frequency, but shows no change in the presence of *n*-heptane. However, the shifts of the P=O band to lower frequency (bond weakened) and the P–O–C band to higher frequency (bond strengthened) are in the direction which would be expected for hydrogen bonding to the phosphoryl oxygen.

TABLE III

POSITION OF P=O BANDS OF PHOSPHORYL COMPOUNDS

Phosphoryl compd.	CCl_4 soln. alone, cm.$^{-1}$	Phosphoryl compd. and acceptor solvent in CCl_4 soln.[a]			
		$CHCl_3$, cm.$^{-1}$	$CHCl_2$–CCl_3, cm.$^{-1}$	$CHCl_2$–$CHCl_2$, cm.$^{-1}$	*n*-C_7H_{16}, cm.$^{-1}$
$POCl_3$	1305	1302	1303	1302	1305
$(C_2H_5O)_3PO$	1263[c]	1260	1260	1265[b]	1263[c]
	1275[c]	1271 (sh)[d]	1274 (sh)[d]		1275[c]
$(n$-$C_4H_9)_3PO$	1168	1160	1160	1160	1168

[a] 4/1 moles of acceptor solvent to phosphoryl compound. [b] Broad band. [c] Band of doublet. [d] Shoulder.

The fact that $(n$-$C_4H_9)_3P{=}O$ shows a greater shift of the P=O absorption band on hydrogen bonding with $CHCl_3$ than do $(C_2H_5O)_3P{=}O$ and $POCl_3$ indicates that the oxygen atom of the phosphoryl group has a variable negative charge, this charge being greatest in the trialkyl phosphine oxide.

It was mentioned in a previous paper[14] that trialkylphosphine oxides hydrogen bond with catechol and phenol. The shifts in the phosphoryl absorption due to hydrogen bonding with a hydroxyl hydrogen are greater than shifts in phosphoryl absorption due to hydrogen bonding with the hydrogen of a C–H group.

[14] J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, THIS JOURNAL, **76**, 5189 (1954).

ARMY CHEMICAL CENTER, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Acid–Base Reactions in Non-dissociating Solvents. Acetic Acid and Diethylamine in Carbon Tetrachloride and Chloroform

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The reactions between acetic acid and diethylamine in carbon tetrachloride and chloroform were studied by infrared spectroscopy. Structures for the various ion-pair products have been deduced from the observed spectral changes. These are discussed in terms of their expected stabilities. As in the triethylamine–acetic acid system, interaction with chloroform molecules greatly alters the electronic structure of the ion pairs. Equilibrium constants were determined for several of the reactions and were compared with previous results.

The reactions of organic acids and bases in non-dissociating solvents produce ion-pair products.[1,2,3] The use of infrared spectroscopy allows the extent of the acid–base reaction to be followed, and therefore equilibrium constants to be obtained, and the nature of the ion-pairs to be deduced. The latter is concerned with the number of species present in the ion-pair, the manner in which the ions are linked, and the role of the solvent in the ion-pair. Furthermore, infrared spectroscopy is applicable to a wide range of acids and bases and is not restricted to compounds with convenient absorption bands in the visible region.[4,5]

A previous study of the system of acetic acid and triethylamine[6] has shown that the association between ion-pairs is a specific interaction, leading to particular hydrogen bonded structures, rather than only a general electrostatic attraction. A relatively strong interaction of the ion-pair with a hydrogen bonding solvent molecule was also observed to lead to a specific structure. The role of such solvents cannot, therefore, be understood in terms of the dielectric constants alone.

It is of interest now to investigate the ion-pair species, their structures and the equilibrium constants for the reaction of acetic acid with a secondary amine. Structural features rather different from those encountered with a tertiary amine are to be expected. The diethylamine–acetic acid system is chosen as a model for reactions involving secondary amines with carboxylic acids. Diethylamine and acetic acid are spectroscopically convenient. Carbon tetrachloride is taken as a completely non-interacting solvent and the effect of a hydrogen bonding solvent is studied using chloroform. Equilibrium constants are calculated to test the validity of the proposed species and are compared with previous results.

Experimental

The spectra discussed were obtained using a Baird Associates instrument with rock salt optics. Only the intensities of fairly low absorptions were used for quantitative work so that Beer's law could be assumed without appreciable error. The rock salt cells were 0.089 and 0.103 mm. thick, as determined by interference patterns, and 1.10, 9.3, 10.67 and 20.6 mm. thick, by direct measurement with a micrometer. The temperature of the samples was not controlled and was between room temperature, 25°, and that of the instrument, 30°.

The acetic acid, carbon tetrachloride and chloroform were purified as previously described.[6] The other reagents were prepared and purified as follows:

Diethylamine: Eastman Kodak white label diethylamine was dried over KOH and distilled. The constant boiling fraction at 55.6° was stored over KOH.

Diethylammonium acetate: equimolar quantities of diethylamine and acetic acid were mixed and cooled in an ice-bath. The resulting crystals, m.p. 26°, were dried under vacuum.

Diethyldideuteroammonium acetate: diethylammonium acetate was exchanged under vacuum with two samples of

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[1] M. M. Davis and E. A. McDonald, *Bur. Standards J. Research*, **42**, 595 (1949).

[2] A. A. Maryott, *ibid.*, **41**, 1, 7 (1948).

[3] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 3614 (1933).

[4] M. M. Davis and H. B. Hetzer, *Bur. Standards, J. Research*, **48**, 381 (1952), and references to previous work.

[5] R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952).

[6] G. M. Barrow and E. A. Yerger, THIS JOURNAL, **76**, 5211 (1954).

deuterium oxide, 99.8%, from the Stuart Oxygen Company. The product was dried under vacuum.

Ethyl acetate: Eastman Kodak ethyl acetate was distilled; the fraction boiling at 114–115° was used.

Cyclohexane: Eastman Kodak cyclohexane was stirred overnight with concentrated sulfuric acid to remove olefinic, aromatic or oxygen containing impurities. It was then washed, dried and distilled. The constant boiling fraction, 81°, was used.

The more concentrated acetic acid–diethylamine solutions tended to precipitate in the infrared cells, giving rise to interfering carboxylate bands. With such solutions, therefore, background spectra with the sample cell containing only the solvent were taken before and after each spectrum. Only those spectra which were followed by a relatively clear background trace were considered. The precipitate was removed from the cells by washing with *n*-butyl alcohol.

I. Nature of Intermediates and Products

Interpretation of the Spectra.—The spectrum of acetic acid is fairly well understood and has recently been discussed in detail by Hadzi and Sheppard.[7] Only certain bands useful in the present study need be mentioned. Convenient bands characteristic of the acetic acid dimer are the in-plane and out-of-plane OH deformations at 7.75 and 10.7 μ, respectively. Absorption in the carbonyl region due to acetic acid occurs at 5.84 μ for the dimer and 5.66 μ for the monomer. Other species, however, may also absorb in this region and a "carbonyl-like" absorption band indicates the presence of a species in which the oxygens are not equivalent, *i.e.*, one oxygen of the carbonyl group is essentially in a carbonyl bond. Equivalently bound oxygens are shown by the presence of carboxylate bands in the 6.2 to 6.45 and the 7.1 to 7.7 μ regions.[8]

A carbonyl frequency shift might be expected if hydrogen bonding occurred between diethylamine and the carbonyl group of the acetic acid monomer or of any of the ion-pair products. The effect of diethylamine on the carbonyl band of ethyl acetate was therefore studied. No shift from the value obtained in CCl_4 was produced by the addition of diethylamine. Ethyl acetate solutions of diethylamine also failed to exhibit any new bands in the carbonyl or carboxylate region.

A detailed discussion of the characteristic bands of diethylamine is unnecessary since only the C–N stretching[8] band at 8.8 μ is helpful. This band is characteristic of unreacted diethylamine and is not found in the diethylammonium salts. The amine salt bands at 4.05 and 5.1 μ[6,9] indicate the formation of a quaternary nitrogen atom. A band attributable to free N–H stretching was not observed for either the amine or its salts.

A fairly sharp, intense peak at 6.14 μ also appeared in the spectra of the reaction products and in that of pure diethylammonium acetate run as a liquid film or in solution. In similar spectra of diethyldideuteroammonium acetate, the 6.14 μ, 1629 cm.$^{-1}$, band disappeared and was replaced by its deutero equivalent at 8.7 μ, 1150 cm.$^{-1}$. The 4.05 μ band likewise disappeared in the spectrum of the deutero compound. The 6.14 μ band can therefore be assigned to the $^{+}NH_2$ bending mode. This assignment corresponds to that made for some amino acid hydrochlorides.[8]

Species Present in Carbon Tetrachloride.—The species occurring in the acetic acid–diethylamine mixture in CCl_4 may be identified with the aid of the bands discussed above. Spectra were examined for acetic acid concentrations of 0.3, 0.1, 0.02, and 0.0008 *M* with various concentrations of diethylamine. In addition solutions with a diethylamine–acetic acid ratio of 2:1 were observed for 0.0025, 0.005, 0.0075 and 0.01 *M* acetic acid.

In dilute solution, 0.0008 *M*, only the one-to-one species, $AcOH{\cdot}HNEt_2$, appears to be formed. The principal evidence for the composition of this species is the calculation of a satisfactory equilibrium constant. This species is, moreover, a reasonable result of the break up, on dilution, of the species found at higher concentrations. As shown in Fig. 1, the formation of this species is accompanied by the appearance of the 4.05 μ salt band, the 6.14 μ $^{+}NH_2$ bending band, and a new carbonyl band at 5.75 μ just intermediate between the 5.66 μ monomer and the 5.84 μ dimer carbonyl band. Thus the ion-pair, $AcO^{-}\ H_2{}^{+}NEt_2$, would be expected to have a carbonyl-like group but is clearly an ion-pair salt since the $^{+}NH_2$ group is present. Structure I, Fig. 2, is postulated for this one-to-one species in preference to structure VI since no free N–H stretching vibration is observed for the salt. Structure I is not necessarily planar but most probably, as recently suggested by Schneider,[10] the hydrogen bonding occurs in the direction of the non-bonded orbitals which project at approximately tetrahedral angles from the C–O bond direction.

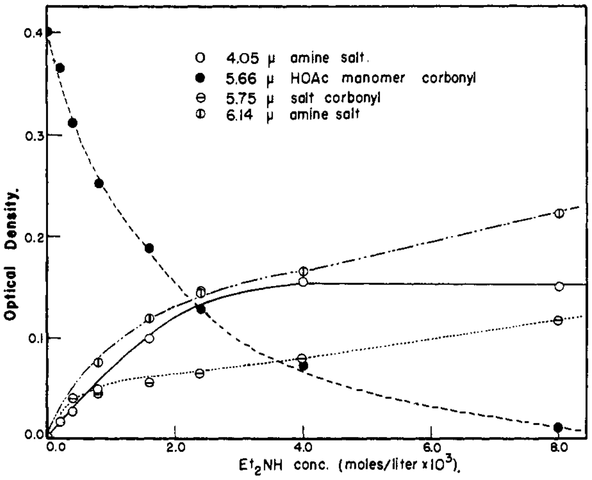

Fig. 1.—The optical density of some absorption bands in the system 0.0008 *M* acetic acid-diethylamine in CCl_4.

This relatively simple behavior of the system in dilute solution gives way to a more complicated one as the concentration is increased. In 0.3 and 0.1 *M* acetic acid solutions, Fig. 3, the complete disappearance of the 7.76 and 10.7 μ acetic acid dimer bands occurs at half neutralization indicating that then the acetic acid dimer is no longer present. Furthermore, the 5.84 μ carbonyl band has decreased to less than half its value and carboxylate bands have appeared at 6.46 and 7.2 μ, Fig. 4. The

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

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

[9] R. C. Lord and R. E. Merrifield, *J. Chem. Phys.*, **21**, 166 (1953).

[10] W. G. Schneider, *ibid.*, **23**, 26 (1955).

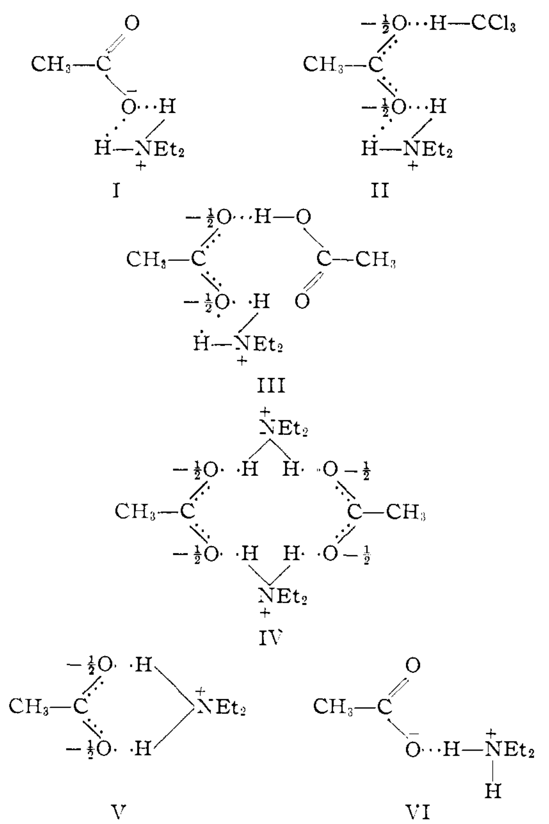

Fig. 2.—Proposed structures for the system diethylamine–acetic acid in CCl_4: I, III, IV; in $CHCl_3$: II, III; also considered: V, VI.

formation of a species $(AcOH)_2HNEt_2$, containing both carbonyl and carboxylate groups is indicated. Salt formation is shown by the presence of the 4.05, 5.1 and 6.14 μ salt bands. These characteristics lead to the postulation of structure III for this species analogous to the intermediate reported previously for the triethylamine–acetic acid system.[6] The intermediate character of III is indicated by the further decrease of the 5.84 μ carbonyl band after half neutralization, the fact that the 6.46, 7.2 and 7.8 μ bands all exhibit maxima at half neutralization and subsequently disappear, and the continued increase of the 4.05, 5.1 and 6.14 μ amine salt bands. The apparent shift of the 7.76 μ in-plane OH deformation of the acetic acid dimer to a band of slightly higher frequency, 7.8 μ, is interpreted as being due to the modified environment of the remaining acetic acid molecule. As in species I, the structure of the ion-pair is not necessarily planar. A hydrogen bond may exist from the diethylammonium ion to the acetic acid carbonyl but more probably there is only a general electrostatic attraction of the negative carbonyl oxygen to the nearby cation.

The stoichiometric composition, $AcOH{\cdot}HNEt_2$, of the final species is shown by the almost complete disappearance of the 5.84 μ carbonyl band and the leveling off of the 4.05, 5.1 and 6.14 μ amine salt bands at diethylamine concentrations greater than the acetic acid concentration. The 8.8 μ diethylamine band appears at the one-to-one diethylamine–acetic acid ratio and increases linearly indicating no additional species. A new carboxylate band

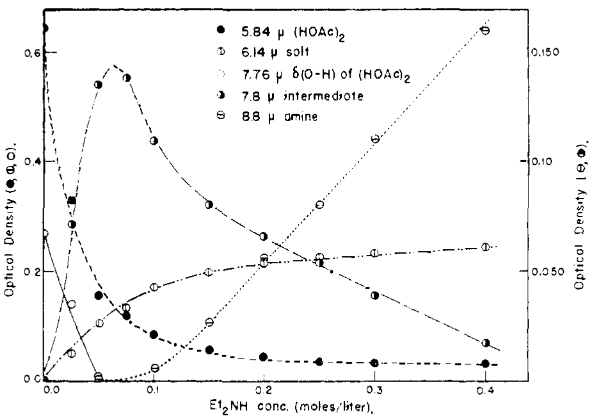

Fig. 3.—The optical density of some absorption bands in the system 0.1 M acetic acid–diethylamine in CCl_4.

appears at 6.33 μ for diethylamine concentrations greater than half neutralization and levels off at diethylamine concentrations of greater than the one-to-one ratio, Fig. 4. Since the final product in concentrated solutions has carboxylate character rather than the carbonyl character found in more dilute solutions, a dimer, IV, of species I found for the dilute solution product is proposed. The carboxylate character of this species might also be explained by structure V. Such a species would not, however, be favored in concentrated solutions while I is favored in dilute solutions. To verify that this salt product is a dimer the behavior of the 5.75 μ carbonyl band of species I was observed for solutions of intermediate acetic acid concentrations, 0.0025, 0.005, 0.0075 and 0.01 M, containing a diethylamine–acetic acid ratio of 2 : 1. The increase in the observed intensity of the 5.75 μ band was not as great as the linear increase predicted by Beer's law. Likewise, the increase in the carboxylate band at these concentrations was greater than predicted by Beer's law; cyclohexane was used as the solvent since CCl_4 is not very transparent in this region. The dimer IV can be considered as the association of ion-pairs of the type I in which the polarization of the two oxygens of the carboxylate is equalized. As discussed previously the diethylammonium hydrogens are oriented in such a way as to allow maximum interaction with the carboxylate oxygens. The partial double bond character of the C–O bond probably requires these hydrogens to be in the plane of the acetate skeleton and at about a 120° angle with the $C{-}O^-$ bond.[10] This suggests that these hydrogens be bound to separate carbonyl oxygens, structure IV,[11] since a dimer with the hydrogen bonding arrangement of species I would not easily lead to an equivalence of the oxygens as required by the observed carboxylate band.

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(11) The suggested structure for the salt dimer, IV, would lead to a zero dipole moment for a rigidly planar form. Measurements of the dielectric constants of solutions of amines and acetic acid in CCl_4 lead, however, to molar polarization of about 290 cc. per mole for the ion-pair Et_3NHOAc and a similar value calculated on the basis of a dimer species, $(Et_2NH_2OAc)_2$. The latter result would be near 150 on the basis of a monomer salt product and this would appear to be rather inconsistent with the Et_3N result. On the other hand, the dimer salt of Et_2NH would not have been expected to yield a value as high as 300. This is, however, probably compatible with structure IV in view of its expected high polarizability and the possibilities of a non-rigid planar configuration.

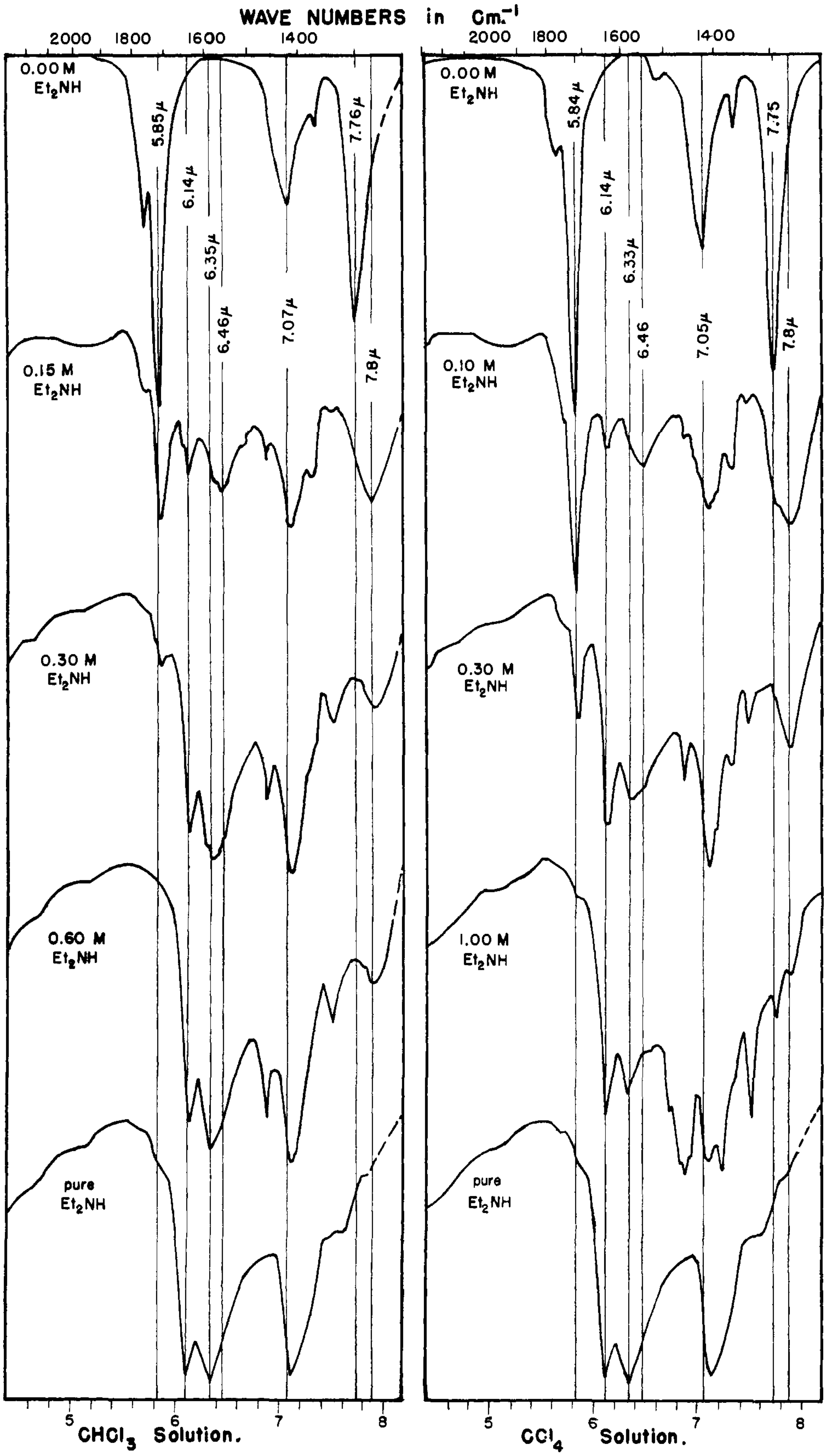

Fig. 4.—Some typical absorption curves for the system 0.3 M acetic acid–diethylamine.

The species present in the system acetic acid–diethylamine in carbon tetrachloride can therefore be quite definitely deduced from the infrared spectra. At high acetic acid concentrations a species III is formed which on further addition of diethylamine goes over to species IV. In the more dilute solutions species I is the most important reaction product.

Species Present in Chloroform.—The species present in the diethylamine–acetic acid system in chloroform have been determined in a manner similar to those in CCl_4. For higher acetic acid concentrations, 0.3 and 0.1 *M*, as shown in Fig. 5 at half neutralization the 7.76 μ dimer band has almost disappeared, the 5.85 μ carbonyl band has diminished to less than half its original value, and the carboxylate bands at 6.46 and 7.2 and the OH deformation band at 7.8 μ have reached their maximum intensities. This is accompanied by the appearance of the amine salt bands at 4.05, 5.1 and 6.14 μ. Since this behavior parallels that observed in CCl_4, the same intermediate III is postulated.

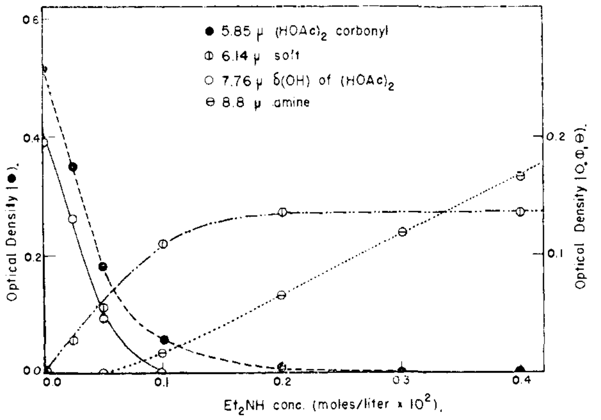

Fig. 5.—The optical density of some absorption bands in the system 0.1 *M* acetic acid–diethylamine in $CHCl_3$.

The final product in $CHCl_3$ is a one-to-one species, $AcOH{\cdot}HNEt_2$, as in CCl_4. This is shown by the complete disappearance of the 5.85 μ carbonyl band, Fig. 5, the leveling off of the 4.05, 5.1 and 6.14 μ amine salt bands and the appearance and linear increase of the 8.8 μ diethylamine band when the 1:1 ratio is exceeded. As in CCl_4, a new 6.35 μ carboxylate band, Fig. 4, appears after half neutralization and levels off at higher diethylamine concentrations. In $CHCl_3$ the carboxylate nature of the final product is attributed to stabilization of the salt by hydrogen bonding with the solvent, structure II, as in the triethylamine–acetic acid system.[6] This solvent stabilization is thought to prevent the formation of IV which is spectroscopically indistinguishable from II. The formation of II rather than IV is borne out by the equilibrium constant calculations.

In more dilute solutions, 0.0008 *M* acetic acid, there is no evidence for the formation of an intermediate III and only the one-to-one product is formed. The disappearance of the 5.71 and 5.85 μ acetic acid carbonyl bands is not accompanied by the formation of any new carbonyl bands but the 4.05 and 6.14 μ amine salt bands do appear. The appearance of a carboxylate band could not be determined since it would be obscured by the strong solvent absorption in the carboxylate region. Thus the final product is species II as postulated in the more concentrated solutions.

Thus certain deductions can also be made about the species present in the diethylamine–acetic acid system in $CHCl_3$ from the infrared spectra. At high acetic acid concentrations III is formed initially and is converted to II, or possibly the spectroscopically indistinguishable IV, at higher diethylamine concentrations. The postulation of a salt dimer, IV, is not necessary to explain the results in $CHCl_3$ and as will be shown does not lead to a satisfactory equilibrium constant. In the more dilute solutions II is formed directly.

II. Calculation of Equilibrium Constants

Determination of the species present in the diethylamine–acetic acid system makes it possible to calculate the constants for the equilibria involved. The equilibrium constants for the dimerization of acetic acid in chloroform and carbon tetrachloride have been evaluated previously[12] for concentrations to about 0.0008 *M*. The presence of interacting impurities was observed to increase the values of these constants. In contrast to acetic acid, the relatively weak association between diethylamine molecules would not be expected to alter significantly its effective concentration and was neglected in the calculation of the equilibrium constants. The change in solvent properties due to the addition of diethylamine was also assumed negligible for the equilibria involved.

Acid–Base Equilibrium Constants in Carbon Tetrachloride.—In very dilute solutions, 0.0008 *M* acetic acid, the reaction proceeds directly from the acetic acid monomer to the final product I according to reaction 1.

$$AcOH + HNEt_2 \rightleftarrows AcOH_2NEt_2 \qquad (1)$$

The concentration of the acetic acid monomer in 0.0008 *M* acetic acid solution was calculated from an equilibrium constant of 2000 l. moles^{-1} for the acetic acid dimerization.[12] From the observed intensity of the 5.66 μ monomer band, αl for this band was determined and Beer's law, $C = (1/\alpha l) \log I_0/I$, used to calculate the monomer concentration at the various diethylamine concentrations. The concentration of the dimer was determined in a similar manner from the intensity of the 5.84 μ band. The observed deviation of the dimerization constant calculated from these values is probably due to the presence of an interfering compound, *i.e.*, the excess diethylamine or the salt, and does not introduce an appreciable error in the calculations. The concentrations of I and diethylamine could then be calculated from the stoichiometry of the reaction. An average value of 2800 l. mole^{-1} for the equilibrium constant of reaction 1 was obtained as shown in Table I.

This equilibrium constant was then used to calculate the concentration of the acetic acid monomer and the salt at various diethylamine values. Suitable values of αl for the acetic acid and the salt were chosen so that a calculated optical density

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(12) G. M. Barrow and E. A. Yerger, THIS JOURNAL, **76**, 5248 (1954).

TABLE I

THE EQUILIBRIUM CONSTANT FOR THE REACTION

$CH_3COOH + Et_2NH \rightleftarrows CH_3COOH_2NEt_2$

Acetic acid concentration equals 0.0008 *M*

			$C \times 10^4$, moles l.$^{-1}$				
M_{HNEt_2}	log (I_0/I) 5.66μ	log (I_0/I) 5.84μ	HOAc	(HO-Ac)$_2$	Et$_2$-NH$_2$-OAc	Et$_2$-NH	*K*
0.0000	0.402	0.748	(3.40)	(2.30)	..	...	..
.0002	.365	.660	3.09	2.03	0.85	1.15	(2460)
.0004	.311	.584	2.63	1.80	1.77	2.23	3050
.0008	.252	.450	2.13	1.38	3.11	4.89	2990
.0016	.187	.297	1.58	0.91	4.60	11.40	2550
.0024	.127	.258	1.08	0.79	5.34	18.66	2640
.0040	.071	.204	0.60	0.65	6.10	33.90	3000
						Av.	2800

could be plotted against the amine concentration. As shown in Fig. 6 the calculated curves agreed closely with the experimental values of the 5.66 μ monomer and the 4.05 μ salt bands; the 5.75 μ carbonyl band also agrees closely with the calculated salt curve. This agreement indicates that the assumption that I is the only amine salt species present at these concentrations is valid.

Calculation of the dimerization constant for the salt was made at salt concentrations of 0.0001 to 0.002 *M*, where the 5.75 μ band does not increase as much as predicted by Beer's law. The 5.75 μ band was assumed to be due only to the salt monomer, I, and a value of α determined from the intensity of this band in very dilute solutions containing only I. The values for the monomer salt concentration were then calculated from intensity of the 5.75 μ band. The free acetic acid and diethylamine were calculated from the equilibrium constant for reaction I and the concentration of the dimer was obtained from the stoichiometry. The salt dimerization constant was then determined to be 240 l. mole^{-1} as shown in Table II. This value predicts that less than 10% of the salt monomer would dimerize at the concentrations used for the calculation of the equilibrium constant for reaction I confirming the validity of the assumption made in calculating this constant. Further it predicts that in the 0.1 and 0.3 *M* acetic acid solutions only about 10% of the salt is present as monomer.

TABLE II

EQUILIBRIUM CONSTANT FOR SALT DIMERIZATION

$2CH_3COOH_2NEt_2 \rightleftarrows (CH_3COOH_2NEt_2)_2$

				$C \times 10^3$, moles l.$^{-1}$		
M_{HOAc}	M_{Et_2NH}	$M_{AcOH_2NEt_2}$	1/*l*. log (I_0/I) 5.75 μ	AcOH$_2$-NEt$_2$	(Ac-OH$_2$-NEt$_2$)$_2$	*K*
0.0008	0.0016	0.000518	0.00573	(0.518)	..	..
.0025	.005	.0020	.0148	1.34	0.43	240
.0050	.010	.0044	.0253	2.29	1.23	230
.0075	.0150	.0068	.0340	3.07	2.10	230
.0100	.0200	.0093	.0382	3.45	3.18	270
					Av.	240

The equilibrium constant for the formation of III, reaction 2, appeared too large to calculate, *i.e.*, the reaction

$$(AcOH)_2 + HNEt_2 \rightleftarrows (AcOH)_2HNEt_2 \qquad (2)$$

is essentially stoichiometric. The constant for the formation of IV, reaction 3, can, however, be approximated in the solutions containing 0.1 and 0.3 *M* acetic acid. The concentration of III was obtained from the intensities of the 6.46 and 7.2 μ bands by assuming that only III was present at an acetic acid–diethylamine molar ratio of two-to-one. From a consideration of their equilibrium constants only the acetic acid and salt dimers could be assumed to be present. An average of 16 l. mole^{-1} was obtained for the equilibrium constant of reaction 3 as shown in Table III. Combination of this value with the constants previously calculated leads to a value of approximately 1.5 × 10^4 l. mole^{-1} for reaction 2 confirming that this reaction proceeds essentially stoichiometrically at acetic acid concentrations of 0.1 *M*.

$$(AcOH)_2HNEt_2 + HNEt_2 \rightleftarrows (AcOH_2NEt_2)_2 \qquad (3)$$

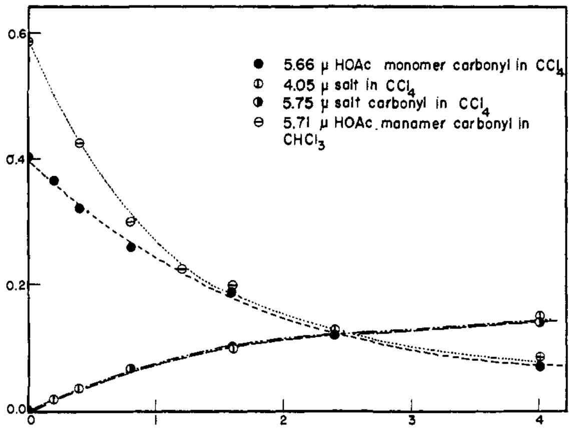

Fig. 6.—The calculated optical density of some absorption bands in the system 0.0008 *M* acetic acid–diethylamine.

TABLE III

EQUILIBRIUM CONSTANT FOR THE REACTION IN CARBON TETRACHLORIDE

$HNEt_2 + (AcOH)_2HNEt_2 \rightleftarrows (AcOH_2NEt_2)_2$

			C (mole l.$^{-1}$)			
$M_{(HOAc)_2}$	M_{Et_2NH}	log (I_0/I) 6.46 μ	(AcOH)$_2$-HNEt$_2$	(AcOH$_2$-NEt$_2$)$_2$	Et$_2$NH	*K*
0.15	0.15	0.115	(0.15)	...	...	..
.15	.20	.094	.122	0.028	0.022	10
.15	.25	.073	.095	.055	.045	13
.15	.30	.050	.065	.085	.065	20
.15	.35	.042	.055	.095	.105	16
.15	.40	.030	.039	.111	.139	20
		log (I_0/I) 7.20 μ				
0.05	0.05	0.066	(0.05)	...	...	..
.05	.075	.044	.030	0.020	0.005	13
.05	.10	.023	.016	.034	.016	13
.15	.15	.218	(0.150)	...	...	..
.15	.20	.172	.118	.032	.018	15
.15	.25	.137	.095	.055	.045	13
.15	.30	.110	.066	.084	.066	19
.15	.35	.090	.062	.088	.112	13
.15	.40	.060	.041	.109	.122	22
					Av.	16

Acid–Base Equilibrium Constants in Chloroform.—Calculation of the equilibrium constant for the formation of II, reaction 4, was made using the results obtained with 0.0008 *M* acetic acid.

$$AcOH + HNEt_2 + HCCl_3 \rightleftarrows AcOH_2NEt_2 \cdot HCCl_3 \qquad (4)$$

As in CCl_4, the acetic acid monomer concentration was calculated from the intensity of the 5.71 μ monomer band. The value of αl was obtained from the intensity of this band with no diethylamine present using the acetic acid dimerization constant of 200 l. mole^{-1}.[12] The dimer concentration was calculated from the monomer concentration and the dimerization constant since the intensity of the 5.85 μ band could not be accurately determined in $CHCl_3$. This constant might be expected to show deviations as it did in CCl_4 but again the error thus introduced is comparatively small. The salt and diethylamine concentrations were calculated from the stoichiometry of the reaction. The equilibrium constant, 3000 l. mole^{-1}, was then determined as shown in Table IV and a theoretical curve was calculated for the intensity of the 5.71 μ band agreed well with the experimental values, Fig. 6, and was much more sensitive to the value of the acid–base equilibrium constant than that calculated for CCl_4 solutions due to the decrease in the dimerization constant of acetic acid.

TABLE IV

ACID–BASE EQUILIBRIUM CONSTANT IN CHLOROFORM

$$CH_3COOH + Et_2NH \rightleftharpoons CH_3COOH_2NEt_2$$

Acetic acid equals 0.0008 M

M_{Et_2NH}	log (I_0/I) 5.71 μ	$C \times 10^4$, moles l.$^{-1}$ HOAc	$(HOAc)_2$	$AcOH_2$-NEt_2	Et_2NH	K
0.0000	0.584	(6.37)	(0.81)	..	...	..
.0004	.426	4.65	.43	2.49	1.51	3540
.0008	.299	3.27	.21	4.31	3.69	3570
.0012	.228	2.49	.12	5.27	6.73	3150
.0016	.210	2.29	.10	5.51	10.49	2300
.0024	.120	1.31	.03	6.63	17.37	2920
.0040	.084	0.92	.02	7.04	32.96	2320
					Av.	3000

The formation of III in $CHCl_3$ appeared to proceed essentially to completion as in CCl_4. There was still, however, some unreacted amine at half neutralization so that the equilibrium constant for reaction 5 could not be calculated from the inter-

$$(AcOH)_2HNEt_2 + HNEt_2 + 2HCCl_3 \rightleftharpoons 2AcOH_2NEt_2{\cdot}HCCl_3 \quad (5)$$

mediate bands as with CCl_4. Therefore this equilibrium constant had to be calculated from the intensity of the 6.35 μ carboxylate band which is difficult to sort out from the 6.46 μ band. It is, however, the only band available which could be assumed to be due only to II. The intensity of this band at the two highest diethylamine concentrations of Table IV was assumed to represent complete salt formation and was used to calculate αl for this band. The concentration of III and diethylamine were then determined by considering the stoichiometry of the reaction. The value of 100 l. mole^{-1} for reaction 5 was obtained as shown in Table V and was then used to approximate an equilibrium constant for reaction 2 in $CHCl_3$. This constant indicated that only about 10% of III would not be formed at equimolar amounts of acetic acid dimer and diethylamine. Thus the assumption that no acetic acid dimer remains after this point would be expected to produce only a small error in the equilibrium constant as calculated in Table V but might account for the lowest value obtained.

TABLE V

EQUILIBRIUM CONSTANT FOR THE REACTION IN CHLOROFORM

$$(AcOH)_2HNEt_2 + HNEt_2 \rightleftharpoons 2AcOH_2NEt_2$$

$M_{(HOAc)_2}$	M_{Et_2NH}	log (I_0/I) 6.35 μ	$C \times 10^2$, moles l.$^{-1}$ Et_2NH_2-OAc	$(AcOH)_2$-$HNEt_2$	Et_2NH	K	K
0.05	0.10	0.125	4.16	0.84	0.84	100	290
.05	.20	.150	(5.00)	...	..	..	..
.05	.40	.151	(5.00)	...	..	..	..
.15	.20	.147	4.87	10.13	0.13	70	180
.15	.25	.276	9.15	5.85	0.65	90	120
.15	.30	.377	12.60	2.40	2.40	110	110
.15	.35	.420	13.90	1.10	6.10	120	100
.15	.40	.449	(15.00)	...	..	..	..
.15	.60	.456	(15.00)	...	..	..	..
					Av.	100	

Since, as discussed previously, the formation of a dimer, IV, was also possible an equilibrium constant, K', was calculated for dimer reaction 3 in $CHCl_3$. As shown in Table V, this constant was fairly satisfactory for the data from the solutions 0.15 M in acetic acid dimer. However, the poor agreement of the value obtained with a concentration of 0.05 M acetic acid dimer is outside of experimental error and must be considered as evidence against the formation of the dimer, IV, in chloroform solutions.

III. Discussion

Ion-pair structures involving hydrogen bonding between the ions and with the solvent have been demonstrated in previous work with triethylamine and acetic acid.[6] The exact nature of the salt structures in the diethylamine system could not, however, have been easily predicted. Structures I, V and VI as well as structures requiring hydrogen bonding of diethylamine to the salt appeared feasible. The preferential formation of I and the formation of the dimer IV in CCl_4 can be understood. The relative values of the equilibrium constants in the triethylamine– and diethylamine–acetic acid systems may also be explained.

A simple electrostatic calculation on the basis of a model similar to those of Schneider[10] indicates that I is about 1.6 kcal. more stable than VI. The energy loss due to the non-linearity of the O · · ·H–N system is adequately compensated for by the fact that two hydrogen bonds are formed in I whereas only one linear hydrogen bond may be formed in VI. Similar calculations lead to the relative stability of the non-linear hydrogen bonded structures II, III and IV over corresponding models having only one linear hydrogen bond. The preferential formation of I over V is understood when the relative dimensions of the two ions are considered. In structure V, the closest non-bonded orbitals of the two carboxylate oxygens are parallel to each other at a distance of about 2.5 Å. Since the distance between the two hydrogens on the diethylammonium ion is about 0.9 Å. less than this, the formation of two hydrogen bonds as shown in V is highly improbable. This is probably the chief reason for the failure to observe this more symmetrical structure.

The formation of the dimer IV in CCl_4 may be regarded as an extreme result of the dipole–dipole attraction of ion-pairs. The ability of the cation to bridge the two anions leads to the observed spectral changes and probably explains the stability of the dimer. The absence of such dimers in the triethylamine–acetic acid system[6] is then expected since there could be no similar cation bridge. Specific solvent hydrogen bonding in $CHCl_3$ as indicated by II would tend to prevent dimerization and explains the absence of the dimer in $CHCl_3$. This effect is also demonstrated by the larger dimerization constant of acetic acid in CCl_4 than in $CHCl_3$.[12]

The specificity of the hydrogen bonding of chloroform to the ion-pairs and between the elements of the ion-pairs in the triethylamine–acetic acid and diethylamine–acetic acid systems suggests that similar structures are also to be expected for solvation of ions in dissociating solvents. Structural arrangements of water molecules have been proposed for cation solvation in water.[13,14] A model involving linear hydrogen bonding for anion solvation has been discussed by Verwey.[15] The structures for the diethylamine–acetic acid complexes reported here suggest that two hydrogens from the same water molecule may hydrogen bond to the same anion. This non-linear model is not intended to replace that of Verwey but would be favored in cases where additional good hydrogen acceptors are not readily available.

It is of interest, also, to consider the relative base strength of tri- and diethylamine toward acetic acid in CCl_4 and $CHCl_3$. On the basis of the inductive effect, triethylamine is expected to be a stronger base than diethylamine.[16] The relative basicity of these compounds may, however, be altered by differences in solvation. Assuming that there is no solvent interaction due to CCl_4, the larger equilibrium constant for the direct salt formation, reaction 1, and hence increased basicity of diethylamine when compared with triethylamine in CCl_4 must be attributed to differences in the ability of the acetate ion to interact with or "to solvate" the cation. This "solvation" by the acetate ion might be expected to be greater for diethylammonium ion than for triethylammonium ion since the former ion forms two hydrogen bonds with the acetate ion. Some steric effect due to increased shielding of the lone pair of electrons on the nitrogen atom of triethylamine[16] is also possible. In $CHCl_3$ there are, in addition to the differences in ion–ion interactions, solvent effects due to the relative hydrogen bonding energies of $CHCl_3$ to the amines and to the ion-pairs. The equivalence of the equilibrium constants for the reaction of diethylamine and triethylamine with acetic acid observed in $CHCl_3$ probably stems from the fact that although the diethylammonium ion is better "solvated" by the acetate ion, diethylamine forms a better hydrogen bond to $CHCl_3$ than does triethylamine.[17] The equivalence of the equilibrium constants for direct salt formation between diethylamine and acetic acid in CCl_4 and $CHCl_3$ indicates furthermore that the reactants and the products are equally well stabilized by hydrogen bonding to $CHCl_3$.

These results emphasize the important role of the solvent and of the ion-pair structures in determining relative basicities. The necessity of an accurate knowledge of the detailed structure of the products before equilibrium constants may be compared is also pointed out. These structures may also be of more general theoretical value in the interpretation of solvent-ion structures such as occur in aqueous solution.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES OF THE UNIVERSITY OF CHICAGO]

Anions as Bridging and Non-bridging Ligands in Reactions of Co(III) Compounds with Cr^{++}

BY HENRY TAUBE

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Transfer of X to Cr takes place in the reaction of $(NH_3)_5Co(III)X$ with Cr^{++} when X is thiocyanate, azide, phosphate, pyrophosphate, acetate, butyrate, crotonate, oxalate, succinate or maleate. The rates of reaction are approximately the same with X = acetate, butyrate, crotonate or succinate, but are at least 100 times greater with oxalate or maleate as the bridging groups. The participation of some anions as non-bridging ligands has been demonstrated. Pyrosphosphate adds efficiently to Cr on reaction of $Co(NH_3)_5H_2O^{+++}$ with Cr^{++}, and $SO_4^{=}$ does so less efficiently. When $Co(NH_3)_5Cl^{++}$ is the oxidizing agent, and pyrophosphate is present, both Cl and pyrophosphate add to Cr. The reaction of Cr^{++} with Co en_2 *o*-phen^{+++} is more rapid than that of Cr^{++} with Co en_3^{+++}.

The study of reactions of Cr^{++} with substitution-inert cationic oxidizing agents[1-3] has led to some definite conclusions about the geometry of the activated complexes involved. Each system studied thus far has furnished evidence for a "bridged activated complex"—one in which the central atoms in oxidant and reductant share a common group during the electron transfer process. The particular systems for which this feature of the transition state, as well as others, can be readily demonstrated provide models also for systems in which a similar direct demonstration of geometry is difficult

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