HYDROGEN BOND AND PROTON TRANSFER IN COMPLEXES OF TRIOCTYLAMINE WITH HALOGENOACETIC ACIDS

G. S. DENISOV, G. V. GUSAKOVA AND A. L. SMOLYANSKY

Institute of Physics, Leningrad State University and Institute of Milk, Vologda (U.S.S.R.)

(Received 1 September 1972)

ABSTRACT

The infrared spectra of solutions containing trioctylamine and mono-halogenoacetic acids have been investigated in the region 1500–1800 cm^{-1}. Two forms of complexes 1:1 acid–amine, the molecular complex with hydrogen bond OH $\cdots$ N and the ionic pair, resulting from proton transfer from acid to amine, have been found to exist in equilibrium with each other.

INTRODUCTION

Information about the potential energy surface in proton donor–acceptor systems may be deduced from spectroscopic investigation of equilibria in solutions with strong hydrogen bonds. In particular, the simultaneous existence of two stable complexes—the molecular complex with a hydrogen bond and the ionic complex (ionic pair), caused by the proton transfer from a donor to an acceptor, is a criterion for the existence of two minima on the potential energy surface. The spectral and energetic characteristics of carboxylic acid–secondary amine complexes have been studied previously[1-4]. In this paper the infrared spectra of complexes formed by monochloro-, monobromo- and monoiodoacetic acids with trioctylamine are studied.

DISCUSSION

There are two bands, 1640 and 1730 cm^{-1} in the $\nu C=O$ region of the infrared spectrum of monochloroacetic acid solution in trioctylamine. The intensity of the first band decreases with rise in temperature while the intensity of the second one
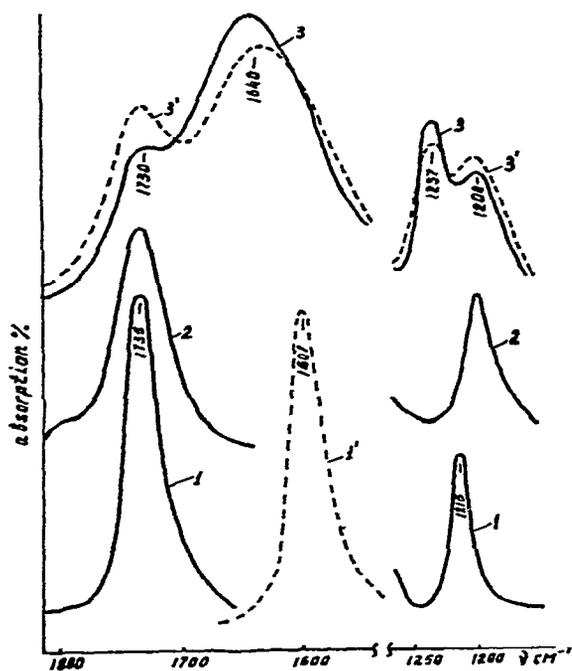
Fig. 1. Spectra of monochloroacetic acid. 1 — in C_2Cl_4: $C = 0.14$ M; 1′ — in D_2O: 0.07 M+0.07 M of triethylamine; 2 — in CCl_4: 0.14 M+ 0.14M dimethyl sulphoxide;3, 3′ — in trioctylamine: 0.5 M; $t°C$: 1,1′,2,3 – 20°C, 3′ – 80°C; cell 45.7 μ.
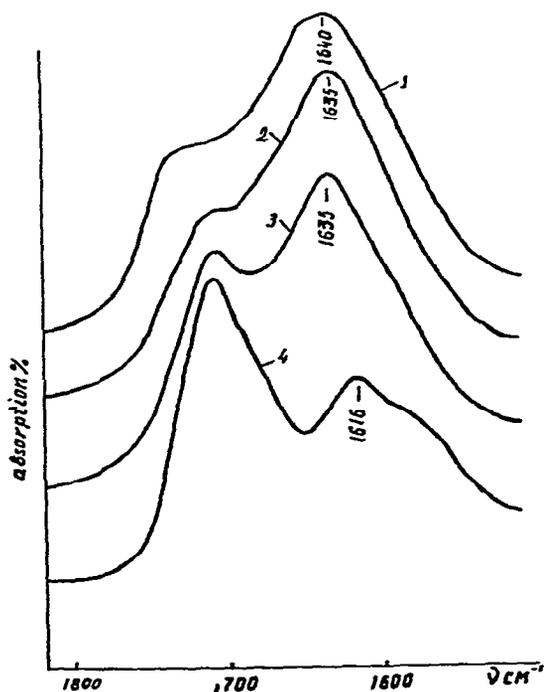

Fig. 2. Spectra of acids (0.5 M) and trioctylamine (1.5 M) solutions in C_2Cl_4: 1 = $CH_2ClCOOH$, 2 = $CH_2BrCOOH$, 3 = CH_2ICOOH, 4 = CH_2ICH_2COOH; cell 45.7 μ.

increases (Fig. 1). The spectrum of solution in C_2Cl_4, containing 0.5 M of acid and three-fold excess of amine has the same appearance. The solutions of mono-bromo- and monoiodoacetic acids in the same conditions have similar spectra (Fig. 2). The conclusion drawn from these results is that the complexes of composition 1 : 1 formed in solutions of monohalogenoacetic acids and excess trioctyl-amine exist in two forms: that of hydrogen bonded molecular complex $RCOOH \cdots NR_3$ and of ionic pair $RCOO^- \cdots NH^+R_3$, arising from proton transfer from acid to amine. The spectral indication of a molecular complex for monohalogenoacetic acids is the $\nu C{=}O$ band in the interval 1710–1730 cm^{-1}. The frequency of this band is close to the frequency of a dimer, which is typical for acid molecules forming the strong hydrogen bond as proton donors. For instance, a $\nu C{=}O$ band of monochloroacetic acid in a molecular complex with dimethyl sulphoxide is shown in Fig. 1 (in these conditions the dimers do not exist[5]). The spectral indication of an ionic pair is the band in the region 1630–1640 cm^{-1}, belonging to the acid anion. The frequency $\nu_a CO_2^-$ for monochloroacetic acid 1640 cm^{-1} does not differ from typical values $\nu_a CO_2^-$ of metal chloroacetates (ref. 6), but it is noticeably higher than $\nu_a CO_2^-$ of symmetric chloroacetate ion in D_2O solution containing monochloroacetic acid and triethylamine (by 0.07 M each), the frequency $\nu_a CO_2^-$ is 1601 cm^{-1} (Fig. 1).

The ionic and molecular complexes are in equilibrium with each other[7]. The position of equilibrium, as one can see from the relative intensity of the $\nu C{=}O$ and $\nu_a CO_2^-$ bands, depends on the proton-donating power of an acid and shifts to the ionic form, as the acid strength increases (Fig. 2). The spectrum of a weaker proton donor, iodopropionic acid, is also shown in Fig. 2, for which the subsequent shift of the equilibrium to the molecular complex occurs. On the other hand, for the extreme case of strong donors, trichloroacetic and heptafluorobutyric acids, the equilibrium at room temperature is completely shifted to the ionic form[8]. The increase of temperature is accompanied by the shift of equilibrium to the molecular complex, therefore the ionic form is energetically preferable to the molecular form. For the systems studied as well as those previously described[2,4,9] the second minimum on the potential energy surface is deeper than the first.

The energy difference between ionic and molecular complexes can be estimated by temperature dependence of the intensity of the $\nu C{=}O$ and $\nu_a CO_2^-$ bands of the acid solution in trioctylamine. Such measurements were performed for monochloroacetic acid at 22 ° and 100 °C. The ΔH value has been calculated from

$$\Delta H = R \frac{T_1 T_2}{T_1 - T_2} \ln \frac{K_1}{K_2}.$$

The ratio of the equilibrium constants of unimolecular proton transfer reaction at 22 ° and 100 °C K_1/K_2 has been expressed through the integral intensities B^{1640} and B^{1730} of bands 1640 and 1730 cm^{-1} at these temperatures. Assuming the ratio of the integral absorption coefficients to be independent of temperature one

can write

$$\frac{K_1}{K_2} = \frac{B_1^{1640}}{B_2^{1640}} \frac{B_2^{1730}}{B_1^{1730}}.$$

The value ΔH, found in this way, is equal to 3.8 ± 0.8 kcal/mole. Similar experiments with bromo- and iodoacetic acids failed because of their chemical instability at high temperatures.

The molecular complex–ionic pair equilibrium is the only one for monohalogenoacetic acids in excess of amine. However at equimolar acid/amine concentrations in solution the spectrum becomes more complicated: besides the bands mentioned above, a new band appears in the region 1580–1600 cm^{-1}, the intensity of the $\nu C{=}O$ band of molecular complex increases (Fig. 3). In excess acid the intensity of this new band increases at the expense of the $\nu_a CO_2^{-}$ band of $1:1$ ionic complex (Fig. 4). In these conditions the formation of complexes containing two or more acid molecules whose existence was indicated by various authors (refs. 9–12) is possible. It was shown recently[8] in the case of trioctylammonium trichloroacetate and heptafluorobutyrate that the addition of the second acid molecule to the ionic pair in solution results in lowering the $\nu_a CO_2^{-}$ by ~ 40 cm^{-1}. At the same time the $\nu C{=}O$ band of acid molecule forming the hydrogen bond with the anion lies in the region $\nu C{=}O$ of dimer. If there is the molecular complex–ionic

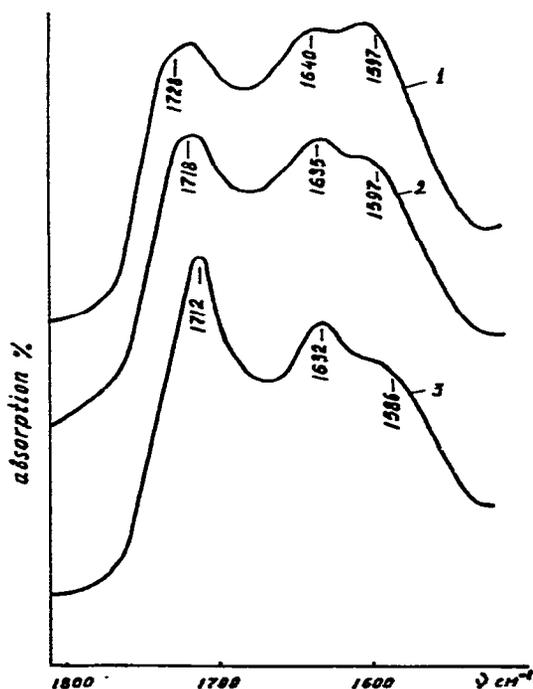Fig. 3. Spectra of equimolar acid/trioctyltamine solutions (0.25 M) in C_2Cl_4: $1 = CH_2ClCOOH$, $2 = CH_2BrCOOH$, $3 = CH_2ICOOH$, cell $150\,\mu$.
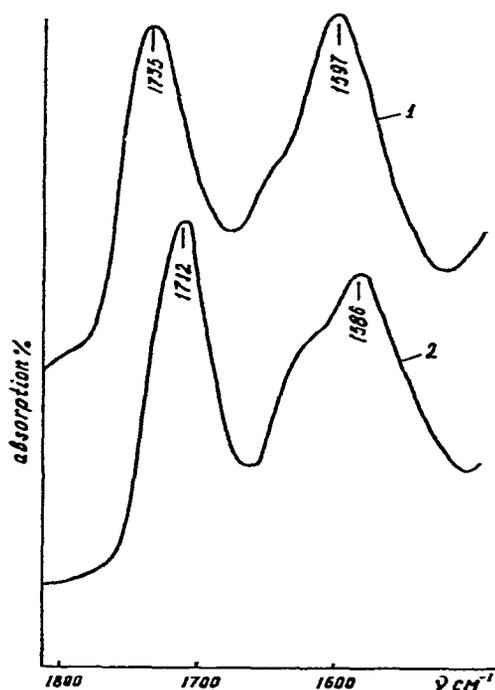
Fig. 4. Spectra of acids (1.0 *M)* and trioctylamine (0.5 *M)* in C_2Cl_4: 1 = $CH_2ClCOOH$, 2 = CH_2ICOOH, cell 45.7 μ.

pair equilibrium in solution, the connection of the second acid molecule to the molecular complex results in the proton transfer to the amine, so the complex 2 : 1 always contains the anion[12]. Therefore, the band in the interval 1580–1600 cm^{-1} should be ascribed to the vibration $v_aCO_2^-$ of the anion in the complex 2 : 1, and the band in the region vC=O of dimer to the vC=O vibration of the second acid molecule.
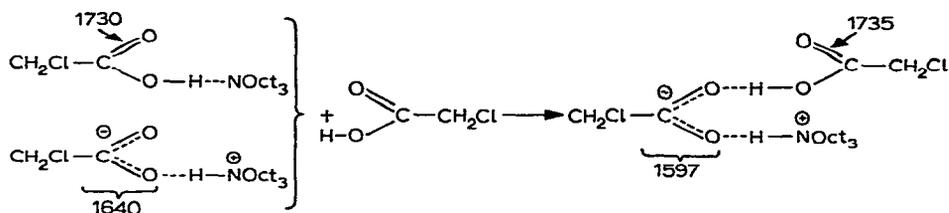
CONCLUSION

Thus in solutions containing similar quantities of acid and amine besides molecular and ionic complexes 1 : 1 there are also complexes of constitution 2 : 1. All these complexes are in equilibrium, the proportion of the latter decreasing as the concentration of amine increases. The relative content of the complexes 1 : 1

and 2 : 1 under comparable conditions depends strongly on the proton donating power of an acid. If for the strong acids C_3F_7COOH and CCl_3COOH the complex 2 : 1 is formed only at the excess of the acid, then for weaker monohalogeno-acetic acids the equilibrium can be completely shifted to complex 1 : 1 only at three-fold excess of amine (Fig. 2). For iodopropionic acid the band of complex 2 : 1 is still seen under these conditions.

Supplementary arguments concerning equilibria in the above systems can be obtained from the absorbance in the region near 1200 cm^{-1} where there is a band of a carboxylic group sensitive to intermolecular interaction. The $\nu C{=}O$ frequency of monochloroacetic acid's dimer 1215 cm^{-1} diminishes in forming strong molecular complexes with dimethyl sulphoxide (Fig. 1) and trimethylphosphinoxide to 1200 and 1211 cm^{-1}. In the spectrum of the acid solution in amine (Fig. 1) there is a band 1200 cm^{-1} in this region whose presence signifies that the molecular complex with a hydrogen bond exists in this system. The 1237 cm^{-1} band belongs to the monochloroacetate ion, (apparently δCH_2), because its intensity reduces with temperature. Simultaneously the intensity of the band 1200 cm^{-1} increases in accordance with the picture observed in the region $1500–1800 \text{ cm}^{-1}$.

REFERENCES

1 G. V. Gusakova, G. S. Denisov and A. L. Smolyansky, *Zh. Prikl. Spektrosk.*, 16 (1972) 320.
2 G. V. Gusakova, G. S. Denisov and A. L. Smolyansky, *Zh. Prikl. Spektrosk.*, 16 (1972) 503
3 G. S. Denisov, G. V. Gusakova and A. L. Smolyansky, *Spectrosk. Lett.*, 4 (1971) 237.
4 G. V. Gusakova, G. S. Denisov and A. L. Smolyansky, *Zh. Prikl. Spektrosk.*, 17 (1972) 666
5 G. V. Gusakova and A. L. Smolyansky, *Opt. Spektrosk.*, 32 (1972) 509.
6 A. W. R. Warrier and P. S. Narayanan, *Spectrochim. Acta*, 23A (1967) 1061.
7 K. Bauge and J. W. Smith, *J. Chem. Soc. (A)*, (1966) 616.
8 G. V. Gusakova, G. S. Denisov and A. L. Smolyansky, *Opt. Spektrosk.*, 32 (1972) 922.
9 G. V. Gusakova, G. S. Denisov, A. L. Smolyansky and V. M. Schreiber, *Dokl. Akad. Nauk SSSR*, 193 (1970) 1065.
10 S. Bruckenstein and D. E. Untereker, *J. Amer. Chem. Soc.*, 91 (1969) 5741.
11 A. A. Lipovsky and M. G. Kuzina, *Zh. Neorg. Khim.*, 12 (1967) 236.
12 G. M. Barrow, *J. Amer. Chem. Soc.*, 78 (1966) 5802.