[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY]

The Rate of Exchange of the Phosphorus Bonded Hydrogen in Phosphorous Acid[1]

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The hydrogen bonded to phosphorus in a solution of phosphorous acid exchanges with the deuterium of heavy water with a half life of about 200 minutes at 23°. The reaction is followed by observing the change with time of certain characteristic frequencies in the Raman spectrum. The rate of exchange is markedly increased by increasing the acidity of the solution through addition of HCl in H_2O, or of DCl in D_2O solutions. In solutions of salts of the acid the exchange rate is very low. A mechanism consistent with the facts is proposed and the Raman spectra of the normal and deuterated phosphorous acid are recorded.

Phosphorous acid is dibasic and hence the structure $H_2(HPO_3)$ is usually assigned to it, the H inside the parentheses being bound to phosphorus rather than to oxygen. Trialkyl esters of both possible tautomeric forms, RPO_3R_2 and PO_3R_3, have been prepared and their infrared and Raman spectra recorded.[2–4] On the other hand, the dialkyl esters exist predominantly in the phosphonate, $R_2(HPO_3)$, form.[5] The oxygen bonded hydrogen atoms in phosphorous acid exchange practically instantaneously. An attempt to measure the exchange of the phosphorous bonded hydrogen in D_2O gave random results from which the authors concluded that no exchange took place[6] In this report the latter exchange is reinvestigated by following the alterations in the Raman spectra with time. The exchange rate is conveniently measurable by this technique.

Experimental

Phosphorous acid (H_3PO_3), sodium phosphite ($Na_2HPO_3 \cdot 5H_2O$) and sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) were Fisher products. Other acids and salts were prepared from these by the addition of reagent grade acids or bases. DCl was prepared from D_2O and benzoyl chloride.[7] D_3PO_3 was prepared by the addition of D_2O to H_3PO_3, allowing the solution to stand for at least 20 hr., and subsequently evaporating *in vacuo* over calcium sulfate and magnesium perchlorate. The cycle was repeated five times until there was no observable change in the Raman spectra of the solution.

The Raman spectra were taken on a Cary 81 recording Raman spectrophotometer (Applied Physics Corporation, Monrovia, California). A slit width of 10 cm.$^{-1}$ was used throughout the study. All solutions were clarified with Norit and filtered through a sintered glass funnel before recording the spectra. The brief warming interval when the Raman cell was intermittently inserted into the instrument should not materially affect the values of the rate constants for the half-life periods of this study. The intense line at about 940 cm.$^{-1}$, found in the spectrum of both H_3PO_3 and D_3PO_3 (see Table I below), was considered to be of constant intensity and was used as an internal standard. The intensities of the other lines relative to the 940 cm.$^{-1}$ line were taken to be directly proportional to the concentration of the particular species which gave rise to them.

Results

The Raman spectra of solutions 30% by weight in phosphorous acid are recorded in Table I. The 1172 cm.$^{-1}$ line of H_3PO_3 was not listed in the spectra reported earlier.[8] The Raman spectrum of D_3PO_3 has not been recorded previously. The first, fourth and seventh lines listed are dependent upon the solvent due to the immediate exchange of the oxygen bonded hydrogen atoms. For example when H_3PO_3 is dissolved in D_2O, yielding at first mainly the species $D_2(HPO_3)$, the mentioned lines are at about 412, 933 and 1203 cm.$^{-1}$.

TABLE I

RAMAN SPECTRA OF 30% BY WEIGHT SOLUTIONS OF PHOSPHOROUS ACID[a]

H_3PO_3 in H_2O	D_3PO_3 in D_2O
422 (8)	412 (9)
528 (3)	525 (3)
......	750 (13)
942 (20)	933 (20)
1024 (15)	1036 (3)
Masked?	1066 (5)
1172 (4)	1203 (9)
2457 (22)	1793 (22)

[a] In units of cm.$^{-1}$. The numbers in parentheses represent the relative intensity.

The P–H and P–D stretching vibrations at 2457 and 1793 cm.$^{-1}$, respectively, are widely separated and quite intense, affording convenient markers for following the exchange rate. The line at 750 cm.$^{-1}$ in D_3PO_3 may be considered to be a P–D deformation frequency which should appear at about 1030 cm.$^{-1}$ in the H_3PO_3 spectra. However, there is another line in the same region so that the line in H_3PO_3 at 1024 cm.$^{-1}$ is a superposition of at least two lines.

Upon adding H_3PO_3 to D_2O the lines at 750 and 1793 cm.$^{-1}$ appear and increase in intensity while the lines at 1024 and 2457 cm.$^{-1}$ decrease in intensity. Although all these lines change in intensity at the same rate, the rate is most conveniently followed by the former two lines since the line at 1024 represents a superposition of at least two lines and the line at 2457 is superimposed on the D_2O band.

When D_3PO_3 is added to H_2O, the lines at 750 and 1793 cm.$^{-1}$ decrease in intensity while the lines at about 1025 and 2460 increase in intensity. As above the former two are the most accurately interpreted, though again all change at the same rate.

In Fig. 1 a plot of the relative intensities for several lines relative to the 940 cm.$^{-1}$ line are shown

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[1] This work was supported by grants from the National Science Foundation (G-3230) and the United States Public Health Service (H-3169).

[2] C. D. Meyrick and H. W. Thompson, *J. Chem. Soc.*, 225 (1950).

[3] L. J. Bellamy and L. Beecher, *ibid.*, **475**, 1701 (1952).

[4] M. Baudler, *Z. Elektrochem.*, **59**, 173 (1955).

[5] L. W. Daasch, THIS JOURNAL, **80**, 5301 (1958); C. F. Callis, J. R. Van Wazer, J. N. Shoolery and W. A. Anderson, *ibid.*, **79**, 2719 (1957).

[6] A. D. Brodskii and L. V. Sulima, *Doklady Akad. Nauk. SSSR*, **85**, 1277 (1952); *C. A.*, **47**, 930e (1953); see also *C. A.*, **50**, 4567d (1956).

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[8] A. Simon and F. Feher, *Z. anorg. allgem. Chem.*, **230**, 289 (1937).

as functions of time for two experiments indicating the nature of the data obtained.

Considering first the case of the addition of H_3PO_3 to D_2O, the oxygen bonded atoms may be considered to be instantaneously exchanged as represented by the equation

$$\text{POH} + \text{D} \rightleftarrows \text{POD} + \text{H} \qquad (1)$$

where the equilibrium constant

$$K_1 = (\text{POD})(\text{H})/(\text{POH})(\text{D}) \qquad (2)$$

is expressed in terms of equivalents. The symbols H and D denote the equivalent concentrations of H and D in the water of the system. The value of K_1 was arbitrarily chosen as unity. Since the initial equivalents are known, the utilization of the value for the equilibrium constant allows calculation of the concentrations of all four species at equilibrium. Due to the excess of D_2O the equilibrium values so calculated are not very sensitive to the value of K_1 chosen, and even a value altered by a factor of three would yield substantially the same results.

Following the rapid reaction 1 is the slower, measurable reaction

$$\text{P-H} + \text{D} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{P-D} + \text{H} \qquad (3)$$

As a first approximation the equivalent fractions of D and H in the water present are considered not to change appreciably during the course of the reaction. This approximation makes the kinetic interpretation much simpler and is aided by the buffering effect of reaction 1, since any H produced in (3) will tend to react with the oxygen of the phosphorous acid by the reverse of (1). In the most unfavorable case considered below the change in D is about 5% and that in H about 15%.

Making the above approximations and applying the standard treatment for a reversible reaction, the following equation is obtained, where $(\text{PD})_\text{E}$ is the equivalent fraction of PD at equilibrium.

$$\log \frac{(\text{PD})_\text{E}}{(\text{PD})_\text{E} - (\text{PD})} = \frac{k_1[(\text{PH}) + (\text{PD})](\text{D})t}{2.3(\text{PD})_\text{E}} \qquad (4)$$

Thus a plot of log $[(\text{PD})_\text{E} - (\text{PD})]$ *versus* time should yield a straight line from which k_1 may be calculated from the slope. The equilibrium constant for reaction 3

$$K_2 = (\text{PD})(\text{H})/(\text{PH})(\text{D}) \qquad (5)$$

also may be calculated.

Likewise, for the addition of D_3PO_3 to H_2O the reaction analogous to (3) is

$$\text{P-D} + \text{H} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \text{P-H} + \text{D} \qquad (6)$$

for which, with the same approximations as before, is obtained

$$\log \frac{(\text{PD})_\text{I} - (\text{PD})_\text{E}}{(\text{PD}) - (\text{PD})_\text{E}} = \frac{k_3[(\text{PD}) + (\text{PH})](\text{H})t}{2.3(\text{PH})_\text{E}} \qquad (7)$$

where $(\text{PD})_\text{I}$ is the initial equivalent fraction of PD. Similarly, k_3 may be evaluated as well as the equilibrium constant for equation 6, K_2^{-1}.

The results of the experiments are recorded in Table II. The plots for the determinations of k_1 and k_3 were straight in all cases except the first, where there was some curvature, probably due to the fact that the high concentration of H_3PO_3 was too great for the approximations made in deriving equation 3.

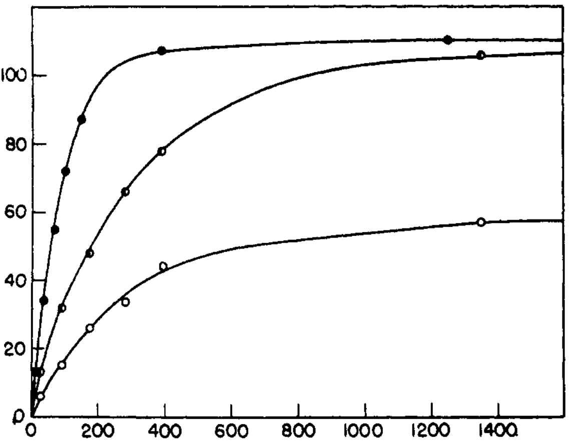

Fig. 1.—Intensity relative to that of the 940 cm.$^{-1}$ line *versus* time in minutes. The 750 cm.$^{-1}$ line (open circles, ○) and the 1793 line (half circles, ◐) for the second experiment of Table II. The 1793 line (closed circles, ●) for the third experiment of Table II.

TABLE II

RESULTS OF KINETIC AND EQUILIBRIUM EXPERIMENTS FOR PHOSPHORUS BONDED HYDROGEN EXCHANGE IN PHOSPHOROUS ACID AT 23°

Initial mixture	k_1^a	k_3^a	$k_{1/2}^b$	K_2
5.0 g. H_3PO_3 + 5.0 ml. D_2O	5.7	..	204	0.74
2.5 g. H_3PO_3 + 5.0 ml. D_2O	5.8	..	198	.79
2.5 g. H_3PO_3 + 5.0 ml. 4.8 *M* DCl	18.3	..	64	.8
5.0 g. H_3PO_3 + 5.0 ml. 11.2 *M* DCl	55	..	23	.82
2.5 g. D_3PO_3 + 5.0 ml. H_2O	..	2.3	540	.67

[a] In units of 10^{-5} sec.$^{-1}$. The terms in equations 4 and 7 were expressed in equivalent fractions in computing this value. [b] In units of minutes.

Additional experiments were performed on the rate of the phosphorus bonded hydrogen exchange. A solution of KH_2PO_3 in D_2O gave only very slow exchange and a solution of Na_2HPO_3 in D_2O no observable exchange. This confirms previous results.[6]

The phosphorus bonded hydrogen in hypophosphorous acid gave a relatively rapid exchange not easily measurable by the Raman technique, in agreement with the results of earlier workers obtained by other means.[6,9] A solution of NaH_2PO_2 in D_2O gave no exchange, also in agreement with previous results.[6,10]

Discussion

The value of K_2 is comparable with the values for the bonds of other elements with hydrogen[11] and agrees with the observation that deuterium tends to concentrate in the bond with the greater force constant. It is not possible to formulate the increase in k_1 with an increase in acidity on a quan-

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(9) W. A. Jenkins and D. M. Yost, *J. Chem. Phys.*, **20**, 538 (1952).

(10) H. Erlenmeyer and H. Gärtner, *Helv. Chim. Acta*, **17**, 970 (1934).

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titative basis because neither the strengths of the acids nor the activities of hydrogen ion in solutions so concentrated in phosphorous acid are known.

For the exchange of the phosphorus bonded hydrogen in phosphorous acid a mechanism consistent with the results is

$$L_2(HPO_3) + L^+ \rightleftarrows L_3(HPO_3)^+ \quad (8)$$

$$L_3(HPO_3)^+ \rightleftarrows L_3(:PO_3) + H^+ \quad (9)$$

$$L_3(:PO_3) + D^+ \rightleftarrows L_3(DPO_3)^+ \quad (10)$$

$$L_3(DPO_3)^+ \rightleftarrows L_2(DPO_3) + L^+ \quad (11)$$

where L is D when read in the forward direction for H_3PO_3 in D_2O and L is H when read in the reverse direction for D_3PO_3 in H_2O. This statement is an oversimplification because in each case all L will not be exclusively either D or H, due to the exchange reaction 1 and also to reactions 3 or 6 respectively, as they proceed producing the species opposite to that originally present in the solvent.

The complete steady-state solution of equations 8–11 is derived easily, but the resulting expression is complex. Reactions 8 and 11 may be considered to be rapid as compared with (9) and (10) which are rate determining. The mechanism accounts for the increase of reaction rate as the solution becomes more acid, and for the lack of any appreciable exchange for the salts of phosphorous acid. A similar mechanism has been proposed for the exchange in hypophosphorous acid.[6]

It is not possible to calculate an isotope effect from the experimentally determined rate constants, since several of the species postulated in the mechanism contribute to the over-all reaction to an unknown extent in each solvent mixture. Considering only the stretching frequency of the P–H and P–D bonds, the maximum isotope effect at 25° may be calculated[12] to be $k_H/k_D = 5.1$. The results and interpretation are consistent with the idea that exchange takes place *via* a free electron pair on the element bonding hydrogen, *e.g.*, $L_3(:PO_3)$.

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[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Saturation Magnetizations of Iron Carbides[1]

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Magnetic characteristics of iron carbides were obtained to permit their quantitative determination in Fischer–Tropsch catalysts and in steels at various stages of tempering. Iron carbides were prepared by reducing iron oxide powder with hydrogen at 208°, carburizing to ε-iron carbide with carbon monoxide at 170° and then tempering *in vacuo* to χ-iron carbide and subsequently to cementite. Specific magnetizations were measured between about 2 and 10 kilo-oersteds from 50° to about 200–350°. The data were corrected for contributions due to impurities and extrapolated to infinite field and 0°K. to obtain the magnetic moments of the carbides: 1.70–1.72 (ε-carbide), 1.72–1.75 (χ-carbide) and 1.72–1.79 (cementite) Bohr magnetons per iron atom. The paramagnetic moments of χ-iron carbide and cementite were 5.55 and 3.89 Bohr magnetons, respectively.

Introduction

Quantitative thermomagnetic determination of crystalline phases involved in solid-phase reactions of steel and of iron Fischer–Tropsch catalysts is possible only with data obtained at or near magnetic saturation, or with saturation data obtained by extrapolation to infinite field strength.[2] Consequently, the saturation magnetizations of the pure phases must be known. Such data are available for α-iron[3] and cementite.[4] They have not been available for the ε- and χ-iron carbides, although their specific magnetizations at room temperature are known to be roughly equal to that of cementite.[5]

Previous preparations of carbides of iron especially those of χ-iron carbide and ε-iron carbide have been relatively impure. Even specimens containing only 50% of the desired compound have been considered reasonably satisfactory.[5] The specimens described here represent an order of magnitude of increased purity with respect to the amount of iron in the desired form. The amount of promoters, copper and sodium oxide, which are present in these preparations are less then 2% and do not dissolve in the carbide phase to any detectable extent according to the known solubility relationships. The methods of synthesis here described should therefore be regarded as the best now available for χ- and ε-iron carbide. Similarly, the magnetic properties reported here are believed to have general significance.

Experimental

Preparation of Carbides.—Direct determination of the specific magnetization of the iron carbides requires specimens in which the carbide in question is the major phase, and the amount of iron present in any paramagnetic form should be as small as possible. Extraction of χ-iron carbide and ε-iron carbide from tempered steels is an uncertain procedure[6] and specimens so obtained are likely to contain

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