Kinetics and Mechanism of the Oxidation of Lower Oxyacids of Phosphorus by Hexamethylenetetramine Bromine

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ABSTRACT: The oxidation of lower oxyacids of phosphorus by hexamethylenetetramine bromine (HABR) in glacial acetic acid resulted in the formation of corresponding oxyacids with phosphorus in a higher oxidation state. The reaction exhibited 2:1 stoichiometry. The reaction is first order with respect to HABR. Michaelis–Menten-type kinetics were observed with respect to the acids. The formation constant of the phenylphosphinic acid–HABR complex also has been determined spectrophotometrically. The thermodynamic parameters for the complex formation and the activation parameters for their decomposition were calculated. The reaction showed the presence of a substantial kinetic isotope effect. It is proposed that the HABR itself is the reactive oxidizing species. It has been shown that the pentacoordinated tautomer of the phosphorus oxyacid is the reactive reductant. A suitable mechanism has been proposed. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 165–170, 2000

INTRODUCTION

Hexamethylenetetramine bromine (HABR) has been reported as a synthetic reagent for the oxidation of alcohols to carbonyl compounds [1]. We have undertaken a study of the kinetics and mechanism of oxidation by HABR. Four reports have been issued from our laboratory on the mechanistic aspects of the oxidation of alcohols [2,3], aldehydes [4], and diols [5]. In this article, the kinetics of oxidation of three lower oxyacids of phosphorus, namely, phosphorous (POA), phosphinic (PA), and phenylphosphinic (PPA) acids, by HABR in glacial acetic acid have been reported. Attempts have been made to identify the reactive oxidizing and reducing species. A suitable mechanism has been proposed.

EXPERIMENTAL

Material

The phosphorus oxyacids were commercial products (Fluka) and were used as supplied. HABR was prepared by the reported method [1] and its purity was checked by an iodometric method and melting point determination. Contrary to the earlier report [1], we found that in acetic acid solutions, the active bromine content of this complex is 2 mol/mol of the reagent. The P—H bonds in PA and POA were deuterated by repeatedly dissolving the acid in deuterium oxide (BARC, 99.4%) and evaporating water and the excess of deuterium oxide in vacuo [6]. This isotopic purity

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of the deuterated PA and POA, as determined from their nuclear magnetic resonance (NMR) spectra, was $92 \pm 5\%$ and $91 \pm 5\%$, respectively. Acetic acid was refluxed with chromium trioxide and acetic anhydride for 6 h and then distilled.

Kinetic Measurements

The reactions were studied under pseudo-first-order conditions by keeping an excess (20 times or more) of the acid over HABR. The solvent was glacial acetic acid. The reactions were studied at constant temperature (± 0.1 K) and were followed by monitoring the decrease in the [HABR] spectrophotometrically at 380 nm for up to 80% reaction. Beer's law was found to be valid for HABR within the concentration range used in our experiments. Pseudo-first-order rate constants, k_{obs} were evaluated from linear plots ($r > 0.9990$) of log [HABR] against time. Duplicate kinetic runs showed that the rates were reproducible to within $\pm 3\%$.

Spectral Analysis

Ultraviolet visible (UV-vis) spectra of HABR, hexamethylenetetramine (HXA), bromine, and the reaction mixture were obtained on an HP diode-array rapid scanning spectrophotometer (Model 8452A) with a scanning speed of 600 nm s^{-1}. To determine the formation constant of the intermediate, spectra of reaction mixtures containing a constant [HABR] and varying [PPA] also were obtained. The solvent was glacial acetic acid and the temperature was 313 ± 1 K. For the individual compounds the blank was glacial acetic acid and for the reaction mixture the blank was a solution of the oxyacid in glacial acetic acid. The time gap between preparation of the reaction mixture and recording of the spectrum was < 10 s.

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 PA or POA. On completion of the reaction, the amount of POA formed in the oxidation of PA and the residual reductant in the oxidation of POA were determined by the reported method [7]. Several determinations indicated that the [POA formed]/[HABR] and [consumed POA]/[HABR] in the case of PA and POA are 2.09 ± 0.06 and 1.96 ± 0.05, respectively. To determine the stoichiometry of the oxidation of PPA, a known excess of HABR was treated with PPA and the residual HABR was determined spectrophotometrically at 380 nm af-

ter the completion of the reaction. The [PPA]/[HABR consumed] was found to be 2.10 ± 0.08.

RESULTS

Oxidation of the phosphorus oxyacids exhibited a 2:1 stoichiometry and the overall reaction can, therefore, be written as Eq. (1).

$$2RH_2PO_2 + (CH_2)_6N_4Br_4 + 4CH_3COOH \longrightarrow$$
$$2RH_2PO_3 + (CH_2)_6N_4 + 4HBr + 4(CH_3CO)_2O$$
$$(1)$$
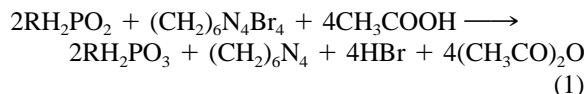
where R = H, OH, or Ph.

The reactions were found to be first order with respect to HABR. Furthermore, the pseudo-first-order rate constants do not depend on the initial concentration of HABR. The rate of the reaction increases with an increase in the concentration of the oxyacid (Table I). The order with respect to PA, PPA, and POA, as determined by the log–log plot, is 0.45 ± 0.04, 0.47 ± 0.05, and 0.44 ± 0.04, respectively. A plot of $1/k_{obs}$ vs. $1/[\text{oxyacid}]$ was linear with an intercept on the rate ordinate (Fig. 1). Thus, Michaelis–Menten-type kinetics were observed with respect to the substrate. This leads to the postulation of the following overall mechanism, Eqs. (2) and (3), and the rate law (4).
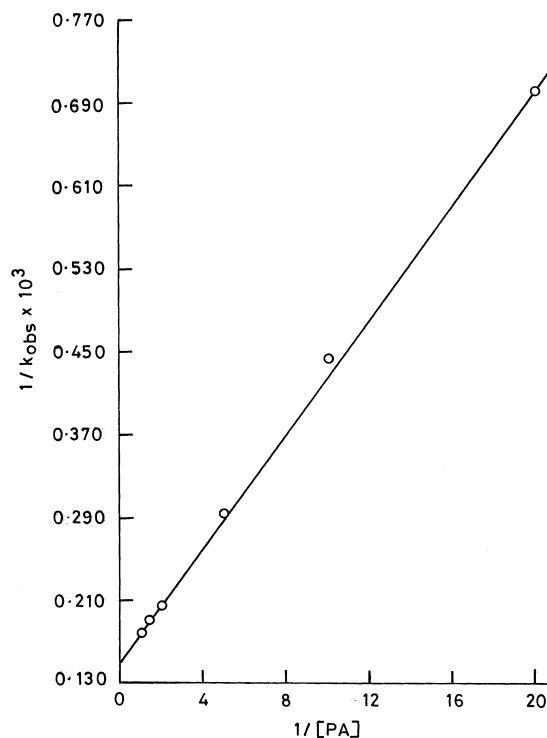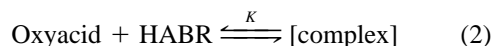
$$\text{Oxyacid} + \text{HABR} \underset{}{\overset{K}{\rightleftharpoons}} [\text{complex}] \quad (2)$$

Figure 1   A plot of $1/[\text{PA}]$ vs. $1/k_{obs}$ in the oxidation by HABR. (Conditions as in Table I.)

Table I   Rate Constants for the Oxidation of Oxyacids of Phosphorus by HABR at 303 K

10^3[HABR] (mol dm^{-3})	[Oxyacid] (mol dm^{-3})	$10^3\,k_{obs}$/(s^{-1})		
		PA	PPA	POA
1.0	0.05	1.40	3.20	0.40
1.0	0.10	2.25	5.26	0.63
1.0	0.20	3.42	8.05	0.96
1.0	0.50	4.85	11.7	1.34
1.0	0.80	5.29	12.4	1.45
1.0	1.00	5.58	13.5	1.55
1.0	1.00	5.60[a]	13.0[a]	1.54[a]
0.5	0.20	3.46	7.91	0.92
0.8	0.20	3.51	7.93	0.90
2.0	0.20	3.44	8.00	0.97
3.0	0.20	3.60	7.88	0.88
4.0	0.20	3.50	8.10	0.86

[a] Contained 0.005 mol dm^{-3} acrylonitrile.

$$[\text{Complex}] \xrightarrow{\ k_2\ } \text{products} \tag{3}$$
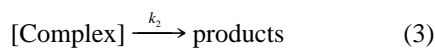
$$\text{Rate} = k_2\,K\,[\text{oxyacid}][\text{HABR}]/(1 + K\,[\text{oxyacid}]) \tag{4}$$

The dependence of k_{obs} on the concentration of oxyacid was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic parameters for the complex formation and activation parameters of the decomposition of the complexes, at 298 K, were calculated from the values of K and k_2, respectively, at different temperatures (Tables II and III).

Induced Polymerization of Acrylonitrile

The oxidation of PA, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Also, an addition of acrylonitrile had no effect on the rate (see Table I).

Kinetic Isotope Effect

To ascertain the importance of the cleavage of the P—H bond in the rate-determining step, the oxidation of deuterated PA and POA was studied. Results recorded in Tables II and III showed that the formation constants of the complexes of ordinary and deuterated oxyacids have similar values but the rates of decomposition of the complexes showed the presence of a substantial kinetic isotope effect ($k_H/k_D = 5.94$ and 5.90 for PA and POA, respectively, at 303 K).

Spectral Analysis

A perusal of UV-vis spectra of HABR (0.001 mol dm^{-3}) and an equivalent amount of bromine (0.002 mol dm^{-3}), in AcOH at $\approx 313 \pm 1$ K, showed that the difference in the nature of the spectra of HABR and bromine was not very striking but their optical densities showed variations. HXA had no appreciable absorption in this range. Moreover, the spectrum of HABR did not show any change in the experimental time period (ca. 2 h). When a solution of HABR in acetic acid was evaporated to dryness under reduced pressure, HABR was recovered unchanged. This confirmed that HABR retained its integrity in acetic acid.

A perusal of the spectra of HABR and of HABR + PPA showed that there is a distinct increase in the absorbance of HABR on the addition of PPA (Fig. 2). Additionally, the value of the absorbance increases with an increase in the concentration of PPA. This supports the postulation of the formation of an intermediate complex in a pre-equilibrium. The for-

Table II   Formation Constants and Thermodynamic Parameters for the Oxyacid–HABR Complexes

Acid	K/dm^3 mol^{-1}			ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
	303 K	313 K	323 K		
PA	5.43	3.90	2.98	-26.9 ± 0.6	-67 ± 2
PPA	5.00	3.54	2.50	-30.7 ± 0.3	-80 ± 1
POA	5.76	4.30	3.38	-24.2 ± 0.5	-58 ± 2
DPA	5.46	3.80	2.86	-28.8 ± 0.9	-73 ± 3
DPOA	5.88	4.49	3.33	-25.6 ± 0.7	$-62. \pm 2$

Table III   Rate Constants for the Decomposition of the Oxyacid–HABR Complexes and Their Activation Parameters

Acid	$10^3 k_2/s^{-1}$			ΔH^a (kJ mol^{-1})	ΔS^a (J mol^{-1} K^{-1})
	303 K	313 K	323 K		
PA	6.53	13.0	27.1	55.3 ± 1.3	−105 ± 4
PPA	16.0	32.8	60.0	51.3 ± 1.0	−111 ± 3
POA	1.77	3.71	6.90	52.9 ± 1.1	−124 ± 3
DPA	1.10	2.30	4.26	52.6 ± 1.1	−129 ± 4
DPOA	0.30	0.65	1.18	53.3 ± 2.1	−137 ± 7
k_H/k_D	5.94	5.65	6.36 (PA)		
k_H/k_D	5.90	5.71	5.85 (POA)		

mation constant of the HABR–PPA complex was determined spectrophotometrically from the absorbance of solutions containing a constant initial [HABR] and varying initial [PPA] by a double reciprocal plot. The value of the formation constant, K, at 313 K was found to be 2.6 dm^3 mol^{-1}, which compares favorably with the value of 3.5 obtained kinetically (cf. Table II).

Effect of Hexamethylenetetramine

The rate of oxidation of oxyacids is not affected by the addition of HXA (Table IV).

Effect of Bromide Ion

The addition of bromide ion has no effect on the rate of oxidation of oxyacids (Table V).

Oxidation by Bromine

For the purpose of comparison, the oxidation of PA by bromine was studied. It was found that the oxidation by bromine exhibits kinetics different than those

Figure 2   UV-vis spectra of (A) 0.001 mol dm^{-3} HABR; (B) 0.001 mol dm^{-3} HABR + 0.018 mol dm^{-3} PPA; (C) 0.001 mol dm^{-3} HABR + 0.020 mol dm^{-3} PPA; (D) 0.001 mol dm^{-3} HABR + 0.0246 mol dm^{-3} PPA; (E) 0.001 mol dm^{-3} HABR + 0.026 mol dm^{-3} PPA; (F) 0.001 mol dm^{-3} HABR + 0.045 mol dm^{-3} PPA; (G) 0.001 mol dm^{-3} HABR + 0.090 mol dm^{-3} PPA; temperature: 313 ± 1 K; solvent: acetic acid.

shown by HABR. The oxidation by bromine, under similar reaction conditions, is much faster than that by HABR (ca. five times) and the order with respect to PA is one. Furthermore, an addition of bromide ions retards the oxidation.

DISCUSSION

In solutions, HABR may dissociate to form molecular bromine [reaction (5)].

$$(CH_2)_6N_4Br_4 \rightleftharpoons (CH_2)_6N_4 + 2Br_2 \qquad (5)$$

However, nil effect of both bromide ions and HXA on the rate showed that the equilibrium in reaction (5) is not participating in the oxidation process. Moreover, the isolation of unchanged HABR, from a solution in acetic acid, indicated that HABR retained its integrity in acetic acid. Therefore, it is proposed that the reactive oxidizing species is HABR itself. The different kinetic pictures obtained in the oxidation of PA by bromine and HABR support this postulation.

Nothing much is known about the structure of HABR. For the sake of convenience, we have shown the reactive part as $\diagdown\!\!\diagup$N···Br···Br. However, an alternative form can be Br—N$^+$ Br$_3^-$. There is no evidence for any of these suggestions.

Lower oxyacids of phosphorus are reported to exist in two tautomeric forms [8,9]. The predominant species is the pentacoordinated form (A). The value [10] of the equilibrium constant, K_t, in aqueous solutions is of the order of 10^{-12}. Although in acetic acid solution, the value of K_t might be different, the order is likely to be the same.
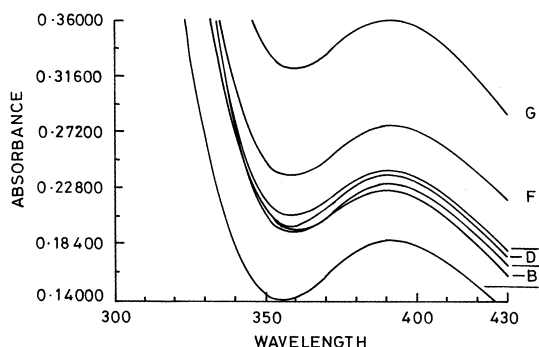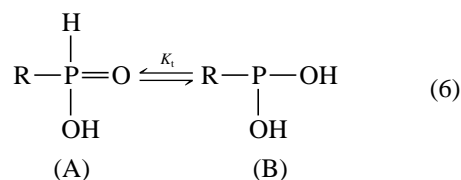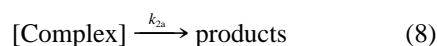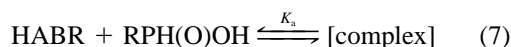
$$\underset{(A)}{R-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{P}}=O} \underset{K_t}{\rightleftharpoons} \underset{(B)}{R-\underset{\underset{OH}{|}}{P}-OH} \qquad (6)$$

Table IV   Effect of Hexamethylenetetramine on the Oxidation of Phosphinic Acid by HABR[a]

10^3[HXA]/mol dm^{-3}	0.0	0.5	1.0	2.0	3.0	5.0
$10^3\,k_{obs}$/s^{-1}	4.85	4.80	4.91	4.84	4.75	5.05

[a] [HABR] = 0.001 mol dm^{-3}; [PA] = 0.50; and T = 303 K.

Hence, two alternative broad mechanisms can be formulated. By assuming in the first instance that pentacoordinated tautomer (A) is the reactive reducing species, the following mechanism, Eqs. (6)–(8), can be written, which leads to the rate law (9).
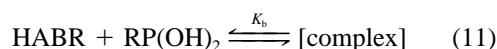
$$\text{HABR} + \text{RPH(O)OH} \xrightleftharpoons{\;K_a\;} \text{[complex]} \quad (7)$$

$$\text{[Complex]} \xrightarrow{k_{2a}} \text{products} \quad (8)$$

$$\text{Rate} - \frac{k_{2a} K_a \,[\text{oxidant}]\,[\text{RHP(O)OH}]_0}{1 + K_t + K_a \,[\text{RHP(O)OH}]_0} \quad (9)$$

where [RHP(O)OH]$_0$ represents the initial concentration of the phosphorus oxyacid. Because $1 \gg K_t$, Eq. (9) is reduced to Eq. (10).

$$\text{Rate} = \frac{k_{2a} K_a \,[\text{oxidant}]\,[\text{RHP(O)OH}]_0}{1 + K_a \,[\text{RHP(O)OH}]_0} \quad (10)$$

Another mechanism can be formulated assuming the tricoordinated form (B) as the reactive reducing species, Eqs. (6), (11), and (12).

$$\text{HABR} + \text{RP(OH)}_2 \xrightleftharpoons{\;K_b\;} \text{[complex]} \quad (11)$$

$$\text{[Complex]} \xrightarrow{k_{2b}} \text{products} \quad (12)$$

The corresponding rate law is given by Eq. (13). In view of the relation $1 \gg K_t$, Eq. (13) is reduced to Eq. (14).

$$\text{Rate} = \frac{k_{2b} K_t K_b \,[\text{oxidant}]\,[\text{RHP(O)OH}]_0}{1 + K_t + K_b K_t \,[\text{RHP(O)OH}]_0} \quad (13)$$

$$\text{Rate} = \frac{k_{2b} K_b K_t \,[\text{oxidant}]\,[\text{RHP(O)OH}]_0}{1 + K_b K_t \,[\text{RHP(O)OH}]_0} \quad (14)$$

Thus, the two rate equations conform to the experimental rate law, Eq. (4), and are kinetically indistinguishable.

In the plots of $1/k_{obs}$ vs. $1/$[substrate], values of the slope and the intercept, using Eqs. (10) and (14), are as follows:

$$\text{Slope} = (K_a k_{2a})^{-1}$$

and

$$\text{Intercept} = 1/k_{2a}$$

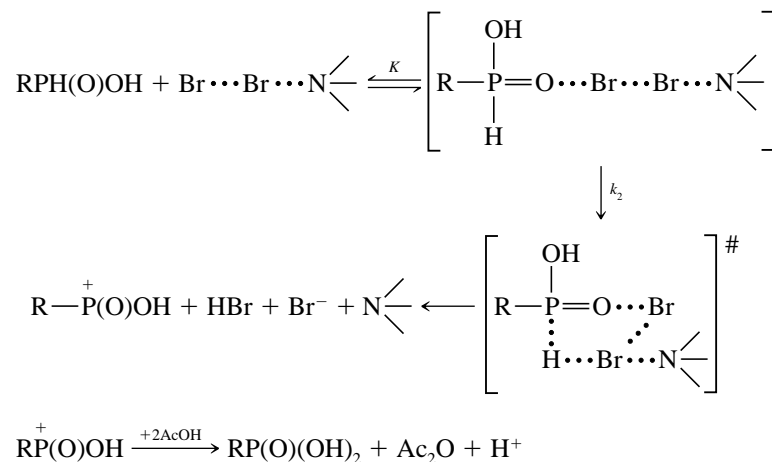$$\text{Slope} = (K_t K_b k_{2b})^{-1}$$

and

$$\text{Intercept} = 1/k_{2b}$$

It is thus seen that $k_2 = k_{2a} = k_{2b}$, which means that the rate constant for the disproportionation of the complex is not affected by the reactive form of the oxyacid. However, the values of the equilibrium constant from the rate laws (10) and (14) are $K = K_a = K_t K_b$ respectively. Therefore, $K_b = 10^{12} K$ or K_b for PA at 303 K should have a value of ca. 5×10^{12} dm^3 mol^{-1}. Polyhalides are not reported to form a highly stable series of complexes. In the oxidation of PA with benzyltrimethylammonium dichloroiodate [11] and benzyltrimethylammonium tribomide [12], the complex formation was not detected, implying that if the complex is formed the formation constants have very small values. HABR has been found to form complexes with alcohols [2] and aldehydes [4] but the values of formation constants range from 4 to 7 dm^3 mol^{-1}. Thus, the very high value of the formation constant of the HABR–oxyacid complex is improbable, and it is highly unlikely that form (B) is involved in the oxidation process. The very small value of K_t means that in 0.05 mol oxyacid the concentration of form (B) is too small to form a sufficient amount of the intermediate complex.

Table V   Effect of Bromide Ion on the Oxidation of Phosphinic Acid by HABR[a]

10^3[Br$^-$]/mol dm^{-3}	0.0	0.5	1.0	2.0	3.0	5.0
$10^3\,k_{obs}$/s^{-1}	4.85	5.08	4.89	4.84	4.99	5.05

[a] [HABR] = 0.001 mol dm^{-3}; [PA] = 0.50; and T = 303 K.

$$RPH(O)OH + Br\cdots Br\cdots N \diagup_{\diagdown} \underset{K}{\rightleftharpoons} \left[\begin{array}{c} OH \\ | \\ R-P=O\cdots Br\cdots Br\cdots N \diagup_{\diagdown} \\ | \\ H \end{array} \right]$$

$$\downarrow k_2$$

$$R-\overset{+}{P}(O)OH + HBr + Br^- + N \diagup_{\diagdown} \longleftarrow \left[\begin{array}{c} OH \\ | \\ R-P=O\cdots Br \\ \vdots \qquad \vdots \\ H\cdots Br\cdots N \diagup_{\diagdown} \end{array} \right]^{\#}$$

$$R\overset{+}{P}(O)OH \xrightarrow{+2AcOH} RP(O)(OH)_2 + Ac_2O + H^+$$

Scheme I

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 give 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 [13] is 460 kJ mol^{-1}, while that for a P—H bond [14] is 321 kJ mol^{-1}. Thus, the experimental results can be accounted for in terms of formation of an intermediate complex in a pre-equilibrium that subsequently yields phosphonium cation in the rate-determining step (Scheme I). With the present data it is not possible to state definitely the structure of the intermediate complex. In oxidations by several polyhalides [15,16], it has been proposed that the intermediate complex is formed by an interaction of the nonbonded electron pair of oxygen and the halogen atom. The proposed mechanism also is supported by the observed values of entropy of activation. 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.

The rate of oxidation follows the order PPA > PA > 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 the 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 III revealed that the reaction rates are controlled mainly by the entropy of activation.

BIBLIOGRAPHY

1. Yavari, I.; Shaabani, G. J Chem Res (S) 1994, 274.
2. Pareek, A.; Kothari, S.; Banerji, K. K. Indian J Chem 1996, 35B, 970.
3. Bohra, A.; Sharma, P. K.; Banerji, K. K. J Indian Chem Soc 1998, 75, 784.
4. Pareek, A.; Varshney, S.; Banerji, K. K. React Kinet Catal Lett 1997, 60, 127.
5. Gangwani, H.; Sharma, P. K.; Banerji, K. K. J Chem Res (S), 1999, 180.
6. Haight, G. P.; Rose, M.; Preer, J. J Am Chem Soc 1968, 90, 4809.
7. Jones, R. T.; Swift, E. H. Anal Chem 1953, 25, 1272.
8. Jenkin, W. A.; Yost, D. M. J Inorg Nucl Chem 1959, 11, 297.
9. Fratiello, A.; Anderson, E. W. J Am Chem Soc 1963, 85, 519.
10. Van Wazer, J. R. Phosphorus and Its Compounds, Vol. 1. Wiley: New York, 1958.
11. Suri, D.; Kothari, S.; Banerji, K.K. Proc Indian Acad Sci (Chem Sci) 1997, 109, 147.
12. Rao, P.S.C.; Goel, S.; Kothari, S.; Banerji, K. K. Indian J Chem 1998, 37B, 1129.
13. Lovering, E. G.; Laidler, K. J. Can J Chem 1960, 38, 2367.
14. Gunn, S. R.; Green, L. G. J Phys Chem 1961, 65, 779.
15. Goel, S.; Kothari, S.; Banerji, K. K. Indian J Chem 1996, 35B, 1180; J Chem Res (S) 1996, 230; (M) 1318.
16. Suri, D.; Banerji, K. K.; Kothari, S. J Chem Res (S) 1995, 274; (M) 1734.