

$J = 2.6$  and  $9.7$  Hz), 2.37 (m), 2.20 (m), 1.85 (m), 1.3 (m), 1.22 (d,  $J = 7.1$  Hz), 0.95 (d,  $J = 6.1$  Hz), 0.92 (d,  $J = 6.5$  Hz);  $^{13}\text{C}$  NMR (50.1 MHz)  $\delta$  174.5, 137.9, 129.2, 90.3, 39.4, 37.3, 36.0, 30.9, 30.7, 22.4, 22.3, 27.6, 17.1, 13.5. Exact mass calcd for  $\text{C}_{14}\text{H}_{24}\text{O}_2$ :  $m/e$  224.1776. Found:  $m/e$  224.1776.

(+)-Prelog-Djerassi Lactonic Aldehyde (2). Ozone was introduced into a solution of the lactone **8** (1.23 mmol) in 30 mL of ethyl acetate at  $-78$  °C. After the solution became blue, the ozone flow was stopped and excess ozone swept from the reaction flask. After 10 min 2 mL of methyl sulfide was added to the solution and the mixture warmed to room temperature (2 h). The solution was concentrated and then dissolved in 20 mL of ethyl ether and treated with 10 mL of 1 M aqueous potassium iodide. The iodine was destroyed with sodium thiosulfate and the aqueous phase extracted with ether. The organic phase was dried ( $\text{MgSO}_4$ ) and concentrated. The product was isolated as a white solid by flash chromatography (1:1 ethyl acetate/hexane) in 83% yield. Recrystallization from hexane-ether provided material of mp  $62$ – $64$  °C;  $[\alpha]_D^{26} +27.3^\circ$  ( $c$  3.11,  $\text{CHCl}_3$ ) (lit.<sup>6b</sup> mp  $57$ – $62$  °C,  $[\alpha]_D^{26} +27.0^\circ$  ( $c$  3.60,  $\text{CHCl}_3$ ));  $^1\text{H}$  NMR (200 MHz)  $\delta$  9.75 (s, 1 H), 4.59 (dd,  $J = 10.2$

and 2.1 Hz, 1 H), 1.65–2.90 (m, 5 H), 1.30 (d,  $J = 7.0$  Hz, 3 H), 1.22 (d,  $J = 7.0$  Hz, 3 H), 1.03 (d,  $J = 6.4$  Hz, 3 H);  $^{13}\text{C}$  NMR (50.1 MHz)  $\delta$  202.5, 173.4, 84.8, 47.4, 37.2, 36.2, 30.4, 17.0, 16.6, 6.3.

**Acknowledgment.** We thank the National Institutes of Health (GM 24517), the Herman Frasch Foundation administered by the American Chemical Society, and the Committee on Research, University of California, Riverside, for financial support. We thank Drs. Robert Lee and Richard Kondrat for obtaining 300-MHz  $^1\text{H}$  NMR and high resolution mass spectral data.

**Registry No.** **2**, 77405-46-0; **3**, 96346-17-7; **3** (*tert*-butyldimethylsilyl ether), 96258-97-8; **4**, 89998-89-0; **4** (ketone), 52066-33-8; **5**, 96391-34-3; **6**, 96258-95-6; **6** (alcohol), 96258-98-9; **6** (diol), 96258-99-0; **6** (isopropylidene derivative), 96259-00-6; **7**, 79563-15-8; **7** (alcohol amide), 74036-66-1; **8**, 96258-96-7; **8** (amide precursor)-Li, 96259-01-7; (+)-(2*Z*,4*S*)-5-methyl-2-hexen-4-ol, 96346-18-8; (*S*)-prolinol propionamide;  $\text{CH}_3\text{CH}(\text{CHO})\text{CH}_3$ , 78-84-2;  $\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$ , 563-47-3;  $\text{CH}\equiv\text{C}-\text{CH}_3$ , 74-99-7.

## Ionization of the PH Bond in Diethyl Phosphonate

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**Abstract:** Diethyl phosphonate is oxidized by halogens in a reaction subject to general base catalysis when the halogen concentration is sufficiently high. Under these conditions the reaction is zero order in iodine or bromine and the Brønsted exponent,  $\beta$ , is, contrary to earlier reports, about 0.7. When the halogen concentration is quite low, but still within the range of the spectrophotometric analysis used, a third-order rate law is obeyed and the product of the ionization constant of the phosphonate and the rate constant for the reaction of the anion with halogen (which is probably diffusion controlled) can be derived. This gives an acid dissociation constant of  $2.5 \times 10^{-15}$ . When the diethyl phosphonate is exchanged with  $\text{D}_2\text{O}$ , a substantial kinetic isotope effect is observed for the oxidation, again contrary to expectation from previous reports on a similar reaction. This reaction is thus closely analogous to the ionization of hydrogen  $\alpha$  to a carbonyl group or a nitro group in all of which the proton transfer is slower than the diffusion-controlled rate in both directions.

In aqueous solution dialkyl phosphonates react with halogens according to eq 1. Using a titrimetric analysis, Nylen<sup>1</sup> found

$$(\text{RO})_2\text{PHO} + \text{I}_2 + 3\text{OH}^- \rightarrow (\text{RO})_2\text{PO}_2^- + 2\text{I}^- + 2\text{H}_2\text{O} \quad (1)$$

that the reaction was subject to general base catalysis and the rate was independent of iodine concentration as long as the concentration was not too small. There was also an acid catalysis with the simple oxidation complicated by some ester hydrolysis. A study of different bases appeared to show conformity with the Brønsted equation with a  $\beta$  value of unity. Although the difficulty of observing very high  $\beta$  values is well-known, as shown (for example) by Bell,<sup>2</sup> the inconsistency was apparently overlooked for a long time. Naturally, large  $\beta$  values can be measured if the point for  $\text{OH}^-$  lies far below the value expected from the Brønsted equation. This can easily happen if the diffusion limit is already reached with weaker bases, but Nylen's rates are far too slow for this to be the case. A further indication of the inconsistency is the natural assumption from the large  $\beta$  value that the reverse reaction (with  $\alpha$  0) is diffusion limited, yet iodine at modest concentrations could compete for the intermediate anion to the exclusion of the reverse protonation. An apparent inconsistency was found again in a study of the exchange rate in  $\text{D}_2\text{O}$  and of the deuterated ester into  $\text{H}_2\text{O}$  by Luz and Silver,<sup>3</sup> who confirmed the general base catalysis, but

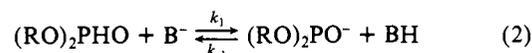
**Table I.** Rate Constants for Attack of Various Bases on Diethyl Phosphonate

base	$k_1$ ( $\text{M}^{-1} \text{s}^{-1}$ )
$\text{CH}_3\text{COO}^-$	$2.98 \times 10^{-3}$
$\text{HPO}_4^{2-}$	$2.25 \times 10^{-1}$
$\text{CO}_3^{2-}$	3.4
$\text{NH}_3$	$2.35 \times 10^{-3}$
$\text{OH}^-$	$\sim 10^4$ <sup>a</sup>

<sup>a</sup>The extrapolation to zero buffer concentration makes this value somewhat uncertain. Furthermore, the value is based only on phosphate buffer data.

found that the isotope effect expected with the general base catalysis was very small with acetate ion as the base. They used an NMR analysis to measure the exchange. They concluded that the r.d.s. was not a simple proton transfer. In work on the acid catalysis<sup>4</sup> they did find an isotope effect. The general base catalysis also showed up less convincingly in a study of the reaction of the dimethyl ester with diazonium salts.<sup>5</sup>

In spite of the problems, the mechanism is plausibly given by eq 2–4.



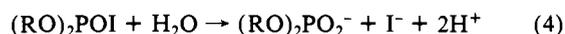
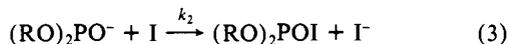
(1) Nylen, P. Z. *Anorg. Allg. Chem.*, **1938**, 235, 161.

(2) Bell, R. P. "Acid-Base Catalysis"; Clarendon Press: Oxford, 1941; Chapter 5.

(3) Silver, B.; Luz, Z. *J. Am. Chem. Soc.* **1962**, 84, 1095.

(4) Silver, B.; Luz, Z. *J. Am. Chem. Soc.* **1962**, 84, 1091.

(5) Lewis, E. S.; Nieh, E. C. *J. Org. Chem.* **1973**, 38, 4402.



We shall assume this mechanism; the kinetics and mechanism of reaction 4 are not relevant to this work since we only measure the disappearance of iodine.

### Results and Discussion

The general base catalysis shows that eq 2 is rate determining at high  $\text{I}_2$  concentrations, but the steady-state approximation for the intermediate  $(\text{RO})_2\text{PO}_2^-$  gives the more general rate expression, eq 5.

$$-d(\text{I}_2)/dt = \frac{k_1 k_2 (\text{B}^-) ((\text{RO})_2\text{PHO})(\text{I}_2)}{k_{-1}(\text{BH}) + k_2(\text{I}_2)} \quad (5)$$

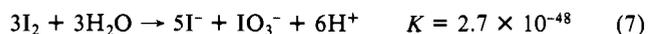
The two limiting rate laws at both high and low iodine concentration are experimentally accessible by a spectrophotometric method, following the iodine concentration at the wavelength of the isobestic point of iodine and the triiodide ion.<sup>6</sup> There are two of these, so it proved practical to measure the high iodine limit at the lower extinction coefficient one of these two, and the low concentration limit at the higher extinction coefficient isobestic point.

All measurements were made with a jacketed cell in the spectrophotometer at 25 °C, to minimize temperature errors which sometimes can be serious in hot or cold circulating systems. Table I shows the results obtained at high iodine concentrations, where the rate law is given in eq 6,

$$-d(\text{I}_2)/dt = ((\text{RO})_2\text{PHO}) \left[ \sum_i k_{1i} \text{B}_i^- \right] \quad (6)$$

The slopes of the straight-line plots of  $\ln(A_t - A_\infty)$  vs. time were the pseudo-first-order rate constants for the disappearance of the phosphonate ester; iodine and base were present in excess. The slope of a plot of these pseudo-first-order constants against the buffer concentration at constant buffer ratio gave the rate constants for the bases of Table I. For several phosphate buffer ratios, the intercepts of these plots, plotted against the  $\text{OH}^-$  concentration, gave a new graph, the slope of which gave the rate constant for hydroxide ion as a base. Because of the uncertainties of this extrapolation, the precision is lower and there is no real assurance that the data correspond to the high  $\text{I}_2$  concentration limiting rate law.

The measurement of these rates at fairly high pH values presents a problem from two different aspects. The first of these is the disproportionation of iodine, eq 7.



Thus, at pH 9, 0.01 M iodine is almost 10% converted to iodate even with 5 M iodide ion. This amount of iodate can be reduced still further by lowering the concentration of iodine substantially, but eventually at the cost of reducing  $k_2(\text{I}_2)$  to the point where it is not large compared to  $k_{-1}(\text{BH})$ . Since the reaction is zero order in iodine and the rates measured were for the pseudo-first-order disappearance of phosphonate (as measured by iodine consumptions) the partial disproportionation of the iodine in a rapidly reversible manner does not introduce error in the rate constants of Table I, unless the iodine concentration is reduced to the point at which it begins to enter the rate equation.

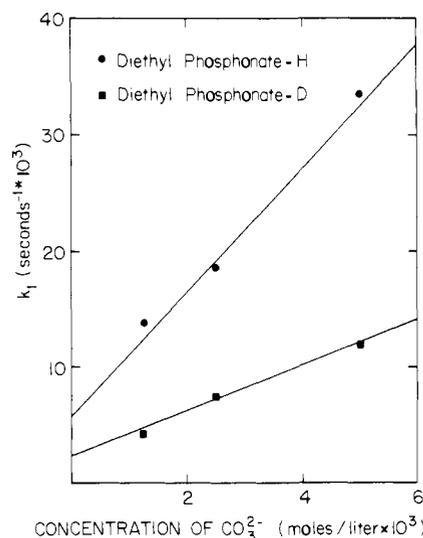
The data for the acetate, the hydrogen phosphate, and carbonate fitted the statistically corrected Brønsted equation with  $\beta = 0.7$  (the highly uncertain point for hydroxide ion also fitted, probably coincidentally). The point for ammonia deviates strongly; the rate is far too slow for the base strength, even though perfect fits for both oxygen and nitrogen are not to be expected.

It is possible that the reaction between iodine and ammonia gives a reactive substance of far lower extinction coefficient al-

**Table II.** Isotope Effects on the Proton Abstraction from Diethyl Phosphonate by Bases

base	$\text{p}K_a$	$k_H/k_D$
$\text{CH}_3\text{COO}^-$	4.8	1.01
$\text{HPO}_4^{2-}$	7.2	1.65
$\text{NH}_3$	9.6	1.84 <sup>a</sup>
$\text{CO}_3^{2-}$	10.3	2.76

<sup>a</sup> Although there is a question about the significance of  $k_1$  for  $\text{NH}_3$  in Table I, because of the Brønsted deviation, the possible presence of major systemic error appears to be present in both the H and D compounds. The isotope effect is therefore believable, if not convincing. The plot of pseudo-first-order rate constant vs. ammonia buffer concentration is as good as that of Figure 1 for carbonate buffers.



**Figure 1.** A plot of the apparent first-order rate constants vs. buffer concentration. Both the general base catalysis and the isotope effect with the base  $\text{CO}_3^{2-}$  are evident.

though this was not suggested by qualitative observation of the initial absorbance. An alternative explanation for the low rate constant is that the iodine concentration used was too low to assure an absolutely zero-order rate law. Although as described above we took this factor into consideration, too low iodine would lead to rate constants too low, and to a possibly imperceptible deviation from first-order kinetics. In spite of this seriously deviant point, there is no question that the report of a Brønsted  $\beta$  of about 1 is quite unable to fit these data.

Diethyl phosphonate-*d* was prepared in a concentrated solution by dissolving the ordinary ester in a large excess of  $\text{D}_2\text{O}$  containing sodium carbonate. Exchange was shown to be virtually quantitative by the disappearance of the proton NMR resonance of the phosphorus-bound proton. A small sample of this solution was then used in the light water buffer and iodine solution to determine the rate of the deuterated material. Contrary to the expectation from the work of Luz and Silver,<sup>3</sup> although not in direct contradiction since the only base in common is acetate with a negligible isotope effect in both studies, there is a significant isotope effect on  $k_1$ , shown in Table II.

The experimental basis of the general base catalysis and the kinetic isotope effect is illustrated in Figure 1, an example of such plots for each base.

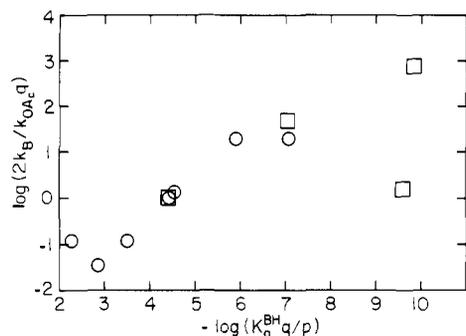
The isotope effects are clearly compatible with the existence of the general base catalysis and compatible with current ideas about rate-determining proton transfers. The maximum effect resulting from complete loss of the PH stretching vibration at this temperature is a factor of 5.6;<sup>4,9</sup> this value might be approached with a base with a conjugate acid of  $\text{p}K_a$  equal to that of the

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**Figure 2.** Brønsted plot statistically corrected combining current data (squares) with those of ref 1 (circles) (both normalized to the common acetate point) and illustrating the essential nonlinearity. See text for discussion of deviant points. Bases are, from left to right, citrate, iodoacetate, glycolate, acetate, propionate, cacodylate,  $\text{HPO}_4^{2-}$ ,  $\text{NH}_3$ , and  $\text{CO}_3^{2-}$ .

phosphonate, which has, as shown below, a  $\text{p}K_a$  of about 14.6.

As expected, the isotope effect increases with increasing base strength, of course implying a maximum with still stronger bases. However, the absence of information on isotope effects for much stronger bases prevents the experimental observation of such a maximum.

It appears impossible by these methods to get a reasonable value for  $k_H/k_D$  for  $\text{OH}^-$  as the base. Not only is the value of  $k_1$  in Table I uncertain but the isotope effects given by the ratio of the intercepts in plots such as that in Figure 1 are exceedingly variable, varying from 1.2 for the phosphate buffer data to 5 for carbonate. Possibly the extrapolated values which ought to give  $k_1$  for  $\text{OH}^-$  in fact do not have enough iodine to suppress the reversal of reaction 2, with 55 M conjugate acid. Thus when deuterated phosphonate is used, it may exchange in the course of the reaction, and thus give an isotope effect far too low. The remaining isotope effects can be treated by the Marcus equation, as described by Kreevoy.<sup>7</sup> An intrinsic barrier of 10–12 kcal/mol is appropriate for the increase in isotope effects with increasing base strength.

Kreevoy's treatment assumes no equilibrium isotope effect, which is clearly not a very good assumption when changing from the rather weak PH bond to the strong OH bond. The problem with substantial equilibrium isotope effect has been attacked recently,<sup>8</sup> the treatment predicts the maximum in isotope effect in this case to occur with bases whose conjugate acids are weaker than the diethyl phosphonate. Our data do not allow a check on this prediction, nor can we expect more data by these methods to be available with stronger bases.

If there were many more reliable points they could be expected to show perceptible but not gross curvature in the Brønsted plot. With the present data, there is no chance of showing this. However, Nylen's  $\beta = 1$  for the weaker bases might be combined with the current ones, except for the temperature difference. Figure 2 shows Nylen's data together with ours on a statistically corrected Brønsted plot. The data (taken at different temperatures) are normalized to the common point of acetate ion catalysis by in each set dividing the rate constant by that for acetate. The line of slope 0.9 for the data clearly do not fit a straight line, neither one of slope 0.9 for the earlier data nor one of 0.7 slope data. The uncertain point for  $\text{OH}^-$ , a concave downward curve, is clearly indicated by the combined data, although hardly suggested by either one alone. The curvature is consistent with the variable isotope effect.

Three points deviate strongly. Nylen's point for base catalysis by citrate probably has a significant error because the acid catalysis contributes more than the base catalysis. Similarly his point for phosphate buffer probably suffers from experimental error; we could not follow the phosphate reaction by his titration method because it was too fast. Even allowing for the five degree temperature difference and his greater practice with the method, we doubt that good precision would be obtainable. The drastic and unexplained deviation of the ammonia catalysis point in our data is mentioned elsewhere.

**Table III.** Values of  $k_2K_a$  Derived from Low Iodine Concentration Kinetics

buffer <sup>a</sup>	$1/(\text{H}^+)^b$	$k_{\text{obsd}} (\text{s}^{-1})$	$k_2K_a^c$
$\text{OAc}^-$ , $\text{HOAc}$ (1:1)	$5.68 \times 10^4$	$4.6 \times 10^{-2}$	$1.25 \times 10^{-5}$
$\text{OAc}^-$ , $\text{HOAc}$ (2:1)	$1.14 \times 10^5$	$8.96 \times 10^{-2}$	$1.22 \times 10^{-5}$
$\text{OAc}^-$ , $\text{HOAc}$ (3:1)	$1.70 \times 10^5$	$1.41 \times 10^{-1}$	$1.29 \times 10^{-5}$
$\text{HPO}_4^{2-}$ , $\text{H}_2\text{PO}_4^-$ (.01:2)	$8.00 \times 10^4$	$6.46 \times 10^{-2}$	$1.25 \times 10^{-5}$
$\text{OAc}^-$ , $\text{HOAc}$ (1:0.5) <sup>d</sup>	$1.14 \times 10^5$	$9.23 \times 10^{-2}$	$1.26 \times 10^{-5}$

<sup>a</sup>The parenthetical numbers are the molar concentrations of the two buffer components, in order. <sup>b</sup>These are calculated from the literature values of the dissociation constants, with no ionic strength correction. <sup>c</sup>Obtained by dividing  $k_{\text{obsd}}$  by  $1/(\text{H}^+)$  and by the phosphonate concentration, in all cases  $6.43 \times 10^{-2}$  M. <sup>d</sup>In this run bromine was used instead of iodine.

The study of the reaction at low iodine concentration provides an approach to a reliable value for the acid-dissociation constant of the phosphonate. At low iodine concentration, eq 5 reduces to the simpler eq 8.

$$d(\text{I}_2)/dt = \frac{k_2K_a((\text{RO})_2\text{PHO})(\text{I}_2)}{(\text{H}^+)} \quad (8)$$

A series of experiments were done with a large excess of the phosphonate ester and low concentrations of iodine showed that iodine disappeared following a first-order course with a rate constant  $k_2K_a((\text{RO})_2\text{PHO})/(\text{H}^+)$ . The derived values of the  $k_2K_a$  product are given in Table III.

The constancy of the last column in the table, covering a factor of 3 variation in  $(\text{H}^+)$ , demonstrates the applicability of eq 7, in that the rate does not depend on buffer concentration or its nature; only the hydrogen ion concentration is in the rate law. The last line in the table is more informative. Since there is no general reason why  $k_2$  for bromine should not be greater than that for iodine, we must look for a specific reason. The most obvious explanation and the one we propose is that both reactions are diffusion controlled. This is plausible since halogens react at diffusion-controlled rates with several nucleophiles, and these phosphonate anions are certainly very good nucleophiles.<sup>10</sup>

The diffusion-controlled rate constant for a neutral-anion reaction is about  $5 \times 10^9$  to  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . The first of these numbers has been used by Dubois and Toullec<sup>11</sup> in their determination of the ionization constants of various ketones. The recent direct observation of enols and their protonation rates<sup>12</sup> gives a number for the keto-enol equilibrium constant for acetone ( $\text{p}K_E = 8.22$ ) slightly different from that determined by Dubois and Toullec ( $\text{p}K_E = 8.46$ ). The two numbers could be brought into perfect agreement by adjustment of the diffusional rate constant, but it is probably not worthwhile since the numbers are very close anyway. We choose the value  $k_2 = 5 \times 10^9$  because our method is virtually identical with that of the French workers. This leads then to the value of  $1.25 \times 10^{-5}/5 \times 10^9 = 2.5 \times 10^{-15}$  for  $K_a$  of diethyl phosphonate.

The constancy of the last column in the table is at first surprising since salt effects on the buffer acid ionization constants were neglected. We must conclude that the salt effect on the ionization of the phosphonate is nearly the same as that on the buffer acid. This cannot be exactly true, since the phosphate buffer has a different charge type. However, a partial cancellation is reasonable. The estimate given is therefore the value expected in the infinitely dilute solution to which the literature values of the acid-dissociation constants apply.

The conclusion from this work, that the Brønsted  $\beta$  is significantly less than unity and that the reaction shows a significant deuterium isotope effect is not really surprising, except for differences from the previous work. Moreover, proton transfers from phosphorus which are below the diffusion-controlled rate are not

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new; thus in addition to the work of Silver and Luz<sup>4</sup> on the acid-catalyzed oxidation which shows an isotope effect, they also showed that proton transfers between phosphines are perceptibly slow in water,<sup>13</sup> and proton transfers from trialkylphosphonium salts are slow in both directions in dimethyl sulfoxide,<sup>14</sup> although in the gas phase phosphites equilibrate with protonated species at rates fast by ICR standards.<sup>15</sup>

Perhaps a more notable conclusion is that the halogenation after proton loss should be as general a method with PH compounds as it is with carbonyl and nitro compounds. The various phosphonates show a wide range of reactivity, thus  $\text{CH}_3\text{OPHO}_2^-$  does not exchange with alkaline  $\text{D}_2\text{O}$  at a significant rate at room temperature, as shown by the stability of the PH proton NMR,<sup>10</sup> so the range of possible reactivities is very large.

Apparently the rate law here is not entirely general, for the iodination of hypophosphorus acid is not zero order in iodine and triiodide ion is slower than iodine. The difference may merely be a slower reaction of iodine with the reactive intermediate.<sup>16</sup>

### Experimental Section

**Materials.** Diethyl phosphonate was a commercial material distilled before use. The proton NMR showed no impurities. A sample was exchanged with heavy water containing sodium carbonate to prepare the deuterated material in  $\text{D}_2\text{O}$  solution. It showed almost complete loss of the phosphorus-bound proton in the NMR (at least 95% D). A small portion of this solution was then put into the buffer solution for the kinetic run. The small solvent kinetic isotope effect from this  $\text{D}_2\text{O}$  in the  $\text{H}_2\text{O}$  solution was neglected as was the small amount of extra base.

**Kinetics.** A mixture of the buffer solution, the ester, and the iodine with iodide was placed in a 1-cm cell jacketed for temperature control at 25 °C in the spectrophotometer, and the absorbance as a function of time was followed. The initial iodine concentration was in the range

0.005 to 0.017. The concentrated solutions of iodine were followed at 560 nm, at which the extinction coefficient is 99; the more dilute runs were followed at 470 nm (extinction coefficient 670). These are isobestic points for iodine and triiodide, thus avoiding the need for correction for the iodide formed in the reaction. Implicit in this method is the assumption that  $\text{I}_2$  and  $\text{I}_3^-$  are equally reactive; the kinetics gave no reason to doubt this assumption. The ester concentration initially was not more than 2% of the buffer concentration, to allow for the 3 mol of acid produced.

At the higher pH values, there was concern about the disproportionation of iodine to iodide and iodate, which would serve as a transparent source of  $\text{I}_2$ , and therefore give rates too low. This was suppressed by the addition of excess iodide, up to 5 M for the carbonate and the ammonia buffers, and by reducing the iodine concentration. Under these circumstances there was no evidence that the iodine concentration was too low for the zero order in iodine assumption. Nevertheless, the low rate constant for  $\text{NH}_3$  buffers suggests the possibility of this problem. We did not study possible salt effect contributions, although Nylén found no experimentally significant salt effects up to 1 M.

In the concentrated iodine solutions the buffer and the iodine were both in excess so the  $A$  vs. time plot was an exponential fall to the infinity value, when the phosphonate was gone. This gave a pseudo-first-order constant for the particular buffer concentration used, except in the case of acetate buffers, for which much higher phosphonate concentrations and the (zero order) fall in iodine concentration were measured. For the dilute iodine solutions the  $A$  vs. time plot was also an exponential decay, when the absorbance was followed in the range 0.1 to 0.0 ( $\text{I}_2 + \text{I}_3^- < 1.5 \times 10^{-4}$ ), giving the  $k_{\text{obsd}}$  values in Table III. In accordance with the rate law, the absorbance vs. time was linear at high absorbance, but then developed curvature leading finally to the exponential section. Because of the pseudo-first-order law, the extinction coefficient of bromine was not needed or determined. Rates not here reported in the high iodine regime with acetate buffers were also measured by the thiosulfate titration method used by Nylén;<sup>1</sup> it gave results in agreement with his considering the temperature difference, but in our hands it was not useful for the faster reactions at the higher pH's.

**Acknowledgment.** We acknowledge the support of this work by the Welch Foundation.

**Registry No.** Diethyl phosphonate, 762-04-9.

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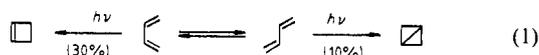
## 185-nm Photochemistry of Cyclobutene and Bicyclo[1.1.0]butane

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**Abstract:** The high quantum yield of the direct 185-nm photolysis of cyclobutene ( $\phi_s = 0.71$ ) leading to 1,3-butadiene is in accord with symmetry-allowed electrocyclic ring opening of a  $\pi, \pi^*$ -excited singlet state of cyclobutene. The formation of ethene, acetylene, and methylenecyclopropane as minor products presumably involves cyclopropylmethylene and cyclobutylidene as carbene intermediates, formed on ( $\pi, 3s$ )-Rydberg excitation of cyclobutene. The 185-nm photolysis of bicyclo[1.1.0]butane resembles that of the homologous bicyclo[ $n.1.0$ ]alkanes. As main products cyclobutene ( $\phi_p = 0.30$ ) and 1,3-butadiene ( $\phi_p = 0.29$ ) are formed. On the other hand, the transformations of methylenecyclopropane on 185-nm irradiation, leading to ethene, acetylene, and 1,3-butadiene, are akin to radiolysis and gas-phase photolysis results of this substrate.

The symmetry-allowed disrotatory electrocyclic closure of 1,3-butadiene into cyclobutene (eq 1) is experimentally and theoretically well understood.<sup>1</sup> However, the reverse process, the



direct photochemical opening of simple cyclobutenes, is only

documented with a few examples.<sup>2</sup> The major reason for this is that simple cyclobutenes show no significant absorption above 200 nm. The same is the case for simple bicyclo[ $n.1.0$ ]alkanes. It is, therefore, not surprising that very little is known on the

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