

on μ is observed for the pQ and pk' values. In the case of the pk_{13}' value (Fig. 2b) this dependence is similar to that observed previously for proton ionization from the $-\text{NH}_3^+$ group of alanine.¹¹

Gorin and Clary² measured the concentration change with μ of the ionized sulfhydryl proton of CYS. They observed that the concentration of this species changed very little as a function of μ except at low μ -values, and concluded that R was likewise invariant with μ . As seen in Fig. 2a, our results show that R does change appreciably with μ . However, the results of Gorin and Clary can be understood by reference to the data in Fig. 2b. Gorin and Clary followed the pk_{12}' ionization and it is seen that over the μ range used in their study ($\mu^{0.5} \sim 0.03$ to $\mu^{0.5} = 2.5$) there is little change in pk_{12}' except at low μ -values. On this point our results and theirs agree. However, R depends upon the relative magnitudes of pk_{12}' and pk_{13}' and not upon that of pk_{12}' alone. It is seen that pk_{13}' has a considerably larger variation with μ than has pk_{12}' . Thus, R is seen to have a considerable μ variation. Furthermore, the data in Fig. 2c show both pk_{132}' and pk_{123}' to have much greater μ dependencies than the corresponding dissociations in the lower pH region.

The ΔS values reported in Table II for proton dissociation from MAA and SMC are of the expected magnitudes considering the ionic charges involved. The relative effects on pQ of the $-T\Delta S$ and ΔH changes between $\mu = 0$ and $\mu = 1$ are shown in Table III.

(11) A. C. Batchelder and C. L. A. Schmidt, *J. Phys. Chem.*, **44**, 880 (1940).

TABLE III

THE EFFECT OF CHANGING μ ON $T\Delta S$, ΔH , AND pQ^a

Reaction	$\frac{\partial(-T\Delta S)}{\partial\mu}\bigg _{\mu=0}$ $\bigg _{\mu=1}$	$\frac{\partial(\Delta H)}{\partial\mu}\bigg _{\mu=0}$ $\bigg _{\mu=1}$	$\frac{2.3RT\partial(pQ)}{\partial\mu}\bigg _{\mu=0}$ $\bigg _{\mu=1}$
H_2CYS^- (I) =			
(II, III) + H^+	0	-0.44	-0.44
(II, III) = CYS^{-2}			
(IV) + H^+	-1.8	+0.72	-1.1
HMAA ⁻ =			
MAA ⁻² + H^+	-1.2	0	-1.2
HSMC ^{+·-} =			
SMC ⁻ + H^+	-0.66	+0.22	-0.44

^a Data in kcal./mole and taken from Tables I and II and Fig. 1; temperature = 25°.

The change in $T\Delta S$ is seen to be the determining factor in the observed decrease of pQ with increasing μ in all cases except the first. The data in Table III also show the large decrease of the pk_{123}' and pk_{132}' values compared to that of the pk_{12}' and pk_{13}' values with increasing μ (Fig. 2c) to be the result of the much larger $T\Delta S$ change with changing μ upon proton ionization from the II, III species.

The method described here for microconstant determinations is more accurate than other reported methods when R is at or near unity and the heats of proton dissociation of the groups involved vary considerably.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, SOUTH CAROLINA]

Ion-Solvent Interaction. The Interactions of Some Amines with Tertiary Ammonium Salts in Low Dielectric Solvents

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The conductances of solutions of tertiary ammonium salts have been studied at 25° in *o*-dichlorobenzene and chlorobenzene as a function of the concentration of added amines, such as pyridine and tri-*n*-butylamine. The results are consistent with the formation of a 1:1 cation-amine complex. The following order of increasing complex stability with tri-*n*-butylammonium ion in *o*-dichlorobenzene is observed: 4-cyanopyridine < acetonitrile < tri-*n*-butylamine < pyridine < 4-methylpyridine. The effect of solvent on the cation-amine complex equilibrium can be accounted for by postulating that the amine displaces one tightly bound solvent molecule in forming the complex.

Specific interaction between an electrophile and an anion or between a nucleophile and a cation, in solution, may be regarded² as a displacement of a solvating solvent molecule from the ion by the incoming electrophile or nucleophile. It would be of interest to study such interactions as a function of solvent, structure of anion and cation, and basicity (or acidity) and structure of the molecule displacing the solvent. It is hoped that some of the factors of importance in ion-solvent interaction may be elucidated in this manner. Fuoss and co-workers^{2,3} are actively engaged in studying anion interactions with solvents and added electrophiles. We report here the results of a study of the conduct-

ances of several amine salt-nucleophile systems in the solvents *o*-dichlorobenzene (ODCB) and chlorobenzene (CB) at 25°. It was hoped that the results could be interpreted in terms of cation-nucleophile interaction. Incidental to the foregoing study, the conductances of tri-*n*-butylammonium bromide and iodide were studied in ethylene chloride (EC). Increasing conductivity with age of solutions of amines in this solvent, indicative of amine-solvent reaction, precluded studies of salt-amine systems in this solvent.

Experimental

Materials.—ODCB (Allied Chemical Co., Solvay Process Division) was passed through alumina (Alcoa grade F-20) on a 30 × 2 cm. column and distilled on a 35 cm. column packed with glass helices. The middle fraction, b.p. 48° (5 mm.), was stored over alumina which had been fired to approximately 800° for 1 hr.

(1) Guy F. Lipscomb Fellow, 1962-1963.

(2) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1722 (1963).

(3) For recent leading references, see M. A. Coplan and R. M. Fuoss, *ibid.*, **68**, 1181 (1964).

Just prior to use the solvent was passed through a 30 × 2 cm. column the bottom half of which was packed with fired alumina and the top half with molecular sieve (Linde Air Products, type 5A). The specific conductance ranged between 3 and 8 × 10⁻¹¹ mhos/cm. CB (Dow Chemical Co.) was treated in exactly the same manner as ODCB, but had b.p. 45° (33 mm.) and specific conductance 7 × 10⁻¹¹ mhos/cm. Ethylene chloride (EC) (Dow Chemical Co.) was treated in the same fashion, b.p. 83.7°, specific conductance 4 × 10⁻¹¹ mhos/cm.

Pyridine (Py) (Merck reagent grade) was distilled from potassium hydroxide and then from barium oxide, b.p. 115–116°. Solutions (0.01 *M*) of Py in ODCB had specific conductances in the range 1–10 × 10⁻¹⁰ mhos/cm. 4-Cyanopyridine (4-CNPy) (Columbia Organic Chemicals Co.) was recrystallized from benzene and dried under vacuum, m.p. 78.0–79.0° (lit.⁴ m.p. 78.5–80.0°). 4-Methylpyridine (4-MePy) (Columbia Organic Chemicals Co.) was distilled under reduced pressure, b.p. 56° (32 mm.). It was necessary to use freshly distilled material since it turns brown on standing. A 0.01 *M* solution in CB had a specific conductance of 5 × 10⁻¹¹ mhos/cm. Tri-*n*-butylamine (TBA) (Matheson Coleman and Bell Division, The Matheson Co., practical grade) was refluxed under reduced pressure over potassium hydroxide for 2 hr. at 3 mm. and then distilled. The middle fraction was refluxed over barium oxide at 3 mm. for 1 hr. and then distilled. The middle fraction was collected, b.p. 57° (3 mm.). Methanol (MeOH) (Matheson Coleman and Bell Division, The Matheson Co., reagent grade) was refluxed over barium oxide for 2 hr. and distilled in a Vigreux column. The middle cut was taken, b.p. 64.8°. Acetonitrile (MeCN) (Matheson Coleman and Bell Division, The Matheson Co., spectral grade) was distilled through a 10 cm. column packed with glass helices, b.p. 81°.

Picric acid (HPi), recrystallized from ethanol, was supplied by R. E. Stamm. Tri-*n*-butylammonium picrate (TBAHPi) was prepared by the method of Witschonke and Kraus.⁵ The salt was recrystallized three times from 95% ethanol, m.p. 106.7° (lit.⁵ m.p. 106.5°). If the salt is subjected to heating under vacuum its melting point decreases, so freshly recrystallized samples were dried under vacuum at room temperature just prior to use. Tri-*n*-butylammonium bromide (TBAHBr) was prepared from TBA and 48% hydrobromic acid in diethyl ether. It was recrystallized seven times from ether, m.p. 74–75° (lit.⁶ m.p. 75°). Tri-*n*-butylammonium iodide (TBAHI) was prepared from 47% hydriodic acid and the amine in 95% ethanol. Recrystallization from ethyl acetate ten times gave a salt, m.p. 101.0–101.5° (lit.⁷ m.p. 101.2–101.7°). Pyridinium picrate (PyHPi)–pyridine solutions were prepared by the addition of picric acid to an excess of pyridine in ODCB. This method was necessary due to the slow rate of solution of the salt in this solvent.

Solutions.—All salts were weighed in a nitrogen-filled drybox. The solutions were made up by weight and the molarities calculated using the density of the solvent. Solutions for conductance measurements were made by adding a concentrated stock solution from a weight buret directly to the conductance cell containing a weighed portion of solvent.

Measurements.—All conductance measurements were made at 25.00° in an oil-filled thermostat. The temperature was constant within ±0.005°. The two conductance cells used were of the Kraus type with bright platinum electrodes. The cell constants, 0.01800 and 0.03063 cm.⁻¹, were determined by comparison with a similar cell with platinized electrodes and a cell constant of 0.6297 cm.⁻¹ as determined using a 0.01 Demal potassium chloride solution.⁸

The conductance bridge used has been described previously.⁹ Densities were determined using a Lipkin pycnometer, calibrated with water and mercury.

Physical constants.—These are given for the three solvents in the order ODCB, EC, and CB: viscosity (cp.), 1.272,¹⁰ 0.785,¹¹ 0.752¹²; density (g./ml.), 1.3007, 1.2455,¹¹ 1.1011; dielectric constant, 10.06,¹³ 10.23,¹¹ 5.621.¹⁴

Results

The equivalent conductances, Λ , of the various salts in the three solvents with and without addends are listed in Table I. In each case, the specific conductance of the solvent, one-hundredth or less of the total, was subtracted from the observed specific conductance to yield the specific conductance presumed due to the salt. Also included in Table I is the conductance of a 1.804 × 10⁻⁴ *M* solution of TBAHPi in ODCB as a function of the concentration of added MeCN. The treatment of the conductance data to yield derived constants is described below for each salt.

TBAHPi in ODCB and EC.—The method of Shedlovsky¹⁵ was used.

$$1/(\Lambda S) = 1/\Lambda_0 + \Lambda C S y_{\pm}^2 / K \Lambda_0^2 \quad (1)$$

where S is the Shedlovsky function¹⁵ and y_{\pm}^2 is calculated from the Debye–Hückel theory. Both of these quantities depend upon the value of the limiting equivalent conductance, Λ_0 , but since neither are different from unity by more than 3% in any of these systems the results are not particularly sensitive to the value of Λ_0 used in calculating them. A plot of $1/(\Lambda S)$ vs. $\Lambda C S y_{\pm}^2$ should yield a straight line. Above 2 × 10⁻⁴ *M*, curvature in the plots of eq. 1 were observed in the pure solvents, presumably due to triple-ion formation. The plots were linear below this concentration. In ODCB the intercept was about 0.5, corresponding to Λ_0 of 2, and in EC the intercept was 0.05, corresponding to a Λ_0 of 20. These values were not used in calculations of either the S function or the activity coefficient. The reason for the low values of Λ_0 will be discussed later, but more realistic values were estimated by assuming the ratio of Λ_0 for the salt to that of tetra-*n*-butylammonium picrate (Bu₄NPi) in either solvent was equal to the same ratio in nitrobenzene, where more unequivocal values have been obtained. The following values of Λ_0 were used in these estimations: Bu₄NPi in PhNO₂¹⁶ 27.9, in EC¹⁷ 57.4, and in ODCB⁹ 36.8; TBAHPi in PhNO₂⁵ 28.9. The values so estimated appear in Table II in column 3 in parentheses. From the slopes of the plots of eq. 1, values of the product $\Lambda_0^2 K$ may be obtained where K is the apparent ion-pair dissociation constant for the salt. In the pure solvents, the quantity K_0 , the ion pair dissociation constant for the salt in the pure solvent, was obtained by dividing the product $\Lambda_0^2 K_0$ by the estimated value of Λ_0^2 . The value of $\Lambda_0^2 K_0$ of 7.18 × 10⁻⁵ in EC compares favorably with the value 7.56 × 10⁻⁵ obtained by Mead, Fuoss, and Kraus¹⁸ using somewhat higher salt concentrations than those employed in this work. When addends were present, the ratio, R , of the slope in pure solvent, $1/(\Lambda_0^2 K_0)$, to that in a given addend solution, $1/(\Lambda_0^2 K)$, was calculated. R is plotted vs. addend concentration in Fig. 1 and Fig. 2. The Shedlovsky plots were linear below 2 × 10⁻⁴ *M* in the pure solvents and were linear

(4) D. G. Leis and B. C. Curran, *J. Am. Chem. Soc.*, **67**, 79 (1945).

(5) C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

(6) J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

(7) H. S. Young and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 4733 (1951).

(8) G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

(9) H. L. Curry and W. R. Gilkerson, *ibid.*, **79**, 4021 (1957).

(10) F. Accascina, E. L. Swarts, P. L. Mercier, and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S.*, **39**, 917 (1953).

(11) D. L. Fowler and C. A. Kraus, *J. Am. Chem. Soc.*, **62**, 2237 (1940).

(12) R. L. McIntosh, D. J. Mead, and R. M. Fuoss, *ibid.*, **62**, 506 (1940).

(13) P. H. Flaherty and K. H. Stern, *ibid.*, **80**, 1034 (1958).

(14) A. Maryott, U. S. National Bureau of Standards, Circular No. 514.

(15) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(16) E. G. Taylor and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1731 (1947).

(17) D. J. Mead, R. M. Fuoss, and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

(18) D. J. Mead, R. M. Fuoss, and C. A. Kraus, *J. Am. Chem. Soc.*, **61**, 3257 (1939).

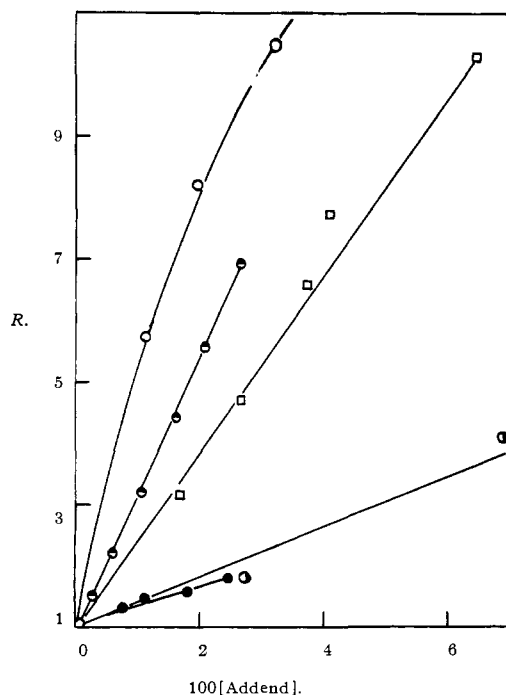


Fig. 1.— R vs. addend concentration; \circ , TBAHPi with TBA in ODCB; \bullet , TBAHPi with MeCN in ODCB; \bullet , TBAHPi with 4-CNPy in ODCB; \bullet , TBAHPi with MeOH in EC; \square , TBAHBr with Py in ODCB (the abscissa in this case is 1000[addend]).

at higher concentrations in the presence of addends. In ODCB-4-MePy solvent mixtures, the Shedlovsky plots were quite linear but gave a small *negative* intercept (about 0.5 reciprocal Λ -units). This is attributed to the presence of a small amount of impurity in the base which could not be removed even by using freshly distilled base. It was assumed that the slope obtained from the four points corresponding to the highest salt concentrations in each case was more nearly representative of the correct value.

Included in Fig. 1 are results calculated from data obtained in the titration of a $1.804 \times 10^{-4} M$ TBAHPi solution of ODCB with MeCN, Table I. At this concentration, the salt is dissociated to such a small extent that eq. 1 reduces to $\Lambda^2 C y_{\pm}^2 \cong \Lambda_0^2 K$. The ratios R in this case were obtained by dividing $\Lambda^2 C y_{\pm}^2$ at a particular acetonitrile concentration by that value in the absence of acetonitrile.

The slopes of the straight lines in Fig. 1 and 2 drawn through the points are recorded in Table II as K_L .

MeOH was the only addend whose effect on the conductivity of TBAHPi solutions in EC could be determined. The nitrogen bases apparently reacted with the solvent as noted in the introduction. As can be seen in Fig. 2, there is considerable departure of this system from a straight line in an R vs. [MeOH] plot. The value of K_L recorded in Table II was obtained from a straight line drawn approximately half-way between the two points.

TBAHPi in CB.—Triple-ion formation was evident at the concentrations of the salt employed. Values of $\Lambda_0^2 K$ in this solvent were obtained by the procedure of Fuoss and Kraus,¹⁹ taking into account the increased conductivity of the solutions due to triple ions. Here the conductance equation is

$$\Lambda C^{0.5} g(C) = \Lambda_0 K^{0.5} + (K^{0.5} \Lambda_3 / k)(1 - \Lambda / \Lambda_0) C \quad (2)$$

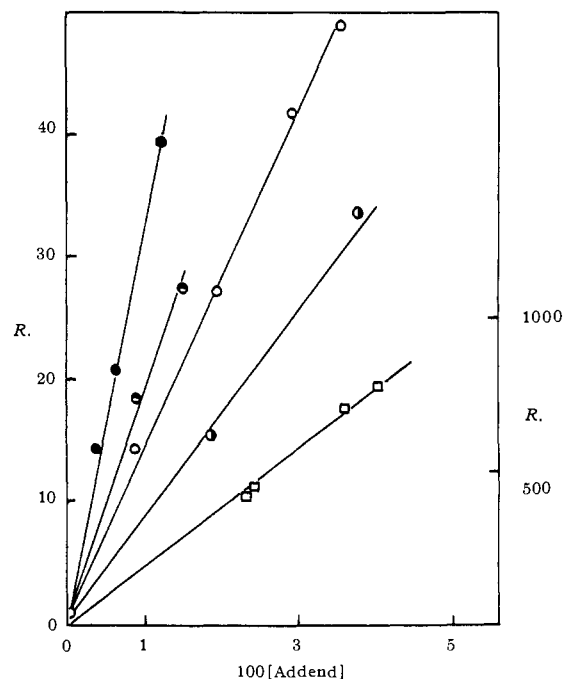


Fig. 2.— R vs. addend concentration; left-hand ordinate: \bullet , TBAHPi with 4-MePy in ODCB; \bullet , TBAHPi with 4-MePy in CB; \circ , TBAHPi with Py in ODCB; \circ , TBAHPi with Py in CB; right-hand ordinate: \square , PyHPi with Py in ODCB.

where $g(C)$ is a known¹⁹ function of Λ_0 , taking into account ion atmosphere effects; $g(C)$ is very close to unity for these solutions. The constant k is the triple-ion dissociation constant and is assumed to be the same for both possible ion triples. In practice this is justified by the linearity of a plot of $\Lambda C^{0.5}$ vs. C (eq. 2). The value of Λ_0 was estimated as described in the case of ODCB and EC as solvents, utilizing in addition Λ_0 (Bu_4Npi in CB) = 36.8.²⁰ K_0 in Table II was thus calculated from the intercept of a plot of eq. 2 in the pure solvent. Values of the ratio R were obtained from the intercepts in the presence of added pyridine and 4-methylpyridine and are plotted vs. addend concentration in Fig. 2. The slopes of these latter plots appear in Table II as K_L .

TBAHBr and TBAHI.—These salts were studied in ODCB in an effort to test the effect of changing the anion in the salt on the interaction with added bases. Conductance data for both salts were sensitive to the solvent conductivity, the iodide more so than the bromide. Data for both in EC are reported here, but only the bromide data are given for the solvent ODCB. These salts showed evidence of triple-ion formation in the 10^{-4} to $10^{-3} M$ concentration range, but plots according to eq. 2 showed decreasing slope with increasing salt concentration. A rough plot of $\Lambda^2 C$ vs. C resulted in a fairly straight line. This suggested to us that perhaps here was another example of unsymmetrical triple-ion formation similar to the $(\text{FHF})^-$ ion. We suppose the one formed here is the cation type, $(\text{TBAH})_2\text{Br}^+$. The conductance function in such a case has been derived by Wooster²¹ (eq. 3)

$$(\Lambda y_{\pm} / m)^2 C / (1 - \Lambda / \Lambda_0) = \Lambda_0^2 K [1 + \frac{hC(1 - \Lambda / \Lambda_0)}{k_+}] \quad (3)$$

(19) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933).

(20) J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, **68**, 1581 (1964).

(21) C. B. Wooster, *J. Am. Chem. Soc.*, **59**, 377 (1937).

TABLE I

EFFECT OF ADDENDS ON EQUIVALENT CONDUCTANCES OF TRISUBSTITUTED AMMONIUM SALTS AT 25°

10°C	10A	10°C	10A	10°C	A	10°C	A
TBAHPi in ODCB				+ 0.03218 M TBA		C (Salt) = 1.804 × 10 ⁻⁴ M C, MeCN	
0.2084	1.369	0.2666	1.217	0.8148	2.329	0.0000	0.5452
0.4457	0.9473	0.5407	0.8643	1.651	1.643	0.00259	0.6746
0.7636	0.7303	0.9493	0.6572	2.632	1.307	0.00586	0.8109
1.119	0.6083	1.344	0.5571	3.545	1.129	0.01063	0.9806
1.491	0.5307	1.753	0.4904	4.711	0.9825	0.01619	1.151
1.870	0.4757	2.166	0.4438			0.02096	1.285
2.343	0.4285	2.559	0.4100			0.02666	1.433
2.790	0.3945	2.974	0.3824				
3.266	0.3669	3.397	0.3600				
+ 0.00890 M Py		+ 0.01951 M Py		10°C	10A	10°C	10A
1.347	2.105	0.4878	5.162	TBAHPi in CB			
3.026	1.418	0.8773	3.673	1.065	1.104	8.331	0.8245
4.995	1.114	1.812	2.559	2.397	0.8982	1.449	0.9944
7.140	0.9385	2.619	2.132	3.595	0.8428	2.773	0.8644
9.400	0.8240	3.956	1.741	4.722	0.8246	4.501	0.8247
+ 0.02902 M Py		+ 0.03559 M Py		6.099	0.8096	6.406	0.8195
0.7553	4.929	1.220	4.223	7.205	0.8149		
1.691	3.282	2.311	3.064	+ 0.00894 M 4-MePy		+ 0.01497 M 4-MePy	
3.331	2.343	5.012	2.088	0.6203	5.610	0.4485	7.935
5.381	1.881	7.529	1.712	1.302	3.958	0.9537	5.483
7.755	1.550	9.821	1.503	1.836	3.406	1.772	4.130
+ 0.00374 M 4-MePy		+ 0.00654 M 4-MePy		2.502	2.999	2.643	3.497
0.2444	5.520	0.2695	6.449	3.297	2.704	3.565	3.114
0.4726	3.857	0.5742	4.249	4.094	2.513	4.280	2.935
0.8754	2.776	0.9154	3.308	4.924	2.370	5.011	2.795
1.211	2.341	1.359	2.683	5.474	2.303	5.819	2.682
1.616	2.015	1.852	2.281	6.198	2.228	6.598	2.595
2.011	1.801	2.282	2.047	+ 0.01872 M Py		+ 0.03781 M Py	
2.413	1.639	2.699	1.878	0.6800	4.701	0.6745	6.874
2.816	1.515	3.132	1.741	1.479	3.324	1.303	5.159
3.258	1.407	3.612	1.620	2.270	2.784	2.162	4.139
+ 0.01219 M 4-MePy		+ 0.00751 M 4-CNPy		3.250	2.443	2.911	3.679
0.2368	9.810	0.3105	1.305	4.087	2.266	3.701	3.372
0.5073	6.404	0.6351	0.9251	5.084	2.128	4.469	3.166
0.7947	5.002	1.139	0.6983	5.960	2.045	5.144	3.019
2.041	3.014	1.575	0.5978	10°C	A	10°C	A
2.490	2.715	2.121	0.5193	TBAHPi in EC			
2.822	2.544	2.619	0.4703	0.1628	2.091	0.9740	0.8749
3.347	2.330	3.090	0.4354	0.2971	1.559	1.742	0.6588
+ 0.01113 M 4-CNPy		3.585	0.4066	0.6405	1.073	2.508	0.5525
0.2279	1.611	4.032	0.3857	+ 0.02743 M MeOH		+ 0.06909 M MeOH	
0.5007	1.101			0.2218	2.131	0.2331	3.482
0.8123	0.8720			0.5192	1.586	0.5430	2.326
1.194	0.7255			0.7836	1.299	0.8391	1.889
1.637	0.6254	+ 0.02465 M 4-CNPy		1.083	1.112	1.197	1.591
2.143	0.5510	0.3060	1.525	1.554	0.9319	1.633	1.357
2.596	0.5027	0.6695	1.043	2.289	0.7725	1.947	1.260
+ 0.01787 M 4-CNPy		1.010	0.8550	10°C	10A	10°C	10A
0.3315	1.375	1.401	0.7310	TBAHBr in ODCB			
0.5823	1.044	1.885	0.6341	+ 0.00167 M Py			
0.9827	0.8317	2.443	0.5607	0.6222	3.587	0.3528	3.560
1.302	0.7058	2.952	0.5135	1.630	3.378	0.8542	3.208
1.779	0.6068	3.545	0.4709	3.408	3.377	1.752	3.084
2.264	0.5409	4.064	0.4422	5.341	3.401	2.898	3.048
2.724	0.4951	+ 0.01980 M TBA		8.097	3.487	3.780	3.016
3.206	0.4584	0.8151	2.089	0.4338	3.688	4.765	3.017
+ 0.01145 M TBA		1.700	1.446	0.6417	3.422	5.643	3.046
1.147	1.493	2.596	1.172	1.097	3.221	6.660	3.035
2.369	1.026	3.513	1.009	2.275	3.434	7.399	3.042
4.022	0.7814	4.423	0.8998	3.791	3.471		
5.614	0.6619	5.488	0.8104				
7.417	0.5771						

TABLE I (Continued)

10°C	10 ² Δ	10°C	10 ² Δ	10°C	Δ	10°C	Δ
+ 0.00268 M Py		+ 0.00375 M Py		TBAHI in EC			
0.5603	3.377	0.6271	3.526	0.1731	6.355	0.1477	0.7647
1.343	3.045	1.022	3.279	0.3324	4.654	0.2237	0.6430
2.247	2.971	1.640	3.130	0.5939	3.512	0.3032	0.5740
3.105	2.943	2.374	3.058	0.7683	3.073	0.3897	0.5265
4.072	2.928	3.127	3.022	0.8392	2.971	0.8447	0.4205
4.857	2.922	3.959	3.003	1.154	2.546	1.366	0.3813
5.746	2.921	4.821	2.993	1.499	2.249	2.522	0.3526
6.449	2.920	5.775	2.988	1.675	2.109	3.644	0.3453
7.263	2.923	6.579	2.985	3.307	1.523		
+ 0.00411 M Py		+ 0.006505 M Py		4.961	1.259		
0.5507	3.726	0.9003	3.652	6.197	1.137		
1.259	3.260	1.798	3.311	10°C	10A	10°C	10A
2.172	3.105	2.730	3.201	PyHPi in ODCB			
3.130	3.049	3.785	3.145	+ 0.03608 M Py		+ 0.04038 M Py	
4.119	3.020	4.656	3.122	1.175	6.874	1.673	6.127
5.260	3.006	5.683	3.109	2.978	4.332	3.816	4.080
6.154	2.999	6.604	3.106	4.346	3.580	6.057	3.229
7.000	2.999	7.380	3.104	6.305	2.944	8.396	2.730
10°C	Δ	10°C	Δ	7.862	2.620	+ 0.01313 M HPi	
TBAHBr in EC				9.013	2.440	12.43	0.08496
0.5277	0.3104	5.658	0.1765	+ 0.02325 M Py		31.32	0.06539
1.222	0.2354	6.874	0.1735	0.8339	6.444	+ 0.02418 M Py	
2.359	0.2008	8.000	0.1715	1.638	4.623	0.8451	6.527
3.168	0.1904	9.275	0.1701	2.656	3.546	2.715	3.657
4.269	0.1824			4.060	2.919	4.042	2.978
				5.791	2.418	5.213	2.656
						6.677	2.282

TABLE II

DERIVED CONSTANTS AT 25°

Solvent	Δ ₀ ^a	10 ¹⁰ K ₀	Addend	K _L
TBAHPI				
ODCB	2 (38.1)	2.86	TBA	560 ± 40
			Py	1370 ± 70
			4-MePy	3240 ± 210
			4-CNPy	40 ± 7
			MeCN	212 ± 6
EC	20 (59.4)	203	MeOH	41
CB	(43.0)	0.0048	Py	820 ± 50
			4-MePy	1830 ± 80
TBAHBr				
ODCB	(45.2)	0.022	Py	1450 ± 90
EC	(70.5)	8.07		
TBAHI				
EC	(69.5)	157		
PyHPi				
ODCB	(46.8)	0.35 ^b	Py	19,000 ± 500

^a Value preceding () obtained by extrapolation in pure solvent. Value in () estimated as described in text. ^b As determined in the presence of 0.01313 M HPi.

where $h = 2\lambda_0/\Lambda_0 - 1 + (1 - \lambda_0/\Lambda_0)^2/(1 + k_+/C)$. The function m^{21} corrects Λ for departures due to ion-atmosphere effects, λ_0 is the limiting equivalent conductance of the salt corresponding to the lone triple ion and counter-ion, and k_+ is the triple-ion dissociation constant. Equation 3 was fitted to the conductance data assuming $\lambda_0/\Lambda_0 = 0.667$. The Wooster plot, eq. 3, for the bromide in ODCB was quite steep, and gave an intercept so close to zero as to be of doubtful value in obtaining $\Lambda_0^2 K_0$. The intercepts were first

obtained in the presence of added pyridine, plotted vs. pyridine concentration and extrapolated to zero pyridine to give the value of $\Lambda_0^2 K_0$. The values of Λ_0 in nitrobenzene used to estimate Λ_0 in the solvents ODCB and EC were calculated from Λ_0 for the picrate in PhNO₂ and the bromide,²² iodide,²³ and picrate²³ ion conductances in PhNO₂. The values of K_0 calculated from the intercepts in the two solvents and the estimated value of Λ_0 are given in Table II. The ratios, R , for TBAHBr in ODCB in the presence of added pyridine are plotted vs. pyridine concentration in Fig. 1. In EC, k_+ was found to be 4.0×10^{-4} for the iodide and 7.5×10^{-5} for the bromide. In ODCB, k_+ was found to be 1.7×10^{-6} for the bromide.

PyHPi in ODCB.—The conductance data in the presence of excess HPi was treated by the method of Fuoss and Kraus,¹⁹ using eq. 2, to yield the intercept, $\Lambda_0^2 K_0$. The estimated value of Λ_0 appearing in Table II was calculated using the value 34.7 as determined in PhNO₂.⁵ K_0 was calculated using this estimate of Λ_0 and appears in Table II. In the presence of excess pyridine, triple-ion formation was no longer apparent. The values of $\Lambda_0^2 K$, from which the ratios, R , were calculated, were obtained from the slopes of Shedlovsky plots (eq. 1). R is plotted vs. pyridine concentration in Fig. 2.

The conductances as a function of added TBA are shown in Fig. 3 for PyHPi in ODCB-Py solution and for 4-methylpyridinium picrate in ODCB-4-methylpyridine solution.

The addition of 0.023 M Py to a 1.5×10^{-4} M solu-

(22) H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 4507 (1959).

(23) E. Hirsch and R. M. Fuoss, *ibid.*, **82**, 1018 (1960).

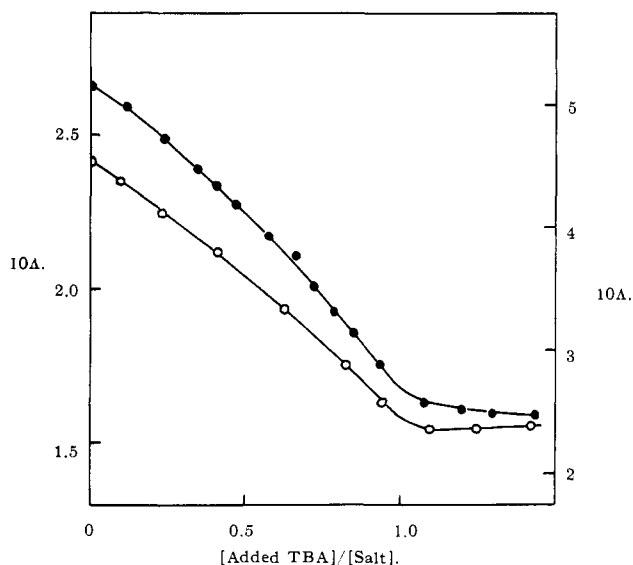
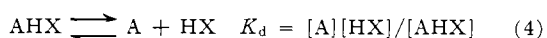


Fig. 3.—Open circles, left-hand ordinate, Λ for $5.652 \times 10^{-4} M$ PyHPi in $0.02326 M$ Py in ODCB *vs.* mole ratio of added TBA to salt. Upper curve, closed circles, right-hand ordinate, a similar plot of Λ for $3.715 \times 10^{-4} M$ 4-MePyHPi in $0.01658 M$ 4-MePy in ODCB *vs.* mole ratio of added TBA to salt.

tion of $Bu_4N^+Pi^-$ in ODCB increased the conductance by only 2%. The addition of $0.033 M$ acetonitrile to a $1.87 \times 10^{-4} M$ solution of the same salt in the same solvent gave a 6% increase in the conductivity.

Discussion

The values of Λ_0 appearing in Table II for TBAHPi in ODCB and EC, obtained by extrapolation, are seen to be quite low compared with what are believed to be the more nearly correct values, those in parentheses. Elliott and Fuoss²⁴ and Kraus and co-workers^{5,16} have shown this effect to be due to acid-base dissociation in the case of amine salts (eq. 4)



where A represents the amine, HX the acid, and AHX the ion pair. Activity coefficients of all uncharged species are assumed to be unity.

According to Elliott and Fuoss,²⁴ the conductance equation (eq. 1) is replaced by

$$1/(\Delta S) = (1 + K_d^{0.5}/K_0^{0.5})/\Lambda_0 + \Delta C S y_{\pm}^2 / K_0 \Lambda_0^2 \quad (5)$$

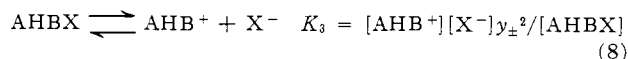
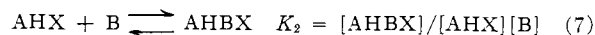
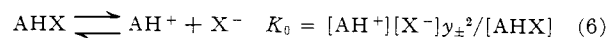
It is seen from eq. 5 that the effect of acid-base dissociation is to change the intercept of a Shedlovsky plot, leaving the slope unchanged (as long as the ion concentration is low enough that the Shedlovsky function and activity coefficients are not too different from unity). Accordingly, we calculate that TBAHPi in ODCB has a K_d of 9×10^{-8} , while in EC it is 7×10^{-8} . Pearson and Vogelsong,²⁵ using a spectrophotometric method, found K_d to be 3.41×10^{-5} in EC at 25° for the salt of the same amine with the weaker acid, 2,4-dinitrophenol.

The increased conductance of solutions of TBAHPi in ODCB in the presence of added TBA is due to some factor other than repression of acid-base dissociation. The ratio R appearing in Fig. 1 and 2 in each case is calculated from the slope of a plot of the modified Shedlovsky equation, eq. 5. As pointed out above,

(24) M. A. Elliott and R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 294 (1939).

(25) R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1038 (1958).

the slope is unaffected by acid-base dissociation. Kraus and Witschonke,⁵ observing similar effects in $PhNO_2$ as solvent, attributed their results to the interaction of the added amine with the acidic hydrogen atom on the cation, resulting in increased ion-pair dissociation. We believe their interpretation to be correct. No such effects were obtained upon addition of either Py or MeCN to solutions of $Bu_4N^+Pi^-$ in ODCB. Such interaction as occurs with TBAHPi can be viewed as proceeding according to the following equilibria, in addition to eq. 4



where for generality B may not be the same as the amine A. Kolthoff and co-workers²⁶ have interpreted conductometric titration curves in acetonitrile in terms of similar equilibria involving complex formation between anions and suitable weak acids. Complex formation between base and protonated base has been postulated²⁷ to explain the behavior of the potentials of cells containing amines and their corresponding ammonium salts in acetonitrile.

In eq. 6, 7, and 8, AHBX represents any complex between base and the ion pair, AHX. AHB⁺ represents a complex between cation AH^+ and the base B. In the following derivation of the conductance equation, acid-base dissociation will be assumed to be repressed, as it would be for B the same as A. In the presence of a large (compared to AHBX or AHB⁺) and constant concentration of B, the equivalent conductance, corrected for ion-atmosphere effects, of a salt solution of concentration C is given by $\Delta S = \alpha_0 \Lambda_0 + \alpha_B \Lambda_B$, where $\alpha_0 = [AH^+]/C$, $\alpha_B = [AHB^+]/C$, and Λ_B is the limiting equivalent conductance of the salt AHBX. Utilizing the fact that $[AHX] + [AHBX] = C(1 - \alpha_0 - \alpha_B)$ and the relation K_2 , we find that

$$[AHX] = C(1 - \alpha_0 - \alpha_B)/(1 + K_2[B])$$

Using the relations K_0 and K_3 , as well as K_2 , we find

$$\alpha_0 = \Delta S / [\Lambda_0(1 + \Lambda_B K_L [B] / \Lambda_0)]$$

where $K_L = K_2 K_3 / K_0$. Also

$$\alpha_0 + \alpha_B = [X^-]/C = \frac{\Delta S(1 + K_L [B])}{\Lambda_0(1 + \Lambda_B K_L [B] / \Lambda_0)}$$

Inserting these relations into $K_0 = C \alpha_0 (\alpha_0 + \alpha_B) y_{\pm}^2 / [AHX]$, and rearranging, we obtain

$$1/(\Delta S) = (1 + K_L [B]) / \Lambda_0(1 + \Lambda_B K_L [B] / \Lambda_0) + \frac{\Delta C S y_{\pm}^2 (1 + K_2 [B])(1 + K_L [B])}{[K_0 \Lambda_0^2 (1 + \Lambda_B K_L [B] / \Lambda_0)^2]} \quad (9)$$

The ratio R can be seen to be given, according to eq. 9, by

$$R = (1 + \Lambda_B K_L [B] / \Lambda_0)^2 / [(1 + K_2 [B])(1 + K_L [B])] \quad (10)$$

The intercepts of the Shedlovsky plots cannot be determined with sufficient precision (they are too close

(26) For leading references, see I. M. Kolthoff and M. K. Chantooni, *ibid.*, **85**, 2195 (1963).

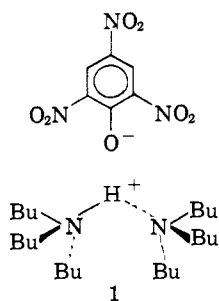
(27) J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, *Talanta*, **11**, 93 (1964).

to zero) in the solutions we are dealing with to allow evaluation of the quantity Λ_B/Λ_0 . We shall assume the latter ratio to be unity here. This is reasonable considering that the value of the ratio $\Lambda_0(\text{Bu}_4\text{N}^+\text{Pi}^-)/\Lambda_0(\text{TBAHPi})$ is 0.965 in PhNO_2 .⁵ Then eq. 10 reduces to

$$R \simeq (1 + K_L[\text{B}]) / (1 + K_2[\text{B}]) \quad (11)$$

The curve in Fig. 1 for TBAHPi in ODCB-TBA mixtures was calculated using $K_L = 560$ (Table II) and $K_2 = 25$. Due to the approximation that $\Lambda_B/\Lambda_0 = 1.00$, we believe these to be the minimum values for K_L and K_2 .

Curvature in R vs. $[\text{B}]$ plots was not observed for any of the other salt-addend systems studied here. It is noteworthy that TBA was the strongest base used in the present work. Similar curvature can be found in the work of Kraus and Witschonke in the case of the relatively strong bases Et_3N and piperidine added to trisubstituted hydroxyammonium salts in PhNO_2 .⁵ The $(\text{TBA})_2\text{HPi}$ complex can be represented by structure 1 where the plane of the benzene ring in



the picrate ion is perpendicular to the $\text{N}-\text{H}\cdots\text{N}$ plane. A Stuart-Briegleb model of the complex shows that the phenolic oxygen on the picrate ion can approach the proton in the complex almost as closely as in the uncomplexed ion pair. At least one butyl group on each amine has lost considerable rotational freedom due to the steric requirements of the picrate ion.

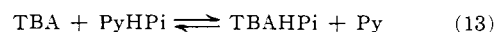
In the presence of excess HPi, acid-base dissociation of PyHPi is presumed repressed in ODCB. Large increases in conductance, and consequently in the ratio R , are observed upon the addition of excess Py to PyHPi solutions in ODCB. The fact that R is linear in the $[\text{Py}]$ is interpreted as meaning that $K_2[\text{Py}]$ is much less than unity. The only complex of importance in this system then is $(\text{Py})_2\text{H}^+$. The large value of K_L for the formation of the latter complex compared to that for the corresponding TBA complex can only be attributed to the increased importance of steric factors in acid-base interaction when the size of the acid, the cation AH^+ here, becomes large compared to the proton, as pointed out by Brown.²⁸ The butyl groups on both TBA molecules undoubtedly hinder the approach of the second TBA molecule to the TBAH^+ cation, compared to the relatively unhindered approach of a second Py molecule to the PyH^+ cation. TBA is still a strong enough nucleophile, compared to Py , that it forms the stable complex, 1 (eq. 7), while Py does not do so with PyHPi .

The values of R as a function of $[\text{B}]$ were linear for TBAHPi in the presence of Py and 4-MePy as B in ODCB and CB and also of 4-CNPy and MeCN as B

in ODCB. Apparently the concentration of any base-ion pair complex, AHB^+ , is so small that eq. 11 reduces to eq. 12

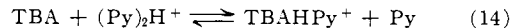
$$R \simeq (1 + K_L[\text{B}]) \quad (12)$$

At the concentrations utilized in the present work, all of the salts exist in solution principally in the form of ion pairs. If TBAHPi is dissolved in a solvent such as ODCB containing a large excess of a base such as pyridine, as weak a base as it is, does the salt exist now as TBAHPi ion pairs or PyHPi ion pairs? A numerical value for the equilibrium constant, K_4 , for the reaction



would be desirable. $K_4 = K_{dP}/K_{dT}$, where K_{dP} is the acid-base dissociation constant for PyHPi and K_{dT} is that for TBAHPi. The latter is known, but the former is not.

It can be seen in Fig. 3 that as TBA is added to a solution of PyHPi in excess Py in ODCB solvent, Λ (calculated here using the stoichiometric concentration of HPi in the system as the electrolyte concentration) decreases almost linearly with increasing TBA concentration until an amount of TBA equivalent to the initial concentration of PyHPi has been added, after which point Λ remains fairly constant as more TBA is added. This result is interpreted as indicating that reaction 13 goes essentially to completion, even in the presence of a 100-fold excess of pyridine. Further, the cation species in solution undergoes the following displacement reaction (eq. 14).



We thus assume that the constants, K_L , for solutions of TBAHPi in the presence of the addends Py , 4-MePy, 4-CNPy, and MeCN all correspond to equilibria of the type $\text{TBAH}^+ + \text{B} \rightleftharpoons (\text{TBA})\text{HB}^+$, where B represents the particular addend involved. The value of K_L , 1450 ± 90 , for solutions of TBAHBr in ODCB in the presence of added Py is seen in Table II to be the same as that for the picrate salt, 1370 ± 70 , within experimental error. This is further confirmation that the effect primarily involves cation and base and is unaffected by the nature of the anion. The order of increasing basicity, as represented by K_L , toward the acid TBAH^+ in ODCB is thus 4-CNPy < MeCN < TBA < Py < 4-MePy. As noted in the paragraph above, TBA is probably reduced in basicity due to steric hindrance. A Hammett plot of $\log K_L$ vs. σ^{29} for the three pyridines in ODCB gives a remarkably straight line with a slope of $\rho = -2.30$. The fact that acetonitrile forms a fairly stable complex was surprising since it is usually considered to be quite weak as a base.³⁰

The ratio of K_L for 4-MePy to that of Py in ODCB is 2.4 ± 0.3 and in CB as solvent it is 2.2 ± 0.2 , the same within experimental error. Specific solvent effects appear to be absent in these two solvents in the displacement of one base by another from the cation

(29) σ -values obtained from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). We are indebted to one of the referees for pointing this out to us.

(30) See E. M. Arnett, "Quantitative Comparisons of Weak Organic Bases," in "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Eds., Interscience Publishers, Inc., New York, N. Y., 1963, p. 278.

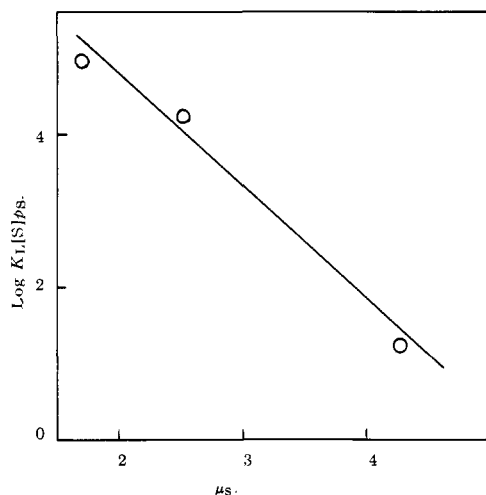
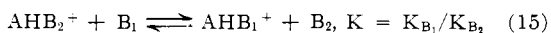
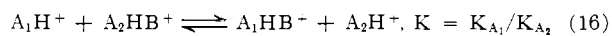


Fig. 4.—Plot of $\log K_L[S]p_S$ vs. solvent dipole moment, μ_S , for TBAHPi and Py in PhNO₂, ODCB, and CB solvents.

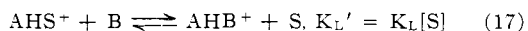
(eq. 15) as long as the structural difference between



the two bases is far removed from the reaction site. Displacement of one cation by another from a base complex does exhibit some variation with solvent. In PhNO₂³¹ at 25°, K_L is 58 for the reaction $\text{PyH}^+ + \text{Py} \rightleftharpoons (\text{Py})_2\text{H}^+$ and is 6.2 for the reaction $\text{TBAH}^+ + \text{Py} \rightleftharpoons (\text{TBA})\text{HPy}^+$. The ratio of the first to the second K_L is then 9.4 in PhNO₂. From Table II, we calculate the ratio to be 14 in ODCB. In this case, the displacement reaction is eq. 16. Specific solvent

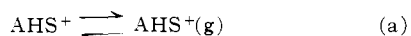


interaction between the negatively substituted benzene solvent molecules and the free pyridines in eq. 15 apparently does not play as important a role as in the case of the cation displacement (eq. 16). We are thus led to write the cation–base equilibrium in the form

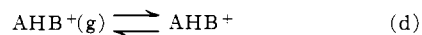


where S represents a solvating solvent molecule being displaced from the cation. This scheme is the cation analog of one proposed by D'Aprano and Fuoss² in connection with interaction between bromide ion and *p*-nitroaniline in acetonitrile solvent.

Changing the solvent had a large effect on the TB-AH⁺–Py association equilibrium. K_L is 6.2 in PhNO₂,³¹ increases to 1370 in ODCB, and decreases to 820 in CB. If eq. 17 is a reasonable representation of the process in solvent S, then there are two opposing factors operative: interaction between S and the cation AH⁺ in the AHS⁺ complex, and interaction between the uncomplexed solvent molecule S and its neighboring solvent molecules. The following stepwise processes will be considered in assessing the role of the various factors in eq. 17; transfer of reactants to the gas phase (a and b), conversion of reactants to products in the gas phase (c), and transfer of products from the gas to the solution phase (d and e). Then



(31) Witschonke and Kraus, ref. 5, have given data from which these values may be calculated if eq. 12 is assumed to be applicable.



where (g) denotes the component in the gas phase. Since $K_L[\text{S}]$ is independent of concentration units, standard states for reactants and products may be chosen as the pure substances for B and S and ideal 1 M solutions for the cations. ΔF° for eq. 17 is the sum of the standard free energies of reactions a through e. If solvent molecule and the base B are not too different in size and shape then the free-energy changes corresponding to a and d should be about equal and are opposite in sign; that is, the interaction between the cation AHS⁺ and surrounding solvent is presumed equal to that between AHB⁺ and the surrounding solvent. The base solutions are dilute enough that we will consider them to be ideal. Then the free-energy change for process b will not vary as the solvent changes. The free-energy change for (e) is given by $\Delta F_e^\circ = RT \ln p_S$, where p_S is the vapor pressure of the solvent, and the gas-phase pressures are taken to be 1 atm. in the standard state. Now $\Delta F_{17}^\circ = \Delta F_b^\circ + RT \ln p_S + \Delta F_c^\circ$, or, rearranging, $\log K_L[\text{S}]p_S = \text{constant} - \Delta F_c^\circ/(2.303RT)$ where the constant contains ΔF_b° . We may define the quantity $\Delta F_c^\circ/(2.303RT)$ as $n_B - n_S$, where n_B is the free-energy change divided by $2.303 \cdot RT$ for the process $\text{AH}^+ + \text{B} \rightleftharpoons \text{AHB}^+$, and n_S is the corresponding value for the process $\text{AH}^+ + \text{S} \rightleftharpoons \text{AHS}^+$. Thus, n_B and n_S are measures of the nucleophilic reactivity of B and S toward the electrophile AH⁺ in the gas phase. We thus obtain eq. 18. We, at

$$\log K_L[\text{S}]p_S = \text{constant} - n_B + n_S \quad (18)$$

the moment, are interested in the principal factors that govern n_S , and thus K_L as a function of solvent. A plot of $\log K_L[\text{S}]p_S$ vs. the solvent dipole moment is shown in Fig. 4 for $\text{TBAH}^+ + \text{Py}$ in PhNO₂, ODCB, and CB. The vapor pressures at 25° used were: PhNO₂³² 0.279 mm., ODCB³³ 1.35 mm., and CB³³ 11.5 mm. The dipole moments³⁴ of the gaseous molecules used were: PhNO₂ 4.27 D., ODCB 2.52 D., and CB 1.70 D. The three points almost fall on a straight line. If an ion-dipole model is used for the interaction between AH⁺ and S, then $n_S = -e\mu_S/(2.303kTr_S^2)$, where e is the charge on the cation, μ_S is the moment of the solvent dipole, and r_S is the distance between the center of the dipole and the charge. The slope is negative in Fig. 4, and from the numerical value of the straight line drawn through the points we calculate an apparent value of r_S of 5.9 Å. The value of r_S so obtained is rather large, but this is reasonable considering the crude model and the assumption of ideality for the Py solutions.

We conclude that the interaction between pyridine and the tri-*n*-butylammonium cation shows a large solvent effect in substituted benzene solvents. This effect may be roughly accounted for in terms of competition between ion–solvent interaction, as measured by the dipole moment of the solvating solvent molecule, and solvent–solvent interaction, as measured by the solvent vapor pressure. Further work is in

(32) Landolt-Bornstein, Zahlenwerte und Funktionen, 6th Ed., Springer-Verlag, Berlin, 1960, Band II, Teil 2, Bandteil a, p. 139, by interpolation.

(33) Ref. 32, p. 106.

(34) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, Chapters 9, 10, and 11.

progress on the effect of structure of the base and of the cation on cation-base interaction in aprotic solvents of low dielectric constant.

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[CONTRIBUTION FROM THE UNION CARBIDE CORPORATION, CHEMICALS DIVISION, RESEARCH AND DEVELOPMENT DEPARTMENT, SOUTH CHARLESTON, WEST VIRGINIA]

The Polyacrolein-Bisulfite Equilibrium

BY T. L. DAWSON AND F. J. WELCH

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To gain a better understanding of the structure and properties of polyacrolein in aqueous HSO_3^- solution the effect of the extent of reaction on the polyacrolein-bisulfite equilibrium has been investigated. Since the rate of dissociation of the polyacrolein-bisulfite adduct in cold aqueous solution is very slow, the extent of reaction of HSO_3^- with polyacrolein at equilibrium can be measured directly by iodine titration of the free HSO_3^- . The observed equilibrium constant for bisulfite addition decreases as the extent of the reaction of HSO_3^- with polyacrolein increases from 40 to 85 mole %, but in all cases rates of addition and dissociation and the observed equilibrium constant are smaller than those for monomeric aldehydes. It is suggested that these phenomena result primarily from changes in the relative concentrations of the various structures of the potential aldehyde and hydroxysulfonate groups in the polymer with the extent of reaction.

Introduction

The structure of polyacrolein prepared by free-radical polymerization processes is a distribution of cyclic intracetal-like groups, aldehyde groups, and interacetal-like crosslinks.^{1,2} The polymers are intractable and insoluble in nonreactive solvents. Kern, Schulz, and co-workers have discussed the structure of polyacrolein and demonstrated the reaction of the polymer with many typical aldehyde reagents.³⁻⁶ These reactions are believed to result in the simultaneous breaking of the interacetal-like crosslinks, since soluble reaction products are usually obtained.^{1,6}

Polyacrolein reacts with HSO_3^- to form a high molecular weight, water-soluble polyelectrolyte. This reaction involves an equilibrium between the polyacrolein, HSO_3^- , and polyacrolein-bisulfite adduct.^{1,3,7} The reaction is of particular interest because the structure of the polymer is complex and because an equilibrium occurs between negatively charged ions and a polymer chain containing negative charges. To the authors' knowledge no description has been given of the extent of the reaction of HSO_3^- with polyacrolein or of the magnitude of the equilibrium constant. To understand the structure of the polyacrolein-bisulfite adduct in aqueous solution and, likewise, to interpret its solution behavior, a quantitative description of the equilibrium properties is required. It is the purpose of this paper to describe some of the properties of the reaction.

Experimental

Preparation of Polyacrolein.—The polyacrolein samples used in this study were prepared by modifications of a previously described suspension polymerization.⁸ To a glass-lined, 5-gal. autoclave fitted with a three-blade stirrer was added under an atmosphere of nitrogen 7.90 kg. of heptane, a solution of 6.6 g. of disodium N-tallow- β -iminodipropionate (Deriphat 154, a product

of General Mills Co.) in 1.31 kg. of deionized water that had been adjusted to pH 4.5 with 2.8 g. of 85% H_3PO_4 , and 2.63 kg. of freshly distilled acrolein (commercial grade product of Union Carbide Corp., Chemicals Division). The temperature was adjusted to 20°, and then 13 g. of $\text{K}_2\text{S}_2\text{O}_8$ and 2.6 g. of AgNO_3 were added as 10% aqueous solutions. After 19-hr. reaction time, the resultant slurry was filtered and the solid product was washed thoroughly with water to remove unreacted acrolein and catalyst residues. It was then washed once with 12 l. of acetone containing 23 g. of phenothiazine and dried *in vacuo* at 65° for 24 hr. The product, 1.87 kg., was obtained as a fine, white powder having a reduced viscosity of 4.2 dl.-g.⁻¹ at 0.2% concentration in water saturated with SO_2 at 30°. The intrinsic viscosity of the sodium bisulfite adduct at 30° in 0.5 M aqueous NaCl solution was 2.0 dl.-g.⁻¹.

Although the theoretical carbon content of polyacrolein is 64.3%, the carbon contents of the polyacrolein samples used in this study were only 58.8 to 60.4%. The samples were found to contain about 1-3% physically absorbed water, based on Karl Fisher analysis. The remaining 4-6% of the polymer was assumed to be chemically bound water, present in the form of aldehyde hydrate and hemiacetal-like structures. The polymers were somewhat hygroscopic. Total water contents as high as 22% were obtained after exposure to 100% relative humidity at room temperature. By rigorous drying, over P_2O_5 at 56° (1 mm.) for 24 hr., the carbon content increased to 62.8%; that is, almost 98% of the theoretical value. In general, the more thoroughly the polyacrolein is dried, the less hygroscopic it is and the slower its rate of reaction with aldehyde reagents.

Two methods of analysis were employed to determine total carbonyl in the polyacrolein. In the first method⁴ the reaction of polyacrolein with hydroxylamine hydrochloride in the presence of pyridine at ambient temperature for 64 hr. was followed by titration of the liberated HCl. After correction for the total water contained in the polyacrolein, this method indicated an increase in the mole % aldehyde reacted from 74 to 80% over the time interval of 16-64 hr. Some difference has been observed in the rate with which polyacrolein reacts with the reagent.⁴ Differences in the degrees of hydration, ring formation, and even particle size and porosity could contribute to this. It is, therefore, quite difficult to choose a final value for the extent of reaction because the reaction is slow at room temperature, particularly at high extents of reaction. Our results obtained by this method are in the same range found by Schulz, *et al.*,^{4,9} for various polyacrolein samples including polymers prepared by oxidation-reduction catalysts in water and the spontaneous polymer, disacryl.

It has been reported that polyacrolein, prepared in a liquid medium with a free-radical-yielding catalyst at a temperature below 30° and in the presence of a material having an OH group, contains over 95% of theoretical aldehyde function as determined

- (1) R. C. Schulz, *Kunststoffe*, **47**, 303 (1957).
- (2) M. V. Chistyakova, *Russ. Chem. Rev.*, **31**, 224 (1962).
- (3) R. C. Schulz and W. Kern, *Makromol. Chem.*, **18/19**, 4 (1956).
- (4) R. C. Schulz, H. Fauth, and W. Kern, *ibid.*, **20**, 161 (1956).
- (5) R. C. Schulz, H. Fauth, and W. Kern, *ibid.*, **21**, 227 (1956).
- (6) R. C. Schulz, *Kunststoffe-Plastics*, **6**, 32 (1959).
- (7) R. C. Schulz, I. Löflund, and W. Kern, *Makromol. Chem.*, **32**, 209 (1959).
- (8) F. J. Welch, U. S. Patent 3,089,389 (1962).

- (9) R. C. Schulz, H. Cherdron, and W. Kern, *Makromol. Chem.*, **24**, 141 (1957).