

bility of iodine in iodide solutions is now expressed as

$$S' = [I_2] + [I_3^-] + 2[I_5^-] + 2[I_6^{2-}] \quad (15)$$

and the concentration of potassium iodide is

$$C_K = [I^-] + [I_3^-] + [I_5^-] + 2[I_6^{2-}] \quad (16)$$

From eq. 1, 2, 3, 14, 15, and 16 it follows that

$$S' = K_0 + K_0 K_3 [I^-] + 2K_0^2 K_3 K_5 [I^-] + 2K_0^2 K_3^2 K_6 [I^-]^2 \quad (17)$$

$$[I^-] = \frac{C_K - S' + K_0}{1 - K_0^2 K_3 K_5} \quad (18)$$

$$K_3' = \frac{K_3 + 2K_0 K_3 K_5}{1 - K_0^2 K_3 K_5} + \frac{2K_0 K_3^2 K_6 (C_K - S' + K_0)}{(1 - K_0^2 K_3 K_5)^2} \quad (19)$$

Equation 19 shows that the apparent value for K_3 would always be higher than the true value, even when the potassium iodide concentration approaches zero, or even if the effect of K_6 is negligible. Assuming that the latter is true for our solutions, we may solve for K_5 with the result

$$K_5 = \frac{K_3' - K_3}{K_0 K_3 (2 + K_0 K_3')} \quad (20)$$

By using eq. 12 for K_3' values, eq. 9 for K_0 values, and eq. 5 for K_3 values, we have calculated K_5 as a function of temperature, with the result

$$\log K_5 \approx 0.954 + 0.0308(t - 25) \quad (21)$$

The thermodynamic values for 25° are: $\Delta F^\circ = -1.3$ kcal./mole, $\Delta H^\circ \approx +12$ kcal./mole, and $\Delta S^\circ \approx 50$ cal./deg. mole, but little reliability can be placed on these values. The value of K_5 at 25° is about 9.

The postulation of I_5^- also accounts qualitatively for the intermediate position of the distribution results for K_3' , since those studies involved intermediate concentrations of I_2 and I_3^- .

Finally, we have determined that the inclusion of the I_5^- results in the interpretation of the distribution data does not materially affect the calculated values of K_6 .

Acknowledgment. This work has been supported by N.S.F. Grant No. G19587, and we are also grateful to the Johnson Wax Fund for a department grant partially used in this research.

Properties of Bases in Acetonitrile as Solvent. IV. Proton Acceptor Power and Homoconjugation of Mono- and Diamines

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The dissociation constants of the conjugate acids of 31 amines of various structural types were measured in anhydrous acetonitrile as solvent by means of a glass electrode shown to respond reversibly to hydrogen ion activity in this solvent. The electrode was calibrated in a series of buffers containing picric acid and tetraethylammonium picrate, using the dissociation constant found for picric acid in a careful study by Kolthoff and Chantooni. All measurements were carried out at a constant and sufficiently low ionic strength to allow extrapolation of equilibrium constants to their limiting values. No simple, quantitative correlation was found between base strengths in acetonitrile and water. Although the pK_a values of the majority of the ammonium ions studied are from 7.2 to 7.9 units greater in acetonitrile than in water, several ions differ significantly from this "norm." Aromatic ions are considerably stronger acids in acetonitrile than would be predicted from the strengths of aliphatic ions. In the series of monoprotonated diamines, $H_2N(CH_2)_nNH_3^+$, the acids with $n = 3$ and 4 derive considerable stability from intramolecular hydrogen bonding. Although acetonitrile is much more inert than water, its solvation of ammonium ions still exerts an important influence. Steric inhibition of solvation appears to be more important in acetonitrile than in water. A correlation exists between the base

strength of an amine, B , and its tendency to form homoconjugated complexes, B_nBH^+ , in acetonitrile.

During recent years considerable evidence has been obtained for the hypothesis, originally proposed by Trotman-Dickenson³ and others, that the relative hydration of an amine and its conjugate acid may influence the proton acceptor power of the amine in water to a marked extent. For example, this hypothesis adequately accounts for the fact that, in aqueous solution, secondary amines generally are the strongest and tertiary amines the weakest proton acceptors, while inductive effects alone would lead to an order of strengths increasing from the primary to the secondary to the tertiary amine. This and other consequences of the solvation hypothesis were discussed for a large number of amines by Hall.⁴

Much less is known about corresponding solvation effects in solvents other than water, with a few notable exceptions. Spectrophotometric studies by Davis and Hetzer⁵ and by Pearson and Vogelsson⁶ of the reaction of certain amines with reference (indicator) acids in low

(3) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

(4) H. K. Hall, Jr., *J. Am. Chem. Soc.*, 79, 5441, 5444 (1957).

(5) M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Std.*, 48, 381 (1952).

(6) R. G. Pearson and D. C. Vogelsson, *J. Am. Chem. Soc.*, 80, 1038 (1958).

(1) Address all correspondence to this author.

(2) From the Ph.D. Thesis of G. R. P., University of Pittsburgh, 1963.

dielectric constant solvents, such as benzene and chlorinated hydrocarbons, showed that a reversal in the order of proton acceptor power may occur on changing the solvent. However, unambiguous interpretation of the results in low dielectric constant solvents would require additional, detailed information about all ion association reactions involved. In principle, solvation effects should be more amenable to study in solvents of higher dielectric constant. Acetonitrile (dielectric constant = 36.0) is an appropriate choice, since its solvation of ammonium ions and particularly free amines should be less extensive than that of water. It is to be expected that the behavior of these species in acetonitrile will be intermediate between those observed in water and in the gas phase.

Semiquantitative potentiometric studies of the relative proton acceptor power of series of amines have been carried out by Hall⁷ and others. In those investigations the values of the potential of a glass electrode at the midpoints in the titration of a series of amines with perchloric acid (usually dissolved in dioxane) were taken as an index of the *relative* strengths of the amines. In no case was it attempted to calibrate the basicity scale on an absolute basis. Results obtained from such titrations can be quite valuable for exploratory purposes but are not suitable for precise correlations, because (1) the titrant introduces a competing proton acceptor (dioxane or water); (2) the ionic strength of the solution as well as the net liquid junction potential changes during the titration; (3) additional species, such as $\text{BH}^+\text{ClO}_4^-$ ion pairs as well as BHB^+ and higher hydrogen-bonded complexes, may be produced; and (4) most important of all, for exact comparisons it cannot be assumed without definite evidence that the glass electrode responds reversibly to hydrogen ion activity in an anhydrous solvent. (However, Hall's results indicate that his glass electrode did indeed measure hydrogen ion activity.)

As part of a systematic investigation in this laboratory concerned with the properties of bases in acetonitrile as solvent, we have measured under carefully controlled conditions the absolute $\text{p}K_a$ values, as well as the formation constants of BHB^+ and higher hydrogen-bonded ("homoconjugated") complexes, of 31 mono- and diamines. Glass electrodes were calibrated in anhydrous acetonitrile and shown to respond reversibly to hydrogen ion activity in this solvent. All measurements were carried out in solutions of adequate buffer capacity and at constant and low ionic strength so that equilibrium constants could be extrapolated to their limiting values. The results show many subtle and certain marked differences in trends from those obtained in water.

Experimental Section

Materials. Sohio acetonitrile was purified as described before.⁸ Polarographic tests for acidic and basic impurities were negative (limit of detection, $5\text{--}10 \times 10^{-6} M$).

The sources of other chemicals used are indicated as follows: Eastman White Label, EWL; Eastman Yellow Label, EYL; Eastman Practical Grade, EPG;

Fisher Certified Grade, F; K & K Laboratories, K; Matheson Lecture Bottle, M.

Triethylenediamine (K) was used without further purification. The solid bases were recrystallized and then dried *in vacuo* as indicated: 1,3-diphenylguanidine (EWL, twice from toluene, 40°); *p*-toluidine (EWL, ether, 25°). The following liquid bases were refluxed over a mixture of sodium metal and sodium hydroxide and then fractionally distilled under vacuum: tri-*n*-butylamine, monoethanolamine, and aniline (EWL); triisooamylamine (EPG); 1,4-diaminobutane and 1,5-diaminopentane (K). The following liquid bases were refluxed over a mixture of sodium metal and sodium hydroxide and then fractionally distilled at atmospheric pressure: diethylamine, triethylamine, *n*-propylamine, tri-*n*-propylamine, di-*n*-butylamine, isobutylamine, diisobutylamine, *t*-butylamine, benzylamine, hydrazine, and 1,2-diaminoethane (EWL); piperidine, pyrrolidine, and 1,3-diaminopropane (EYL); *n*-butylamine and pyridine (F); and morpholine (Fisher Laboratory Chemical). In all cases melting or boiling points agreed closely with literature values.

The following gaseous bases were drawn into acetonitrile: ammonia, methylamine, dimethylamine, and trimethylamine (M) and ethylamine (EWL). The concentrations of the resulting solutions were determined by titration with perchloric acid, using a glass electrode to detect the equivalence point.

Tetraethylammonium perchlorate and picrate were prepared as described before.⁹ The picrates of triethylamine, tri-*n*-butylamine, piperidine, pyrrolidine, monoethanolamine, and aniline were prepared by titrating an ethanolic solution of the base with a saturated ethanolic solution of picric acid, using a glass electrode to detect the equivalence point. The salts generally were recrystallized from ethanol and then dried *in vacuo*. The picrates of benzylamine, diisobutylamine, and triisooamylamine were prepared *in situ* in acetonitrile as solvent. The perchlorates of the remaining monoacid bases, and also of piperidine, pyrrolidine, and aniline, were prepared by titration of the base in an appropriate solvent² with 70% aqueous perchloric acid, followed by recrystallization and drying *in vacuo*. The diperchlorates of the diamines were prepared by titrating to the second equivalence point in an appropriate solvent² and then adding benzene to precipitate the salt. The corresponding monoperchlorates were prepared *in situ* in acetonitrile as solvent by mixing equimolar amounts of the diperchlorate and the amine.

Measurements. The $\text{p}K_a$ value of each amine was determined by measuring the potential of a Beckman General Purpose No. 1190-80 glass electrode in four or five buffer solutions containing a constant concentration of the ammonium perchlorate or picrate ($5.0 \times 10^{-4} M$) as well as of the "inert" electrolyte Et_4NClO_4 ($1.0 \times 10^{-2} M$) and varying concentrations of the amine (generally from $ca. 2 \times 10^{-4}$ to $2 \times 10^{-3} M$). Formation constants of homoconjugated complexes were determined by using a series of eight to fourteen buffer solutions containing a constant concentration of the perchlorate or picrate ($5.0 \times 10^{-4} M$) and varying concentrations (generally up to 0.1 *M* or higher²)

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

(8) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

(9) J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, **66**, 1708 (1962).

Table I. Homoconjugation and Acid Dissociation Constants of Protonated Monoamines in Acetonitrile (AN) as Solvent

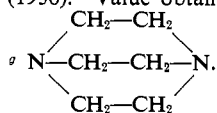
	Amine	$(K_{f_1})_{AN}^a$	$(K_{f_2})_{AN}^b$	$(pK_a)_{AN}^c$	$(pK_a)_W^d$	Δ^e
1	Ammonia	11	2	16.46	9.21	7.25
2	Methylamine	35	2	18.37	10.62	7.75
3	Dimethylamine	31	0.5	18.73	10.64	8.09
4	Trimethylamine	6	...	17.61	9.76	7.85
5	Ethylamine	25	2	18.40	10.63	7.77
6	Diethylamine	2	...	18.75	10.98	7.77
7	Triethylamine	None	...	18.46	10.65	7.81
8	<i>n</i> -Propylamine	19	2	18.22	10.53	7.69
9	Tri- <i>n</i> -propylamine	None	...	18.10	10.65	7.45
10	<i>n</i> -Butylamine	26	2.5	18.26	10.59	7.67
11	Di- <i>n</i> -butylamine	None	...	18.31	11.25	7.06
12	Tri- <i>n</i> -butylamine	None	...	18.09	10.89	7.20
13	<i>t</i> -Butylamine	20	1	18.14	10.45	7.69
14	Isobutylamine	17.92	10.43	7.49
15	Diisobutylamine	None	...	17.88	10.50	7.38
16	Triisobutylamine	None	...	18.04
17	Piperidine	26	...	18.92	11.22	7.70
18	Pyrrolidine	32	2	19.58	11.27	8.31
19	Pyridine	4	...	12.33	5.17 ^f	7.16
20	Aniline	None	...	10.56	4.58 ^f	5.98
21	<i>p</i> -Toluidine	None	...	11.25	5.07 ^f	6.18
22	Benzylamine	15	...	16.76	9.34	7.42
23	Monoethanolamine	24	1.5	17.53	9.50	8.03
24	Morpholine	10	...	16.61	8.36	8.25
25	1,3-Diphenylguanidine	None	...	17.90	10.00 ^g	7.90

^a $K_{f_1} = [BHB^+]/[B][BH^+]$. ^b $K_{f_2} = [B_2BH^+]/[B][BHB^+]$. ^c $K_a = a_{SH^+}[B]/f_1[BH^+]$, where SH⁺ indicates the solvated proton, and f_1 was calculated from the limiting Debye-Hückel equation. ^d Except where noted otherwise, values are from compilation of Hall.⁴ ^e $\Delta = (pK_a)_{AN} - (pK_a)_W$. ^f H. C. Brown, D. H. McDaniel, and O. Häfliger, "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955. ^g Reference 5.

Table II. Homoconjugation and Acid Dissociation Constants of Protonated Diamines in Acetonitrile (AN) as Solvent

Amine	$(K_{f_1})_{AN}^a$	$(K_{f_2})_{AN}^a$	First step ^b			Second step ^c		
			AN	W ^d	AN-W	AN	W ^d	AN-W
Hydrazine	30	6				16.61	7.96 ^e	8.65
1,2-Diaminoethane	40	1.5	13.01	6.90	6.11	18.46	9.95	8.51
1,3-Diaminopropane	22	1.5	14.98	8.49	6.49	19.70	10.47	9.23
1,4-Diaminobutane	10	1.5	15.34	9.20	6.14	20.12	10.65	9.47
1,5-Diaminopentane			16.97 ^e	9.58 ^f	7.39	19.14 ^e	10.85 ^f	8.29
Triethylenediamine ^g	16		10.16	4.18	5.98	18.29	8.19	10.10

^a See footnotes under Table I. ^b pK_{a_1} value given, where $K_{a_1} = ([BH^+][SH^+]/[BH_2^{2+}])(f_1^2/f_2)$. ^c pK_{a_2} value given, where $K_{a_2} = [B][SH^+]/[BH^+]$. ^d C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **62**, 444 (1958). Values obtained by interpolation from those given for 20 and 30°. ^e Evaluated by Noyes' method. For details, see ref. 2. ^f G. Schwarzenbach, *Helv. Chim. Acta*, **16**, 522 (1933); **19**, 178 (1936). Value obtained by extrapolation of that given for 20°, assuming same temperature coefficient as for remaining diamines.



of the amine. The instrumentation was described before.⁹ The electrode was calibrated in picric acid-tetraethylammonium picrate buffers in acetonitrile as solvent, as described before.⁹ Using the recently redetermined pK_a value for picric acid in acetonitrile (11.0),¹⁰ the response (mv. vs. Ag reference electrode) of the particular glass electrode used was represented by the equation

$$E_{\text{glass}} = 714 + 59.1 \log a_{H^+}$$

During the course of this work the response of the electrode was checked every few days in a 1:1 buffer consisting of 1,3-diphenylguanidine and its perchlorate; potentials were reproducible to within ± 3 mv.

We estimate that the relative values of the acid dissociation constants reported in Tables I and II should be accurate to ± 0.05 pK_a unit. The uncertainty in

(10) I. M. Kolthoff and M. K. Chantooni, Jr., private communication; to be published.

the absolute values may be considerably greater in view of the long extrapolation carried out from the calibration point. It would be desirable to design more reference buffers.

Results

The results are presented in Tables I-III and Figures 1 and 2.

Discussion

Formation of Homoconjugated Complexes, B_nBH^+ . Extensive polarographic¹¹ and other evidence indicates that most cations, including ammonium-type ions, have considerably smaller free energies of solvation in acetonitrile than in water. The lower dielectric constant, and also the weaker base properties, of acetonitrile as compared to that of water contribute to

(11) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870, 1852, 6110 (1957).

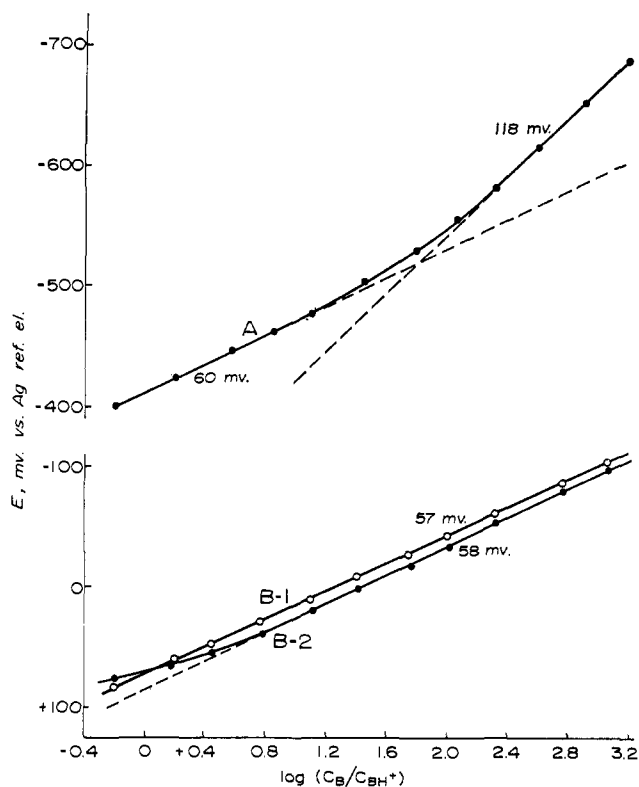


Figure 1. Response of glass electrode in buffer solutions of type $B + BH^+$ at a constant salt concentration of $5.0 \times 10^{-4} M$ in acetonitrile as solvent: (A) piperidine-piperidinium picrate; (B-1) aniline-anilinium perchlorate; (B-2) aniline-anilinium picrate (curvature at low aniline concentrations caused by reversion of salt to parent acid and base).

this lowering in solvation energy. As far as the solvation energy of free amines is concerned, it is known that this quantity varies considerably in different solvents, as is shown by the distribution coefficients quoted by Pearson and Vogelsson.⁶ Little is known about the solvation energies of amines in acetonitrile,

Table III. Values of Kirkwood-Westheimer Effective Dielectric Constant (D_E) for Solutions of Protonated Diamines in Different Media

Amine	R^b	Water		Ethanol-water ^a		Acetonitrile	
		ΔpK_a^c	D_E	ΔpK_a^c	D_E	ΔpK_a^c	D_E
1,2-Diaminoethane	4.45	3.05	22	3.42	19	5.45	11
1,3-Diaminopropane	4.95	1.98	36	2.41	27	4.72	12
1,4-Diaminobutane	5.85	1.45	49	1.86	33	4.78	10
1,5-Diaminopentane	6.45	1.27	56	1.68	35	2.17	24

^a Mixture containing 80% (v./v.) = 73.5% (w./w.) ethanol, with dielectric constant of 36, equal to that of acetonitrile; ΔpK_a values are from reference in footnote *f* under Table II, and are for 20°.

^b C. Tanford, *J. Am. Chem. Soc.*, **79**, 5348 (1957). ^c $\Delta pK_a = pK_a - pK_{a1}$.

but it is to be expected that the lower primary and secondary amines in particular will have lower solvation energies in a nonhydrogen-bonding solvent than in water (with higher, particularly branched, amines opposition from the structure of water would become increasingly important). Certainly amines form mercury(II) complexes much more readily in acetonitrile than in water,¹¹ and they also react extensively with

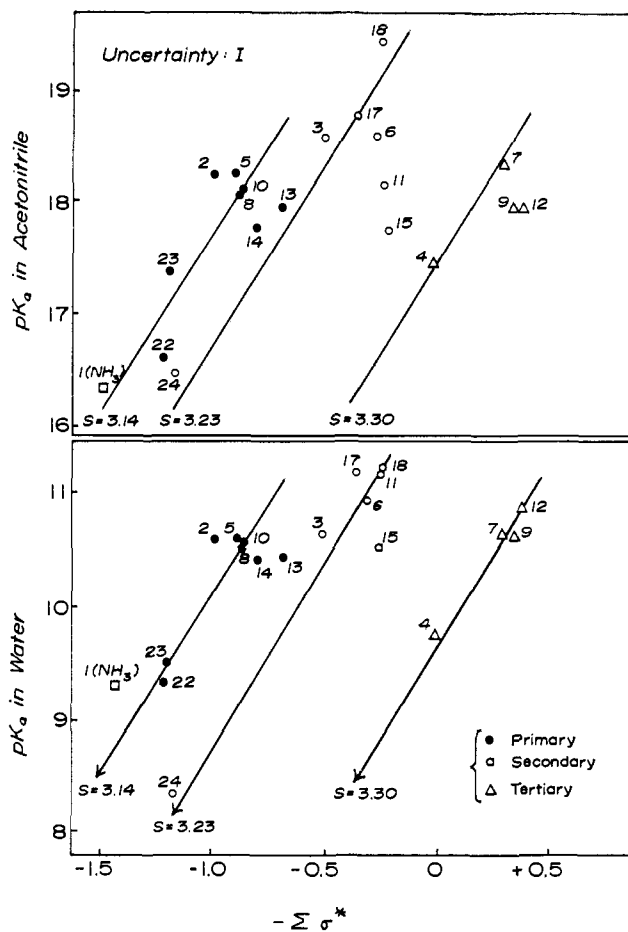


Figure 2. Taft plots for ammonium ions in acetonitrile and water; numbers of acids refer to Table I.

added water in acetonitrile; for example, the formation constant of the monohydrate of *n*-butylamine in acetonitrile is 0.4.¹² The cumulative effect of such decreased stabilization of amines as well as of ammonium ions in acetonitrile is that these species resort to homoconjugation (the formation of hydrogen-bonded complexes, $B_n \cdot BH^+$), reactions which are masked in water. We have discussed these reactions elsewhere.¹³

The stepwise formation constants, K_{f1} and K_{f2} , for the complexes $B \cdot BH^+$ and $B_2 \cdot BH^+$ are included in Tables I and II because a correlation exists between the tendency of an amine to form such complexes and its base strength as expressed by its pK_a value. Furthermore, if an amine forms complexes higher than the 1:1 species, the extent of these reactions must be known in the evaluation of pK_a values.

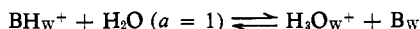
It is evident from Table I that generally homoconjugation increases with increasing strength of base *B* and increasing number of acidic hydrogen atoms in the conjugate acid BH^+ , and also that it has relatively severe steric requirements, as expected. Thus, homoconjugation is most extensive for the lower aliphatic primary amines and aliphatic cyclic secondary amines, such as piperidine, and is insignificant for noncyclic tertiary amines, except trimethylamine. In Figure 1 the behavior of piperidine and aniline is contrasted.

(12) W. S. Muney and J. F. Coetzee, *J. Phys. Chem.*, **66**, 89 (1962).

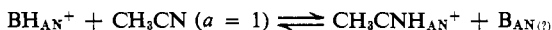
(13) J. F. Coetzee and G. R. Padmanabhan, with G. P. Cunningham, *Talanta*, **11**, 93 (1964).

Proton Acceptor Power of Monoamines. The results given in Table I lead to the following conclusions.

1. All protonated amines are much weaker acids in acetonitrile than in water. The factors contributing to the Δ values in Table I are illustrated by comparing the following equilibria



and



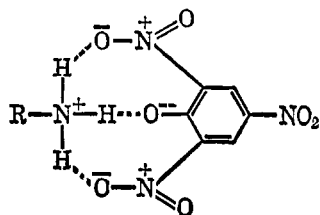
where the subscripts indicate solvation by water and acetonitrile, respectively. Although the solvent influence is complex, the dominant factor must be the fact that the proton acceptor power of acetonitrile is lower than that of water.

2. Although Δ values near 7.6 are found for a number of amines, no simple quantitative correlation exists between $\text{p}K_a$ values in acetonitrile and water. Actually, in view of the scheme given above, no such correlation is to be expected.

3. Leveling of the strongest bases, which was indicated in certain potentiometric titrations,¹⁴ does not occur. Acetonitrile is too weak an acid to level amines.

4. Even though acetonitrile is much more inert than water, it still solvates ammonium ions significantly since in acetonitrile, as in water, tertiary ammonium ions generally are stronger acids than the corresponding secondary or primary ions. This conclusion differs from that of Forman and Hume,¹⁵ who interpreted the results of thermometric titrations of amines with hydrogen bromide on the basis of lack of solvation of ammonium ions by acetonitrile.

5. Virtually the same $\text{p}K_a$ value is obtained with the picrate as with the perchlorate of a given amine. It was pointed out by one of the referees that this fact indicates the absence of specific hydrogen bonding of picrate, which may produce species such as¹⁶



Conductometric data¹⁷ show that in acetonitrile the picrates of aliphatic amines indeed are somewhat more associated than the corresponding perchlorates, but the difference is not large. Such association would be counteracted by solvation of the cation.

6. Aromatic ammonium ions are considerably stronger acids in acetonitrile than would be predicted from the strength of aliphatic amines. This fact indicates either increased solvation of aromatic amines or decreased solvation of aromatic ammonium ions by acetonitrile, or (more probably) the reverse situation in water. This observation may have a bearing on the general applicability of substituted anilines as indicators in H_0 studies.¹⁸

(14) J. S. Fritz, *Anal. Chem.*, **25**, 407 (1953).

(15) E. J. Forman and D. N. Hume, *J. Phys. Chem.*, **63**, 1949 (1959).

(16) G. N. Lewis and G. T. Seaborg, *J. Am. Chem. Soc.*, **62**, 2122 (1940).

(17) J. F. Coetzee and G. P. Cunningham, *ibid.*, **87**, 2534 (1965).

7. The conjugate acids of pyrrolidine, monoethanolamine, and morpholine are significantly weaker acids in acetonitrile than would be predicted from their strengths in water. In the case of the latter two acids it seems likely that in acetonitrile stabilization is derived from intramolecular hydrogen bonding. Hall arrived at the same conclusion.⁷ This increased stability amounts to *ca.* 0.6 pK unit or 0.8 kcal. mole⁻¹. We have observed other cases for which intramolecular hydrogen bonding is greatly enhanced in acetonitrile over that which occurs in water¹⁹ (see also diamines, below).

8. In Figure 2, Taft plots are compared for acetonitrile and water. The slopes of the lines are those found by Hall⁴ for 25 primary, 21 secondary, and 31 tertiary amines in aqueous solution, including examples with lower $\text{p}K_a$ values than the range covered in the present study. The best lines with the same slopes as for water were drawn through the points for acetonitrile. Although this procedure is inexact, it suffices to reveal large differences in the two solvents. The following conclusions can be drawn. First, the existence of three lines supports the Trotman-Dickenson solvation hypothesis for acetonitrile as for water.⁴ Second, steric factors are more important in acetonitrile than in water. In every instance hindered ammonium ions are stronger acids in acetonitrile than would be predicted from their behavior in water, using unhindered ammonium ions as norm (see points 9, 12, 13, and 14, and particularly 11 and 15). The conclusion is that a greater degree of steric inhibition of solvation exists in acetonitrile than in water. This view is supported by the data of Hall,⁴ which show that in both acetonitrile and water the $\text{p}K_a$ value of 2,2,6,6-tetramethylpiperidinium ion (for which steric inhibition of solvation should be important in both solvents) exceeds that of piperidinium ion by only 0.2 unit, whereas the increase from N-methylpiperidinium ion to 1,2,2,6,6-pentamethylpiperidinium ion is 1.1 units in water (strictly a polar effect, since steric inhibition to solvation appears to be unimportant for tertiary amines in water),⁴ but only 0.3 unit in acetonitrile.

9. It is instructive to compare $\text{p}K_a$ values with isothermal heats of neutralization obtained from Forman and Hume's thermometric titrations.¹⁵ Unfortunately exact comparisons are impossible, because the titrant was hydrogen bromide, and bromides of incompletely substituted ammonium bases are somewhat associated at the concentrations used. Nevertheless an approximately linear relationship is found, except for ammonia and morpholine which give larger ΔH_{iso} values, and for tertiary amines (except trimethylamine) and particularly 1,3-diphenylguanidine which give smaller ΔH_{iso} values than would be predicted from the norm established by the majority of amines. The low $-\Delta S$ values for ammonium and morpholinium ions indicate that these ions are most effective in orienting the solvent, whereas the higher tertiary ammonium ions are least effective. The behavior of 1,3-diphenylguanidinium ion is curious.

(18) The Δ values for aniline and *p*-toluidine are approximately 0.9 unit greater than those found spectrophotometrically for several much more weakly basic Hammett indicators: J. F. Coetzee and D. K. McGuire, *J. Phys. Chem.*, **67**, 1810 (1963). This difference may simply reflect the strongly differentiating nature of acetonitrile.

(19) J. F. Coetzee and G. R. Padmanabhan, *ibid.*, **69**, 3193 (1965).

Proton Acceptor Power of Diamines. Diamines exhibit more striking differences in behavior in acetonitrile and in water than those described for monoamines. The results in Table II lead to the following conclusions.

1. Diprotonated diamines are weakened less on being transferred from water to acetonitrile than is the case for the corresponding monoprotated compounds, in agreement with the expectation that the lower dielectric constant of acetonitrile discourages higher charge type ions to a greater degree than is the case in water.

2. In acetonitrile, monoprotated diaminopropane and diaminobutane are weaker acids than would be predicted from the strength of *n*-propyl- and *n*-butylammonium ions. This weakening is attributed to stabilization of the species $H_2N(CH_2)_nNH_3^+$ with $n = 3$ and 4 by intramolecular hydrogen bonding, a reaction which is largely masked in water. In going up the series of diamines, an abrupt increase in acid strength occurs with diaminopentane, which is in agreement with the foregoing, since for the species $H_2N(CH_2)_5NH_3^+$ intramolecular hydrogen bonding would require a seven-membered ring (not counting hydrogen). The same phenomenon is illustrated more strikingly in Table III. In water the difference between the two pK_a values of a given diamine decreases in going up the series and gradually approaches the statistical factor of $\log 4 = 0.60$. In acetonitrile this difference is larger and abruptly decreases at diaminopentane. It is interesting to compare values of the

“effective” dielectric constant, D_E , calculated on the basis of the Kirkwood–Westheimer model,²⁰ in three media for which dissociation constants are available (water, 80% (v./v.) ethanol, and acetonitrile)

$$\log \frac{K_{a1}}{4K_{a2}} = \Delta pK_{a, \text{cor}} = \frac{e^2}{2.303kTRD_E}$$

where $\Delta pK_{a, \text{cor}}$ is the value of ΔpK_a corrected for the statistical factor, R represents the distance (in cm.) between the protons, and other symbols have their usual meaning. It follows that

$$D_E = \frac{2.43 \times 10^{-6}}{R\Delta pK_{a, \text{cor}}}$$

Values of D_E are listed in Table III. For acetonitrile D_E increases abruptly at diaminopentane, whereas in the isodielectric ethanol–water mixture, in which little intramolecular hydrogen bonding is to be expected; D_E smoothly approaches the bulk dielectric constant of the medium. Further calculations probably are not justified in view of the uncertainties associated with the Kirkwood–Westheimer model.²¹

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Rates of Chloride Ion Exchange with Various Phosphonic Chlorides and Phosphorochloridates

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From measurements of the chloride-36 exchange rate with various $RPOCl_2$ compounds and spectroscopic determination of the donor strength of various phosphoryl compounds, it has been possible to examine the electronic effects present in bimolecular displacement reactions on four-coordinate phosphorus. The exchange reaction with $RPOCl_2$ compounds has been shown to follow second-order kinetics in the solvent 1,2-dichloroethane at -30° . The effect of substituent is to decrease the rate in the order $C_6H_5 > CH_3 > OCH_3 \sim Cl > OC_6H_5$. The effect of substituent on the donor strength of the phosphoryl oxygen gives rise to the order $(CH_3)_2N \sim C_6H_5 > CH_3 > OCH_3 > OC_6H_5 > Cl$. The relative importance of inductive and conjugative effects for these substituents has been discussed. These studies aid in the interpretation of some previously published n.q.r. data. Interpreting the donor strength

as an indication of the formal positive charge on phosphorus, it is observed that the rate of exchange is not in direct proportion to this charge. In order to rationalize the rate data, it is necessary to consider the effect that inductive withdrawal of electron density and π bonding have on the relative energies of the ground and transition states.

Introduction

There has been considerable interest in the mechanism of substitution reactions of four-coordinate phosphorus compounds. Much of this interest has arisen from the comparison of the mechanisms of these reactions with substitution reactions on carbon. There has also been considerable interest in the behavior of phosphorus oxychlorides as nonaqueous solvents, and this has served as the motivation for kinetic studies. We report, in this article, work which is pertinent to both of these areas.

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