thors,[12,13] but these are tedious and, in addition, insensitive to small changes in assumed parameters. The method chosen was to treat the data in log–log form as a plot of log $(i\tau^{1/2}/C)$ vs. log $\tau^{1/2}$ and to formulate the theoretical expression in an analogous form. log $(i\tau^{1/2}/i\tau_\infty^{1/2})$ vs. log $(k\tau)^{1/2}$. Superimposition of theoretical and experimental plots allowed the deduction of the rate constant— see Fig. 2.

There are two degrees of freedom in the translation of the theoretical curve to produce best fit with experimental data; one along the ordinate, the other along the abscissa. The former gives an estimate of the diffusion coefficient of the reducible species, the latter an estimate of the rate constant. The diffusion coefficient deduced from Fig. 2 is 0.82×10^{-5} cm.^{2}/sec., which is in excellent qualitative agreement with values for compounds of similar structure determined under the same conditions: nitrobenzene, 1.01×10^{-5} cm.^{2}/sec.; o-nitrophenylacetic acid, 0.70×10^{-5} cm.^{2}/sec.

The pseudo-first order rate constant deduced from Fig. 2 is 0.20 sec.$^{-1}$. Quantitative measure of the accuracy of this value was not attempted because of the large scatter in experimental data. However, a qualitative estimate based on the uncertainty in superimposition of experimental and theoretical curves is $\pm 20\%$.

Conclusions

The reduction of o-nitrophenol at high current densities proceeds with diffusion control and the transfer of four electrons, while at lower current densities up to six electrons are involved. Chronopotentiometric study of the system led to the conclusion that a slow chemical reaction is interposed between two electron transfer steps involving four and two electrons successively. Comparison of the data with exact theory allowed determination of the rate constant of the chemical step.

(12) P. Delahay and S. Oka, THIS JOURNAL, **82**, 329 (1960).

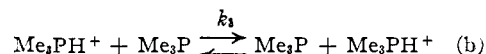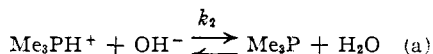(13) O. Fischer and O. Dracka, *Collection Czechoslav. Chem. Commun.*, **24**, 3046 (1959).

Rates and Mechanisms of Protolysis of Trimethylphosphonium Ion in Aqueous Solution Studied by Proton Magnetic Resonance

BY B. SILVER AND Z. LUZ

A kinetic analysis of the protolysis reactions of the trimethylphosphonium ion in aqueous solution has been carried out using the n.m.r technique. Two main mechanisms in the range pH 6.0 to 7.5 were found

$$Me_3PH^+ + OH^- \underset{k_2}{\overset{k_2}{\rightleftharpoons}} Me_3P + H_2O \quad (a) \qquad\qquad Me_3PH^+ + Me_3P \underset{k_1}{\overset{k_1}{\rightleftharpoons}} Me_3P + Me_3PH^+ \quad (b)$$

with second order rate constants of $4.6 \pm 0.9 \times 10^7$ and $1.2 \pm 0.6 \times 10^2$ l. mole^{-1} sec.$^{-1}$, respectively. A minor contribution comes from a pH independent exchange reaction viz., $Me_3PH^+ + H_2O \rightleftharpoons Me_3P + H_3O^+$. The pseudo-first order rate constant for this reaction was found to be dependent on the Me_3PH^+ concentration and varied between 9.8 and 6.2 sec.$^{-1}$ in the concentration range 0.26 to 2.21 M.

Introduction

The nuclear magnetic resonance (n.m.r.) technique has been used recently to study a variety of proton exchange reactions which are too fast to be followed by classical methods. Quantitative studies have been carried out on the protolysis reactions of hydrogen bonded to nitrogen,[1–3] oxygen[4] and sulphur[5] in the case of amines, alcohols and thiols respectively.

The present work extends these studies to the fast protolysis reactions of hydrogen bonded to phosphorus in aqueous solutions of Me_3PHCl. The comparatively slow proton exchange reactions between water and phosphine,[6] hypophosphorous acid[7] and phosphorous acid[8] have previously been studied by isotopic labelling techniques.

Experimental

Spectrometer.—The n.m.r. spectrometer used in this work was the same as that used in previous works[1–5] Cylindrical rotating glass sample holders of 3 mm. internal diameter were used. The resolution of the spectrometer was such that an effective relaxation time of about 1 sec. was measured from the decay of the 'wiggles' after fast passage through a water line. The effective T_2 of a water sample was measured before and after each record.

Preparation of Trimethylphosphonium Chloride Solutions.—Trimethylphosphine was prepared from methyl magnesium iodide[9] (from 24 g. of magnesium and 62 ml. of methyl iodide) in an atmosphere of nitrogen. Me_3P was distilled from the reaction vessel under nitrogen, into a solution of silver iodide (25 g.) in potassium iodide solution (100 g. in 100 ml. of water). The resulting trimethylphosphine–silver iodide complex was filtered off, washed in water and dried at 10μ pressure for several hours, in a tube with a ground-glass joint connected to a three way stopcock of a vacuum system. The tube was then gently heated to decompose the complex, the Me_3P formed being collected in an evacuated tube containing sodium hydroxide pellets and cooled in liquid nitrogen. After standing overnight the Me_3P was distilled into a tared receiver cooled in liquid nitrogen. The receiver was placed in a bath of ice-water and connected with a mercury manometer. A pressure of 15.8 cm. was recorded (quoted[10]: 15.9 and 16.1 cm. at 0°). The Me_3P was neutralized by adding approxi-

(1) E. Grunwald, A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, **27**, 630 (1957).

(2) A. Loewenstein and S. Meiboom, *ibid.*, **27**, 1067 (1957).

(3) S. Meiboom, A. Loewenstein and S. Alexander, *ibid.*, **29**, 969 (1958).

(4) Z. Luz, D. Gill and S. Meiboom, *ibid.*, **30**, 1540 (1959).

(5) M. Sheinblatt, Ph.D. Thesis, Hebrew University, Jerusalem, 1960 (unpublished).

(6) R. E. Weston and J. Bigeleisen, *J. Chem. Phys.*, **20**, 1400 (1952); R. E. Weston and J. Bigeleisen, THIS JOURNAL, **76**, 3074 (1954).

(7) W. A. Jenkins and D. M. Yost, *J. Chem. Phys.*, **20**, 539 (1952); W. A. Jenkins and D. M. Yost, *J. Inorg. Nuclear Chem.*, **11**, 297 (1959).

(8) R. B. Martin, THIS JOURNAL, **81**, 1574 (1959).

(9) F. G. Mann, A. F. Wells and D. Purdie, *J. Chem. Soc. (London)*, 1828 (1937).

(10) N. Davidson and H. C. Brown, THIS JOURNAL, **64**, 316 (1942); A. B. Burg and R. I. Wagner, *ibid.*, **75**, 3873 (1953).
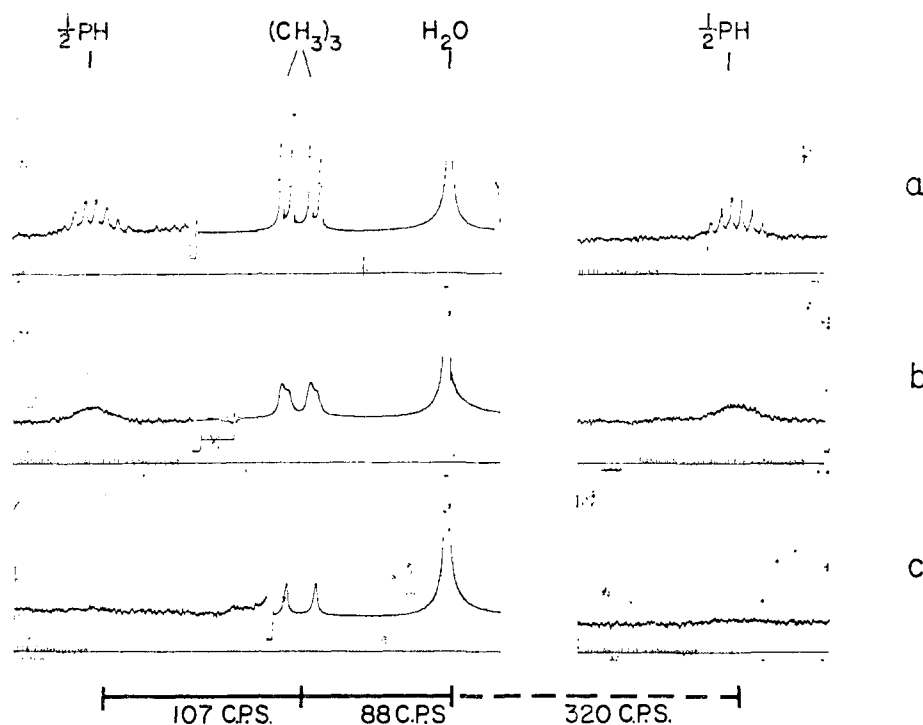
Fig. 1.—Typical proton magnetic resonance spectra of Me_3PH^+ at 31.65 Mc./sec. The two multiplets due to the hydrogen bonded directly to phosphorus were recorded at ten times the amplification of the methyl and water lines. Traces a, b and c correspond to solutions of pH 6.0, 7.1 and 7.6, respectively.

mately the theoretical quantity of $3N$ HCl at $5°$. The solution was adjusted to approximately pH 1 with HCl and made up to a known volume.

The concentration of Me_3PH^+ was calculated from the weight of Me_3P and the volume of the solution. A check on this value was obtained by potentiometric titration as described below.

The solution of trimethylphosphonium chloride obtained as described above was used to prepare solutions of various concentrations by dilution with distilled water.

Determination of pK_A.—The acid dissociation constant, defined as $K_A = \dfrac{[Me_3P][H^+]}{[Me_3PH^+]}$, was determined by potentiometric titration, using a Metrohm E148c pH meter with a Metrohm combined calomel–glass electrode. Measured quantities of the stock solution were diluted with known amounts of distilled water and titrated with standard NaOH $(0.93N)$ solution. The titration curve revealed the presence of two buffered regions, the first, in the range pH 1–2 being due to the slight excess of the HCl present, and the second in the range pH 8.3–8.7, being due to the neutralization of trimethylphosphonium ion. The neutralization of Me_3PH^+ results in the formation of Me_3P, which causes turbidity in the solutions due to its low solubility in water. The pH at which the turbidity was first observed was within the second buffered region and decreased with increasing initial concentration of Me_3PH^+. Values for pK_A were calculated for various concentrations of Me_3PH^+, using the Henderson equation.[11] For this purpose points were selected on the titration curves, in the second buffered region, at pH values lower than those corresponding to the appearance of turbidity. The calculated pK_A values showed no systematic variation in the concentration range 0.2 to 1.8 M Me_3PH^+. An average value was taken for pK_A of 8.80 ± 0.15 at $22 ± 1°$.

The inflexion after the second buffered region of the titration curve corresponds to the complete neutralization of the original Me_3PH^+. The molarity of Me_3PH^+ thus estimated from the titration curve always corresponded to within 2–3% to the molarity of the stock solution as estimated by weighing as described above.

(11) S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 390.

Procedure.—Spectra were recorded for solutions of Me_3-PH^+ of fixed concentration and varying pH. This was done for a variety of Me_3PH^+ concentrations in the range 0.26 to 2.2 M. All measurements were made at $22 ± 1°$. Pronounced changes in spectral lines were observed in the range pH 6.0–7.5. Below pH 6.0 the proton exchange rate is too low to cause changes in the spectrum and above pH 7.5 the loss of Me_3P by evaporation introduces an uncertainty in the interpretation of the results. The procedure was as follows: measured quantities of NaOH solution $(0.93\ N)$ were added to solutions of Me_3PH^+ of known concentration, and the pH determined, using a combined calomel–glass electrode. At varying pH values, samples were taken and their n.m.r. spectra recorded. The pH of the solutions was noted immediately before and after recording the spectra and never differed by more than 0.1 pH unit.

In preliminary experiments all solutions containing Me_3-PH^+ were kept in an atmosphere of analytical nitrogen gas to avoid possible oxidation of Me_3P. It was subsequently found that no observable oxidation occurred in air and the use of nitrogen gas was therefore discontinued.

Results

Typical spectra of Me_3PH^+ for different exchange rates are shown in Fig. 1. At pH values below 6.0, when the exchange rate is negligible, the spectrum is as shown in trace (a). It consists of a double multiplet, due to the exchangeable acidic hydrogen directly bound to the phosphorus atom, and a double doublet due to the three methyl groups. The spin–spin interaction between the phosphorus and the acidic hydrogen is 515 ± 10 c.p.s.[12] The multiplet structure of the acidic hydrogen resonance is caused by the spin–spin interaction with the nine equivalent methyl hydrogens. Theoretically each multiplet should con-

(12) Similar values for the P–H spin–spin interaction have been measured by J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, THIS JOURNAL, 78, 5715 (1956).
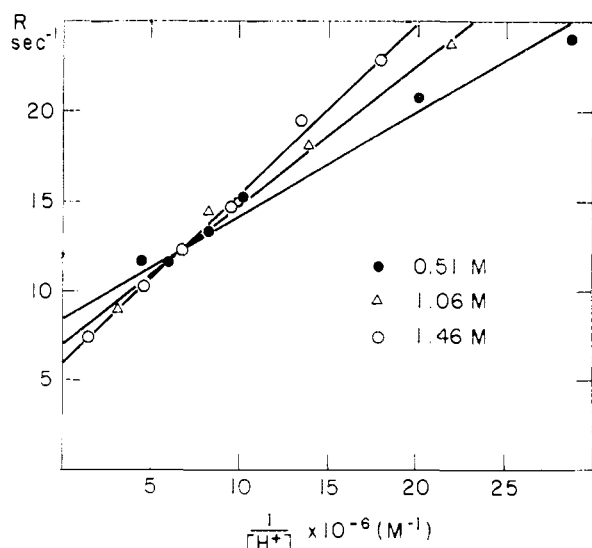
Fig. 2.—Typical graphs showing the total specific rate of exchange, R, (defined a equation 1) as a function of the reciprocal of the hydrogen ion concentration, the concentrations of Me$_3$PH$^+$ of 0.51, 1.06 and 1.46 M, respectively.

tain 10 observable lines, however, due to the low intensity of the outer lines these are indistinguishable from the noise.

The methyl spectrum can be interpreted as a consequence of a major splitting of 16.6 ± 0.8 c.p.s. due to spin–spin interaction with the phosphorus atom and a smaller splitting due to the interaction with the acidic hydrogen. The spin–spin interaction between the methyl hydrogen and the acidic hydrogen should be equal to the splitting of the acidic hydrogen multiplet. A value of 5.48 ± 0.25 c.p.s. was observed for both.

When the exchange rate of the acidic hydrogen is high, at pH values above approximately pH 7.5, the spectra are as shown in trace c. The components of each of the two multiplets have broadened, so that two flat lines are observed, whilst each of the two methyl doublets have collapsed into one line, resulting in the formation of a simple doublet. At intermediate pH values, when the exchange rate is in the range measurable by the n.m.r. technique, the corresponding spectra have a form intermediate between the extreme cases shown in traces a and c; a typical spectrum is shown in trace b.

The fact that the methyl doublet, caused by the spin–spin interaction with the phosphorus atom, shows no tendency to collapse into one line, even at the highest pH value at which measurements were made, indicates that the observed changes in the spectra are due to exchange reactions of the acidic hydrogen only. A measurable exchange of the methyl group would be unexpected on chemical evidence.
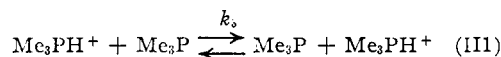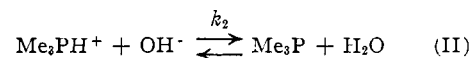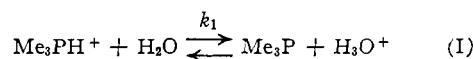
In the pH range in which spectra were recorded, only small changes were observed in the width of the water line.

The line shapes of the Me$_3$PH$^+$ spectra can be interpretated in terms of the mean life-time of the acidic hydrogen between successive exchanges. Two possible exchange reactions must be taken into

consideration, (i) direct exchange between Me$_3$-PH$^+$ ions and (ii) exchange between Me$_3$PH$^+$ ions and water. The line shape of each methyl doublet provides a measure of the total rate of exchange, the water line width gives a measure of reaction (ii), and the line shape of the acidic hydrogen multiplets depends on both reactions (i) and (ii). No attempt was made to interpret the shapes of the latter lines because their low intensity and the laborious theoretical treatment necessary for such an interpretation.

Interpretation of the Methyl Doublet.—The interpretation of the line shape of the methyl doublets was performed using the theoretical line shapes for a doublet, described in ref. 2.

The following protolysis reactions may occur in the system under consideration

$$\text{Me}_3\text{PH}^+ + \text{H}_2\text{O} \underset{\longleftarrow}{\overset{k_1}{\rightleftharpoons}} \text{Me}_3\text{P} + \text{H}_3\text{O}^+ \qquad \text{(I)}$$

$$\text{Me}_3\text{PH}^+ + \text{OH}^- \underset{\longleftarrow}{\overset{k_2}{\rightleftharpoons}} \text{Me}_3\text{P} + \text{H}_2\text{O} \qquad \text{(II)}$$

$$\text{Me}_3\text{PH}^+ + \text{Me}_3\text{P} \underset{\longleftarrow}{\overset{k_3}{\rightleftharpoons}} \text{Me}_3\text{P} + \text{Me}_3\text{PH}^+ \qquad \text{(III)}$$

The total specific rate of exchange, R, is the sum of the rates due, respectively, to reactions I, II and III, $i.e.$

$$\frac{1}{\tau} = R = \frac{1}{[\text{Me}_3\text{PH}^+]}\frac{d[\text{Me}_3\text{PH}^+]}{dt} = k_1' [\text{H}_2\text{O}] +$$
$$k_2 [\text{OH}^-] + k_3 [\text{Me}_3\text{P}] = k_1 +$$
$$\frac{1}{[\text{H}^+]}(k_2 K_\text{W} + k_3 K_\text{A} [\text{Me}_3\text{PH}^+]) \quad (1)$$

where τ is the mean life time of the acidic hydrogen between successive exchanges, k_1', k_2 and k_3 are the respective second order rate constants for reactions I, II and III, and $K_\text{W} = [\text{H}^+][\text{OH}^-]$ is the autoprotolysis constant of water.

In Fig. 2 the total specific rate R is plotted against $1/[\text{H}^+]$ for three different concentrations of Me$_3$PH$^+$. It follows from formula 1 that the intercept on the vertical axis gives a value for the pseudo-first order rate constant k_1, for reaction I and the slope of the plot gives a value for $k = k_2 K_\text{W} + k_3 K_\text{A} [\text{Me}_3\text{PH}^+]$. The results over the complete concentration range of Me$_3$PH$^+$ are given in Table I.

TABLE I

PROTOLYSIS OF TRIMETHYLPHOSPHONIUM AT 22 ± 1°

Conc. Me$_3$PH$^+$ (mole/l.)	$k(= k_2 K_\text{W} + k_3 K_\text{A}$ [Me$_3$PH$^+$]) × 10^5 (mole l.$^{-1}$ sec.$^{-1}$)	k_1 (sec.$^{-1}$)
0.26	0.54	9.8
.30	.56	8.8
.51	.61	8.4
.67	.63	8.1
.78	.76	7.0
1.06	.94	7.2
1.13	.94	7.2
1.46	.97	6.4
2.21	1.07	6.2

Fig. 3 shows a plot of k against concentration of Me$_3$PH$^+$. It follows from the definition of k that the intercept and the slope of this graph give values for $k_2 K_\text{W}$ and $k_3 K_\text{A}$, respectively. In constructing the curve, the point corresponding to the
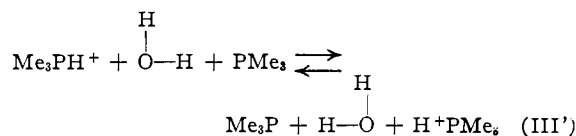
highest concentration of Me_3PH^+ was disregarded since the results at the higher concentrations are considered to be less accurate. The values obtained for k_2 and k_3 were

$$k_2 = 4.6 \pm 0.9 \times 10^7 \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k_3 = 1.2 \pm 0.6 \times 10^2 \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

Interpretation of the Water Line.—Reactions I and II involve water, reaction I directly and reaction II through the participation of the hydroxyl ion. This should manifest itself in a broadening of the water line-width. The broadening observed was of the order of 0.03 c.p.s. within the pH range studied. Using the relevant equations[13] it can be shown by substituting the values obtained for k_1 and k_2 that under the experimental conditions obtained, the maximum broadening of the water line should not exceed 0.04 c.p.s. However, no kinetic interpretation can be based on this broadening, since it is of the same order of magnitude as that observed for changes in the natural line width of water within the same pH range ($\sim$0.01 c.-p.s.).[14,15]

The proton transfer from trimethylphosphonium ion to its conjugate base may be direct as shown in eq. (III) or may involve a water molecule

$$Me_3PH^+ + \overset{\text{H}}{\underset{}{O}}\text{—H} + PMe_3 \underset{\longleftarrow}{\longrightarrow}$$

$$Me_3P + H\text{—}\overset{}{\underset{}{O}} + H^+PMe_3 \quad \text{(III')}$$

These two mechanisms cannot be distinguished by the interpretation of the methyl doublet and therefore the value for k_3, given above, is in fact the sum of the rate constants for reactions (III) and (III'). It is theoretically possible to distinguish reaction (III') from reaction (III) from the broadening of the water line. However even if the observed value of k_3 is assumed to be solely due to reaction (III'), it can be shown[13] that the water line broadening due to this reaction would be too small to provide a practical basis for interpretation.

Discussion

The protolysis reactions of trimethylphosphonium ion were found to proceed *via* three main mechanisms. (i) A direct proton transfer to water, reaction I; (ii) Proton transfer to the conjugate base, reaction III; and (iii) Proton transfer to a hydroxyl ion, reaction II. Rate constants for these reactions are summarized in Table II together with comparable data on Me_3NH^+.

The significant concentration dependence of k_1, shown in Table I, is similar to that observed by Grunwald, et al.,[16] for the analogous reaction between NH_4^+ and water and may be a consequence of the relatively strong dependence of the activity of water on the solute concentration, in the con-

(13) (a) Ref. 1, eq. 12; (b) $\dfrac{2[H_2O]}{[Me_3PH^+]} = \dfrac{\tau_w}{\tau_{Me_3PH^+}}$ where τ_w is the mean life time of a water molecule between successive exchanges with Me_3PH^+, and $\tau_{Me_3PH^+}$ is the mean life time of Me_3PH^+ between successive exchanges with water.

(14) S. Meiboom, Z. Luz and D. Gill, *J. Chem. Phys.*, **27**, 1411 (1957).

(15) S. Meiboom, to be published.

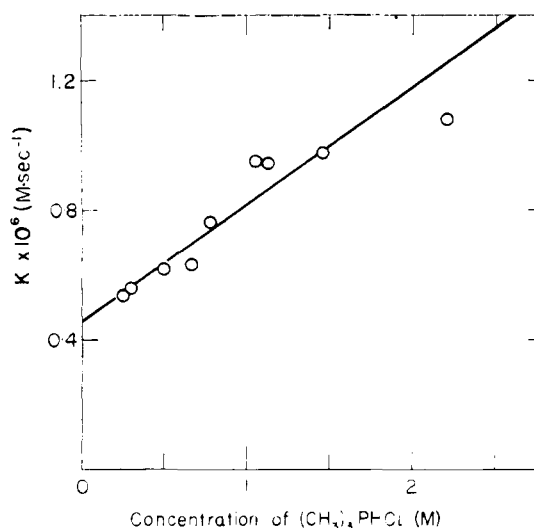(16) T. Emerson, E. Grunwald and R. A. Kromhout, *J. Chem. Phys.*, **33**, 547 (1960).

Fig. 3.—Plot of k ($= k_2K_W + k_3K_A[Me_3PH^+]$) as a function of Me_3PH^+ concentration.

centration range studied. The difference in the values of k_1 for Me_3PH^+ and Me_3NH^+ are those to be expected on the basis of the difference in the corresponding values of pK_A, since both are measures of the proton donating tendency of the conjugate acid.

TABLE II

PROTOLYSIS RATE CONSTANTS OF TRIMETHYLPHOSPHONIUM AND TRIMETHYLAMMONIUM AT $22 \pm 1^{\circ a}$

	k_1 (sec.$^{-1}$)	k_2 (l. mole^{-1} sec.$^{-1}$)	k_3 (l. mole^{-1} sec.$^{-1}$)	pK_A
Me_3PH^+	7.9	0.46×10^8	1.2×10^2	8.80
Me_3NH^+	3	$<10^{11}$	3.1×10^8	9.80

^{a} The values of k_1, k_2 and k_3 for Me_3PH^+ are the rate constants for reactions (I), (II) and (III), respectively, as defined in the text. For the purpose of comparison with Me_3NH^+ the value of k_1 for Me_3PH^+ is given as an average value over the concentration range studied (see Table I). The values for Me_3NH^+ are for the analogous reactions and were taken from ref. 2.

The proton transfer from the trimethylammonium ion to its conjugate base is considerably faster than the analogous reaction of the trimethylphosphonium ion. In the former case the reaction was shown to proceed *via* water and strong evidence was provided that the rate determining step in this reaction is a proton transfer to the conjugate base from a water molecule in its hydration shell. The rate of this step will partially depend on the base dissociation constant $K_B (= K_W/K_A)$. If it is assumed in the case of trimethylphosphonium ion that the direct proton transfer to the conjugate base also proceeds mainly through water, the lower rate of the reaction as compared with trimethylammonium, could be explained in terms of the lower basicity of Me_3P compared to Me_3N.

The rate constant for the proton transfer from Me_3PH^+ to a hydroxyl ion was found to be 0.46×10^8 l. mole^{-1} sec.$^{-1}$. This is three orders of magnitude lower than the rates observed for the combination of ammonium or hydronium ions

with hydroxyl ions.[17] A theoretical estimation[18] based on the rate of formation of short range ion pairs may be made for the rate of reaction of oppositely charged ions in solution and gives a value

(17) M. Eigen and J. Schoen, Z. Elektrochem., 59, 483 (1955); M. Eigen and J. Schoen, Z. Physik. Chem. (Frankfurt), 3, 126 (1955); M. Eigen and L. de Maeyer, Naturwissenschaften, 42, 413 (1955).

(18) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943, pp. 43, 110, eq. (4-7-19).

for the rate constant of approximately 10^{10} l. mole^{-1} sec.$^{-1}$ assuming that every collision results in reaction. Presumably in the case of Me$_3$PH$^+$ not every collision results in a reaction.

High Concentration–Ratio Experiments: Isotope Fractionation at the Methyl Carbon in the Reaction of Cyanide Ion and Methyl Iodide. Isotope Effect under Conditions of Equal Reagent Concentrations
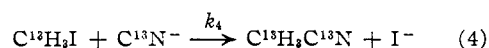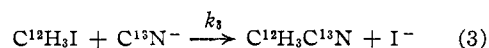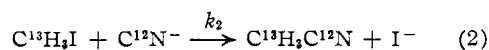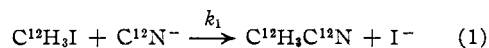
By K. R. Lynn and Peter E. Yankwich

The C^{13} isotope effect for isotopy at the methyl carbon atom has been measured in the cyanization of methyl iodide in water solution between 11.4 and 58.0°. As a check on these results and those previously reported for isotope fractionation at the cyanide carbon atom, experiments were carried out also in which the reagents were present at equal concentrations instead of one being in large excess; the check experiments yield data of considerably higher quality than either set obtained under high concentration-ratio conditions. There is general agreement among the three sets of results, but it is not sufficiently close to permit detailed speculations concerning the nature of the reaction coördinate motion in terms of simple models. The methyl carbon isotope effect in the cyanization is much larger than that observed in the related hydrolysis, a fact which cannot be explained unless account is taken of the details of activation changes in C–H bonding.

Introduction

In a recent publication[1] we reported results of experiments on the temperature dependence of the isotope fractionation at the cyanide carbon atom in the C–C bond-forming reaction of methyl iodide and cyanide ion. To complete the investigation of carbon isotope effects in this reaction, we have studied isotope fractionation at the methyl carbon over the same range of temperature. In the earlier paper the high concentration-ratio technique was employed, as it was in part of the work to be reported below; to check the results obtained by this method, experiments were carried out under more usual conditions, namely those of equal concentrations of the reacting substances.

The isotopic rate constant ratio measured in the previous study was (k_1/k_3) in the following notation

$$C^{12}H_3I + C^{12}N^- \xrightarrow{k_1} C^{12}H_3C^{12}N + I^- \quad (1)$$

$$C^{13}H_3I + C^{12}N^- \xrightarrow{k_2} C^{13}H_3C^{12}N + I^- \quad (2)$$

$$C^{12}H_3I + C^{13}N^- \xrightarrow{k_3} C^{12}H_3C^{13}N + I^- \quad (3)$$

$$C^{13}H_3I + C^{13}N^- \xrightarrow{k_4} C^{13}H_3C^{13}N + I^- \quad (4)$$

while the subject of the present investigation is (k_1/k_2). The experimental conditions were such that there was no likelihood of appreciable exchange of methyl nitrile carbon with methyl iodide.[2,3]

Experimental

Reagents.—Fisher "Certified" sodium cyanide was used without further purification; the methyl iodide samples were center cuts distilled from Eastman "White Label Grade"

material. Solvent water was de-ionized by passage through a mixed-bed resin ion exchanger. Reagents of analytical grade were employed in the analyses of reactants and products.

Cyanization Runs.—Reactions were carried out at two different concentration ratios: (a) 90 ml. of 0.05 M methyl iodide and 10 ml. of 0.015 M sodium cyanide were mixed and allowed to react for at least fifteen times the calculated half-time of reaction[4,5] or (b) 90 ml. of 0.05 M methyl iodide and 9 ml. of 0.5 M sodium cyanide were mixed, allowed to react until approximately 3% conversion to methyl nitrile had occurred, then their reaction quenched by addition of excess saturated aqueous zinc sulfate solution (Mallinckrodt A. R.). In either case, aliquots of sodium cyanide solution and freshly prepared methyl iodide solution were brought to the reaction temperature ($\pm 0.1°$), then mixed in glass-stoppered vessels of appropriate volume.

The details of the gas-chromatographic technique employed in isolation and purification of the methyl nitrile and of the several combustion procedures used to secure carbon dioxide for mass spectrometric analysis are given in the previous paper.[1] The mass spectrometric procedures employed are described in earlier publications from this Laboratory.[6-8]

Calculations.—Complete reaction of the cyanide ions in the presence of an approximately thirty-fold excess of methyl iodide is equivalent to about 3% reaction of the latter. Under these conditions the isotopic constitution of the residual methyl iodide is not altered significantly, the isotopic constitution of the nitrile carbon is that of the original cyanide reagent and that of the methyl carbon in the product reflects the isotope effect related to (k_1/k_2).

Let R_I be the ratio (C^{13}H$_3$I/C^{12}H$_3$I) for the original methyl iodide reactant (equivalent to the corresponding ratio of isotopic carbon dioxides obtained by combustion of the reagent material) and X_I the corresponding C^{13} atom fraction $(X = R/[1 + R])$; let X_C be the atom fraction of C^{13} in the reagent cyanide. Further, let X_N' be the atom fraction of C^{13} in the carbon dioxide obtained by combustion of

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(6) P. E. Yankwich and R. L. Belford, This Journal, 75, 4178 (1953).

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