# Hydrolysis of Toxic Organophosphorus Esters. The Behaviour of the Perborate Anion

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It has been observed that in the hydrolysis of the organophosphorus esters such as paraoxon 1 and ethyl p-nitrophenylmethylphosphonate (2), by aqueous sodium or phosphonium perborate, it is not possible to obtain a complete understanding of the results obtained if the perhydroxide anion is considered to be the sole nucleophilic reagent. In this work we investigate the possibility of perborate anion participation. We propose a new kinetic expression for this kind of hydrolysis taking into account the effectiveness of the perborate anion as a reactive entity.

In a previous communication [1] we reported that the addition of an equimolecular amount of a phosphonium salt to aqueous sodium perborate (Na^+PB^-) greatly enhances the efficiency of Na^+PB^- as a reagent for oxidative decomposition of organophosphorus esters (OP) such as p-nitrophenyl diethylphosphate (1) or ethyl p-nitrophenylmethylphosphonate (2).

$$(EtO)_2P(O)–OC_6H_4–p-NO_2 \quad (EtO)MeP(O)–OC_6H_4–p-NO_2$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}$$
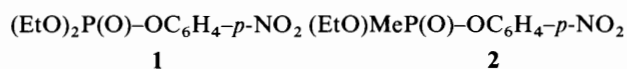
Decomposition of compounds 1 and 2 by nucleophilic anion attack results in the loss of p-nitrophenolate (p-NP), the better leaving group. The liberation of p-nitrophenolate can be monitored by following the change in absorbance at $\lambda = 402$ nm. We observed [1] such decomposition when equimolecular mixtures of sodium perborate and phosphonium salts 3 or ammonium salts 4 were mixed with organophosphorus esters (OP) 1, and 2, at selected experimental conditions as used by Kenley.[2]

$$R^1R^2R^3R^4P^+Br^- \quad R^1R^2R^3R^4N^+Br^-$$
$$\mathbf{3} \qquad\qquad\qquad \mathbf{4}$$
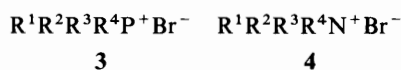
Experimental
Reactions were carried out in CO_2-free solutions (saturated with N_2 and then degassed). Formation of p-nitrophenoxide ions was followed spectrophotometrically at $\lambda = 402$ nm in a Beckman Model DU-40 UV–VIS spectrophotometer equipped with a thermostatted six position cell holder and cell programmer. Temperature control was maintained at 25 ± 0.2 °C by means of a circulating constant-temperature bath. Glass cuvettes of 1 cm pathlength were used throughout; pH readings and adjustments were made by using a potentiometric Metrohm Model E 532.

All kinetic experiments were carried out in water at 25 °C under pseudo-first-order conditions by mixing the substrates 1 or 2 with a large amount of the nucleophilic reactants.[1] Initial concentrations of $[Na^+PB^-]_0$, $[3]_0$ and $[4]_0$ were in at least ten-fold molar excess over the esters 1 or 2. Kinetic solutions also contained the following: 0.1×10^{-3} mol dm^{-3} EDTA; 0.1 mol dm^{-3} sodium borate buffer and KCl added to bring the solution to ionic strength 0.5.

The corresponding values of the rate constant k_{obsd} are provided by the pseudo-first-order kinetic plot of the extinction coefficients A [eqn. (1)] (the subscripts t, 0, α, refer, respectively, to absorbance values taken at time t, taken initially, and taken after a sufficiently long time that (p-NP) liberation had clearly stopped].

$$-\ln[OP]_t/[OP]_0 = -\ln[(A_\alpha - A_t)/ \qquad\qquad (A_\alpha - A_0)] = k_{obsd}\cdot t \quad (1)$$

The pseudo-first-order kinetics of the reaction of Na^+PB^- alone, with different organophosphorus esters is well established, and the participation of the hydroxide and perhydroxide anions as attacking nucleophiles in the hydrolysis of such compounds is expressed [2] in eqn. (2) in which the sodium perborate is assumed to serve as a buffered source of hydrogen peroxide. In this instance, using equimolecular mixtures of Na^+PB^- and 3 or 4, analysis of the variation of k_{obsd} vs. $[PB]_0$ (the initial perborate concentration), shows that the relation is not strictly first-order and therefore not explained by eqn. (2).
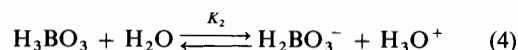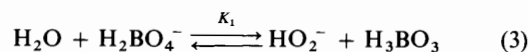
$$-d[OP]/dt = [OP]\cdot\{k_{H_2O}\cdot[H_2O] + [k_{OH}]\cdot[OH^-] + [k_{HO_2}]\cdot[HO_2^-]\} \quad (2)$$

We postulate that under basic conditions the perborate salts give rise to two active nucleophilic entities; perhydroxide anions and perborate anions, which result from the dissociated (into hydrogen peroxide) and undissociated forms of perborate anion respectively.

Little is known of the structure of the perborate anion. According to the results of Carpeni,[3] Hanson [4] and Bougault,[5] this anion appears to behave as tetracoordinated (one hydroxide being a ligand). As a function of the nature of the cation M, the perborate salt may be a pseudo-perborate, or a perborate of general formula: $MBO_3\cdot\frac{1}{2}H_2O$ (e.g. M = K), and $MBO_3\cdot H_2O$ (for example M = Na), respectively. These structures are related to different degrees of cation solvation.
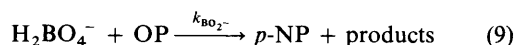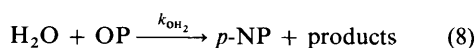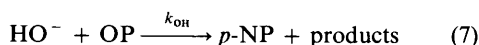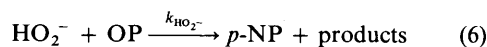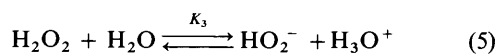
Results and Discussion
In our work [1] reacting equimolecular mixtures of Na^+PB^- and 3 or 4 with the esters 1 and 2 the kinetic data (k_{obsd} vs. $[PB]_0$) obtained are not strictly explained by eqn. (2). We believe that the hydrolysis of the organophosphorus esters under the selected conditions is not adequately described [2] by the eqns. (3)–(8), but also requires consideration of the reaction described by eqn. (9).

$$H_2O + H_2BO_4^- \underset{\qquad}{\overset{K_1}{\rightleftharpoons}} HO_2^- + H_3BO_3 \quad (3)$$

$$H_3BO_3 + H_2O \underset{\qquad}{\overset{K_2}{\rightleftharpoons}} H_2BO_3^- + H_3O^+ \quad (4)$$

Table 1 Variation of the coefficient of dissociation, β, for the perborate anion concentration $[PB]_0$

| pH | $[PB]_0/10^{-3}$ mol dm^{-3} | | | |
	50	25	10	5
8.0	0.78	0.80	0.82	0.84
9.0	0.31	0.32	0.33	0.34
10.0	0.073	0.074	0.075	0.075
10.8	0.043	0.043	0.043	0.043

$$H_2O_2 + H_2O \xrightleftharpoons{K_3} HO_2^- + H_3O^+ \qquad (5)$$

$$HO_2^- + OP \xrightarrow{k_{HO_2^-}} p\text{-NP} + \text{products} \qquad (6)$$

$$HO^- + OP \xrightarrow{k_{OH}} p\text{-NP} + \text{products} \qquad (7)$$

$$H_2O + OP \xrightarrow{k_{OH_2}} p\text{-NP} + \text{products} \qquad (8)$$

$$H_2BO_4^- + OP \xrightarrow{k_{BO_2^-}} p\text{-NP} + \text{products} \qquad (9)$$

So we consider the participation of (i) the solvent (H_2O) whose variation of concentration is negligible, (ii) the hydroxide anion (OH^-) whose variation of concentration is also negligible, since all the reactions are performed in basic conditions in a buffered medium, (iii) the perhydroxide anion (HO_2^-) resulting from the partial dissociation of the perborate and (iv) the undissociated perborate anion ($H_2BO_4^-$).

The contributions of all of these reactions [eqns. (3)–(9)] are taken into account in eqn. (10) which is in best agreement with

$$-d[OP]/dt = [OP]\{k_{H_2O}\cdot[H_2O] + k_{OH}\cdot[OH^-] + \\ k_{HO_2}\cdot[HO_2^-] + k_{BO_2}\cdot[BO_2^-]\} \qquad (10)$$

chemical experiments. According to Kenley,[2] the pseudo-first-order rate constant for the spontaneous hydrolysis of the organophosphorus esters [OP] **1**, or **2** is defined as k_{sp} eqn. (11).

$$k_{sp} = k_{H_2O}\cdot[H_2O] + k_{OH}\cdot[OH^-] \qquad (11)$$

Then eqn. (10) reduces to eqn. (12).

$$-d[OP]/dt = [OP]\cdot\{k_{sp} + k_{HO}\cdot[HO_2^-] + \\ k_{BO_2}\cdot[BO_2^-]\} \qquad (12)$$

$[BO_2^-]$ and $[HO_2^-]$ may be related to $[PB]_0([PB]_0$ and $[PB]$ are the initial perborate concentration and the remaining perborate concentration after dissociation, respectively) by the coefficient of dissociation β of the perborate anion in H_2O [eqn. (13)]; combining eqns. (13) and (14) leads to eqn. (15), and

$$\beta = [HO_2^-] + [H_2O_2]/[PB]_0 = \\ [PB]_0 - [PB]/[PB]_0 \qquad (13)$$

$$K_3 = [HO_2^-][H_3O^+]/[H_2O_2] \qquad (14)$$

$$K_3 = [HO_2^-][H_3O^+]/\beta[PB]_0 - [HO_2^-] \qquad (15)$$

combining eqns. (15) and (13) gives eqn. (16).

$$-d[OP]/dt = [OP]\cdot\{k_{sp} + \beta\cdot k_{HO_2}\cdot[PB]_0\cdot[K_3/(K_3 + \\ [H_3O^+])] + (1 - \beta)k_{BO_2}\cdot[PB]_0\} \qquad (16)$$

With strict control of concentration ($[PB]_0 \gg [OP]_0$), pH (value between 8 and 10.8 using borate buffer), I, and temperature, we can consider the coefficient β to be constant. Therefore $K_3/(K_3 + [H_3O^+])$ is negligible, taking into account

the value of the pK_a of hydrogen peroxide of 11.8. Consequently eqn. (16) becomes eqn. (17).

$$-d[OP]/dt = k_{obsd}\cdot[OP] = \\ k_{sp} + (1 - \beta)\cdot k_{BO_2}\cdot[PB]_0 \qquad (17)$$

Combining the following expressions for the constants K_1, K_2 and K_3, and the previous eqns., we obtain eqn. (18), where C_T is the borate buffer concentration.

$$K_1 = [HO_2^-][H_3BO_3]/[H_2BO_4^-]$$
$$K_2 = [H_2BO_3^-][H_3O^+]/[H_3BO_3]$$
$$K_3 = [HO_2^-][H_3O]/[H_2O_2]$$
$$\therefore K_2 = (C_T + \beta\cdot[PB]_0 - [H_3BO_3])\cdot[H_3O^+]/ \\ [H_3BO_3] \qquad (18)$$

The boric acid concentration $[H_3BO_3]$ is a function of C_T and β as indicated in eqns. (19) and (20).

$$[H_3BO_3] + [H_2BO_3^-] = C_T + \beta\cdot[PB]_0 \qquad (19)$$
$$[H_3BO_3] = [H_3O+]\cdot(C_T + \beta\cdot[PB]_0)/ \\ [H_3O^+] + K_2 \qquad (20)$$

Combining these eqns. gives rise to the expression [eqn. (21)] for the constant K_1, which may be written as a quadratic expression in β [eqn. (22)].

$$K_1 = [H_3O^+]\cdot(C_T + \beta\cdot[PB]_0)\cdot(K_3\cdot\beta\cdot[PB]_0)/ \\ ([H_3O^+] + K_2)\cdot(K_3 + [H_3O^+])\cdot(1 - \beta)\cdot[PB]_0 \qquad (21)$$

$$\beta^2\cdot\{K_3\cdot[H_3O^+]\cdot[PB]_0\} + \beta\cdot[K_1K_2K_3 + \\ K_1(K_2 + K_3) + K_3C_T]\cdot\{[H_3O^+] + K_1\cdot[H_3O^+]^2\} - \\ \{K_1K_2K_3 + K_1(K_2 + K_3)[H_3O^+] + \\ K_1[H_3O^+]^2\} = 0 \qquad (22)$$

On the basis of the literature values[2] for the constants K_1, K_2 and K_3, which are 1.2×10^{-4}, 6.6×10^{-11} and 2.5×10^{-12} mol dm^{-3} respectively, and at a concentration $C_T = 0.1$ mol dm^{-3} we obtain, at different pH values, the following relations [eqns. (23)–(26)].

$$\text{pH 8: } 2.5\ [PB]_0\beta^2 + 1.458\beta - 1.208 = 0 \qquad (23)$$

$$\text{pH 9: } 25\ [PB]_0\beta^2 + 3.782\beta - 1.282 = 0 \qquad (24)$$

$$\text{pH 10: } 25\ [PB]_0\beta^2 + 2.704\beta - 0.204 = 0 \qquad (25)$$

$$\text{pH 10.8: } 39.62\ [PB]_0\beta^2 + 4.142\beta - 0.180 = 0 \qquad (26)$$

The solution of these equations gives the positive values for β reported in Table 1.

In a comparison of hydroxide and perhydroxide anion activities towards organophosphorus esters **1** or **2**, Kenley[2] points out that the extraordinary reactivity exhibited by the perhydroxide anion confirms it to be a 'super' or 'α-effect' nucleophile. The perborate anion should display a greater 'α-effect' than the perhydroxide anion as a result of the respective electronegativities of the hydrogen and boron atoms: $\chi_H = 2.1$ and $\chi_B = 1.8$. This may be reflected in the rate constant $k_{H_2BO_4}$, and will be examined below.

Figs. 1 and 2 are kinetic plots for various $[PB]_0$ obtained by mixing, in equimolecular proportions, Na^+PB^- and salts **3** or **4** with ester **1** and **2**, respectively.

At this point in the discussion it is possible to rationalise the difference in the shapes of the plots k_{obsd} vs. $[PB]_0$ obtained[2] using Na^+PB^- alone, or in presence of the salts **3** or **4**. This is
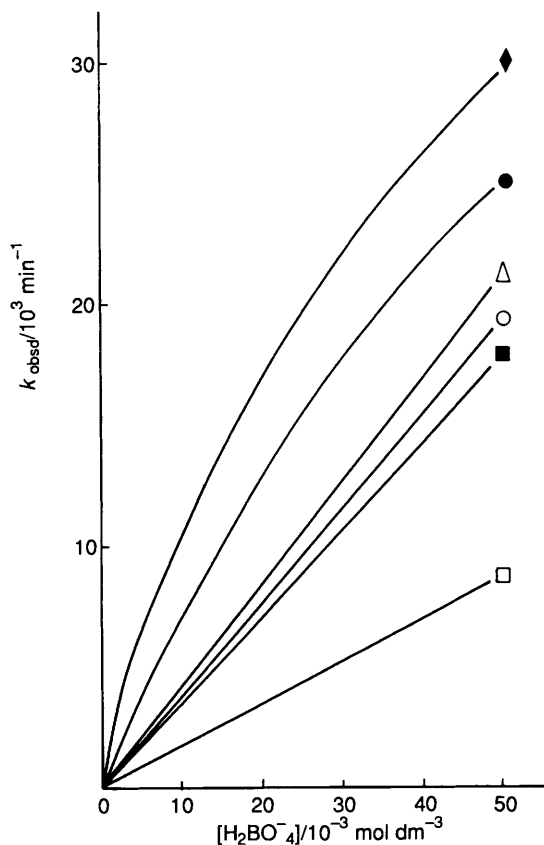
Fig. 1 Pseudo-first-order kinetic plot of $k_{obsd} = \ln[(A_\alpha - A_t)/A_\alpha - A_0)]$ vs. initial concentration of perborate anion $[PB]_0 = [H_2BO_4]_0$, for the production of p-nitrophenolate from the reaction of mixture of sodium perborate Na^+PB^- and onium salts **3** or **4**, with ester **1** at 25 °C, pH 10, and $I = 0.5$. $\square = Na^+PB^- + 3$ ($R^1 = R^2 = R^3 = Ph_3P$, $R^4 = CH_2CH_2CO_2H$); $\blacksquare = Na^+PB^-$; $\bigcirc = Na^+PB^- + 3$ ($R^1 = R^2 = R^3 = Ph_3P$, $R^4 = CH_3$); $\triangle = Na^+PB^- + 4$ ($R^1 = R^2 = R^3 = Me_3$, $R^4 = $ cetyl); $\bullet = Na^+PB^- + 3$ ($R^1 = R^2 = R^3 = Bu^n_3$, $R^4 = $ cetyl); $\blacklozenge = Na^+PB^- + 3$ ($R^1 = R^2 = R^3 = Ph_3P$, $R^4 = $ cetyl).

achieved by comparison of the two expressions established for k_{obsd}.

In this work,

$$k_{obsd} = k_{sp} + (1 - \beta) \cdot k_{BO_2} \cdot [PB]_0 \qquad (17)$$

where the β value depends not only on the borate buffer concentration and the pH value but also on the initial concentration $[PB]_0$. In all the cases investigated by Kenley,

$$k_{obsd} = k_{sp} + k_{HO_2} \cdot \alpha \cdot [PB]_0(K_2/K_2 + [H^+]) \qquad (27)$$

At any pH within the range 8–10.8, attained using a borate buffer, this eqn. (27) becomes $k_{obsd} = k_{sp} + \text{constant} \cdot [PB]_0$, giving a linear dependence of k_{obsd} on $[PB]_0$. The plots of k_{obsd} vs. $[PB]_0$ shown in Fig. 1 are nearly straight lines and clearly different from those drawn in Fig. 2. This behaviour is explained by the values for β shown in Table 1. Fig. 2 shows the kinetic plots for the borate-buffered ($C_T = 0.10$ mol dm^{-3}) hydrolysis of ethyl p-nitrophenylmethylphosphonate **2** conducted at pH 8. The non-linear shape of the plots k_{obsd} vs. $[PB]_0$ is in good agreement with the effectively greater influence of $[PB]_0$ variations on the β values.

In this case we can express the rate constant for the ester **2** according to eqns. (17) and (25) as follows:

$$k_{obsd} = k_{sp} + 0.29 \cdot k_{H_2BO_4} + \tfrac{1}{5} \cdot (2.126 +$$
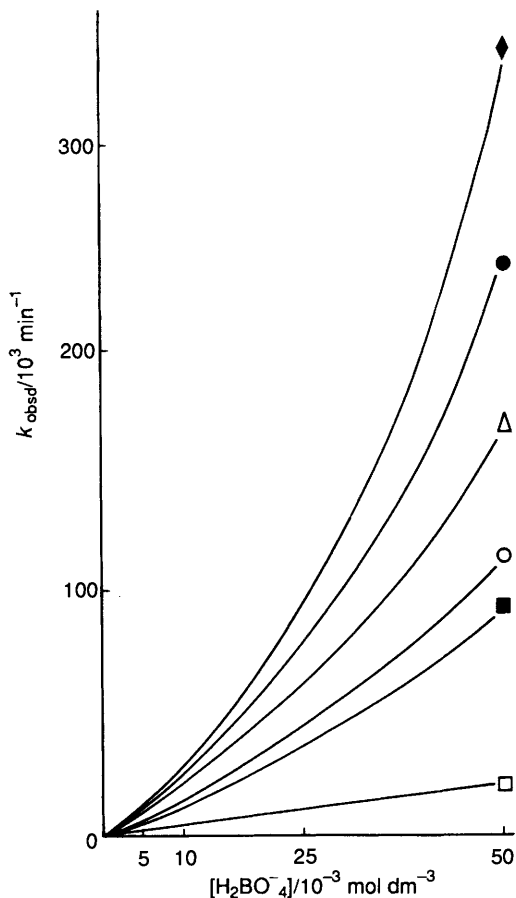$$12.08 \cdot [PB]_0)^{\frac{1}{2}} k_{H_2BO_4} + k_{H_2BO_4} \cdot [PB]_0 \qquad (28)$$

Fig. 2 Pseudo-first-order plot of $K_{obsd} = -\ln[(A_\alpha - A_t)/A_\alpha - A_0)]$ vs. initial concentration of perborate anion $[PB]_0 = [H_2BO_4]$, for the production of p-nitrophenolate from the reaction of mixture of sodium perborate Na^+PB^- and onium salts **3** or **4**, with ester **2** at 25 °C, pH 8, and $I = 0.5$. $\square = Na^+PB^- + 3$ ($R^1 = R^2 = R^3 = Ph_3P$, $R^4 = CH_2CH_2CO_2H$); $\blacksquare = Na^+PB^-$; $\bigcirc = Na^+PB^- + 3$ ($R^1 = R^2 = R^3 = Ph_3P$, $R^4 = CH_3$); $\triangle = Na^+PB^- + 4$ ($R^1 = R^2 = R^3 = Me_3$, $R^4 = $ cetyl); $\bullet = Na^+PB^- + 3$ ($R^1 = R^2 = R^3 = Bu^n_3$, $R^4 = $ cetyl); $\blacklozenge = Na^+PB^- + 3$ ($R^1 = R^2 = R^3 = Ph_3P$, $R^4 = $ cetyl).

If we define Y and X as:

$$Y = k_{obsd} \text{ and } X = (2.126 + 12.08 \cdot [PB]_0)^{\frac{1}{2}}$$

then eqn. (28) becomes:

$$Y = k_{sp} + 0.29 \cdot K_{H_2BO_4} + (X/5) \cdot k_{H_2BO_4} +$$
$$(X^2 - 2.126)/12.08) \cdot k_{H_2BO_4} \qquad (29)$$

Then, eqn. (29) reduces to (30).

$$Y = aX^2 + bX + c \qquad (30)$$

with $a = k_{H_2BO_4}/12.08$, $b = -k_{H_2BO_4}/5$ and $c = k_{sp} + 0.1156 \cdot K_{H_2BO_4}$.

The mathematical form of eqn. (30) is in good agreement with the shape of the plots presented in Fig. 2, and this result demonstrates the validity of our assumption concerning the participation of perborate anions as nucleophilic reagents in the oxidative decomposition of this kind of ester (OP). On the other hand, Fig. 1 shows kinetic plots for paraoxon **1** at pH 10, in the presence of a borate buffer, ($C_T = 0.10$ mol dm^{-3}). Under these conditions the values of β are small and nearly identical in the range of $[PB]_0$ studied.

In the same manner for ester **1** we obtain eqn. (31) which is in

Table 2 k_{BO_2} values calculated from the value of (a') determined by regression analysis assimilating the representative curve of the paraoxon **1** hydrolysis [at pH = 10(borate 0.1 mol dm^{-3}) and $I = 0.5$ M(KCl)] by equimolecular solutions of sodium perborate and organic bromides Q^+Br^-] to a second-order equation $Y' = a'X'^2 + b'X' + c'$

Q^+	Coefficient a'	$k_{BO_2}/10^3$ dm^3 mol^{-1} min^{-1}	$k_{sp}/10^3$ dm^3 mol^{-1} min^{-1}
Na$^+$	0.124 ± 0.0015	253 ± 32	0.73 ± 0.42
Ph$_3$P$^+$Me	0.0123 ± 0.0023	251 ± 47	0.84 ± 0.51
Bu$^n_4$P$^+$	0.0176 ± 0.0005	360 ± 12	0.53 ± 0.21
Ph$_3$P$^+$C$_{16}$H$_{33}$	0.0306 ± 0.0049	624 ± 99	0.48 ± 0.42
Bu$^n_3$P$^+$C$_{16}$H$_{33}$	0.0172 ± 0.0032	350 ± 66	1.04 ± 0.65
Ph$_3$P$^+$CH$_2$CH$_2$CO$_2$H	0.0018 ± 0.0005	38 ± 13	0.78 ± 0.33
Ph$_3$P$^+$(CH$_2$)$_3$P$^+$Ph$_3$	0.0220 ± 0.0079	449 ± 161	0.92 ± 0.85
Bu$^n_4$N$^+$	0.0125 ± 0.0028	254 ± 56	0.83 ± 0.52
Me$_3$N$^+$C$_{16}$H$_{33}$	0.0216 ± 0.0029	441 ± 58	0.41 ± 0.38

Table 3 k_{BO_2} values calculated from the value of (a) determined by regression analysis assimilating the representative curve of the methylphosphonate **2** hydrolysis [at pH 8 (borate 0.1 mol dm^{-3}) and $I = 0.5$ mol dm^{-3} (KCl) by equimolecular solutions of sodium perborate and organic bromides Q^+Br^-] to a second-order equation $Y = aX^2 + bX + c$

Q^+	Coefficient a	$k_{BO_2}/10^3$ dm^3 mol^{-1} min^{-1}
Na$^+$	0.220 ± 0.017	2 665 ± 211
Ph$_3$P$^+$Me	0.300 ± 0.038	3 628 ± 467
Bu$^n_4$P$^+$	0.218 ± 0.056	2 642 ± 678
Ph$_3$P$^+$C$_{16}$H$_{33}$	0.908 ± 0.140	10 977 ± 169
Bu$^n_3$P$^+$C$_{16}$H$_{33}$	0.672 ± 0.113	8 116 ± 136
Ph$_3$P$^+$CH$_2$CH$_2$CO$_2$H	0.023 ± 0.001	281 ± 6
Ph$_3$P$^+$(CH$_2$)$_3$P$^+$Ph$_3$	0.402 ± 0.029	4 856 ± 351
Bu$^n_4$N$^+$	0.239 ± 0.007	2 890 ± 86
Me$_3$N$^+$C$_{16}$H$_{33}$	0.443 ± 0.049	5 357 ± 593

good agreement with the experimental data, for the reactions carried out under these conditions (Fig. 1).

$$Y' = a'X'^2 + b'X' + c' \tag{31}$$

With $Y' = k_{obsd}$, $X' = (7.312 + 20.4 \text{ [PB]}_0)^{\frac{1}{2}}$ and $a' = k_{H_2BO_4}/20.5$, $b' = -k_{H_2BO_4}/50$, $c' = k_{sp} - 0.3043 k_{H_2BO_4}$.

Finally we wished to evaluate $k_{H_2BO_4}$. It can be determined from eqns. (30) and (31) and from the plots in Figs. 2 and 1, respectively.

These plots are reproduced by computer simulations confirming the second-order relation for k_{obsd} *vs.* [H$_2$BO$_4^-$], that can be expressed by the general quadratic form: $Y =$

Table 4 Second-order rate constants $(K_{Nu}/10^3$ dm^3 mol^{-1} min$^{-1})$ for the hydrolysis of organophosphorus esters **1** and **2** by the nucleophilic reagents NaOH, HOOH and NaH$_2$BO$_4$

Ester	K_{OH}	K_{HO_2}	K_{BO_2}
1	1.04 ± 0.004[a]	83 ± 30[a]	382 ± 18
2	70.5 ± 4.8	2500 ± 640	2665 ± 211

[a] Ref. 2.

$aX^2 + bX + c$. The values of the constants a, b and c, obtained by regression analysis provide the values for $k_{H_2BO_4}$ reported in Tables 2 and 3, and corrected respectively to the parameters of the hydrolysis of the paraoxon **1** by equimolecular aqueous solutions of Na$^+$PB$^-$ and **3** or **4** in given conditions (pH 10, borate buffer $C_T = 0.1$ mol dm^{-3}, $I = 0.5$) and the second table correspond to the hydrolysis of the ester **2** by equimolecular aqueous solutions of Na$^+$PB$^-$ and **3** or **4** in given conditions (pH 8, borate buffer $C_T = 0.1$ mol dm^{-3}, $I = 0.5$).

The dependence of the kinetic rate constants on the nature of the phosphonium or ammonium perborate entities for the reactions examined is strongly indicated by the variation of the collected $k_{H_2BO_4}$ values.

In conclusion, all the results obtained point to the influence of the perborate anion on the kinetic rate constants, for the hydrolysis of organophosphorus esters **1** and **2**. The comparison of the $k_{H_2BO_4}$ and k_{HO_2} values given in Table 4, confirms the greater 'α' effect of a boron atom compared to a hydrogen atom. Thus, the important observations of Kenley and collaborators[2] who demonstrated that aqueous solutions of sodium perborate afford substantial enhancements in rates of decomposition of organophosphorus esters relative to rates of alkaline hydrolysis by OH$^-$, result from the activities of the perhydroxide and the perborate anions as nucleophiles. In addition we have shown that a further increase in the rate of the decomposition of phosphorated esters may be achieved by including quaternary ammonium or phosphonium salts in the reaction mixture.

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