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Organophosphorus Ester Reactions with Aqueous Sodium Perborate

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We investigated the decomposition kinetics of four organophosphorus (OP) esters dissolved in aqueous sodium perborate. The esters conformed to the general structure $R_1R_2P(O)OC_6H_4NO_2$ where $R_1, R_2 = C_2H_5O, C_2H_5O$, $R_1, R_2 = C_2H_5O, CH_3$, $R_1, R_2 = C_2H_5, C_2H_5$, and $R_1, R_2 = HO, CH_3$. The decomposition reactions were studied as a function of pH (8–12), temperature (290–320 K), perborate concentration (0–50 mM), buffer type (borate vs. phosphate), and buffer strength (5–100 mM borate). We find that sodium perborate greatly accelerates OP ester decomposition and that the reactions are best described by perhydroxyl ion (which is in equilibrium with perborate) undergoing nucleophilic attack on phosphorus. At 300 K, calculated bimolecular rate constants (M^{-1} min^{-1}) for perhydroxyl attack are 83 ($R_1, R_2 = C_2H_5O, C_2H_5O$), 2500 ($R_1, R_2 = C_2H_5O, CH_3$), 8300 ($R_1, R_2 = C_2H_5, C_2H_5$), and 0.12 ($R_1, R_2 = HO, CH_3$). Overall decomposition kinetics depend on the following equilibria: H_2O_2/HO_2^-; $B(OH)_3/B(OH)_4^-$; $HO_2B(OH)_3^-/B(OH)_3$. These studies illustrate the potential utility of sodium perborate for decontaminating hazardous organophosphorus wastes.

Introduction

Organophosphorus ester reaction mechanisms have evoked considerable attention because many of these reactions play a central role in biological chemistry.[1] In a more mundane context, organophosphorus esters find widespread application in agriculture for pest control[2] and in warfare as casualty agents.[3] In this practical context, interest remains high in developing new and better methods for destroying hazardous organophosphorus ester wastes. The search for effective organophosphorus ester decontaminants has largely focused on potent nucleophiles that rapidly attack tetrahedral phosphorus. Examples include hypochlorite anion[4,5] and various hydroxylamine derivatives.[1,6-10] Early work[10-15] demonstrated the enormously high reactivity of the perhydroxyl anion toward phosphorus esters, but hydrogen peroxide never achieved acceptance as a large-scale decontaminating agent. Presumably, the poor storage stability of hydrogen peroxide solutions has limited their practical application for destroying hazardous wastes.

However, a possible alternative to hydrogen peroxide solutions exists, namely sodium perborate, $Na^+HO_2B(OH)_3^-$ (PB). As the tetrahydrate, sodium PB is a storage-stable powder used industrially as a bleaching agent.[16] In alkaline aqueous solution, PB equilibrates with borate and perhydroxyl anion[17] thus raising the obvious possibility that such solutions might effectively destroy organophosphorus esters.

Surprisingly, the literature does not report reaction kinetics of aqueous sodium perborate solutions toward organophosphorus esters. Given the absence of published kinetic evidence and the likely usefulness of PB as a decontaminating agent, we have undertaken to directly determine rate constants for reaction of PB with four structurally related organophosphorus esters, $R_1R_2P(O)OC_6H_4NO_2$, where $R_1, R_2 = C_2H_5O, C_2H_5O$ (**1**), $R_1, R_2 = CH_3, C_2H_5O$ (**2**), $R_1, R_2 = C_2H_5, C_2H_5$ (**3**), and $R_1, R_2 = HO, CH_3$ (**4**). We chose this series of phosphoric, phosphonic, and phosphinic acid esters to cover a wide range of susceptibilities toward nucleophilic attack[6,7] while maintaining a constant leaving group (*p*-nitrophenolate). The convenient spectrophotometric determination of *p*-nitrophenolate (λ 402 nm) and available literature data for reactions of the above organophosphorus esters with various nucleophiles further supported our substrate choice. For comparison, we also determined reaction kinetics of PB with *p*-nitrophenyl acetate, **5**.

We find that aqueous sodium perborate greatly accelerates the decomposition of compounds **1**–**5** and that perhydroxyl anion is the reactive species. The reactions are kinetically well behaved, but several participating equilibria complicate the overall reaction scheme. Despite the complicating factors, the enormously high inherent reactivity of the perhydroxyl anion and the commercial availability of sodium perborate combine to recommend PB as a cleaning agent for surfaces contaminated with organophosphorus esters.

Experimental Section

Materials. The following chemicals were obtained and used without further purification: diethyl *p*-nitrophenyl phosphate (**1**), *p*-nitrophenyl acetate (**5**), sodium perchlorate (Aldrich Chemical Co.), sodium perborate tetrahydrate (Alfa Products), sodium borate (anhydrous), anhydrous sodium phosphate dibasic (Malinckrodt, Inc.), disodium ethylenediaminetetraacetate (Fisher Scientific Co.), sodium hydroxide (J.T. Baker Co.), tetraethyldiphosphine disulfide (Chemical Procurement Laboratories), and diethyl methylphosphonate (Specialty Organics, Inc.). *p*-Nitrophenyl methylphosphonic acid (**4**), $(HO)CH_3P(O)OC_6H_4NO_2$, was obtained from Ash Stevens, Inc. and purified by repeated crys-

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Table I. Experimental Data for Reaction of Sodium Perborate with 3 at 300 K, pH 8

	cuvette				
	1	2	3	4	5
$[PB]_0$, mM	0	0.500	1.00	2.50	5.00
$[\mathbf{3}]_0$, μM	5.08	4.98	4.88	4.57	4.07
$[PNP]_\infty/[\mathbf{3}]_0$	1.08	1.08	1.08	1.09	1.07
$t_{1/2}$, min[a]	417	245	142	90	56
$10^{-3}k_{obsd}$,[b] min^{-1}	1.66	2.83	4.87	7.71	12.4

[a] $t_{1/2} = 0.693/k_{obsd}$. [b] k_{obsd} calculated according to eq 13.

tallization until exhaustive alkaline hydrolysis of 4 showed quantitative (>99%) liberation of *p*-nitrophenolate. Water for kinetic experiments was obtained from a Milli-Q reverse osmosis/ion exchange system and was glass distilled before use.

Ethyl *p*-Nitrophenyl Methylphosphonate (2), $C_2H_5O(CH_3)P(O)OC_6H_4NO_2$. By the method of Edwards,[18a] reaction of diethyl methylphosphonate with phosphorus pentachloride followed by reaction with sodium *p*-nitrophenolate yielded 2, which was purified by distillation at reduced pressure. Anal. Calcd for $C_7H_{12}NO_5P$: C, 44.1; H, 4.93; N, 5.71. Found C, 43.9; H, 4.77; N, 4.59 [**Caution**! Compound 2 is a ***VERY TOXIC NERVE POISON***; the subcutaneous lethal dose (LD50) in mice is 350 μg/kg (R. Howd and R. Kenley, unpublished results), and the material should be handled with extreme care at all times.]

***p*-Nitrophenyl Diethylphosphinate (3), $(C_2H_5)_2P(O)OC_6H_4NO_2$.** Reaction of tetraethyldiphosphine disulfide with $SOCl_2$ by the method of Parshall[18b] yielded $(C_2H_5)_2P(O)Cl$. Subsequent reaction of the phosphinochloridate with *p*-nitrophenol following the general method of Douglas and Williams[18c] yielded the desired product, which was purified by vacuum distillation. Anal. Calcd for $C_{10}H_{14}NO_4P$: C, 49.28; H, 5.74; N, 5.74. Found: C, 49.08; H, 5.83; N, 5.59.

Apparatus. Reaction progress was measured by the appearance of *p*-nitrophenolate. *p*-Nitrophenolate production was monitored with a Perkin-Elmer Model 554 UV-visible spectrophotometer equipped with a thermostatted 5 × 5 position cell holder and cell programmer. Temperature control was maintained within 0.2 °C with a Forma Scientific circulating constant temperature bath. Reaction temperatures were determined in the cuvettes with a National Bureau of Standards calibrated thermometer. Quartz 1.000-cm pathlength cuvettes were used throughout. pH readings and adjustments were made by using a potentiometric Metrohm Model E526 automatic titrator/pH meter.

Methods. All experiments with compounds 1–5 were conducted in aqueous solution with PB in at least 10-fold molar excess over the other reactant. Kinetic solutions also contained the following: 0.1 mM disodium ethylenediamminetetraacetate, 0.1 M buffer (sodium borate unless otherwise specified), and $NaClO_4$ added to bring the solution to ionic strength 0.50.

Typically, PB was accurately weighed to the appropriate buffer volume and used immediately. Organophosphorus reagents were transferred via microliter syringe to a second buffer solution. The reactions were initiated by transferring an appropriate volume of PB solution (via Pipetman™ automatic pipettor) to a cuvette, then adding organophosphorus ester solution (also via the automatic pipettor) to bring the total reaction volume to 3.00 mL.

p-Nitrophenolate (PNP) production was monitored at 402 nm and quantitated by using extinction coefficients experimentally determined for each reaction medium. The fraction of reactant conversion to product was given by the ratio $(A_t - A_0)/(A_\infty - A_0)$, 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 liberation was clearly stopped.

Rate constants were determined by linear least-squares regression analysis, and error limits are reported as ± standard deviations (SD).

Control experiments demonstrated that PB solutions were stable under the reaction conditions employed: at pH 8–10.8, over a 24-h period at 300 K, less than 4% peroxygen content loss occurred.

Results and Discussion

For simultaneous reactions of added organophosphorus (OP) ester with base, water, and perborate (PB) to yield *p*-nitrophenolate (PNP), we must consider the following minimum reaction set:

$$PB \overset{K_1}{\rightleftharpoons} HO_2^- + B(OH)_3 \tag{1}$$

$$H_2O_2 \overset{K_2}{\rightleftharpoons} H^+ + HO_2^- \tag{2}$$

$$H_2O + B(OH)_3 \overset{K_3}{\rightleftharpoons} B(OH)_4^- + H^+ \tag{3}$$

$$HO_2^- + OP \xrightarrow{k_{HO_2}} PNP + \text{products} \tag{4}$$

$$HO^- + OP \xrightarrow{k_{OH}} PNP + \text{products} \tag{5}$$

$$H_2O + OP \xrightarrow{k_{H_2O}} PNP + \text{products} \tag{6}$$

From this scheme, we can obtain eq 7:

$$+d[PNP]/dt = -d[OP]/dt = [OP](k_{H_2O}[H_2O] + k_{OH}[OH] + k_{HO_2}[HO_2]) \tag{7}$$

If we define the pseudo-first-order rate constant for OP ester spontaneous hydrolysis as in eq 8,

$$k_{sp} = k_{H_2O}[H_2O] + k_{OH}[OH] \tag{8}$$

then eq 7 reduces to eq 9:

$$-d[OP]/dt = [OP](k_{sp} + k_{HO_2}[HO_2]) \tag{9}$$

To calculate the fraction of added PB present as perhydroxyl at any pH, we first accounted for the hydrogen peroxide/perhydroxyl equilibrium, [eq 2] according to eq 10:

$$[HO_2^-]/[H_2O_2] = K_2/(K_2 + H^+) \tag{10}$$

Next we define the equilibrium fraction, α, of initially added perborate present as hydrogen peroxide by eq 11:

$$\alpha = ([PB]_0 - [PB])/[PB]_0 \tag{11}$$

Combining eq 9–11 gives

$$-d[OP]/dt = [OP]\left\{k_{sp} + \alpha k_{HO_2}[PB]_0\left(\frac{K_2}{K_2 + [H^+]}\right)\right\} \tag{12}$$

when $[PB]_0 \gg [OP]$, pseudo-first-order kinetics obtain, and

$$-\ln [OP]_t/[OP]_0 = k_{obsd}t \tag{13}$$

where $-\ln [OP]_t/[OP]_0 = -\ln [(A_t - A_0)/(A_\infty - A_0)]$ in our spectrophotometric assay (see Experimental Section). Finally, combining eq 12 and 13 gives

$$k_{obsd} = k_{sp} + k_{HO_2}\alpha[PB]_0\left(\frac{K_2}{K_2 + [H^+]}\right) \tag{14}$$

Thus for all esters at any pH, a plot of k_{obsd} vs. $[PB]_0$ should be linear with intercept = k_{sp} and slope = $\alpha k_{HO_2}[K_2/(K_2 + [H_+])]. + [H^+])]$.

Table I summarizes selected experimental conditions and results for the PB reaction with 3 at pH 8, 300 K. Figure 1 is a pseudo-first-order kinetic plot for various $[PB]_0$ reacting with 2 at pH 8, 300 K. Figure 2 is a kinetic plot of k_{obsd} vs. $[PB]_0$ for PB reaction with 1 at 300 K and three different pH values. The data in Table I and Figures

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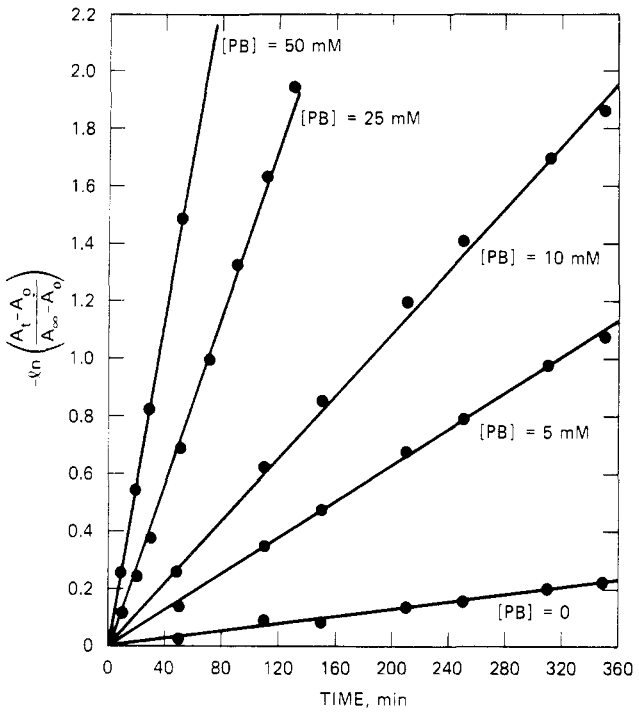

Figure 1. Pseudo-first-order kinetic plot of $-\ln (A_t - A_0)/(A_\infty - A_0)$ vs. time for production of p-nitrophenolate from reaction of sodium perborate at various concentrations with compound **2** at 300 K, pH 8.

1 and **2** are typical for all the compounds tested and detailed results are not shown for other cases. Table I demonstrates the k_{obsd} dependence on $[\mathrm{PB}]_0$ and the fact that the reactions typically proceeded to completion ($[\mathrm{PNP}]_\infty/[\mathbf{3}]_0$ = unity). Table I also shows the substantial rate enhancements afforded by relatively low initial PB concentrations: 5 mM PB decreased the half-life for **3** decomposition 7.5-fold relative to alkaline hydrolysis at pH 8.

Figure 1 shows that PNP production rates adhered to eq 13 to long conversions for the range of $[\mathrm{PB}]_0$ studied. Figure 2 demonstrates that eq 14 holds over the pH range employed.

Having thus determined that the reaction system was kinetically well-behaved, we determined k_{sp} and $\alpha k_{\mathrm{HO_2}}$ values from least-squares linear regression of k_{obsd} vs. $[\mathrm{PB}]_0[K_2/(K_2 + [\mathrm{H}^+)]$ data at various pH. In these calculations we used the literature[19] value of $K_2 = 2.5 \times 10^{-12}$ [19] and deferred calculating the factor α to a subsequent step (vide infra). Table II lists the kinetic constants so obtained. The data show good adherence to eq 14 within individual kinetic runs (linear regression correlation coefficients were >0.99 in all cases and relative standard deviations about slope and intercept were small) as well as good reproducibility between runs at a given pH. It is also clear from Table II that the product αk_{HO2} decreased at increasing pH for all experiments conducted in borate buffer. For the case of **1** decomposition at pH 10.8 in borate buffer, vs. pH 12 in phosphate buffer, the trend toward lower $\alpha k_{\mathrm{HO_2}}$ at higher pH reversed.

The best explanation for these results is perhydroxyl complexation with boric acid, as shown in eq 1. The fraction, α, of initially added PB present as $\mathrm{HO_2}^-$ will depend on the equilibrium constant K_1 and therefore on equilibrium concentrations of perhydroxyl [reaction 2] and boric acid [reaction 3] at any pH. To determine α, we estimated K_1 (1.2×10^{-4} M), K_2 (2.5×10^{-12} M) and K_3 (6.6×10^{-11} M) at 300 K from available literature data[19-22] and numerically modeled[23] the reaction set 1–3. For the reaction system with 0.1 M borate present, the modeling study provided the following results for α (pH): 0.78 (8), 0.39 (9), 0.25 (10), 0.24 (10.8). Substituting α values into Table II containing $\alpha k_{\mathrm{HO_2}}$ values yields $k_{\mathrm{HO_2}}$ values. At pH 8–10, calculated $k_{\mathrm{HO_2}}$ values were reasonably constant (see below). However, at pH 10.8 (where the correction for α is greatest) calculated $k_{\mathrm{HO_2}}$ values were lower (by approximately a factor of five) than the $k_{\mathrm{HO_2}}$ values calculated at pH 8–10. Probably, the failure to correctly predict α at pH 10.8 resulted from inaccuracies in our estimated K_1, K_2, and K_3 values. Without directly determining the equilibrium constants under our actual experimental conditions we cannot provide better $k_{\mathrm{HO_2}}$ value estimates.

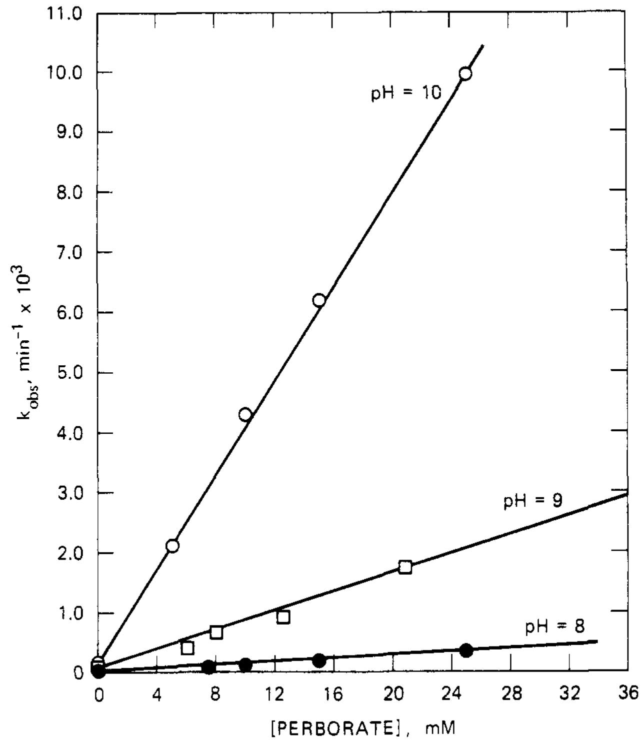

Figure 2. Kinetic plot of pseudo-first-order rate constant for reaction of compound **1** (k_{obsd}) vs. concentration of added sodium perborate at 300 K at various pH in 0.1 M borate buffer.

To demonstrate the validity of our $k_{\mathrm{HO_2}}$ values, we averaged the individual values for compounds **1**, **2**, and **3** calculated at pH 8, 9, and 10 and compared the mean values to literature values obtained by using hydrogen peroxide solutions as a perhydroxyl source. For compound **4** we assumed $\alpha = 1$ (and used the $k_{\mathrm{HO_2}}$ data for pH 12 in phosphate buffer) and for **5** we used $\alpha = 0.78$ and the pH 8 data of Table II.

Our k_{OH} values for **1**, **4**, and **5** were different from the literature values by factors of 2.6, 0.6, and 5.9, respectively. Because there is a 3×10^5-fold difference in (our) k_{OH} values and differences in experimental conditions, the

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Table II. Kinetic Constants for Perborate Reactions at 300 K and Various pH in 0.10 M Borate Buffer

no.	pH	10^3k_{sp} (± SD),[a] min^{-1}	αk_{HO} (± SD),[a] $M^{-1}\,\mathrm{min}^{-1}$
1	8	0.00192 ± 0.011	51.8 ± 3.0
	9	0.028 ± 0.024	45.9 ± 2.2
	10	0.238 ± 0.029	16.1 ± 0.27
	10.8	0.936 ± 0.043	5.07 ± 0.07
	12[b]	10.5 ± 0.080	42.1 ± 0.22
2	8	0.207 ± 0.30	2790 ± 84
	8	0.544 ± 0.071	2380 ± 80
	8	0.310 ± 0.20	2360 ± 31
	mean	0.354 ± 0.17	2510 ± 243
	9	3.26 ± 0.074	834 ± 11
	10	10.2 ± 0.50	755 ± 40
	10	17.2 ± 0.13	296 ± 5.8
	mean	13.7 ± 3.5	536 ± 240
	10.8	57.7 ± 1.4	216 ± 14
3	8	1.58 ± 0.082	7130 ± 65
	8	2.51 ± 0.19	8010 ± 300
	8	1.38 ± 0.22	7780 ± 166
	8	1.24 ± 0.18	7800 ± 276
	mean	1.68 ± 0.57	7680 ± 380
	9	3.03 ± 0.29	4390 ± 62
	10	26.8 ± 4.0	996 ± 50
	10.8	63.5 ± 0.12	381 ± 20
4	12[b]	0.181 ± 0.23	0.122 ± 0.00023
5	8	5.29 ± 2.2	152 000 ± 14 000
	8	5.32 ± 2.1	116 000 ± 3 400
	mean	5.31 ± 0.021	134 000 ± 26 000

[a] Calculated by linear regression according to eq 14. [b] In 0.10 M Na_2HPO_4 buffer.

Table III. Bimolecular Rate Constants for Organophosphorus Ester Reactions with Hydroxide and Perhydroxyl Anions in Aqueous Solution at 300–305 K

no.	k_{OH},[a] $M^{-1}\,\mathrm{min}^{-1}$	k_{HO2},[b] $M^{-1}\,\mathrm{min}^{-1}$	ref
1	1.04 ± 0.0040	83 ± 30	this work
	0.40	60.4	24, 25, 11
2	70.5 ± 4.8	2500 ± 640	this work
	c	*c*	*c*
3	121 ± 20	8300 ± 3700	this work
	c	*c*	*c*
4	0.0181[d]	0.122[e]	this work
	0.030	0.155	26, 13
5	5300[d]	171 000[f]	this work
	890	220 000	27, 10

[a] Values of this work from least-squares linear regression of k_{sp} vs. [OH] data according to eq 8. Values shown ±SD about the regression slope. [b] Mean value (±SD) of three determinations at pH 8, 9, 10. Data at pH 10.8 not included. See text and Table II. [c] Not available. [d] Calculated according to the expression $k_{OH} = (k_{sp})/[OH]$ at a single pH. See eq 8, Table II. [e] Determined at pH 12 in phosphate buffer assuming α^{-1} = unity. [f] Determined at pH 8 only in borate buffer, using $\alpha^{-1} = 1.28$. See text and Table II.

agreement between our data and literature values seem reasonable. In our experiments we did not extrapolate k_{OH} values to zero buffer concentration and buffer participation in the hydrolysis reactions probably explains at least part of the difference between our data and comparable literature values. The k_{HO_2} data compare similarly. Thus, our k_{HO_2} values differed from literature values by 20–40%. Again, considering the 10^6-fold activity range of the compounds employed, the agreement is acceptable. We consider that the good comparison of our data with literature rate constants establishes perhydroxyl ion as the reactive species in our system and proves that reactions 1–8 adequately describe the chemistry of the aqueous alkaline perborate solutions in the pH 8–10 range.

An additional point concerns the k_{HO_2}/k_{OH} rate constant ratio. For our rate constants we find the following k_{HO_2}/k_{OH} (reactant): 80 (1), 35 (2), 69 (3), 7 (4), 32 (5). Thus for all the neutral ester substrates, k_{HO_2}/k_{OH} ratios ranged from 30 to 80 (mean = 54 ± 24), but for 4 (which dissociates to the phosphonic acid anion in alkaline solution) the perhydroxyl/hydroxide reactivity ratio dropped to 7. Clearly perhydroxyl exhibits extraordinary activity toward neutral esters, confirming its identification as a "super"[15] or "α-effect"[10] nucleophile. Vs. anionic substrates (i.e., 4), charge repulsion lowers both the overall reactivity of PB and the PB activity relative to hydroxide.

Finally, we wished to investigate the temperature dependence of the PB reactions. To do so, we determined k_{obsd} values at pH 9 for PB reaction with 2 as a function of temperature and borate buffer concentration. We did not attempt to reduce the observed pseudo-first-order rate constants to k_{HO_2} values because we could not accurately estimate the various equilibrium constants (K_1, K_2, and K_3) over the temperature range employed. Table IV summarizes the k_{obsd} vs. temperature and buffer concentration data and provides apparent Arrhenius parameters. From Table II it is apparent that k_{obsd} values decreased with increasing borate buffer concentration, again demonstrating the intervention of the perhydroxyl/perborate equilibrium [reaction 1]. The apparent activation parameters at 5 and 10 mM buffer concentrations were not significantly different, and the reaction 1 equilibrium apparently lies far to the right at these low buffer concentrations. Assuming negligible k_{sp} values (see Table I), α = unity, and $K_2/(K_2 + [H^+])$ calculated from the data of Uri and Evans[20] at zero ionic strength at all temperatures, we can use eq 14 and the apparent activation parameters for 5 mM borate buffer to calculate activation parameters for the bimolecular rate constant, k_{HO_2}. Doing so gives k_{HO_2} ($M^{-1}\,\mathrm{min}^{-1}$) $= 10^{(5.75\pm0.38)} \exp[(-2990 \pm 540)/RT]$ for reaction with compound 2.

Conclusions

Sodium perborate serves as a buffered source of hydrogen peroxide and perhydroxyl anion. The fraction of

Table IV. Temperature and Borate Buffer Concentration Dependence of Pseudo-First-Order Rate Constants (k_{obsd}) for PB (5.0 mM) Reactions with 2 at pH 9

	$10^3\,k_{obsd}$,[a] min^{-1} at [borate buffer], mM				
temp, K	100	50	25	10	5.0
290	5.89 ± 0.075	8.60 ± 0.098	11.5 ± 0.18	17.8 ± 0.27	23.0 ± 0.42
300	14.9 ± 0.19	19.4 ± 0.42	26.2 ± 0.28	37.3 ± 0.62	50.4 ± 0.50
310	32.9 ± 0.92	41.3 ± 1.4	55.6 ± 1.7	71.1 ± 2.7	95.0 ± 3.4
320	83.4 ± 3.8	101 ± 4.4	125 ± 5.2	153 ± 5.8	213 ± 6.3
E_a,[c] kcal/mol	16.2 ± 0.5	15.0 ± 0.6	14.6 ± 0.3	13.1 ± 0.4	13.5 ± 0.5
ln A,[d] min^{-1}	22.8 ± 0.8	21.3 ± 1.0	20.8 ± 0.5	18.7 ± 0.7	19.6 ± 0.9

[a] From linear least-squares regression of [*p*-nitrophenolate] vs. time data according to eq 13. [b] From linear least-squares regression of k_{obsd} vs. temperature data according to the expression $\ln k_{obsd} = \ln A - E_a/RT$. [c] Activation energy. [d] Pre-exponential factor.

perborate dissociated to perhydroxyl depends on the reaction medium pH and the concentration of borate present: increasing pH and increasing borate concentration decrease the perhydroxyl ion concentration. Aqueous sodium perborate solutions afford substantial enhancements in organophosphorus ester decomposition rates relative to alkaline hydrolysis rates, the ratio $k_{\mathrm{HO_2^-}}/k_{\mathrm{HO^-}}$ is approximately 50 for neutral esters.

We can put the available rate enhancements into perspective as follows. At pH 9, 300 K, with 100 mM perborate present, estimated half-times for phosphorus ester degradation are 13, 0.4, and 0.13 min, respectively, for compounds **1**, **2**, and **3**. For any neutral organophosphorus ester whose reactivity toward alkaline hydrolysis is known, we can approximate the decomposition rate in aqueous perborate by using the ratio $k_{\mathrm{HO_2^-}}/k_{\mathrm{HO^-}} = 50$ and eq 14. A survey of the available literature reveals that a great variety of phosphorus esters will react extremely rapidly in moderately alkaline solutions of saturated sodium perborate. Because it has such high reactivity and commercial availability, we strongly recommend sodium perborate as a cleaning agent for removing hazardous organophosphorus ester residues.

Registry No. **1**, 311-45-5; **2**, 3735-98-6; **3**, 7531-39-7; **4**, 81349-02-2; **5**, 830-03-5; PB, 93184-29-3.

Halogenation and Rearrangement Reactions of Substituted Tricyclo[2.1.0.0^{2,5}]pentan-3-ones

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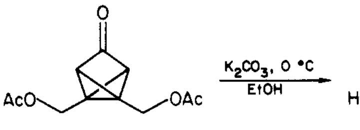
Hydrolysis of 1,5-bis(acetoxymethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (I) with potassium carbonate in methanol yielded 1,5-bis(hydroxymethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (II). Treatment of the latter with triphenylphosphine and carbon tetrabromide in acetonitrile yielded 1,5-bis(bromomethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (V). The analogous reaction with triphenylphosphine and carbon tetrachloride yielded little 1,5-bis(chloromethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (V). Instead, 3-oxabicyclo[3.3.0]octa-1,4-dien-7-one (VI) was found. An authentic sample of VI was synthesized by treating 3,4-bis(chloromethyl)furan (VII) with methyl (methylsulfinyl)methyl sulfide, yielding 3-oxa-7-(methylthio)-7-(methylsulfinyl)bicyclo[3.3.0]octa-1,4-diene (VIII). Treatment of VIII with acid yielded an authentic sample of the ketone VI. The dichloride V was prepared by the following alternative route. 1,4-Dichlorobut-2-yne was reacted with *tert*-butyl diazoacetate yielding *tert*-butyl 1,2-bis(chloromethyl)cyclopropene-3-carboxylate (XII). Deesterification with trifluoroacetic acid yielded 1,2-bis(chloromethyl)cyclopropene-3-carboxylic acid (XIII) that was converted with oxalyl bromide to 1,2-bis(chloromethyl)cyclopropene-3-carbonyl bromide (XIV). The latter was reacted with diazomethane and yielded 3-(diazoacetyl)-1,2-bis(chloromethyl)cyclopropene (XV) which was closed to V using dirhodium tetraacetate as catalyst. Rearrangement of the diol II upon treatment with triphenylphosphine and carbon tetrachloride may proceed by conversion to the [3.1.1]propellane IX followed by valence tautomerization to the cyclopentadienone X and prototopic rearrangement to the product VI. Likewise, treatment of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one with iodine probably also results in the formation of 3,4-dimethylcyclopentadienone which dimerizes to XVIII. An authentic sample of XVIII was prepared by bromination of 3,4-dimethylcyclopent-2-en-1-one with *N*-bromosuccinimide, yielding 4-bromo-3,4-dimethylcyclopent-2-en-1-one (XX). Treatment of XX with triethylamine yielded an authentic sample of dimer XVIII. Reaction of XVIII with sodium methoxide in MeOD–D_2O resulted in the exchange of eight protons yielding XVIII-d_8. The high number of deuteriums incorporated is a consequence of a facile Cope rearrangement.

Halogenation and Rearrangement

In the course of learning how to prepare functionalized derivatives of the tricyclo[2.1.0.0^{2,5}]pentan-3-one system,[2] several rearrangments were observed that provide insight into the strain and reactivity which are properties of this carbon skeleton. This is unexplored territory. Only the dimethyl, di-*n*-propyl, and diphenyl derivatives of the tricyclo[2.1.0.0^{2,5}]pentanone system were known before this work was begun.[2] Following the pioneering work of Doering[2a] and Masamune[2b] of 20 years ago, nothing had been added to this area until the very recent work of Maier.[2d]

The key substance in this research is the diol II, which



I

II

is prepared by mild hydrolysis of the diacetate I[1] using potassium carbonate in ethanol at 0 °C. The keto diol II was converted, in 45% yield, to the crystalline dibromide III, mp 68–69 °C, by treatment with triphenylphosphine and carbon tetrabromide at 50 °C in acetonitrile.[3] The

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(1) (a) H. Irngartinger, A. Goldman, R. Schappert, P. Garner, and P. Dowd *J. Chem. Soc., Chem. Commun.*, 455 (1981); (b) P. Dowd, P. Garner, R. Schappert, H. Irngartinger, and A. Goldmann, *J. Org. Chem.*, **47**, 4240 (1982). Part of this work has been published in preliminary form: P. Dowd, R. Schappert, and P. Garner, *Tetrahedron Lett.*, 3 (1982).

(2) The earliest tricyclo[2.1.0.0^{2,5}] systems were (a) the 1,3-dimethyl derivative of W. Doering and M. Pomerantz, *Tetrahedron Lett.*, 961 (1964); (b) the 1,5-diphenyl derivative of S. Masamune, *J. Am. Chem. Soc.*, **86**, 736 (1964); (c) see also G. Maier, H. P. Resenauer, and H. A. Freitag, *Tetrahedron Lett.*, 121 (1978); (d) G. Maier, M. Hoppe, and H. P. Reisenauer, *Angew. Chem., Int. Ed. Engl.*, **22**, 990 (1983).

(3) J Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968).

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