

SPECTROSCOPIC DETERMINATION OF THE ENERGIES OF COMPLEXES OF WATER WITH TRICHLOROACETIC AND TRIFLUOROACETIC ACIDS IN SOLUTION IN CCl₄

G. S. Denisov, A. L. Smolyanskii,
A. A. Trusov, and M. I. Sheikh-Zade

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It is difficult to estimate quantitatively the capacity of water molecules for forming hydrogen bonds when acting as proton acceptors on account of the low solubility of water in inactive solvents. On the other hand, if one uses solvents that will form hydrogen bonds of OH . . . Y type, the proton-acceptor capacitor of the water will be increased because of the raised electron density near the free pairs. Then the thermodynamic characteristics of the RXH . . . OH₂ complexes in such solvents will differ from those for the vapor state by much more than they will for CCl₄, for example, for which the hydrogen-bond energy has been examined in most detail. Therefore, if one is to determine reliably the equilibrium constant of



at component concentrations in the range 10⁻³-10⁻² M, which are limited by the solubility of water [1, 2], it is best to use a donor with the maximum proton-donor capacity.

We have measured the enthalpy of formation for complexes of water with trichloroacetic acid and trifluoroacetic acid in CCl₄ on the basis of infrared spectra. The solutions contained 4-8 · 10⁻³ M water and 0.6-4 · 10⁻³ M acid and were used at 12-72°C. The measurements were made with a UR-20 instrument with a spectral slit width of 5 cm⁻¹ (νOH region) in a cell of thickness 2 cm with fluorite windows.

In the OH region of water, the RCOOH . . . OH₂ complex results in a reduction in ν_a and ν_s by 20 cm⁻¹ [3, 4], which is comparable with the half-width (Fig. 1), so one cannot separate the bands of the free and bound water with the necessary precision. The νOH band of the acid in the water complex very much overlaps the νOH band of the acid dimers, which are present even in the most dilute solutions, and it is best for quantitative purposes to use the νOH bands of the monomer at 3516 cm⁻¹ (CCl₃COOH) and 3505 cm⁻¹ (CF₃COOH). In the νC = O region, the RCOOH . . . OH₂ complex gives a band between the bands of the monomer and dimer [3, 4], and this can also be used to determine the concentrations of the three forms of the acid (Fig. 2). The concentration of free acid is determined from the integral intensity of the νOH band of the monomer, while the dimerization correction is applied by the scheme of [5]. The results for the νC = O bands, although subject to considerable error give similar values. The water content in the initial CCl₄ was determined from the νOH band. The integral absorption coefficient of [6, 7] gave the absorption coefficient at the band peak as ν_aOH₂ 3709 cm⁻¹, ε_M = 56 liter/mole · cm, and this value was used in the quantitative measurements. We found that ε_M had an appreciable negative temperature coefficient, which was incorporated together with the temperature dependence of the density in processing the results. The integral absorption coefficients for the νOH and νC = O bands were found from the solutions of the acid in CCl₄ carefully dried with zeolite, together with the equilibrium constants of (1), the concentration range being 0.1-0.001 M.

TABLE 1. Equilibrium Constants and Enthalpies of Formation for CCl₃COOH . . . OH₂ and CF₃COOH . . . OH₂

Acid	K, M ⁻¹					-ΔH kcal/mole
	12°C	22°C	38°C	55°C	72°C	
CCl ₃ COOH	216	122	69	41	—	7,2
CF ₃ COOH	294	164	84	42	25	8,4

Vologod Milk Institute. A. A. Zhdanov Leningrad University. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 4, pp. 142-144, April, 1974. Original article submitted June 11, 1973; revision submitted July 31, 1973.

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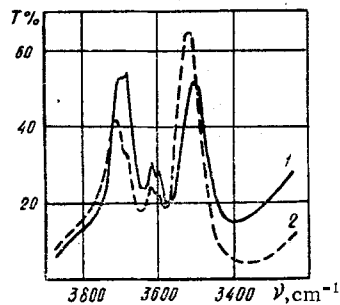


Fig. 1

Fig. 1. Spectra in the νOH region for CF_3COOH and water, acid $3 \cdot 10^{-3}$ M, water $8 \cdot 10^{-3}$ M: 1) 22; 2) 72°C. Layer 2 cm.

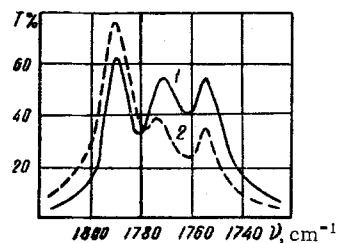


Fig. 2

Fig. 2. Spectra in the $\nu\text{C}=\text{O}$ region of CCl_3COOH , acid concentration $0.8 \cdot 10^{-3}$ M, water $4 \cdot 10^{-3}$ M: 1) 22; 2) 38°C. Layer 2 cm.

Table 1 gives the equilibrium constants of (1) for various temperatures together with the enthalpies of the $\text{RCOOH} \dots \text{OH}_2$ complexes in CCl_4 as found from these results. It is clear that the equilibrium constants and the enthalpies of reaction indicate that trifluoroacetic acid is a stronger proton donor than trichloroacetic. The energy of the $\text{RCOOH} \dots \text{OH}_2$ hydrogen bond substantially exceeds that of a bond in an acid dimer and is comparable with the dimer formation energy [8, 9]. We wish particularly to emphasize that the $\text{RCOOH} \dots \text{OH}_2$ complexes in CCl_4 have a molecular structure; there is no complete transfer of the proton to the water molecule with formation of ion pairs. It appears clear [8] that the proton transfer does not occur either when trichloroacetic acid interacts with stronger bases such as dimethylsulfoxide ($H = 10.1$ kcal/mole), triphenylsulfoxide (13.9 kcal/mole), or diphenylcelluloxide (15.9 kcal/mole), but there is a tendency for symmetrical $\text{O} \dots \text{H} \dots \text{O}$ hydrogen bond to form.

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