Infrared studies of complexes between carboxylic acids and tertiary amines in argon matrices

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Infrared Studies of Complexes between Carboxylic Acids and Tertiary Amines in Argon Matrices

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The infrared spectra of the complexes formed between acetic and trifluoroacetic acids and tertiary amines [$N(CH_3)_3$, $N(C_2H_5)_3$] in argon matrices and for two-component solid mixtures of acid and amine have been recorded. The spectra show that both 1:1 and 2:1 complexes of acetic acid and amine isolated in argon matrices have molecular forms characterized by broad ν_{OH} absorption at ≈ 2000 cm^{-1}. In an acidic environment in both highly concentrated argon matrices and in two-component solid mixtures the proton transfer form $CH_3CO_2^- \ldots H^+NR_3$ was identified. The 2:1 complexes of trifluoroacetic acid and amine isolated in argon matrices have an ionic form as identified by the appearance of characteristic carboxylate group absorption. The spectra also suggest that the 1:1 complex forms an ion pair in an argon matrix but this is not conclusive.

One of the most interesting problems in studying the nature of hydrogen bonding is proton transfer and the possibility of ion pair formation between the two interacting molecules. Since the pioneering work of Barrow and Yerger [1] much experimental evidence for proton transfer in hydrogen-bonded systems has been found but all relate to the condensed phase. In contrast, theoretical studies performed in recent years for isolated bimolecular hydrogen-bonded complexes have not provided any evidence for ion pair formation even in very strongly hydrogen-bonded complexes.[2-6] This contradiction indicates the importance of the environment; the ideal medium in which experimental studies should be done to compare them with theoretical results is the gas phase at low pressures. In the pure liquid or solid phases the environment strongly affects the nature of the hydrogen bond formed and, in extreme cases, can lead to proton transfer effects.

Studies in the gas phase pose many practical difficulties (particularly for strongly hydrogen-bonded systems) but many of these are overcome by the matrix-isolation technique. In highly diluted matrices the studied molecule (or two interacting molecules) may be expected to be isolated and the perturbation of the system by the neutral matrix environment is usually negligible. Pimentel and coworkers [7, 8] were the first to apply this technique to studies of very strongly hydrogen-bonded systems. These authors found proton transfer effects in few very strongly hydrogen-bonded systems and presented the vibrational correlation diagram which displays the relative base strength (measured by proton affinity) needed for proton transfer in the hydrogen bond.[8]

We present here the results of infrared matrix-isolation studies of the nature of complexes formed between acetic and trifluoroacetic acids with trimethylamine and triethylamine. These systems have been examined very extensively in various solvents.[1, 9-14] The complexes formed between acetic acid and amine are molecular or ionic in nature depending on the solvent used but those involving trifluoroacetic acid always exist in the ionic form. The vibrational correlation diagram of Pimentel

and coworkers [8] cannot be used in these systems as no experimental thermodynamic data are accessible for the RCOO⁻ ion in the gas phase.   The infrared matrix-isolation spectra should explicitly define the nature of these complexes because the ionic form should be strongly manifested in the spectrum by the appearance of CO_2^- absorption.

EXPERIMENTAL

The matrix-isolated samples were prepared by standard methods.   An appropriate pressure of amine or acid was introduced into a 1 dm³ bulb and then sufficient argon was added to reach the desired concentration.   Experiments were performed using simultaneous deposition of the two gaseous mixtures from two bulbs and separate jets onto a CsI window maintained at 20 K by the Helium Cryocooler model 21.   The infrared spectra between 4000 and 400 cm⁻¹ were recorded with a Perkin Elmer 180 spectrophotometer.

An all Pyrex vacuum system was used to prepare the gas mixtures.   Teflon jets and stainless steel needle valves were used to deposit the mixtures on the cold CsI window.   It was noticed that small amounts of both acids were adsorbed on the surface of the needle valves during deposition of the gas mixture and this slightly altered the composition of the matrix in comparison with the composition of the prepared gas mixture (which is reported in the paper).   After each experiment the deposition system was blown off with argon.

RESULTS

ACETIC ACID–TERTIARY AMINE SYSTEMS

Fig. 1(a) shows the spectrum of the $CH_3COOH:N(CH_3)_3:Ar = 1:3:600$ matrix mixture prepared in a two-jet deposition.   The bottom curve (b) in fig. 1 shows the spectrum of acetic acid in argon at a mole ratio of $1:700$; the parent molecules spectra are in general agreement with these reported in the literature.[15-16]   Five
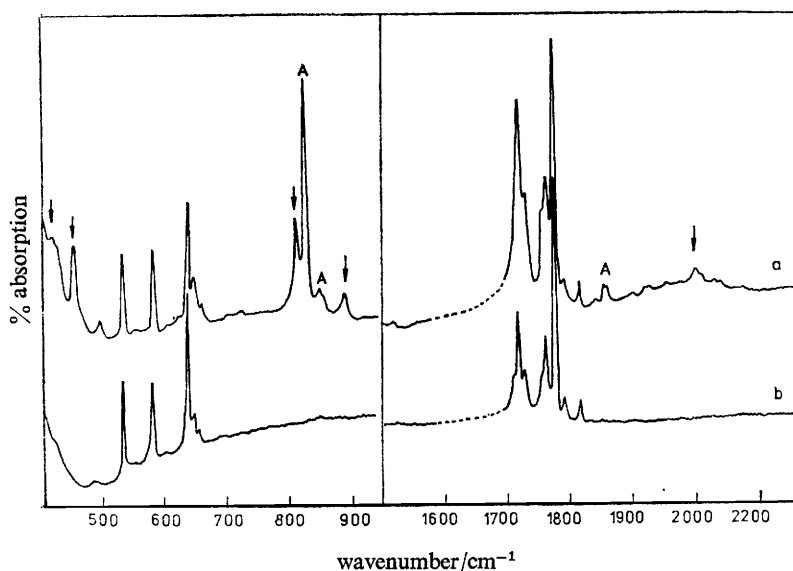

FIG. 1.—(a) Infrared spectrum of co-deposited CH_3COOH and $N(CH_3)_3$ with

$$CH_3COOH:N(CH_3)_3:Ar = 1:3:600.$$

The bands due to complex are marked with arrows, the bands due to amine are marked with A. (b) Infrared spectrum of the matrix of composition $CH_3COOH:Ar = 1:700$.   The bands due to water impurities have been removed from the figures.

absorption features not observed in the parent molecules spectra are observed in the spectrum of the mixture: at ≈ 2000, 885, 809, 450 and 418 cm^{-1}. Bands due to water impurity were also observed in the spectrum. It was found that water impurity did not affect the absorption pattern characteristics for the $CH_3COOH + NR_3$ mixture. The band observed at ≈ 2000 cm^{-1} is very broad (half-width 150 cm^{-1}) with a characteristic structure. The half-widths of the other four features are, respectively, 12, 5, 10 and 10 cm^{-1}. The spectra were recorded for different ratios of $CH_3COOH : N(CH_3)_3$ ranging from 1:1 to 1:5 and for different ratios of acid or amine to argon ranging from 1:800 to 1:50. All the new bands reported above were observed in all cases and, moreover, a new absorption feature at 1570 cm^{-1} appeared in highly concentrated matrices (at ratios of $CH_3COOH : Ar \geqslant 1:100$).
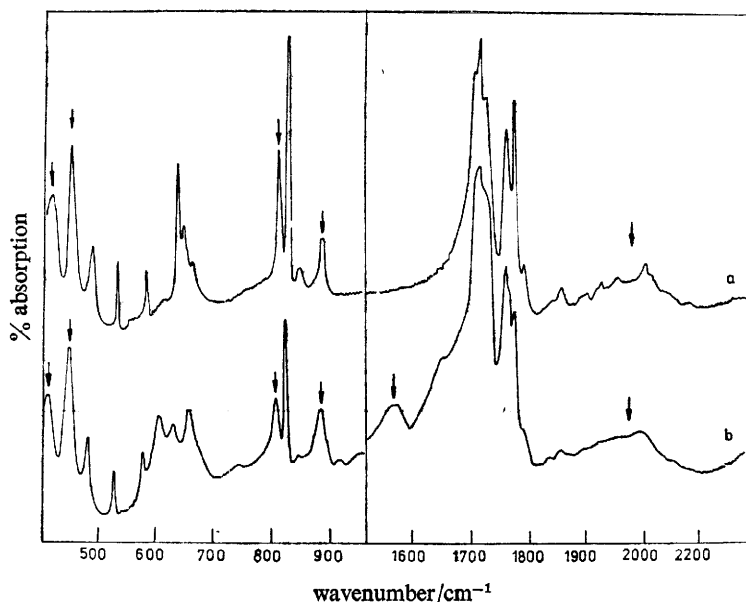

FIG. 2.—Infrared spectra of co-deposited CH_3COOH and $N(CH_3)_3$ with
$CH_3COOH : N(CH_3)_3 : Ar = 1:4:200(a)$ and $1:1:100(b)$.
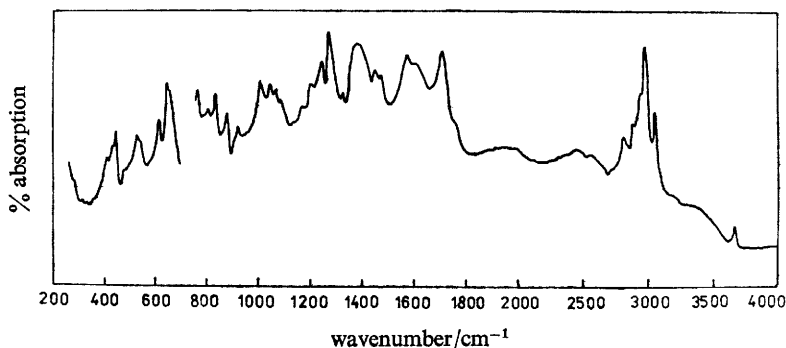

FIG. 3.—Infrared spectrum of acetic acid with triethylamine in CH_2Cl_2 (0.3 mol dm^{-3} acid + 0.3 mol dm^{-3} amine, path length 0.053 mm).

The structure of the broad band at ≈ 2000 cm^{-1} seemed also to be changed in concentrated matrices; the fine structure disappeared and the band contour became smoother. In fig. 2 the spectra of matrices of composition

$$CH_3COOH : N(CH_3)_3 : Ar = 1:4:200 \ (a) \ \text{and} \ 1:1:100 \ (b)$$
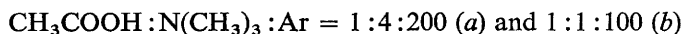
are presented. For comparison, the spectrum of the two component solid mixture $CH_3COOH : N(CH_3)_3 = 1:1$ prepared in a two-jet deposition was recorded. All the characteristic bands observed in the spectra of concentrated argon matrices are also observed here with comparable frequencies, except the band at 810 cm^{-1}. Instead, in the spectrum of the solid mixture, a new band at 668 cm^{-1} is observed.

TABLE 1.—ABSORPTION FREQUENCIES (cm^{-1}) OF ACETIC ACID AND TERTIARY AMINE MIXTURES

$CH_3COOH + N(CH_3)_3$ argon matrix 20 K	$CH_3COOH + N(C_2H_5)_3$ argon matrix 20 K	$CH_3COOH + N(CH_3)_3$ solid state 20 K	$CH_3COOH + N(C_2H_5)_3$ CH_2Cl_2 soln. room temp.	tentative assignment
			2450	$\nu(\overset{+}{N}$—H$\ldots$O$^-$)
≈ 2000 [b]	≈ 2020 [b]	≈ 2000 [b]	≈ 1975	$\nu(N\ldots H$—O)
			1712	$\nu(C{=}O)$
			1610	$\nu(CO_2^-)$ in 1:1 ion pair
			1574	$\nu(CO_2^-)$ in 2:1 ion pair
1575 [a]	1570 [a]	1560		$\nu(CO_2^-)$ in n:1 ionic complex (acidic environment)
			1240	$\nu(C$—O)
885	885	885	880	$\nu(C$—C)
809			833	$\nu(C$—N)
		668	647	$\delta(CO_2^-)$
450	439	450	450	$\left.\begin{array}{c}\\\\\end{array}\right\} \delta(CCO) + \omega(COOH)$
418	426	418	412(?)	

[a] Appears only in highly concentrated matrices; [b] broad.

Very similar results were obtained using triethylamine. In the spectra of dilute $CH_3COOH + N(C_2H_5)_3 + Ar$ matrices four characteristic absorption features are observed at ≈ 2020, 885, 439 and 426 cm^{-1}. In concentrated matrices an additional band appears at 1570 cm^{-1}.

Fig. 3 presents the spectrum of $CH_3COOH + (C_2H_5)_3N$ mixture in CH_2Cl_2 solution which was recorded for comparison. All observed frequencies characteristic for the spectra of $CH_3COOH + NR_3$ (R = CH$_3$, C$_2$H$_5$) mixtures are listed in table 1.

TRIFLUOROACETIC ACID–TRIMETHYLAMINE SYSTEM

In fig. 4(a) the spectrum of the $CF_3COOH : N(CH_3)_3 : Ar = 1:1:800$ matrix mixture prepared in a two-jet deposition is presented. [The spectrum of the CF_3COOH molecule was recorded for comparison and this is in general agreement with the spectrum reported in ref. (17)]. Four absorption features which are not observed in the parent molecules spectra are marked with arrows. The band at 1685 cm^{-1} is rather broad with half-width 40 cm^{-1}, the two bands at lowest frequencies (800 and 721 cm^{-1}) are sharp with half-width 8 cm^{-1}, while that at 994 cm^{-1} is slightly broader with half-width 15 cm^{-1}. The spectra were recorded for different ratios of $CF_3COOH : N(CH_3)_3 : Ar = 1:2:300, \ 1:2:400, \ 1:6:600, \ 1:1:800, \ 1:2:1000$. In fig. 4($b$) the spectrum of the matrix of composition $CF_3COOH : N(CH_3)_3 : Ar = 1:2:400$ is shown. All the new bands observed in dilute matrices also appear here and, moreover, a new absorption feature at 1740 cm^{-1} is observed. In more concentrated matrices the band at 1685 cm^{-1} seems to have a second component at
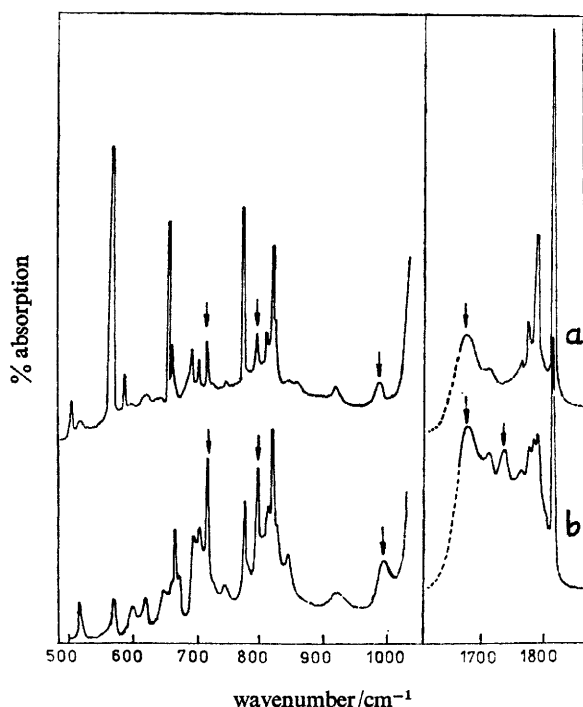
FIG. 4.—Infrared spectra of co-deposited CF_3COOH and $N(CH_3)_3$ with

$CF_3COOH : N(CH_3)_3 : Ar = 1 : 1 : 800$ (*a*) and $1 : 2 : 400$ (*b*).

The bands due to water impurities have been removed from the figures.

1680 cm^{-1} which grows in intensity as the concentration is increased.   In the spectrum of a matrix containing a high excess of amine broad weak absorption at ≈ 2500 cm^{-1} is observed.   The small amount of water impurity observed in the matrix spectra did not affect the absorptions characteristic for $CF_3COOH + NR_3$ mixtures.

The spectrum of the two component solid mixture: $CF_3COOH : N(CH_3)_3 = 1 : 1$ was recorded for comparison.   Four bands due to trifluoroacetic acid–amine complexes are observed at 1675, 992, 800 and 721 cm^{-1}.

DISCUSSION

ACETIC ACID–TERTIARY AMINE SYSTEMS

The spectral and structural characteristics of complexes formed between carboxylic acids and tertiary amines in aprotic solvents have been very extensively studied.[1, 9-14] The main spectral feature of these systems in solution is a broad, relatively strong general absorption (see also fig. 3).   There has been some disagreement regarding the structure of the complexes formed between acetic acid and tertiary amines in such non-polar solvents as CCl_4.   Barrow and Yerger[1] and Smith and Vitoria[9] suggested the formation of $2 : 1$ (AHA$^-$BH$^+$) and $1 : 1$ (A$^-$BH$^+$) ion pairs whereas DeTar and Novak[10] interpreted their spectra as indicative of hydrogen bonding without ionization (AHB).   Gusakova *et al.*[11] concluded that the $1 : 1$ complex can exist in two forms, as a molecular complex or as an ion pair, but the tautomeric equilibrium between these two forms is strongly shifted to the molecular form.

Barrow postulated in his paper [18] that attachment of the second acid molecule to the molecular complex existing in tautomeric equilibrium with an ionic form always effects proton transfer to the amine so the 2:1 complex has an ionic form $AHA–BH^+$. Recently Kulbida and Schreiber [19] studied the $CX_3COOH + N(CH_3)_3$ (X = H, F) systems in the vapour phase and they suggested formation of molecular complexes for both systems.

$$\text{I} \qquad\qquad \text{II} \qquad\qquad \text{III}$$

$$\text{IV} \qquad\qquad\qquad \text{V}$$
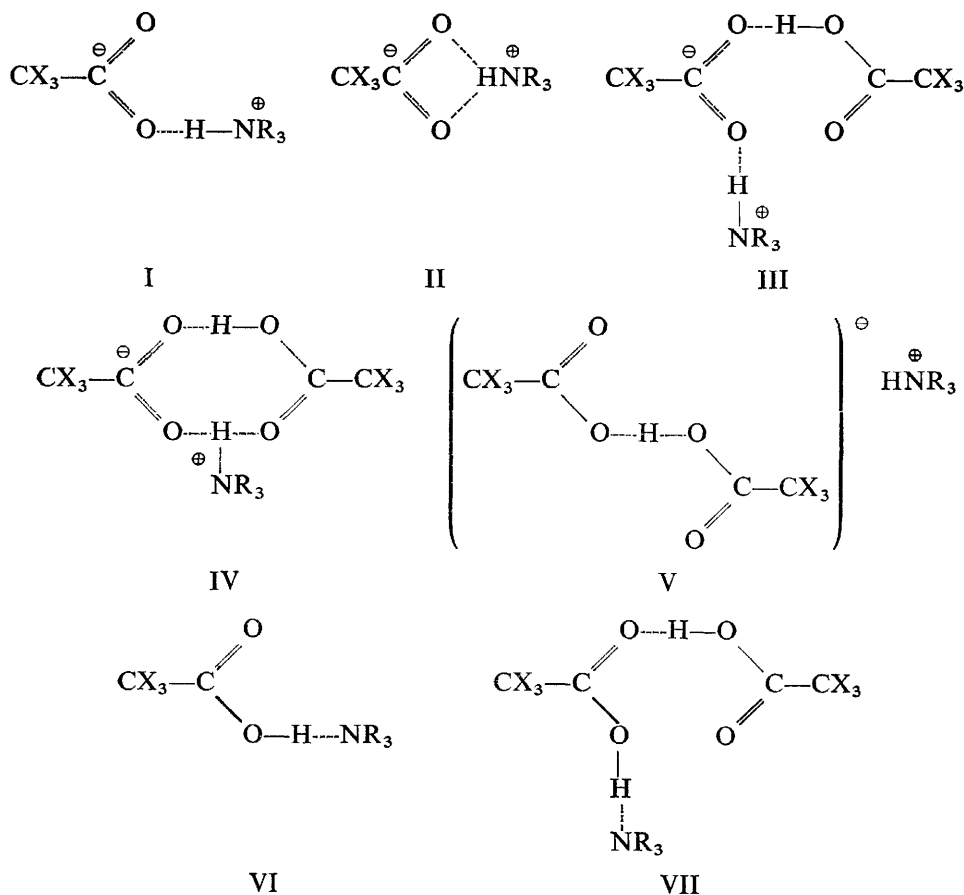
$$\text{VI} \qquad\qquad\qquad \text{VII}$$

FIG. 5.—Five possible prototype structures for ionic 2:1 and 1:1 complexes and two possible structures for molecular 2:1 and 1:1 complexes formed between carboxylic acids and amine.

Fig. 5 shows seven distinct structures of $CX_3COOHNR_3$ and $(CX_3COOH)_2NR_3$ complexes; the first five represent ionic forms, the other two represent molecular complexes. The formation of complexes of type I-III between acetic acid and tertiary amines in solution is strongly demonstrated by the appearance of $\nu(CO_2^-)$ absorption in the region 1620-1550 cm^{-1} [11] (see also table 1 and fig. 3). The possibility that 2:1 complexes exist in form IV was discussed both by Barrow and Yerger [1] and Smith and Vitoria [9] but the cyclization was not regarded as proved. In this form the carboxylate group is also present and its characteristic absorption frequencies should be observed. The acetic acid anion of type V appears in salts of acetic acid. Two carboxylic groups in such an anion can be equivalent, as in the case of the sodium salt,[20] or one can have the character of a carboxylate ion and the second one the

character of a neutral group, as in the case of the potassium salt.[21]   The existence of complexes of type V seems to be possible in solution but their formation should be discouraged by the matrix environment.   The characteristic absorption features due to carbonyl groups appear in the spectra of acetic acid salts in the region 1715-1620 cm^{-1}.

No absorption feature which could be assigned to acetic acid–tertiary amine complexes was observed in the studied matrix spectra in the region 1550-1710 cm^{-1} unless the matrices were highly concentrated.   Even in matrices of low concentrations both monomers as well as dimers and higher polymers of the acid are present (CH$_3$COOH dimer absorptions are identified by using even higher ratio Ac:Ar than 1 : 1000)[15] and we should expect that both 1 : 1 and 2 : 1 complexes exist in the studied matrices.   Lack of any absorption band in the region 1700-1550 cm^{-1} in the spectra of dilute matrices definitely excludes structures I-IV as well as structure V with two non-equivalent carbonyl groups.   There is some doubt about structure V with a centrosymmetric anion as the only v(C=O) band observed in the infrared spectrum of the sodium acid salt (1715 cm^{-1})[20] is very close to the v(C=O) band of the (CH$_3$COOH)$_2$ dimer (1720 cm^{-1}) and could be overlapped by one of the bands appearing in the v(C=O) region.   But there are other facts associated with the spectra which exclude this structure, as will be discussed later.

We are left with structures VI and VII, corresponding to the formation of 1 : 1 and 2 : 1 molecular complexes.   The solution studies showed that the v(C=O) frequency of both the 1 : 1 complex and the bonded acid molecule in the 2 : 1 complex are very close to the v(C=O) frequency of acetic acid dimer [11, 12] and this may be the reason why no characteristic absorption could be assigned to C=O stretching in molecular complexes.   In matrix spectra the region of v(C=O) absorption is rather difficult to study.   The bands due to v(C=O) vibrations in cyclic and open dimers, to some combination bands and to v(C=O) of higher polymers are observed in this region.   So the v(C=O) band of the molecular complex can be overlapped by one of the bands due to acids.

The broad band at $\approx$ 2000 cm^{-1} is assigned to the v_{as}(O—H . . . N) vibration. This is in agreement with our studies of (C$_2$H$_5$)$_3$N + CH$_3$COOH complexes in CH$_2$Cl$_2$ solution.   It is quite obvious from the spectrum (fig. 3) that in CH$_2$Cl$_2$ solution a tautomeric equilibrium between ionic pairs and the molecular form of the CH$_3$COOHNR$_3$ complex exists.   Two bands characteristic of molecular complex [1245 cm^{-1}, v(C—O); 1712 cm^{-1}, v(C=O)][11] and two bands characteristic of ion pairs [1610 cm^{-1}, v(CO$_2^-$) in 1 : 1 complex; 1570 cm^{-1}, v(CO$_2^-$) in 2 : 1 complex] appear in the region of carboxyl group absorption.   Accordingly, two broad bands observed at $\approx$ 1950 and $\approx$ 2500 cm^{-1} are assigned to v_{as}(O—H . . . N) and v_{as}(O$^-$ . . . H—N$^+$).   A band near 1900 cm^{-1} was observed by Smith and Vitoria [9] in their studies of complexes formed between some carboxylic acids and tri-n-propylamine in CCl$_4$ and CHCl$_3$ solutions.   Their assignment is different from ours as they interpreted the spectra as indicative of ion pair formation, but their observation that the intensity of this band increases with decreasing strength of the acid is in accord with our interpretation since this shifts the tautomeric equilibrium towards the molecular form of the complex.   The present studies do not provide any explanation for the fine structure of the broad band which is observed in diluted (CH$_3$)$_3$N + CH$_3$COOH + Ar matrices.   The fact that it appears in diluted matrices seems to indicate that it is characteristic of the v(O—H . . . N) band in a specific type of complex (2 : 1 or 1 : 1) and is not due to different types of complexes (1 : 1, 2 : 1, 3 : 1).

The band observed at 885 cm^{-1} in the spectra of all matrices is assigned to v(C—C) (probably in the 2 : 1 complex).   The corresponding band appears as a weak absorp-

tion at 890 cm^{-1} in the acetic acid dimer [22] but it increases in intensity in the spectra of acid salts of acetic acid.[21] The change in charge distribution within the acetic acid dimer when the 2:1 complex with amine is formed may be the reason for the relatively strong intensity of this band in the spectrum of this complex. On the other hand, the frequency of this band seems to be too low to assign it to γ(OH ... O) or γ(OH ... N) in the 2:1 system. The γ(OH ... O) mode is observed at ≈ 940 cm^{-1} in acetic acid dimer [22] and the O—H ... O bond is expected to be stronger in the $(CH_3COOH)_2NR_3$ complex than in the acid dimer.[23] The band at 809 cm^{-1} observed in the spectra of complexes with trimethylamine can be easily assigned to perturbed C---N stretching vibration of bonded amine; it is very close to the corresponding band in free trimethylamine (825 cm^{-1}).[16] The relative intensity of this band decreases when the matrix concentration is increased (see fig. 2). Two bands in the low region (418 and 450 cm^{-1} in AcOH–TMA; 426 and 439 cm^{-1} in AcOH–TEA) are assigned to two δ(CCO) vibrations in the 2:1 complex [possibly coupled with ω(CO$_2$) vibrations] in agreement with the assignments proposed for acetic acid monomer,[15] dimer [22] and acid salts of acetic acid.[20, 21] In the spectra of acetic acid monomer [15] and dimer [22] the bands due to corresponding modes are of weak or medium intensity but they become very intense in infrared spectra of acid salts containing the $(CH_3CO_2H)^-$ anion. This is probably due to a change in the charge distribution within the carboxyl group. The bands observed at 450 cm^{-1} (AcOH–TMA) and 439 cm^{-1} (AcOH–TEA) are the most intense bands due to the complex. The ratio $I_{max}(450)/I_{max}(418)$, $I_{max}(439)/I_{max}(426)$ varies in the studied spectra and seems to increase with dilution when the amount of 1:1 complexes in the matrix increases. It can mean that the δ(CCO) vibration in the 1:1 complex is near 450 cm^{-1} in trimethylamine and near 439 cm^{-1} in triethylamine complexes. The considerable effect of amine on the position of both observed bands seems to provide additional proof against structure V. In this type of complex the position of both bands should be less sensitive to the amine.

The spectra of highly concentrated matrices and two-component solid mixtures show all the bands observed in dilute matrices [except the ν(C—N) complex band in the spectrum of the two-component solid mixture] thus indicating the presence of molecular complexes. Two additional bands are observed at 1570 and 669 cm^{-1} (the last one only in the spectrum of the two-component mixture). The frequency of the first band is close to $\nu_{as}(CO_2^-)$ in the 2:1 ionic AcHAc$^-$HB$^+$ complex (table 1 and fig. 3) in solution.[11] The appearance of this band indicates the formation of an ion pair $R_3NH^+ ... CO_2^-CH_3(CH_3COOH)_n$ by proton transfer in an acidic environment. This result is in agreement with studies in solution [10] and with recent infrared matrix isolation studies on $(CH_3)_2CO$–HCl complexes.[24] A conceivable explanation for the presence of two different types of complexes (ion pair and molecular) is the existence of the different arrangements of the interacting molecules in the studied mixtures. The band observed at 669 cm^{-1} in the solid state can be assigned to δ(CO$_2^-$).

TRIFLUOROACETIC ACID–TERTIARY AMINE SYSTEMS

The studies performed for complexes of trifluoroacetic acid with strong nitrogen bases in various solvents [13, 14, 18] clearly indicate the formation of ion pairs regardless of the solvent used.

In our spectra of all studied matrices containing CF$_3$COOH and N(CH$_3$)$_3$ mixtures the absorption feature characteristic of the $\nu_{as}(CO_2^-)$ vibration appears at ≈ 1680 cm^{-1}, proving that the ionic complexes are present. Even in very dilute

matrices (1 : 2 : 1000) small amounts of trifluoroacetic acid dimers were present and in addition to 1 : 1 complexes small amounts of 2 : 1 complexes also exist.   The question then arises, does the observed $v_{as}(CO_2^-)$ absorption originate from 2 : 1 and 1 : 1 complexes or from 2 : 1 complexes alone?   The presence of small amounts of dimers in very dilute matrices as well as the lack of any absorption band which could be assigned to molecular complexes seems to indicate that the band at ≈ 1680 cm^{-1} originates from both complexes.   This would mean that both 2 : 1 as well as 1 : 1 complexes exist in matrices in an ionic form.   The results obtained give no information on the structure of the 1 : 1 complexes, whether they form unsymmetrically bonded type I or symmetrically bonded type II systems.   Of interest is the appearance of the band at 1740 cm^{-1} in concentrated matrices in which large amounts of dimers, trimers, higher oligomers and their corresponding complexes exist.   The frequency of this band is too low to assign it to the $v(C{=}O)$ vibration of an acid molecule bonded to a carboxylate ion.   The most reasonable explanation for this band seems to be the formation of type V complexes in which the centre of symmetry is lost in highly concentrated matrices.   In the sodium acid salt of trifluoroacetic acid two $v(C{=}O)$ bands are observed at 1790 cm^{-1} (i.r.) and 1720 cm^{-1} (Raman).[25]   Again no useful information can be obtained from the studied spectra on the geometry of 2 : 1 complexes.

The observed shift of the $v(CO_2^-)$ band with increasing matrix concentration is probably due to perturbation of the ion by the environment.

The band observed at 721 cm^{-1} is due to $\delta(OCO)$ of the $CF_3CO_2^-$ ion, its frequency being close to that found for the $CF_3CO_2^-$ ion in aqueous solution.[26] The two bands observed at 800 and 994 cm^{-1} are assigned to $v(C{-}N^+)$ of the $(CH_3)_3NH^+$ species.

The region 2400-2800 cm^{-1} in which $v(NH^+)$ absorption falls [10] is difficult to study.   The band corresponding to this vibration is usually broad and relatively weak [10] (see also fig. 3).   This is the reason why we do not observe it in the spectra of very dilute matrices (1 : 1 : 800, 1 : 2 : 1000) in which relatively small amounts of complexes are present.   In more concentrated matrices (1 : 2 : 300, 1 : 2 : 400) the absorption due to broad OH stretching of the trifluoroacetic acid dimer appears in this region. Broad absorption with a maximum at ≈ 2500 cm^{-1} is observed in the spectrum of a matrix containing diluted CF_3COOH and a large excess of amine

$$CF_3COOH : NR_3 : Ar = 1 : 6 : 600.$$
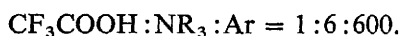
This band is probably due to $v(NH^+)$ vibration.

CONCLUSION

The matrix spectra show clearly that both $CH_3COOHNR_3$ (R $=$ CH$_3$, C$_2$H$_5$) as well as $(CH_3COOH)_2NR_3$ complexes exist in matrices in molecular form.   In contrast to the spectra of these complexes in solution no continuous absorption was observed in the spectra of matrices.   The most likely explanation of continuous absorption observed for strongly hydrogen-bonded complexes in condensed media is one involving cooperative effects due to the interaction of close neighbouring molecules of the complex.[27]   The spectra of $CH_3COOH + NR_3$ complexes in argon matrices strongly suggest that this is the case.   In an acidic environment proton transfer from an acid to a base molecule occurs and ion pairs are formed.

The spectra of argon matrices containing $CF_3COOH + NR_3$ mixtures indicate that the $(CF_3COOH)_2NR_3$ complex exists in an ionic form in solid argon.   The spectra also suggest that the $CF_3COOHNR_3$ complex forms an ion pair in an argon matrix but this is not conclusive.

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