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INTERMOLECULAR HYDROGEN BONDING OF CHLORO-SUBSTITUTED ACETIC AND PROPIONIC ACIDS IN CARBON TETRACHLORIDE

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ABSTRACT

A calorimetric enthalpy of dilution technique has been applied to the investigation of the self-association of several chloro-substituted carboxylic acids in dilute solutions in anhydrous carbon tetrachloride at 25 °C. Calorimetric data are expressed in terms of relative apparent molar enthalpies, Φ_L. The values of Φ_L are shown to be consistent with the monomer-dimer model. Values of the equilibrium constant, standard enthalpy, and standard entropy of dimerization are given for seven acids. Results are discussed in terms of the effect of substitution on the electrostatic nature of the hydrogen bond.

INTRODUCTION

It is generally agreed that dimerization is the predominant self-association equilibrium reaction occurring in dilute solutions of carboxylic acids in "inert" solvents. Several such systems have been extensively studied using a variety of experimental techniques, and many of the thermodynamic data have been tabulated for a number of acids[1,2].

Recently we have applied a calorimetric enthalpy of dilution technique to the study of dimerization of acetic acid in carbon tetrachloride and benzene[3]. By this technique we have shown that it is possible to determine the thermodynamic quantities $\Delta G°$, $\Delta H°$, and $\Delta S°$ of dimerization from a single experiment.

In this paper we report the results of applying this calorimetric technique to a study of the hydrogen-bonding dimerization of several chloro-substituted acetic and propionic acids in carbon tetrachloride at 25 °C.

EXPERIMENTAL

Reagent grade chloroacetic, trichloroacetic, propionic, 2-chloropropionic, and 3-chloropropionic acids, and practical grade dichloroacetic acid, were used. Spectrophotometric grade CCl_4 that was used in the preparation of solutions and in the

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calorimetric dilution experiments was analyzed by gas chromatography and found to contain no more than 0.002% water. Care was taken to prepare and keep all solutions and solvents free of water. All measurements were made at 25.00±0.03 °C.

Heats of dilution of all acid solutions in anhydrous CCl_4 were measured with the Tronac 450 Titration Calorimeter (50 ml vessel) coupled to the Tronac 1040 Precision Temperature Controller and a Sargent–Welch SRG recorder. The apparatus was modified to include a Metrohm Herisau Dosimat piston buret. All results are reported in terms of the calorie defined equal to 4.184 J. All solute concentrations are expressed in terms of molarities and activity coefficients are assumed to be unity[4].

CALCULATIONS AND RESULTS

A general equation which relates heats of dilution to the thermodynamic properties K_n and ΔH_n° for any self-association reaction

$$nA \rightleftharpoons A_n \tag{1}$$

has been developed previously[4]. The equation makes use of the relative apparent molar enthalpy, Φ_L, which is equal to the negative of the enthalpy of dilution of one mole of solute from a solution of specified molarity to infinite dilution. Application of this general equation to the dimerization of carboxylic acids in inert solvents ($n = 2$ in eqn 1) yields

$$\Phi_L = (\Delta H_2^\circ/2) + (-\Delta H_2^\circ/4K_2)^{1/2}(-\Phi_L/M)^{1/2} \tag{2}$$

Plots of $-\Phi_L$ versus $(-\Phi_L/M)^{1/2}$ for acetic acid in CCl_4 and in benzene are seen to be straight lines[3].

Values of Φ_L are obtained as follows. As the solution of acid enters the pure solvent at a known rate, the enthalpy of dilution is recorded at regular intervals, corresponding to

$$M_t \rightarrow M_1 \qquad \Delta H_1 \tag{3a}$$

$$M_t \rightarrow M_2 \qquad \Delta H_2 \tag{3b}$$

$$\vdots \qquad\qquad \vdots$$

$$M_t \rightarrow M_i \qquad \Delta H_i \tag{3i}$$

where M_t is the formal acid concentration of the titrant. The enthalpy of dilution of the titrant to infinite dilution corresponds to

$$M_t \rightarrow 0 \qquad \Delta H_0 = -\Phi_{Lt} \tag{4}$$

Combination of eqns (3) and (4) yields

$$M_1 \rightarrow 0 \qquad -\Phi_{L1} \tag{5a}$$

$$M_2 \rightarrow 0 \qquad -\Phi_{L2} \tag{5b}$$

$$\vdots \qquad\qquad \vdots$$

$$M_i \rightarrow 0 \qquad -\Phi_{Li} \tag{5i}$$

Theoretically, the correct value of ΔH_0 can be found by extrapolation of a plot of ΔH_i versus M_i to zero concentration. The uncertainties in ΔH_i and in M_i are often large at small concentrations, however. Consequently, an extrapolated value of ΔH_0 is often uncertain.

We have observed that if a chosen value of ΔH_0 is too low, the resulting plot of $-\Phi_L$ versus $(-\Phi_L/M)^{1/2}$ is convex, whereas if a chosen value of ΔH_0 is too high the plot is concave. It is known that the presence of other polymeric species (*i.e.*, trimers, tetramers, etc.) could also cause convex curvature in such a plot[4], but it is generally accepted that monomers and dimers are the only species present in dilute solution[1,2].

Based on these observations, we have developed a computer program which determines the value of ΔH_0 for which the resulting plot of $-\Phi_L$ versus $(-\Phi_L/M)^{1/2}$ best fits a straight line. In Table 1 we list representative Φ_L values obtained by this method. These values are based on a large number of enthalpy of dilution measurements (eqn 3). Also included are values for acetic acid which we consider to be slightly more reliable than the values we previously reported[3]. In Fig. 1 we show the application of eqn (2) to the data in Table 1.

TABLE 1

RELATIVE APPARENT MOLAR ENTHALPIES OF CARBOXYLIC ACIDS IN CARBON TETRACHLORIDE AT 25 C (tabulated as $-\Phi_L$, cal/mole)

ml tirated[a]	*Acetic* 0.5412 *M*	*Chloro-acetic* 0.3589 *M*	*Dichloro-acetic* 0.6360 *M*	*Trichloro acetic* 0.3784 *M*	*Propionic* 0.6884 *M*	*2-Chloro-propionic* 0.4163 *M*	*3-Chloro-propionic* 0.5084 *M*
0.2219	2849	2000	1835	741	2714	1825	2508
0.4439	3154	2410	2161	1071	3006	2190	2834
0.6658	3311	2632	2328	1263	3147	2372	3003
0.8878	3409	2769	2430	1396	3233	2487	3107
1.1097	3482	2870	2502	1490	3291	2572	3178
1.3317	3542	2943	2552	1565	3335	2640	3232
1.5536	3589	3000	2590	1627	3369	2693	3271
1.7756	3631	3047	2620	1680	3396	2738	3304
1.9975			2641	1725	3419	2779	3328
2.2195			2656	1766	3437		3349
titrant[b]	4140	3715	3000	2531	3738	3280	3730

[a] Titrated into 50.00 ml anhydrous carbon tetrachloride. [b] Equation 4.

In order to eliminate the necessity of finding ΔH_0, an alternate method of calculations based on differences in Φ_L values was used. Following a derivation made earlier[3], we have

$$K_2 = \frac{x}{2M(1-x)^2} \tag{6a}$$

and

$$\Delta H_2^{\circ} = \frac{2(\Phi_{Li} - \Phi_{Lj})}{(x_i - x_j)} \tag{6b}$$

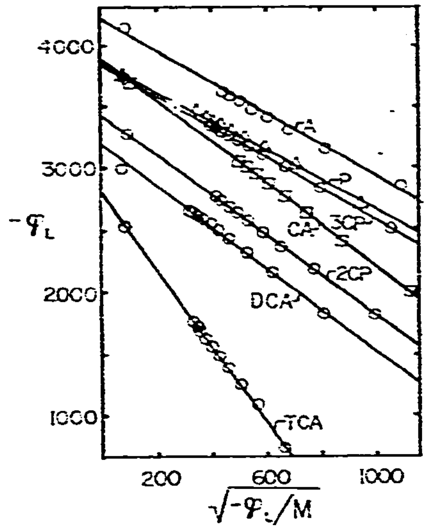


Fig. 1. Plots of the data in Table I according to eqn (2). TCA, trichloroacetic acid; DCA, dichloroacetic acid; 2CP, 2-chloropropionic acid; CA, chloroacetic acid; 3CP, 3-chloropropionic acid; P, propionic acid; and A, acetic acid.

where α represents the fraction of monomers that is associated at a particular concentration. By referring to eqns (3) and (5), one readily sees that eqn (6b) is equivalent to

$$\Delta H_2^\circ = \frac{2(\Delta H_i - \Delta H_j)}{(\alpha_i - \alpha_j)} \qquad (6c)$$

and both are independent of ΔH_0.

The value of K_2 in eqn (6a) can be varied until the most consistent value of ΔH_2° is obtained for each acid from Φ_L and concentration data such as that given in Table I.

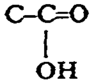
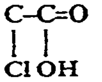
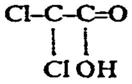
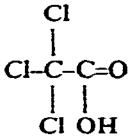
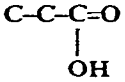
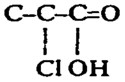
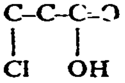
Using the two methods based on eqns (2) and (6) we have determined the "best" thermodynamic values for the self-association of each of the acids in Table 1 in anhydrous CCl_4 solvent at 25 °C. The results are given in Table 2.

DISCUSSION

IR spectroscopic methods have been used frequently to study the dimerization of various carboxylic acids in anhydrous carbon tetrachloride[5–9]. The results of these studies are not always in close agreement. Barrow and Yerger[5] report an association constant for acetic acid that is concentration-dependent, varying from 1000 in 0.05 M acid to 2650 in 1.12×10^{-4} M acid. Wenograd and Spurr[6] report a value of K_2 of 2375 for acetic acid, while Harris and Hobbs[7] report values of 3225 and 5555 at different concentrations. They also report a value for the association constant for trichloroacetic acid of 526, while Affsprung *et al.*[8] report a value of 269. The ΔH_2° of dimerization for trichloroacetic acid has been reported as −7.9 and −10.3 kcal[9].

TABLE 2

"BEST" VALUES OF THERMODYNAMIC FUNCTIONS FOR DIMERIZATION OF CARBOXYLIC ACIDS (eqn 1 with $n = 2$) IN CARBON TETRACHLORIDE AT 25 °C

Acid	K_2	$-\Delta H_2^\circ$ *(kcal)*	$-\Delta S_2^\circ$ *(cal/K)*
 $\mathrm{C-\underset{OH}{\underset{\mid}{C}}=O}$	1400 (±400)	8.4 (±0.3)	13.8 (±1.7)
 $\mathrm{\underset{Cl}{\underset{\mid}{C}}-\underset{OH}{\underset{\mid}{C}}=O}$	700 (±200)	7.8 (±0.5)	13.1 (±2.3)
 $\mathrm{Cl-\underset{Cl}{\underset{\mid}{C}}-\underset{OH}{\underset{\mid}{C}}=O}$	600 (±300)	6.7 (±0.7)	9.7 (±3.7)
 $\mathrm{Cl-\overset{Cl}{\overset{\mid}{\underset{Cl}{\underset{\mid}{C}}}}-\underset{OH}{\underset{\mid}{C}}=O}$	150 (±20)	5.6 (±0.3)	8.7 (±1.3)
 $\mathrm{C-C-\underset{OH}{\underset{\mid}{C}}=O}$	1400 (±250)	7.6 (±0.3)	11.1 (±1.4)
 $\mathrm{C-\underset{Cl}{\underset{\mid}{C}}-\underset{OH}{\underset{\mid}{C}}=O}$	700 (±200)	6.9 (±0.3)	10.1 (±1.7)
 $\mathrm{\underset{Cl}{\underset{\mid}{C}}-C-\underset{OH}{\underset{\mid}{C}}=O}$	1200 (±300)	7.5 (±0.5)	11.1 (±2.3)

The values of K_2 and ΔH_2° we report in Table 2 are generally lower than those based on infrared spectroscopy, but the same trends are evident. There is an increase of nearly 1 kcal/mole in ΔH_2° for each acid in the series acetic acid–trichloroacetic acid. The difference in ΔH_2° of 2.8 kcal between acetic acid and trichloroacetic acid is in agreement with the difference reported by Affsprung *et al.*[8]. There is a similar but smaller increase in ΔG_2° in this series. The difference in ΔG_2° between acetic acid and trichloroacetic acid is 1.3 kcal, which agrees well with the 1.2 kcal difference reported by Harris and Hobbs[7].

These trends can be explained readily in terms of an electrostatic model of the hydrogen bond. Pimentel and McClellan[1] point out that the long hydrogen bond (2.8 Å) can be considered essentially electrostatic in nature. It has been shown by X-ray diffraction that the bond distance in gas-phase acetic dimers is 2.76 ±0.06 Å[10]. These bonds may thus be treated as if they are almost entirely electrostatic.

The substitution of the electronegative element chlorine for hydrogen in acetic acid causes a decrease in the electron density on the carboxyl group. Born electrostatic theory predicts that a decrease in charge would result in a more positive ΔG° and a more positive ΔH° for dimerization, and this trend is evident in our results.

The decrease in the influence of chlorine on the electrostatic nature of the hydrogen bond when the chlorine atom is moved from the α to the β position is seen by examining the three propionic acids. In the α position, chlorine substitution increases ΔG_2° and ΔH_2° just as in chloroacetic acid. On the other hand, the presence of chlorine in the β position causes only a very slight increase in ΔG_2° and ΔH_2°, and the thermodynamic values for dimerization of 3-chloropropionic acid are very similar to those of propionic acid.

By comparing acetic acid with propionic acid and chloroacetic acid with 2-chloropropionic acid, we see an unexpected effect of the methyl group. Even though ΔG_2° does not change, ΔH_2° increases by nearly 1 kcal upon the addition of the methyl group in both cases. The methyl group is slightly more electronegative than hydrogen[11], so one would expect a slight increase in both ΔG_2° and ΔH_2° as with chlorine substitution. It is unreasonable to assume that the change in ΔH_2° which we observe is due solely to this effect. Further study will be necessary to examine the effect of the methyl group on the thermodynamic values for carboxylic acid dimerization reactions.

ACKNOWLEDGMENT

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