[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Kinetics of the Exchange of Hydrogen between Phosphine and Water: A Kinetic Estimate of the Acid and Base Strengths of Phosphine[1]

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The rate of approach to equilibrium in the hydrogen exchange between phosphine and water containing 3% deuterium has been measured by following the uptake of deuterium in the phosphine. Under conditions where the diffusion from the gaseous to the liquid phase is not rate-determining, the fraction of exchange as a function of time follows the usual McKay rate law. The rate expression may be written as $d(PH_2D)/dt = (PH_3)\{\Sigma_i k_{HA_i}(HA_i) + k_{OH^-}(OH^-)\}$ where HA_i represents a general acid with exchangeable proton. By making reasonable assumptions concerning rate constants, an estimate of 10^{-28} is made for the base dissociation constant of phosphine in water. A similar estimate of 10^{-29} is made for the acid dissociation constant.

As part of a general program of research on reactions involving stable isotopes, we have recently reported an investigation of the equilibrium in the exchange of hydrogen between phosphine and water.[2] From the experimental conditions required to attain this equilibrium, it was evident that phosphine was behaving as a weak base. Since nothing had been reported in the literature on the basicity of phosphine (other than the fact that it is considerably weaker than its analog, ammonia), a kinetic investigation of the exchange mechanism was undertaken, with the object of determining something about the acid and base properties of phosphine in aqueous solution. The method of isotopic exchange which was used appears to be generally applicable to studies of other weak acids and bases.

Experimental

The methods used for the preparation of phosphine and for mass spectrometric analysis of phosphine have been previously described.[2]

Buffer solutions were made up by dissolving C.P. or Analytical Grade reagents in gravimetrically prepared mixtures of distilled water and 99.8% heavy water. A Beckman model G *p*H meter with glass electrode was used to determine the *p*H of these solutions; for alkaline solutions a Type E glass electrode was used. The deuterium content of the solutions was about 3 atom per cent. and its effect on the *p*H was therefore neglected.

Ten ml. of solution was pipetted into a conical reaction vessel, and the solution was degassed by repeated cycles of freezing, evacuation and thawing. With the solution at −78°, a measured pressure of phosphine was added, the liquid was thawed quickly, and the vessel was placed in a shaking device immersed in a thermostat. Typical values were 300-400 mm. for the phosphine pressure, and 120-150 ml. for the gas phase volume. The temperature control was within ±0.02°, with an absolute accuracy of ±0.1° determined by comparison with a thermometer calibrated at the National Bureau of Standards. Unless otherwise stated, the temperature was 27.0°. At measured elapsed times, the vessel was removed from the thermostat to the vacuum line, and a sample of the gas phase was removed for analysis as described previously.[2]

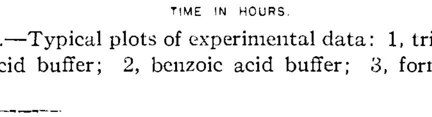

Fig. 1.—Typical plots of experimental data: 1, trimethylacetic acid buffer; 2, benzoic acid buffer; 3, formic acid buffer.

For each experiment, a plot was made of log $(1 - f)$ against time. The fraction of exchange, f, is defined by $f = (D - D_0)/(D_\infty - D_0)$, where D, the fraction of deuterium in phosphine at time t, is obtained from mass spectrometric analysis; D_0 is the natural abundance of deuterium; and D_∞, the fraction of deuterium in phosphine at complete exchange, is calculated from the known exchange equilibrium constant[2] and the fraction of deuterium initially in the aqueous phase. In all cases, straight lines were obtained, in agreement with the McKay law for isotope-exchange reactions.[3] Typical experimental plots are shown in Fig. 1. From the plot a value of the half-time for the exchange, $t_{1/2}$(obs), was read off, and from this the rate constant calculated as described below.

A correction must be made for the fact that the exchange occurs only in the aqueous phase, while a large volume of undissolved phosphine is also present. This correction may be easily determined by a consideration of a general first-order reaction

$$A_g \underset{}{\overset{\text{Rapid}}{\rightleftarrows}} A_s \xrightarrow{k_s} \text{Products}$$

where the subscripts refer to the gas and solution phases. Assuming the solution equilibrium to be maintained at all times, the actual rate is given by $-dA/dt = k_sA_s$. However, we measure a first-order rate constant for the rate expression $-dA/dt = k(\text{obs})A$, where $A = A_g + A_s$. Hence, $k_s = k(\text{obs})A/A_s = k(\text{obs})\ [1 + V_g/K_sV_s)]$, where $K_s = (A_s)/(A_g)$ is the Ostwald solubility coefficient and the V's are the volumes of the two phases. The determination of the solubility coefficient of phosphine is described elsewhere.[4] A 27°, the temperature at which most experiments were performed, $K_s = 0.195$ in distilled water. This is not changed, within experimental error, at the salt concentrations used in most of the buffer solutions. The empirical first-order rate constant was then calculated from the relationship

$$k_e = \ln 2\ [1 + (V_g/K_sV_s)]/t_{1/2}(\text{obs})$$

This method of calculating the empirical first-order rate constant may be illustrated by the following typical data: buffer solution, 0.01 *M* trimethylacetic acid-0.01 *M* sodium trimethylacetate; measured *p*H, 4.95; V_s, 10 ml.; V_g, 119 ml.; temperature, 27.0°; observed half-time (*cf.* line 1 of Fig. 1), 272 hr. Hence, $k_e = 0.693\ [(1 + (119)/(0.195)(10)]/(272)(3600) = 4.38 \times 10^{-5}$ sec.$^{-1}$. The correction for general acid catalysis is $k_{HA}(HA) = (5.8 \times 10^{-4})\ (0.01)$, and the corrected value of k_e is 3.80×10^{-5} sec.$^{-1}$.

Experimental Results

Acid Catalysis.—The uncatalyzed reaction was found to be rather slow.[2] Hydrogen ion was found

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] R. E. Weston, Jr., and J. Bigeleisen, *J. Chem. Phys.*, **20**, 1400 (1952).

[3] *Cf.* for example, "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, editors, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 7.

[4] R. E. Weston, Jr., THIS JOURNAL, **76**, 1027 (1954).

to be an efficient catalyst. A study was therefore made of both general acid and base catalysis and salt effects to elucidate the reaction mechanism. To determine the effect of hydronium ion, experiments were carried out over the *p*H range 3.40 to 4.95, using buffer solutions 0.01 *M* in both carboxylic acid and the corresponding sodium salt. The acids used were mandelic, pK_a = 3.38; formic, pK_a = 3.75; benzoic, pK_a = 4.20; acetic, pK_a = 4.76; trimethylacetic, pK_a = 5.05.

The empirical rate constants given in Table I were calculated from the observed half-times after a correction for the small effect of general acid catalysis (see below) produced by the 0.01 *M* acid present. This correction was applied simply by subtracting from the calculated first-order rate constant the term for general acid catalysis: k_{HA}(HA). The values of k_{HA} for benzoic and mandelic acids were obtained from a log–log plot of k_{HA} against K_{HA}(the acid dissociation constant), using the data described below. A log–log plot of corrected rate constant against hydronium ion concentration yields a straight line with a slope of unity (Fig. 2), within experimental error, hence the reaction is first order with respect to hydronium ion. The rate constant for hydronium ion catalysis obtained from the experimental plot is $k_{H_3O^+}$ = 3.6 liters/mole second at 27°.

TABLE I

EFFECT OF HYDRONIUM ION CONCENTRATION ON EXCHANGE RATE AT 27°

All buffer solutions were 0.01 *M* in the acid listed and in its sodium salt.

Acid	*p*H[a]	k_e, sec.$^{-1}$
Mandelic	3.40	12.9 × 10^{-4}
Formic	3.75	6.23 × 10^{-4}
Benzoic	4.18	2.31 × 10^{-4}
Benzoic	4.18	2.39 × 10^{-4}
Acetic	4.71	0.832 × 10^{-4}
Acetic	4.71	.742 × 10^{-4}
Acetic	4.75	.779 × 10^{-4}
Acetic	4.75	.681 × 10^{-4}
Acetic	4.69	.676 × 10^{-4}
Trimethylacetic	4.95	.380 × 10^{-4}
Trimethylacetic	4.95	.406 × 10^{-4}

[a] Measured with glass electrode at 22–23°. Temperature correction is negligible.

An experiment was performed using 0.01 *N* sulfuric acid (*p*H 2.08) as a catalyst, and the observed half-time was about one hour. However, by applying the rate constant for hydronium ion catalysis (*cf.* the preceding paragraph) one would predict a half-time of ten seconds. Evidently, under these conditions diffusion is the rate-determining step, with a half-time of one hour under these particular conditions of agitation (which were the same in all experiments). For this reason, all other experiments were designed (by the choice of catalyst concentration) so that the homogeneous rate was slower than the measured diffusion rate by a factor of at least four; in most cases the factor was greater than ten.

A study of general acid catalysis was made by varying the concentration of buffer solution at a fixed buffer ratio of 1:1. The acids used were formic, acetic and trimethylacetic. For each acid, the empirical rate constants at the various concentrations were corrected to a value for the *p*H of the 0.01 *M* buffer solution (since the *p*H varies slightly with buffer concentration). The first-order dependence of rate on hydronium ion concentration was used, *i.e.*, $\Delta \log k_e = -\Delta p\text{H}$.

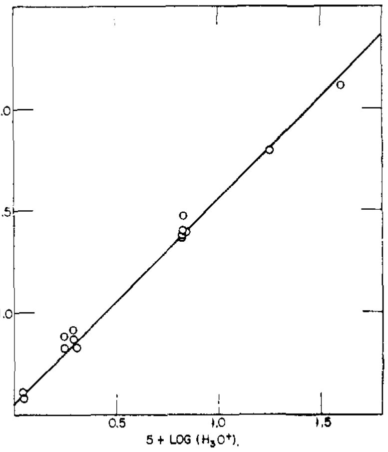

Fig. 2.—Empirical rate constant as a function of hydronium ion concentration.

A plot of the corrected rate constant against concentration of undissociated acid gives a straight line, within a rather large experimental error, for each case. This is shown in Fig. 3, where ($k_e - k_e^0$) (k_e^0 is the rate constant extrapolated to zero acid concentration) is plotted against undissociated acid concentration. From the slopes of the lines these rate constants are obtained: formic acid, k_{HA} = 21 × 10^{-4}; acetic acid, k_{HA} = 9.4 × 10^{-4}; trimethylacetic acid, k_{HA} = 4.7 × 10^{-4} (all in liters/mole second at 27°). These rate constants are actually upper limits, since at the ionic strengths used, an appreciable amount of the catalysis is due to the salt of the buffer. A rough estimate of this effect was made using the data obtained for the effect of sodium chloride (see below); this indicates that the rate constants may be high by nearly 50%, although the linearity of the relationship between rate constant and acid concentration is maintained. It would be necessary to determine the

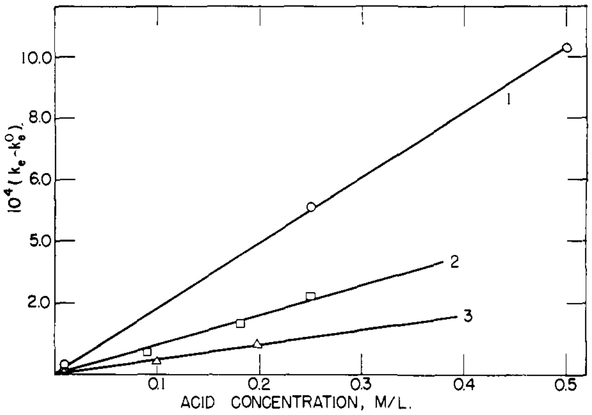

Fig. 3.—Empirical rate constant as a function of undissociated acid concentration: 1, formic acid; 2, acetic acid; 3, trimethylacetic acid.

salt effect for each buffer salt to obtain a more accurate correction. The trend of the catalytic rate constants is in the direction which one would predict from the Brönsted catalysis law[5] and the pertinent acid dissociation constants. However, the range of dissociation constants is too small to give the Brönsted law parameters with any accuracy.

Base Catalysis.—Experiments were performed in the *p*H range 10.0 to 11.9 using sodium carbonate–sodium bicarbonate buffers, disodium phosphate–trisodium phosphate buffers, and unbuffered 0.01 *N* sodium hydroxide. The ionic strengths of the buffer solutions were kept below 0.1 *M* to reduce salt effects. Work in this *p*H region is complicated by the scarcity of suitable buffers which do not have high ionic strengths at reasonable concentrations (because of the multivalent ions). The results are collected in Table II. A log–log plot of the empirical rate constant against hydroxyl ion concentration gives a straight line of slope unity, within experimental error (Fig. 4). We conclude that the reaction is first order with respect to hydroxyl ion. The value thus obtained for the catalytic rate constant of hydroxyl ion is $k_{OH^-} = 0.40$ liters/mole second at 27°.

TABLE II

EFFECT OF HYDROXYL ION CONCENTRATION ON EXCHANGE RATE AT 27°

Buffer	*p*H	$-\log(OH^-)^a$	k_e, sec.$^{-1}$
0.00834 *M* $NaHCO_3$ .00834 *M* Na_2CO_3	10.06^b	3.87	0.570×10^{-4}
.00467 *M* $NaHCO_3$ .01205 *M* Na_2CO_3	10.45^b	3.48	1.23×10^{-4}
.00987 *M* Na_2HPO_4 .00995 *M* Na_3PO_4	11.52^b	2.41	15.0×10^{-4}
0.01 *N* NaOH	11.75^c	2.18^d	29.2×10^{-4}
0.01 *N* NaOH	11.75^c	2.18^d	22.6×10^{-4}

^{a} Using $pK_w = 13.930$ (ref. 8). ^{b} *p*H measured with Type E glass electrode at 22° corrected to 27° using data of I. M. Kolthoff and F. Tekelenburg, *Rec. trav. chim.*, 46, 33 (1925). ^{c} *p*H from data for 0.01 *N* NaOH in ref. b. ^{d} This value, rather than 2.00, is used so as to minimize the influence of the activity coefficient in converting from *p*H as measured by the glass electrode to log (OH^-).

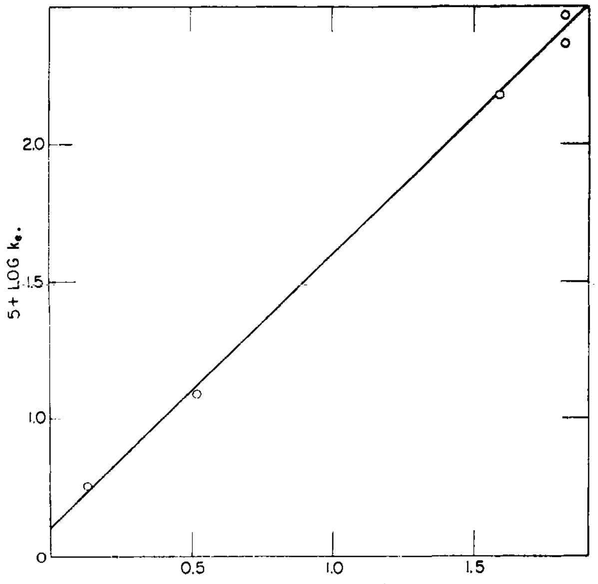

Fig. 4.—Empirical rate constant as a function of hydroxyl ion concentration.

An attempt was made to detect general base catalysis by anions of weak acids. Using the same buffer solution, salts of weak acids were compared with salts of strong acids of the same valence type. The results are given in Table III. Evidently the difference between the effects produced by different salts is no larger than would be predicted from the primary salt effect on the reaction rate.

TABLE III

EFFECT OF INERT SALT CONCENTRATION ON EXCHANGE RATE AT 27°

Added salt	*p*H^a	k_e, sec.$^{-1}$
In 0.02 *M* $NaHCO_3$–0.02 *M* Na_2CO_3 buffer solution		
0.2 *M* NaCl	10.00	0.383×10^{-4}
.5 *M* NaCl	9.84	0.494×10^{-4b}
.2 *M* NaOAc	10.09	$.321 \times 10^{-4b}$
.5 *M* NaOAc	9.94	$.364 \times 10^{-4b}$
In 0.01 *N* NaOH solution		
0.1 *M* Na_2CO_3	12.24	25.6×10^{-4}
.3 *M* Na_2CO_3	12.03	43.3×10^{-4c}
.3 *M* Na_2SO_4	11.98	40.2×10^{-4c}
In 0.01 *M* benzoic acid–0.01 *M* sodium benzoate buffer solution		
None	4.18	2.38×10^{-4}
0.0195 *M* NaCl	4.12	2.39×10^{-4d}
.0505 *M* NaCl	4.08	2.55×10^{-4d}
.1005 *M* NaCl	4.06	2.64×10^{-4d}
.199 *M* NaCl	4.04	3.24×10^{-4d}

^{a} *p*H measured at 22° and corrected to 27° using data of I. M. Kolthoff and F. Tekelenburg, *Rec. trav. chim.*, 46, 33 (1925). ^{b} Corrected to *p*H 10.00. ^{c} Corrected to *p*H 12.24. ^{d} Corrected to *p*H 4.18.

Phosphine Concentration.—Several experiments were carried out using the same buffer solution but different partial pressures of phosphine. It was found that the half-time for exchange was independent of phosphine pressure, as shown by the data of Table IV. Hence the reaction is first order with respect to phosphine.

TABLE IV

EFFECT OF PHOSPHINE PRESSURE ON EXCHANGE RATE AT 27°

Pressure, mm.	k_e, sec.$^{-1}$
At *p*H 4.17, 0.01 *M* benzoic acid–0.01 *M* sodium benzoate buffer	
103	2.55×10^{-4}
196	2.47×10^{-4}
397	2.99×10^{-4}
523	2.48×10^{-4}

Effect of Added Inert Electrolyte.—A series of experiments was performed using 0.01 *M* benzoic acid–0.01 *M* sodium benzoate buffers with various amounts of sodium chloride added. After correction to a common *p*H (as described in the discussion of general acid catalysis), the empirical rate constants are linearly proportional to the total salt concentration of the solution. This is shown in Fig. 5, where $(k_e - k_e^0)$ (k_e^0 is the extrapolated rate

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[5] See, for example, R. P. Bell, "Acid-Base Catalysis," Oxford University Press, Oxford, 1941, p. 82 ff.

constant for zero salt concentration) is plotted against salt concentration. This is in agreement with the theory of the effect of inert electrolytes on an ion–dipole reaction.[6]

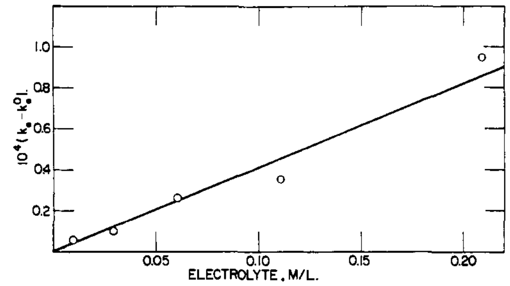

Fig. 5.—Empirical rate constant as a function of sodium chloride concentration.

Effect of Temperature.—Two series of experiments were carried out: one using acetic acid–sodium acetate buffer solutions at 300.0, 313.2 and 322.7°K., and another using sodium bicarbonate–sodium carbonate buffers at 300.0, 309.2 and 318.3°K. The empirical rate constants were corrected for the temperature dependence of (a) the isotope-exchange equilibrium constant,[2] (b) the solubility of phosphine,[4] (c) the *p*H of the buffer solution,[7] and (d) the ionization constant of water.[8] Plots of the logarithms of the corrected rate constants, $k_e/(H_3O^+)$ and $k_e/(OH^-)$, against $1/T$ give straight lines in each case (Figs. 6 and 7). The slopes correspond to an activation energy of 17.6 ± 2 kcal./mole for hydronium ion catalysis and 17.6 ± 2 kcal./mole for hydroxyl ion catalysis.

From these values and the rate constants at 27°, one obtains $k_{H_3O^+} = 2.4 \times 10^{13} \exp(-17{,}600/RT)$ and $k_{OH^-} = 2.7 \times 10^{12} \exp(-17{,}600/RT)$. The pre-exponential terms may be compared with the average collisional rate constant of $\sim 3 \times 10^{11}$ liters/mole second.[9] In terms of the absolute reaction rate theory, the pre-exponential terms give $\Delta S^{\ddagger}_{H_3O^+} = +0.69$ e.u./mole and $\Delta S^{\ddagger}_{OH^-} = -3.65$ e.u./mole, making the usual assumption that $\kappa = 1$.

Other Effects.—To test for the effect of surface on the rate, an experiment was performed using acetate buffer with glass helices added to the reaction vessel. The calculated increase in surface was a factor of about three. The experimental points, when plotted on the usual semi-logarithmic plot, show considerably more scatter than usual (perhaps because of variations in the diffusion rate caused by the added helices). However, there is no systematic deviation from a similar plot for the results using an unpacked vessel.

Two experiments using formic acid–sodium formate buffer but with different concentrations of heavy water (2.99 and 6.64 mole % D_2O) gave identical rate constants.

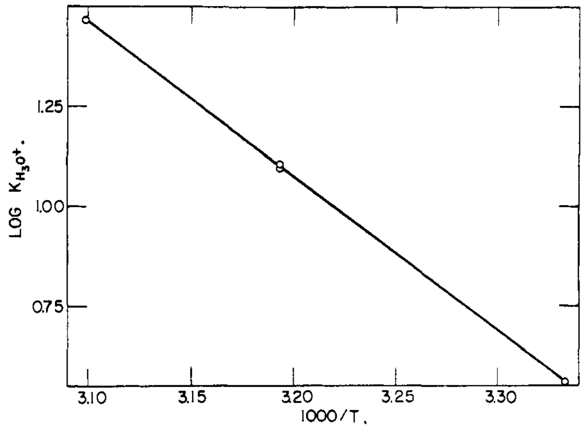

Fig. 6.—Rate constant for hydronium ion catalysis as a function of temperature.

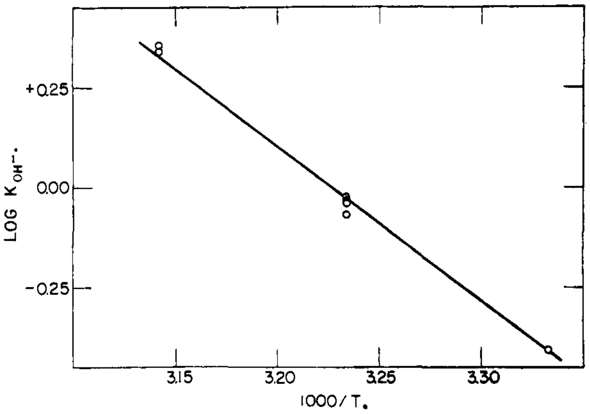

Fig. 7.—Rate constant for hydroxyl ion catalysis as a function of temperature.

Discussion

Exchange Mechanism.—The experimental results reported above may be summarized in the empirical rate expression

$$d(PH_2D)/dt = (PH_3)\{\Sigma_i k_{HA_i}(HA_i) + k_{OH^-}(OH^-)\}$$

where HA_i represents a general acid with an exchangeable proton.

The mechanism suggested by this for acid-catalyzed exchange is

$$PH_3 + DA_i \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PH_3D^+ + A_i^- \qquad (1)$$

$$PH_3D^+ + A_i^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} PH_2D + HA_i \qquad (2)$$

$$HA_i + HDO \overset{\text{rapid}}{\rightleftharpoons} H_2O + DA_i$$

It may be noted that the phosphonium ion, PH_4^+, is known to exist in solid phosphonium halides of the type PH_4X.

The rate expression derived from this mechanism may be integrated by substituting initial and equilibrium concentrations, and by noting that (HA_i) and (DA_i) are constant in a given experiment. The result is

$$-\ln(1-f) = \left[\frac{k_1k_2(DA_i)}{(k_{-1}+k_2)(HA_i)} + \frac{k_{-1}k_{-2}}{k_{-1}+k_2}\right](HA_i) \times t$$

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[6] Reference 5, p. 21ff.

[7] I. M. Kolthoff and F. Tekelenburg, *Rec. trav. chim.*, **46**, 33 (1925).

[8] H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 977 (1940).

[9] E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford University Press, Oxford, 1947, p. 68ff.

which has the form of the McKay law. It has been pointed out[10] that in general, exchange reactions will not obey the McKay law when the exchange equilibrium constant differs from unity, as in the present case. However, (DA_i) and (HA_i) are large compared with (PH_3) and (PH_2D), so that $(DA_i)/(HA_i)$ is constant during a given experiment. In this case the McKay law is obeyed, within the limits of experimental error.

From the exchange equilibrium constant $K_{eq} = (PH_2D)(HA_i)/(PH_3)(DA_i) = k_1k_2/k_{-1}k_{-2}$, one obtains

$$k_e = \frac{k_1k_2}{k_{-1} + k_2}\left[\frac{(DA_i)}{(HA_i)} + \frac{1}{K_{eq}}\right](HA_i)$$

In the particular case of hydronium ion catalysis, one can obtain K_{eq} by multiplying the two known equilibrium constants

$$(PH_2D)(H_2O)/(PH_3)(HDO) = 1/1.63,^{2} \text{ and}$$
$$(H_3O^+)(HDO)/(H_2DO^+)(H_2O) = 3.76^{11}$$

$$\text{Finally } k_e = \frac{k_1k_2}{k_{-1} + k_2}\left[\frac{(H_2DO^+)}{(H_3O^+)} + 0.434\right](H_3O^+)$$

In our experiments $(H_2DO^+)/(H_3O^+) \simeq 0.02\text{–}0.04$, and we see that the independence of the empirical rate constant on deuterium concentration at low concentration is predicted by the mechanism. Also, using $k_{H_3O^+} = 3.6$ liters/mole second, $k_1k_2/(k_{-1} + k_2) = 8.0$. If we make the further assumption that the intramolecular isotope effect for transfer of a proton or a deuteron from the PH_3D^+ ion to a water molecule is negligible,[12] then $3k_{-1} = k_2$, and $k_1 = (4/3)(k_{H_3O^+})(K_{eq})$, so that step 1 of the mechanism is rate determining. The rate constant for this is 11 liters/mole second in the case of hydronium ion catalysis.

In the case of base catalysis, the experimental facts suggest the mechanism

$$PH_3 + B_i^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} PH_2^- + B_iH \qquad (3)$$

$$B_iH + HDO \overset{\text{rapid}}{\rightleftarrows} B_iD + H_2O$$

$$PH_2^- + B_iD \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} PH_2D + B_i^- \qquad (4)$$

The ion PH_2^- has been recently proposed as an intermediate in the liquid ammonia reaction of phosphine with methyl chloride to form methylphosphine and dimethylphosphine[13]; it is, of course, formally analogous to the amide ion in the ammonia system.

The rate expression is integrated to give

$$-\ln(1 - f) = \left[\frac{k_4k_3}{Rk_{-3} + k_4} + \frac{k_{-3}k_{-4}R}{Rk_{-3} + k_4}\right](B_i^-) \times t$$

where $R = (B_iH)/(B_iD)$. Considerations similar to those for acid catalysis show that this is identical with the McKay law. In the case of hydroxyl ion catalysis, some simplification can be introduced by using the exchange equilibrium constant $k_{-3}k_{-4}/k_3k_4 = (PH_3)(HDO)/(PH_2D)(H_2O) = 1.63$. Then $k_{OH^-} = k_4k_3(1 + 1.63\,R)/(Rk_{-3} + k_4)$. We again assume the absence of an isotope effect,[14] which makes $k_{-3} \sim 2k_4$, and note that in our experiments $R \sim 1/0.06$, so that $1.63\,R >> 1$ and $Rk_{-3} >> k_4$. Using the observed value of $k_e = 0.40$ for hydroxyl ion catalysis, $k_3 \sim 0.49$ liter/mole second at 27°.

A Kinetic Estimate of the Acid and Base Strengths of Phosphine.—From our kinetic data and the exchange mechanism, it is possible to arrive at an estimate of the equilibrium constant $K_B = (PH_4^+)(OH^-)/(PH_3)(H_2O)$. This constant may be rewritten as $K_B = [(PH_4^+)(H_2O)/(PH_3)(H_3O^+)][(H_3O^+)(OH^-)/(H_2O)^2]$. The first term in brackets is just k_1'/k_c, the equilibrium constant for the reaction $PH_3 + H_3O^+ \underset{k_c}{\overset{k_1'}{\rightleftarrows}} PH_4^+ + H_2O$. Again neglecting the isotope effect, $k_1' \sim k_1 \sim 11$ liters/mole second (the rate constant for hydronium ion catalysis). The reverse reaction is assumed to proceed at the collisional rate,[15] so that $k_c \sim 10^{11}$ liters/mole second. Combining these values with the ionization constant of water, $K_B \sim 4 \times 10^{-28}$.

Similarly, $K_A = (PH_2^-)(H_3O^+)/(PH_3)(H_2O)$ may be approximated using the hydroxyl ion catalytic constant, with the same assumptions concerning isotope effect and collision rate. This leads to $K_A \sim 1.6 \times 10^{-29}$.

If our estimates above are at all correct, then equilibrium measurements in aqueous solutions cannot reveal any acidic or basic properties of phosphine; the latter might be detectable in some solvent such as 100% sulfuric acid. The fact that strong acids and bases produce no large increase in the solubility of phosphine in water[4] substantiates this statement.

There are some independent data, however, from which another estimate of the base strength can be made. Measurements have been made by Sujishi[16] of the base dissociation constants of dimethylphosphine and trimethylphosphine in aqueous solution. Methylphosphine was too weak a base to be measurable. If one assumes that substituent methyl groups in phosphine produce a change in the base strength which is the same for each additional group, as suggested by Brown, *et al.*,[16b] a value of $K_B \sim 10^{-22}$ is obtained by extrapolation. Considering the assumptions made in both cases, the disparity of a factor of a million may be taken as rather good agreement.

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(10) G. M. Harris, *Trans. Faraday Soc.*, **47**, 716 (1951).

(11) F. Brescia, This Journal, **60**, 2811 (1938).

(12) The intramolecular isotope effect, $k_2/3k_{-1}$, is expected to be of the order of $\sqrt{2}$. This would decrease k_1 by about 10% below the value obtained upon assumption of no isotope effect.

(13) R. I. Wagner and A. B. Burg, This Journal, **75**, 3869 (1953).

(14) The intermolecular isotope effect, k_{-3}/k_4, is given by $k_{-3}/k_4 = (m_D/m_H)^{1/2} f_{HDO}/f^{\ddagger}$. Approximately, $f_{HDO}/f^{\ddagger} = (f_{HDO}/f_{PH_2D}) \cdot (\sigma_{PH_3}/\sigma^{\ddagger}) = 3K_{ex}$, so that $k_{-3}/k_4 = 6.9$. The f's and σ's are defined by J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949). The result of this is to increase k_3 by a factor of 3.5 over the value estimated with the assumption of no isotope effect. It can be shown that another reaction, $PH_2^- + HDO \leftrightarrows PH_3 + OD^-$, does not contribute to the rate expression at the low deuterium concentrations used.

(15) This is undoubtedly a much larger approximation than the neglect of isotope effects throughout has been. However, since phosphonium halides decompose spontaneously into phosphine and hydrogen halide when dissolved in water, the activation energy may be small. The steric factor in the pre-exponential term of the rate constant is near unity (*cf.* the entropies of activation).

(16) (a) S. Sujishi, Ph.D. Thesis, Purdue University, 1949; (b) H. C. Brown, E. A. Fletcher, E. Lawton and S. Sujishi, Abstracts of 121st Meeting, American Chemical Society, p. 9N.