TABLE IV

"*a*" AND "*b*" VALUES FOR THE HYDROGENATION OF *p*-NITROPHENOL OVER NICKEL POWDER IN AQUEOUS SOLUTION

| Amount catalyst, g. | *a*, *M*/min. | *b* |
|---|---|---|
| 0.345 | 0.0030 | 4.5 |
| 0.74 | .0030 | 10.5 |
| 1.27 | .0029 | 23.8 |
| 2.97 | .0030 | 95.5 |
| 5.10 | .0029 | 1273.0 |

catalyst increases and is first order with respect to hydrogen pressure. The rate of reaction also increases with increasing amount of catalyst and then levels off. No reaction intermediate other than the final products was isolated. The apparent activation energy for hydrogenation of *p*-nitrophenol is 9.8 kcal./mole as compared to 15.2 kcal./mole and 13.2 kcal./mole obtained for the same reaction over Pd and Rh, respectively.

The integrated form of equation 1 is

$$\frac{1}{b}\ln\frac{C_0}{C} + (C_0 - C) = at \qquad (3)$$

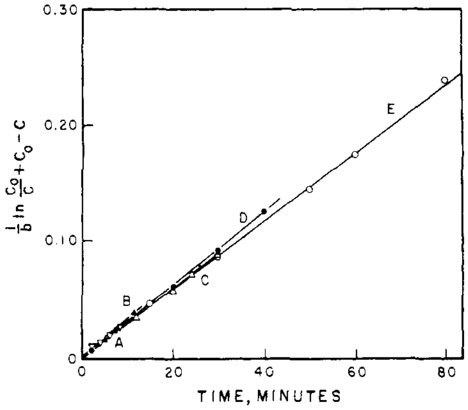

Fig. 7.—Replot of results in Fig. 6 with $\frac{1}{b}\ln\frac{C_0}{C} + C_0 - C$ *vs.* time: A, B, C, D, E, are the same as those in Fig. 6.

Application of this equation to results of Fig. 6 is shown in Fig. 7. The linearity obtained indicates the validity of the equation for the hydrogenation of nitrocompound over the nickel powder catalyst. The "*a*" and "*b*" values calculated from the results are listed in Table IV.

**Acknowledgments.**—The authors wish to thank the National Science Foundation for financing this work. They are also indebted to Dr. Hans Schaefer for helpful discussions.

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[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

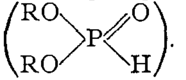
# The Oxidation of Diethylphosphonate. Kinetics and a Kinetic Isotope Effect

BY B. SILVER AND Z. LUZ

RECEIVED JULY 17, 1961

The mechanism of the acid catalyzed formation of the phosphite tautomer of diethylphosphonate has been studied. The dependence on acidity of the oxidation reaction of diethylphosphonate was determined from 0.05 *N* to 4.5 *N* HCl, and a decrease was observed in the apparent acid catalysis constant with increasing acidity. A comparison was made between the oxidation rates of normal and deuteriated $(EtO)_2PO \cdot D$, diethylphosphonate, a value of 4 being found for the kinetic isotopic effect ($k^H/k^D$) on the acid catalyzed reaction. A change in solvent from $H_2O$ to $D_2O$ increases the rate of the acid catalyzed oxidation reaction. The results are interpreted in terms of a pre-equilibrium protonation on the phosphoryl group followed by the rate-determining fission of the phosphorus hydrogen bond.

## Introduction

The structure of dialkyl phosphonates has been shown[1] to involve a hydrogen atom directly bonded to the phosphorus atom of the phosphoryl group, . There are many chemical reactions of these compounds which imply the existence of a tautomeric equilibrium between the normal or phosphonate form and an "active" or phosphite form,[2] *i.e.*, $(RO)_2PO{\cdot}H \rightleftarrows (RO)_2P{\cdot}OH$. However, physical measurements have failed to prove the existence of the phosphite form.[2] The chemical evidence is mainly based on kinetic data, for example Nylen[3] found the oxidation of phosphonates to phosphates by halogens to be independent of the concentration of oxidizing agent at high halogen concentrations. This led him to suggest the existence of the above tautomerism in which the phosphite form is the active species, undergoing oxidation. Recently Luz and Silver[4] have studied the kinetics of the acid catalyzed exchange of the phosphorus bonded hydrogen in several dialkyl phosphonates. It was found that the exchange reaction follows the same rate law as that found for oxidation, *i.e.*

$$k = \frac{R}{[\text{phosphonate}]} = k_w + k_H[H^+] \qquad (1)$$

where $R$ is the reaction rate. The values of $k_w$ and $k_H$ for exchange were found to be similar to those given by Nylen for the oxidation reaction. The results are best interpreted in terms of the above tautomeric equilibrium. Fox[5] also has used such an equilibrium to explain his results for hydrogen exchange of dibutylphosphonate in butyl alcohol.

On the basis of the above evidence a general scheme was suggested[4] to describe the mechanism of both the acid catalyzed exchange and oxidation reactions.

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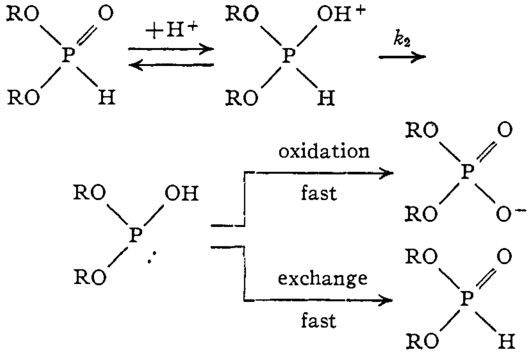
(1) J. R. Van Wazer, "Phosphorus and its Compounds," Interscience Publishers, Inc., New York, N. Y., 1958, Chap. 7.

(2) G. O. Doak and L. D. Freedman, *Chem. Revs.*, **61**, 31 (1961).

(3) P. Nylen, *Z. anorg. u. Allgem. Chem.*, **235**, 161 (1938).

(4) Z. Luz and B. Silver, *J. Am. Chem. Soc.*, **83**, 4518 (1961).

(5) R. B. Fox, NRL Report 5242, January 8, 1959.


(I)

The first step shows a reversible protonation of the phosphoryl group followed by the fission of the phosphorus hydrogen bond, resulting in the formation of the phosphite form. It was shown[4] that the rate of formation of the phosphite form is the rate determining step in both oxidation and exchange reactions since this form is very active, rapidly reverting to the phosphonate form in the presence of a proton donor, or being immediately oxidized in the presence of excess oxidizing agent. The rate law (eq. 1) obeyed by the exchange and oxidation reactions is consistent with the suggested scheme but fails to distinguish between (i) a fast pre-equilibrium, followed by a slow rate determining fission of the P–H bond, or (ii) a slow rate determining proton transfer to the phosphoryl group. The aim of the present work was to distinguish between mechanisms (i) and (ii). The approach was based on a study of the oxidation reaction of diethylphosphonate. In principle a study of the hydrogen exchange reaction of diethylphosphonate would yield the same information as that obtained by studying the oxidation reaction. However the oxidation reaction was chosen, since the kinetics may be followed with greater accuracy.

To determine whether the fission of the P–H bond is rate-determining, a comparison was made between the rates of acid catalyzed oxidation of the normal and deuteriated forms of diethylphosphonates. On the basis of much previous evidence[6] the substitution of deuterium for hydrogen in a given bond would be expected to reduce the rate of any step in a reaction involving the breaking of this bond.

In order to obtain additional data that would aid in distinguishing between mechanisms (i) and (ii), the oxidation reaction of diethylphosphonate was studied at acidities up to 4.5 *N* HCl. Both the acid-catalyzed oxidation[3] and exchange[4] of dialkyl phosphonates have been studied for concentrations of acid less than 1 *N*, in which range the reaction rate was found to be linearly dependent on acid concentration, as expressed in equation 1. The same behavior was observed for the acid-catalyzed hydrolysis of dialkyl phosphonates[7] and fluorophosphonates[8] at low acid concentrations. However, at higher acidities the apparent acid catalysis constant for hydrolysis of these compounds decreases with increasing acid concentration. This behavior has been explained[9] on the basis of Euler's ionization theory,[10] which involves the existence of a pre-equilibrium between the substrate and its conjugate acid, the equilibrium constant for the protonation being of the order of unity. In the present work it is shown that a similar deviation from linearity occurs at higher acid concentration for the acid catalyzed oxidation reaction of dialkyl phosphonates.

The effect on reaction rate of a change in solvent from $H_2O$ to $D_2O$ has been used in studies of acid catalysis to distinguish between a pre-equilibrium protonation and one-step slow proton transfer.[11,12] In this paper some results are given for the oxidation of diethylphosphonate in acidic $D_2O$ solutions.

**Material.**—**Diethylphosphonate**, (b.p. 72–73° (9 mm.)) was made by the reaction of $PCl_3$ with ethanol[13] and was double-distilled before use.

**Diethylphosphonate-*d*,** $(EtO)_2PO{\cdot}D$, (b.p. 72–73°(9 mm.)) was made from $PCl_3$ and ethanol-*d*. Ethanol-*d* was made by hydrolyzing diethyl oxalate[14] with $D_2O$ and distilling the product. The diethylphosphonate so obtained contained 9±2% of the normal diethylphosphonate, as estimated by n.m.r. intensity measurements on the resonance line of the phosphorus bonded hydrogen.[4]

**DCl solution** was made by passing DCl gas into $D_2O$. The DCl was obtained from the reaction of benzoyl chloride and $D_2O$.[15] $D_2O$ (99.5%) was purchased from Norsk Hydro-elektrik; KI and $I_2$ were Analar reagents.

**Procedure.**—In aqueous acidic solutions of oxidizing agents, dialkyl phosphonates undergo simultaneous oxidation, to phosphates, and hydrolysis, to monophosphonates. In order to allow for the hydrolysis reaction in studying the oxidation kinetics, the general procedure of Nylen[3] was adopted. The decrease in oxidizing agent (iodine) was followed by titrating samples of the reaction mixture with sodium thiosulfate solution (0.01 *N*). Concurrent determination of the extent of hydrolysis was made as follows. At measured times samples of the reaction solution were mixed with disodium phosphate solution, slightly in excess of that needed to neutralize the acid present and allowed to stand at room temperature for 15 min. Under these conditions, the oxidation of the diethylphosphonate proceeds to completion, and the oxidation of the monoethylphosphonate is negligible, as is the hydrolysis of the diethylphosphonate. At the end of this time the residual iodine is titrated against standard alkaline arsenite solution (0.01 *N*). The decrease in iodine as determined by the thiosulfate titration measures the amount of phosphonate oxidized at the time of titration. The increase in the value of the arsenite titration measures the amount of hydrolysis as a function of time. All runs were followed to about 75% reaction. The compositions of the reaction solutions are given under Results.

Analysis of the experimental data was based on the procedure of Nylen,[3] except that the acid produced by the formation of HI and monoethylphosphonate was neglected. This introduces an error of about 3 to 6% in the measured rate constants for the lowest acidities (0.1–0.2 *N*) and a much lower error (<2%) at higher acidities. The relevant rate equation is

$$\ln\left(\frac{[\text{phosphonate}]_0}{1+\varphi} - [\text{phosphonate}]_t\right) = -k(1+\varphi)t + \ln\frac{[\text{phosphonate}]_0}{1+\varphi} \qquad (2)$$

which is a form of the general rate equation for two competing first order reactions[16] and applies in the present case

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[6] K. B. Wiberg, *Chem. Revs.*, **56**, 713 (1955).

[7] P. Nylen, *Svensk Kem. Tidskr.*, **49**, 29 (1937).

[8] M. Kilpatrick and M. L. Kilpatrick, *J. Phys. and Colloid Chem.*, **53**, 1371 (1949).

[9] G. Aksnes, *Acta Chem. Scand.*, **14**, 1526 (1960).

[10] R. P. Bell, "Acid-Base Catalysis," Oxford, 1941, p. 122.

[11] F. A. Long and M. A. Paul. *Chem. Revs.*, **57**, 935 (1957).

[12] F. A. Long, *Ann. N. Y. Acad. Sci.*, **84**, 596 (1960).

[13] H. McCombie, S. C. Saunders and G. J. Stacie, *J. Chem. Soc.*, 380 (1945).

[14] J. Beersman and J. C. Jungers, *Bull. soc. chim. Belges*, **56**, 72 (1947).

[15] H. C. Brown and C. Groot, *J. Am. Chem. Soc.*, **64**, 2223 (1942).

[16] "Kinetics and Mechanism," A. A. Frost and R. G. Pearson, John Wiley and Sons, Inc., New York, N. Y., 1953, Chap. 8.

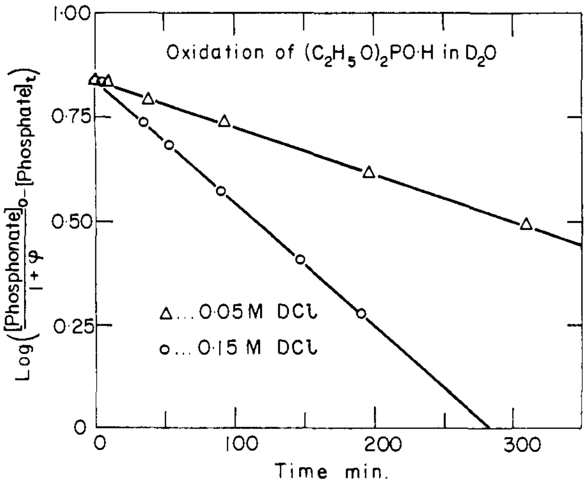

Fig. 1.—Kinetics of oxidation of diethylphosphonate in $D_2O$ in 0.05 *M* and 0.15 *M* DCl at 22 ± 1°.

since both the oxidation and hydrolysis reaction show first order kinetics under the experimental conditions. In the rate equation, $k$ is the observed first order rate constant for oxidation at any given acidity, the term $[\text{phosphonate}]_0$ is the initial concentration of diethylphosphonate and $[\text{phosphate}]_t$ is the concentration of phosphate formed up to time $t$. $\varphi$ is the ratio of first order rate constants of hydrolysis to oxidation and is equal to the ratio of the products of hydrolysis and oxidation at any time. In practice plots were made of $\log\left(\frac{[\text{phosphonate}]_0}{1+\varphi} - [\text{phosphate}]_t\right)$ against time. From equation 2 such plots should be linear with a slope of $k(1 + \varphi)$. Linearity was in fact observed, the estimated error in $k$, obtained from the slopes, is less than 5% at lower acidities and about 10% above 2 *N* acid. In the study of the oxidation of diethylphosphonate in $D_2O$, the question arises whether some of the phosphorus bonded hydrogen exchanges during the reaction, resulting in the formation of the deuteriated form of diethylphosphonate. Such an exchange should be manifested by a deviation from linearity in the plots for the reactions since, as will be shown later, the isotopic isomers have appreciably different reaction rates. As may be seen from Fig. 1 no such deviation is detectable, indicating the absence of significant exchange. The same applies to the case of diethylphosphonate-*d* in $H_2O$.

The synthesis of diethylphosphonate-*d* gave a product containing 9 ± 2% of the normal form, and correction was made for this in calculating the rate constants for the oxidation of diethylphosphonate-*d*.

## Results

To extend Nylen's[3] results for the oxidation reaction to higher acidities, aqueous solutions were prepared containing 0.0078 *M* diethylphosphonate, 0.14 *M* KI, 0.03 *M* $I_2$ and varying amounts of HCl. The oxidation reaction was followed as described under Procedure, and the first order rate constants obtained are shown in Table I and plotted in Fig. 2.

As seen from Fig. 2 the plot of $k$, against acid concentration, falls away from linearity at higher acid concentration. The possibility that this deviation is due to the dependence of the oxidation rate on iodine concentration is ruled out by the fact that even at the highest acidities the logarithmic plots were found to be linear. This zero-order dependence on iodine concentration also is indicated by the results for the three runs carried out in 4 *N* HCl (Table I). Doubling both the concentration of KI and $I_2$ gives a small increase in rate which is seen to be due mainly to the additional KI.

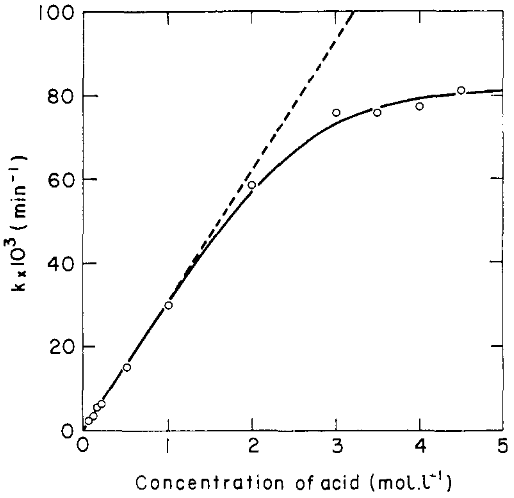

Fig. 2.—Variation with stoichiometric acidity of observed first-order rate constant $k$ for the oxidation of diethylphosphonate at 22 ± 1°.

To determine the effect on the oxidation rate of substituting deuterium for the phosphorus bonded hydrogen, parallel sets of runs were carried out on the normal and deuteriated forms of diethylphosphonate. The solutions were 0.0078 *M* in diethylphosphonate, 0.14 *M* in KI and 0.03 *M* in $I_2$ and contained varying amounts of HCl. The values obtained for the first-order rate constants for the deuteriated compound are compared in Table II, with the values of $k$ already given for the normal compound at comparable acidities. These results are included in Fig. 3.

TABLE I

OBSERVED FIRST ORDER RATE CONSTANTS $k$ FOR THE OXIDATION OF DIETHYLPHOSPHONATE FOR DIFFERENT CONCENTRATIONS OF HCl (TEMP. 22.0 ± 1.0°)

| HCl, *M* | $k \times 10^3$ min.⁻¹ | HCl, *M* | $k \times 10^3$ min.⁻¹ |
|---|---|---|---|
| 0.05 | 2.14 | 3.0 | 76.0 |
| .10 | 3.37 | 3.5 | 76.0 |
| .15 | 5.48 | 4.0 | 77.5 |
| .20 | 6.46 | 4.0[a] | 83.0 |
| .50 | 15.2 | 4.0[b] | 82.0 |
| 1.0 | 30.0 | 4.5 | 81.5 |
| 2.0 | 58.5 | | |

[a] In this run the concentration of $I_2$ and KI were doubled (0.06 *M* $I_2$ and 0.28 *M* KI). [b] In this run the concentration of KI was doubled (0.03 *M* $I_2$ and 0.28 *M* KI).

TABLE II

OBSERVED FIRST ORDER RATE CONSTANTS $k$ FOR THE OXIDATION OF DIETHYLPHOSPHONATE AND DIETHYLPHOSPHONATE-*d* AT DIFFERENT HCl CONCENTRATIONS IN $H_2O$. (TEMP. 22.0 ± 1.0°)

| HCl (*M*) | 0.050 | 0.100 | 0.125 | 0.150 | 0.200 | 0.275 |
|---|---|---|---|---|---|---|
| $k \times 10^3$ (min.⁻¹) for $(EtO)_2PO{\cdot}H$ | 2.14 | 3.37 | .. | 5.48 | 6.46 | .. |
| $k \times 10^3$ (min.⁻¹) for $(EtO)_2PO{\cdot}D$ | 0.71 | .. | 1.36 | .. | 1.88 | 2.72 |

The results show that the substitution of deuterium for phosphorus bonded hydrogen decreases the oxidation rate appreciably. The values of $k$ vary linearly with acid concentration in the range studied.

To investigate the effect on the reaction of a change in solvent from $H_2O$ to $D_2O$, oxidation runs

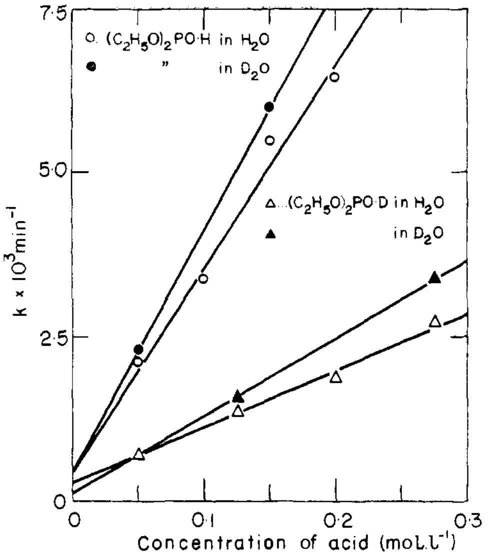

Fig. 3.—Variation with stoichiometric acidity of observed first-order rate constant $k$ for the oxidation of normal and deuteriated diethylphosphonate in $H_2O$ and $D_2O$ at 22 ± 1°.

were carried out in $D_2O$ using the same concentrations of diethylphosphonate, KI and $I_2$ as used in the above experiments. Similar runs were carried out using diethylphosphonate-*d*, and the results are shown in Table III and plotted in Fig. 3.

TABLE III

OBSERVED FIRST ORDER RATE CONSTANTS $k$ FOR THE OXIDATION OF DIETHYLPHOSPHONATE AND DIETHYLPHOSPHONATE-*d* IN $D_2O$ (TEMP. 22.0 ± 1.0°)

| DCl ($M$) | 0.050 | 0.125 | 0.150 | 0.275 |
|---|---|---|---|---|
| $k \times 10^3$ (min.$^{-1}$) for $(EtO)_2PO\cdot H$ | 2.31 | .. | 6.00 | .. |
| $k \times 10^3$ (min.$^{-1}$) for $(EtO)_2PO\cdot D$ | .. | 1.57 | .. | 3.40 |

These results show that the rate of oxidation is higher in $D_2O$ than in the corresponding $H_2O$ solutions.

## Discussion

The results of the present work are consistent with a pre-equilibrium protonation followed by the rate-determining fission of the phosphorus–hydrogen bond.

From the results, the observed first order rate constant for oxidation, $k$, is the sum of two terms, one due to the acid catalyzed reaction and another acid-independent term $k_w$. The term for the acid catalyzed reaction, derived from Scheme I, is equal to the specific rate of formation of the phosphite form, $\frac{1}{[\text{phosphonate}]} \times \frac{d[\text{phosphite}]}{dt}$. The observed first order rate constant therefore is given by

$$k = k_w + \frac{1}{[\text{phosphonate}]} \times \frac{d[\text{phosphite}]}{dt} = k_w + \frac{k_2K[H^+]}{1 + K[H^+]} \quad (3)$$

where $K = \frac{[(RO)_2POH\cdot H^+]}{[(RO)_2PO\cdot H][H^+]}$, and $k_2$ is the first order rate constant for the fission of the P–H bond. If $K[H^+] \ll 1$, the rate equation reduces to $k = k_w + k_H[H^+]$ where $k_H = k_2K$. This is the rate law observed by Nylen[3] for the oxidation reaction in dilute acid. If $K[H^+]$ is of the order of unity, the first order rate constant $k$ no longer shows a linear dependence on $[H^+]$. Such a deviation from linearity occurs in the present case and indicates the presence of a pre-equilibrium protonation.[10,11] The possibility that the observed deviation is due to a large negative salt effect, is excluded by the observation in preliminary work that the oxidation reaction is in fact subject to a small positive salt effect in both dilute and strong acid media.

The hydrolysis of dialkyl phosphonates has been analyzed recently by Aksnes[9] in terms of a pre-equilibrium protonation on the phosphoryl group followed by the rate determining attack of water on the phosphorus atom. Values of $K$, the equilibrium constant for the protonation, were derived from the experimental data of Nylen and independent estimates of $K$ for the same compounds were made on the basis of shifts in the O–D frequency in the infrared spectrum of small amounts of $D_2O$ dissolved in these compounds. The different values of $K$ (in mole$^{-1}$ l.) for diethylphosphonate given in ref. 9 are ~1.1, from kinetic data, and ~0.4 from infrared measurements. In view of the fact that $K$ has an unknown dependence on ionic strength the value derived from kinetic data can indicate only the order of magnitude of $K$. For this reason no attempt was made in the present work to obtain a value for $K$; however, from the experimental data $K$ may be stated to be of the order of unity, in agreement with the above values. Aksnes[9] interprets $K$ as a so-called association constant for the hydrogen-bonded complex between phosphonate and hydroxonium ion. The reason given for this interpretation is that if $K$ represents a conventional dissociation constant a significant change in $p$H would be expected on dissolving dialkyl phosphonates in water. This seems incorrect since on the basis of the above values for $K$, very slight changes in the $p$H of a solution would be expected on the addition of diethylphosphonate.

The hypothesis that the breaking of the P–H bond is the rate-determining step in the formation of the phosphite form was tested by substituting deuterium for the phosphorus bonded hydrogen of diethylphosphonate. From the results plotted in Fig. 2 values of $k_H$ and $k_w$, as defined in equation 1, were derived for the normal and deuteriated forms at 22° and are tabulated below.

TABLE IV

| | $(EtO)_2PO\cdot H$ | $(EtO)_2PO\cdot D$ |
|---|---|---|
| $k_H$, $M^{-1}$ min.$^{-1}$ | $3.1 \pm 0.2 \times 10^{-2}$ | $0.8 \pm 0.1 \times 10^{-2}$ |
| $k_w$, min.$^{-1}$ | $0.5 \pm 0.2 \times 10^{-3}$ | $0.3 \pm 0.1 \times 10^{-3}$ |

The ratio of the acid catalysis constants $k_H^H/k_H^D$ in $H_2O$ is 4 where the superscripts H and D refer to the normal and deuteriated forms, respectively. This large effect proves that fission of the P–H bond is the rate-determining step in acid catalyzed phosphite formation.

The theoretical maximum kinetic isotope effect, associated with the breaking of the P–H bond, can be calculated from the vibration frequencies of the P–H and P–D bonds.[6] For diethylphosphonate the respective frequencies were found[17] to be 2460

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[17] Thanks are due to Dr. S. Pinchas of this Institute for carrying out the infrared measurements.

and 1770 cm.$^{-1}$, from which a maximum isotope effect at 22° may be calculated to be $k^{\mathrm{H}}/k^{\mathrm{D}} = 5.3$. A similar value (5.1 at 25°) also was obtained by Martin[18] for the analogous bond in phosphorous acid. The observed value of $k^{\mathrm{H}}/k^{\mathrm{D}}$ is not far below the calculated maximum value, indicating considerable stretching of the P–H bond in the transition state. It should be noted that the maximum kinetic isotope effect was calculated from the vibration frequencies of the liquid phosphonate and therefore does not apply exactly to the protonated phosphonate in aqueous solution.

The isotope effect for the spontaneous reaction $k_{\mathrm{w}}^{\mathrm{H}}/k_{\mathrm{w}}^{\mathrm{D}}$ is approximately 1.7 and though subject to considerable error, appears to be significantly lower than that for the acid catalyzed reaction. Swain[19] recently has discussed the variation of isotope effect with the strength of the catalyzing acid for some keto–enol isomerizations and postulates that, other things being equal, the kinetic isotope effect increases with acid strength. The lower value of the kinetic isotope effect for the spontaneous reaction, in the present case, possibly is to be explained in a similar manner, assuming water to be the catalyzing acid in the spontaneous reaction.

The effect of solvent $D_2O$ on the oxidation reaction of diethylphosphonate is shown in Table III and Fig. 3. The rates in $D_2O$ are seen to be systematically 15–30% higher than the corresponding runs in $H_2O$. An increase of this kind has been considered to provide evidence for the existence of a pre-equilibrium protonation.[6] Long[12] has estimated numerical limits for the expected solvent isotope effects $k^{\mathrm{D_2O}}/k^{\mathrm{H_2O}}$ in acid catalysis, giving approximate limits of 1.4 to 3.0 for pre-equilibrium and 0.7 to 1.4 (with less than unity values being more likely), for a slow proton transfer. Although the present studies in $D_2O$ therefore do not exclude the possibility of a slow proton transfer, neither do they rule out the existence of a pre-equilibrium.

This investigation was supported in part by a research grant (RG 5842) from the Division of Research Grants, U.S. Public Health Service. One of us (B.S.) is the holder of a Max and Rebecca Schrire Medical Research Grant.

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[18] R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1574 (1959).

[19] C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *ibid.*, **80**, 5885 (1958).

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[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

# N.m.r. Study of the Exchange of Phosphorus Bonded Hydrogen in Dimethyl- and Diethylphosphonate, Catalyzed by Acetate Ion

BY Z. LUZ AND B. SILVER

RECEIVED JULY 17, 1961

The exchange of the phosphorus-bonded hydrogen with deuterium in $D_2O$ solutions of sodium acetate has been studied for dimethyl- and diethylphosphonate using a nuclear magnetic resonance technique previously described.[1] The exchange was found to be linearly dependent on the acetate ion concentration. From a comparison of the data obtained with those found for the oxidation of the same compounds, it is suggested that the phosphite form of the dialkyl phosphonate serves as a common intermediate for both the exchange and oxidation reactions. The substitution of deuterium for the phosphorus bonded hydrogen in diethylphosphonate had a negligible effect on the oxidation rate. This result is discussed in terms of possible mechanisms for the formation of the phosphite form.

## Introduction

The oxidation of dialkyl phosphonates[2] and the exchange of the phosphorus bonded hydrogen[1] in the same compounds have been found to be acid catalyzed. The mechanisms of both reactions have been interpreted in terms of a tautomeric equilibrium between the normal (phosphonate) form and an active (phosphite) form.[1–4] The rate determining step in both reactions was shown to be the formation of the phosphite form which serves as a common intermediate for both oxidation and exchange. It is known[2] that the oxidation of dialkyl phosphonates also is subject to general base catalysis, and it was therefore of interest to determine whether the exchange of the phosphorus bonded hydrogen is similarly catalyzed. That this is in fact the case was determined by preliminary experiments, and a quantitative study of this exchange was performed with the n.m.r. technique previously used[1] in studying the acid catalyzed exchange. The basic catalyst used in the present work was acetate ion, for which comparable data for oxidation are available.[2] No attempt was made to study hydroxide ion catalysis of exchange since the hydrolysis of dialkyl phosphonates is strongly catalyzed by hydroxide ion. The exchange reaction was studied for dimethyl- and diethylphosphonate. An attempt to study the reaction for di-*n*-propylphosphonate failed since this compound was salted out of solution by the addition of the catalyst.

## Experimental

The n.m.r. spectrum of a dialkyl phosphonate includes a doublet due to the phosphorus bonded hydrogen. The rate of exchange of this hydrogen with solvent $D_2O$ may be measured by observing the decrease, with time, of the relative intensity of one component of this doublet (P–H line). The procedure in the present work is identical with that described in reference 1. The reaction solutions contained varying amounts of dialkyl phosphonate, sodium acetate and acetic acid in $D_2O$. First-order rate constants $k$ for the exchange reaction were evaluated from a plot against time of the logarithm of the relative intensity of a P–H line. Since under the present experimental conditions the hydrolysis of dialkyl phosphonates is negligible,[5] hydrolysis

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[1] Z. Luz and B. Silver, *J. Am. Chem. Soc.*, **83**, 4518 (1961).

[2] P. Nylen, *Z. anorg. u. allgem. Chem.*, **235**, 161 (1938).

[3] B. Silver and Z. Luz, *J. Am. Chem. Soc.*, **84**, 1091 (1962).

[4] G. O. Doak and L. D. Freedman, *Chem. Revs.*, **61**, 31 (1961).

[5] P. Nylen, *Svensk Kem. Tidskr.*, **49**, 79 (1937).