

## KINETICS AND MECHANISM OF THE OXIDATION OF LOWER OXYACIDS OF PHOSPHORUS BY QUINOLINIUM BROMOCHROMATE

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### ABSTRACT

Oxidation of lower oxyacids of phosphorus by quinolinium bromochromate (QBC) in dimethylsulfoxide (DMSO) 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 with respect to QBC. Michaelis-Menten type of kinetics was observed with respect to the reductants. The reaction does not induce polymerization of acrylonitrile. Reactions are catalysed by hydrogen-ion. The hydrogen-ion dependence has the form:  $k_{\text{obs}} = a + b[\text{H}^+]$ . The oxidation of deuterated phosphinic and phenylphosphinic acids exhibited a substantial primary kinetic isotope effect. The oxidation was studied in nineteen different organic solvents. The solvent effects were analysed in terms Taft's and Swain's multiparametric equations. The effect of solvent indicates the solvent polarity plays a major role in the process. It has been shown that the pentacoordinated tautomer of the phosphorus oxyacid is the reactive reductant and it has been concluded that tricoordinated forms of phosphorus oxyacids does not participate in the oxidation process. A mechanism involving transfer of a hydride ion in the rate-determining step has been proposed.

**Key words :** Kinetics, Oxidation, Oxy acids, Phosphorous, Quinolinium bromochromate

### INTRODUCTION

Quinolinium bromochromate (QBC) has been used as a mild and selective oxidizing reagent in synthetic organic chemistry<sup>1</sup>. Though there are a few reports on the mechanistic aspects of oxidation reactions of QBC available in literature<sup>2-4</sup>. We have been interested in the kinetic and mechanistic studies of the reactions of chromium (VI) species and have already reported the mechanistic studies by several halochromates viz. pyridinium fluoro, chloro- and bromochromates (PFC, PCC and PBC) and 2,2'-bipyridinium chlorochromates<sup>5-8</sup>. It was observed that PFC and PCC presented different kinetic pictures. Further the lower oxyacids are reported to exist in two tautomeric forms<sup>9-10</sup>, and it is of interest to determine the nature of the oxyacid acid involved in the oxidation process. There seems to be no report on the oxidation of oxyacids of phosphorus by QBC. Therefore, we report here the kinetics of oxidation of phosphinic (PA), phenylphosphinic (PPA) and phosphorous (POA) acids by QBC in dimethylsulfoxide (DMSO) as a solvent. A suitable mechanism has also been proposed.

## EXPERIMENTAL

The phosphorus oxyacids were commercial products (Fluka) and were used as supplied. QBC was prepared by the reported method<sup>1</sup> 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<sup>11</sup>. The isotopic purity of the deuterated PA and POA, as determined from their NMR spectra, was 92±5% and 94±5%, respectively. Due to the non-aqueous nature of the medium, toluene - p- sulphonic acid was used as a source of hydrogen ions. TsOH is a strong acid and in non-polar solvents like DMSO, it is likely to be completely ionised. Other solvents were purified by their usual methods<sup>12</sup>.

### 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 phosphorous acids were determined by reported method<sup>13</sup>. To determine the stoichiometry of the oxidation of PPA, a known excess of QBC was treated with PPA and the residual QBC was determined spectrophotometrically at 354 nm after the completion of the reaction. The oxidation state of chromium in the completely reduced reaction mixture, determined by iodometric titration, was 3.96±0.10. The oxidation exhibited 1:1 stoichiometry and the overall reaction may therefore, be written as:



(R = H, Ph or OH)

QBC undergoes two-electron change. This is in accordance with the earlier observations with PFC<sup>5</sup>, QFC<sup>14</sup> and QBC<sup>4</sup>.

### Kinetic measurements

The reactions were studied under pseudo-first order conditions by keeping an excess (x 15 or greater) of the [oxyacid] over [QBC]. The solvent was DMSO, unless specified otherwise. The reactions were studied at constant temperature (±0.1 K) and were followed by monitoring the decrease in the [QBC] spectrophotometrically at 354 nm for up to 80% reaction. Pseudo-first-order rate constants,  $K_{obs}$  were evaluated from linear plots ( $r > 0.9990$ ) of  $\log[QBC]$  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

### Rate laws

The reactions were found to be first order with respect to QBC. The reactions exhibited the Michaelis-Menten type of kinetics with respect to the oxyacids (Table 1). A plot of  $1/[\text{oxyacid}]$  versus  $1/k_{\text{obs}}$  is linear with an intercept at the rate ordinate. This indicates the following overall mechanism (equation 2 and 3) and the rate law (4).



$$\text{Rate} = k_2 K [\text{QBC}] [\text{Oxyacid}] / (1 + K [\text{Oxyacid}]) \quad \text{....(4)}$$

**Table 1. Rate constants for the oxidation of oxyacids of phosphorus by QBC at 298 K**

$10^3 [\text{QBC}]$ (mol dm <sup>-3</sup> )	[oxyacid] (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}/(\text{s}^{-1})$		
		PA	PPA	POA
1.00	0.10	1.54	6.21	0.57
1.00	0.20	2.42	9.01	0.89
1.00	0.40	3.39	11.6	1.22
1.00	0.80	4.24	13.6	1.51
1.00	1.50	4.81	14.8	1.69
1.00	3.00	5.20	15.6	1.81
2.00	0.40	3.95	12.3	1.75
4.00	0.40	3.14	11.0	1.10
6.00	0.40	3.80	12.4	1.62
8.00	0.40	3.42	11.5	1.08
1.00	0.20	2.51*	11.7*	0.91*

\* Contained 0.005 mol dm<sup>-3</sup> acrylonitrile.

The dependence of reaction rate on reductant concentration was studied at four different temperatures and the value of  $K$  and  $k_2$  were evaluated from the double reciprocal plots. The thermodynamic and activation parameters were also calculated from the values of  $K$  and  $k_2$ , respectively, at different temperatures (Table 2 and 3).



**Table 2. Rate constants and activation parameters of the oxidation of -phosphorus oxyacids by QBC**

Acid	$10^3 k_2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )				$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\Delta S^*$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^*$ (kJ mol <sup>-1</sup> )
	288 K	298 K	308 K	318 K			
PA	3.26	5.67	10.4	18.2	41.3±0.8	-169±2	91.5±0.6
PPA	10.2	16.4	26.6	44.1	34.6±0.8	-183±2	88.8±0.6
POA	1.03	1.96	3.76	7.11	46.5±0.6	-160±2	94.1±0.1
DPA	0.53	0.98	1.87	3.51	45.5±0.8	-169±3	95.8±0.6
DPOA	0.17	0.35	0.72	1.41	51.3±0.4	-159±1	98.3±0.3
$k_H/k_D$	6.15	5.79	5.56	5.19 (PA)			
$k_H/k_D$	6.06	5.60	5.22	5.04 (POA)			

**Table 3. Formation constants and thermodynamic parameters of the oxidation of phosphorus oxyacids complexes by QBC**

Acid	$K$ / (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )				$\Delta H^*$ (KJ mol <sup>-1</sup> )	$\Delta S^*$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^*$ (kJ mol <sup>-1</sup> )
	288K	298K	308K	318K			
PA	4.36	3.72	3.12	2.55	-165±0.5	-35±2	5.71±0.4
PPA	6.73	6.10	5.51	4.88	-10.6±0.3	-13±1	6.69±0.2
POA	4.80	4.14	3.55	2.88	-15.3±0.7	-32±2	5.98±0.6
DPA	3.96	3.41	2.80	2.38	-15.6±0.4	-34±1	5.48±0.3
DPOA	5.10	4.55	3.91	3.28	-13.7±0.6	-26±2	6.19±0.8

#### Induced polymerization test

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).

#### Kinetic isotope effect

To ascertain an 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).

#### Effect of acidity

The reaction is analysed by hydrogen ions (Table 4). The hydrogen - ion dependence has the following form  $k_{\text{obs}} = a + b [H^+]$ . The values of  $a$  and  $b$ , for PPA, are  $6.15 \pm 0.13 \times 10^{-4} \text{ s}^{-1}$  and  $21.2 \pm 0.21 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , respectively ( $r^2 = 0.9996$ ).

**Table 4. Effect of hydrogen ion concentration on the oxidation of PPA by QBC**

[QBC] = 0.001 mol dm <sup>-3</sup> ; [PPA] = 1.0 mol dm <sup>-3</sup> ; Temp. = 298 K						
[H <sup>+</sup> ]	0.10	0.20	0.40	0.60	0.80	1.00
10 <sup>4</sup> k <sub>obs</sub> /S <sup>-1</sup>	8.34	10.5	14.4	18.9	23.0	27.5

**Effect of solvents**

The oxidation of PPA was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of QBC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics were similar in all the solvents. The values k<sub>z</sub> at 298 K for the oxidation of PPA are recorded in Table 5.

**Table 5. Effect of solvents on the oxidation of phenylphosphinic acid by QBC at 298 K**

Solvents	K (dm <sup>-3</sup> mols <sup>-1</sup> )	10 <sup>4</sup> k <sub>z</sub> (s <sup>-1</sup> )	Solvents	K (dm <sup>-3</sup> mols <sup>-1</sup> )	10 <sup>4</sup> k <sub>z</sub> (s <sup>-1</sup> )
Chloroform	5.22	28.8	Toluene	5.70	7.08
1,2-Dichloroethane	5.78	39.8	Acetophenone	6.32	57.5
Dichloromethane	5.52	34.7	THF	6.24	13.2
DMSO	6.10	164	t-butyl alcohol	5.66	7.94
Acetone	5.81	32.4	1,4-Dioxane	4.90	15.8
DMF	6.63	72.4	1,2 Dimethoxyethane	6.48	6.17
Butanone	5.64	20.4	CS <sub>2</sub>	5.55	2.95
Nitrobenzene	4.88	50.1	Acetic acid	6.16	2.09
Benzene	5.10	9.55	Ethyl acetate	5.80	10.5
Cyclohexane	5.51	0.44			

**DISCUSSION**

The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one is acid-independent and the other is acid dependent. The acid-catalysis may well be attributed to protonation of QBC to yield a protonated Cr (VI) species which is a stronger oxidant and electrophile.



Formation of a protonated Cr (VI) species has earlier been postulated in the reactions of structurally similar PCC<sup>15</sup> and PBC<sup>16</sup>.

**Solvent effect :** The rate constants of the oxidation,  $k_2$ , in eighteen solvents ( $\text{CS}_2$  was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (LESR) of Kamlet and Taft<sup>17</sup>.

$$\log k_2 = A_0 + \rho\pi^* + b\beta + a\alpha \quad \text{.....(6)}$$

In this equation,  $\pi^*$  represents the solvent polarity,  $\beta$  the hydrogen bond acceptor basicities and  $\alpha$  is the hydrogen bond donor acidity.  $A_0$  is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for  $\alpha$ . The results of correlation analyses in terms of equation (6), a biparametric equation involving  $\pi^*$  and  $\beta$ , and separately with  $\pi^*$  and  $\beta$  are given below as equations (7) - (10).

$$\log k_2 = -3.79 + 2.21(\pm 0.27)\pi^* + 0.24(\pm 0.22)\beta + 0.37(\pm 0.21)\alpha \quad \text{.....(7)}$$

$$R^2 = 0.8611; \text{ sd} = 0.25; n = 18; \psi = 0.41$$

$$\log k_2 = -3.70 + 2.26(\pm 0.27)\pi^* + 0.12(\pm 0.22)\beta \quad \text{.....(8)}$$

$$R^2 = 0.8303; \text{ sd} = 0.26; n = 18; \psi = 0.44$$

$$\log k_2 = -3.72 + 2.29(\pm 0.26)\pi^* \quad \text{.....(9)}$$

$$r^2 = 0.8272; \text{ sd} = 0.26; n = 18; \psi = 0.43$$

$$\log k_2 = 2.99 + 0.52(\pm 0.44)\beta \quad \text{.....(10)}$$

$$r^2 = 0.0638; \text{ sd} = 0.59; n = 18; \psi = 0.99$$

Here  $n$  is the number of data points and is the Exner's statistical parameter<sup>18</sup>.

Kamlet's<sup>17</sup> triparametric equation explains ca 86% of the effect of solvent on the oxidation. However, by Exner's criterion<sup>18</sup> the correlation is not even satisfactory (*cf.* equation (6)). The major contribution is of solvent polarity. It alone accounted for ca 85% of the data. Both  $\beta$  and  $\alpha$  play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's<sup>19</sup> equation (11) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \quad \text{.....(11)}$$

Here  $A$  represents the anion-solvating power of the solvent and  $B$  the cation-solvating power.  $C$  is the intercept term. ( $A + B$ ) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of equation (8), separately with  $A$  and  $B$  and with ( $A + B$ ).

$$\log k_2 = 0.55(\pm 0.03)A + 2.34(\pm 0.02)B - 3.50 \quad \text{.....(12)}$$

$$R^2 = 0.9985; \text{ sd} = 0.02; n = 19; \psi = 0.04$$

$$\log k_2 = 0.21(\pm 0.77)A - 2.89 \quad \text{.....(13)}$$

$$r^2 = 0.0045; \text{ sd} = 0.62; n = 19; \psi = 1.02$$



$$\log k_2 = 2.30 (\pm 0.09) B - 3.68 \quad \text{.....(14)}$$

$$r^2 = 0.9694; \text{sd} = 0.11; n = 19; \psi = 0.18$$

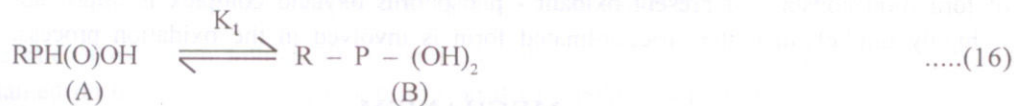
$$\log k_2 = 1.75 \pm 0.23 (A + B) - 2.56 \quad \text{.....(15)}$$

$$r^2 = 0.7723; \text{sd} = 0.39; n = 19; \psi = 0.71$$

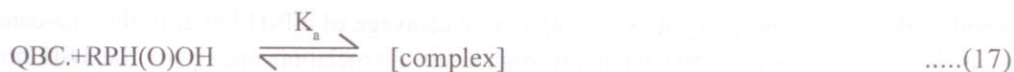
The rates of oxidation of PPA in different solvents showed an excellent correlation in Swain's equation (cf. equation 11) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for ca. 99% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for ca. 77% of the data. In view of the fact that solvent polarity is able to account for ca. 77% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of  $\log k_2$  against the inverse of the relative permittivity is not linear ( $r^2 = 0.5149$ ;  $\text{sd} = 0.44$ ;  $\psi = 0.71$ ).

#### Reactive reducing species

Lower oxyacids of phosphorus are reported to exist in two tautomeric forms<sup>9-10</sup>. The predominant species is the pentacoordinated form (A). The value<sup>20</sup> of the equilibrium constant,  $K_t$ , in aqueous solutions, is of the order of  $10^{-12}$ .



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 (19).



$$\text{Rate} = k_a K_a [\text{Oxyacid}]_0 [\text{QBC}] / 1 + K_t K_a [\text{oxyacid}]_0 \quad \text{.....(19)}$$

Where  $[\text{oxyacid}]_0$  represents the initial concentration of the oxyacid. Equation (19) can be reduced to (20) as  $1 \gg K_t$ .

$$\text{Rate} = k_a K_a [\text{Oxyacid}]_0 [\text{QBC}] / 1 + K_a [\text{oxyacid}]_0 \quad \text{.....(20)}$$

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





$$\text{Rate} = k_b K_b K_t [\text{Oxyacid}]_0 [\text{QBC}] / 1 + K_t + K_t K_b [\text{oxyacid}]_0 \quad \text{.....(23)}$$

This mechanism leads to the rate law (23), which can be reduced to (10), again acknowledging  $1 \gg K_t$ .

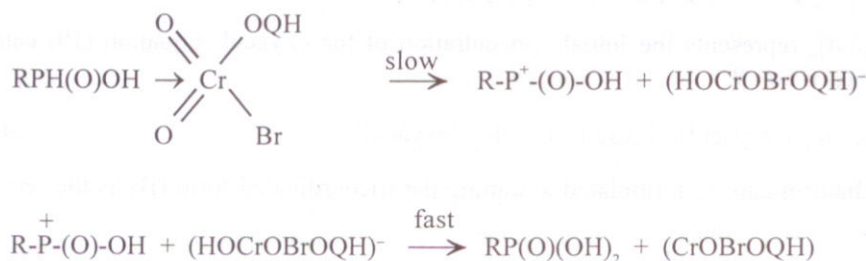
$$\text{Rate} = k_b K_b K_t [\text{Oxyacid}]_0 [\text{QBC}] / 1 + K_t K_b [\text{oxyacid}]_0 \quad \text{.....(24)}$$

Therefore, in the plots of  $1/k_{\text{obs}}$  versus  $1/[\text{oxyacid}]$ , the slope and the intercept are equivalent to the values given-below. Slope  $= (k_b K_b K_t)^{-1}$ , intercept  $= 1/k_b$ , intercept/slope  $= K_b K_t$ .

It is thus seen that  $k_2 = k_a = k_b$  which means that the rate constant for the decomposition of the complex is not affected by the reactive form of the phosphorus oxyacid. However,  $K = K_t K_b$ , so that  $K_b = 10^{-12} K$  or  $K_b$  for PPA should have value of the order of  $10^{12}$ . Generally chromium (VI) does not give rise to extensive and highly stable series of complexes<sup>21</sup>. Further, the reported values<sup>5,22,23</sup> of the formation constant for the chromic acid PPA complexes are  $6.12 \pm 0.3$ ,  $11 \pm 2$  and  $19 \pm 4 \text{ dm}^3 \text{ mol}^{-1}$ . Similarly, the formation constant of complex<sup>24</sup> between triethylamine and Cr (VI) diperoxide derivative is  $0.0014 \text{ dm}^3 \text{ mol}^{-1}$ . Thus the very high value of formation constant of present oxidant - phosphorus oxyacid complex is improbable, and it is highly unlikely that the tricoordinated form is involved in the oxidation process.

## 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<sup>25</sup> is  $460 \text{ kJ mol}^{-1}$ , while that for a P-H bond<sup>26</sup> is  $321 \text{ kJ mol}^{-1}$ . Therefore, a hydride ion mechanism may be proposed for the oxidation of these oxyacids.



Scheme I



The proposed mechanism involving the hydride ion transfer in the rate determining step is also supported by the observed major role of cation-solvating power of the solvents.

It has already been shown that both PFC<sup>27</sup> and PCC<sup>28</sup> act as two electron oxidants and are reduced to chromium (IV) species by determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies

In the chromic acid oxidation of phosphinic acid, Sengupta and Chakaldar<sup>23</sup> postulated the participation of tricoordinated tautomer. However, no evidence has been presented and author did not take into consideration the small value of  $K_t$ . However, Sharma and Mehrotra<sup>22</sup> reported that in the chromic acid oxidation it is not possible to pinpoint the reactive form of the compound. The formation of a phosphinium ion in the rate determining step has been postulated by the earlier workers<sup>22-23</sup>.

It is of interest to compare the mode of oxidation of lower oxyacids of phosphorus by PFC<sup>5</sup>, PCC<sup>6</sup> and QBC. The oxidation by PCC exhibited the second order kinetics, first with respect to each reactant. The oxidation by PFC and QBC presented similar kinetic picture i.e. Michaelis-Menten type of kinetics. The rate-law, acid dependence, kinetic isotope effect are similar in both the cases. In all the three oxidations, excellent correlation were obtained in terms of Swain's equation with the cation solvating power of the solvents playing the major role.

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.

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