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SPECTROSCOPIC INVESTIGATION OF THE DIMERIZATION OF HALOGENATED ACETIC ACIDS

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In the present work we investigated the association of a number of carboxylic acids, viz., halogenated acetic acids, in CCl_4 solutions according to their IR absorption spectra. The goal of the work was to measure the heat of dimerization of monochloroacetic acid $CH_2ClCOOH$ (MCAA), dichloroacetic acid $CHCl_2COOH$ (DCAA), trichloroacetic acid CCl_3COOH (TCAA), tribromoacetic acid CBr_3COOH (TBAA), and trifluoroacetic acid of CF_3COOH (TFAA) for the purpose of ascertaining the role of the proton-donor and proton-acceptor abilities of the carboxyl group in varying the energy of dimerization upon the introduction of electronegative atoms into the radical. In addition, the values of the equilibrium constants for the dimerization of the acids at different temperatures are needed for the determination of the enthalpy of complexes of carboxylic acids with proton acceptors [1]. Although the dimerization of the acids enumerated (besides TBAA) has been investigated repeatedly, according to some data the dimerization energy remains unchanged along the series of acids from acetic acid to TCAA within the range of random errors [2, 3], while according to other data, it regularly decreases along this series (in [4] from 8.4 to 5.6 kcal/mole), the difference in the values given for the same systems sometimes reaching several kilocalories per mole (according to the data in [5] and [6], the energy of formation of the TFAA dimer in the gaseous phase is 12.0 and 17.5 kcal/mole, respectively). A concentration dependence of the equilibrium constants was discovered in [2], and Bulmer and Shurvell [7] stress that the dimerization constant is not dependent on the concentration.

The measurements were carried out on a UR-20 instrument according to the νOH and νC=O bands of the monomers and dimers of the acids. Solutions of the acids in CCl_4 with different concentrations in the 0.001-0.1-mole/liter range were investigated in fluorite cuvettes at 22, 38, 55, and 72°C. The solvent was dried by zeolite NaA. The water content in the solution was monitored according to the band at 3709 cm^{-1} and was $4 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ mole/liter in the most dilute solutions of the acids. At the same time no interaction between the acids and water was observed either in the νC=O bands of the acids [8] or in the νOH bands of water. The dependence of the density of the solvent on the temperature was taken into account in measuring the intensity. The results were treated by three independent methods based on the schemes in [9, 10]. In the case of TFAA and TCAA, we constructed plots of the dependence of B_d/C_0d on B_m/C_0d (B is the integral intensity, d is the optical path, and C_0 is the original concentration of the acid) for the dimeric and monomeric νC=O bands, which were separated graphically, and their areas were determined by planimetry. In the case of MCAA and DCAA, the separation of the νC=O bands is complicated by the fact that these bands have a structure due to the existence of rotational isomers [11]. Figure 1a shows these plots for TFAA. The points corresponding to different temperatures lie on the same straight line. This shows that the integral extinction coefficients of the νC=O absorption bands of the monomer and the dimer do not depend on the temperature in the working range from 22 to 72°C. A similar plot was constructed for all the acids from the intensities of the monomeric and dimeric νOH bands (Fig. 1b). The x and y intercepts provide the values of the integral extinction coefficients of the monomer and the dimer A_m and A_d of the νC=O and νOH bands (see Table 1), which were used for the determination of the dimerization constant of the acids D_d from the integral intensities of these bands [10]. Finally, plots were constructed in B_m/d versus C_0d/B_m coordinates (B_m is the integral intensity of the νOH band of the monomer) according to the method in [9]. The points satisfactorily lie on straight lines for each temperature. At the same time, the straight lines for different temperatures intersect practically at a single point. This means that K_d is not dependent on the concentration in the 0.001-0.1-mole/liter range, and A_m is not dependent on the temperature in the 22-72°C

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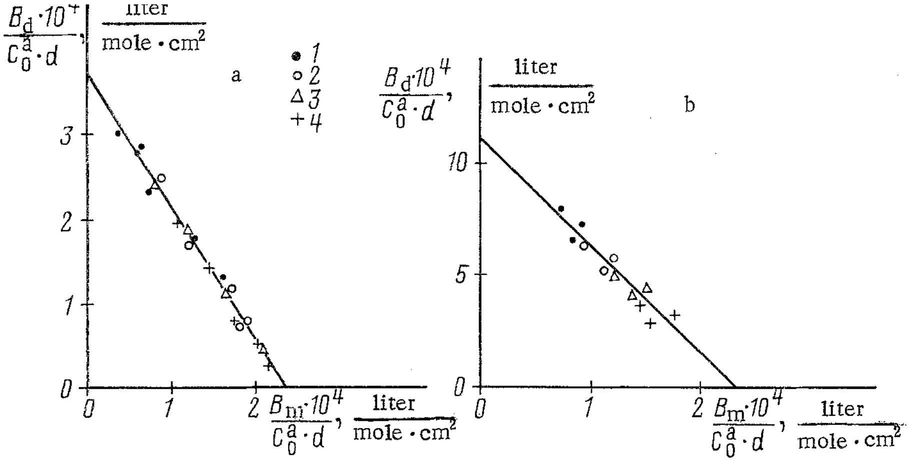

Fig. 1. Dependence of B_d/C_0d on B_m/C_0d for solutions of TFAA in CCl_4 for νC=O (a) and νOH (b) bands. T = 22 (1), 38 (2), 55 (3), and 72°C (4).

TABLE 1. Spectral Characteristics of the νOH and νC=O Bands of Halogenated Acetic Acids in CCl_4 Solutions

Acid	νOH band				νC=O band			
	ν_m, cm^2	$\Delta\nu_{1/2}^{m}$, cm^{-1}	$A_m \cdot 10^{-4}$, liter/mole · cm^2	$A_d \cdot 10^{-4}$, liter/mole · cm^2	ν_m, cm^{-1}	ν_d, cm^{-1}	$A_m \cdot 10^{-4}$, liter/mole · cm^2	$A_d \cdot 10^{-4}$, liter/mole · cm^2
$CH_2ClCOOH$	3527	34	1,9	14,1	1768, 1798	1798, 1740	—	—
$CHCl_2COOH$	3518	42	2,3	14,9	1768, 1789	1748	—	—
CBr_3COOH	3508	54	2,7	—	1771	1736	—	—
CCl_3COOH	3511	53	2,7	15,7	1789	1751	2,7	3,1
CF_3COOH	3505	54	2,3	11,0	1810	1778	2,3	3,7

range. Figure 2 presents these plots for TBAA. The location of the points near straight lines is about the same for the other acids. The values of A_d and A_m for the νOH band were determined from the parameters of these straight lines.

From Table 1 it is seen that the formation of a dimer is accompanied by a five- to sevenfold increase in the extinction coefficient of the νOH band, this increase being maximal for MCAA and decreasing somewhat along the series MCAA, DCAA, TCAA, TFAA. The extinction coefficient of the νC=O band also increases upon the formation of a dimer by 15-20%, and in the case of TFAA it increases by more than 1.5 times. The dimerization constants obtained by the three independent methods are in good agreement with each other at each temperature. This is shown in Table 2 in the example of TFAA. The mean value of K_d was found, and then the enthalpy change ΔH and entropy change ΔS upon dimerization of the acids were found from the dependence of log D_d on 1/T according to the van't Hoff equation. Figure 3 presents these plots for the acids studied. It is seen that the points lie close to straight lines. The results of the determination of the thermodynamic quantities are presented in Table 3. The mean-square error in the determination of the enthalpy change estimated from the spread of the points on the straight lines in Fig. 3 amounts to 0.3 kcal/mole. This value does not reflect the errors introduced upon separation of the bands or, apparently, the other systematic errors and is underestimated. It may be assumed on the basis of a comparison of the experimental data obtained by different methods that the values of ΔH presented in Table 3 are reliable with an accuracy of 0.6 kcal/mole. The values of ΔH obtained for MCAA and DCAA were somewhat higher than those recently found by other workers [2-4, 12]. The range of values of ΔH for TCAA according to the data of those workers is very broad (from 10.4 [3] to 5.6 [4] kcal/mole), but the values of H for TFAA and TBAA are in good agreement with the values given in [3] and [13].

From the data in Table 3 it is seen that the values of the dimerization constants decrease along the MCAA—DCAA—TCAA and TBAA—TCAA—TFAA series with increasing number or electronegativity of the substituents in the radical. The heat of dimerization also decreases along

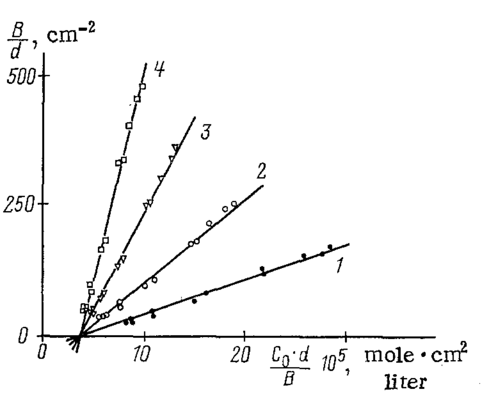

Fig. 2

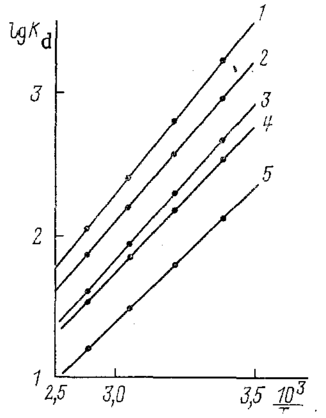

Fig. 3

Fig. 2. Dependence of B_m/d on C_0d/B_m of the νOH band for a solution of TBAA in CCl_4 at T = 22 (1), 38 (2), 55 (3), and 72°C (4).

Fig. 3. Dependence of log K_d on 1/T for halogenated acetic acids in CCl_4: 1) MCAA; 2) DCAA; 3) TBAA; 4) TCAA; 5) TFAA.

TABLE 2. Dimerization Constants D_d (liter/mole) of TFAA Obtained from Measurements of the Integral Intensity of the νC=O (I) and νOH (II) Bands of the Monomers and Dimers and According to the Method in [9] (III)

T, °C	CF_3COOH		
	I	II	III
22	162	137	122
38	62	60	63
55	28	30	30
72	15	17	17

TABLE 3. Thermodynamic Characteristics of the Dimerization of Halogenated Acetic Acids in CCl_4 Solutions

Acid	K_d, liter/mole	$-\Delta H$, kcal/mole	$-\Delta S$, cal/mole·deg
$CH_2ClCOOH$	1600	10,8	20,8
$CHCl_2COOH$	930	10,4	21,7
CBr_3COOH	460	10,0	21,6
CCl_3COOH	400	9,2	19,2
CF_3COOH	140	8,8	19,9

these series, but this decrease only slightly exceeds the measurement error. Therefore, the decrease in the proton-acceptor ability of the C=O group along these series is almost completely compensated by the increase in the proton-donor ability of the OH group, so that the energy of the dimer remains approximately the same for all the acids investigated. If the increase in the energy of the interaction of the monomer acid molecules with the solvent along these series is taken into account [14], it may be concluded that the dimerization energy, which is governed only by the electronic configuration of the molecules, may even increase somewhat along these series in accordance with the results obtained in the gaseous phase when the dimerization of acetic acid and TFAA is compared [6, 15], in contradiction to the hypothesis advanced in [16].

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