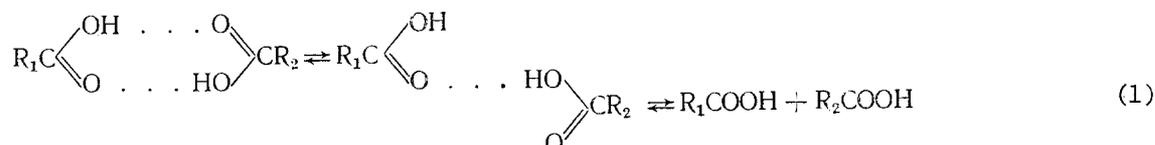
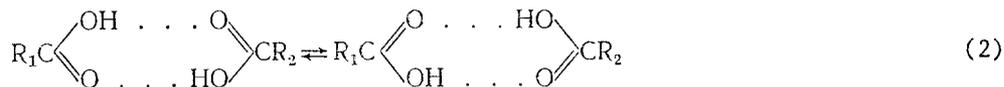


The study of asymmetric (consisting of different molecules) dimers of carboxylic acids is of interest in two respects. In the first place, when there is a significant difference in the electronegativities of the radicals such as, for example, in the case of the $\text{CF}_3\text{COOH}\cdot\text{CH}_3\text{-COOH}$ dimer, it might be expected that there would be a large difference in the strength of the two hydrogen bonds in the dimer and this would increase the probability for the appearance of an open dimer with a single hydrogen bond. A study of the equilibria



would enable one to estimate the magnitude of the mutual effect of the two hydrogen bonds in the dimer which it is generally assumed determines the high thermodynamic stability of the cyclic structure. In the case of symmetric dimers open forms have not been observed either in the gas phase or in inert solvents even at high temperatures [1]. (The authors of [4] were unable to detect the bands ascribed in [2, 3] to the open forms of trifluoroacetic acid. These bands apparently belong to complexes of the acid with a water impurity [5, 6].) Secondly, it becomes theoretically possible to obtain information on the frequency of the degenerate intracomplex proton exchange between the two positions with are now nonequivalent.



The estimation of the lower limit of the frequency of proton migration in the dimer of formic acid at -160°C as $\tau^{-1} > 10^3 \text{ sec}^{-1}$, which was accomplished using the contour of the triplet OH signal in the PMR spectrum, is rather low and, according to the NMR spectra of mixed dimers in which the two hydrogen bonds differ greatly both with respect to their energy and, consequently, with respect to the proton chemical shift, it should be possible to substantially improve on this estimate.

In the present work we have investigated the IR spectra of solutions containing mixtures of trifluoroacetic and trimethylacetic (pivalic) acids as well as several of their isotopically substituted species in pentane (from -120 to $+30^\circ\text{C}$) and in hexadecane $\text{C}_{16}\text{H}_{34}$ (from $+30$ to 250°C) at concentrations from 10^{-3} to 10^{-1} mole/liter. The low temperature NMR spectra (-170°C) were recorded in a mixture of the freons $\text{CDF}_3 + \text{CDF}_2\text{Cl}$. Moreover, the IR spectra of the $\text{RCOOH} + \text{CF}_3\text{COOH}$ ($\text{R} = \text{CH}_3, \text{H}, \text{o-OH-C}_6\text{H}_4$) systems and of several model systems were recorded in pentane at room temperature. Mixtures of trifluoroacetic acid with aliphatic acids have previously been studied in the gas phase using their microwave [8] and far IR spectra [9] and vapor pressure measurements [10] and, in the condensed phase using ultrasonic absorption [11] and methods of physicochemical analysis [12]. In every case, the formation of a strong complex, which is usually classified as an asymmetric cyclic dimer, was noted.

The chemically pure grade trifluoroacetic acid, after the addition of a small amount of the anhydride in order to remove any water present, was triply vacuum distilled at -40°C . The deuterated acid was prepared by dissolving a calculated amount of D_2O in trifluoroacetic anhydride followed by vacuum distillation. The pivalic acid in hexane solution was dried using type 4A zeolite and, after the solvent had been distilled off, it was doubly distilled under vacuum at 50°C . The alkanes which were employed as the solvents were successively

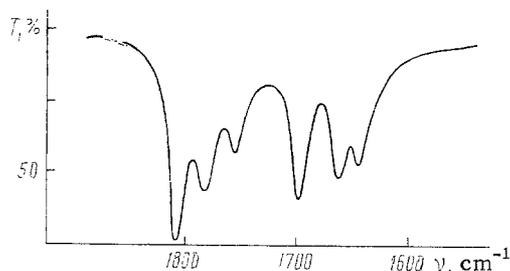


Fig. 2. The spectrum of a solution containing CF_3COOH ($6 \cdot 10^{-3}$ mole/liter) and salicylic acid ($4 \cdot 10^{-3}$ mole/liter) in pentane at $+20^\circ\text{C}$.

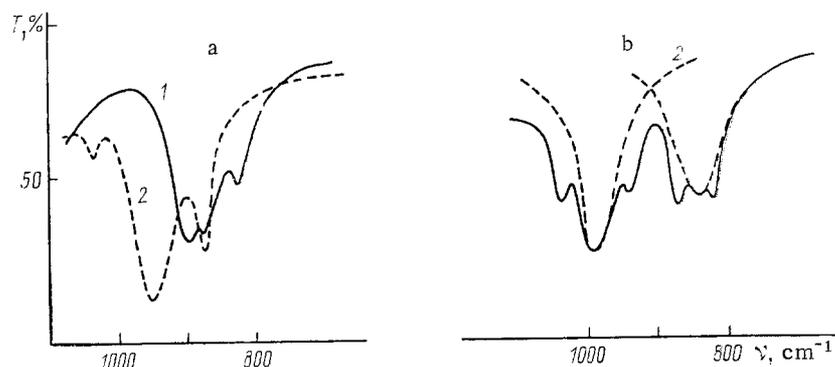


Fig. 3. IR spectra of solutions in pentane. Separate components (a): CF_3COOH (1) and $(\text{CH}_3)_3\text{CCOOH}$ (2) at concentrations of 0.1 mole/liter and -40°C . (b) A mixed solution of these acids under the same conditions (the ν_{OH} bands of the asymmetric dimer are approximately resolved by the dashed line).

the temperature from -120°C up to 0°C does not bring about the appearance of any new bands, and only a certain redistribution of the intensities in favor of the symmetric dimers can be noted. A natural result of increasing the temperature up to 250°C is the growth of the monomer bands at the expense of the bands due to both types of dimers. No new bands whatsoever, which could be assigned to an open dimer, were observed. The spectra of all mixed solutions containing CF_3COOH and a carboxylic acid look similar. All six $\text{C}=\text{O}$ group vibrational bands are best separated in the case of salicylic acid (Fig. 2) and the bands due to the corresponding mixed dimer at 1644 and 1760 cm^{-1} are not broadened in comparison with the bands due to the symmetric dimers. We also note that the width of the $\nu_{\text{C}=\text{O}}$ bands of all of the other mixed dimers is appreciably reduced upon deuteration of the acids. The reason for this remains unclear. It is possible that this broadening is associated with rapid degenerate proton exchange within the dimer which is retarded upon deuteration and is absent in the dimer of salicylic acid. Two strongly overlapping bands at 3540 and 3500 cm^{-1} , belonging to the $(\text{CH}_3)_3\text{CCOOH}$ and CF_3COOH monomers are observed at high temperature in the region of the free OH group valence vibrations. No traces of a third band which could have been assigned to the vibration of the free OH group in the open dimer, were visible.

TABLE 1. Frequencies ν_{OH} and ν_{OD} of the Out-of-Plane Deformation Vibration of the Hydroxyl Group in the Carboxylic Acid Dimers $\text{CF}_3\text{COOH} \cdot \text{RCOOH}$

R	Symmetric dimer		Asymmetric dimer			
	ν_{OH}	ν_{OD}	CF_3COOH		RCOOH	
			ν_{OH}	ν_{OD}	ν_{OH}	ν_{OD}
$(\text{CH}_3)_3\text{C}$	945	690	997	725	845	610
CH_3	942	690	970	705	848	615
H	925	670	935	680	870	630
CF_3	890	647	890	647	890	647

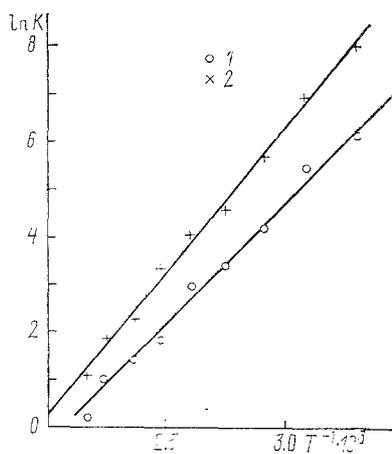


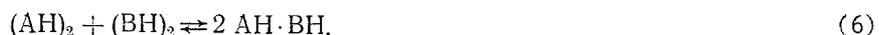
Fig. 4. Relationships between the logarithm of the dimerization constant K (liter/mole) for CF_3COOH (1) and $(\text{CH}_3)_3\text{CCOOH}$ (2) in hexadecane and the inverse temperature.

The 800–1100 cm^{-1} region of the spectra is depicted in Fig. 3 in which the ν_{OH} bands of the carboxylic acid complexes appear. In the spectrum of a mixed solution, the bands at 890 and 945 cm^{-1} , which belong respectively to the dimers of trifluoroacetic and pivalic acids [16] are reduced in intensity and, instead, as many broad bands appear at 997 and 845 cm^{-1} . These bands disappear upon deuteration and bands arise at 725 and 610 cm^{-1} . It has been shown in [16, 17] that the frequencies of the ν_{OH} vibrations correlated fairly well with the energies of the hydrogen bond which is formed by the OH group. It may therefore be postulated that the 997- cm^{-1} band belongs to the CF_3COOH molecule which forms an appreciably stronger hydrogen bond than that in the symmetric dimer (the shift in the ν_{OH} frequency is +110 cm^{-1}). Likewise, the second hydrogen bond in the mixed dimer is significantly weaker than that in $[(\text{CH}_3)_3\text{CCOOH}]_2$. As the value of ΔpK_a for the two acids decreases, the difference in the frequencies of the two ν_{OH} vibrations decreases (Table 1).

The use of the correlation relationship [17]

$$\nu_{\text{complex}}^2 - \nu_{\text{free}}^2 = 6.5 \cdot 10^4 \Delta H \quad (3)$$

is apparently the only available method of estimating the energies of the two bonds in the mixed dimer separately. (It is not possible to resolve the broad bands due to the bound OH group valence vibrations.) However, for this purpose one requires a knowledge of the ν_{OH} frequencies in the monomers and the bands arising from the corresponding vibrations could not be unambiguously identified. Hence, using Eq. (3), we solely found the magnitude of the differences in the bond energies in the mixed and symmetric dimers. A direct comparison of the frequencies in the symmetric and asymmetric dimer may appear unjustified since, in the first case, the absorption band corresponds to an antisymmetric vibration of two bonds which vibrate practically independently in the second case. However, the interaction between the vibrations is very small in the symmetric dimer (for example, the difference in the frequencies of the two ν_{OH} vibrations of A_u and B_g symmetry in $(\text{HCOOH})_2$ is 2 cm^{-1}) which means that the above-mentioned effect can be neglected. Then, in the case of the $\text{CF}_3\text{COOH} \cdot (\text{CH}_3)_3\text{CCOOH}$ dimer, one of the bonds is stronger than that in $(\text{CF}_3\text{COOH})_2$ by 3.1 kcal/mole while the other is weaker than that in $[(\text{CH}_3)_3\text{CCOOH}]_2$ by 2.9 kcal/mole such that, on the whole, the mixed dimer is somewhat more favorable from the energetic point of view. Subsequently, the magnitude of the enthalpy changes for the processes



where $\text{AH} = \text{CF}_3\text{COOH}$, $\text{BH} = (\text{CH}_3)_3\text{CCOOH}$, were determined by the thermodynamic method using the temperature dependence of the equilibrium constant. The equilibria (4) and (5) were studied

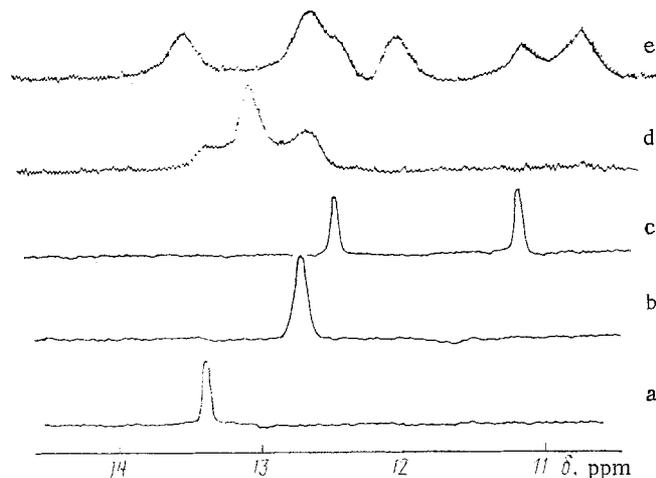


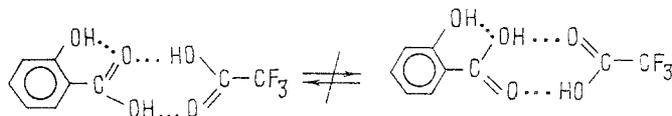
Fig. 5. ^1H NMR spectra of solutions containing $(\text{CH}_3)_3\text{CCOOH}$, $5 \cdot 10^{-3}$ mole/liter (a); CF_3COOH , 10^{-2} mole/liter (b); *o*- $\text{HOC}_6\text{H}_4\text{COOH}$, $5 \cdot 10^{-3}$ mole/liter (c); $(\text{CH}_3)_3\text{CCOOH}$, $5 \cdot 10^{-3}$ mole/liter and CF_3COOH , 10^{-2} mole/liter (d); and *o*- $\text{HOC}_6\text{H}_4\text{COOH}$, $5 \cdot 10^{-3}$ mole/liter and CF_3COOH , 10^{-2} mole/liter (e) in a mixture of the freons $\text{CDF}_3 + \text{CDF}_2\text{Cl}$ at -170°C .

using the $\nu_{\text{C=O}}$ bands of the monomer and the dimer (the procedure for treating the spectra and carrying the calculations has been described in [18]) in hexadecane over a temperature range of $30\text{--}200^\circ\text{C}$. The relationships between $\ln K$ and T^{-1} are shown in Fig. 4. As the result of this, a value $\Delta H = 10.8 \pm 0.3$ kcal/mole was obtained for the energy of dimerization of CF_3COOH and a value of 12.2 ± 0.4 kcal/mole for the energy of dimerization of $(\text{CH}_3)_3\text{CCOOH}$. The first value lies between the values of 8.8 kcal/mole obtained in [18] in CCl_4 solution and the value of 12.2 kcal/mole found in [1] for the gas phase. Hence, the energy of one bond in the mixed dimer is equal to 8.5 kcal/mole and the energy of the other equal to 3.2 kcal/mole with an accuracy corresponding to the validity of the correlation equation (3) (values of 11–12 and 5–6 kcal/mole were found in [10] for the $\text{CF}_3\text{COOH} \cdot \text{CH}_3\text{COOH}$ dimer in the gas phase.) The equilibrium (6) was studied in pentane at -120 to -20°C , when the equilibria (4) and (5) are completely displaced to the left. The bands at 1708 cm^{-1} of the $(\text{BH})_2$ dimer and at 1667 cm^{-1} of the $\text{AH} \cdot \text{BH}$ dimer, which can be resolved graphically with comparative ease, were employed as the analytical bands. Subject to the condition that $[\text{AH}] = [\text{BH}] = 0$, the equilibrium constant expressed in terms of the concentrations of $(\text{BH})_2$ and $\text{AH} \cdot \text{BH}$ is equal to

$$K = \frac{[\text{AH} \cdot \text{BH}]^2}{[(\text{AH})_2] \cdot [(\text{BH})_2]} = \frac{4[\text{AH} \cdot \text{BH}]^2}{([\text{AH}]_0 - [\text{AH} \cdot \text{BH}])([\text{BH}]_0 - [\text{AH} \cdot \text{BH}])} = \frac{2([\text{BH}]_0 - 2[(\text{BH})_2])^2}{[(\text{BH})_2] \cdot ([\text{AH}]_0 - [\text{BH}]_0 + 2[(\text{BH})_2])},$$

where $[\text{AH}]_0$ and $[\text{BH}]_0$ are the initial concentrations of the acid. The integral absorption coefficients of the bands at 1667 and 1708 cm^{-1} can be measured separately since, in the absence of trifluoroacetic acid, all of the pivalic acid exists as the dimer and, when there is a great excess of trifluoroacetic acid, in the form of the mixed dimer. They turned out to be equal to $4.6 \cdot 10^4$ and $6.4 \cdot 10^4$ liter/mole $\cdot\text{cm}^2$, respectively. The enthalpy change involved in process (6) was found to be equal to $\Delta H = 0.6 \pm 0.2$ kcal/mole which is in good agreement with the value of $\Delta H = 2(8.5 + 3.2) - 10.8 - 12.2 = 0.4$ kcal/mole, obtained using the correlation relationship described by Eq. (3).

The low-temperature NMR spectra of solutions containing the mixed dimers of trifluoroacetic and pivalic acids (Fig. 5d) and of trifluoroacetic and salicylic acids (Fig. 5e) are sketched in Fig. 5. The assignment of the signals becomes obvious upon comparison with the spectra of solutions which contain the above-mentioned acids separately. In the case of salicylic acid, apart from the signals due to the symmetric dimer, two signals are observed in the spectrum at $\delta = 12.2$ and 13.6 ppm which are assigned to the two nonequivalent protons of the mixed dimer. This means that degenerate intracomplex proton exchange is absent. The reason for this probably lies in the fact that the intramolecular hydrogen bond with the carbonyl group in the salicylic acid molecule makes one of the species, which are equivalent in the absence of this bond, energetically unfavorable



Internal rotation with the rupture of an intramolecular hydrogen bond (IHB) takes place slowly on an NMR time scale [19] in *o*-carbonyl-substituted phenols at -170°C [9] and, hence, the IHB hinders the process involving the transfer of protons within the dimer. In the mixed complex the signal due to the phenolic proton is shifted to stronger fields in comparison with the symmetric dimer since the carbonyl group simultaneously forms two hydrogen bonds and, in this case, the reinforcement of one of them brings about a weakening of the other.

In the case of the mixed dimer of trifluoroacetic and pivalic acids, a single averaged signal, lying between the signals due to the symmetric dimers, is observed in the spectrum. The application of the correlation relationship which relates the chemical shift of the OH proton to the energy of the hydrogen bond which is formed by carboxylic acids [20] provides an estimate of the difference in the chemical shifts of the two nonequivalent protons of ≈ 5 ppm since the difference in the energies of the two hydrogen bonds was estimated as 5.3 kcal/mole. Since no broadening of the signal from the mixed dimer was observed when the signal was compared with those from the symmetric dimers, the lower limit of the proton transfer frequency within this dimer at -170°C can be estimated as $\tau^{-1} > 10^5 \text{ sec}^{-1}$ using the formula $\Delta\nu_{1/2} = 2\pi P_A^2 P_B^2 (\Delta\nu)^2 \tau$, where $\Delta\nu$ is the difference in the frequencies of the overlapping signals, τ is the average lifetime of the two species, and $P_A = P_B = 1$.

To sum up, the following conclusions may be drawn.

1. In spite of the fact that the difference in the energies of the two hydrogen bonds in the mixed dimer of trifluoroacetic and pivalic acids is about 5 kcal/mole the open dimer is thermodynamically unfavorable in comparison with the cyclic dimer and is not formed in measurable amounts over the whole of the temperature range studied (-170 to $+250^{\circ}\text{C}$). This can apparently be explained by some additional stabilization of the cyclic dimers due to a mutual polarization of the bonds in the conjugated system. Furthermore, the increase in entropy upon passing from the cyclic dimer to the open dimer must be insignificant and cannot compensate for the reduction in the enthalpy. This transition is to some extent similar to *cis-trans* isomerization in molecules of the orthonitrophenol type which is not accompanied by any noticeable increase in the entropy, as a consequence of which rupture of the comparatively weak (≈ 5 kcal/mole [21]) hydrogen bond is not observed up to $+250^{\circ}\text{C}$.

2. Even in the case of two very nonequivalent hydrogen bonds degenerate proton exchange within the dimer takes place with a frequency greater than 10^5 sec^{-1} at -170°C . We do not know of any quantum mechanical calculations on such systems. However, in the case of the symmetric dimer of formic acid, a value for the tunnelling frequency in the ground vibrational state of the order of 10^7 sec^{-1} was obtained in one of the calculations [22].

The authors are grateful to L. Kimtis for making available a sample of high purity deuterated pivalic acid.

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