

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

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Abstract. Oxidation of lower phosphorus oxyacids by benzyltrimethylammonium dichloroiodate (BTACI), in the presence of zinc chloride, resulted in the formation of the corresponding oxyacids with phosphorus in a higher oxidation state. The reaction is first order with respect to the concentration of BTACI, oxyacid and zinc chloride. The reaction exhibited the presence of a substantial kinetic isotope effect. Addition of benzyltrimethylammonium chloride enhances the reaction rate. It is proposed that the reactive oxidizing species is $[\text{PhCH}_2\text{Me}_3\text{N}]^+ [\text{Zn}_2\text{Cl}_6]^{-2} \text{I}^+$. It has been shown that the pentacoordinated tautomer of the phosphorus oxyacid is the reactive reductant. A mechanism involving a hydride-ion transfer from the P–H bond to the oxidant in the rate-determining step has been postulated.

Keywords. Phosphorus oxyacids; kinetic isotope effect; benzyltrimethylammonium dichloroiodate.

1. Introduction

Benzyltrimethylammonium polyhalides are widely used halogenating reagents (Fujisaki *et al* 1988; Kajigaeshi *et al* 1989b). These compounds are more suitable than molecular halogens because they are solids, and of their ease of handling, stability, selectivity and excellent product yields. However, their utility as non-halogenating oxidizing agents has not been investigated much (Kajigaeshi *et al* 1989a, 1991; Kakinami *et al* 1991). We are interested in the kinetics and mechanism of action of the newer oxidizing agents and here report studies on three lower oxyacids of phosphorus, viz. phosphinic (PA), phenylphosphinic (PPA) and phosphorous (POA) acids by benzyltrimethylammonium dichloroiodate (BTACI) in acetic acid, in the presence of zinc chloride. Since the lower oxyacids of phosphorus are reported to exist in two tautomeric forms (Jenkins and Yost 1959; Fratiello and Anderson 1963), the nature of the reactive reducing species has been discussed.

2. Experimental

2.1 Materials

BTACI was prepared by the reported method (Fujisaki *et al* 1988) and its purity was checked iodometrically. The phosphorus oxyacids were commercial products

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(Fluka) and were used as supplied. Acetic acid was refluxed for 6 h with CrO_3 and acetic anhydride and then fractionated. The P–H bonds in PA and POA were deuterated by repeatedly dissolving the acid in deuterium oxide (BARC, 99.4% purity) and evaporating the excess of deuterium oxide and water *in vacuo* (Haight *et al* 1968). The isotopic purity of deuterated PA (DPA) and POA (DPOA), as determined by their NMR spectra, were $92 \pm 5\%$ and $91 \pm 4\%$ respectively.

BTACI is only slightly soluble in acetic acid at room temperature. However, addition of zinc chloride makes this reagent soluble in acetic acid. We found that in the absence of ZnCl_2 , the strength of a saturated solution of BTACI in acetic acid is $0.0005 \text{ mol dm}^{-3}$. Addition of ZnCl_2 ($0.002 \text{ mol dm}^{-3}$) increased the solubility of BTACI and a saturated solution of BTACI, under these conditions, has a strength of $0.0016 \text{ mol dm}^{-3}$. It has been proposed earlier that a species like $[\text{PhCH}_2\text{Me}_3\text{N}]^+ [\text{ZnCl}_4]^{-2} \text{I}^+$ is formed (Kajjgaeshi *et al* 1989).

2.2 Stoichiometry

The oxidation of lower oxyacids of phosphorus by BTACI leads to the formation of the corresponding oxyacids containing phosphorus in a higher oxidation state.

Reaction mixtures were prepared containing a known excess of phosphinic or phosphorous acid. On completion of the reaction, the amounts 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 (Jones and Swift 1953). To determine the stoichiometry of the oxidation of PPA, a known excess of BTACI was treated with PPA and the amount of BTACI consumed was determined iodometrically after completion of the reaction. The observed stoichiometries for PA, PPA and POA are 1.04 ± 0.05 , 0.96 ± 0.04 and 1.09 ± 0.02 respectively. The oxidation of PA resulted in the formation of POA. PA is oxidised at approximately thrice the rate of oxidation of POA. To reduce the effect of further oxidation of POA on the kinetics and stoichiometry of the oxidation of PA, the concentration of oxyacid was always kept in large excess over the concentration of BTACI.

2.3 Spectral studies

UV-Vis spectra of $0.0005 \text{ mol dm}^{-3}$ of BTACI alone and in the presence of 0.002 , 0.003 and $0.006 \text{ mol dm}^{-3}$ of ZnCl_2 were obtained using a HP-diode array spectrophotometer (Model 8452A), at $300 \pm 3 \text{ K}$. The solvent as well as the blank was glacial acetic acid. The scanning speed was 600 nm s^{-1} .

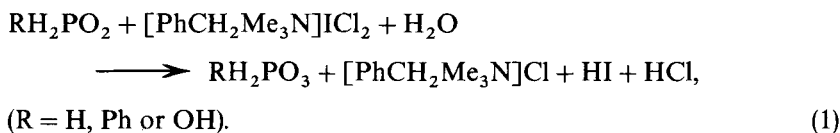
2.4 Kinetic measurements

Reactions were carried out under pseudo-first-order conditions by maintaining a large excess of the oxyacid ($\times 15$ times or more) over BTACI. The solvent was glacial acetic acid. The reactions were followed at constant temperature ($\pm 0.1 \text{ K}$), and were carried out in the presence of zinc chloride and were monitored by spectrophotometrically determining the decrease in $[\text{BTACI}]$ at 364 nm for at least three half-lives. No other reactant or product has any appreciable absorption at this wavelength. The pseudo-first-order rate constant, k_{obs} , was evaluated from the linear ($r > 0.990$) plots of $\log [\text{BTACI}]$ against time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. The experimental third order rate constant, k_3 , was determined from the relationship $k_3 = k_{\text{obs}}/[\text{oxyacid}] [\text{ZnCl}_2]$. Corrections were

applied to the rate constants of the deuterated compounds for the hydrogen-1 content by using the formula $(\text{observed } k_{\text{H}}/k_{\text{D}} \times 100)/\%$ isotopic purity.

3. Results

Oxidation of phosphorus oxyacids exhibited 1:1 stoichiometry and the overall reaction can, therefore, be written as



A comparison of the UV-Vis spectra (figure 1) of BTACl alone and in the presence of different concentrations of ZnCl_2 showed that the nature of the spectra is not very different but there is a definite and regular change in the absorbance of BTACl on the addition of increasing amounts of ZnCl_2 . This clearly showed that a complex is formed whose concentration increases with increase in the concentration of ZnCl_2 .

The order of the reaction with respect to BTACl is one. Further, the pseudo-first-order rate constants do not depend on the initial concentration of BTACl. The reaction rate increases linearly with an increase in the concentration of the oxyacid (table 1). With increase in concentration of zinc chloride, reaction rate increases (table 2). A plot between k_{obs} against $[\text{ZnCl}_2]$ is linear ($r = 0.9995$) and passes through the origin. Rates of oxidation of the three oxyacids were determined at different temperatures and the activation parameters calculated (table 3).

To ascertain the importance of the cleavage of a P-H bond in the rate-determining step, the oxidation of deuterated PA and POA was studied. Results showed (table 3) the

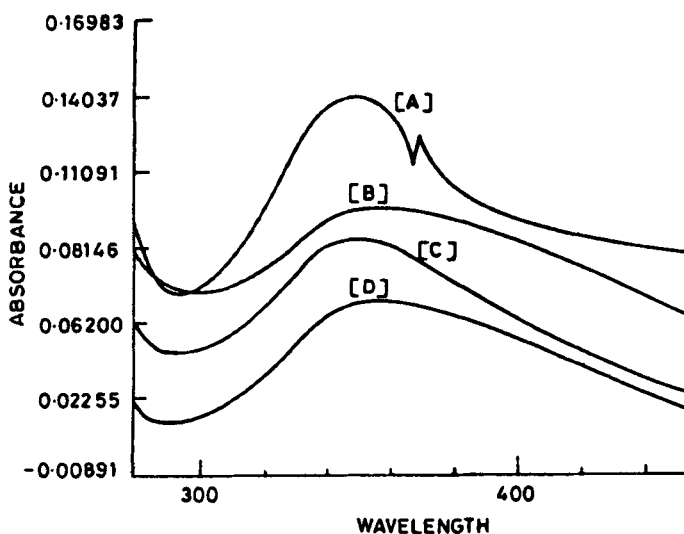


Figure 1. UV-Vis spectra of [A]— $0.0005 \text{ mol dm}^{-3}$ BTACl, [B]—[A] + $0.002 \text{ mol dm}^{-3}$ ZnCl_2 , [C]—[A] + $0.003 \text{ mol dm}^{-3}$ ZnCl_2 and [D]—[A] + $0.006 \text{ mol dm}^{-3}$ ZnCl_2 ; solvent—glacial acetic acid temperature— $300 \pm 3 \text{ K}$.

Table 1. Rate constants for the oxidation of oxyacids of phosphorus by BTACI containing 0.002 M ZnCl₂ at 318 K.

[oxyacid] (mol dm ⁻³)	10 ³ [BTACI] (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)		
		PA	PPA	POA
0.1	1.0	9.64	22.2	3.73
0.2	1.0	19.4	44.1	7.90
0.3	1.0	29.1	67.0	11.7
0.4	1.0	37.5	92.0	15.1
0.6	1.0	58.3	137	21.8
0.8	1.0	76.0	174	30.8
1.0	1.0	97.2	224	36.9
0.1	1.0	9.81*	22.5*	3.68*
0.1	0.2	10.2	21.1	3.56
0.1	0.3	9.58	22.6	3.85
0.1	0.5	9.70	21.8	3.79
0.1	0.8	9.85	22.0	3.64

*Containing 0.005 M acrylonitrile

Table 2. Effect of zinc chloride on the oxidation of phosphinic acid by BTACI. [BTACI] = 0.001 mol dm⁻³; [PA] = 0.1 mol dm⁻³; T = 318 K

10 ³ [ZnCl ₂] (mol dm ⁻³)	2.0	3.0	4.0	5.0	6.0	7.0	8.0
10 ⁴ k _{obs} (s ⁻¹)	9.64	14.1	19.5	24.3	28.5	34.0	39.4

Table 3. Rate constants at different temperatures and activation parameters for the oxidation of oxyacids of phosphorus by BTACI.

Acid	10 ² k ₃ (mol ⁻² dm ⁶ s ⁻¹) at				ΔH [#] (kJ mol ⁻¹)	ΔS [#] (J mol ⁻¹ K ⁻¹)
	298 K	308 K	318 K	328 K		
PA	9.12	21.9	48.2	105	63.5 ± 0.2	-52 ± 1
PPA	25.2	55.5	111	218	55.7 ± 0.3	-70 ± 1
POA	3.62	8.50	18.7	38.2	61.4 ± 0.3	-67 ± 1
DPA	1.65	4.12	8.75	18.1	62.0 ± 0.9	-71 ± 3
DPOA	0.65	1.65	3.56	7.20	62.4 ± 1.1	-78 ± 3

presence of a substantial primary kinetic isotope effect ($k_H/k_D = 5.51$ for PA and 5.25 for POA at 318 K).

Addition of benzyltrimethylammonium chloride (BTMACI) slightly enhances reaction rate (table 4). A plot between $1/k_{obs}$ and $1/[BTMACI]$ is linear ($r = 0.9986$) with an intercept on the rate-ordinate.

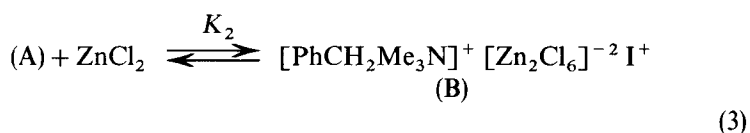
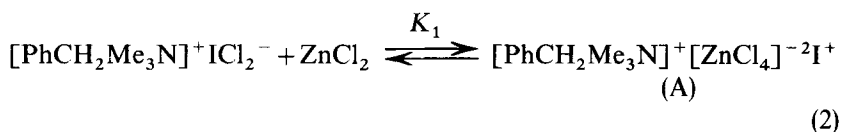
The oxidation of oxyacids, under a nitrogen atmosphere, failed to induce polymerization of acrylonitrile. Further, an addition of acrylonitrile had no effect on the rate (table 1).

Table 4. Effect of benzyltrimethylammonium chloride on the oxidation of PA by BTACI.[BTACI] = 0.001 mol dm⁻³; [PA] = 0.1 mol dm⁻³; T = 318 K

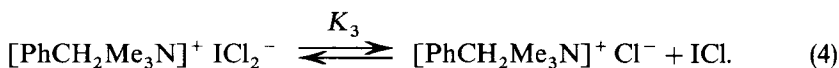
10 ³ [BTMACl] (mol dm ⁻³)	0.0	0.4	0.6	1.0	1.6	3.0	4.0
10 ⁴ k _{obs} (s ⁻¹)	9.64	10.5	12.3	15.2	17.1	17.5	19.4

4. Discussion

From our data on the solubility of BTACI in the absence and presence of ZnCl₂, the value of the equilibrium constant, K₁, is ≈ 2400 mol⁻¹ dm³. This indicates that even at the lowest concentration of ZnCl₂ used, almost the whole of BTACI will be in the form of complex (A), (2) below. The linear increase in the rate with [ZnCl₂] points to a further complexation, see (3) below

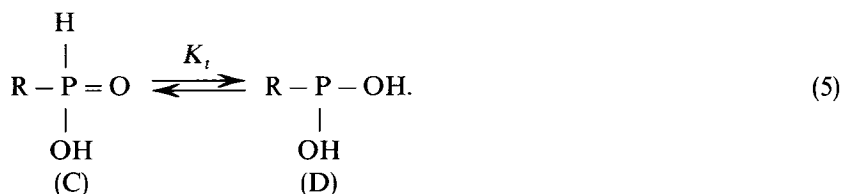


The observed dependence on the concentration of zinc chloride indicates that the equilibrium between complexes (A) and (B) is rapid, that the equilibrium constant, K₂, is small and the reaction is not complete even at high concentrations of ZnCl₂, and that only the complex (B) is reactive. The small rate-enhancing effect of BTMACl suggests that iodine monochloride is not involved in the oxidation process, i.e.



Therefore, (B) is the only reactive oxidizing species in the oxidation of phosphorus oxyacids. Formation of the complex is supported by spectral studies also. The existence of the anion [Zn₂Cl₆]⁻², in tetrahydrofuran, has been confirmed by X-ray crystallography (Cotton *et al* 1983).

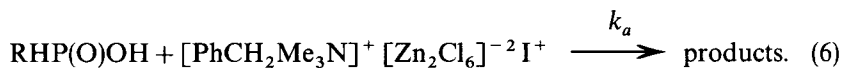
Lower oxyacids of phosphorus are reported to exist in two tautomeric forms (Jenkins and Yost 1959; Fratiello and Anderson 1963),



The predominant species is the pentacoordinated form (C). Formation of a tricoordinated form (D) in an equilibrium has been proposed in the study of acid-catalysed

exchange of phosphorus-bonded hydrogen with deuterium and tritium. The value of the equilibrium constant, K_t (Van Wazer 1958), is of the order of 10^{-12} .

Two alternative broad mechanisms can be formulated, one assuming the form (C) as the reactive reducing species,



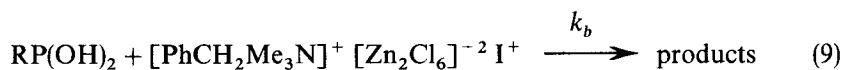
The rate law for the sequence of reactions (3)–(6), will have the form

$$\text{rate} = \frac{K_2 k_a [\text{BTACl}] [\text{RHP(O)OH}]_0 [\text{ZnCl}_2]}{(1 + K_t)(1 + K_2) [\text{ZnCl}_2] + K_3 [\text{BTMACl}]^{-1}}, \quad (7)$$

where $[\text{RHP(O)OH}]_0$ denotes the initial concentration of the oxyacid. In view of the observed relationships between k_{obs} and $[\text{ZnCl}_2]$ and the low concentration of ZnCl_2 used ($\approx 0.002 \text{ M}$), one can assume that $1 \gg K_2 [\text{ZnCl}_2]$. Further, since $1 \gg K_t$, (7) can be reduced to

$$\text{rate} = \frac{K_2 k_a [\text{BTACl}] [\text{RHP(O)OH}]_0 [\text{ZnCl}_2]}{1 + K_3 [\text{BTMACl}]^{-1}}. \quad (8)$$

Similarly a mechanism [(3)–(5) and (9)] can be proposed involving form (D) as the reactive species leading to rate law (10), which can be reduced to (11), in view of the earlier assumptions.



$$\text{rate} = \frac{K_2 K_t k_b [\text{BTACl}] [\text{RHP(O)OH}]_0 [\text{ZnCl}_2]}{(1 + K_t)(1 + K_2 [\text{ZnCl}_2] + K_3 [\text{BTMACl}]^{-1})}, \quad (10)$$

$$\text{rate} = \frac{K_2 K_t K_b [\text{BTACl}] [\text{RHP(O)OH}]_0 [\text{ZnCl}_2]}{1 + K_3 [\text{BTMACl}]^{-1}}. \quad (11)$$

Thus the two rate laws (8) and (11) are kinetically indistinguishable.

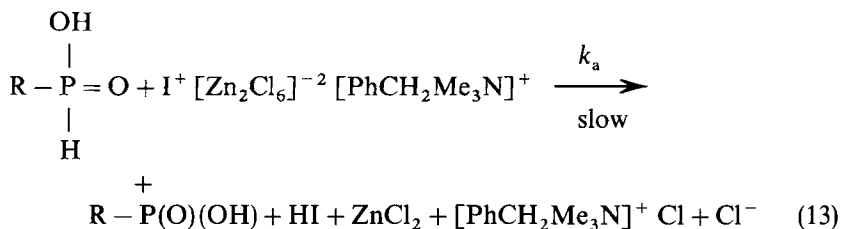
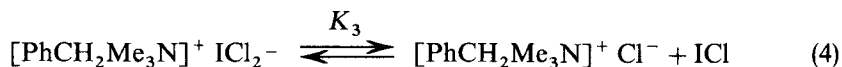
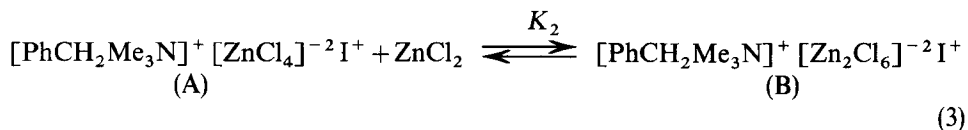
If the form (D) is the reactive reducing species and reactions (3)–(5) and (9) represent the mechanism of the reaction, then the experimental third order rate constant, k_3 , is given by

$$k_3 = K_2 K_t k_b. \quad (12)$$

The value of K_2 is not known. However, it cannot be very high as the rate is not levelled off even at higher concentrations of zinc chloride. Since the value of K_t is of the order of 10^{-12} , the value of the rate-limiting constant, k_b , equals/exceeds the rate constants of diffusion-controlled rate processes (Vetter 1967). 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 indicate the absence of one-electron oxidation giving rise to free radicals. The presence of substantial kinetic isotope effect confirms the cleavage of a P–H bond in the rate-determining step. The 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 (Lovering and Laidler 1960) of the bond dissociation energy of an O–H bond is 460 kJ mol^{-1} , while that for a P–H

bond (Gunn and Green 1961) is 321 kJ mol^{-1} . Therefore, the following mechanism may be proposed for the oxidation (scheme 1),



Scheme 1.

Based on scheme 1 and assuming that $1 \gg K_2 [\text{ZnCl}_2]$, in view of the observed relationships between k_{obs} and $[\text{ZnCl}_2]$ and the low concentration of ZnCl_2 used ($\approx 0.002 \text{ M}$), the rate law for scheme 1 can be written as,

$$-d[\text{BTACl}]/dt = \frac{k_a K_2 [\text{ZnCl}_2] [\text{oxyacid}] [\text{BTACl}]}{1 + K_3 [\text{BTMACl}]^{-1}} \quad (15)$$

This rate law is able to explain all the observed kinetic features. The value of K_3 calculated from the experimental data is $3.97 \pm 0.17 \times 10^{-4} \text{ mol dm}^{-3}$. We were unable to study the effect of polarity, which might have provided evidence supporting our mechanism, because of the decomposition of the oxidant in water and its insolubility in any other suitable solvent.

Acknowledgement

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