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INTERMOLECULAR HYDROGEN BONDING OF ACETIC ACID IN CARBON TETRACHLORIDE AND BENZENE

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ABSTRACT

The hydrogen bonding dimerization of acetic acid in anhydrous CCl_4 and benzene solutions at 25° has been investigated by a dilution calorimetric technique. The calorimetric data are analyzed in terms of relative apparent molar enthalpies, Φ_L. The values of Φ_L are shown to be consistent with the monomer–dimer model. The results lead to the following values of the equilibrium constant (molar concentrations) and standard enthalpy for formation of dimers from monomers: in CCl_4, $K_2 = 900$ (± 100) and $\Delta H_2^\circ = -8.1$ (± 0.2) kcal/mole of dimer; in benzene, $K_2 = 270$ (± 50) and $\Delta H_2^\circ = -7.4$ (± 0.2) kcal/mole of dimer.

INTRODUCTION

Many studies have shown that compounds containing –OH groups are intermolecularly hydrogen bonded when in "inert" solvents. Often the associated species are stable enough to identify the extent of aggregation and to determine their thermodynamic properties. The wide variety of experimental techniques utilized in studies of the hydrogen bond are discussed by Pimentel and McClellan[1].

Recently, a calorimetric titration technique has been developed which enables us to determine from one experiment the thermodynamic quantities ΔG°, ΔH°, and ΔS° for the self-association of hydrogen bonded solutes[2,3]. It has been shown that independent determination of the extent of association (dimers, trimers, etc.) is helpful but not necessary in determination of numerical values of these thermodynamic quantities[2].

We have chosen to study the hydrogen bonding association of acetic acid in carbon tetrachloride and in benzene by this calorimetric technique because of the general agreement that the predominant equilibrium reaction for these systems is the dimerization of acetic acid[1,4,5] represented by

$$2A \rightleftharpoons A_2 \tag{1}$$

$$K_2 = [A_2]/[A]^2 \tag{2}$$

In Eqn. (2), $[A_2]$ and $[A]$ represent molarities of acetic acid dimer and monomer, respectively.

EXPERIMENTAL

Reagent grade glacial acetic acid and spectrophotometric grade carbon tetrachloride and benzene were used. Considerable care was taken to prepare and keep all solutions and solvents free from water. All measurements were made at 25.0 ±0.2°C.

Heats of dilution of acetic acid in anhydrous CCl_4 and in anhydrous benzene were measured with the Tronac 450 Titration Calorimeter (50 ml vessel) coupled to the Tronac PTC-1000A Temperature Controller and a Sargent–Welch SRG recorder. All results of our measurements are reported in terms of the calorie defined equal to 4.184 J. All solute concentrations are described in terms of molarities.

CALCULATIONS AND RESULTS

Our heat of dilution results are reported and used in the form of Φ_L values. The relative apparent molar enthalpy, Φ_L, is equal to the negative of the enthalpy of dilution of one mole of acetic acid from a solution of specified molarity to infinite dilution. We assume the differences between actual Φ_L values and $\Phi_L = 0$ for ideal solutions are caused by dissociation of acetic acid dimers to monomers[2].

TABLE I

RELATIVE APPARENT MOLAR ENTHALPIES OF ACETIC ACID IN ANHYDROUS CCl_4

M (moles acid/liter of solution)	*$-\Phi_L$ (cal/mole of acid)*	*M (moles acid/liter of solution)*	*$-\Phi_L$ (cal/mole of acid)*
0.00114	1970	0.01230	3239
0.00160	2203	0.01339	3270
0.00228	2452	0.01448	3298
0.00273	2575	0.01556	3320
0.00341	2698	0.01664	3343
0.00453	2840	0.01772	3365
0.00566	2932	0.01879	3382
0.00678	3007	0.01986	3401
0.00789	3072	0.571_4	3900
0.00900	3127	1.120_9	3950
0.01010	3169		
0.01120	3208		

Our Φ_L data for acetic acid in CCl_4 and benzene are listed in Tables I and II. These values are based on several separate calorimetric dilution runs in which titrant solutions were prepared independently. The titrant solutions had acetic acid molarities of $M = 1.120_9$ and $M = 0.571_4$ in CCl_4 solvent, and $M = 1.229_7$ and $M = 0.594_2$ in benzene solvent.

Our interpretation of the Φ_L *versus* M data follows that given earlier[2]. We consider the dilution of a solution containing acetic acid from an initial molarity M to

TABLE II

RELATIVE APPARENT MOLAR ENTHALPIES OF ACETIC ACID IN ANHYDROUS BENZENE

M (moles acid/liter of solution)	$-\Phi_L$ *(cal/mole of acid)*	*M (moles acid/liter of solution)*	$-\Phi_L$ *(cal/mole of acid)*
0.00119	1162	0.01279	2539
0.00166	1281	0.01393	2575
0.00237	1558	0.01506	2609
0.00284	1640	0.01618	2644
0.00354	1781	0.01731	2661
0.00472	1990	0.01842	2698
0.00588	2116	0.01954	2722
0.00705	2222	0.02065	2744
0.00820	2312	0.594_2	3400
0.00936	2383	1.229_7	3500
0.01051	2435		
0.01165	2485		

infinite dilution. For this process we write

$$M\,\Phi_L = \Delta H_2^\circ\,[\mathrm{A_2}] \tag{3}$$

in which ΔH_2° represents the molar enthalpy of the reaction shown in Eqn. (1). Rearrangement of Eqn. (2) leads to

$$[\mathrm{A_2}] = K_2\,[\mathrm{A}]^2 \tag{4}$$

Combination of Eqns. (3) and (4) and subsequent rearrangement gives us

$$[\mathrm{A}] = (M\,\Phi_L/\Delta H_2^\circ\,K_2)^{\frac{1}{2}} \tag{5}$$

Substitution of Eqns. (4) and (5) into the equation for material balance

$$M = [\mathrm{A}] + 2[\mathrm{A_2}] \tag{6}$$

followed by rearrangement yields

$$\Phi_L = (\Delta H_2^\circ/2) - (-\Delta H_2^\circ/4K_2)^{\frac{1}{2}}\,(-\Phi_L/M)^{\frac{1}{2}} \tag{7}$$

A graph of our experimental $-\Phi_L$ *versus* $(-\Phi_L/M)^{\frac{1}{2}}$ values is shown in Fig. 1. The slopes and intercepts of these lines lead to $K_2 = 883$ (±200) in $\mathrm{CCl_4}$ and $\Delta H_2^\circ = -8.0_6$ (±0.2) kcal/mole of acetic acid dimer in $\mathrm{CCl_4}$ and $K_2 = 290$ (±60) in benzene and $\Delta H_2^\circ = -7.2_7$ (±0.2) kcal/mole of acetic acid dimer in benzene.

Since at any finite concentration there will be both monomeric and dimeric acetic acid present, while at infinite dilution all dimers are dissociated to monomers, we can express the enthalpy of dilution to infinite dilution in terms of

$$\Phi_L = (\alpha/2)\,\Delta H_2^\circ \tag{8}$$

where α represents the fraction of monomers that is associated. Thus we have $[\mathrm{A}] = M(1-\alpha)$ and $[\mathrm{A_2}] = \alpha M/2$, which we substitute into Eqn. (4) to obtain

$$K_2 = \alpha/2M(1-\alpha)^2 \tag{9}$$

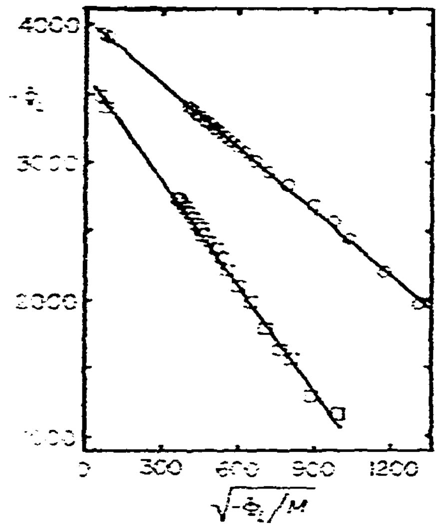

Fig. 1. Results of enthalpy of dilution measurements displayed as suggested by Eqn. (7): ○, acetic acid in CCl_4; □, acetic acid in benzene.

We have tested Eqns. (8) and (9) with our Φ_L results using a computer to find the value of K_2 that leads to the most consistent value of ΔH_2° over the entire range of concentrations. These calculations lead to $K_2 = 865$ and $\Delta H_2^\circ = -8.07$ (± 0.025) kcal/mole in CCl_4 and $K_2 = 255$ and $\Delta H_2^\circ = -7.46$ (± 0.072) kcal/mole in benzene.

We have also devised an approach based on differences in Φ_L values at finite M values. We take Φ_{L1} and Φ_{L2} to indicate relative apparent molar enthalpies at two molarities of acetic acid, M_1 and M_2. From Eqn. (8) we obtain

$$\Delta H_2^\circ = 2(\Phi_{L2} - \Phi_{L1})/(x_2 - x_1) \tag{10}$$

where x_2 and x_1 refer to the fraction of monomers associated in the two solutions.

We have tested Eqns. (9) and (10) with our Φ_L results using a computer to find the value of K_2 that leads to the most consistent value of ΔH_2° over the entire range of concentrations. These calculations lead to $K_2 \sim 950$ and $\Delta H_2^\circ \sim -8.2$ kcal/mole in CCl_4 and $K_2 \sim 260$ and $\Delta H_2^\circ \sim -7.5$ kcal/mole in benzene.

Since the thermodynamic values obtained by these two computer approaches are in agreement with the results of the graphical method [Eqn. (7) and Fig. 1], we conclude that the "best" thermodynamic values are $K_2 = 900$ (± 100) and $\Delta H_2^\circ = -8.1$ (± 0.2) kcal/mole in CCl_4 and $K_2 = 270$ (± 50) and $\Delta H_2^\circ = -7.4$ (± 0.2) kcal/mole in benzene.

From these "best" K_2 values we obtain $\Delta G_2^\circ = -4.0_3$ (± 0.07) kcal/mole and $\Delta G_2^\circ = -3.3_2$ ($\pm 0.1_2$) kcal/mole for the dimerization reaction in Eqn. (1), in CCl_4 and in benzene, respectively. Combination of these ΔG_2° values (based on molar concentrations of monomer and dimer) and the "best" ΔH_2° values leads to $\Delta S_2^\circ = -13._7$ (± 1) kcal/mole/°K and $\Delta S_2^\circ = -13._7$ (± 1) kcal/mole/°K for the dimerization reaction in Eqn. (1), in CCl_4 and in benzene, respectively. These values are summarized in Table III.

TABLE III

THERMODYNAMICS OF ACETIC ACID DIMERIZATION IN ANHYDROUS BENZENE AND CCl_4[a]

	Benzene	CCl_4
K_2[b]	270 (±50)	900 (±100)
ΔG_2^0 (kcal/mole)[b]	-3.3_2 ($\pm 0.1_2$)	-4.0_3 ($\pm 0.0_7$)
ΔH_2^0 (kcal/mole)	−7.4 (±0.2)	−8.1 (±0.2)
ΔS_2^0 (kcal/mole/°K)[b]	$-13._7$ (±1)	$-13._7$ (±1)

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[a] We use ± to indicate total uncertainty in values (see Ref. 2). [b] Values based on molar concentrations of monomer and dimer (see Ref. 2).

DISCUSSION

Acetic acid in benzene has been investigated by a variety of techniques that lead to reasonably consistent values of K_2[1,6,7,8]. Much of the compiled data is derived from acetic acid–water–benzene distribution measurements in which the benzene phase contains significant amounts of water. Such data are not necessarily comparable in a direct manner with our Φ_L measurements in anhydrous benzene because of the probable presence of hydrated acetic acid species in the benzene phase[2,6,7]. Christian and coworkers[6] have attempted to correct earlier acetic acid–water–benzene distribution data for hydration effects. They conclude that K_2 values valid for anhydrous benzene are two or three times as large as the apparent K_2 values obtained from distribution experiments in the temperature range of 15–35°C.

Apparent K_2 values at 25°C from distribution data on acetic acid–water–benzene are generally in the range of 130–170[1,4,7]. Using the factor of two or three from Christian and coworkers[6], K_2 in anhydrous benzene should be between 260 and 510. Our $K_2 = 270$ (±50) from Φ_L data in anhydrous benzene is in good agreement with this estimate.

Pimentel and McClellan[1] also give K_2 values from 0° to 70°C derived from dipole moment data of acetic acid in anhydrous benzene by Smyth and Rogers[8]. We have calculated $\Delta H_2^0 = -5._3$ kcal/mole at 25°C using these K_2 values, density (ρ) data for anhydrous benzene[9], and Eqn. (11)[2].

$$\Delta H_2^0 = RT^2\,(\mathrm{d}\ln K_2/\mathrm{d}T) + RT^2\,(\mathrm{d}\ln \rho/\mathrm{d}T) \qquad (11)$$

Interpolation of the K_2 values gives $K_2 = 170$ at 25°C. We note that these values are somewhat lower than the values in Table III.

We now turn to a discussion of the thermodynamic values for acetic acid in CCl_4 obtained by our Φ_L method as compared to previous work. Values of K_2 obtained by various methods appear to be more uncertain in anhydrous CCl_4 than in anhydrous benzene. The three IR spectroscopic studies cited by Pimentel and McClellan[1] give K_2 values ranging from 1000 to 4000 at 25°C, somewhat higher than our $K_2 = 900$ (±100). Distribution measurements on acetic acid–water–CCl_4 give[1] $K_2 = 483$ at 25°C. As with K_2 in benzene, this $K_2 = 483$ cannot necessarily be compared in direct manner with our K_2 in anhydrous CCl_4. Pimentel and McClellan[1] also cite $\Delta H_2^\circ = -10.76$ kcal/mole of dimer in anhydrous CCl_4 from IR spectroscopic data, somewhat more negative than our "best" value of -7.4 (± 0.2) kcal/mole.

We conclude that the calorimetric dilution technique and method of calculation described here and elsewhere[2] provide a good approach for the investigation of intermolecular hydrogen bonding of carboxylic acids. The experimental procedure is performed readily with the calorimetric equipment described in this paper. Treatment of the calorimetric enthalpy of dilution data is straightforward. Thermodynamic values derived from these methods are in reasonable agreement with corresponding values obtained by other methods.

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REFERENCES

1 G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman and Co., San Francisco, 1960.
2 E. M. Woolley, J. G. Travers, B. P. Erno, and L. G. Hepler, *J. Phys. Chem.*, in press.
3 E. Calvet and C. Paoli, *Compt. Rend.*, 257 (1963) 3376.
4 M. M. Davis, *Acid–Base Behavior in Aprotic Organic Solvents*, National Bureau of Standards Monograph 105, U. S. Government Printing Office, Washington, D. C., 1968.
5 S. Kishida and K. Nakamoto, *J. Chem. Phys.*, 41 (1964) 1558.
6 S. D. Christian, H. E. Affsprung, and S. A. Taylor, *J. Phys. Chem.*, 67 (1963) 187.
7 I. Kojima, M. Yoshida, and M. Tanaka, *J. Inorg. Nucl. Chem.*, 32 (1970) 987.
8 C. P. Smyth and H. E. Rogers, *J. Amer. Chem. Soc.*, 52 (1930) 1824.
9 J. Timmermans, *The Physico-chemical Constants of Binary Systems in Condensed Solutions*, Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1960, p. 152.