Heteroatom Chemistry
Volume 1, Number 4, 1990

Toxic Organophosphorus Esters Hydrolysis Enhanced by Onium Perborates

Henri-Jean Cristau,* Eliane Torreilles,* and Jean-François Ginieys

U.A. 458, Laboratoire de Chimie Organique, E.N.S.C.M., 8 Rue de l'Ecole Normale, 34075 Montpellier, France

Received 27 November 1989

ABSTRACT

The addition of equimolecular quantities of phosphonium salts to an aqueous sodium perborate solution (Na^+PB^-) greatly enhances the efficiency of Na^+PB^- as a reagent that destroys organophosphorus esters, such as p*-nitrophenyldiethyl phosphate or ethyl* p*-nitrophenyl methylphosphonate.*

INTRODUCTION

In an investigation of methods for the destruction of wastes containing hazardous phosphorus esters, we have found that aqueous organic cation perborates decompose organophosphorus esters more completely than does aqueous sodium perborate.

Kenley et al. [1] recently evaluated the different reagents used as potent nucleophiles in the dephosphorylation of *p*-nitrophenyl phosphoric and phosphinic esters. They found that aqueous sodium perborate, Na^+PB^-, functions as the perhydroxyl anion, and appears to be the effective dephosphorylating agent [2].

We are studying the use of phosphonium salts as reagents in organic synthesis [3], and we are exploring the possible reactivity of some phosphonium perborates. We are investigating the real efficiency of the perborate anion as a reactive nucleophile and the effect of the nature of the phosphonium ion on its reactivity. We have chosen two phosphorus esters $RPO(OC_2H_5)OC_6H_4NO_2$, $R = OC_2H_5$ (**1**), and $R = CH_3$ (**2**).

In the literature, the preparations of inorganic perborate salts are given [4], but syntheses of organic perborate salts **3** have not been described. Taking into account the possibility that pure compounds of type **3** may be dangerous to handle, we have used mixtures of equimolecular amounts of Na^+PB^- and a phosphonium bromide **4** or an ammonium bromide **5** for comparison. In water, all these salts are dissolved and dissociated; the solutions probably contain some amount of organic cation-perborate anion intimate pairs.

EXPERIMENTAL

Materials

The preparation and purification of the substrates **1** [4, 5] and **2** [1] have been described. The phosphonium and ammonium salts used in these studies are listed in Table 1. Triphenyl 2-carboxyethyl phosphonium bromide **4e** [6] and 1,3-trimethylenebis(triphenylphosphonium) dibromide **4f** [7] were prepared according to the literature. The other salts were obtained from commercial sources and were used without further purification. Water for kinetic experiments was distilled twice. Freshly prepared solutions were used in all experiments. The acetonitrile was distilled. ^{31}P-NMR spectra were taken at 80 MHz on a Bruker WP 80.

The determination of the saturation concentration of the PB^- anion in the presence of each of the substrates **4** or **5** relies on the basic physical and chemical measurements that are used for the determination of solubility in general [8]. The obtained solubility data are given in Table 1. In the different media used, the stability of the phosphonium salts is monitored by ^{31}P-NMR spectroscopy.

---

*To whom correspondence should be addressed.

1042-7163/90/$3.50 + .25

TABLE 1 Na^+PB^- solubility in H_2O, at 25°C, in the presence of phosphonium or ammonium salts Y^+Br^-.

Salt		*Sol. [8]*	*Salt*		*Sol. [8]*
Y^+Br^-	*Y^+*	*mol/l*[a]	*Y^+Br^-*	*Y^+*	*mol/L*[a]
	Na^+	0.220 (2)	**4e**	$Ph_3P^+(CH_2)_2CO_2H$	0.440 (15)
4a	Ph_3P^+Me	0.160 (4)	**4f**	$Ph_3P^+(CH_2)_3P^+Ph_3Br^-$	0.180 (7)
4b	nBu_4P^+	0.120 (4)	**5a**	nBu_4N^+	0.130 (<2)
4c	$Ph_3P^+C_{16}H_{33}$	0.205 (8)	**5b**	$Me_3N^+C_{16}H_{33}$	0.130 (<2)
4d	$nBu_3P^+C_{16}H_{33}$	0.180 (2)			

[a] Number in parentheses indicates half time of Na^+PB^- dissolution in minutes [8].

Kinetics

Reactions were carried out in CO_2-free solutions saturated with N_2 and then degassed. Formation of *p*-nitrophenoxide ion was followed spectrophotometrically at 402 nm by use of a DU-40 Beckman Model UV-visible spectrophotometer equipped with a thermostated 6 positions cell holder and cell programmer. Temperature control was maintained at 25°C ± 0.2°C with a circulating constant temperature bath. One cm pathlength glass cuvettes were used throughout. Readings of pH and adjustments were made by use of a potentiometric Metrohm Model E-532 meter.

Methods

All experiments were carried out as recommended by Kenley [1]. The dephosphorylation of substrates **1** and **2** were conducted in aqueous solution with Na^+PB^- present in at least a 10-fold molar excess over each substrate. Na^+PB^- and salts **4** or **5** are used in equimolecular amounts. Kinetic solutions contained 0.1 mM EDTA, 0.1 M sodium borate buffer, and KCl, which were added to bring the solution to an ionic strength of 0.5 M. The reactions were followed as realized by Kenley [1]. The *p*-nitrophenolate (*p*NP) anion production was monitored at 402 nm and was quantitated by use of extinction coefficients that were experimentally determined for each reaction medium. The fraction of reactant converted to product was given by the ratio $(A_\infty - A_t)/(A_\infty - A_0)$, where the subscripts *t*, 0, and ∞ refer, respectively, to absorbance values taken at time *t*, taken initially, and taken at long reaction times when *p*-nitrophenolate anion liberation had clearly stopped.

RESULTS AND DISCUSSION

The homogeneity and the stability of solutions $(Na^+PB^- + \mathbf{4})$ and $(Na^+PB^- + \mathbf{5})$ were tested by different control experiments.

The aqueous kinetic solutions contain equimolecular quantities of Na^+PB^- and either phosphonium salts **4** or ammonium salts **5** at a concentration of 0 to 50 mmol/l; bromides **4c** and **4d** needed the addition of EtOH (25% in vol.) to obtain homogeneous solutions. There are no modifications in the ^{31}P NMR spectra of most of these solutions over a 2-day period. Anion chromatography shows the absence of BrO_3^-. This verifies that in all the kinetic mixtures used during a 7-day period of observation Br^- is not oxidized. Less than 4% peroxide is lost over a 24 h period at 25°C, pH = 10. The diminution of the Na^+PB^- solubility in the presence of compounds **4** or **5** (Table 1) cannot be attributed to a salt effect but is probably a consequence of the counterion nature (phosphonium and ammonium). The addition of Na^+Br^- does not change the Na^+PB^- solubility.

Without going into a discussion of the mechanism of nucleophilic substitution of the leaving group (*p*-nitrophenolate, *p*NP) of the organic phosphorus esters (OP), **1** or **2**, we can regard the cleavage of the P—O bond as a monomolecular reaction.

In all cases $[Na^+PB^-]_0 >> [OP]_0 = 2.10^5$ mol/l, so pseudo-first-order kinetics are computed according to Equations (1)–(3) [1].

$$-d[OP]/dt = (ks[H_2O] + k_{OH}[OH^-] + k_{HOO}[HOO^-])\,[OP] \qquad (1)$$

$$-\ln[OP]_t/[OP]_0 = k_{obsd} \cdot t \qquad (2)$$

$$-\ln(A_\infty - A_t)/(A_\infty - A_0) = k_{obsd} \cdot t \qquad (3)$$

For the esters **1** and **2** at a given pH, a plot of $-\ln(A_\infty - A_t)/(A_\infty - A_0)$ versus *t* is impracticable because of the lack of precision in the A_∞ determination. Consequently, we chose Guggenheim's method, as expressed in Equation (4).

$$A = a\,e^{-k \cdot t} + b \qquad (4)$$

with *a*,*b* coming from Equation (5), which expresses the linear relation between [*p*NP] and the absorbance *A*, α and β being constants.

$$A = \alpha\,[pNP] + \beta \qquad (5)$$

Because the kinetic reactions being studied are of the pseudo-first-order type, we can take into account the exponential relationship between [*p*NP] and time *t* and relate A_t values and time *t* as in Equation (6).

$$\ln(A_{t+\Delta t} - A_t) = k \cdot t + c \qquad (6)$$

Therefore a plot of $\ln(A_{t+\Delta t})$ versus t should be linear with k_{obsd} as the slope.

Tables 2 and 3 list the kinetic rate constants obtained for **1** at pH = 10 and for **2** at pH = 8. These kinetic data indicate that organic cation perborates enhance the decomposition rate of organophosphorus esters in comparison to sodium perborate hydrolysis rates. This effect is more accentuated for the ester **2**. The hydrolysis rate of **1** is significantly affected by the nature of the counterion R_4P^+ or R_4N^+. Maximum rate enhancements are found when one substituent R is a normal alkyl chain with a length of sixteen carbon atoms. We note a decrease with the introduction of a polar group as in compound **4e**. Similar results are obtained in the hydrolysis of ester **2**.

Table 4 shows the pH dependence of k_{obsd} for reactions of **1** at the given ionic strength I = 0.5 mol/l (KCl) and the buffer borate concentration at 0.1 mol/l. In the range of pH values investigated (8.0–10.8), it can be seen that for all equimolecular mixtures (Na^+PB^- + **4** or **5**) tested, the hydrolysis rate of ester **1** is greatly accelerated when the basicity of the medium is increased.

Furthermore, the pseudo-first-order rate constants listed in Table 4, show that, at any pH, the nature of the organic counterion of **4** or **5** significantly influences the rate of hydrolysis of **1** when the reaction is carried out in borate buffer at a given concentration (0.1 M). As indicated in Table 5, the buffer concentration changes also affect the rate of *p*-nitrophenoxide ion formation in the hydrolysis of **2**. We can observe that the decrease of borate buffer concentration causes an increase in the reaction rate and that, at any concentration value, the onium nature of compounds **4** and **5** also has an important effect.

When sodium perborate is used alone, our data and literature values (1) are in agreement. We can conclude that Na^+PB^- reactivity depends on the

TABLE 2 Kinetic rate constants (k_{obsd}) for the Paraoxon **1**. Reactions with equimolecular mixtures of Na^+PB^- and Y^+Br^- **4** or **5**.

	$k_{obsd} \times 10^3\ min^{-1}$ *at equimolecular concentrations*			
Y^+Br^-	*50 mM*	*25 mM*	*10 mM*	*5 mM*
Na^+Br^-	18.0 ± 0.4	10.40 ± 0.50	4.57 ± 0.04	2.51 ± 0.03
4a	18.7 ± 0.3	11.08 ± 0.09	4.64 ± 0.06	2.83 ± 0.11
4b	21.0 ± 2.0	11.06 ± 0.10	4.80 ± 0.34	2.83 ± 0.04
4c	30.2 ± 0.9	19.30 ± 0.10	8.80 ± 0.20	4.26 ± 0.16
4d	25.7 ± 0.9	15.20 ± 0.10	6.39 ± 0.81	3.63 ± 0.23
4e	6.8 ± 0.2	4.21 ± 0.03	2.49 ± 0.03	1.61 ± 0.02
4f	25.0 ± 0.3	11.09 ± 0.10	6.34 ± 0.10	4.45 ± 0.04
5a	18.7 ± 0.2	11.13 ± 0.09	4.48 ± 0.11	2.93 ± 0.09
5b	25.0 ± 0.4	13.76 ± 0.09	5.12 ± 0.32	3.02 ± 0.03

Conditions: pH = 10 (borate buffer 0.1 M) and I = 0.5 M (KCl); when $H_2BO_4^-$ = 0.0 k_{obsd} = 0.102 ± 0.003 × 10^{-3} min^{-1}.

TABLE 3 Kinetic rate constants (k_{obsd}) for the methyl phosphonate **2**. Reactions with equimolecular mixtures of Na^+PB^- and Y^+Br^- salts **4** or **5**.

	$k_{obsd} \times 10^3\ min^{-1}$ *at equimolecular concentrations*			
Y^+Br^-	*50 mM*	*25 mM*	*10 mM*	*5 mM*
Na^+Br^-	91 ± 4	35 ± 1	10.0 ± 0.5	4.09 ± 0.10
4a	115 ± 3	39 ± 1	11.0 ± 0.3	4.27 ± 0.06
4b	106 ± 2	57 ± 1	10.1 ± 0.3	4.08 ± 0.07
4c	325 ± 4	98 ± 2	25.2 ± 0.4	7.65 ± 0.16
4d	234 ± 8	67 ± 1	15.8 ± 0.4	5.93 ± 0.19
4e	19 ± 1	11 ± 1	5.1 ± 0.1	3.03 ± 0.03
4f	152 ± 4	55 ± 1	11.1 ± 0.1	3.84 ± 0.04
5a	102 ± 2	42 ± 1	11.2 ± 0.6	3.98 ± 0.05
5b	170 ± 7	59 ± 2	15.5 ± 0.2	5.60 ± 0.21

Conditions: pH = 8 (borate buffer 0.1 M) and I = 0.5 M (KCl). When $H_2BO_4^-$ = 0.0. k_{obsd} = 0.42 ± 0.04 × 10^{-3} min^{-1}.

TABLE 4 pH Dependence of pseudo-first-order rate constants (k_{obsd}) for 50 mM. Reactions with Paraoxon **1** at I = 0.5 M (KCl) and borate buffer (0.1 M).

	$k_{obsd} \times 10^3\ min^{-1}$ at various pH values			
Y^+Br^-	8.00 ± 0.02	9.00 ± 0.02	10.0 ± 0.02	10.8 ± 0.02
Na^+Br^-	4.81 ± 0.39	5.55 ± 0.04	18.0 ± 0.4	64 ± 1
4a	4.61 ± 0.10	5.42 ± 0.06	18.7 ± 0.3	65 ± 1
4b	4.65 ± 0.09	6.93 ± 0.08	21.0 ± 2.0	62 ± 1
4c	7.23 ± 0.42	8.30 ± 0.12	25.7 ± 0.9	94 ± 1
5a	4.31 ± 0.14	5.30 ± 0.03	18.7 ± 0.2	61 ± 1
5b	5.46 ± 0.22	5.99 ± 0.04	25.0 ± 0.4	92 ± 1

TABLE 5 Borate buffer concentration dependence of pseudo-first-order rate constants (k_{obsd}) for Na^+PB^- + Y^+Br^- equimolecular mixtures = 10 mM. Reactions with the methyl phosphonate **2** at pH = 9 and I = 0.5 M (KCl).

	$k_{obsd} \times 10^3\ min^{-1}$ at borate buffer concentration				
Y^+Br^-	0.1 M	0.05 M	0.025 M	0.01 M	0.005 M
Na^+Br^-	39.1 ± 0.9	55.3 ± 0.9	89 ± 1	149 ± 3	166 ± 8
4a	33.9 ± 1.0	60.0 ± 1.0	84 ± 1	128 ± 2	110 ± 4
4b	44.4 ± 0.7	54.0 ± 0.4	99 ± 2	126 ± 2	220 ± 10
4c	76.0 ± 2.0	94.0 ± 4.0	171 ± 9	185 ± 4	199 ± 11
5a	40.0 ± 0.5	61.8 ± 0.8	106 ± 5	119 ± 3	166 ± 5
5b	73.0 ± 2.0	91.0 ± 2.0	134 ± 6	151 ± 9	275 ± 16

pH of the reaction medium and the concentration of borate. However, in our systems (Na^+PB^- + **4** or **5**) the great influence of the cation nature of **4** or **5** is well demonstrated. These supplementary effects give rise to the question of whether the cleavage of the P—OAr bond in the types **1** and **2** organophosphorus esters are occurring only by the nucleophilic attack of the HOO^- present in the medium or also by another reactive species, the undissociated perborate anion. We are currently studying this last point of view and the possible use of this onium salt as a micellar catalyst.

REFERENCES AND NOTES

[1] R. A. Kenley, G. C. Lee, J. S. Winterle, *J. Org. Chem.*, *50*, 1985, 40.

[2] L. Horner, A. Parg, *Liebigs Ann. Chem.* 1977, 61.

[3] H. J. Cristau, E. Torreilles, P. Morand, H. Christol, *Phosphorus and Sulfur*, *25*, 1985, 357. H. J. Cristau, E. Torreilles, P. Morand, H. Christol, *Tetrahedron Letters*, *27*, 1986, 177. H. J. Cristau, A. Bazbouz, P. Morand, E. Torreilles, *Tetrahedron Letters*, *27*, 1986, 2965.

[4] H. McCombie, B. C. Saunders, G. J. Stracey, *J. Chem. Soc.*, 1945, 380.

[5] G. W. Kenne, N. R. Williams, *J. Chem. Soc.*, 1955, 522.

[6] H. Hoffman, *Chem. Ber.*, *94*, 1961, 1331.

[7] L. Horner, H. Hoffmann, W. Klink, H. Ertel, V. G. Toscano, *Chem. Ber. 95*, 1962, 581.

[8] 25 mL of distilled water are added to mixture of powdered solids: $Na^+PB^- \cdot 4\ H_2O$ (1.6153 g, 0.0105 mol.) and salt **4** or **5** in equimolecular quantities. At time *t*, the stirring is started and periodic prelevements are carried out and analysed.

[9] K. J. Laidler: *Chemical Kinetics*, McGraw-Hill, New York, 1950.