and ketones relative to hydrocarbons.[20] It is probable that at least part of the deviations arises from subtle differences in conformations. In any event, the heavy dependence of ^{13}C chemical shifts upon steric forces in these systems heralds the development of a potent tool in the study of conformations.

Acknowledgment. The authors are indebted to Professor S. J. Angyal for generous advice and gifts of samples.

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Carboxylic Acid–Amine Equilibria in Nonaqueous Solvents[1,2]

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Abstract: A survey of the infrared and ultraviolet spectra of mixtures of amines and carboxylic acids has shown that the expected formation of ion pairs A^-BH^+ and AHA^-BH^+ often takes place. However, tertiary amines exhibit two types of abnormal behavior. In solvents of low dielectric constant such as carbon tetrachloride, cyclohexane, or carbon disulfide strong tertiary amines such as triethylamine interact with carboxylic acids such as acetic acid and benzoic acid by hydrogen bond association with little ionization. Furthermore, the ionization which does occur in solvents such as chloroform or acetonitrile leads to unusual species. There is an absence of identifiable NH^+ infrared absorption and the whole curve is underlaid by a strong genreal absorbance. These spectra have been interpreted qualitatively and in two cases also quantitatively.

Because an understanding of acid–base equilibria underlies much of chemistry, the development of modern techniques has led to a rejuvenation of interest in medium strength acids and bases, particularly with reference to nonaqueous systems.[3] Techniques that have been applied include conductivity,[4] indicator titrations,[3] measurements of ultraviolet,[5] infrared[6–12] and nmr spectra,[13] potentiometric titrations,[14] measurements of colligative properties,[15,16] calorimetric measurements,[17] and measurements of dielectric constants.[18] Chemical methods based on reaction kinetics might be included, but reaction systems are usually too complicated to provide firm conclusions about acid–base equilibria.[19,20]

Each technique provides useful types of information. The purpose of the present work is to develop further the spectrophotometric techniques. In favorable systems these permit direct observation of ion pair and other equilibria and hence serve to complement techniques which depend primarily on observation of free ions or which count the number of molecules present.

The present work has been greatly facilitated by the pioneering studies of Barrow and his students[6–10] and by other studies, only a selection of which has been specifically cited. Yet there are two fundamental points upon which we disagree with previous workers. (1) We interpret the spectra of solutions of acetic acid and triethylamine in nonpolar solvents such as carbon tetrachloride as indicative of hydrogen bonding without ionization. Previous workers have suggested the formation of 2:1 salts AHA^-BH^+ and 1:1 salts A^-BH^+.[6,12] (2) Systems of tertiary amines and carboxylic acids show a broad relatively strong general absorbance which we interpret as indicative of uncertainty in the position of the proton. This phenomenon is much less pronounced for mixtures of carboxylic acids with primary or secondary amines and does not occur with mixtures of amines and phenols.

Qualitative Results. Typical ir spectra are shown in Figure 1 and uv spectra are shown in Figure 2. In a solvent such as dimethyl sulfoxide, addition of sufficient triethylamine to a solution of benzoic acid causes disappearance of the benzoic acid peak at 1714 cm^{-1} and appearance of typical benzoate peaks at 1575 and 1604 cm^{-1} (Figures 1-1 and 1-8). It is also possible to identify the NH^+ absorption at 2450 and 2600 cm^{-1} (Figures 1-3 and 1-8). These spectral features indicate that ionization has occurred. Other evidence shows that there is relatively little dissociation into free ions.

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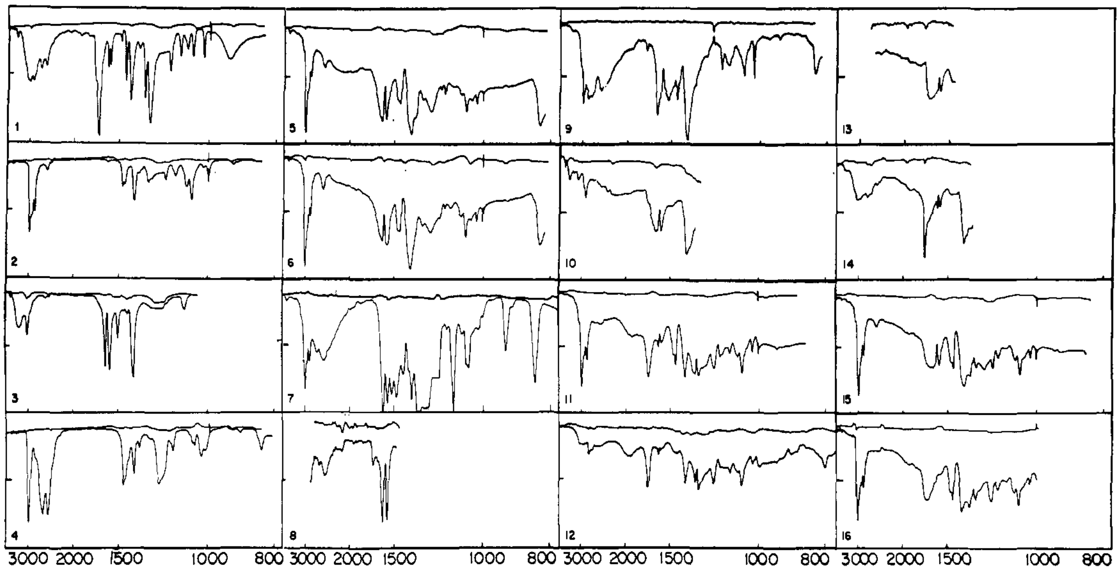

Figure 1. Infrared spectra of acids and bases: (1) upper curve solvent, against solvent; lower curve benzoic acid (0.088 *M*) in chloroform, against chloroform; cell thickness 0.2 mm; sodium chloride; same cell for all spectra except 3, 10, and 12; ordinate is per cent transmittance. (2) Triethylamine (0.079 *M*) in chloroform, against chloroform. (3) Tetramethylammonium benzoate (0.040 *M*) in chloroform + 2% ethanol, against chloroform + 2% ethanol; cell thickness 0.2 mm; calcium fluoride; the ethanol was used to increase solubility; except for the OH peak at 3300 cm^{-1}, the spectrum is the same as that of more ragged curves using dilute solutions without ethanol. (4) Triethylammonium bromide (0.080 *M*) in chloroform, against chloroform. (5) Benzoic acid (0.108 *M*) plus triethylamine (0.172 *M*) in chloroform, against chloroform. (6) Deuteriobenzoic acid (0.088 *M*) plus triethylamine (0.163 *M*) in chloroform, against chloroform. (7) 2,4-Dinitrophenol (0.1 *M*) plus triethylamine (0.2 *M*) in chloroform, against chloroform. (8) Benzoic acid (0.064 *M*) plus triethylamine (0.160 *M*) in dimethyl sulfoxide, against dimethyl sulfoxide. (9) Benzoic acid (0.100 *M*) plus diethylamine (0.200 *M*) in carbon tetrachloride, against carbon tetrachloride. (10) Benzoic acid (0.076 *M*) plus triethylamine (0.13 *M*) in propionitrile, against propionitrile (calcium fluoride cell). (11) Benzoic acid (0.084 *M*) plus triethylamine (0.161 *M*) in carbon tetrachloride, against carbon tetrachloride. (12) Benzoic acid (0.025 *M*) plus triethylamine (0.05 *M*) in cyclohexane, against cyclohexane; cell thickness 0.5 mm; sodium chloride. (13) Benzoic acid (0.101 *M*) plus triethylamine (0.302 *M*) in 1,4-dioxane, against 1,4-dioxane. (14) Benzoic acid (0.102 *M*) plus triethylamine (0.200 *M*) in tetrahydrofuran, against tetrahydrofuran. (15) Benzoic acid (0.090 *M*) plus triethylamine (0.168 *M*) in 70% carbon tetrachloride–30% chloroform, against 70% carbon tetrachloride-30% chloroform. (16) Benzoic acid (0.105 *M*) plus triethylamine (0.200 *M*) in trichloroethylene, against trichloroethylene.

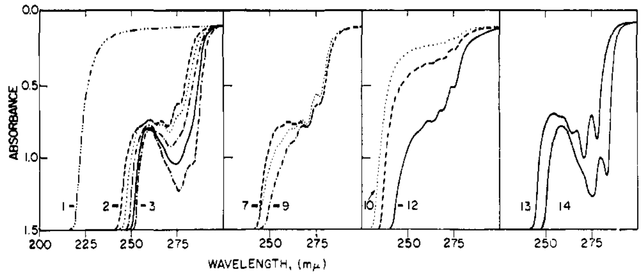

Figure 2. Ultraviolet spectra, cell thickness 0.010 cm, chloroform solutions: (1) chloroform solvent; (2) 0.104 *M* benzoic acid plus 0.0828 *M* triethylamine; (3) 0.103 *M* benzoic acid; the intermediate curves all have 0.104 *M* benzoic acid with the following amounts of triethylamine: 0.021, 0.041, and 0.062 *M*; (7) 0.104 *M* benzoic acid, 0.104 *M* triethylamine; (9) 0.104 *M* benzoic acid, 0.207 *M* triethylamine; the intermediate curve has 0.145 *M* triethylamine; (10) 0.027 *M* tetraethylammonium benzoate; (12) 0.133 *M* tetraethylammonium benzoate; the intermediate curve is 0.053 *M*; (13) 0.010 *M* benzoic acid plus 0.020 *M* triethylamine in cyclohexane; cell thickness 0.1 cm; (14) 0.010 *M* benzoic acid in cyclohexane; cell thickness 0.1 cm.

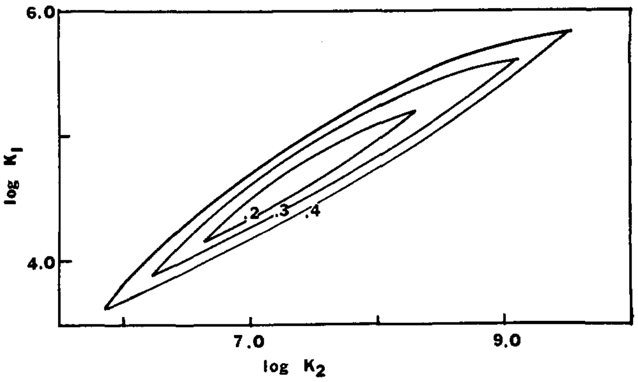

Figure 3. Contour diagram showing variance of per cent transmittance values $[\epsilon(T_{\text{obsd}} - T_{\text{cald}})^2]/(n - 2)$ as a function of K_1 and K_2 for benzoic acid and triethylamine in chloroform.

Ion pair formation is also observed with benzoic acid and triethylamine in chloroform (Figure 1-5) in propionitrile (Figure 1-10), and in many other solvents of intermediate polarity. With benzoic acid changes in the uv spectra also indicate proton transfer to form ion pairs; Figure 2-3 shows the benzoic acid curve while 2-10 and 2-12 show tetramethylammonium benzoate. Mixtures of benzoic acid and triethylamine show progressive increase of benzoate uv bands with increasing triethylamine (Figures 2-3 to 2-9).

While ion pair formation is the expected behavior and appears to be general for primary and secondary amines, we have observed a new and potentially important property of strong tertiary amines. Thus mixtures of triethylamine and acetic acid or benzoic acid in carbon tetrachloride undergo little ionization (Figure 1-11). A solution of acetic acid in carbon tetrachloride shows five principal regions of absorption: 3000, 1715, 1414, 1289, and 939 cm^{-1}.[12] Except for the carbonyl stretching band at 1715 cm^{-1} all are at least in part due to OH–O vibrations of the dimer.[21] Addition of progressive amounts of triethylamine causes those spectral changes expected to result from modification of the hydrogen bonding pattern: (1) pronounced broadening or shifting of all of the OH–O bonds, (2) some diminution of the 1715-cm^{-1} carbonyl band, and (3) appearance of a general absorbance which seems characteristic of certain extreme forms of hydrogen bonding.[22] Similar changes occur to a lesser degree upon addition of water to acetic acid.[21] Even in the presence of a 100% excess of triethylamine the carbonyl absorption at 1715 cm^{-1} is only slightly diminished. With benzoic acid there is no appearance of benzoate peaks.

In other solvents of low dielectric constant such as cyclohexane and carbon disulfide the major species are also hydrogen bonded but un-ionized molecules. While triethylamine ionizes in excess acetic acid used as solvent, it is interesting that a 1:1 molar mixture is a highly mobile fluid, and the ir spectrum shows relatively little proton transfer. The uv spectra, Figure 2-13, also point to hydrogen bonding without proton transfer. The benzoic acid curve is shown in Figure 2-14.

Hydrogen bond formation without ionization has been reported previously for the weak base pyridine with carboxylic acids[8] and for the weak acid *p*-nitrophenol with triethylamine.[23] It does not appear to have been noted previously for bases as strong as triethylamine interacting with acids as strong as acetic acid or benzoic acid. There is evidence that triethylamine gives appreciable ion pair formation in carbon tetrachloride with stronger acids such as trifluoroacetic and even with chloroacetic acid since there is separation of a crystalline solid or of an oil phase.

Interpretation of the Spectra of Mixtures of Benzoic Acid and Triethylamine in Chloroform. While the infrared spectra of mixtures of carboxylic acids and tertiary amines in solvents such as chloroform show many of the characteristics expected for ion pair formation, there are a number of unusual features which need to be accounted for before such conclusions may be accepted. We have therefore examined these spectra in two stages, first qualitatively and then quantitatively.

Three equilibria are expected to be important in these systems, eq 1–3. The formation of a 1:1 ion

$$\mathrm{BzOH + Et_3N = BzO^-Et_3NH^+} \qquad (1)$$

$$\mathrm{2BzOH + Et_3N = BzOH{\cdot}BzO^-Et_3NH^+} \qquad (2)$$

$$\mathrm{2BzOH = (BzOH)_2} \qquad (3)$$

pair is the simplest reaction, and the formation of 2:1 complexes (eq 2) has been extensively documented.[6, 24–28] Dimerization of acids has also received considerable study.[29–32] In these solutions one might therefore expect to find ir peaks typical of benzoic acid, of dimer, of benzoate ion, and of triethylammonium ion. This expectation proves only partly true.

Benzoic acid in chloroform (Figure 1-1) shows a dimer peak at 1714 cm^{-1}, a small spur due to monomer at about 1746 cm^{-1}, and the typical hydrogen bond pattern in the 3000-cm^{-1} region. Triethylamine (Figure 1-2) is relatively transparent in the region of interest except for relatively strong C–H absorption. The most typical features of the benzoate ion spectrum (Figure 1-3) are the doublet at 1562 and 1600 cm^{-1} and the strong peak at 1366 cm^{-1}. This latter is often obscured by solvent absorption. The peak at 3200 cm^{-1} is apparently an enhanced absorption due to hydrogen bonding between the benzoate ion and the 2% ethanol used to promote solubility. The effectiveness of solvent compensation in this run is apparent from the upper curve. Poorer spectra of dilute solutions in the absence of ethanol show the same benzoate ion peaks.

The NH$^+$ absorption of triethylammonium ion has numerous complicating features. Thus triethylammonium halides as fluorocarbon or mineral oil mulls show complex series of peaks in the 2500–2800-cm^{-1} region.[33] The details observable depend upon the dispersion of the instrument. Our data using a grating instrument (PE521) more or less corroborate the values published for the peaks obtained with a LiCl prism.[33] However, the present work was based primarily on instruments of lower resolution, the Perkin-Elmer Models 21 and 137 with sodium chloride optics which showed dominant NH$^+$ peaks for triethylammonium bromide (KBr pellet) at 2500, 2690, and 2770 cm^{-1}.

A solution of triethylammonium bromide in chloroform (Figure 1-4) is quite different. It shows peaks at 2470 and 2584 cm^{-1}, while the deuterated compound shows peaks at 1923 and a doublet at 1988 and 2020. The H/D frequency ratios are about 1.29, which seems normal.[34] In propionitrile the peaks appear at about 2500 and 2600 (137), the *p*-toluenesulfonate in acetonitrile shows peaks at 2488 and 2667 cm^{-1}. The doublet or multiplet peak structures have apparently not been explained. These spectra all show relatively sharp peaks. They appear to represent the $\mathrm{(C_2H_5)_3NH^+}$ stretching band as perturbed by hydrogen bonding to solvent or to anion. Examples of perturbation by anions have been reported.[36]

Further examples of NH$^+$ absorption are shown by triethylammonium trifluoroacetate in chloroform (2350, 2500, 2680 cm^{-1} on the PE137), 2,4-dinitrophenol plus triethylamine in 80% chloroform–20% carbon tetrachloride (2500 and 2650 cm^{-1}) (Figure 1-7),[37] and triethylammonium bromide in dimethyl sulfoxide (2480 and 2600 cm^{-1}).

Although caution is clearly necessary in using one ammonium salt in one solvent or as a crystalline solid as a model for another, the examples suggest that tri-

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(34) Figure 3–21,[35] (p 111) p 107 seems to have been incorrectly identified. The spectra are not those of triethylammonium halides.

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(37) Ultraviolet spectra indicate that the proton has transferred in toluene,[5] and it is therefore expected to transfer in a mixture of $\mathrm{CCl_4}$ and $\mathrm{CHCl_3}$ as well.

ethylammonium benzoate will show one or two peaks in the 2500–2600-cm^{-1} region.

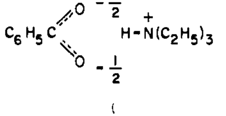
The spectra of mixtures of benzoic acid and triethylamine (1:1.7) in chloroform are shown in Figure 1-5, a mixture of deuteriobenzoic acid and triethylamine is shown in Figure 1-6, and Figure 1-10 shows a spectrum of ordinary benzoic acid and triethylamine in propionitrile. In each of these curves the benzoic acid peak at 1714 cm^{-1} has disappeared and the C–H pattern of the ethyl group of triethylamine is clear. Benzoate absorption near 1550–1600 and 1370 cm^{-1} is also clearly apparent although the peaks are broad.

However, the spectra exhibit two unusual features: the absence of NH$^+$ peaks[38] and the presence of very broad and strong general absorbance underlying the whole curve. While the broad absorbance around 2500 cm^{-1} may indeed be due to NH$^+$ absorption, the spectra lack definitive features. The broad general absorbance begins at about 3300 cm^{-1} and continues across the spectrum. In the 800–400-cm^{-1} region (PE521) the valleys between peaks do not return to the base line, but it is not possible to decide whether this results from overlapping peaks or to a continuation of the general absorbance. With deuteriobenzoic acid this general absorbance is somewhat less pronounced in the 2700–200-cm^{-1} region; it appears to begin at slightly lower frequencies.

The general absorbance does not arise from such trivial causes as incipient precipitation or fogging of windows. It has been observed in a wide variety of solvents (*e.g.*, Figure 1-10), and in cells with sodium chloride windows, with calcium fluoride windows, and in cavity cells without spacer. Furthermore the salt solutions in chloroform and other solvents are crystal clear and show no trace of Tyndall effect.

Mixtures of triethylamine and 2,4-dinitrophenol (Figure 1-7) do not show the general absorbance, and neither do diethylamine–benzoic acid mixtures (Figure 1-9). The phenomenon appears to be limited to mixtures of carboxylic acids with sufficiently strong tertiary amines,[39] but with these systems it is an important fundamental property.

The infrared spectra suggest clearly that ion pairs (equation 1 or 2) have formed, for the benzoic acid peak at 1714 cm^{-1} has been replaced by benzoate peaks. But some special explanation is required for the absence of the N–H$^+$ stretch in the 2500-cm^{-1} region and for the general background absorbance. We have suggested that proton tunneling may be invoked.[2] Thus the lowest energy form of the ion pair might be presumed to be the symmetrical arrangement **1**. Perhaps there are actually several low energy forms of type **2** in which the N–H is bent away from the nominal symmetry axis. If there are two such energy minima, or if there are several energy minima separated by very low barriers, then the position of the proton could be indeterminate. This would explain the absence of a definite N–H$^+$ stretching peak and could account for part of the very broad general absorbance.[40,41]



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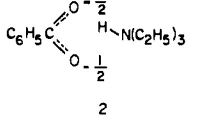

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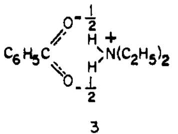

3

The situation is related to the general problem of explaining the strong oscillator strengths and the broad absorption pattern of ordinary hydrogen bonds (see Figure 1-1).[42–45] However, the present example is an extreme one.[22] The relative absence of general absorption (apart from typical hydrogen bond absorption) in $C_6H_5COO^-H_2N(C_2H_5)_2{}^+$ (**3**) (Figure 1-9) can be explained on the basis that both minima are occupied, while the absence in $O_2NC_6H_4O^-NH(C_2H_5)_3$ could be due to the presence of a single minimum. Although the NH$^+$ stretching bands are discernible in $C_6H_5COO^-H_2N(C_2H_5)_2{}^+$ (Figure 1-9), they are broad, and so are the benzoate bands, presumably as a consequence of hydrogen bonding. Some general absorbance also occurs in mixtures of triethylamine and benzoic acid in carbon tetrachloride (Figure 1-11) and in cyclohexane (Figure 1-12) where the extent of proton transfer is relatively small.

Quantitative Study of the Triethylamine–Benzoic Acid Equilibria in Chloroform. In view of the general absorbance, it is of considerable importance to discover whether the infrared spectra are in quantitative accord with expected ionization equilibria. For solutions in chloroform such equilibria might be evaluated quantitatively from the disappearance of the acid carbonyl peak at 1714 cm^{-1} and the appearance of benzoate peaks at 1562 and 1600 cm^{-1}. Two approaches were used to treat the complication of the general absorbance. Fortunately these led to the same result: the carbonyl bands could be measured from a base line at about 2000 cm^{-1} or else the background absorption could be treated hypothetically as being due to salts, molar absorbance indexes being computed for the salts.

It is easy to show rigorously that an equilibrium involving only the 1:1 salt (eq 1) cannot account for the data, and it is also possible to show that an equilibrium involving only the 2:1 salt (eq 2) is unsatisfactory. However, a combination of both equilibria gives a satisfactory fit. There may well be further complexes such as A_3B, A_4B, and so on, but the present data provide no certain evidence about these.

It is also necessary to reckon with the dimerization of benzoic acid (eq 3). In spite of extensive studies of acid dimerization,[31] the uncertainties in the determination of an equilibrium constant are large and discrepancies of factors of five or more in the equilibrium constants are not uncommon. We have used the value 400 M^{-1} for benzoic acid in chloroform.[32]

Actually there are too many unknowns in this system to give a specific solution: besides the acid dimerization (eq 3) for which a fixed value was used there are two equilibrium constants K_1 (eq 1) and K_2 (eq 2) plus molar

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[38] The small spur at about 2700 cm^{-1} in Figure 1-5 is a peak characteristic of triethylamine itself and is present even with the deuterated samples (Figure 1-6). It has nothing to do with NH$^+$ absorption.

[39] Pairs tested include benzoic acid and benzylamine, benzoic and diethylamine, 2,4-dinitrophenol and triethylamine which do not, and benzoic acid and tri-*n*-butylamine, benzoic acid and triethylamine which do show the general absorbance.

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absorbancy indexes of both salts at all wavelengths plus the separately measurable molar absorbancy indexes of benzoic acid and triethylamine. As a consequence the parameters are correlated and many pairs of $K_1 - K_2$ values will accommodate the data. Representative values are shown in Figure 3 and Table I.

Table I. Molar Absorbancy Indexes for the Triethylamine–Benzoic Acid Equilibrium in Chloroform for Two Selected Pairs of $K_1 - K_2$ Values

Peak position, cm^{-1}	C_6H_5COOH[a]	$(C_6H_5COOH)_2 \cdot$ TEA[a]	$C_6H_5COOH \cdot$ TEA[a]
For $K_1 = 2 \times 10^4\ M^{-1}$		$K_2 = 6 \times 10^6\ M^{-2}$	
1714	634.6 ± 6	399.8 ± 10	101.8 ± 2
1619	83.4 ± 2	375.1 ± 10	270.9 ± 4
1583	26.6 ± 1	344.1 ± 10	265.2 ± 4
For $K_1 = 5 \times 10^4\ M^{-1}$		$K_2 = 3 \times 10^7\ M^{-2}$	
1714	635.4 ± 6	444.3 ± 10	101.6 ± 2
1619	83.4 ± 2	371.5 ± 10	270.0 ± 4
1583	26.6 ± 1	335.4 ± 10	264.4 ± 4

[a] The values tabulated are molar absorbancy indexes: $a = \epsilon cl$ where $a = \log (T/_{100}T)$, c = molar concentration, l = path length in centimeters. T_{100} is the per cent transmittance of solvent, and $100(T/T_{100})$ is the normalized per cent transmittance. The absorbance due to triethylamine was negligible at the three peaks used and at the concentrations present.

The ultraviolet spectra of solutions of benzoic acid and of triethylamine in chloroform (Figure 2-9) have yielded useful confirmatory information although they do not permit a precise calculation of equilibrium constants due to a progressive charge-transfer shift of the solvent spectrum as the triethylamine concentration is increased.

Benzoic Acid and Triethylamine in Dimethyl Sulfoxide. Spectra of mixtures of benzoic acid and triethylamine in dimethyl sulfoxide provide a useful contrast to those in chloroform or acetonitrile. In dimethyl sulfoxide there is a relatively clear evidence for NH absorption, due to $Et_3NH^+C_6H_5COO^-$ and the benzoate peaks are also sharp. Although absorbance near 2500 cm^{-1} due to C_6H_5COOH overlaps absorbance due to NH^+, the absorbance at 2000 and 1900 cm^{-1} due to ND^+ is quite well separated from absorbance by C_6H_5COOD at 2200 and 2010 cm^{-1}. Strong absorbance by the solvent limits observation to the 2700–1500-cm^{-1} region.

Kolthoff, Chantooni, and Bhowmik report an extensive potentiometric study of the ionization of acids in dimethyl sulfoxide.[46] From their dissociation constants for benzoic acid and triethylammonium ion the equilibrium constant for formation of dissociated ions (eq 4)

$$C_6H_5COOH + (C_2H_5)_3N = C_6H_5COO^- + (C_2H_5)_3NH^+ \quad (4)$$

is about 0.01. We have analyzed the infrared spectra of a series of solutions of benzoic acid and of 0.01 M benzoic acid with varying concentrations of triethylamine and find an equilibrium constant of about 70 M^{-1} l. for ion pair formation (eq 1). Thus the equilibrium constant for dissociation of the ion pair is about 1.4×10^{-4}. The advantages of employing several methods of evaluating acid–base equilibria are well illustrated by this example.

The molar absorbancy index for the salt (ion pairs) at 1608 is about 435 while that for tetraethylammonium benzoate is about 680. This apparently reflects the effect of hydrogen bonding by the triethylammonium ion and parallels the observed decrease in intensity of nitro group intensity upon hydrogen bonding.[47]

As observed previously[4] benzoic acid is very much weaker in dimethyl sulfoxide (and also in ethanol) than in chloroform. This means that in dimethyl sulfoxide (and in ethanol) reactants are solvated in preference to products while in chloroform ion pair solvation is relatively favorable. Triethylamine has a limited solubility in dimethyl sulfoxide and solvation is therefore poor; however, hydrogen bond association between benzoic acid and dimethyl sulfoxide is expected to be strong and this apparently is the dominant factor.

Experimental Section

Reagents and Spectra. The solvents and reagents were high grade commercial products. Ethanol stabilizer was removed from the chloroform by passing the solvent through aluminas. Spectra were observed using a Perkin-Elmer Model 21 spectrophotometer for quantitative studies and a Model 137 for survey purposes. A few spectra were run on a Perkin-Elmer Model 137 for survey purposes. A few spectra were run on a Perkin-Elmer Model 521 spectrophotometer. Uv spectra were run on a Perkin-Elmer Model 202 spectrophotometer. Fixed cells were used for quantitative studies. In some cases it was found that sodium chloride cells exchanged with the solutions. This was observable by finding that the solvent spectrum still showed benzoate peaks. Such spectra were discarded. Spectra run in calcium fluoride cells were free from complications.

In all cases ambient temperature was used.

Computation of Equilibrium Constants. For computing K_1 and K_2 for solutions of benzoic acid and triethylamine in chloroform the following procedure was adopted: (a) a preliminary analysis of the data provided suitable initial $K_1 - K_2$ pairs, and a series of K_1 and K_2 values were chosen so as to cover the region of interest. (b) For a given $K_1 - K_2$ pair, concentrations of each standard solution were computed for the free benzoic acid, the free triethylamine, salt 1, and salt 2 (eq 1–3). The value used for K_3 was 400 M^{-1}. Computation of concentrations is tedious and was performed by the computer program REMECH.[48,49] (c) By a least-squares technique, best values of molar absorbancy indexes were computed for all species at several wavelengths for each of the standard solutions with concentrations as defined in section b. The systems were highly overdetermined and it was therefore possible to back calculate per cent transmittance values for the infrared curve of each standard solution. This computation was performed by the computer program ANALYZ.[50] (d) The goodness of fit was now judged on the basis of the variance of the calculated *vs.* observed per cent transmittance values. Figure 3 shows a contour plot of this variance as a function of K_1 and K_2. Table I gives molar absorbancy indexes computed for two typical $K_1 - K_2$ pairs.

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