where $\delta_{Internal}$ is the internal chemical shift, $\delta_X - \delta_B$ or $\delta_X - \delta_A$ in c.p.s. at 60 Mc. between the X proton and the adjacent proton in question, E is the electronegativity of the substituent and ϕ is the dihedral angle between the X proton and the proton in question on the adjacent carbon atom. The two solid lines are calculated for $\phi = 0°$ and $\phi = 120°$ corresponding to the dihedral angles between the protons in the bicyclic chloro compounds. The internal chemical shift for the corresponding ethyl derivatives, being a rotational average over all possible orientations of the methylene protons with respect to the methyl protons, can be calculated from the chemical shifts at 120° and 0° for any given compound by

$$\delta_{1nt.\ Av.} = \tfrac{1}{3}[2\delta_{1nt}(\phi = 120°) + \delta_{1nt}(\phi = 0°)]$$

The values for this average chemical shift are represented by the dashed line and are found to correspond to the internal chemical shift for the individual ethyl derivatives (the square points) as determined by Cavanaugh and Dailey. In view of the highly anisotropic environment of the protons on the bicyclic chloro compounds, it is surprising that any single relationship can be found between these chemical shifts and those of the corresponding ethyl derivatives; therefore the relationship observed above may be purely fortuitous. It is known, for instance, that a proton lying in the plane of a double bond is shielded and a proton located above the plane of a double bond is deshielded with respect to an unperturbed proton.[26] This phenomenon has been employed by Fraser[27] to establish the configuration of carboxylic acid derivatives of bicyclo-[2.2.1]-hept-2-enes. As in the bicyclic chloro compounds the *endo* protons in Fraser's compounds are usually found at higher fields than the *exo* protons since the *endo* proton lies above the plane of the double bond and the *exo* proton is in a position approximately in the plane of the double bond.

In the series of bicyclic chloro compounds there are undoubtedly both paramagnetic and diamagnetic contributions to the shieldings of the three protons arising from the presence of the anisotropic double bond, and the bridge and bridgehead chlorine atoms. However, these shielding contributions should remain essentially constant through the series of compounds. The observed differences in internal chemical shifts are therefore functions of the substituent *and* presumably (as calculated above) also functions of the dihedral angles

(26) L. M. Jackman. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London. 1959. p. 129.
(27) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

between the protons. However, internal chemical shifts for only two angles have been obtained, therefore the angular dependence of this internal chemical shift is not well established. It is clear, however, despite fairly wide variations of some of the points that the differences in internal chemical shifts are dependent on the electronegativity[28] of the substituent.

Experimental

The proton magnetic resonance spectra were obtained with a Varian Associates DP-60 high-resolution n.m.r. spectrometer operating at a frequency of 60 Mc./sec. The line positions were obtained by the side band technique with graphical interpolation and are the average of about ten measurements. Chemical shifts are considered accurate to ±1 c.p.s. and coupling constants to ±0.2 c.p.s. Each sample was run as a ten per cent solution in carbon disulfide containing tetramethylsilane as an internal reference. The samples were sublimed at 0.4 mm. at 120° and had the melting points given in Table III. Despite the fairly wide melting point ranges observed, the samples were homogeneous as far as could be ascertained from the n.m.r. spectra with no extraneous lines appearing in any of the spectra.

TABLE III

DIELS–ALDER ADDUCTS OF HEXACHLOROCYCLOPENTADIENE AND MONOSUBSTITUTED ETHYLENES

I R =	M.p. found. °C.	M.p. reported, °C.	Ref.
CN^a	143–145.5	143	c
COOH^a	178–180	181–182.5	d
C₆H₅^a	72–73	73–76	e
Cl^{a,b}	130–142.5	125–136	f
OH^b	156–157	155	g
OAc^{a,b}	42–42.5	44	g

^{a} Sample from Hooker Electrochemical Co., Niagara Falls, N. Y.; ^{b} Sample from Monsanto Chemical Co., St. Louis, Mo.; ^{c} E. A. Prill, *J. Am. Chem. Soc.*, **69**, 62 (1947); ^{d} S. B. Soloway, J. G. Morales and J. Van Overbeek, U. S. Patent 2,758,918, *C.A.*, **50**, 17307b (1956); ^{e} S. H. Herzfeld, R. E. Lidov and H. Bluestone, U. S. Patent, 2,606,910, *C.A.*, **47**, 8775b (1953); ^{f} H. Bluestone, U. S. Patent 2,676,132 *C.A.*, **48**, 8474b (1954); ^{g} E. K. Fields, *J. Am. Chem. Soc.*, **78**, 5821 (1956).

(28) It has been pointed out by Dr. Norman Sheppard (private communication) that the apparent electronegativities derived from chemical shift data on the ethyl compounds probably include not inconsiderable contributions from magnetic anisotropies within them. therefore the linear correlations observed between the internal chemical shifts in these cyclic compounds and Cavanaugh and Dailey's internal shifts may well reflect a parallelism in magnetic anisotropies as well as "true" electronegativities.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INCORPORATED, MURRAY HILL, NEW JERSEY]

Kinetic Study of the H₂POOH–D₂O Exchange by Nuclear Magnetic Resonance

BY A. FRATIELLO AND E. W. ANDERSON

The exchange with D₂O of the phosphorus bonded hydrogens of hypophosphorous acid has been studied using a nuclear magnetic resonance technique. Intensity measurements were used to follow concentration changes during the exchange. The rate law for the exchange, which is acid catalyzed, was found to be: rate $= k_1[H_3PO_2]^2 + k_2\cdot[H_3PO_2][H^+ + D^+]$. The rate constants for the reaction are compared to those determined for the tritium exchange and an isotope effect is discussed.

Introduction

Several studies have been made on the exchange of phosphorus bonded hydrogens. Luz and Silver[1,2] and

Hammond[3] made nuclear magnetic resonance investigations of the exchange of several dialkyl phosphonates with D₂O, and Martin[4] has studied deuterium exchange

(1) Z. Luz and B. Silver. *J. Am. Chem. Soc.*, **83**, 4518 (1961).
(2) Z. Luz and B. Silver. *ibid.*, **84**, 1095 (1962).

(3) P. R. Hammond. *J. Chem. Soc.*, (London). 1365 (1962).
(4) R. B. Martin. *J. Am. Chem. Soc.*, **81**, 1574 (1959).
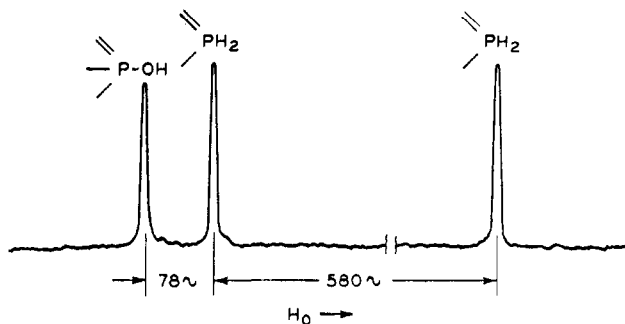
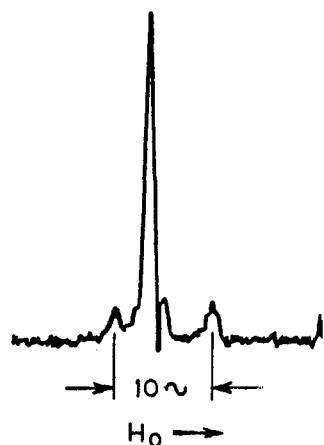Fig. 1.—N.m.r. spectrum of anhydrous hypophosphorous acid at 25°.

Fig. 2.—N.m.r. spectrum of one of the doublet components of the phosphorus bonded hydrogens in a mixture of $H_2POOH(D)$ and $HDPOOH(D)$.

with phosphorous acid by a Raman technique. Jenkins and Yost[5] followed the hypophosphorous acid exchange with water using tritium labeling.

The purpose of this work is to carry out a kinetic study of the exchange of hypophosphorous acid with D_2O. A nuclear magnetic resonance technique is utilized for the measurements. Previous kinetic studies of this system, both by Raman spectroscopy[4] and by deuterium analysis,[6] were unsuccessful due to the rapidity of the exchange.

Experimental

The hypophosphorous acid and salts used in this work were reagent grade. Anhydrous H_3PO_2 was prepared by drying the 50% acid (Fisher) at room temperature under vacuum. Anhydrous NaH_2PO_2 was obtained from $NaH_2PO_2 \cdot H_2O$ (Fisher) by heating for 2 hours at ~200° under vacuum. A 2.5 molar stock solution of DCl was prepared by adding D_3PO_4 to freshly dried NaCl (Baker) to liberate DCl gas which subsequently was passed through 99.5% D_2O (General Dynamics). The D_3PO_4 was made by the addition of D_2O to anhydrous P_2O_5 (Allied Chemical).

All measurements were made on a Varian DP 60 spectrometer at 29.5 ± 1°. The spectrum of hypophosphorous acid, shown in Fig. 1, consists of a widely spaced doublet (~580 c.p.s.) due to the phosphorus bonded hydrogens, and a third peak, at lower field, due to the acid hydroxyl proton and the protons from any small amount of water (~1%) which may be present in the system. Since the water and acid protons exchange rapidly the position of this peak varies greatly with water concentration.

Since the intensity of a peak is proportional to the concentration of the species producing it, exchange of the phosphorus bonded protons on the acid with D_2O results in a decrease in the intensity of the doublet. As the doublet intensity decreases, a broad triplet signal, with an over-all splitting of 10 c.p.s., appears at the base of each component of the doublet. This is illustrated in Fig. 2. The triplet arises from $HDPOOH(D)$ formed in the first step of the exchange. The line width of the

(5) W. A. Jenkins and D. M. Yost, *J. Inorg. Nuclear Chem.*, **11**, 297 (1959).

(6) A. D. Brodskii and S. V. Sulima, *Doklady Akad. Nauk. S.S.S.R.*, **85**, 1277 (1952); *C. A.*, **47**, 930e (1953).
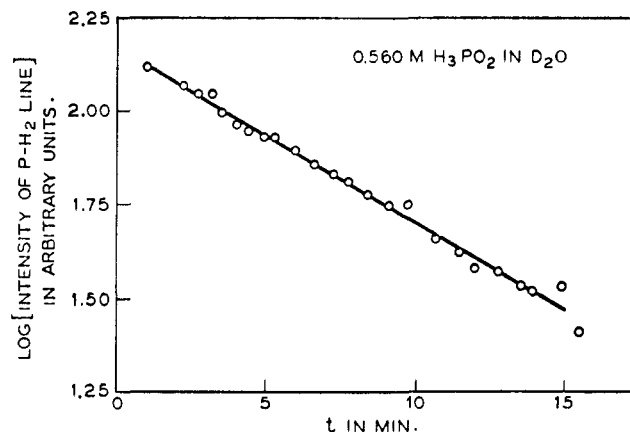

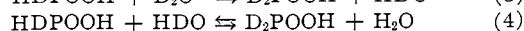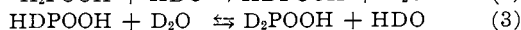Fig. 3.—Plot of the logarithm of the intensity of one of the PH_2 components of H_3PO_2 versus time.

triplet components was only slightly greater than that of the doublet components which was ~1 c.p.s. Owing to an isotope shift, the center of the triplet is not perfectly superimposed on the doublet components, but rather, as also illustrated in Fig. 2, the triplet is displaced approximately one cycle upfield.

The experiments were carried out by mixing known concentrations of the reactants and recording spectra as soon as possible after mixing, usually about one minute. The temperature of the reactants before mixing was kept as close as possible to that of the probe to ensure rapid attainment of thermal equilibrium. After mixing, the decrease in acid concentration was followed with time by sweeping rapidly (2–3 c.p.s.) through one of the doublet components. The peak height was used as a measure of the concentration. In early experiments, peak areas, measured with a planimeter, were used as an indication of the acid concentration. However, the slow field sweeps necessary to produce measurable areas were non-linear and, as a result, the precision of these measurements was only half as good as that which resulted from the peak height measurements. In addition the faster sweeps made possible by measuring peak heights rather than areas allows one to take more data per run and to use higher r.f. voltages before saturation appears. The increase in r.f. level gives an apparent increase in signal to noise which is helpful at low acid concentrations.

Since the intensity of all peaks in the spectrum varied during the course of the exchange, one could not check the peak height calibration during a run. However, since most of the runs were of relatively short duration (<30 min.), errors arising from fluctuations in r.f. intensity were most likely within experimental precision. As a result of the isotopic shift previously mentioned, the contribution of the triplet to the doublet peak height was small and was ignored.

Results

The stoichiometric reactions which occur in a mixture of H_3PO_2 and D_2O, neglecting exchange of the acid hydroxyl proton, are

$$H_2POOH + D_2O \rightleftharpoons HDPOOH + HDO \quad (1)$$
$$H_2POOH + HDO \rightleftharpoons HDPOOH + H_2O \quad (2)$$
$$HDPOOH + D_2O \rightleftharpoons D_2POOH + HDO \quad (3)$$
$$HDPOOH + HDO \rightleftharpoons D_2POOH + H_2O \quad (4)$$

An analysis of these reactions for the experimental conditions of our study, that is, $[D_2O] \gg [H_3PO_2]$ and $[H_2O]$, yields the first order expression

$$\ln \{[H_3PO_2]/[H_3PO_2]_0\} = 4k[D_2O]t \quad (5)$$

where k is the specific rate for the exchange of one proton. The brackets indicate molar concentration while the subscript indicates initial concentration of acid. A typical example of the linear plots of $\ln [H_3PO_2]$ vs. time obtained from our data is given in Fig. 3.

From the slopes of such plots, R, defined[7] as the gross rate of exchange of a phosphorus bonded hydrogen with water, could be calculated from the following considerations. R is related to the specific rate of the exchange by

$$R = \{2\Sigma[H_3PO_2] \times 2[D_2O]\}k \quad (6)$$

(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 179.

where

$$\Sigma[H_3PO_2] = [H_3PO_2] + [H_2PO_2^-]$$

Since the experimentally observed slope, S, is given by $S = 4k[D_2O]$

$$R = S \times \Sigma[H_3PO_2] \qquad (7)$$

In order to study the dependence of the specific rate constant, k, on reactant concentrations, the following reactions were carried out. First, since preliminary work[5] had indicated that the exchange is acid catalyzed, runs were carried out in the presence of a high concentration of NaH_2PO_2, thereby reducing the proton concentration to a negligible value. In this way, the acid independent term of the rate equation

TABLE I

[H₃PO₂]	[H⁺]+[D⁺]ᵃ	[H₂PO₂⁻]	k_1	k_3	
0.752	0.014	4.51	0.148	0.10	
.579	< .01	4.55	.146	.08	
.438	< .01	4.32	.146	.06	
			k_2	k_4	k_5
0.385	0.175	0.175	0.57	0.22	1.30
.390	.177	.177	.49	.24	1.36
.405	.180	.180	.53	.21	1.19
.549	.209	.209	.43	.25	1.22
.765	.247	.247	.40	.33	1.37
.239	.812	.023	.41	.10	0.12
.297	1.19	.017	.47	.14	.11
.347	1.20	.023	.43	.15	.12
.243	1.59	.013	.36	.09	.06
.353	2.38	.013	.50	.17	.08

ᵃ $K_{H_3PO_2} = 0.0796$ (ref. 5).

was determined. Then, various amounts of DCl were added to the reactant mixtures to determine the acid catalyzed term of the rate law. The results of all runs are given in Table I, in which the rate constants k_1 and k_2 are defined by the complete rate expression

$$k = k_1[H_3PO_2] + k_2([H^+] + [D^+]) \qquad (8)$$
or
$$R = k_1[H_3PO_2]^2 + k_2[H_3PO_2]([H^+] + [D^+]) \qquad (9)$$

Values of k_1 and k_2 were 0.15 and 0.46, respectively, in units of liter/mole min., with an estimated precision of $\pm 15\%$. The other rate constants, shown in Table I for comparison, were calculated using the expressions

$$k_3 = R/[H_3PO_2]; \quad k_4 = (R - k_1[H_3PO_2]^2)/([H^+] + [D^+])$$
and
$$k_5 = (R - k_1[H_3PO_2]^2)/([H^+] + [D^+])^2$$

Several runs were carried out at 16.5° to determine activation energies for the two exchange processes. From the values of the rate constants at this temperature, $k_1 = 0.013$ and $k_2 = 0.073$, activation energies

of 31 and 24 kcal./mole were calculated for the acid independent and acid catalyzed exchange processes, respectively.

Discussion

The rate expression given by equation 9 is the same as that determined by Yost and Jenkins[5] for the exchange of hypophosphorous acid with tritiated water at 27°. Their values of the corresponding rate constants were $k_1 = k_2 = 0.038$, approximately 4 and 12 times smaller than those determined in this study. Since the temperature difference of the two investigations can account for only 15% of this difference, an isotope effect must be considered.

Yost and Jenkins have shown that in their investigation the rate constants which they measure refer to the reaction

$$HTPOOH + H_2O \longrightarrow H_2POOH + HTO \qquad (10)$$
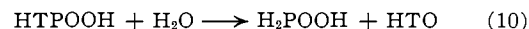
for which the rate determining step is the fission of the P–T bond. In our study, owing to the small concentration of acid used compared to D_2O, the only reaction of significance is

$$H_2POOH + D_2O \longrightarrow HDPOOH + HDO \qquad (11)$$

neglecting the hydroxyl proton exchange. Thus, assuming that the fission of the P–H bond is the rate determining step of equation 11, to predict an isotope effect one must, according to absolute reaction rate theory, compare the energies of the P–T and P–H bonds. Due to the lack of spectroscopic data available for the P–T bond, this comparison cannot be made directly. However, using the vibrational frequency of the P–H bond as obtained from infrared measurements,[8] $\nu_{P-H} = 2460$ cm.$^{-1}$, and the approximation $\nu_{P-T} = \nu_{P-H}/\sqrt{3}$, an isotope effect of ~ 10 can be expected.[9] This expectation is manifest in the case of the rate constant for the acid catalyzed exchange. However, the observed isotope effect of ~ 4 for the acid independent exchange is much smaller than predicted. It may be mentioned that Silver and Luz[8] in their investigation of the oxidation of diethylphosphonate observed a similar anomaly. They attributed this effect to an observation by Swain[10] that in acid catalyzed reactions the kinetic isotope effect increases with acid strength.

(8) B. Silver and Z. Luz, J. Am. Chem. Soc., **84**, 1091 (1962).
(9) K. B. Wiberg, Chem. Revs., **55**, 713 (1955).
(10) C. G. Swain, F. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, J. Am. Chem. Soc., **80**, 5885 (1958).