1-Chlorocyclohexene-2,6,6-d_3 and Phenyllithium. 1-Chlorocyclohexene-2,6,6-d_3[6] (4.5663 g, 0.03815 mole) and 100 ml of 1.00 M phenyllithium (0.100 mole) in ether were heated at 150 ± 10° for 1.3 hr. The reaction products included 2.13 g (46.6%; XEA, 90°, 35 cc/min) of 1-chlorocyclohexene-2,6,6-d_3 and 0.79 g (12.5%) of deuterated 1-phenylcyclohexene. Both compounds were isolated utilizing preparative glpc. The nmr and infrared spectra of the recovered chloride were virtually identical with those of the starting material. Proton nmr analysis of the deuterated 1-phenylcyclohexene indicated the presence of 0.82 ± 0.09 deuteron and 1.93 ± 0.11 deuterons in the olefinic and saturated ring positions, respectively.

Proton Transfers in Dipolar Aprotic Solvents. III. Transfers from Triphenylmethane in Dimethyl Sulfoxide Solution[1,2]

Calvin D. Ritchie and R. E. Uschold

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received January 25, 1967

Abstract: The reactions of triphenylmethane with *t*-butoxide, *n*-propoxide, and dimsyl ions in dimethyl sulfoxide solution have been studied. Triphenylmethane reacts with dimsyl ion and *n*-propoxide ion to form trityl anion with second-order rate constants of 8×10^3 and 6×10^3 M^{-1} sec^{-1}, respectively. The reaction of triphenylmethane with *t*-butoxide ion is too slow to measure under our reaction conditions, and an upper limit of 8×10^2 M^{-1} sec^{-1} is set on the rate constant for this reaction. Equilibrium constants for the reactions of triphenylmethane with dimsyl ion, *t*-butoxide ion, and *n*-propoxide ion are 1.6×10^4, 0.5, and 0.1, respectively.

As part of a continuing study of solvent effects on the rates of proton transfer reactions, we have measured the rates and equilibrium constants for the reactions of triphenylmethane with dimsylcesium, potassium *t*-butoxide, and potassium *n*-propoxide in dimethyl sulfoxide solution. Since the results obtained are pertinent to a number of recently reported studies of rates and equilibria of carbon acids,[3] we wish to report these data now. Several corrections are made to a preliminary report of this work.[4]

Experimental Section

All materials were purified, stored, and handled under an atmosphere of purified argon.[5]

Materials. Dimethyl sulfoxide was purified by the method previously described,[5] and was found to contain less than 5×10^{-6} M acidic and basic impurities, and less than 20 ppm of water.

Dimsylcesium solutions of *ca.* 0.3 M were prepared from cesium amide as previously described.[5] Less concentrated solutions were prepared by dilution. The ultraviolet spectrum of a 2.4×10^{-2} M solution of cesium dimsyl in a 0.1-mm cell showed an absorption shoulder at 260 mμ (ϵ 1.5×10^3 M^{-1} cm^{-1}), and no peaks or shoulders at longer wavelengths. The 60-Mc nmr spectrum of a 0.24 M solution showed a single sharp peak for the solvent and *no* other visible bands within 800 cps on either side of the solvent peak. Any band with an intensity of as much as *0.5%* of that of the solvent would have been seen. The infrared spectrum of a 0.24 M solution of dimsylcesium *vs.* pure dimethyl sulfoxide showed a single band at 840–850 cm^{-1} ($\epsilon \simeq 1.2 \times 10^2$ M^{-1} cm^{-1}) which we believe to be due to the S–O stretch of the dimsyl ion.

Potassium *t*-butoxide (MSA Research Corp.) was twice sublimed under vacuum at *ca.* 100° prior to use.

Potassium *n*-propoxide was prepared by reaction of metallic potassium with dry deoxygenated *n*-propyl alcohol, followed by removal of excess *n*-propyl alcohol under vacuum. The resulting product was dried under vacuum at *ca.* 100° for 3 hr. Titration of a weighed sample of the alkoxide with aqueous standard acid indicated a purity of better than 99.5%.

Triphenylmethane was recrystallized from ethanol and dried under vacuum prior to use.

A sample of triphenylmethane-d_1 was kindly supplied by Professor P. T. Lansbury. Infrared analysis of the material showed greater than 90% isotopic purity.

Apparatus. Equilibrium measurements were carried out on a Cary Model 14 spectrophotometer fitted with the mixing cell apparatus diagrammed in Figure 1, and further described below.

Kinetic measurements were carried out on a small-scale stopflow apparatus which we have previously described.[6]

Equilibrium Measurements. Solutions of triphenylmethane (the concentrations of triphenylmethane in the various measurements ranged from 5×10^{-6} M to *ca.* 10^{-4} M in each determination) were added incrementally by means of a micrometer syringe, whose tip extended into the bulb of the apparatus shown in Figure 1, to 10.0 ml of the base solutions contained in the mixing cell. The solutions were mixed after each addition by simply tipping the cell back and forth several times. Care was taken that the solutions did not contact the rubber serum cap through which the syringe was inserted.

Plots of absorbance at 495 mμ, the wavelength of maximum absorption of the trityl anion, *vs.* concentration of triphenylmethane added gave straight lines whose slopes are the apparent extinction coefficients, ϵ'. Several experiments utilizing *ca.* 10^{-1} M solutions of dimsylcesium gave the true extinction coefficient of the trityl anion, ϵ, as 3.12×10^4 M^{-1} cm^{-1}. At lower concentrations of dimsyl anion, the observed apparent extinction coefficients can be used to calculate the ratio of trityl anion to triphenylmethane concentrations in the solution by eq 1.

$$(\text{Ar}_3\text{C}^-)/(\text{Ar}_3\text{CH}) = \epsilon'/(\epsilon - \epsilon') \qquad (1)$$

This technique of measurement is necessary because of small amounts of impurities present which react with either the trityl anion or triphenylmethane. The fact that non-zero intercepts are obtained in the plots of absorbance *vs.* concentration show the presence of such impurities. One such plot is shown in Figure 2.

(1) This work was supported by Grant No. GM 12832 from Public Health Service, National Institutes of Health.

(2) For previous papers in this series, see: C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1730 (1967); **86**, 4488 (1964).

(3) See, for example: (a) G. A. Russell and A. G. Bemis, *ibid.*, **88**, 5491 (1966); (b) J. I. Brauman and D. F. McMillen, *ibid.*, in press; (c) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(4) C. D. Ritchie and R. E. Uschold, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p 1475.

(5) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1721 (1967).

(6) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2063 (1967).
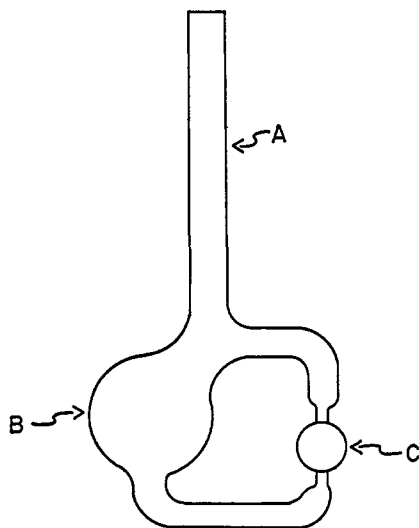
Figure 1. Mixing cell used for triphenylmethane titrations: A, 4.0-mm i.d. Pyrex tubing; B, bulb, *ca.* 12-ml capacity; C, cylindrical quartz window cell, 1.0-cm path.

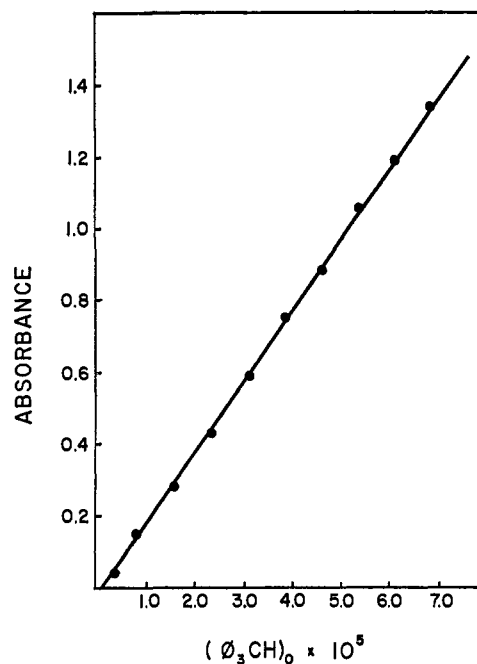Figure 2. Absorbance at 495 mμ *vs.* concentration of triphenylmethane in 1.64 $\times$ 10^{-3} M dimsylcesium in DMSO.

Once the equilibrium constant for the reaction of triphenylmethane with dimsyl ion has been obtained, then the equilibrium constants for the reactions of alcohols with dimsyl ion, and thus, with triphenylmethane, can be obtained. Analogous experiments to those described above in which triphenylmethane is added to solutions of the alkoxides are used to obtain the ratio of trityl ion to triphenylmethane concentrations at given alkoxide concentrations. From these ratios and the equilibrium constant for the dimsyl-triphenylmethane reaction, the concentration of dimsyl ion at given concentrations of added alkoxide can be calculated, and from this, the desired equilibrium constants are evaluated.

The values obtained for the various equilibrium constants are shown in Table I. The precision and accuracy of the data are discussed below.

Table I. Equilibrium Constants at 25° for the Reactions
HA + CH₃SOCH₂⁻ = A⁻ + CH₃SOCH₃

HA	Initial base concn $\times$ 10³, M	$K \times 10^{-4}$
Triphenylmethane	2.4	1.8
	1.2	1.3
	0.60	2.1
	6.0	1.4
	2.4	1.2
	1.2	1.5
	0.60	1.5
	6.5	2.7
	1.6	1.5
	Av	1.6 ± 0.4
t-Butyl alcohol	74.0	6.2
	1.8	5.6
	7.0	0.72
	4.2	1.2
	2.1	2.3
	1.1	1.0
	Av	3.0 ± 2.0
n-Propyl alcohol	5.1	7.7
	2.6	10.0
	1.2	29.0
	0.61	26.0
	5.2	5.9
	6.2	8.3
	4.3	8.3
	8.0	18.0
	Av	14.0 ± 7.0

Kinetic Measurements. Solutions of known concentration of base and of triphenylmethane were prepared under an argon atmosphere and transferred to gas-tight syringes and then into the stop-flow apparatus. The reactions were followed by the appearance of the absorbance of the trityl anion at 495 mμ. Details of the general procedure used on the stop-flow apparatus have been given previously.[6]

In all runs, the concentration of base was much greater than the equilibrium concentration of trityl ion and the kinetics observed were those of pseudo-first-order reversible reactions. In the reactions with dimsyl ion, treatment of the data was straightforward using eq 2

$$\ln (C_a{}^\infty - C_a) = -k_\psi(C_0/C_a{}^\infty)t + \ln C_a{}^\infty \quad (2)$$

where $C_a{}^\infty$ is the concentration of trityl ion at equilibrium, C_a is the concentration of trityl ion at time t, and C_0 is the initial concentration of triphenylmethane. The second-order rate constant for the reaction is equal to the pseudo-first-order constant, k_ψ, divided by the concentration of base. Some typical data for the reaction of dimsyl ion are shown in Table II.

Table II. Reaction of Triphenylmethane with Cesium Dimsyl at 25°

Concn of cesium dimsyl $\times$ 10³, M	Slope[a]	$C_a{}^\infty/C_0$[b]	$k_2 \times 10^{-3}$, M^{-1} sec^{-1}
2.42	24.1	0.750	7.5
2.42	22.0	0.665	6.0
1.21	14.2	0.525	6.2
1.21	16.3	0.551	7.4
0.61	15.7	0.464	12.0
0.61	13.9	0.392	8.9
			8.0 ± 1.5
$k_H/k_D = 4.7 \pm 0.4$			

[a] Slope of the plot of ln ($C_a{}^\infty - C_a$) *vs.* time (sec). [b] Ratio of trityl ion concentration at equilibrium to initial triphenylmethane concentration. In each run, the initial concentration of triphenylmethane was *ca.* 3 $\times$ 10^{-5} M.

The reaction of triphenylmethane with solutions of the alkoxides involves simultaneous reactions with dimsyl ion and alkoxide ion since appreciable amounts of dimsyl ion are formed by reaction of

the alkoxide with solvent. In each kinetic run, we have calculated the concentration of dimsyl ion present from the observed ratio of trityl ion to triphenylmethane concentrations at equilibrium in the reactions. Knowing the concentration of dimsyl ion and the rate constant for reaction of dimsyl ion, the observed first-order rate constants in alkoxide solutions can be corrected for the reaction of dimsyl ion and the second-order rate constants for reaction of the alkoxides calculated. This calculation involves the implicit assumption that the concentration of dimsyl ion does not change during the run. Since a dilution is involved in mixing the reactants in the stop flow, and since the ratio of concentration of dimsyl ion to that of alkoxide is concentration dependent, the assumption is that the alkoxide-solvent equilibrium is established much more rapidly than reaction with triphenylmethane. The constancy of the the observed rate constants with varying initial concentration of base provides support for this assumption, as does the observed linearity of the kinetic plots. The data obtained for the reactions of the alkoxides are summarized in Table III.

Table III. Reactions of Triphenylmethane with Potassium Alkoxides at 25°

Initial base concn × 10^3, M	R^a	Dimsyl concn^b × 10^4	C_a^∞/C_0	k_{exptl},^{c} sec^{-1}	k_{cor},^{d} sec^{-1}	k_2^e × 10^{-3} M^{-1} sec^{-1}
		Potassium *t*-butoxide				
4.2	1.86	17.4	0.650	13.1	−0.8	0.0
2.1	0.91	8.5	0.477	6.65	0.15	0.0
1.1	0.77	7.2	0.436	5.85	0.10	0.0
		Potassium *n*-propoxide				
5.1	0.93	8.8	0.442	28.4	21.4	5.1
2.6	0.57	5.4	0.364	17.9	13.6	6.5
1.2	0.24	2.2	0.192	7.58	5.81	5.8
0.61	0.17	1.6	0.148	4.27	2.98	6.1
					Av	5.9 ± 0.4

^{a} Ratio of trityl ion to triphenylmethane concentration at equilibrium. The initial concentrations of triphenylmethane were from 2–5×10^{-5} M. ^{b} Concentration of dimsyl ion, calculated from R. ^{c} Pseudo-first-order rate constant defined by eq 2. ^{d} Pseudo-first-order rate constant for reaction with alkoxide ion. ^{e} Second-order rate constant for reaction with alkoxide ion.

The reaction of triphenylmethane-d_1 with dimsyl ion was also studied. This reaction involves formation of trityl ion simultaneous with hydrogen–deuterium exchange, and the rate expression cannot easily be put into the form of a plot. The integrated rate expression is given by eq 3

$$C_a^\infty - C_a = C_0\{(k_1 - k_1')/[k_1(C_0/C_a^\infty) - k_1']\}e^{-k_1't} + \{k_1(C_0 - C_a^\infty)[k_1(C_0/C_a^\infty) - k_1']\}e^{-k_1(C_0/C_a^\infty)t} \quad (3)$$

where k_1 is the pseudo-first-order rate constant for reaction with triphenylmethane, k_1' is the analogous constant for reaction of triphenylmethane-d_1, and the other symbols are defined as in eq 2.

Rate constants were calculated by means of the method of steepest descents using a program written in Fortran IV language for this particular problem. A single kinetic run gave values for both k_1 and k_1' independent of the value previously obtained for the rate constant for the undeuterated compound. An average value of $k_H/k_D = 4.7$ was obtained at 25°. Rate contants for the reaction of the hydrogen compound calculated from these data were in good agreement with the independently determined value.

Sources of Error and Accuracy of Data. The very basic carbanion solutions dealt with in the present work are extremely sensitive to small amounts of impurities. It is known that oxygen reacts with triphenylmethane anion to produce hydroperoxide anions^{3a} very rapidly. In addition, any compound which could act as even a weak acid ($pK < 30$) would react with dimsyl ion to make our solutions less basic than we expect on the basis of titrations for dimsyl ion.

The fact that the plots obtained from the titrations of the base solutions with triphenylmethane, as typically shown in Figure 2, have intercepts at *ca.* 10^{-6} M indicates that we do not have appre-

ciable amounts of oxygen in the solutions used there. Since equilibrium constants calculated from the equilibrium concentrations in the kinetic runs agree with those determined by the titration technique fairly well, we may assume that appreciable amounts of oxygen were not present in these runs. Titrations of the solvent for acidic impurities^5 would have shown the presence of any acid with a pK up to *ca.* 25. Standardization of the dimsyl solutions by titration of formanilide in dimethyl sulfoxide and by titration with standard acid in water ensures that no acidic species with pK less than *ca.* 21 is present.

Sulfides, sulfones, and water probably all have pK's greater than 20 and less than that of dimethyl sulfoxide, and could reasonably go undetected and yet cause serious errors in the measurements reported here. Although water would have been detected at concentrations greater than *ca.* 10^{-3} M (18 ppm), there could be enough present to cause some difficulty. We have observed, however, that the addition of a drop of water to a 5×10^{-4} M solution of dimsylcesium causes a marked cloudiness of the solution. It therefore appears that cesium hydroxide is probably too insoluble to cause difficulty in base solutions of greater than *ca.* 10^{-3} M. We believe that the most likely source of error is the presence of traces of dimethyl sulfone. It would be interesting to know the pK of this compound.

Steiner^7 has reported a value for the equilibrium constant of the reaction of triphenylmethane with dimsyl ion as 3×10^4. In view of the difficulties mentioned above, we are satisfied with the agreement within a factor of 2 of our value with this one.

If Steiner's value for the equilibrium constant of the reaction of triphenylmethane with dimsyl ion is used in place of the value reported in this paper, the equilibrium constants for the reactions with the alcohols and dimsyl ion would be increased by a factor of 2, as would the rate constant for the reaction of dimsyl ion with triphenylmethane. These errors, however, would have little effect on the reported values for the rate and equilibrium constants for the reactions of the alkoxides with triphenylmethane.

In any case, the fair agreement of our values for the equilibrium constants with those reported by Steiner indicates that the values reported in the present paper are accurate to within a factor of ~ 2. Considering the difficulties of the measurements, and for the present purposes, we are content with this accuracy.

Discussion

In a preliminary report of this work,^{4} we overlooked the possibility of the reactions of the alkoxides with solvent to form appreciable amounts of dimsyl ion in solution.^{8} The rate and equilibrium constants reported there are, therefore, completely in error. The two most serious errors are in the reported values for the reverse rate constants of the reactions of the alkoxides and in the value for the rate of reaction of *t*-butoxide.

The fact that *t*-butoxide contributes virtually nothing to the rate of formation of trityl ion in solutions of potassium *t*-butoxide is quite surprising and raises the question of the identity of the active base in other studies of proton abstraction in solutions of *t*-butoxide.^{3} Since *n*-propoxide reacts with triphenylmethane quite rapidly, even though it is a weaker base than *t*-butoxide, it appears that the slowness of reaction of *t*-butoxide must be due to a steric effect. Examination of molecular models shows that this is a reasonable postulate, and, in fact, Streitwieser has suggested that a steric effect may be responsible for the slowness of reaction of methoxide ion with triphenylmethane in methanol solution.^{9} It seems possible, also, that the reactions of both *n*-propoxide and dimsyl ion with triphenylmethane are subject to a steric effect if Streitwieser's suggestion is correct.

(7) E. C. Steiner, preprint of paper to be presented in Petroleum Chemistry Section, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

(8) This possibility was pointed out to us by Dr. E. C. Steiner. We would like to express our appreciation to him for this suggestion, and for many later discussions and suggestions.

(9) A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, **3**, 58 (1965).

Data have been reported[9,10] which allow the calculation of a second-order rate constant of ca. 10^{-9} M^{-1} sec^{-1} for the reaction of triphenylmethane with methoxide ion in methanol at 45°. We can, therefore, estimate that n-propoxide in dimethyl sulfoxide reacts at least 10^{14} times faster than does methoxide in methanol with triphenylmethane. This tremendous rate enhancement must be attributed to a solvent effect if we reasonably assume that methoxide and n-propoxide would react at the same rate in a given solvent. (Unfortunately, the solubility of potassium methoxide in pure dimethyl sulfoxide is too low to allow easy measurement of its reactions.) With the analogous assumption that the basicity of methoxide and n-propoxide would be nearly the same in a given solvent,[11] we can estimate that the change of solvent from methanol to dimethyl sulfoxide increases the basicity of n-propoxide by a factor of not more than 10^{11}. If one uses Steiner's recently reported[7] value of 26.9 for the pK of methanol in DMSO with the value of 18.3 for the pK

of methanol in methanol,[6] the increase in basicity of methoxide is only 8.6. We therefore conclude that factors other than solvation of the alkoxide[3c] contribute to the enhanced rates of proton abstraction on going from hydroxylic to nonhydroxylic solvents.

A reasonable explanation of the origin of this extra rate-enhancing factor is the postulate of the necessity of solvent reorganization which we have recently used to explain the enhanced rates of reactions of nucleophiles with carbonium ions in nonhydroxylic solvents.[6] In a hydroxylic solvent, the base must be hydrogen bonded to solvent molecules. At the transition state, this solvation is lost and compensation by solvent–solvent hydrogen bonding has not fully occurred. Thus, the rate of reaction is slowed in both directions. In the reverse direction, solvent molecules which are in the initial state hydrogen bonded to other solvent molecules must break away and start to reorganize to solvate the products.

As we have pointed out previously,[6] this idea is a simple extension of the concepts suggested by earlier workers.[12]

(10) A. Strietwiser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, J. Am. Chem. Soc., 87, 384 (1965).

(11) There is a great deal of evidence that the basicities of the simple alcohols are not far different from one another in any single solvent; see: R. P. Bell, "The Proton in Chemistry," Cornell University Press, Inc., Ithaca, N. Y., 1959, p 45.

(12) E. A. Moelwyn-Hughes, Proc. Roy. Soc. (London), A164, 295 (1938); A212, 260 (1952); E. F. Caldin, J. Chem. Soc., 3345 (1959); K. T. Leffek, R. E. Robertson, and S. Sugamori, J. Am. Chem. Soc., 87, 2097 (1965); and other references cited in these works.

Proton Exchange of Triethylammonium Ion in Aqueous Solution[1]
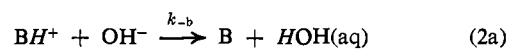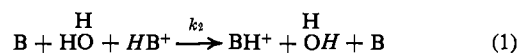
E. K. Ralph, III, and Ernest Grunwald

Contribution from the Lecks Chemical Laboratories, Brandeis University, Waltham, Massachusetts 02154. Received January 13, 1967

Abstract: Rates of exchange of NH protons of triethylammonium ion (BH$^+$) with H_2O and D_2O have been measured by nuclear magnetic resonance techniques in acid solutions over a range of pH. The following reactions and rate constants (corrected to infinite dilution) were found: BH$^+$ + OH$^-$, k_{-b} = (1.7 ± 0.5) × 10^{10} sec^{-1} M^{-1} at 30°; BH$^+$ + OH$_2$ + B (symmetrical exchange), k_2 = (1.82 ± 0.08) × 10^8 sec^{-1} M^{-1} at 30°; B + H$_3$O$^+$, k_{-a} = 2 × 10^{10} sec^{-1} M^{-1} at 25°; B·HOD + D$_2$O → B·DOD + HOD, k_H* = (3.1 ± 0.5) × 10^9 sec^{-1}. Of these rate constants, only k_2 is considerably smaller than expected from data for methylamines, probably due to steric hindrance. Acid dissociation constants are reported for BH$^+$ as a function of BHCl concentration; pK_A° = 10.81 at 25°. H_2O–D_2O solvent isotope effects on K_A are discussed.
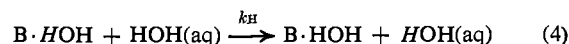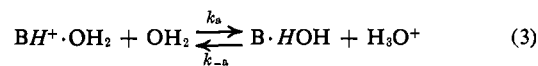
We wish to report nuclear magnetic resonance (nmr) measurements of the rate of proton exchange between triethylammonium ion and water in light and heavy water. The substrates, triethylammonium ion and triethylamine (which are in equilibrium at the given pH), are of interest because the site at which N–H proton transfer takes place in these molecules is under steric compression.[2] Both chemical evidence and space-filling molecular models suggest that the volume that would normally be assigned to the hydrogen atom or the unshared electron pair on nitrogen is invaded by part of an ethyl group.[2]

We find that the following proton transfer reactions of triethylammonium ion (BH$^+$) are kinetically significant in the pH range 5–8: (i) symmetrical proton

exchange (eq 1), and (ii) reaction with hydroxide ion (2a followed rapidly by 2b).

$$\text{B} + \overset{\text{H}}{\text{HO}} + H\text{B}^+ \xrightarrow{k_2} \text{BH}^+ + \overset{\text{H}}{\text{O}H} + \text{B} \qquad (1)$$

$$\text{B}H^+ + \text{OH}^- \xrightarrow{k_{-b}} \text{B} + H\text{OH(aq)} \qquad (2a)$$

$$\text{B} + \text{HOH(aq)} \xrightarrow{k_b} \text{BH}^+ + \text{OH}^- \qquad (2b)$$

At pH <1, acid dissociation produces an amine hydrate (eq 3), which subsequently exchanges its water molecule (eq 4).

$$\text{B}H^+ \cdot \text{OH}_2 + \text{OH}_2 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \text{B} \cdot H\text{OH} + \text{H}_3\text{O}^+ \qquad (3)$$

$$\text{B} \cdot H\text{OH} + \text{HOH(aq)} \xrightarrow{k_H} \text{B} \cdot H\text{OH} + H\text{OH(aq)} \qquad (4)$$

On comparing the new data with previously reported rate constants for similar reactions of ammonia and the

(2) H. C. Brown and S. Sujishi, J. Am. Chem. Soc., 70, 2878 (1948).