and in 25 *m* choline chloride. The titration curves in water and in the choline salt solution are similar and show quite poor end points (see Table II). However, in the *n*-Bu_4NBr solution, because of the expanded acidity scale and the increased basicity of the hydroxyl ion, the end point is easily detectable (a similar result is found in 20 *m* Me_4NCl).

Figure 6 shows the titration of 0.02 *M* *dl*-α-alanine with 1 *M* HCl in water, in 7.75 *m* *n*-Bu_4NBr, in 20 *m* Me_4NCl, in 15 *m* choline iodide, in 25 *m* choline chloride, and 25 *m* choline bromide. The titration end points are poor in water and in the tetra-*n*-butylammonium bromide solution, but for reasons which are not yet understood they are satisfactory in the Me_4NCl solution and in the choline salt solutions. However, it must be said that these titrations are not necessarily useful, since α-amino acids, unlike many other organic compounds, do not appear to be salted into quaternary ammonium salt solutions.

Acknowledgments. We gratefully acknowledge the support of part of this work by the U. S. Atomic Energy Commission (through Contract AT(30-1)-2544). J. S. thanks the National Research Council of Italy and the Institute of Organic Chemistry of the University of Padua for a research fellowship which made some of this work possible. He is indebted to the late Professor S. Bezzi and Professor E. Scoffone (of the Institute) for their kindness and cooperation, and Professor L. Gotte and Dr. A. Fracassini-Serafini of the Department of Histology of the Medical School, for their courtesy and help. The technical assistance of Drs. E. Peggion and A.-M. Mattucci of the Institute is deeply appreciated.

Acid–Base Reactions in Concentrated Aqueous Quaternary Ammonium Salt Solutions. II. Steric Effects

Joseph Steigman and Donald Sussman[1]

Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York, and the Institute of Organic Chemistry, University of Padua, Padua, Italy. *Received March 15, 1967*

Abstract: A series of monosubstituted benzoic acids were titrated at 25.0° with KOH in 7.75 *m* aqueous tetra-*n*-butylammonium bromide. Unlike their behavior in water, the *ortho*-substituted acids (fluoro-, chloro-, bromo-, iodo-, nitro-, methyl-, methoxy-, and phenylbenzoic acids) had mixed acidity constants which were almost the same as those of their *para* isomers. The *ortho* effect in the ionization of these acids had disappeared. The *ortho* effect is attributed to the disruption of hydrogen-bonded water clusters above and below the plane of the ring by π electrons and the encounter between the carbonyl and alcohol groups of the acid and water molecules from these disrupted clusters. Its disappearance is attributed to the very strong solvent organization through hydrogen bonding caused by the quaternary ammonium salt. This hypothesis is generalized further. Ionol (2,6-di-*t*-butyl-*p*-cresol) is a sterically hindered phenol which ordinarily is very weakly acidic. In 10 *m* tetra-*n*-butylammonium bromide it dissolved and was titrated at 25.0° with KOH. Its mixed acidity constant was $^1/_{25}$th that of phenol in the same medium. The difference in acidity constants is attributed to inductive effects on the phenolic group by the alkyl groups. The disappearance of the steric hindrance is thought to be caused by the incorporation of the ionol into a strongly hydrogen-bonded medium in which the water molecules have restricted molecular rotation and are properly aligned for proton jumps.

This paper describes the disappearance of the *ortho* effect in the ionization of monosubstituted benzoic acids and of steric hindrance in the ionization of a hindered phenol when the solvent is a concentrated aqueous solution of a quaternary ammonium salt.

Experimental Section

1. **Materials. a. Substituted Benzoic Acids.** The various substituted benzoic acids were the highest purity acids of Eastman Kodak, Matheson Coleman and Bell, Fluka, Aldrich, Fisher, or K & K. Each was recrystallized several times from water and dried *in vacuo*. The melting points were close to the literature values. An indirect check on the purity of each acid was made from the stoichiometry of each titration.

b. Substituted Phenols. The various nitrophenols were reagent grade chemicals obtained from Eastman, Matheson Coleman and Bell, Fisher, or K & K. Each was recrystallized several times from water, and dried *in vacuo*. The melting points were in good agreement with those reported in the literature. Ionol (2,6-di-*t*-butyl-*p*-cresol) was obtained through the courtesy of The Shell Chemical Co. Three recrystallizations were made from carbon tetrachloride, followed by drying *in vacuo*. D_2O was 99.7% pure (Columbia Organic Chemicals).

c. Other Reagents. All other reagents have been previously described.[2]

2. **Potentiometric and Spectrophotometric Measurements.** Some of these techniques have been previously described.[2] Infrared measurements were made on a Perkin-Elmer Model 521 recording infrared spectrophotometer. The spectra of solutions in water and in D_2O were determined in C.I.C. demountable cells with CaF_2 windows and 0.1- or 0.2-mm Teflon spacers. Both cells were filled with the electrolyte solutions and base lines were run with adjustment of the thickness of the sample cell until the transmission in the region of interest was equal in the two cells. The benzoic acid solution was run immediately afterwards in one of the cells.

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(1) From a thesis submitted by D. Sussman to the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) J. Steigman and D. Sussman, *J. Am. Chem. Soc.*, **89**, 6400 (1967).

Results and Discussion

1. Substituted Benzoic Acids. The *ortho* Effect. It is well known that nearly all *ortho*-substituted benzoic acids have acidity constants in water which are considerably larger than those of the *meta* and *para* isomers. The effect, which is known as the *ortho* effect, is commonly ascribed to a steric inhibition of resonance. The group in the *ortho* position forces the carboxyl group to twist out of the plane of the ring. The resulting interference in the coplanar alignment of either the acid or the carboxylate ion decreases the resonance energy of each, but the decrease is larger for the acid. Hence it is less stable and transfers a proton more readily, becoming a stronger acid.

Table I shows the thermodynamic constants (called pK_A) in water at 25° of benzoic acid and a number of substituted benzoic acids, together with the mixed acidity constants[3] (called pK') calculated from the titration of 0.02 *M* solutions of these acids at 25.0° with 1 *M* KOH in 7.75 *m* aqueous tetra-*n*-butylammonium bromide (called *n*-Bu_4NBr).

Table I. pK_A Values of Substituted Benzoic Acids in Water at 25° and Their pK' Values in 7.75 *m* *n*-Bu_4NBr

Acid	p$K_A$$^{a-c}$	pK'
Benzoic	4.20	6.30 ± 0.01
o-Hydroxybenzoic	2.98	4.01 ± 0.03
m-Hydroxybenzoic	4.08	6.42 ± 0.02
p-Hydroxybenzoic	4.58	7.16 ± 0.02
o-Fluorobenzoic	3.27	5.81 ± 0.03
m-Fluorobenzoic	3.87	5.91 ± 0.02
p-Fluorobenzoic	4.14	5.71 ± 0.02
o-Chlorobenzoic	2.94	5.70 ± 0.02
m-Chlorobenzoic	3.83	5.60 ± 0.02
p-Chlorobenzoic	3.98	5.60 ± 0.03
o-Bromobenzoic	2.85	5.58 ± 0.02
m-Bromobenzoic	3.81	5.50 ± 0.02
p-Bromobenzoic	3.97	5.48 ± 0.02
o-Iodobenzoic	2.86	5.75 ± 0.01
m-Iodobenzoic	3.85	5.74 ± 0.01
p-Iodobenzoic	3.93	5.70 ± 0.02
o-Nitrobenzoic	2.17	4.79 ± 0.02
m-Nitrobenzoic	3.49	4.93 ± 0.01
p-Nitrobenzoic	3.43	4.57 ± 0.03
o-Methoxybenzoic	4.09	6.60 ± 0.02
m-Methoxybenzoic	4.09	6.08 ± 0.03
p-Methoxybenzoic	4.47	6.69 ± 0.02
o-Methylbenzoic	3.91	6.67 ± 0.02
m-Methylbenzoic	4.27	6.43 ± 0.03
p-Methylbenzoic	4.37	6.54 ± 0.03
o-Phenylbenzoic	3.46	6.37 ± 0.01
m-Phenylbenzoic	3.99	5.89 ± 0.04
p-Phenylbenzoic	4.20	6.14 ± 0.02

[a] See ref 3. [b] H. C. Brown, D. H. McDaniel, and O. Haflinger, in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955. [c] G. Kortum, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth and Co., Ltd., London, 1961.

The hydroxybenzoic acids must be examined separately. In water, the *ortho* isomer is a much stronger acid than the *meta* and *para* compounds, but the effect is attributed to the great stability of an internally hydrogen-bonded anion which can form a six-membered ring.[4] In the quaternary ammonium salt solution the *ortho* isomer is still a much stronger acid than the other two. In the light of the behavior of the other *ortho*-substituted acids it can be concluded that the internally hydrogen-bonded anion is the probable cause of the greater acidity constant of the *ortho* isomer in the salt solution.

The other substituted benzoic acids all show a different phenomenon: the disappearance of the *ortho* effect in the concentrated *n*-Bu_4NBr solution. In the case of methoxybenzoic acid the *para* isomer is weaker than the *ortho* compound by 0.1 pK' unit. For all the other acids the *ortho* isomer is weaker than the *para* compound by 0.1–0.2 pK' unit. We conclude that the *ortho* effect arises from an interaction of the solute acid with the solvent. Since the effect is seen in water and is not evident in 7.75 *m* *n*-Bu_4NBr, it should reappear at some intermediate salt concentrations. Alternatively, the effect might be expected to reappear in more concentrated solutions of the acid. This is shown in Table II, in which the three isomeric bromobenzoic acids are titrated with 1 *M* KOH in 7.75 *m* *n*-Bu_4NBr at different initial acid concentrations. The *meta* and *para* acids show very small changes in their mixed acidity constants with increasing acid concentration, whereas the *ortho* acid becomes stronger at higher concentrations.

The *ortho* effect represents an interaction of the aromatic acid with water, and the benzenoid compound may well have an effect on the water structure. Némethy and Scheraga have shown that aliphatic hydrocarbons dissolved in water are more efficient than aromatic hydrocarbons in promoting the organization of hydrogen-bonded water clusters around themselves.[5] This is seen in Table III. The negative entropies and the large heat capacities both reflect the increase in hydrogen bonding of the water by the hydrocarbon solutes. The aliphatic hydrocarbon molecules promote structure-making in the water around themselves. The aromatic hydrocarbons will promote water-structure-making around the molecular periphery in the plane of the ring, because of the σ bonds. However, above and below the plane of the ring the π electrons will polarize the water molecules and will disrupt the hydrogen-bonded clusters which would otherwise form. The net effect of these two opposing tendencies for benzene will be to increase the hydrogen bonding of water, but to a significantly smaller extent than by a corresponding aliphatic compound. This is evident from the data of Table III, in which benzene in water displays a smaller entropy change and a smaller heat capacity than paraffins of lower molecular weight.

We propose that the *ortho* effect in aqueous solutions of monosubstituted benzoic acids is due to the polarization of water molecules above and below the plane of the ring by the π electrons, with the consequent disruption of the water structure. In the normal aro-

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(3) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., Ltd., London, 1962.

(4) G. E. K. Branch and D. L. Yabroff, *J. Am. Chem. Soc.*, **56**, 2568 (1934).

(5) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382, 3401 (1962).

Table II. p*K'* Values for Bromobenzoic Acids in 7.75 *m* *n*-Bu$_4$NBr at 25.0° at Different Acid Concentrations

ortho		*meta*		*para*	
Acid, *M*	p*K'*	Acid, *M*	p*K'*	Acid, *M*	p*K'*
0.0040	5.58 ± 0.02	0.0055	5.58 ± 0.02	0.0055	5.58 ± 0.03
0.0100	5.58 ± 0.04	0.0101	5.57 ± 0.01	0.0105	5.58 ± 0.04
0.0200	5.58 ± 0.02	0.0212	5.50 ± 0.02	0.0111	5.55 ± 0.03
0.0444	5.36 ± 0.01	0.0443	5.56 ± 0.01	0.0274	5.49 ± 0.02
0.0614	5.21 ± 0.01			0.0349	5.59 ± 0.01
				0.0480	5.53 ± 0.01

Table III. Entropy and Heat Capacity Changes in Solutions of Hydrocarbons in Water at 25°[6]

Hydrocarbon	$\Delta S°$, eu	ΔC_p, cal/deg mole
Methane	−15.3	64
Ethane	−18.8	79
Butane	−23.0	99
Benzene	−13.7	73
Toluene	−15.7	85

matic acids, like benzoic acid, the COOH is aligned in the plane of the ring. In this position both the carbonyl and the hydroxyl groups encounter organized water clusters and hydrogen-bond with them, thus stabilizing themselves. (The exact manner of the interaction of carboxyl groups with water is not yet known.) However, the carboxyl group of an *ortho*-substituted benzoic acid is forced out of the plane of the ring by steric factors. In this position, the carbonyl on one side of the ring and the hydroxyl group on the other side will encounter groups of water molecules which are subjected to disruptive polarization by the π electrons. Hence the carboxyl group cannot enter into an organized water structure and will therefore not be stabilized to the extent of the *meta* and *para* isomers. As a consequence, the *ortho* acid will be stronger than the other two. In 7.75 *m* *n*-Bu$_4$NBr solution, the carboxyl group is, of course, still twisted out of the plane of the ring. However, the water is now very strongly organized, so that there is a greatly decreased effect of the π electrons on the water structure above and below the plane of the ring. The carbonyl and the hydroxyl groups will now interact with organized water clusters more or less in the same way as the carboxyl groups of the *para* isomer. The concentration dependence of the mixed acidity constant for *o*-bromobenzoic acid may reflect increasing disorganization in the solvent structure caused by the increasing concentration of π electrons.

This interpretation assumes that the *ortho* effect is caused by an interaction between the acid and water and its elimination is brought about by a stronger interaction between the two species. Preliminary infrared studies of benzoic acid in D_2O and in H_2O containing *n*-Bu$_4$NBr support this hypothesis. In D_2O saturated with deuterated benzoic acid, the carbonyl peak appears at 1680 cm^{-1} (which compares well with 1685 cm^{-1} in the solid dimer[6]). In 0.5 *m* *n*-Bu$_4$NBr the peak shifts to 1685 cm^{-1}, and in 7.75 *m* *n*-Bu$_4$NBr it shifts further to 1690 cm^{-1} (with a shoulder at 1700). At the same time, the C–O–D frequency (representing C–O stretch and O–D bend interactions) in D_2O is at 1348 cm^{-1},[7] and moves down to 1339 cm^{-1} in 7.75 *m* *n*-Pr$_4$NBr (which is equivalent to *n*-Bu$_4$NBr in its titration curves). This suggests that the carbonyl group is less hydrogen-bonded in quaternary ammonium salt solutions than in water itself and that the C–O–D groups of the carboxyl is more strongly hydrogen-bonded in *n*-Bu$_4$NBr solution than in water. Finally, in solid benzoic acid there is a well-defined pair of small bands near 2670 and 2560 cm^{-1}. These are attributed to overtones and combinations of bands at 1287 and 1420 cm^{-1}, which are due to OH deformation and C–O stretching.[8] These two vibrations are strongly coupled in the carboxyl group. In H_2O these two small benzoic acid bands are replaced by a broad, flat, very shallow band centering at 2600, but extending from 2700 to 2500 cm^{-1}. In 7.75 *m* *n*-Bu$_4$NBr two very well-developed bands reappear, one at 2620 cm^{-1} and the other at 2515 cm^{-1}. Similar but more marked effects are seen with *o*-bromobenzoic acid. If both acids are incorporated by hydrogen bonding into clusters of organized water molecules in the quaternary ammonium salt solution, it is reasonable to expect a lower frequency for the C–O and O–D combination, as well as less freedom of rotation on the part of the individual groups (C–O and O–H) and hence a more sharply defined spectrum near 2600 cm^{-1}.

If the *ortho* effect is caused by the interaction of π electrons with solvent molecules, the acidity of an out-of-plane COOH group of an *ortho*-substituted benzoic acid will be determined in part by the degree of polarity and of organization of the particular solvent. If the solvent is very well organized (as, for example, in concentrated aqueous solutions of organic electrolytes), the difference between solvent molecules in the plane of the ring and above and below the plane should disappear, and there should be no *ortho* effect. This could also be true of concentrated sulfuric acid as a solvent. It is a liquid which is very strongly hydrogen-bonded, certainly to a much greater extent than water.[9] The only data on this point are found in an early paper by Hammett, in which he reported that *o*-nitrobenzoic acid and *p*-nitrobenzoic acid (behaving as bases) had almost the same p*K* values.[10] In polar liquids which are less strongly organized than H_2SO_4, one would expect to find a difference in solvent structure in the plane of the ring and in the vicinity of the π electrons. Thus the *ortho* effect is found not only in water but in the lower alcohols (methanol and 1-butanol). On the other hand, if the solvent is poorly organized and relatively nonpolar, there should be practically no *ortho* effect

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(6) M. St. C. Fleet, *Trans. Faraday Soc.*, **44**, 767 (1948).

(7) D. Hadzi and N. Sheppard, *Proc. Roy. Soc.* (London), **A216**, 247 (1953).

(8) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, p 258.

(9) R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

(10) L. A. Flexser and L. P. Hammett, *J. Am. Chem. Soc.*, **60**, 885 (1938).

since the interactions between solvent molecules and the π electrons would be weaker than in a polar solvent. Davis and Hetzer[11] measured the formation constants of the reactions between diphenylguanidine and 40 aromatic acids in benzene and found no *ortho* effect for methyl-, chloro-, bromo-, and iodobenzoic acids. They concluded from their measurements that the *ortho* effect in monosubstituted benzoic acids is due to an interaction with the solvent. The results reported here support their conclusion.

2. **2,6-Di-*t*-butyl-*p*-cresol. Steric Hindrance.** Ionol (2,6-di-*t*-butyl-*p*-cresol) is a sterically hindered compound which normally is very weakly acidic. It does not dissolve in concentrated aqueous sodium hydroxide. It dissolves readily in ethanol but reacts incompletely even with 5 *M* NaOH, whereas phenol is completely converted to the phenolate anion in dilute alkali (less than 0.1 *M* NaOH).[12]

Ionol dissolved readily in aqueous 10 *m* *n*-Bu_4NBr. A 0.015 *M* solution of the phenol in this medium was titrated with 1 *M* KOH at 25°. The end point was poor, and hence the value of the mixed acidity constant is uncertain. An attempt was therefore made to measure its p*K'* spectrophotometrically. Figure 1 shows the ultraviolet–visible absorption spectrum at 25° of 7×10^{-4} *M* ionol in 10 *m* *n*-Bu_4NBr solutions containing different concentrations of KOH. The glass electrode readings of the various solutions are listed in the figure. Unfortunately, it was not possible to obtain a limiting curve by adding a large excess of KOH because a coacervate formed.[2] Nevertheless, the spectra do show that a phenolate peak near 310 mμ is becoming more and more prominent as the solutions are made more alkaline.

At 25° in 7.75 *m* *n*-Bu_4NBr, phenol has a mixed acidity constant (p*K'*) of 12.08.[2] In 10 *m* salt, its p*K'* is about 12.6. In the same medium, the p*K'* of ionol is approximately 14.0. Hence the dissociation constant of phenol is approximately 25 times greater than that of ionol in 10 *m* *n*-Bu_4NBr.

Part I of this paper shows that in concentrated Bu_4NBr solutions, the *ortho* effect has disappeared for monosubstituted benzoic acid. If we assume that there is no steric hindrance for *ortho*-substituted phenols as well, that the σ value for a group in the *para* position can be used for the same group in the *ortho* position, and that σ values of several groups in the same molecule are additive, then it is possible to evaluate the difference in the dissociation constants of phenol and ionol in the 10 *m* salt solution. Table IV shows the mixed acidity constants of a number of nitro- and dinitrophenols in water and in 7.75 *m* *n*-Bu_4NBr, together with ρ values obtained on the basis of the assumptions. These compounds yield an average ρ value of 3.2 for the dissociation of phenols in 7.75 *m* *n*-Bu_4NBr. A similar calculation for the ionol (assuming σ values of −0.170 for the methyl group, −0.197 for each *t*-butyl group,[13] and a combined value of −0.564 for the three alkyl substituents) yields a value of approximately 2.5 for ρ in 10 *m* *n*-Bu_4NBr. In view of the large experimental uncertainties in the determinations of the mixed acidity constants of acids as weak as ionol and phenol in this solvent, the agreement is surprisingly good. It can be concluded that the difference in acidity between phenol and ionol in the 10 *m* salt solution is due to inductive effects, and that the steric hindrance commonly associated with the acidity of this phenol has disappeared.

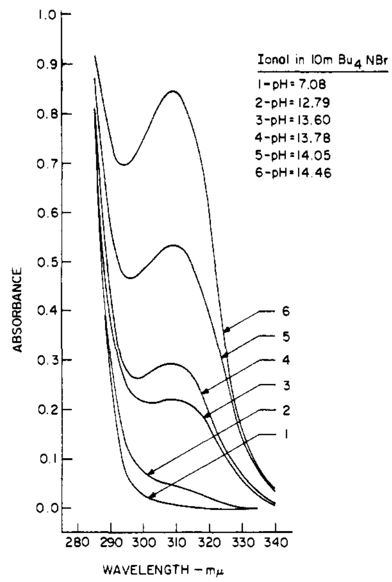

Figure 1. Ultraviolet–visible spectra of 7×10^{-4} *M* ionol in 10 *m* *n*-Bu_4NBr containing different concentrations of KOH.

Table IV. Acidity Constants of Phenols in Water and Their Mixed Constants in 7.75 *m* *n*-Bu_4NBr at 25.0°, with ρ and σ Values

Compound	pK_A[a]	p*K'*	σ[b]	ρ
Phenol	9.99	12.08 ± 0.01	...	...
o-Nitrophenol	7.23	8.26 ± 0.01	+1.27	3.01
m-Nitrophenol	8.40	9.93 ± 0.03	+0.7	3.03
p-Nitrophenol	7.15	7.95 ± 0.03	+1.27	3.25
2,4-Dinitrophenol	4.09	3.53 ± 0.04	+2.54	3.37
2,5-Dinitrophenol	5.17	5.55 ± 0.03	+1.96	3.30

[a] See footnote *b*, Table I. [b] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

This conclusion can be explained qualitatively in terms of the effects of the concentrated quaternary ammonium salts on the water structure. They organize the water around themselves very strongly, and the ionol molecule can enter a void in the inmediate vicinity of a quaternary ion, and perhaps even further strengthen the hydrogen bonding of adjacent molecules of water because of the bulky *t*-butyl groups. The phenolic OH group probably hydrogen bonds to molecules of water in its immediate vicinity (a model shows that some contact can be established). The hydroxyl group may be incorporated into a relatively rigid water structure as a consequence. Proton transfer can now take place with relative ease because the extensive hydrogen bonding of the water molecules restricts their freedom of rotation. In water adjacent molecules participating in a proton transfer must rotate to achieve the proper orientation before the jump occurs.[14] The rotational

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(11) M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Std.*, 60, 569 (1958).

(12) N. D. Coggeshall and A. S. Glessner, Jr., *J. Am. Chem. Soc.*, 71, 3150 (1949).

(13) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958).

(14) M. Eigen and L DeMaeyer in "The Structure of Aqueous Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959.

energy barrier is believed to be the principal obstacle to the actual proton jump. In ice where the neighboring molecules of water are already aligned, the mobility of protons is several orders of magnitude greater than in water at the same temperature.[14] In 10 *m* *n*-Bu_4NBr, "ice-like" water is well organized so that the rotational barrier to the proton jump is very small, although it is probably larger than in crystalline ice. It is, then, the diminution in rotational freedom of the water molecules in the quaternary ammonium salt solutions which is responsible for the virtual disappearance of the steric hindrance commonly found with ionol.

Acknowledgments. The support of part of this work by U. S. Atomic Energy Commission Contract AT-(30-1)-2544 is gratefully acknowledged. J. S. thanks the National Research Council of Italy and the Institute of Organic Chemistry of the University of Padua for a research fellowship for some of this work. The late Professor S. Bezzi, former director of the Institute, and Professor E. Scoffone, its present director, were particularly kind. He thanks Professor L. Gotte and Dr. A. Fracassini-Serafini of the Department of Histology of the University for their generous help. Technical assistance by Dr. E. Peggion is deeply appreciated.

The Effect of Conformer Stability on Cation–Ligand Association[1a]

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Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received June 28, 1967*

Abstract: Cation–ligand association constants have been determined by a conductance method for piperidinium, 1-methylpiperidinium, and 1-ethylpiperidinium cations with free amine, triphenylphosphine oxide, and 2,6-dimethylpyridine as ligands in chlorobenzene as solvent and with the first two as ligands in nitrobenzene as solvent, all at 25°. The results are interpreted in terms of equatorial–axial conformational equilibria for the substituted piperidinium cations and amines. Values of the equilibrium constants are calculated and compared with other pertinent values in the literature.

We have determined cation–ligand association constants, K_L (eq 1), for a variety of ligands, L,

$$AH^+ + L \rightleftarrows AH^+,L \quad K_L = [AH^+,L]/[AH^+][L] \qquad (1)$$

principally with tri-*n*-butylammonium cation in several low dielectric solvents at 25° using a conductance method.[2] We now report the measurement of the conductances of piperidinium ($PipH^+$), 1-methylpiperidinium ($MePipH^+$), and 1-ethylpiperidinium ($EtPipH^+$) picrates with and without added free amine as ligand and added triphenylphosphine oxide (Ph_3PO) as ligand in nitrobenzene ($PhNO_2$) solvent and in chlorobenzene (PhCl) solvent, all at 25°. 2,6-Dimethylpyridine (Lut) was also used as a ligand in the latter solvent. This work was undertaken to extend our information on the effect of cation structure on cation–ligand association.

Experimental Section

Chlorobenzene was purified as before.[2a] Nitrobenzene was purified using a modification[2f] of a procedure due to Witschonke and Kraus.[3] Picric acid (HPi) was recrystallized from ethanol. The piperidines (Columbia Organic Chemicals Co., Inc.) were distilled under reduced pressure, a middle fraction being taken. The picrate salts of each of these amines was prepared in the same way[2a] as the tributylammonium picrate previously used: PipHPi, mp 151–152° (lit.[4] mp 150.5–151.5°); MePipHPi, mp 230–231° (lit.[5] mp 226°); EtPipHPi, mp 172–173° (lit.[5] mp 170°). 2,6-Dimethylpyridine was distilled at atmospheric pressure, a middle fraction being taken. Ph_3PO was purified as before.[2c] Conductance measurements were carried out using the bridge, bath, and cells previously described.[2a] The physical constants of the solvents, $PhNO_2$ and PhCl, have been listed before.[2e,f]

Results

The equivalent conductances, Λ (cm^2 ohm^{-1} $equiv^{-1}$), as a function of molar salt concentration, *C*, for a number of salts in $PhNO_2$ solvent with and without added ligands, at 25°, appear in Table I. The solvent specific conductance has been subtracted from that of the solution in each case to obtain the specific conductance presumed due to the salt alone. The solvent conductance was no more than 0.2% of that of the most dilute salt solution. No attempt was made to check or correct for polarization. We have already found[2f] that the correction for this effect with a similar salt, Bu_3NHPi, amounted to no more than 0.1%. The conductance data in Table I were treated by the method of Shedlovsky,[6] where *S* is the Shedlovsky function and $y_{\pm}^2$ is calculated from the Debye–Hückel theory. Λ_0^0 is the limiting

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[1] (a) This research was supported in part by a National Science Foundation Grant, GP-3955; (b) author to whom inquiries should be addressed.

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