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 analogousa ssumption 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]

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(10) A. Strietweiser, 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]

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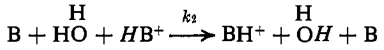
Abstract: Rates of exchange of NH protons of triethylammonium ion (BH^+) with H_2O and D_2O have been measured by nuclear magnetic reasonance techniques in acid solutions over a range of pH. The following reactions and rate constants (corrected to infinite dilution) were found: $BH^+ + OH^-$, $k_{-b} = (1.7 \pm 0.5) \times 10^{10}$ sec^{-1} M^{-1} at 30°; $BH^+ + OH_2 + B$ (symmetrical exchange), $k_2 = (1.82 \pm 0.08) \times 10^8$ sec^{-1} M^{-1} at 30°; $B + H_3O^+$, $k_{-a} = 2 \times 10^{10}$ sec^{-1} M^{-1} at 25°; $B \cdot HOD + D_2O \rightarrow B \cdot DOD + HOD$, $k_H^* = (3.1 \pm 0.5) \times 10^9$ 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).



$$B + \overset{H}{HO} + \mathit{H}B^+ \xrightarrow{k_2} BH^+ + \overset{H}{O\mathit{H}} + B \tag{1}$$

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

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

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

$$B\mathit{H}^+ \cdot OH_2 + OH_2 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} B \cdot \mathit{H}OH + H_3O^+ \tag{3}$$

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

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

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(1) Work supported by the National Science Foundation under Grant GP 3921.

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

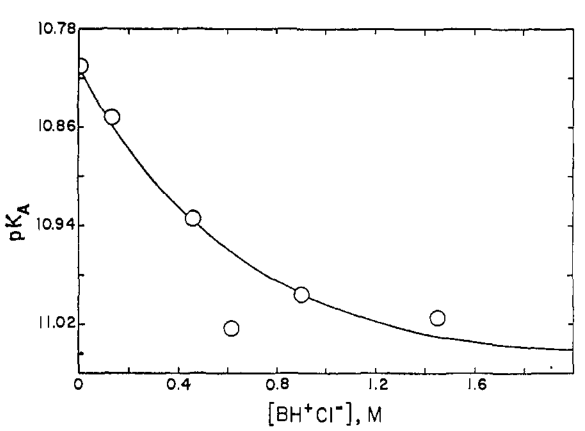

Figure 1. pK_A for triethylammonium ion as a function of triethylammonium chloride concentration, water, 25°.

methylamines,[3a] we find that k_2 is only one-fifth the value that we would have predicted if there were no steric hindrance, while k_{-b}, k_a, and k_{-a} are "normal." k_H also appears to be "normal"; it is smaller than the values reported for the methylamines and smoothly continues the trend for k_H to decrease with increasing number and size of alkyl substituents on nitrogen.[3]

Results

In the pH range 5–8, the rate of proton exchange between triethylammonium ion and water was measured by nmr line-broadening techniques, using water of normal isotopic composition. In the pH range <1, the rate was too slow for those techniques and isotopic exchange between BH^+ and D_2O–DCl was measured instead. Since both measurements extended up to moderately high BH^+ concentrations, we also report K_A for BH^+ as a function of concentration.

K_A Measurements. Acid dissociation constants were measured by a differential potentiometric method,[4] using triethylammonium chloride as the substrate. K_A is defined in eq 5, where the terms in brackets denote molar concentrations. Results are shown in Figure 1.

$$K_A = [B][H^+]/[BH^+] \qquad (5)$$

Extrapolation to infinite dilution yields the thermodynamic constant, $pK_A{}^\circ = 10.81$ at 25°, which may be compared with previously reported $pK_A{}^\circ$ values of 10.75,[5] 10.87,[6] and 10.67[7] at 25°. K_A values at 30° (needed in the kinetic analysis) were obtained from the data in Figure 1 and a previously reported[6] value of 12.24 kcal for $\Delta H_A{}^\circ$.

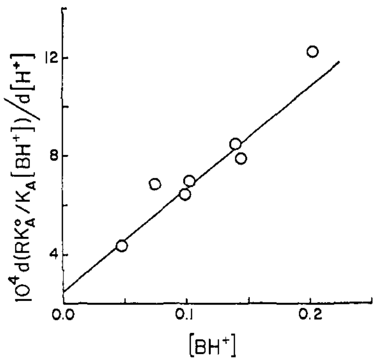

Figure 2. Plot of kinetic data for NH-OH proton exchange according to eq 8: triethylammonium ion in H_2O at 30°.

Proton Exchange, pH 5–8. In the measurements reported in this section, the temperature was 30°, the solvent was H_2O, the solute was 0.05–0.2 *M* triethylammonium chloride, and the pH was adjusted by adding NaOH and measured with a pH meter Under these conditions, the rate law for NH-OH proton exchange throughout the pH range 5–8 was found to be given by eq 6, where *R* denotes the rate of exchange (in moles/l.

$$R = k_{-b}[BH^+][OH^-] + k_2[BH^+][B] \qquad (6)$$

sec). To allow for kinetic salt effects in the calculation of the rate constants, it is convenient to introduce eq 7 in which k^0 (or K^0) denotes the respective rate (or equilibrium) constant at infinite dilution, and y denotes the molar activity coefficient with respect to the infinitely dilute reference state. In (7a) and (7b), the

$$k_{-b} = k_{-b}{}^0\, y_{BH^+}y_{OH^-}/y^{\ddagger}{}_{B\cdot\cdot H\cdot\cdot OH} \approx k_{-b}{}^0 y_{BH^+}y_{OH^-}/y_B \qquad (7a)$$

$$k_2 = k_2{}^0 y_{BH^+}y_B a_{H_2O}/y^{\ddagger} \approx k_2{}^0 \qquad (7b)$$

$$[OH^-] = K_w{}^0/[H^+]y_{H^+}y_{OH^-} \qquad (7c)$$

$$K_A = K_A{}^0 y_{BH^+}/y_B y_{H^+} \qquad (7d)$$

equal sign introduces formal expressions based on Brønsted's rate equation[8]; the approximate expressions that follow try to evaluate $y^{\ddagger}$ for the transition-state complex in terms of measurable activity coefficients for stable model substances. In (7c), $K_w{}^0$ is the autoprotolysis constant of water. On substituting eq 5 and 7 in (6) and rearranging, we obtain (8).

$$\frac{R}{[BH^+]}\frac{K_A{}^0}{K_A} = \frac{k_{-b}{}^0K_w{}^0 + k_2{}^0K_A{}^0[BH^+]}{[H^+]} \qquad (8)$$

Equation 8 was applied as follows: (a) $[H^+]$ was computed from pH and y_H; y_{H^+} was taken to be the same as $y_\pm$ for 0.01 *M* HCl in a KCl solution[9] of the same ionic strength as the reaction mixture. (b) Plots were made of $RK_A{}^0/K_A[BH^+]$ *vs.* $[H^+]^{-1}$ at constant $[BH^+]$. (c) The slopes obtained in (b) were plotted *vs.* $[BH^+]$.

The result is shown in Figure 2, where the straight line is based on a weighted least-squares analysis of the data. According to (8) we identify the intercept as $k_{-b}{}^0K_w{}^0$, and the slope as $k_2{}^0K_A{}^0$. On introducing known values for $K_w{}^0$ and $K_A{}^0$, we finally obtain $k_{-b}{}^0 = (1.7 \pm 0.5) \times 10^{10}$ sec^{-1} M^{-1} at 30° and $k_2{}^0 = (1.82 \pm 0.08) \times 10^8$ sec^{-1} M^{-1} at 30°.

Proton-Deuteron Exchange, pH <1. In the measurements reported in this section, the temperature was 25°, the solvent was D_2O–DCl, and the solute was 0.5–

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[3] (a) For a recent review, see E. Grunwald and M. Cocivera, *Discussions Faraday Soc.*, **39**, 105 (1965). (b) Further analysis of k_H will be presented in a forthcoming paper: E. Grunwald and E. K. Ralph, III, *J. Am. Chem. Soc.*, in press.

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[7] W. S. Fyfe, *J. Chem. Soc.*, 1347 (1955).

[8] J. M. Brønsted, *Z. Physik. Chem.*, 102, 169 (1922).

[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p 575.

1.8 *M* triethylammonium chloride. Exchange was followed by measuring the height, *h*, of the HOD proton nmr line as a function of time under conditions where *h* is proportional to [HOD]. Experimental plots of log $(h - h_t)$ *vs.* time were linear, within the experimental error, with slope k_e. Since the deuterium isotope was present in large excess, the conversion of BH^+ to BD^+ at equilibrium was virtually complete and the rate of the back-reaction, $BD^+ \rightarrow BH^+$, could be neglected. Thus k_e is the pseudo-first-order rate constant for the forward reaction, $BH^+ \rightarrow BD^+$, as in (9), where R^* is the rate of proton–deuteron exchange (in moles/l. sec).

$$k_e = R^*/[BH^+] \qquad (9)$$

Experimental results are summarized in Table I. The high acidity of the reaction mixtures reduces the rate of reactions 1 and 2 to less than 5% of R^*, so that these reactions can be neglected. The dominant mechanism for exchange consists of reactions 3 and 4, and the rate law is given accordingly by (10), where starred symbols are used to denote that the N–*H* compound is in D_2O. As it turned out that $k_H^*/k_{-a}^*[D^+]$

$$k_e = k_a^*k_H^*/(k_{-a}^*[D^+] + k_H^*) \qquad (10)$$

< 0.5 in all experiments, it was convenient to rewrite (10) in the form (11), where $K_A^* = k_a^*/k_{-a}^*$. According

$$k_e = K_A^*k_H^*/[D^+](1 + k_H^*/k_{-a}^*[D^+]) \qquad (11)$$

to (11), at high acidities k_e varies as $[D^+]^{-1}$, with slope equal to $K_A^*k_H^*$; at lower acidities there is negative curvature, which affords the value of k_H^*/k_{-a}^*. However, as is well known, there are substantial deviations from dilute-solution behavior at acid and substrate concentrations of the magnitude we are using (see Table I). We allowed for these deviations as follows: (a) k_H^*/k_{-a}^* is regarded as independent of concentration. This assumption is not crucial since $k_H^*/k_{-a}[D^+] < 0.5$, and it is consistent with previous measurements on trimethylammonium ion in aqueous HCl.[10] (b) The

$$k_H^* = k_H^{*0}\eta^{*0}/\eta^* \qquad (12)$$

medium effect on k_H^* is given by (12), where η^* is the bulk viscosity of the solution and the superscript zero denotes the value of the property at zero solute concentration, as before. Equation 12 has been verified for other amines in H_2O.[11] (c) The medium effect on K_A^* was obtained from (13). This equation assumes that medium effects due to BHCl and HCl are additive

$$\log(K_A^*/K_A^{*0}) = \log(K_A/K_A^0)_{[BHCl]} + \log(K_A/K_A^0)_{[HCl]} \qquad (13)$$

and evaluates the additive terms in H_2O rather than D_2O. The first term is shown as a function of [BHCl] in Figure 1. The second term was evaluated as

$$\log(K_A/K_A^0)_{[HCl]} = -0.32[HCl]$$

on the basis of Arnett and Mach's H_0''' acidity function.[12] For anilines it has been shown that medium effects on K_A due to HCl in H_2O and DCl in D_2O are closely similar.[13]

Table I. Data for Protium–Deuterium Exchange of Triethylammonium Chloride in D_2O–DCl at 25°

$[Et_3NHCl]$	[DCl]	$10^3 \times k_e$	η^*/η^{*0} [a]	K_A^*/K_A^{*0} [b]
1.27	0.349	10.3 ± 1.2	1.21	0.476
1.48	0.463	5.98 ± 0.12	1.28	0.436
1.05	0.431	11.3 ± 1.1	1.16	0.464
0.917	0.437	11.5 ± 0.06	1.13	0.470
0.506	0.466	10.9 ± 1.1	1.07	0.520
1.64	0.546	5.76 ± 0.23	1.33	0.397
1.80	0.798	3.30 ± 0.06	1.42	0.328
1.56	0.807	4.54 ± 0.90	1.32	0.330
1.85	0.965	2.90 ± 0.20	1.45	0.290
1.45	1.35	1.33 ± 0.07	1.33	0.223
1.84	1.37	1.78 ± 0.23	1.43	0.215

[a] The viscosity of the Et_3NHCl–DCl solution in D_2O relative to that of pure D_2O. [b] Computed as described in text; see eq 13.

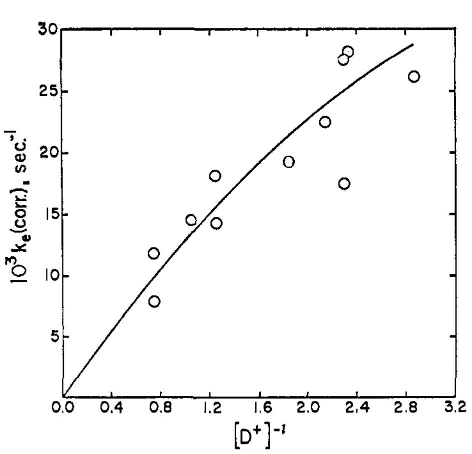

Figure 3. Plot of kinetic data for NH–OD proton exchange according to eq 14 and 15: $(C_2H_5)_3NH^+$ in D_2O–DCl at 25°.

Let us define a parameter k_e(cor) according to (14).

$$k_e(\text{cor}) = k_eK_A^{*0}\eta^*/K_A^*\eta^{*0} \qquad (14)$$

It then follows from (a) to (c) above that (11) can be recast in the form

$$k_e(\text{cor}) = K_A^{*0}k_H^{*0}/[D^+](1 + k_H^*/k_{-a}^*[D^+]) \qquad (15)$$

The plot of k_e(cor) *vs.* $[D^+]^{-1}$ based on the experimental data is shown in Figure 3. $K_A^{*0}k_H^{*0}$ is evaluated from the limiting slope at high acidity as $(1.45 \pm 0.2) \times 10^{-2}$; k_H^*/k_{-a}^* is evaluated from the curvature as 0.14 ± 0.07. The precision measures include our estimate of determinate errors resulting from the treatment of medium effects. During the course of this work we tried various schemes for making the corrections, including making no correction at all. The initial slope, $K_A^{*0}k_H^{*0}$, was always between 0.012 and 0.018. The curvature, and therefore k_H^*/k_{-a}^*, was far less well defined and in one scheme even appeared to be zero.

Evaluation of K_A^{*0} and the Rate Constants According to the theory represented above K_A^{*0} is the "equilibrium constant" for reaction 16 in dilute solution.

$$Et_3NH^+\cdot OD_2 + D_2O \overset{K_A^{*0}}{\rightleftharpoons} Et_3N\cdot HOD + D_3O^+ \qquad (16)$$

We now wish to evaluate K_A^{*0} from K_A^0 (eq 17) and established theories of the H_2O–D_2O solvent isotope

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[10] E. Grunwald, *J. Phys. Chem.*, **67**, 2211 (1963).

[11] M. T. Emerson, E. Grunwald, M. L. Kaplan, and R. A. Kromhout, *J. Am. Chem. Soc.*, **82**, 6307 (1960).

[12] E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964).

[13] E. Högfeldt and J. Bigeleisen, *ibid.*, **82**, 15 (1960).

effect.[14–17] To solve the relevant ratio (18), we introduce

$$\mathrm{Et_3NH^+\cdot OH_2 + H_2O \overset{K_A{}^0}{\rightleftharpoons} Et_3N\cdot HOH + H_3O^+} \qquad (17)$$

the parameter L, defined in (19), which has been evaluated[15] as 11.0 at 25°. The result is (20), with Φ

$$\frac{K_A{}^{*0}}{K_A{}^0} = \frac{[\mathrm{B\cdot HOD}][\mathrm{D_3O^+}][\mathrm{H_2O}][\mathrm{BH^+\cdot OH_2}]}{[\mathrm{B\cdot HOH}][\mathrm{H_3O^+}][\mathrm{D_2O}][\mathrm{BH^+\cdot OD_2}]} \qquad (18)$$

$$L = [\mathrm{H_3O^+}]^2[\mathrm{D_2O}]^3/[\mathrm{D_3O^+}]^2[\mathrm{H_2O}]^3 \qquad (19)$$

defined in (21). Note that Φ is a fractionation factor

$$K_A{}^{*0}/K_A{}^0 = L^{-1/2}\Phi \qquad (20)$$

$$\Phi = \frac{[\mathrm{B\cdot HOD}][\mathrm{D_2O}]^{1/2}[\mathrm{BH^+\cdot OH_2}]}{[\mathrm{B\cdot HOH}][\mathrm{H_2O}]^{1/2}[\mathrm{BH^+\cdot OD_2}]} \qquad (21)$$

for specific water isotopes in different microscopic environments: adjacent to B, adjacent to BH^+, or in bulk solvent. We now wish to show that Φ is approximately unity.

Within the framework of the quoted theories,[14–17] we may assume that hydrogen isotope fractionation factors are independent of the macroscopic solvent medium and, therefore, of the microscopic environment. Moreover, for water isotopes the distribution at isotopic equilibrium is essentially statistical.[15] Thus, when each molecule exists in an aqueous environment, K for reaction 22 has the statistical value of 4.

$$\mathrm{H_2O(aq) + D_2O(aq) \xrightarrow{K} 2HOD(aq)} \qquad (22)$$

On the same basis, when each molecule is adjacent to B, K' for the analogous reaction 23 has the statistical value of unity. Moreover, $[\mathrm{B\cdot HOD}] = [\mathrm{B\cdot DOH}]$

$$\mathrm{B\cdot HOH + B\cdot DOD \xrightarrow{K'} B\cdot HOD + B\cdot DOH} \qquad (23)$$

and, in view of $K' = 1$, both are equal to $[\mathrm{B\cdot HOH}]^{1/2}\cdot[\mathrm{B\cdot DOD}]^{1/2}$. Thus we may rewrite (21) in the form

$$\Phi = \frac{[\mathrm{B\cdot DOD}]^{1/2}[\mathrm{D_2O}]^{1/2}[\mathrm{BH^+\cdot OH_2}]}{[\mathrm{B\cdot HOH}]^{1/2}[\mathrm{H_2O}]^{1/2}[\mathrm{BH^+\cdot OD_2}]} \qquad (24)$$

Each of the three factors in (24) is a fractionation factor involving H_2O and D_2O in a different microscopic environment. Thus, if fractionation factors are indeed independent of the environment (as suggested by the success of the theory[14–17]), $\Phi = 1$.

Applying eq 20, we then find that $K_A{}^{*0} = K_A{}^0L^{-1/2} = 4.7 \times 10^{-12}$. Using this value and results given in the previous section, we obtain $k_H{}^{*0} = (3.1 \pm 0.5) \times 10^9$ sec^{-1} at 25° in D_2O and $k_{-a}{}^{*0} = 2 \times 10^{10}$ sec^{-1} M^{-1} at 25° in D_2O. Both rate constants are of a magnitude appropriate to diffusion-controlled processes in an aqueous medium and should vary approximately inversely with the viscosity, as assumed above (eq 12). Thus, to obtain $k_H{}^0$ and $k_{-a}{}^0$ in H_2O, we multiply the above values by the relative viscosity η_{D_2O}/η_{H_2O} or 1.23 at 25°.

Discussion

Kinetic and thermodynamic constants for proton transfer of ammonia, the methylamines, and triethylamine are compared in Table II. For ammonia and the methylamines, $k_{-b}{}^0$ and $k_{-a}{}^0$ are of the correct magnitude for diffusion-controlled reactions.[18,19] The new values of $k_{-b}{}^0$ and $k_{-a}{}^0$ for triethylamine fit smoothly into this pattern. The fact that they are slightly smaller than those for the substrates of lower molecular weight is plausible in view of the lowering of molecular mobility and "steric factor" for reaction[20] that accompanies the increase in alkyl size. Clearly, whatever steric hindrance exists in triethylamine or its conjugate ion is insufficient to alter the diffusion-controlled mechanism of the respective reactions with hydrogen ion or hydroxide ion.

It is probable that the reaction measured by k_2 involves one water molecule, as stated in eq 1.[3,21] For ammonia and the methylamines, the rate constant k_2 varies monotonically with base strength as measured by K_B, as shown in Table II.[21b] From this monotonic relationship we would expect that a base of the strength of triethylamine reacts with $k_2 \approx 9 \times 10^8$ sec^{-1} M^{-1} at 25°. Since the actual value of k_2 for triethylamine is only 1.8×10^8 sec^{-1} M^{-1} at 25°, there seems to be a (possibly steric) retardation of k_2 by a factor of one-fifth. As a matter of fact, when models of the transition-state complex $\mathrm{Et_3N\cdot H_2O\cdot HNEt_3^+}$ are constructed from space-filling atomic models, it is apparent that there is significant steric hindrance, both in formation and solvation of the transition-state complex.

Table II. Data for Proton Transfer of Ammonia, Alkylamines, and Their Conjugate Acids in Water

Amine (B in eq 1–5)	$10^4K_B{}^0$ [a] (25°)	$10^{-10}\cdot$ $k_{-b}{}^0$ [b] (20 or 30°)	$10^{-10}\cdot$ $k_{-a}{}^0$ [b] (25°)	$10^{-8}\cdot$ $k_2{}^0$ [b] (25 or 30°)
NH_3	0.18	3.4[d]	4.3[e]	0.9[e]
CH_3NH_2	4.1	3.7[d]	. . .	5.3[e]
$(CH_3)_2NH$	6.0	3.1[d]	. . .	9.0[e]
$(CH_3)_3N$	0.64	2.1[d]	3.0[e]	3.4[e]
$(Et)_3N$	6.5[f]	1.7[g]	2.7[c,f]	1.8[g]

[a] $K_B = [BH^+][OH^-]/[B]$; data based on Table I, ref 3. [b] Units: sec^{-1} M^{-1}. [c] Assume that $k_H{}^{*0}/k_H{}^0 = k_{-a}{}^{*0}/k_{-a}{}^0 = \eta^0{}_{H_2O}/\eta^0{}_{D_2O} = 1.23$. [d] Data at 20°; see ref 18. [e] Data at 25° based on Table I, ref 3. [f] Present work, 25°. [g] Present work, 30°.

Experimental Section

Materials. Deuterium chloride was prepared by the addition of dichlorodimethylsilane (Aldrich) to 99.5 mole % D_2O[22] (Matheson Coleman and Bell). H_2O was distilled from KOH in all-glass ap-

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(14) W. E. Nelson and J. A. V. Butler, *J. Chem. Soc.*, 1361 (1936).

(15) E. L. Purlee, *J. Am. Chem. Soc.*, **81**, 263 (1959).

(16) C. G. Swain and R. F. W. Bader, *Tetrahedron*, 10, 182 (1960); C. G. Swain, R. F. W. Bader, and E. R. Thornton, *ibid.*, **10**, 200 (1960). We are indebted to Dr. C. G. Swain for a helpful discussion of this problem.

(17) P. Salomaa, L. L. Schaleger, and F. A. Long, *J. Phys. Chem.*, **68**, 410 (1964).

(18) M. Eigen, W. Kruse, G. Maass, and L. De Maeyer, "Progress in Reaction Kinetics," Vol. 2, G. Porter, Ed., Pergamon Press, Inc., New York, N. Y., 1964, p 308.

(19) M. T. Emerson, E. Grunwald, and R. A. Kromhout, *J. Chem. Phys.*, **33**, 547 (1960); E. Grunwald, *J. Phys. Chem.*, **67**, 2208 (1963).

(20) M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **82**, 5952 (1960).

(21) (a) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **39**, 366 (1963). (b) If OH bond breaking is more important in the transition state than B–H bond breaking ($BH^+\cdot(OH^-)\cdot HB^+$ makes an important contribution) we expect k_2 to increase with basicity, as found. It should be noted also that the data in Table II have not been corrected for statistical factors (for example, $g = 4$ for the unsolvated ammonium ion). The relationship of k_2/g *vs.* K_Bg is *not* monotonic. However, there is some question whether the statistical factor for the solvated ion is the same as g for the unsolvated ion.

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paratus. Triethylammonium chloride (Eastman) was recrystallized three times from absolute ethanol.

pH Measurements. A Beckman research pH meter was used. The pH of the reaction mixtures was measured in a small glass reservoir fused directly to the top of the nmr sample tube. A glass–Ag|AgCl combination electrode (Beckman Model 39030) was used in all measurements.

Proton Exchange in H_2O. The rate of NH-OH proton exchange between triethylammonium ion and water was determined from nmr measurements of exchange broadening of the dominant water line. The exchange broadening was taken as $T_2^{-1} - T_1^{-1}$. T_2 and T_1 were measured by spin-echo techniques and rates were calculated as described previously.[23] The chemical shift between NH and OH protons was found to be 4.32 ppm in moderately dilute aqueous solution at 30°. The rate calculations also required knowledge of J_{NH}, the ^{14}N–H spin–spin coupling constant, and of T^I, the relaxation time of the ^{14}N nucleus in triethylammonium ion. However, the result is not sensitive to these variables and semiquantitative estimates are sufficient. We used the values, $J_{NH} = 55$ Hz and $T^I = 2.5 \times 10^{-3}$ sec, that were obtained for trimethylammonium ion. (Actual measurements were made in methanol; the T^I value obtained in methanol was then corrected for the change in solvent viscosity to yield the value listed above.)

Proton–Deuteron Exchange in D_2O–DCl. Production of HOD in D_2O–DCl after introduction of triethylammonium chloride was measured by repeated scanning of the HOD proton nmr line in quasi-slow passage. A known weight of BHCl salt was introduced quickly into an nmr sample tube containing a known amount of D_2O–DCl at room temperature (25°). The mixture was stirred at once to dissolve the BHCl, and placed in the sample probe of the nmr magnet. Scanning of the HOD line was begun immediately. Since the D_2O initially contained *ca.* 0.5 *M* HOD, the plot of HOD signal height *vs.* time consisted of two distinct regions: (1) an initial, rapid, increase (with time constant T_1) as the HOD protons in the sample attain equilibrium with the magnetic field; (2) a subsequent, slower, increase as the HOD concentration increases due to exchange with BH^+. This second portion was used to evaluate k_e. T_1 for the HOD protons in representative reaction mixtures was found to be 5–7 sec.

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Nuclear Magnetic Resonance Spectroscopy. Benzene-^{13}C[1a]

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Abstract: The high-resolution ^{13}C spectrum of benzene has been analyzed. The long-range carbon–proton coupling constants, $J_{CCH} = +1.0$ Hz, $J_{CCCH} = +7.4$ Hz, and $J_{CCCCH} = -1.1$ Hz, have been related to proton–proton coupling constants in selected model compounds.

The practical use of ^{13}C nuclear magnetic resonance has been hindered by low natural abundance of this nucleus (1.1%), low inherent sensitivity to nmr detection (1.6% relative to protons at constant field), and long relaxation times. Various methods have been used to overcome these difficulties including the use of enriched materials,[2] observation of the spectrum under rapid-passage conditions in either the dispersion or absorption mode[3] (which sacrifices resolution for better signal-to-noise ratios), complete proton decoupling[4] which enhances the signal-to-noise ratios at the expence of coupling information, internuclear double resonance,[5] and flow techniques.[6] The development of field-frequency stabilization techniques[7] has made time-averaging[8] techniques both possible and practical.

Previously reported ^{13}C spectra of benzene were obtained either under rapid-passage conditions[3] and showed only a broad doublet due to the one-bond C–H coupling, or with proton decoupling[4] and gave only a single line. Bernstein[9] has recently studied the proton spectrum of 2,3,4,5-tetradeuterio-1,2-$^{13}C_2$-benzene and has determined the four coupling constants in this AA′XX′ system. The especially interesting result is the two-bond coupling J_{CCH} which was found to be +1.0 Hz. The one-bond coupling J_{CH} has been determined by several workers and is ~159 Hz.[3,10]

Experimental Section

The benzene sample used in this study contained 10% carbon disulfide and 10% tetramethylsilane (v/v). The sample was degassed and sealed under nitrogen in a 10-mm, precision-bore sample tube.[11]

The deuteriobenzenes were obtained from Merck Sharpe and Dohme of Canada.

The spectrometer used in this work was a special instrument developed for us by F. Nelson and V. Burger of Varian Associates and features a digital frequency sweep for ^{13}C at 15 MHz provided by a Hewlett-Packard 5110-5100A frequency synthesizer controlled by a Varian Associates V-4355 digital programmer. The probe was double tuned to 15 and 60 MHz with the 60 MHz for field-frequency stabilization being derived from the stable driver frequency of the synthesizer. The field was locked by conventional techniques to the proton resonances in the sample, in the present case to tetramethylsilane. Spectra were accumulated on a Varian C-1024 computer of average transients. A block diagram of the spectrometer system is shown in Figure 1.

Comparison spectra for the seven-spin system of ^{13}C and six protons were calculated using the Swalen–Reilly NMRIT[12] program

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