>313 K</td>
<td></td>
</tr>
<tr>
<td>PA</td>
<td>5.16</td>
<td>9.95</td>
<td>19.5</td>
<td>37.1</td>
</tr>
<tr>
<td>PPA</td>
<td>17.7</td>
<td>30.4</td>
<td>51.0</td>
<td>88.6</td>
</tr>
<tr>
<td>POA</td>
<td>1.12</td>
<td>2.55</td>
<td>5.02</td>
<td>10.7</td>
</tr>
<tr>
<td>DPA</td>
<td>0.95</td>
<td>1.88</td>
<td>3.78</td>
<td>7.39</td>
</tr>
<tr>
<td>DPOA</td>
<td>0.21</td>
<td>0.50</td>
<td>1.02</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>$k_0/k_D$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.43</td>
<td>5.29</td>
<td>5.16</td>
<td>5.02 (PA)</td>
</tr>
<tr>
<td></td>
<td>5.33</td>
<td>5.10</td>
<td>4.92</td>
<td>4.82 (POA)</td>
</tr>
</tbody>
</table>

$TBATB + RPH(O)OH \rightarrow \text{Products}$ ... (5)

$\text{Rate}=k_4 [\text{Oxyacid}]_0 [\text{TBATB}] / (1 + K_t)$ ... (6)

Equation (6) can be reduced to (7) as $1 \gg K_t$.

$\text{Rate}=k_4 [\text{Oxyacid}]_0 [\text{TBATB}]$ ... (7)

Another mechanism can be formulated assuming the tricoordinated form (B) as the reactive reducing species.

$TBATB + RP(OH)_2 \rightarrow \text{Products}$ ... (8)

This mechanism leads to the rate law (9), which can be reduced to (10), again acknowledging $1 \gg K_t$.

$\text{Rate}=K_i k_b [\text{Oxyacid}]_0 [\text{TBATB}] / (1 + K_t)$ ... (9)

$\text{Rate}=K_i k_b [\text{Oxyacid}]_0 [\text{TBATB}]$ ... (10)

Thus the two rate equations confirm to the experimental rate law, and are kinetically indistinguishable. If equations (4) and (8) represent the mechanism of the oxidation of oxyacids of phosphorus then the experimental specific rate constant, $k_2=K_i k_b$. Since the value of $K_i$ is of the order of $10^{-12}$, therefore, the value of rate limiting constant $k_b$, ranges between $10^8$ and $10^9$. This value equals/exceeds the rate constants of diffusion-controlled rate processes$^{18}$. Therefore, the participation of tricoordinated form can be ruled out.

Mechanism

The absence of any effect of the radical scavenger on the reaction rate and the failure to induce polymerization of acrylonitrile point against a one-electron oxidation giving rise to free radicals. The presence of a substantial kinetic isotope effect confirms the cleavage of a P–H bond in the rate-determining step.

A preferential cleavage of a P–H bond, in the rate-determining step, is likely in view of the relatively high bond dissociation energy of the O–H bond. The mean value of the bond dissociation energy of an O–H bond$^{19}$ is 460 kJ mol$^{-1}$, while that for a P–H bond$^{20}$ is 321 kJ mol$^{-1}$. Therefore, the following mechanism may be proposed for the oxidation of these oxyacids.

$$R \text{P} (O) \text{OH} + \text{Br}_3^- \rightarrow R - P -(O) - \text{OH} + \text{HBr}$$

+ 2 Br$^-$

$$R - P -(O) - \text{OH} + \text{H}_2\text{O} \rightarrow \text{RP(O)(OH)}_2 + H^+$$

Scheme 1

The proposed mechanism is supported by the observed values of entropy of activation also. As the charge separation takes place, during the rate-determining step, the charged ends become highly solvated. This results in an immobilisation of a large number of solvent molecules, reflected in the loss of entropy$^{21}$.

The rate of oxidation follows the order PPA > PA > POA. The faster rate of PPA could be explained on the basis of stabilisation of a positively polarized phosphorus, in the transition state, by the phenyl group through resonance. The slower rate of POA may well be due to the electron-withdrawing nature of hydroxyl group causing an electron-deficiency at the phosphorus atom. This makes the departure of an anion more difficult. A perusal of the activation parameters in Table 2 revealed that the reaction rates are controlled mainly by the entropy of activation.
Acknowledgement

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References