

## A Calorimetric Study of the Dimerization of Acetic Acid in 1,2-Dichloroethane

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The equilibrium constant and enthalpy change for the dissociation of the acetic acid dimer in 1,2-dichloroethane have been determined from calorimetric measurements. The values found are  $K = (11.6 \pm 0.6) \times 10^{-2} \text{ (mol l}^{-1}\text{)}^{1/2}$  and  $\Delta H = 16.5 \pm 0.5 \text{ kJ/mol HAc}$ . Monomeric and dimeric forms of acetic acid are the only important species in the concentration region covered, 0.008–0.48 mol l<sup>-1</sup>.

The enthalpy of solution of acetic acid to solvated monomer in 1,2-dichloroethane solution was needed in a study of the donor-acceptor interaction between acetic acid and antimony pentachloride. Solutions of the concentration range that can be used in a calorimetric study with equipment available to us contain both monomeric and dimeric forms. As the monomer-dimer equilibrium in 1,2-dichloroethane seems not to have been studied, we undertook the determination of the equilibrium constant and enthalpy change for the dimer dissociation by solution calorimetry.

### EXPERIMENTAL

*Materials.* Acetic acid (Merck) was dried with Molecular Sieves 4A and distilled at atmospheric pressure on a Nester/Faust Auto Annular Teflon Spinning Band Distillation Column. The purity of the sample was checked by analytical gas chromatography, using a Porapak Q column, and by titration with a strong base, and was judged to be better than 99.8 %. The water content of the sample was checked separately by a gas chromatographic method<sup>1</sup> and found to be less than 0.035 % by volume.

*1,2-Dichloroethane* (Fisher Certified Reagent) was fractionally distilled and kept with Molecular Sieves 4A beads. The purity was checked by analytical GLC, using a dioctylphthalate on Chromosorb P column. The water content of the solvent as determined by gas chromatography was about 8 ppm (by volume). It is judged that the amount of water present in each experiment did not exceed  $5 \times 10^{-5}$  mol.

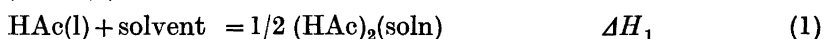
*Apparatus.* The calorimetric measurements were carried out in an LKB 8721 Reaction Solution Calorimeter. The calorimeter is of the constant-temperature-environment type, and a thermistor is used as temperature sensor. Glass reaction vessels of 100 and 25 ml volume were used.

*Calorimetric procedure.* The calorimeter was charged with 1,2-dichloroethane, and after equilibration the reaction was started by breaking the 1 ml sealed glass ampoule containing the acetic acid. The reaction period was less than 3 min. Corrected resistance values ( $R_i$  and  $R_f$ ) were computed by extrapolating the fore and after periods to the time corresponding to 0.63 of the resistance change (Dickinson's extrapolation method). For the electrical calibrations, extrapolations were taken to the time corresponding to 0.50 of the temperature change. The expression  $(R_i - R_f)/(R_i + R_f)$  was used as being proportional to the temperature change.

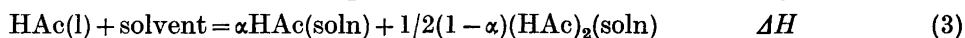
The results of the calorimetric experiments refer to the isothermal process at 25°C and to the true mass.

### RESULTS AND DISCUSSION

The dissolution of acetic acid in 1,2-dichloroethane can be represented by reactions (1) and (2):



The actual calorimetric experiment can then be described by reaction (3):



$$\Delta H = \Delta H_1 + \alpha \Delta H_2 \quad (4)$$

The equilibrium constant for reaction (2) is defined by eqn. (5):

$$K = \left( \frac{2\alpha^2 C}{1 - \alpha} \right)^{1/2} (\text{mol l}^{-1})^{1/2} \quad (5)$$

$C$  denotes the total concentration of acetic acid.

Combination of eqns. (4) and (5) gives the following relation:

$$(\Delta H_2)^2 - \Delta H_2(\Delta H - \Delta H_1) - \frac{2C}{K^2}(\Delta H - \Delta H_1)^2 = 0 \quad (6)$$

Table 1. Results of the calorimetric measurements on dissolution of acetic acid in 1,2-dichloroethane.

$\frac{10^3 n \text{ HAc}}{\text{mol}}$	$V/\text{ml}$	$h/\text{J}$
0.816	100.34	7.81
0.938	100.34	8.68
1.128	100.35	9.68
1.031	25.29	5.55
1.452	26.01	6.91
1.799	25.27	7.72
4.508	27.01	13.19
5.326	27.06	14.44
5.987	27.10	15.38
6.990	27.15	16.71
12.290	27.06	22.20
12.928	26.74	22.67

From a series of calorimetric experiments with varying concentration of acetic acid, the three unknowns,  $\Delta H_1$ ,  $\Delta H_2$ , and  $K$ , can be calculated.

The results of the calorimetric measurements are given in Table 1. The first column gives the amount of acetic acid, and the second the total volume of the solution. The measured enthalpy change,  $h$ , corrected for evaporation of solvent and condensation of acetic acid, when breaking the incompletely filled ampoule, is given in the last column. The error in  $h$  is estimated to be  $\pm 0.05$  J.

For the evaluation, the sum of squares of deviations (7) was minimized

$$U(\Delta H_1, \Delta H_2, K) = \sum_{i=1}^k [Y_i - Y_i(\text{calc.})]^2 \quad (7)$$

with  $Y$  representing either  $\Delta H$ , the apparent molar enthalpy change, or  $h (= n \Delta H)$ .  $k$  is the number of experiments.

With a constant  $\Delta H_1$  value,  $U(\Delta H_2, K)$  was calculated for a network of  $\Delta H_2$  and  $K$  values and  $U_{\min}(\Delta H_2, K)$  located. The calculations were repeated for an array of  $\Delta H_1$  values. The set of values that gave the smallest  $U_{\min}$  was taken to be the best choice of parameter values to be determined. The two different methods of calculating the sum of squares of deviations, (7), which represent different weighting, gave essentially the same result. The following values were found:  $\Delta H_1 = -(0.07 \pm 0.04)$  kJ mol<sup>-1</sup>;  $\Delta H_2 = (16.5 \pm 0.5)$  kJ mol<sup>-1</sup>, and  $K = (11.6 \pm 0.6) \times 10^{-2}$  (mol l<sup>-1</sup>)<sup>1/2</sup>. The error limits were estimated from an analysis of the sum of squares deviations, (7), as a function of the parameter values. The calculations were carried out, using a Univac 1108 computer.

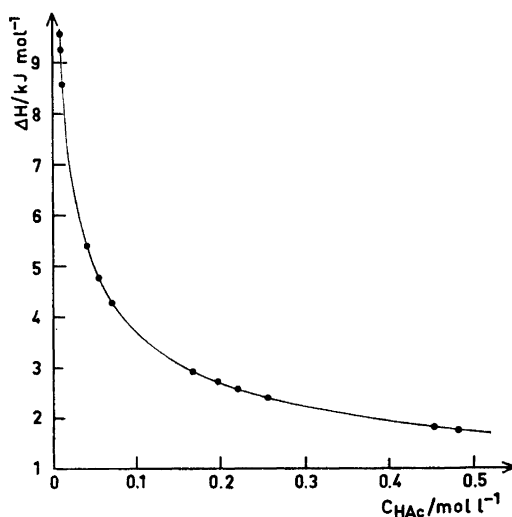


Fig. 1. Apparent molar enthalpy change against concentration of acetic acid. Continuous curve:  $\Delta H = f(c)$  calculated, using parameter values given in text. ●: experimentally determined values.

The continuous curve in Fig. 1 shows  $\Delta H$ , the enthalpy change of reaction (3), as a function of concentration, calculated from the above-mentioned values of  $\Delta H_1$ ,  $\Delta H_2$ , and  $K$ . The points in the figure represent the experimentally determined values. The close agreement between the calculated and experimentally determined  $\Delta H$  values shows that monomeric and dimeric forms of acetic acid are the only important species in 1,2-dichloroethane in the concentration range 0.008 – 0.48 mol l<sup>-1</sup>.

Christian *et al.*<sup>2</sup> have studied the influence of water on the monomer-dimer equilibrium in benzene solutions and have evaluated an equilibrium constant of 26 l mol<sup>-1</sup> (15°C) and 7.1 l mol<sup>-1</sup> (35°C) for the association between water and monomeric acetic acid. We assume the conditions for acetic acid-water interactions in 1,2-dichloroethane solutions to be similar to those in benzene, and judge the small amount of water present in the solvent to be without significant influence in our study.

Some representative values of the equilibrium constant and enthalpy and entropy changes for the acetic acid dimerization in the gas phase and in various solvents are given in Table 2. A review of the thermodynamic properties of

Table 2. Thermodynamic properties for the formation of acetic acid dimer.  $K$  in original units converted to  $K$  in atm<sup>-1</sup>.

State	$T/^\circ\text{C}$	$\log K$	$-\Delta H/\text{kJ mol}(\text{HAc})_2^{-1}$	$-\Delta S/\text{J K}^{-1} \text{mol}(\text{HAc})_2^{-1}$
Gas <sup>a</sup>	27	3.11	65 ± 3	150 ± 8
Heptane <sup>b</sup>	30	3.18		
Carbon tetrachloride <sup>c</sup>	25	2.26	45 ± 5	106 ± 17
<i>o</i> -Dichlorobenzene <sup>d</sup>	28	1.47		
Benzene <sup>d</sup>	28	1.30		
Chloroform <sup>e</sup>	Ambient?	0.69		
1,2-Dichloroethane <sup>f</sup>	25	0.48	33 ± 1	103 ± 3

<sup>a</sup> Ref. 3. <sup>b</sup> Ref. 4. <sup>c</sup> Ref. 5. <sup>d</sup> Ref. 6. <sup>e</sup> Ref. 7. <sup>f</sup> This work.

carboxylic acid dimerization can be found in Ref. 8. The strong influence of different solvents on the acetic acid monomer-dimer equilibrium is clearly revealed in the values of the association constant. There seems to be a corresponding variation of the enthalpy changes, but more reliable  $\Delta H$ -values are needed before any meaningful discussion can be attempted of the influence of various solvents on the thermodynamic properties of acetic acid dimerization. The results found in our study make us believe that high precision solution calorimetric experiments will give valuable contributions to the study of the dimerization of carboxylic acids in organic solvents.

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