

## Kinetics and mechanism of the oxidation of phosphinic, phenylphosphinic and phosphorous acids by benzyltrimethylammonium tribromide

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The oxidation of phosphorus-(I) and -(III) oxyacids by benzyltrimethyl ammonium tribromide (BTMAB), in 9:1 (v/v) acetonitrile-acetic acid, leads to the formation of corresponding phosphorus-(III) and -(V) oxyacids. The reaction is first order with respect to each of the BTMAB and oxyacid. There is no effect of benzyltrimethylammonium chloride or bromide ion on the reaction rate. The oxidation of deuteriated phosphinic and phosphorous acids exhibit the presence of a substantial kinetic isotope effect. The rate decreases with an increase in the proportion of acetic acid in the solvent. It has been shown that the reactive reducing species is the penta-coordinated form of the oxyacid. Tribromide ion has been postulated as the reactive oxidizing species. A mechanism involving a hydride-ion transfer in the rate-determining step has been proposed.

Benzyltrimethylammonium tribromide (BTMAB) has been used as an effective halogenating and oxidizing agent in synthetic organic chemistry<sup>1-3</sup>. We are interested in the kinetic and mechanistic studies of the newer oxidizing agents and have reported the kinetics of the oxidations of primary aliphatic alcohols<sup>4</sup>,  $\alpha$ -hydroxy acids<sup>5</sup> and organic sulfides<sup>6</sup> by BTMAB in aqueous acetic acid solution. We now report herein the kinetics and mechanism of the oxidation of three lower oxyacids of phosphorus namely, phosphinic acid (PA), phenylphosphinic acid (PPA) and phosphorous acid (POA), by BTMAB in 9 : 1 (v/v) acetonitrile-acetic acid solvent. Attempts have been made to determine the nature of the reactive oxidizing and reducing species.

### Materials and Methods

The phosphorus oxyacids were commercial products (Fluka) and were used as supplied. Their aqueous solutions were standardized by alkalimetry. BTMAB was prepared by the reported method<sup>1</sup> and its purity was checked by an iodometric method. The P-H bonds in PA and POA were deuteriated by repeatedly dissolving the acid in deuterium oxide (BARC, 99.4%) and evaporating water and the excess of deuterium oxide in vacuo<sup>7</sup>. The isotopic purity of the deuteriated PA and POA, as determined from their NMR spectra, was  $91\pm 4\%$  and  $93\pm 5\%$

respectively. Acetic acid was refluxed with  $\text{CrO}_3$  and acetic anhydride for 6 hr and then distilled. Acetonitrile was purified by the usual method<sup>8</sup>.

### Stoichiometry

The oxidation of phosphorus-(I) and -(III) oxyacids leads to the formation of corresponding phosphorus-(III) and -(V) oxyacids.

Reaction mixtures were prepared containing a known excess of phosphinic or phosphorous acid. On the completion of reaction, amount of phosphorous acid formed in the oxidation of phosphinic acid and the residual reductant in the oxidation of phosphorous acid were determined by the reported method<sup>9</sup>. To determine the stoichiometry of the oxidation of PPA, a known excess of BTMAB was treated with PPA and the residual BTMAB was determined spectrophotometrically at 354 nm after the completion of the reaction.

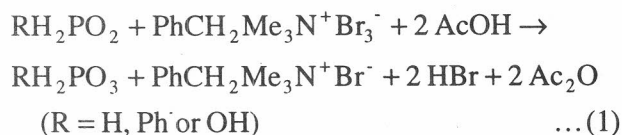
### Kinetic Measurements

The reactions were studied under pseudo-first-order conditions by keeping an excess ( $\times 15$  or greater) of the substrate over BTMAB. The solvent was 9:1 (v/v) acetonitrile-acetic acid, unless mentioned otherwise. The reactions were studied at constant temperature ( $\pm 0.1$  K) and were followed by monitoring the decrease in the concentration of BTMAB at 354 nm for up to 80% reaction.

Pseudo-first-order rate constants,  $k_{\text{obs}}$ , were evaluated from linear plots ( $r > 0.990$ ) of  $\log[\text{BTMAB}]$  against time. Duplicate kinetic runs showed that the rate constants are reproducible to within  $\pm 3\%$ . The second order rate constant,  $k_2$ , was determined from the relation  $k_2 = k_{\text{obs}}/[\text{oxyacid}]$ .

## Results

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



The reactions are of first order with respect to BTMAB. Further, the pseudo-first order rate constant,  $k_{\text{obs}}$ , does not depend on the initial concentration of BTMAB. The rate of reaction is linearly dependent on the concentration of oxyacids (Table I). Addition of benzyltrimethylammonium chloride (BTMACl) or bromide ions had no effect on the rate of oxidation (Table I). The oxidation of the oxyacids, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation (Table I).

Table I—Rate constants for the oxidation of oxyacids of phosphorus by BTMAB at 313 K

$10^3[\text{BTMAB}]$ (mol dm <sup>-3</sup> )	[oxyacid] (mol dm <sup>-3</sup> )	$10^3 k_{\text{obs}}/(\text{s}^{-1})$		
		PA	PPA	POA
1.0	0.03	15.5	38.2	0.12
1.0	0.09	47.0	114	0.37
1.0	0.15	78.3	195	0.68
1.0	0.24	122	308	0.94
1.0	0.30	148	378	1.09
1.0	0.50	230	640	2.01
2.0	0.03	15.3	37.7	0.13
4.0	0.03	15.1	38.5	0.15
6.0	0.03	16.0	38.9	0.12
8.0	0.03	15.7	38.0	0.13
1.0	0.03	15.9 <sup>a</sup>	37.9 <sup>a</sup>	0.16 <sup>a</sup>
1.0	0.03	15.0 <sup>b</sup>	38.7 <sup>b</sup>	0.11 <sup>b</sup>
1.0	0.03	15.4 <sup>c</sup>	38.4 <sup>c</sup>	0.14 <sup>c</sup>

<sup>a</sup> contained 0.005 mol dm<sup>-3</sup> acrylonitrile

<sup>b</sup> contained 0.005 mol dm<sup>-3</sup> benzyltrimethylammonium tribromide

<sup>c</sup> contained 0.005 mol dm<sup>-3</sup> bromide ion

## Effect of temperature

The rate constants for the oxidation of PA, PPA, POA, deuteriated phosphinic (DPA) and deuteriated phosphorous acids (DPOA) were determined at different temperatures and the activation parameters were calculated (Table II).

## Kinetic isotope effect

To ascertain the importance of the cleavage of the P-H bond in the rate-determining step, the oxidation of deuteriated PA and POA was studied. Results recorded in Table II showed the presence of a substantial primary kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 5.43$  for PA and = 5.18 for POA at 313 K)

## Solvent Effect

The oxidation of phosphinic acid was studied in solvents containing different proportions of acetic acid (10 - 80%) and acetonitrile. The rate of reaction decreases as the amount of acetic acid in the solvent mixture is increased.

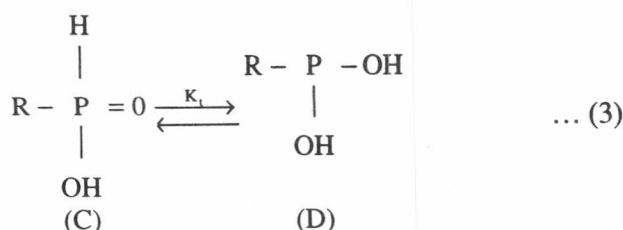
## Discussion

We have carried out some conductivity measurements to determine the nature of BTMAB in acetonitrile-acetic acid solution. It was observed that acetonitrile has very low conductivity. Addition of BTMAB increases the conductivity of acetonitrile sharply. We measured the conductivity of BTMAB in solvents containing different proportions of acetonitrile (100 - 20%) and acetic acid also. It was found that the conductivity decreases slowly as the acetic acid content is increased. Therefore, BTMAB can be considered as an ionic compound which exists under our reaction conditions as benzyltrimethylammonium and tribromide ions (Eq. 2). No effect of added benzyltrimethylammonium ion (Table I) also indicates that the equilibrium (2) lies far towards the right.



The absence of any effect of bromide ion on the reaction rate rules out any role of Br<sub>2</sub> and HOBr in the oxidation process. Therefore, the most likely reactive oxidizing species, in this reaction, is tribromide ion.

Lower oxyacids of phosphorus are reported to exist in two tautomeric forms<sup>10,11</sup>.



The predominant species is the pentacoordinated form (C). The value of the equilibrium constant<sup>12</sup>,  $K_t$ , is of the order of  $10^{-12}$ . Two alternative broad mechanisms can be formulated, one assuming the form (C) as the reactive reducing species and another assuming the form (D) as the reactive species. The rate laws for the two mechanisms will have the form (4) and (5) which are kinetically indistinguishable.

$$\text{Rate} = k_a [\text{BTMAB}] [\text{RHP(O)OH}]_0 \quad \dots (4)$$

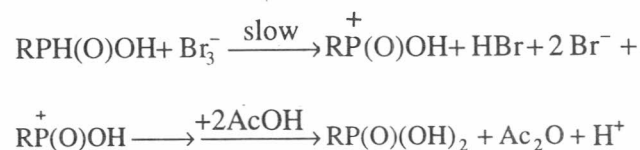
$$\text{Rate} = K_t k_b [\text{BTMAB}] [\text{RHP(O)OH}]_0 \quad \dots (5)$$

If the form (D) is the reactive reducing species then the experimental second order rate constant,  $k_2$ , is given by (6).  
 $k_2 = K_t k_b \quad \dots (6)$

Since the value of  $K_t$  is of the order of  $10^{-12}$ , the value of rate-limiting constant,  $k_b$ , ranges between  $10^8$  and  $10^{10}$ . This value equals/ exceeds the rate constants of diffusion-controlled rate processes<sup>13</sup>. Therefore, one can rule out the participation of the tautomer (D) in the oxidation process.

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 increase in the value of  $k_2$  with an increase in the polarity of the medium suggests

that, in the rate-determining step, the transition state is more polar than the reactant. 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 a O-H bond<sup>14</sup> is  $460 \text{ kJ mol}^{-1}$ , while that for a P-H bond<sup>15</sup> is  $321 \text{ kJ mol}^{-1}$ . Therefore, the following mechanism may be proposed for the oxidation (Scheme I). 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 immobilization of a large number of solvent molecules, reflected in the loss of entropy.



Scheme I

The rate of oxidation follows the order  $\text{PPA} > \text{PA} > \text{POA}$ . The faster rate of PPA could be explained on the basis of stabilization 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 II revealed that the reaction rates are controlled by both the enthalpy and entropy of activation.

Table II—Rate constants at different temperatures and activation parameters for the oxidation of oxyacids of phosphorus by BTMAB

Acid	$10^2 k_2 / (\text{mol}^{-1} \text{dm}^3 \text{s}^{-1})$		313 K	323 K	$\Delta H^*$ KJ mol <sup>-1</sup>	$\Delta S^*$ KJ mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G^*_{298 \text{ K}}$ KJ mol <sup>-1</sup>
	293K	303 K					
PA	13.6	29.2	51.7	101	49.3±1.1	-94±4	77.0±0.8
DPA	2.21	5.02	9.52	19.8	54.3±1.0	-92±3	81.5±0.8
PPA	29.2	64.1	127	231	51.7±0.8	-79±3	75.1±0.7
POA	0.70	1.72	4.05	9.43	65.6±0.5	-63±2	84.2±0.4
DPOA	0.11	0.30	0.78	2.07	74.2±0.9	-49±3	88.6±0.7

$k_H/k_D$  6.15 5.81 5.43 5.10 (PA)  
 $k_H/k_D$  6.35 5.80 5.18 4.56 (POA)

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