Acid–Base Reactions between Amines and Carboxylic Acids in Hexane

Stanley Bruckenstein and D. F. Untereker

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214.
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Abstract: The reactions of carboxylic acids (HX) and amine bases (B) were studied in the solvent hexane at 25° using the differential vapor pressure method and infrared spectroscopy. In general, the following equilibria are required to interpret the experimental results: $2HX \rightleftharpoons (HX)_2$; $B + HX \rightleftharpoons (1/m)(BH^+X^-)_m$; and $(1/m)(BH^+X^-)_m + HX \rightleftharpoons (1/n)(BH^+HX_2^-)_n$. Detectable association of cyclohexyl- and *n*-hexylamines occurs at the 0.01 *M* level, while trichloroacetic and benzoic acids appear to be quantitatively dimerized at the same concentration. Some evidence for the $BH^+H_2X_3^-$ species is given. The results in hexane are compared to a previous study by Bruckenstein and Saito[1] in benzene as solvent. Compared to hexane, in benzene values of *m* and *n* are smaller, and trichloroacetic acid is far less dimerized, clearly indicating that benzene is capable of solvating the species participating in the acid–base and concurrent equilibria.

It is of considerable interest to compare acid–base equilibria involving carboxylic acids and amine bases in hexane with the results of similar studies in benzene.[1] Hexane is of interest because it is an extreme example of a very nonpolar and low dielectric constant solvent (ϵ 1.89 at 25°[2]) of low solvating ability. However, no systematic acid–base studies in hexane seem to have been reported in the literature.

It is generally recognized that the interaction of an amine base, B, with a carboxylic acid, HX, in benzene, is described by the following equations.

$$B + HX \rightleftharpoons \frac{1}{m}(BH^+X^-)_m \qquad (1)$$

$$\frac{1}{m}(BH^+X^-)_m + HX \rightleftharpoons \frac{1}{n}(BH^+HX_2^-)_n \qquad (2)$$

BH^+X^- represents a simple ion pair while the homoconjugate ion pair, $BH^+HX_2^-$, represents an ion pair containing the homoconjugate ion, HX_2^-. Species of the form $(BH^+H_2X_3^-)$ are also known to exist.[1] This study verifies that equilibria similar to reactions 1 and 2 are also important in hexane. However, the values of *m* and *n* found in hexane are greater than those found in benzene, as might be expected by a comparison of the two solvent's properties.

The experimental approach, in which a nonsteady state colligative property technique and infrared spectroscopy were used, paralleled the earlier work of Bruckenstein and Saito.[1] The differential vapor pressure (DVP) technique was chosen in preference to other colligative property techniques because it yielded data at 25° and because of its speed compared to equilibrium vapor pressure measurements. For a detailed discussion of the principles of this technique and the interpretation of the raw experimental data, the reader is referred to the earlier benzene work.[1] Infrared spectroscopic experiments were used to aid in the interpretation of the DVP data. Absorption peaks used were associated principally with the COO^- and COOH groups.

A typical experiment was performed by mixing a fixed amount of base with varying amounts of acid in a series of volumetric flasks, and diluting each amine–acid mixture to volume with hexane. The ratio of the concentration of acid to base, *R*, was varied between 0 and 4. Separate DVP and infrared measurements were then carried out by using portions of the solutions in the volumetric flasks.

From the DVP experiments the van't Hoff *i* value was determined. Since the total analytical concentration of base was held constant and independent of *R*, the numerical value of *i* is a direct measure of the extent of association of all species in solution. For example, if a base, B, is monomeric, at $R = 0$ (no added HX) $i = 1$. If the ion pair formed by reacting B with HX is trimeric and quantitatively formed, at $R = 1$ (equal amounts of B and HX) $i = {}^1/_3$. If upon addition of more HX the dimeric conjugate ion pair $(BH^+HX_2^-)_2$ forms quantitatively, then $i = {}^1/_2$ at $R = 2$. Finally if no further reaction occurs on adding HX, and HX is itself a dimer, $i = 1$ at $R = 3$. Other hypothetical examples have been considered earlier.[1] Plots of *i vs. R* constructed from the DVP data are interpreted in a manner similar to that given above.

Table I. Qualitative Observations Involving Acids and Bases in Hexane

Amine	Acid	Observations
Dodecylamine	Trichloroacetic	Both acid and amine soluble; no precipitate for $0 < R < 3$
Dodecylamine	Benzoic	Benzoic acid only sparingly soluble; all adducts formed appear to be soluble
Dibenzylamine	Trichloroacetic	Amine soluble; precipitate forms at $R \simeq 1$ and redissolves in excess acid in range $2 < R < 3$
Tribenzylamine	Trichloroacetic	Amine soluble; precipitate forms at $R \simeq 1$ and redissolves only in large excess of acid
Cyclohexylamine	Trichloroacetic	Amine soluble; precipitate forms by $R \simeq 1$ and redissolves in excess acid by $R = {\sim}3$

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[1] S. Bruckenstein and A. Saito, *J. Am. Chem. Soc.*, **87**, 698 (1965). References to earlier benzene literature are given here.

[2] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, p 45.

Table II. *Infrared Studies of Reactions of Bases with Trichloroacetic Acid and Benzoic Acid*

Compound (molarity)	*R*	Frequency and intensity of principal absorption peaks						
TCA (0.01)	...	1780 (0.057)	1742 (0.319)				1240 (0.021)	
DDA (0.01)	...							
	1			1670–1675 (0.215)		1320 (0.122)	1230–1240 (0.096)	
	2	1780 (0.036)	1742 (0.142)	1655 (0.160)		1315 (0.092)	1230–1240 (0.167)	
	3	1780 (0.066)	1745 (0.334)	1640–1650 (0.216)		1310 (0.73)		
DBA (0.01)	...					1292 (0.023)		
	1					None		
	2	1780 (0.031)	1742 (0.121)	1657 (0.119)		1315 (0.054)	1220–1240 (0.074)	
	3	1783 (0.058)	1745 (0.255)	1620–1660 (0.068)		1310 (0.031)	1230–1240 (0.110)	
CHA (0.01)	...							
	1					None		
	2	1785 (0.048)	1748 (0.255)				1240 (0.070)	
	3	1782 (0.079)	1745 (0.535)			1260 (0.052)	1244 (0.144)	
TBA (0.01)	...							
	1					None		
	2		1745 (0.011)					
	3		1740 (0.012)				1225 (0.017)	
	4	1785 (0.070)	1748 (0.365)			1245 (0.092)	1205 (0.017)	
	5	1785 (0.099)	1748 (0.62)			1247 (0.160)	1210 (0.050)	
	6	1782 (0.135)	1743 (0.700)			1243 (0.265)	1208 (0.070)	
HBZ (0.01)	...	1740 (0.039)	1690–1695 (0.340)	1597 (0.036)	1578 (0.030)	1308 (0.088)	1273 (0.094)	
DDA (0.01)	...							
	1		1660–1670 (0.054)	1590 (0.110)	1540–1550 (0.119)			
	2	1740 (0.027)	1690 (0.224)	1590 (0.142)	1530–1540 (0.151)	1305 (0.088)	1255 (0.122)	1235 (0.100)
	3	1740 (0.055)	1690–1695 (0.501)	1597 (0.177)	1530–1540 (0.155)	1308 (0.189)	1270 (0.233)	1235 (0.148)

Experimental Section

Vapor Pressure Apparatus. The DVP apparatus used was described by Bruckenstein and Farm,[3] who discuss the detailed theory and operation of this instrument. The method relies on the difference in vapor pressure between solvent and solution which produces a temperature difference between the solvent and solution thermometer of the DVP apparatus. This temperature difference is recorded as a voltage difference across the opposite arms of a Wheatstone bridge, which consists of the two thermistors in adjacent arms, and two other low-temperature coefficient resistors, one of which can be adjusted to balance the bridge when solvent is placed on both thermistors. The unbalanced Wheatstone bridge emf is (for practical purposes) a linear function of the total concentration of all dissolved species, assuming all activity coefficients are unity.

All data were obtained at 25.0 ± 0.001°.

Infrared Technique. Infrared data were obtained with a Perkin-Elmer Model 521 spectrometer in the programmed slit mode. The sample cell had sodium chloride windows and a fixed path length of 428 μ. The reference cell was of a variable path length type and was adjusted to compensate for the hexane absorption in each solution. No data are reported in Table II in a given frequency range unless 10% transmission was observed for the pure solvent.

Infrared data are more difficult to interpret in hexane than in benzene because of the extensive solvent absorption, which obscures many functional groups of interest. Hence, we were forced to limit ourselves primarily to the absorptions associated with carbonyl and carboxylate groups. The carbonyl group of a carboxylic acid has two characteristic frequencies, associated with the stretching modes of the monomeric and dimeric forms. These frequencies are to be expected around 1800 cm^{-1}, that of the monomer being slightly higher than that of the dimer.[4] In hexane the observed frequencies are 1780 and 1742 cm^{-1}, respectively. The carboxylate ion has an asymmetric and a symmetric stretch. The general locations of these are 1550–1610 and 1300–1400 cm^{-1}, respectively.[5]

Chemicals. Hexane. Fisher reagent grade hexane, which is a mixture of isomers, was used. After drying by shaking with activated alumina, the solvent gave irreproducible DVP data; *i.e.*, the base lines were drawn out and slow to reach equilibrium. Solutions of trichloroacetic acid in this alumina-dried hexane exhibited various colors, ranging from red to green. Addition of bromine to the alumina-dried hexane indicated the presence of unsaturated compounds. 3-Methyl-2-pentene, 2-hexane, and 3-hexene have boiling points very near normal hexane. Gas–liquid chromatograms on a squalene 60–80 Chromosorb P column at 30° showed five components. The unsaturated impurities were removed from the Fisher solvent by distilling from sulfuric acid in 4-l. lots using a 4-ft vacuum-jacketed fractionating column with Teflon packing and a reflux ratio of 5:1. The boiling point range of the fraction collected was always between 67 and 69°. The yield was about 40% of the starting material. During the distillation the color of the sulfuric acid phase became deep red, and after the distillation there was a black oily material left in the distillation pot.

After purification, each solvent batch was analyzed for water by Karl Fisher titration. The concentration of water was always less than 3×10^{-3} *M*. Distilled solvent was free of sulfuric acid and unsaturated compounds.

Different batches of hexane were always too dissimilar in vapor pressure to be used interchangeably on the solvent and solute probes in the DVP apparatus. This difficulty arose whenever different hexane batches were used because the DVP technique measures the difference in vapor pressure between drops of liquid on the solvent and solute thermistor probes. The temperature difference, produced as a result of the differing solvent batch composition, masks the effect to be studied. However, this problem does not occur if the same solvent batch (composed of a mixture of similar compounds of similar vapor pressures) is used to prepare all solutions and also for the reference in the DVP cell. This condition is met by using "hexane" distilled as described above.

The hexane was stored in, and dispensed from, an all-glass, gravity-fed vessel made from a 2-l. round-bottom flask. A 25-cm long, 3.5-cm diameter column ending in a 2-mm bore Teflon stopcock was sealed to the bottom of the flask. The column was filled with alumina through which the solvent was perculated before being dispensed *via* the stopcock. Ten milliliters of hexane could be dispensed from this container in a matter of a few seconds with minimal exposure to water vapor in the atmosphere.

Acids. Mallinckrodt AR benzoic acid and Fisher ACS trichloroacetic acid were used. Approximately 0.1 *M* solutions of benzoic acid could be prepared in hexane. Stock solutions of benzoic acid were standardized by titration according to the procedure given by Kolthoff and Sandell.[6] Direct aqueous titration of the trichloroacetic acid yielded a purity of 95.5%, the principal impurity apparently being water. Solutions of this acid were dehydrated by dissolving the acid in hexane (~1 *M* solutions), adding phosphorus pentoxide, shaking, filtering, and repeating the pro-

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[3] R. J. Farm and S. Bruckenstein, *Anal. Chem.*, 40, 1651 (1968).

[4] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 28.

[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p 174.

[6] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1952, p 529.

1130 (0.017)			940 (0.017)	835 (0.065)	818 (0.060)		670–680 (0.048)	
1150 (0.023)		962 (0.071)	935 (0.028)					
1140 (0.021)		970 (0.044)	940 (0.031)		825 (0.111)		670 (0.020)	
1137 (0.046)		968 (0.064)	940 (0.057)	835 (0.236)	830 (0.254)		670 (0.086)	660 (0.084)
1135 (0.056)		970 (0.068)	940 (0.084)	835 (0.352)	825 (0.333)		670 (0.114)	660 (0.111)
							680 (0.136)	
				834 (0.181)	825 (0.185)		670–680 (0.127)	
				835 (0.225)	825 (0.211)		660–680 (0.114)	
1135 (0.035)		975 (0.039)	940 (0.039)				790 (0.039)	
1135 (0.035)		970 (0.047)	940 (0.052)	838 (0.063)	826 (0.038)		660–690 (0.021)	
1130 (0.038)		970 (0.044)	940 (0.064)	838 (0.256)	826 (0.211)		660–690 (0.050)	
1110 (0.040)			955 (0.31)	850 (0.080)			685 (0.240)	
					825 (0.029)		670 (0.020)	
					825 (0.027)		670–680 (0.025)	
1125 (0.017)		940 (0.027)	940 (0.027)	850 (0.023)	840 (0.134)	822 (0.122)	670–690 (0.053)	
1130 (0.027)		942 (0.056)		850 (0.125)	841 (0.318)	823 (0.296)	660–690 (0.091)	
1125 (0.040)		940 (0.053)	940 (0.053)	850 (0.221)	840 (0.381)	821 (0.356)	665 (0.140)	635 (0.060)
1167 (0.033)	1012 (0.017)		925 (0.025)				696 (0.127)	
1150 (0.023)		962 (0.071)	935 (0.028)					
1160 (0.038)		960–970 (0.038)	935 (0.031)			815 (0.044)		
1160 (0.078)	1010 (0.046)	960 (0.095)	920–940 (0.042)			817 (0.029)	692 (0.114)	
1163 (0.123)	1112 (0.055)	1012 (0.027)	925 (0.065)			820 (0.034)	696 (0.346)	

cedure until the water concentration (determined by Karl Fisher method) was lower by a factor of 100 than the acid concentration. Trichloroacetic acid solutions in hexane were standardized by extraction into water and titration with a standard sodium hydroxide solution.

Amines. All amines used were Eastman Kodak White Label products, with the exception of the dodecylamine which was donated by General Mills Central Research Laboratories. The water content of the amine stock solution was less than 0.01 *M*. Each amine solution was analyzed by titration with standard perchloric acid in glacial acetic acid using crystal violet as an indicator.

All amine solutions in hexane were prepared immediately before use, since in some cases, *e.g.*, for tribenzylamine, a precipitate formed after standing (24 hr).

Naphthalene. Reagent grade naphthalene was sublimed before use. Naphthalene solutions were prepared by weight.

Dodecane. Matheson Coleman and Bell dodecane (99 + % purity) was used. Solutions were prepared by weight.

Solution Preparation. All glassware was dried overnight at 120° and then stored in a dessicator. Solutions for use in the DVP apparatus were prepared in 5- or 10-ml volumetric flasks by dispensing the required quantities of stock acid or amine solutions from glass or Teflon piston-type microburets into half-filled volumetric flasks, and then diluting to volume with hexane.

Results and Discussion

Behavior of Single Solutes. It is apparent that the state of aggregation of individual acids and bases in hexane must be known in order to interpret the *i vs. R* curves of their mixtures. Figure 1 is a plot of the Wheatstone bridge unbalance emf *vs.* molarity of solute for five bases: dodecylamine (DDA), dibenzylamine (DBA), tribenzylamine (TBA), *n*-hexylamine (HA), and cyclohexylamine (CHA); two acids: benzoic acid (HBZ) and trichloroacetic acid (TCA); and the standard monomeric solute dodecane. With the exception of CHA and HA the bases were essentially monomeric at the 0.01 *M* level. At 0.01 *M* $i = 0.85$ for cyclohexylamine and $i = 0.67$ for HA. Benzylamine was experimentally indistinguishable from zero at all concentration levels. It was discovered that the index of refraction of BA was very close to that of the solvent, and, even though the BA appeared to dissolve, it was actually quite insoluble in hexane. 1,3-Diphenylguanidine proved to be insoluble in hexane.

The two acids had *i* values experimentally indistinguishable from 0.5 at 0.01 *M* and appear to be dimers.

The behavior of the bases listed above was quite similar to amine bases in benzene,[1] while the acids were considerably more associated in hexane. Trichloroacetic acid is a monomer at 0.01 *M* in benzene, while HBZ at the same analytical concentration in hexane is present as a monomer to the extent of 38%, *i.e.*, $i = 0.69$.[1] The lesser extent of dimerization of these carboxylic acids in benzene than in hexane illustrates the basic character of benzene compared to hexane. This difference in dimerization of carboxylic acids in the two solvents was not unexpected, but the magnitude of the effect was somewhat surprising. The value of dimerization constants of a carboxylic acid in different, weakly basic solvents could prove to be a convenient quantitative measure of

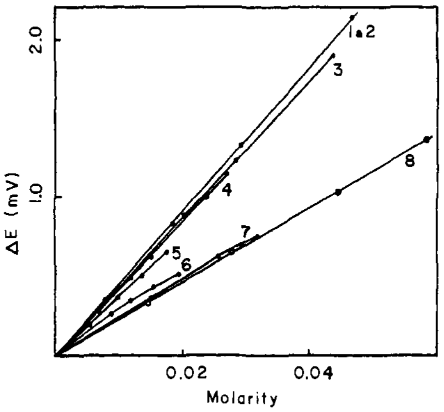

Figure 1. DVP calibration curves in hexane: (1) dodecane, (2) dodecylamine, (3) dibenzylamine, (4) tribenzylamine, (5) cyclohexylamine, (6) *n*-hexylamine, (7) trichloracetic acid, (8) benzoic acid.

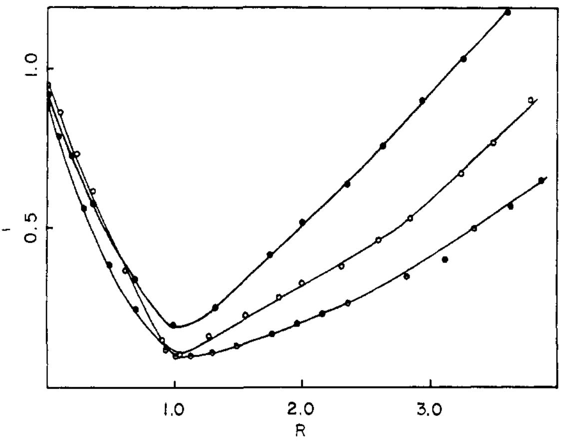

Figure 2. Reaction of DDA with TCA and HBZ: ○, 0.01 *M* DDA with TCA; ◒, 0.05 *M* DDA with TCA; ●, 0.01 *M* DDA with HBZ.

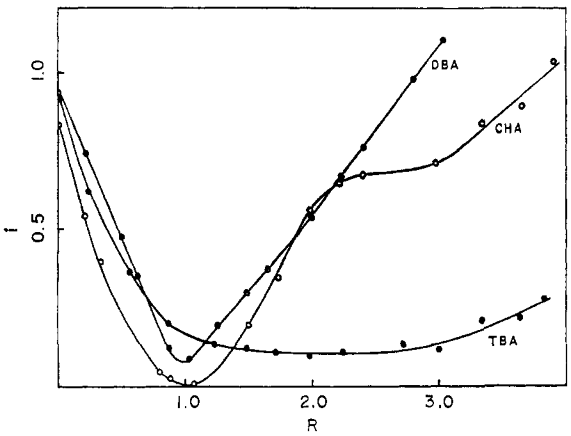

Figure 3. Reaction of TCA with DBA, CHA, and TBA, all with 0.01 *M* base: ○, CHA; ◒, DBA; ●, TBA.

the relative basicities of these solvents, provided adequate corrections for medium effects are made.

Reactions between Amines and Acids. Qualitative visual tests were performed on all amine–acid mixtures to be studied. The results are summarized in Table I. For all cases, except DDA, at least one of the adducts formed was insoluble.

Figure 2 shows the *i vs. R* curve of DDA (0.01 and 0.05 *M* DDA) with TCA and with HBZ (0.01 *M* DDA). Trichloroacetic acid reacts more quantitatively with DDA than does HBZ, as is indicated by the more pronounced rounding in the DDA–benzoic acid curve at $R = 1$ as compared to the 0.01 *M* DDA–TCA curve.

The DDA–TCA reaction at 0.01 and 0.05 *M* DDA shows quantitative formation of a 1:1 DDA–TCA adduct, BHX. The values of $1/i$ at $R = 1$ are 10 (observed value) and ~20 (extrapolated).

The proton in BHX has been transferred from TCA to DDA as shown by the infrared data in Table II. At $R = 1$ we observe the asymmetric and symmetric carboxylate stretches at 1670 and 1320 cm^{-1}, respectively, while the carbonyl bands at 1780 and 1742 cm^{-1}, which are characteristic of TCA, are absent.

In Figure 2 the rounding of the 0.05 *M* DDA–TCA curve in the region $0 < R < 1$, and its position with respect to the 0.01 *M* line, suggests $B_2 \cdot HX$ may form at sufficiently high concentrations of base.

The slope of the 0.01 *M i vs. R* curve, $1 < R < 2$, shows 54% of the added acid forms $BH^+HX_2^-$, assuming the extent of association of the $BH^+HX_2^-$ is approximately the same as that of BH^+X^-. Assuming that the infrared absorption at 1742 cm^{-1} is caused by the carbonyl group in TCA, the data at $R = 2$ show 46% of the added increment of acid is unreacted, which is in excellent agreement with the conclusions drawn from the DVP data. The 0.05 *M* DDA–TCA data are also consistent with these conclusions.

The change in slope of the *i vs. R* plots for DDA–TCA at $R = 3$ strongly supports the formation of a $BH^+HX_2^-$ species.

Beyond $R = 3$, the DVP data indicates further reaction of DDA with TCA leading to the partial formation of $BH^+H_2X_3^-$. In the infrared spectrum of such solutions the carboxylate bands are very distorted and broadened, and the symmetric stretch is about 50% as intense as at $R = 1$. This result suggests that the COO$^-$ environment is shifting toward that of the parent acid, as compared to the free ion which was observed at $R = 1$.

The slope of -1 in the plot of *i vs. R* for 0.01 *M* DDA–HBZ (Figure 2) in the region where $R < 1$ demonstrates that a 1:1 adduct of DDA and HBZ is formed. In benzene such a species had three infrared absorptions resulting from ion-pair formation.[1] These absorptions lie at ~1600, ~1500, and 1380–1420 cm^{-1} and are also present in ammonium and sodium benzoate (KBr and Nujol). Two bands, one at 1590 cm^{-1} and one at 1540-50 cm^{-1}, are observable in the spectrum of the 1:1 HBZ–DDA adduct in hexane. The third band, if present, is obscured by very strong hexane absorption near 1400 cm^{-1}. We conclude that the 1:1 adduct is the ion pair.

The slope of the *i vs. R* curve, $1 < R < 4$ for the 0.01 *M* DDA–HBZ mixture, approaches $^1/_2$ as would be expected if there is relatively little further reaction between BH^+Bz^- and HBz. The infrared absorptions at 1740 and 1690 cm^{-1} show that 70% of the HBZ added between $R = 1$ and $R = 2$ appears to be unreacted. The DVP and infrared data can easily be reconciled by assuming nonquantitative formation of $(BH^+HBZ_2^-)_m$, where $m \simeq 2$.

The extent of association of the 1:1 adducts of DDA with TCA and HBZ is quite surprising. The observed values of $1/i$, the average association number, are 5 and 10 for the HBZ and TCA ion pairs. The molecular weight of the DDA–TCA adduct is on the order of 3500.

Figure 3 gives the *i vs. R* curves for the reactions of DBA, CHA, and TBA with TCA. In each of these cases at least one of the reaction products was insoluble. The reaction of DBA and TCA has been studied in benzene, and 1:1 and 2:1 adducts were found.[1] The 1:1 adduct in benzene, as in hexane, was insoluble. Infrared data at $R = 1$ (Table II) show no absorptions bands, again demonstrating that the 1:1 adduct is very insoluble, and that species such as $BH^+HX_2^-$ have not yet formed. The *i vs. R* data, $1 < R < 3$, has a slope of $^1/_2$ as would be expected if no further reaction occurs between insoluble BH^+X^- and HX. However, the precipitate which forms initially redissolves by $R = 2.5$, demonstrating that a new adduct, *e.g.*, $(BH^+HX_2^-)_2$, is formed. The infrared absorption at 1742–1745 cm^{-1} indicates that 40% of the acid added in the region 1 <

$R < 2$ does not react with DBA. While the formation of $BH^+H_3X_4^-$ is not ruled out, no strong evidence for its existence exists.

The reaction of CHA and TCA was studied in the range $0 < R < 4$. CHA is slightly associated and the DVP data in Figure 3 suggest it forms a B_2HX adduct when CHA is in excess. This inference is drawn from the observation that the slope of the *i vs. R* curve is less than -1 at low values of R. At $R = 1$ both the DVP and infrared data indicate complete precipitation of a 1:1 adduct. The precipitate redissolves as more TCA is added, producing an increase in i between $R = 1$ and $R = 2$. The shape of the plot suggests that a species such as $(BHX)_nHX$ may form to a limited extent in addition to $BH^+HX_2^-$. The slope of the *i vs. R* plot, $3 < R < 4$, is 0.32, showing that TCA is still reacting with CHA. Changes in the infrared spectrum at 1244, 838, and 826 cm^{-1}, $2 < R < 3$, substantiate this conclusion.

An apparent discrepancy between the DVP and infrared data exists. The absorptions accredited to the carbonyl group at $R = 2$ and $R = 3$ are higher than the values that would be predicted from the DVP data. However, it seems likely that the carbonyl environment in the species $BH^+HX_2^-$ is very similar to the environment in $(HX)_2$ and thus could have an absorption maxium at about 1740 cm^{-1}. The peaks observed at $\sim$1740 cm^{-1}, for R values of 2 and 3, are much broader than in the pure acid.

The reaction between TBA and TCA is somewhat surprising. As seen from the *i vs. R* curve in Figure 3, one molecule of TBA can react quantitatively with four molecules of TCA, a result which is unexpected for a base as large as TBA. The first compound is an insoluble 1:1 adduct. The early rounding in the *i vs. R* plot indicates the conversion of insoluble $B\cdot HX$ to slightly soluble $B\cdot 2HX$ well before $R = 1$. Slightly soluble $B\cdot 3HX$ and $B\cdot 4HX$ appear to be forming since, as shown in Table I, a large excess of acid is required to dissolve the precipitate which formed initially. Weak infrared absorptions are seen in TBA–TCA solutions at $R = 2$ and $R = 3$. Infrared spectra at $R = 4$, 5, and 6 show that TCA is still adding a nonquantitative manner to form higher adducts.

Conclusion

Trichloacetic and benzoic acids react with a number of organic amines to form associated, uncharged ionic aggregates. Depending upon the reacting acid and base, the associated species include the simple ion pair, the homoconjugate ion pair, and ion pairs consisting of the protonated amine and more complex homoconjugate ions carrying a single negative charge. Evidence for species with a stoichiometry B_kHX ($k > 1$) is given. Association of aggregates is considerably greater in hexane than in benzene.

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Metal Ion–Aromatic Complexes. VII. The Crystal and Molecular Structure of Bis(*m*-xylene)silver Perchlorate

I. F. Taylor, Jr., E. A. Hall, and E. L. Amma[1]

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received March 6, 1969*

Abstract: The crystal and molecular structure of bis(*m*-xylene)silver(I) perchlorate has been determined by single-crystal X-ray diffraction from 672 counter intensities measured at ambient temperature. The crystals were found to be orthorhombic: $a = 16.594$ (8) Å, $b = 8.861$ (5) Å, $c = 5.795$ (3) Å; space group $P2_12_12_1$. The structure was refined by full-matrix least squares to a final conventional R factor of 0.050. The structure may be described as alternating tetrahedra of ClO_4^- ions and four coordinate Ag(I) sharing an oxygen vertex. The coordination tetrahedron of Ag(I) is composed of the two Ag–O interactions and two bonds to the π electrons of *m*-xylene rings. This tetrahedron is very flattened with an Ag–O distance of 2.49 ± 0.01 Å and O–Ag–O angle of 125.0 ± 0.8° together with an Ag–C distance of 2.45 ± 0.02 Å and C–Ag–C′ angle of 161.7 ± 0.8°. The next shortest Ag–C distance is 2.61 ± 0.02 Å. Hence, the Ag(I) is asymmetrically located relative to the nearest C–C bond of the aromatic ring. The shortest Ag–C distance is *ortho* and *para* to the methyl ring substituents. The aromatic moiety is normal within experimental error. It is clear that the perchlorate group plays a significant role in stabilizing this metal ion–aromatic complex.

The existence of donor–acceptor complexes between aromatic moieties and Ag(I) has been known for some time.[2–4] The 1:1 complexes are well known and the crystal structures of $C_6H_6\cdot AgClO_4$[5] and $C_6H_6\cdot AgAlCl_4$[6] have been determined. The former has been shown to be a polymeric complex and the latter a 1:1 complex with a five-coordinate Ag(I) entity. However, solution evidence,[2–7] composition phase diagrams,[8] and

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[1] Address all correspondence to this author.

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