However, Denison and Ramsey in their original paper report good agreement in ethylene chloride and ethylidene chloride.

Gilkerson has derived an equation for K^{-1} in terms of free volume. However, it cannot be used to calculate K from experimental data or present theory because it contains a quantity E_s, the difference in solvation energy between the ion-pair and the free ions. His equation is

$$K^{-1} = \left(\frac{2\pi\mu kT}{h^2}\right)^{-3/2} (gv\sigma)^{-1} \exp(E_s/RT)\exp(\epsilon^2/aDkT) \quad (13)$$

The terms are defined in the original paper. If we assume $a_G = a_{DR}$, it is apparent that the last exponential term is just $K_{DR}{}^{-1}$.

The entropy change predicted by this theory can be obtained by differentiation of (13) with respect to T. If this is done, assuming g, σ, v, and a temperature independent we obtain

$$\Delta S^0{}_G/R = [\ln(2\pi\mu kT/h^2)^{3/2}(gv\sigma) + 3/2] + (1/R)(dE_s/dT) + \frac{\epsilon^2}{ak}\left(\frac{d(1/D)}{dT}\right) \quad (14)$$

This can be compared with the entropy obtained from the Bjerrum and Denison–Ramsey theories. For the former we obtain from equation 7

$$\Delta S^0{}_B/R = \ln(4\pi Na^3/1000) + \frac{\epsilon^2}{ak}\left(\frac{d(1/D)}{dT}\right) \quad (15)$$

while for the latter

$$\Delta S^0{}_{DR}/R = \frac{\epsilon^2}{ak}\left(\frac{d(1/D)}{dT}\right) \quad (16)$$

A comparison of (14), (15) and (16) shows why the entropy obtained from the D–R theory is so bad. Even the first term of (15) amounts to 9 e.u. for large ions. A comparison with (14) is difficult because at the present state of the theory E_s is an adjustable parameter.

One further point needs to be made. The parameter a appears in all three theories, yet methods used for the calculation of a from experimental data yield a different a depending on which theory is used. Arguments used to justify acceptance of an a value (and implicitly of the theory on which it is based) usually have rested on (1) the "reasonableness" of the value and (2) its constancy for a given salt in several solvents. However, if theories are to correspond to events in a real physical system, it would be desirable that the meaning of a be less ambiguous. One way of doing this would be to accept some measurement of dipole moment as yielding a. The dipole moment of Bu_4NPi in benzene[24] is 3.74 Å. The Bjerrum a is 1 Å. and the D–R a 2 Å. larger, whereas Gilkerson's a is 1 Å. smaller. Dipole measurements of the salt in the gas phase would certainly be of interest.

Acknowledgment.—We wish to thank Professor R. M. Fuoss for some very helpful suggestions.

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[24] (a) J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936); (b) G. S. Hooper and C. A. Kraus, THIS JOURNAL, **56**, 2265 (1934).

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Acid–Base Equilibrium Constants for 2,4-Dinitrophenol and Some Aliphatic Amines in Non-aqueous Solvents

BY R. G. PEARSON AND D. C. VOGELSONG[1a,b]

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Equilibrium constants for ion-pair formation determined spectrophotometrically for 2,4-dinitrophenol and some primary, secondary and tertiary amines show that the solvent has a marked effect on the order of basicity. Tertiary amines are the strongest bases in chloroform, chlorobenzene and ethylene dichloride. Secondary amines are the strongest bases in *n*-heptane, benzene and dioxane, while primary amines are the strongest bases of the three types in ethyl acetate. The importance of specific solvation of the acidic protons of an ammonium ion is shown by the effect of small amounts of added substances. It is estimated that each replacement of H by CH_3 in $NH_4{}^+$ leads to a loss of 8 kcal. in the heat of hydration.

Consideration of inductive effects alone would predict that the base strength of aliphatic amines should increase in the order primary, secondary, tertiary, the tertiary being the strongest base. However, it is well known that the base strength of amines, as observed in water, does not follow this order. Trimethylamine is the weakest base in the methylamine series.[2] Diethylamine is a stronger base than triethylamine and, in general, secondary amines are the strongest bases.

To account for the orders observed, Brown, Bartholomay and Taylor[3] have advanced the theory of B- or back strain. The theory involves the assumption that the bond angles in the free amine are somewhat greater than the normal tetrahedral value. In order to demonstrate basicity a fourth group must be introduced into the vacant position on the nitrogen atom, thereby forcing the molecule into a tetrahedral configuration. The methyl, or other alkyl groups in tertiary amines, are thus crowded toward each other setting up a strain which reduces the stability of the addition compound. Hence, even a proton as a reference acid can cause B-strain.

Others[4–6] have attributed the tertiary amine weakness, as found in water, to solvation effects. The argument here is that the solvation or hydration energy of the ammonium ion decreases with in-

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[1] (a) Taken in part from a dissertation submitted by D. C. Vogelsong to the graduate school of Northwestern University in partial fulfillment of the requirements for the Ph.D. degree, August, 1956; (b) predoctoral fellow, E. I. du Pont de Nemours and Co., 1955–1956.

[2] N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

[3] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *ibid.*, **66**, 435 (1944).

[4] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941).

[5] R. G. Pearson, THIS JOURNAL, **70**, 204 (1948).

[6] A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

creasing alkyl substitution, while the solvation energy of the free amines remains fairly constant. This would have an adverse effect on the equilibrium

$$B + HA = BH^+ + A^- \qquad (1)$$

where HA is a reference acid and B an amine, such that the tertiary amine would show the smallest increase in equilibrium constant for (1), while ammonia would show the largest.

The solvation of the ammonium ion is considered to take place in two ways. First, the acidic protons of the ammonium ion are specifically solvated by electron rich areas of the solvent molecules in a manner analogous to an acid–base type reaction. This effect would depend upon the electron donating properties of the solvent. Secondly, there is the more conventional solvation of an ion by the polarization of the solvent, depending upon the dielectric constant of the solvent. According to Altshuller's[7] estimate, the heat of solvation of the ammonium ion consists of 10 kcal./mole due to the first mechanism and 69 kcal./mole due to the second. That is to say, the heat of hydration is 10 kcal. greater than for an ion of the same size, such as Rb^+, which cannot form hydrogen bonds.

To assess the importance of solvation and steric effects it would be desirable to have the equilibrium constants for the reaction

$$B(g) + H^+(g) = BH^+(g) \qquad (2)$$

the energy of which is conveniently called the proton affinity. This quantity has been calculated for ammonia,[7] but not for the alkyl amines, the missing data being the thermodynamic quantities for the formation of the alkyl ammonium ions in the gas phase.

In order to throw some light on the magnitude of solvation effects, the present investigation involves the measurement of equilibrium constants for several amines in some non-aqueous solvents using 2,4-dinitrophenol as the reference acid.

Experimental

Chloroform and Ethylene Dichloride.—The day before use both of these solvents were washed several times with concentrated sulfuric acid to remove alcohol added as an oxidation inhibitor. They were then washed with water until free of acid, and dried over calcium chloride and Drierite under an atmosphere of nitrogen. Immediately before use these solvents were fractionated through an 80 cm. packed column, the first and last 100 ml. of about 800 ml. total being discarded, the remaining portions distilling within a 0.2° region.

Benzene.—Thiophene-free benzene was refluxed over sodium for several hours, then fractionated through a packed column, the first portion being discarded.

Chlorobenzene and *n*-Heptane.—These solvents were dried over and distilled from fresh phosphorus pentoxide.

Dioxane.—Carbide and Carbon commercial dioxane was refluxed over sodium for several hours, then distilled. The distillate was again refluxed over sodium for another 24 hours or until no further reaction appeared to take place. The dioxane was then fractionated through a packed column, the first 100 ml. of 800 ml. being discarded.

Ethyl Acetate.—U. S. Industrial 99% pure ethyl acetate was washed with aqueous potassium carbonate, then with water until the wash water was no longer basic to phenolphthalein. The ester was then dried over activated alumina and fractionated from phosphorus pentoxide.

2,4-Dinitrophenol.—Eastman Kodak material was recrystallized several times from water acidified with dilute hydrochloric acid, and finally from carbon tetrachloride; m.p. 113°.

Methylamine, Dimethylamine, Trimethylamine and Ethylamine.—The first three amines were liberated from C.P. hydrochlorides by concentrated sodium hydroxide solution. The hydrochlorides were purified by the procedure of Everett and Wynne-Jones.[4] The latter amine was liberated from its 33% aqueous solution by alkali. The gaseous amines were then passed through two 12-inch drying towers packed with potassium carbonate and potassium hydroxide, and bubbled into the appropriate solvent. Concentrations were determined by adding small aliquots to excess 0.1 *N* HCl and then titrating the excess HCl with standard 0.1 *N* NaOH to an end-point determined by a mixed indicator which changed color at a *p*H of 4.3.

Diethylamine, Triethylamine, *n*-Butylamine, Di-*n*-butylamine, Tri-*n*-butylamine and *n*-Hexylamine.—These amines were dried over and distilled from fresh potassium hydroxide immediately before use. Small, constant boiling center cuts were taken. Concentrations were determined by weight.

Tetraethylammonium 2,4-Dinitrophenolate.—Silver oxide was added to a solution of tetraethylammonium iodide in methyl alcohol. After standing several hours with shaking at intervals, the silver iodide was filtered. To the filtrate was added an alcoholic solution of 2,4-dinitrophenol. The volume of the resulting solution was reduced on a steambath until the tetraethylammonium 2,4-dinitrophenolate could be crystallized in an ice-bath. Recrystallization from methyl alcohol produced a yellow salt which melted at 111.5°.

Spectra of Acid and Ion-pairs.—In order to determine an appropriate wave length for measuring the equilibrium constants, spectra of 2,4-dinitrophenol in water were taken in both 0.1 *M* HCl and 0.1 *M* NaOH solutions by means of a Cary Model 11, Recording Spectrophotometer. Figure 1 reveals that the anion of 2,4-dinitrophenol has two absorption peaks, one at about 400 mμ, the other at 360 mμ. The free acid does not appear to absorb at 400 mμ in the concentration range used. The isosbestic point occurs at 325 mμ.

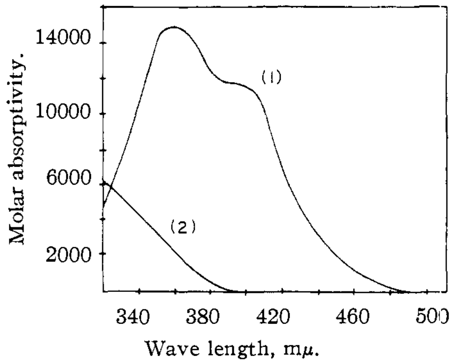

Fig. 1.—Spectra of 2,4-dinitrophenol in water at 25°: (1) 0.1 *N* NaOH present; (2) 0.1 *N* HCl present.

Figures 2 and 3 show spectra which are typical of the reaction products, assumed to be amine-2,4-dinitrophenolate ion-pairs, found in the solvents used in this investigation. Figure 3 shows that both peaks in the spectrum of the tetraethylammonium 2,4-dinitrophenolate ion-pair in chloroform are shifted to somewhat higher wave lengths. This is probably the result of not having a proton coördinated to the anion.

Procedure for Obtaining Equilibrium Constants.—For each determination enough 2,4-dinitrophenol was weighed into a volumetric flask to make a solution of about 0.0005 *M*. An amine stock solution of about 0.002 *M* also was made up in this same way, or by the other procedure described under the experimental section for the gaseous amines. After sufficient solvent had been added, these stock solutions were placed in a 25.0° constant temperature bath for 15 minutes. Aliquots of both stock solutions were then mixed in 25-ml. volumetric flasks and diluted so that the initial concentration of acid and amine were known. In general, the initial acid concentration (about 0.0001 *M*) remained constant while the amine concentrations were

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(7) A. Altshuller, THIS JOURNAL, **77**, 3480 (1955).

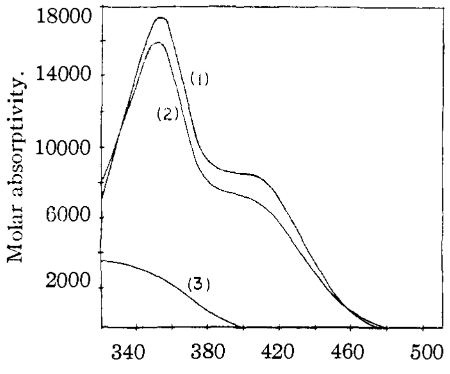

Fig. 2.—Spectra of 2,4-dinitrophenol in benzene at 25°: (1) excess triethylamine added; (2) excess diethylamine added; (3) no base added.

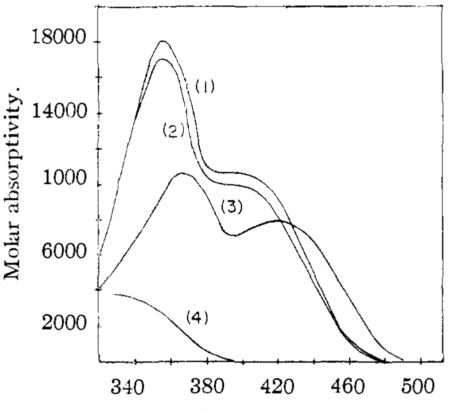

Fig. 3.—Spectra of 2,4-dinitrophenol in chloroform at 25°: (1) excess triethylamine added; (2) excess diethylamine added; (3) as tetraethylammonium salt; (4) no base added.

varied. These new solutions were placed in the water-bath for another 15 minutes, after which the absorbancies were measured at 400 mμ by means of a Beckman Quartz Spectrophotometer. Water at 25° was circulated through the spectrophotometer during all readings.

Method Used for Obtaining Equilibrium Constants.—All equilibrium constants were calculated assuming the reaction to be

$$\text{Acid} + \text{base} = \text{ion-pair} \qquad (3)$$

and that Beer's law is valid over the concentrations used. Plots of absorbancy^{-1} *vs.* base concentration^{-1} usually yielded straight lines from which the equilibrium constants readily could be obtained. The validity of plotting these reciprocal values is shown as

Let (C) = initial concn. of acid
(X) = concn. of ion-pair = A/E
A = absorbancy of solutions
E = molar absorptivity of ion-pair
(B) = base concn. = initial base concn. minus (X)

$$K = \frac{(\mathrm{BH}^+, \mathrm{A}^-)}{(\mathrm{HA})\,(\mathrm{B})} = \frac{(\mathrm{X})}{(\mathrm{C} - \mathrm{X})\,(\mathrm{B})} \qquad (4)$$

Rearranging and replacing X by A/E gives

$$1/A = 1/(B)KE(C) + 1/E(C) \qquad (5)$$

where E, C and K are constants for a given determination. (B) was obtained by assuming an initial value for E and plotting $1/A$ *versus* 1/(B). Extrapolation to the intercept gave a new value of E and the process was repeated until linearity was obtained. The equilibrium constants were obtained from the final plots. In a few cases equilibrium constants were also calculated from absorbancies measured at 360 mμ. These values agreed quite well with those obtained at 400 mμ.

Determination of Partition Coefficients.—Solutions of the amines dissolved in water were shaken with the appropriate organic solvent for two hours, in a water-bath at 25°, by means of an automatic Burrell shaker. The two layers were then separated and the concentration in each layer determined by titration of aliquots with standard 0.1 N HCl. At least four different concentrations of base were used. The amines in some cases were initially dissolved in the organic layer, the results being the same as with the former procedure. The results are summarized in Table II.

Results

Straight lines were obtained from plots of reciprocal absorbancy *versus* reciprocal amine concentration as expected from equation 5 for both secondary and tertiary amines. Figure 4 is representative of the lines obtained. In the case of primary amines, however, there was considerable deviation with the exception of results in the solvents dioxane and ethyl acetate. This deviation from linearity probably was due to the formation of higher aggregates and solvation by the amine itself. Unfortunately the weak basic strength of the primary amines in solvents other than the two mentioned requires a large excess of amine to produce any visible color reaction with 10^{-4} M 2,4-dinitrophenol. Going to higher initial acid concentration also was tried, but this too led to higher values of the equilibrium constants. Likewise, precipitation of the salts of ethyl- and methylamine in these solvents indicated higher aggregates. Thus the values for the primary amines are the values obtained from measurements at high dilution using the extinction coefficients of the secondary and tertiary amine ion-pairs. Molar absorptivities were all of the order of 10^4 and equal to within 10% for secondary and tertiary amines. The equilibrium constants found are summarized in Table I.

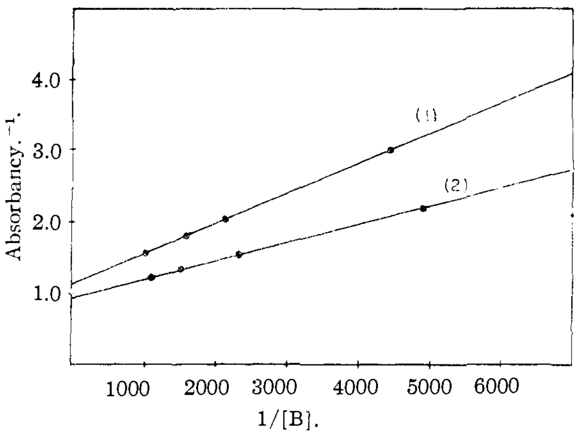

Fig. 4.—2,4-Dinitrophenol in chlorobenzene at 25°; plot of reciprocal absorbancy against reciprocal concentration: (1) B = di-n-butylamine; (2) B = tri-n-butylamine.

Discussion of Results

Table I reveals, as expected, that the base strengths of the amines vary with solvent in a complex manner depending upon dielectric constant and solvating properties of the solvent. It is seen that in chloroform and chlorobenzene the tertiary

TABLE I

EQUILIBRIUM CONSTANTS FOR THE REACTION OF 2,4-DINITROPHENOL AND SOME AMINES AT 25° IN NON-AQUEOUS SOLVENTS

Amines	Heptane	Benzene	Dioxane	Chloroform	Chloro-benzene	Ethyl acetate	Ethylene dichloride	Water[a]
Methyl	..	..	4800	35	..	....	....	3.36
Dimethyl	..	880	5410	1230	1070	....	....	3.29
Trimethyl	..	802	382	2680	1380	....	. .	4.28
Ethyl	..	..	4900	...	..	65,500	....	3.25
Diethyl	..	1240	6230	1730	2500	47,500	....	2.90
Triethyl	..	2940	1460	15800	9680	11,900	....	3.25
n-Butyl	..	..	3760	45	..	38,100	....	3.39
Di-*n*-butyl	360	950	4010	2580	2500	36,000	12,000	2.69
Tri-*n*-butyl	100	614	425	9100	3800	2,520	29,300	3.17
n-Hexyl	..	50	4300	53	80	50,200	....	3.36
Dielectric constant	1.9	2.3	2.2	4.8	5.6	6.3	10.2	78

[a] pK_b in aqueous solution.

amines are the strongest bases. The base strengths, however, do not vary linearly in going from primary to secondary to tertiary, the latter never being as strong as required. Nevertheless the chlorinated solvents show the expected trend in reducing solvent effects. For example, in water dimethylamine is ten times stronger as a base than trimethylamine, but in chloroform trimethylamine is stronger by a factor of two. Thus, between water and chloroform, solvation has accounted for a factor of twenty in relative base strength. Likewise, between methylamine and dimethylamine, solvation has accounted for a factor of twenty-nine.

Going to solvents of lower dielectric constant would lead one to expect even more pronounced changes. Such is not the case as may be seen from the results in benzene and *n*-heptane. To explain these results other factors must be considered. First, there is a considerable electrostatic energy holding together the cation and anion of the ion-pair inversely proportional to the distance of charge separation. With the primary and secondary ammonium cations there is the possibility of having the anion either in direct line with one of the protons on the nitrogen atom, or having it bridged between the protons forming bi- and trifurcated structures.[8] Simple electrostatic calculations indicate that the latter situation is favored energetically. Thus the primary and secondary ammonium cations may have this added stability over tertiary ammonium cations which have only one proton.

In addition, steric factors also must be considered. First, there probably is a certain amount of B-strain present. Second, in an ion-pair, the bulky alkyl groups exhibit F-strain[3] which is the term usually given to all the repulsion terms occurring at the front of the nitrogen atom including van der Waals repulsion and shielding of the electron pair.

If one uses the Born equation, or other equations based on classical electrostatic theory, it may be shown that a solvent of dielectric constant equal to 2, which is about the lowest value found in any liquid, will still have considerable solvating power. Thus a change from the gas phase ($D = 1$) to a non-polar, non-specific solvent ($D = 2$) produces as much solvation energy as a change from the non-polar solvent ($D = 2$) to a non-specific solvent of infinite dielectric constant. Hence no solvent can approximate the gas phase where charged particles are concerned.

A fourth factor to consider is that the solvation energies of the amines vary greatly in going from one solvent to another. This would, of course, change relative base strengths considerably in that a strongly solvated amine would behave as a weaker base. Table II shows some data on distribution coefficients (equal to the concentration of the amine in water/concentration of amine in the organic phase) for ammonia and the methylamines. These do vary greatly, by about a factor of 100 between NH_3 and $(CH_3)_3N$. The result is to make the tertiary amine relatively a weaker base by the same factor.

TABLE II

PARTITION COEFFICIENTS OF THE METHYLAMINES BETWEEN WATER AND FIVE ORGANIC SOLVENTS AT 25°

	CCl_4	Benzene	Chloro-benzene	Ethyl ether	$CHCl_3$
Ammonia	246[a]	210[b]	179	180[c]	26[e]
Methylamine	31.1	27.8[b]	57.6	43.5[d]	11.4[f]
Dimethylamine	13.5	11.2[b]	13.6	18.2[d]	2.75[f]
Trimethylamine	1.3	2.1	2.0	2.2[d]	0.45[f]

[a] A value of 212 is reported by H. W. Smith, *J. Phys. Chem.*, **26**, 256 (1922). [b] W. Harz and E. Stenner, *Z. physik. Chem.*, **A128**, 399 (1927). [c] N. Lofman, *Z. anorg. Chem.*, **107**, 241 (1919). [d] R. Collander, *Acta Chem. Scand.*, **3**, 717 (1949). [e] H. M. Dawson, *J. Chem. Soc.*, **89**, 1668 (1906). [f] W. A. Felsing and E. Ball, THIS JOURNAL, **63**, 2525 (1941). All other values determined in this investigation.

A further observation to be made from Table I is that solvents with basic oxygen atoms exhibit pronounced solvation effects as may be seen from the results in dioxane and ethyl acetate. Primary and secondary amines are stronger bases in these solvents in comparison to solvents of the same dielectric constant but lacking the basic oxygen atoms. Presumably, this is because the electron rich areas of the solvent can stabilize the ion-pairs through hydrogen bonding. Tertiary amines do not show this effect because their proton is already hydrogen bonded to the oxygen of the nitrophenolate anion. In ethyl acetate the primary amines are seen to be the strongest bases. Hall[9] has observed the same effect in ethyl acetate, and Rumpf, Girault-Verlearski and Schaal[10] in 72% dioxane–water mixtures.

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(8) E. A. Yerger and G. M. Barrow, THIS JOURNAL, **76**, 5211 (1954); **77**, 4474, 6206 (1955).

(9) H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 63 (1956).

(10) P. Rumpf, M. Girault-Verlearski and R. Schaal, *Bull. soc. chim.*, 554 (1955).

Hall also found that in ethylene dichloride triethylamine is a stronger base than diethylamine, both of which are considerably stronger than isobutylamine. The technique employed in both of these investigations involves the measurement of e.m.f. values at half-neutralization during titration of the amines with a strong acid such as perchloric. The agreement with these authors and with the work of Barrow and Yerger[8] who used infrared measurements shows that it is indeed a proton transfer reaction which is being studied in each case.

Further evidence showing the importance of specific solvation effects is found upon the addition of small amounts of alcohol and salts having a common cation to reaction mixtures in these solvents. Table III and Table IV summarize these results. Several interesting phenomena are to be noted from these tables. First, addition of small amounts of ethyl alcohol to chloroform has no effect on the trimethylamine–2,4-dinitrophenol equilibrium constant. About four mole % ethyl alcohol increases the equilibrium constant for dimethylamine by a factor of about ten, and for methylamine by about a hundred. The relative solvating properties of ethyl alcohol, ether and dioxane are shown by the results for *n*-hexylamine in chloroform. Adding small amounts of water to dioxane shows that the *n*-hexylammonium-2,4-dinitrophenolate ion-pairs are already sufficiently stabilized by dioxane molecules.

TABLE III

THE EFFECTS OF ADDING SMALL AMOUNTS OF OTHER SOLVENTS ON THE EQUILIBRIUM $B + HA = BH^+,A^-$ IN CHLOROFORM AND DIOXANE AT 25°

1. Chloroform

Amine	Mole % EtOH	*K*	Added solvent	Mole %	*K*
Methylamine	0.00	35	*n*-Hexylamine		
	1.79	662	Ethyl alcohol	0.00	53
	5.20	5830		1.49	360
Dimethylamine	0.00	1230		3.42	1490
	1.12	3520			
	4.30	12700	Ethyl ether	3.08	166
Trimethylamine	0.00	2680		6.24	343
	1.46	2680			
	4.71	2680	Dioxane	3.72	166

2. Dioxane

Amine	Mole % water	*K*
n-Hexylamine	0.00	4300
	0.72	5420
	1.25	5800
	2.25	7180
	5.52	15300

Table IV shows the strong interaction of added ions with the ion-pair formed from a primary amine and 2,4-dinitrophenol. Secondary amines show a smaller interaction and a tertiary amine only a very weak one. There is little doubt that in these cases, as in those of Table III, the interaction involves the added substance and the excess acidic protons of the ammonium ion. Presumably one proton of BH^+ must always be bonded to A^-.

TABLE IV

THE EFFECTS OF ADDING SALTS WITH A COMMON CATION TO BENZENE AND CHLOROFORM ON THE EQUILIBRIUM $B + HA = BH^+,A^-$ AT 25°

1. Benzene, *n*-Hexylamine

Added *n*-hexylammonium *p*-toluenesulfonate, *M*	*K* (molar^{-1})
0.00	50
7.03×10^{-4}	714
3.58×10^{-3}	2360

Di-*n*-butylamine

Added di-*n*-butylammonium *p*-toluenesulfonate, *M*	*K* (molar^{-1})
0.00	950
7.98×10^{-4}	2050
2.15×10^{-3}	2980

2. Chloroform, Triethylamine

Added triethylammonium hydrochloride, *M*	*K* (molar^{-1})
0.00	15800
1.48×10^{-3}	19000
8.60×10^{-3}	21800

Diethylamine

Added diethylammonium hydrochloride, *M*	*K* (molar^{-1})
0.00	1730
2.63×10^{-3}	3690
4.57×10^{-3}	4240

It may be noted that a common ion, BH^+, is added in the experiments shown in Table IV. The fact that the equilibrium constants increase rather than decrease is good evidence that equation 3 is correct rather than equation 1 for the reactions in these solvents. Addition of BH^+ would drive equation 1 to the left, but would have no direct effect on the equilibrium.

$$B + HA = BH^+,A^- \qquad (6)$$

It would be desirable to have the equilibrium constant for reaction 1 in various solvents to avoid the complication due to the strong "solvation" of the ions by each other. This constant could be obtained from the constant for reaction 6 and the dissociation constant of the ion-pair

$$BH^+,A^- = BH^+ + A^- \qquad (7)$$

Kraus and Witschonke[11] have measured the dissociation constant for reaction 7 in the case of the ion-pairs of mono-, di- and tributylamine with picric acid in the solvent nitrobenzene. The three constants were virtually identical for the primary, secondary and tertiary amines. This might not be true in a poorer solvent than nitrobenzene, however, since the latter is capable of solvating the excess acidic protons of the primary and secondary ammonium ions.

An attempt was made in this work to measure the equilibrium constant of (7) for dibutyl- and tributylammonium picrate in the solvents chloroform, chlorobenzene and ethylene dichloride. A conductance method was used but was rendered very difficult by the low concentrations possible and by the low degrees of dissociation encountered. After correcting for triple-ion formation according to Fuoss and Kraus,[12] it was concluded that the dissociation constant for (7) was greater for the tertiary

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[11] C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947).

[12] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933).

amine than for the secondary amine by a factor of from two to five in the three solvents tested. Solvents of lower dielectric constant gave resistances much too large to be measured accurately.

Effect of Methyl Groups on Heat of Hydration of NH_4^+.—An inspection of Tables I and II reveals that replacement of one N–H bond by an $N-CH_3$ bond can cause relative changes in the free energies of solvation of the substituted ammonium ions as large as 3 kcal. in passing from one solvent to another. It would be of interest to know how great a variation in solvation energy is produced, for example, in changing from NH_4^+ to $CH_3NH_3^+$, in the extreme case of transfer from the gas phase to water solution.

The heat and free energy of hydration are known accurately[7] for NH_4^+, being -79 and -76 kcal., respectively, at 25°. The corresponding quantities for the several methylammonium ions are not available because the free energies and heats of formation of the gaseous ions are unknown. However, in the case of the nearly spherically symmetrical tetramethylammonium ion, the heat of hydration can be calculated in two independent ways, requiring only a knowledge of the ionic radius and the experimental heat of solution of a salt such as $(CH_3)_4NCl$.

The crystal structure of $(CH_3)_4NCl$ is known[13] from X-ray data. It crystallizes in the tetragonal system with a distorted face-centered arrangement. The closest cation–anion distance is 4.35 Å. which corresponds to a cationic radius of 2.54 Å.

The free energy of hydration can now be estimated by the use of the modified Born equation suggested by Latimer, Pitzer and Slansky.[14]

$$\Delta Fel = -\frac{Ne^2}{2(r_c + 0.85)}\left(1 - \frac{1}{D}\right) \qquad (8)$$

where r_c is the cationic radius and D the dielectric constant of water. This equation works well for simple, spherically symmetrical cations. The result for the free energy is -48 kcal., and, from the temperature variation of the dielectric constant of water, the corresponding heat of hydration is -49 kcal.

The second method of calculation depends upon finding the lattice energy of the solid salt and subtracting from the heat of solution to get the sum of the heats of hydration of the cation and anion. Because of its irregular structure the exact lattice energy of $(CH_3)_4NCl$ cannot be calculated easily. However, the method of Kapustinsky,[15] which does not depend on knowing the correct Madelung constant, can be used to give a fairly reliable value. The only data needed are the cationic and anionic radii. The latest version of the equation is[15b]

$$= \frac{574.4}{(r_c + r_a)}\left[1 - \frac{0.345}{(r_c + r_a)} + 0.00435(r_c + r_a)\right] \qquad (9)$$

Using this equation gives 160 kcal. for the lattice energy of NH_4Cl and 124 kcal. for $(CH_3)_4NCl$. Correcting for van der Waals attraction energies (London dispersion energies) but neglecting polarization and zero point energies gives 164.5 and 131 kcal.[16] Combining with the heats of solution of solid $(CH_3)_4NCl$ and NH_4Cl[17] gives a value of 31 kcal. for the *difference* between the heats of hydration of NH_4^+ and $(CH_3)_4N^+$.

Therefore both methods agree in showing that replacement of all four hydrogen atoms in NH_4^+ by methyl groups leads to a reduction of about 30 kcal./mole in the heat of hydration. While it will almost certainly not be a constant change per methyl group, it may be taken as a rough approximation that replacement of each hydrogen by methyl leads to a drop of about 8 kcal. in the heat of hydration in passing through the series NH_4^+, $CH_3NH_3^+$, $(CH_3)_2NH^+$, $(CH_3)_3NH^+$ and $(CH_3)_4N^+$.[18]

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[13] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, Vol. 1, Chap. 3, Table 28.

[14] W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

[15] (a) A. F. Kapustinsky, *J. Phys. Chem., U.S.S.R.*, **1**, 59 (1934); (b) A. F. Kapustinsky and K. B. Yatsimirsky, *J. Gen. Chem., U.S.S.R.* (*English translation*), April, p. 1069 (1956).

[16] The first figure may be compared with an accurate value of 171.4 kcal. (A. May, *Phys. Rev.*, **52**, 339 (1937)) for NH_4Cl. However, the neglected terms will certainly nearly cancel in a comparison between the two salts.

[17] F. A. Askew, E. Bullock, K. T. Smith, R. K. Gatty and J. H. Wolfenden, *J. Chem. Soc.*, 1368 (1934); F. D. Rossini, D. D. Wayman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Standards Circular 500, Washington, D. C., 1952, p. 62.

[18] The negative heats of hydration at 25° of NH_3, CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ are 8.0, 10.4, 11.0 and 11.3 kcal. G. Briegleb, *Z. Elektrochem.*, **53**, 350 (1949).