maintained at room temperature for 11 days. Another sample of this solution heated at 100° in a sealed tube for 11 days gave an iodine analysis of 6.03×10^{-3} M. These results suggested that the unknown was primarily isobutylene dibromide containing a small amount (as indicated by its reaction with iodide ion at room temperature)[13] of isobutylene chloroiodide.

The unknown was characterized as an isobutylene dihalide through its conversion to isobutyraldehyde on hydrolysis.[14] A 0.6-g. sample was heated at 100° with 10 cc. of water in a sealed tube for 24 hours. By this time the lower dihalide phase had disappeared and an oily phase had formed on the surface of the water. The water phase gave a positive Fehling test and provided a methone derivative, according to standard procedures,[15] of m.p. 152–154°. This material showed no depression in a mixed melting point determination with an authentic sample of isobutyraldehyde dimethone.

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[13] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 836 (1948).

[14] W. L. Evers, H. S. Rothrock, H. M. Woodburn, E. E. Stahly and F. C. Whitmore, *ibid.*, **55**, 1136 (1933).

[15] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 172.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Rates of Ionization of Pseudo Acids. VI.[1,2] Catalytic Behavior of Alkylamines in the Ionization of Nitroethane

BY RALPH G. PEARSON AND FORREST V. WILLIAMS

RECEIVED AUGUST 26, 1953

The effect of structure of the amine on the velocity of the reaction $C_2H_5NO_2 + B \rightarrow C_2H_4NO_2^- + BH^+$ has been studied. When the rate constants and corresponding equilibrium constants of the various amines are compared, it is found that successive replacement of the hydrogen atoms in ammonia by alkyl groups leads to an *increase* in the relative rates. A comparison of quinuclidine and piperidine with triethylamine and diethylamine shows that tying back the alkyl groups to prevent shielding of the nitrogen lone pair causes a further increase in rate. These results are interpreted as meaning that there is some slowing down of the rate of proton removal by alkylamines due to F-strain. However, this is more than compensated for by another factor which is rate increasing. This is the inductive effect which increases the electron density at the nitrogen atom. The usual ionization constants in water, which show tertiary amines to be weaker bases than secondary amines are not a true measure of this electron density. The ionization constants are reduced by decreased solvation energy in the 'onium ion whenever an N–H group is replaced by an N-alkyl. The effect of B-strain appears to be unimportant.

In studying the influence of structure of amine catalysts on the rates of two reactions of the type $HA + B \rightarrow BH^+ + A^-$ it has been noticed that increasing alkyl substitution in ammonia and in aniline increases the catalytic efficiency above what would be expected on the basis of a Brönsted relationship between rates and equilibria.[3] Thus trimethylamine reacts with nitroethane twice as fast as methylamine, though it is only one-tenth as strong as a base. This accelerating effect was ascribed to the circumstance that the ordinary basic ionization constant of an amine in water is not a true measure of the electron availability at the nitrogen atom.[3,4] In particular solvation energies, which are important in stabilizing the 'onium ion, would be progressively less as hydrogen atoms on the nitrogen are replaced by alkyl groups. Thus trimethylamine is not as extensively ionized as it should be because the trimethylammonium ion is not strongly solvated.

However, Brown[5] has blamed the low ionization constant of trimethylamine, and other trialkylamines, on B-strain in the 'onium ion. That is, the methyl groups are forced back on the addition of a fourth group to the nitrogen atom till they interfere with each other and cause steric strain. This effect, unlike frontal or F-strain,[5] is independent of the steric requirements of the incoming group so that even a proton could cause B-strain. Pitzer and Spitzer[6] have argued that in the case of the trimethylamine complex with trimethylboron, B-strain is too small to be significant whereas F-strain is important.

The present work was done to determine the relative importance of solvation and steric effects in the reaction rates of a series of aliphatic amines with nitroethane in water at 0°

$$B + C_2H_5NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} BH^+ + C_2H_4NO_2^- \qquad (1)$$

By sufficient variation of the structure of B it was hoped to get enough information to sort out the several factors affecting the rates.

Experimental

Materials.—The more volatile amines were purified by crystallization of their chloride salts and fractional distillation of an aqueous solution made alkaline with sodium hydroxide. They were collected as aqueous solutions and titrated to determine concentrations. Quinuclidine was obtained as the picrate salt through the kindness of Dr. Stanley Wawzonek and distilled as above.

The nitroethane, piperidine and *n*-hexylamine were fractionated through a 10-plate column and small middle cuts taken. Diisopropylamine, a gift from the Carbon and Carbide Chemical Corp., and *t*-butylamine, a gift from the Rohm and Haas Co., were treated in the same manner.

Reaction 1 goes essentially to completion for the amines used in this study. It is complicated by the simultaneous reaction of nitroethane with hydroxide ion

$$OH^- + C_2H_5NO_2 \xrightarrow{k_3} H_2O + C_2H_4NO_2 \qquad (2)$$

However, k_3 is known and its effect can be corrected for.

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[1] For previous papers see R. G. Pearson and F. V. Williams, THIS JOURNAL, **75**, 3073 (1953).

[2] Presented at the American Chemical Society National Meeting, March, 1953, San Francisco.

[3] (a) R. G. Pearson, THIS JOURNAL, **70**, 204 (1948); (b) R. P. Bell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1286 (1949).

[4] A. F. Trotman-Dickenson, *ibid.*, 1293 (1949).

[5] H. C. Brown, M. D. Taylor, M. Gerstein and H. Bartholomay, THIS JOURNAL, **66**, 431, 435 (1944).

[6] K. S. Pitzer and R. Spitzer, *ibid.*, **70**, 1261 (1948).

The integrated rate equation becomes, for equal concentrations of base and nitroethane[3a]

$$t = \frac{k_3K_b}{(ak_1 + k_3K_b)^2} \ln \frac{(a - x)}{(k_1x + k_3K_b)} + \frac{1}{(ak_1 + k_3K_b)}\,\frac{a}{(a - x)} + C \quad (3)$$

where K_b is the ionization constant of the amine, a is the initial concentration of amine and nitroethane, x the concentration reacted and C a constant of integration.

The kinetics can be conveniently followed by measuring the change in electrical conductivity as reaction proceeds. The apparatus and procedure previously described[3a] were used. One correction was made to equation 11 of reference 3a in that R_0 was set equal to the measured resistance of a solution containing the amine only, at the appropriate concentration, times the factor $(aK_b)^{1/2}$. This is more accurate than the previous method. Values of the rate constant, k_1, calculated by the older procedure are 1–2% high.

It was necessary to measure the ionization constants of the amines used since the values at 0° were generally unknown. A Beckman model G pH meter was used to measure the pH of a solution half neutralized with hydrochloric acid. The pH was set equal to the pK_a and pK_b found from the ionization constant of water at 0°.

The results obtained are shown in Table I. Concentrations in the kinetic runs were equal and in the range 0.01 to 0.03 M. Runs were made in triplicate, at least, for each reactant, except n-butylamine and quinuclidine where only two runs were made. No trends with concentration were noted.

Discussion

In Fig. 1 we have plotted log k_1 against log K_b for the amines studied in this work and also ammonia and the methylamines previously studied.[3a] A straight line with a slope of 0.65 has been drawn through the cluster of points representing the primary amines. This slope was selected because it is the one found experimentally in the ionization of nitroethane catalyzed by substituted pyridines and quinolines,[1] and catalyzed by carboxylate acid anions.[7] The position of the line passing through the primary amines was selected arbitrarily since an extrapolation of the pyridine-carboxylate ion data actually comes closer to the secondary amine points. However, such a long extrapolation is not very safe and it is more convenient to use the primary amines since they are more numerous. It makes no difference except that the primary amines are taken as standards and deviations from the line are discussed in terms of differences between the other amines and the primary ones.

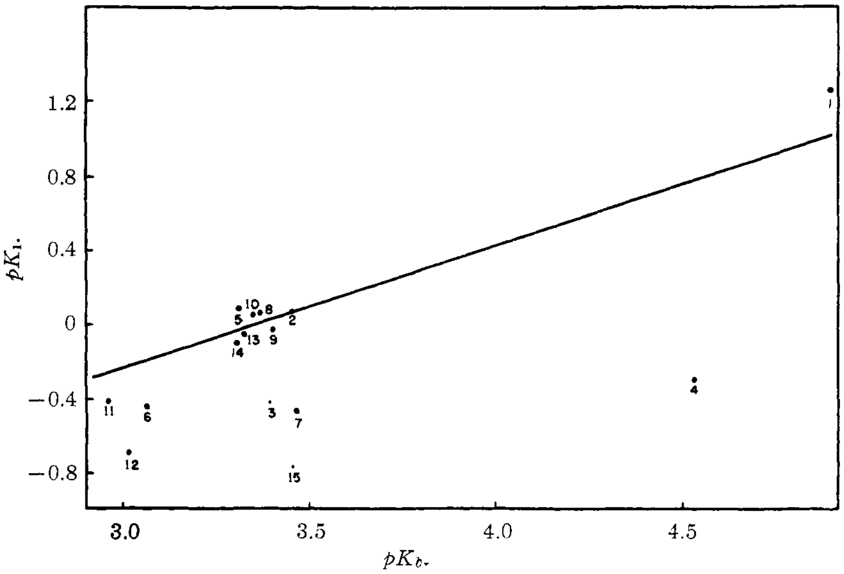

Fig. 1.—Compounds numbered as in Table I.

One might also expect that a slope of 0.65 valid for bases of $K_b \simeq 10^{-9}$ might be reduced somewhat for bases with $K_b \simeq 10^{-4}$. This is because the slope is the value of the coefficient β in the Brönsted equation $k_1 = GK_b{}^{\beta}$. As the strength of the catalyzing base increases β should get smaller.[8] However, ranges of base strength much greater than five powers of ten have frequently been covered by a single value of β.[8]

TABLE I

	Amine	pK_b at 0°	k_1, l./mole min.	$-\Delta pk_1$
1	Ammonia	4.90	0.057[a]	−0.23
2	Methylamine	3.45	0.85[a]	0.0
3	Dimethylamine	3.39	2.60[a]	+0.39
4	Trimethylamine	4.53	2.05[a]	+1.08
5	Ethylamine	3.31	0.85 ± 0.02[b]	−0.06
6	Diethylamine	3.06	2.78 ± .08	+ .25
7	Triethylamine	3.46	3.12 ± .24	+ .55
8	n-Propylamine	3.36	0.89 ± .13	− .04
9	Isopropylamine	3.40	1.14 ± .07	+ .06
10	n-Butylamine	3.35	1.13 ± .15	− .05
11	Di-i-propylamine	2.96	2.60 ± .07	+ .17
12	Piperidine	3.01	4.97 ± .03	+ .48
13	n-Hexylamine	3.32	1.13 ± .04	+ .03
14	t-Butylamine	3.30	1.13 ± .04	+ .07
15	Quinuclidine	3.45	5.91 ± .26	+ .84

[a] From reference 3a. [b] Average deviations.

It is seen from Fig. 1 that the alkylated amines show a positive rate deviation from the linear free energy relationship expressed by the straight line. The effect is greater for tertiary amines than for secondary ones. Ammonia, on the other hand, has a negative rate deviation, reacting more slowly than it should relative to the primary amines. Piperidine and quinuclidine are of interest since they can be compared to diethylamine and triethylamine which are their analogs with the alkyl groups capable of free rotation. Both the cyclic amines show a greater positive rate deviation than their open chain analogs. Diisopropylamine has a smaller deviation than the other secondary amines. Table I shows the Δpk_1 for each amine as estimated from Fig. 1.

The fact that triethylamine has a smaller deviation than quinuclidine and trimethylamine, and diethylamine less than piperidine and dimethylamine, may be interpreted as meaning that there is some F-strain present in the transition state

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[7] R. Junell, Thesis, Uppsala University, 1935.

[8] R. P. Bell, "Acid–Base Catalysis," Oxford University Press, 1941, Chapter VIII.

with nitroethane. This agrees with the prediction that the steric requirements of the preferred configurations of diethylamine and triethylamine are about the same as 2,6-lutidine[9] since the latter compound shows a similar retardation of rate in reacting with nitroethane.[1] Also for diisopropylamine the reduced rate may be blamed on F-strain since molecular models show the nitrogen atom to be rather inaccessible in this compound. There is no evidence and little reason to expect F-strain in any amine with lower steric requirements than diethylamine (compare reference 1).

After allowing for the slowing down caused by F-strain, it is obvious that all the observed deviations can be accounted for on the basis of the solvation theory previously proposed.[3,4] The important change is evidently the replacing of an N–H group by an N-alkyl, with variations in the nature of the alkyl group having little effect. Thus a methyl is just as effective as a *t*-butyl or *n*-hexyl group.

As Brönsted originally showed and Bell and his co-workers confirmed,[10] deviations such as are shown in Fig. 1 can be completely removed if ionization constants for the amines measured in rather non-solvating media such as anisole, chlorobenzene and *m*-cresol are used. This is true for rates determined both in water and in anisole.

The ionization constants of the alkylamines used in our work are not known in such media, but recently[10c] the *n*-butylamines have been studied in chlorobenzene. For the observable equilibrium (using 2,6-dinitrophenol as a reference acid)

$$\mathrm{B} + \mathrm{HA} \rightleftarrows \mathrm{BH}^+, \mathrm{A}^- \text{ (ion-pair)} \tag{4}$$

the constants measured for mono-, di- and tri-*n*-butylamine were 1600, 17000 and 69000, respectively, at 25°. Thus a regular increase in base strength with alkyl substitution is found. This is in contrast to the same amines in water solution where pK_b's of 3.39, 2.69 and 3.11 are found.[11] The former order of base strengths agrees with the rates found in this work, while the order in water does not.

As further evidence for the influence of the solvent on observed ionization constants of bases, some results with the methylanilines can be cited. The ionization constants in several solvents are given in Table II. Changes of 2000 in relative basicity are observed in going from ethanol to *m*-cresol solvent. Thus aniline is the strongest base in ethanol because the anilinium ion is strongly solvated by the highly negative oxygen atom of the alcohol.[12] In *m*-cresol, where a weakly negative oxygen atom only is available, or in chlorobenzene, inductive effects are dominant and dimethylaniline is the strongest base.

TABLE II

pK_b OF ANILINES IN VARIOUS SOLVENTS

	Water[a]	Ethanol[a]	*m*-Cresol[b]	Chlorobenzene[c]
Aniline	9.36	13.8	8.10	−1.0
N-Methylaniline	9.15	14.6	7.26	−1.8
N,N-Dimethylaniline	8.99	15.1	6.18	−2.8

[a] B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 559, 565 (1953). [b] J. N. Brönsted, A. Delbanco and A. Tovborg-Jensen, *ibid.*, **A169**, 361 (1934). [c] R. P. Bell and J. W. Bayles, ref. 10c. Reference acid bromphenol blue.

If it were not for these observed variations with solvent, the rate data in Fig. 1 could equally well be explained on the basis of B-strain. It is only necessary to postulate that the transition state in the rate process has less B-strain than the final product, a not unreasonable situation. However, since B-strain should be independent of the solvent, the observed changes with solvent of the ionization constants are difficult to explain by this hypothesis.

Another indication that B-strain is relatively small in the simple alkylamines is the equality of base strengths of quinuclidine and triethylamine and of piperidine and diethylamine. Such a result would be expected on the basis of inductive and solvation effects but is unexpected in the B-strain theory. Thus it has been shown[13] that in the oxygen series, water, alcohols, ethers, B-strain does seem important. Here the cyclic ether, dioxane, is at least five times stronger as a base than *n*-butyl ether. Also it should be mentioned that, unlike the oxygen series, there is no evidence from bond angle data that B-strain exists in the simple amines.

Brown has used as an argument for the B-strain hypothesis the fact that the phosphine bases show a regular increase in base strength with methyl substitution.[14] This holds true in the gas phase as well as in solution. However, this result could be equally well explained by the solvation theory. Thus the gas phase order is the natural one because of inductive effects. The order in solution is not changed because solvation effects are not nearly so great in changing a non-polar P–H group to a non-polar P–CH_3 compared to the corresponding nitrogen case.

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(9) H. C. Brown and M. D. Taylor, THIS JOURNAL, **69**, 1332 (1947).

(10) (a) J. N. Brönsted, A. L. Nicholson and A. Delbanco, *Z. physik. Chem.*, **A169**, 379 (1934); (b) Bell and Trotman-Dickenson, ref. 3b; (c) R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952).

(11) (a) N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932); (b) P. Damsgaard-Sorensen and A. Unmack, *Z. physik. Chem.*, **A172**, 389 (1935). The value for pK_b of tri-*n*-butylamine given by the latter authors appears to be correct, while that given by Hall and Sprinkle, 4.07, while often quoted, appears to be in error.

(12) For similar results for ammonia and the methylamines see Gutbezahl and Grunwald, footnote *a* in Table II.

(13) J. Hine and M. Hine, THIS JOURNAL, **74**, 5266 (1952).

(14) H. C. Brown, *ibid.*, **67**, 503 (1945); Reaction Mechanism Conference, Northwestern University, August, 1950.