A Novel Isothermal Precision Calorimeter For Measuring Enthalpies of Hydrogen Bonded Complex Formation of Hydrogen Fluoride with Proton Acceptor in Dilute Solution

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A new isothermal reaction calorimeter was designed and constructed for direct measurement of the enthalpy of hydrogen bonded complexes of hydrogen fluoride (HF) with proton acceptor in dilute solution. The enthalpy of mixing of chlorobenzene with benzene was measured at 298.15 K and the formation enthalpy (ΔH_c) of hydrogen bonded complex of HF with diethyl ether was also measured in cyclohexane solution at 298.15 K. The performance of the calorimeter was evaluated on the basis of these results and comparisons were made with previously published data. The results obtained with the present calorimeter were internally consistent to ±0.07 J for the system of chlorobenzene and benzene. The reproducibility of ΔH_c of hydrogen bonded complex of HF with diethyl ether was within ±0.08 kJ.

1. INTRODUCTION

One of the unique physico-chemical properties of hydrogen fluoride (HF) is a strong tendency to form hydrogen bonded complexes with various organic molecules.[1,2] Many theoretical studies involving molecular orbital calculations for HF hydrogen bonding systems have been carried out because of simple geometrical and electronic structure.[3] However, reliable values for the formation enthalpies (ΔH_c) of hydrogen bonding complex have been quite limited on account of experimental difficulties.

In previous papers, we have studied the hydrogen bonding complexes of HF with organic compounds having a proton accepting group by the infrared spectral measurements[4,5] and by quantum mechanical calculations.[6] The infrared study could not be applied in some cases (e.g., HF-amine systems), because the absorption peak due to HF-amine complex was very broad and partly overlapped with the absorption of N-H vibrational frequency of amines. Furthermore, no hydro-

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carbons such as cyclohexane or hexane could be used as inert solvents in infrared measurements for the reason of using the cell with a long optical path length (15 mm). Calorimetric methods can eliminate these problems. Moreover, calorimetric methods are superior to spectroscopic methods in obtaining more reliable values of ΔH_c, that is, they permit an evaluation of ΔH_c without recourse of the van't Hoff equation and uncertainties derived from the differentiation of experimental results with respect to temperature.

These situations lead us to attempt the construction of new isothermal reaction calorimeter. This is a very difficult task because all the materials of this calorimeter which have a chance to contact with sample solution must be completely resistant to highly reactive HF. No glass and metals can be used for this purpose and Teflon and other appropriate materials must be exclusively used. We could overcome these difficulties and succeed to construct a new calorimeter for direct measurement of ΔH_c in dilute HF solution. The performance of this calorimeter was examined by measuring enthalpies of mixing for the system of benzene + chlorobenzene and ΔH_c of HF with diethyl ether in dilute cyclohexane solution.

In this paper, our new calorimeter is described somewhat in detail and the results of calibration measurements are presented and discussed.

2. EXPERIMENTAL

2.1 Apparatus

The calorimeter consists of a mixing vessel, a component feeding system and a circuit for detecting electric energy. Details of the mixing vessel are given in Figure 1. In order to use this calorimeter with HF solutions, all parts of the calorimeter are made of Teflon and Kel-F. The lid A and the vessel B are made of Teflon. The inner volume of B is as large as 130 cm³. The mixing vessel is separated into two compartments by an intervening disk-like diaphragm C which is made of Kel-F. The volumes of each compartment can be varied by using diaphragms with different diameter. The volumes of two compartments were determined from the density and weight of cyclohexane with which each of them was filled. The diaphragm is movable vertically so that separated components can be mixed. The circumference edge of the diaphragm and the wall of the upper compartment are tapered to eliminate frictional energy on raising up the diaphragm, and completely lapped to fit with each other.

At the bottom of the mixing vessel, there exist the thermistor F, the cooling-module J, the heater
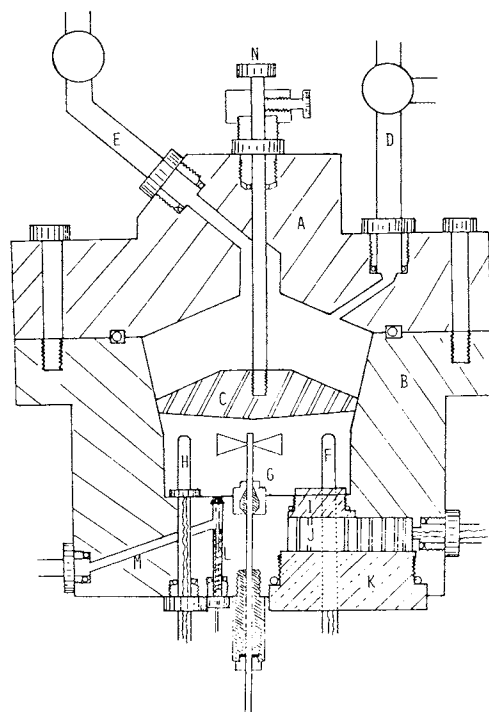

Fig. 1. The mixing vessel of the calorimeter.
(A) Teflon lid; (B) Teflon mixing vessel; (C) Kel-F diaphragm; (D) sample inlet to upper compartment; (E) air bubble outlet; (F) thermistor; (G) stirrer; (H) heater; (I), (K) heat sink; (J) cooling module; (L) spring valve; (M) sample inlet to lower compartment; (N) rod connected to the center of the diaphragm.
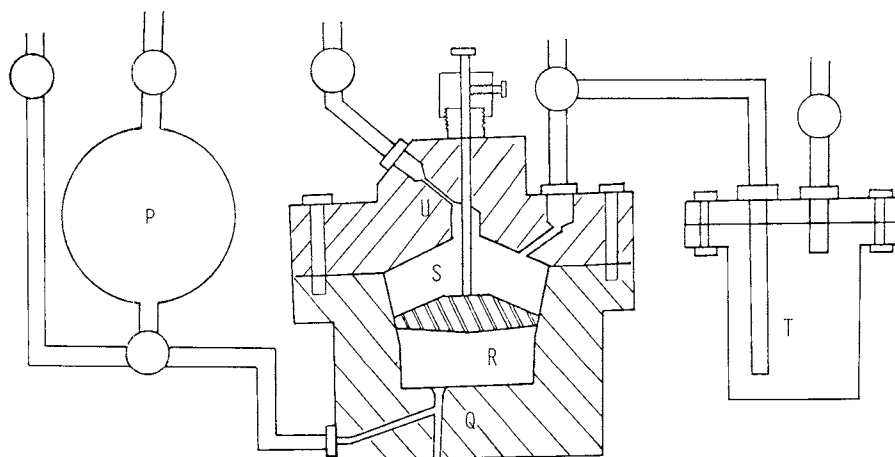

Fig. 2. The block diagram of the calorimeter system.
(P) reservoir of acceptor solution; (Q) mixing vessel; (R) lower compartment; (S) upper compartment; (T) reservoir of donor (HF) solution; (U) air bubble outlet.

H and the stirrer G. They are all covered with a thin Teflon or Kel-F film. The thermistor (Fenwall Elec., GB3298, 2kΩ at 298 K) for detecting temperature change in the vessel is balanced against a Wheatstone bridge and its output signal is amplified by a dc-ac converted amplifier and fed to a recorder. The heater made of manganin wire has resistance of about 25Ω at 298 K. The cooling-module of 16-couple (Sharp Elec., HTM 0516, 5A) is sandwiched between two aluminum heat sinks used as a cooling assembly. Before sandwiching, the surface of the cooling-module was coated with silicone grease to ensure good thermal contact. The stirrer G is made of Kel-F with a Teflon-coated steel shaft. A leak-free seal around the shaft of the stirrer was achieved with two mechanical seals. The upper seal is the same as that described by Featherstone and Dickinson.[7] The shaft is connected to a constant speed motor O with a flexible steel tube. The stirrer is rotated at ca. 300 min^{-1}, which is sufficient for complete mixing. A schematic drawing of the present calorimeter system is given in Figure 2 where P and T are the reservoir of solution containing proton acceptor and proton donor, respectively.

2.2 Operation

The whole calorimetric system is immersed in a large double water thermostat, the temperature of which is controlled within ±0.005 K. Prior to use, the whole system is dried with flowing dehydrated nitrogen gas. First, two liquids to be mixed are charged separately into the reservoir P and T without exposing to atmosphere. One liquid is then introduced into R from P and confined to the lower compartment by pulling down the diaphragm. The excess amount of the sample on the diaphragm is removed through a thin Teflon tube and the upper compartment is dried again with flowing nitrogen gas. Then another liquid is introduced into S from T and small bubbles remained in S can be excluded through the air bubble outlet U. Thus the sample liquids are charged in the mixing vessel without any vapor space.

As the thermistor is equipped at the bottom of the mixing vessel, it is impossible to check directly the attainment of thermal equilibrium of the sample liquid in the upper compartment at the set temperature. In order to examine how long it takes the liquid in the upper compartment to reach thermal equilibrium, blank runs were made, that is, cyclohexane in both compartments was mixed. These runs showed that it is necessary to wait two hours to reach thermal equilibrium. After the attainment of thermal equilibrium, the base line is determined on the recorder which displays the imbalance of the Wheatstone bridge at the set temperature and then the stirrer is activated. The stirring energy could be completely compensated by Peltier cooling and the current level of the cooling-module was as large as 50 mA.

The mixing of two components can be done simply by pulling up the rod connected to the diaphragm. At the same time, a quantity of solution, which is equal to the volume of the rod in the upper compartment, is supplied to the lower compartment from the reservoir. This eliminates the necessity of correcting for changes in the volume of the mixing vessel due to the raise of the diaphragm. During a run, the temperature deviation from the set value is compensated by Joule heating and Peltier cooling and the electrical energy needed to compensate is determined in the same manner as described previously.[8]

As the present calorimeter is of batch type, a mixing is instantaneously completed with only one operation. This brings about more difficulty to maintain isothermal condition during a run, as compared with the measurement by dilution calorimeter. In order to minimize the deviation from the isothermal condition in an exothermic run, the temperature in the vessel is suitably lowered before the run.

2.3 Materials and Determination of HF Concentration

In the calorimetric studies of hydrogen bonding systems containing HF, use of completely dehydrated samples becomes necessary. The method of purification of HF and cyclohexane used as an inert solvent was the same as that described in previous studies.[4,5] Other materials used in this study were spectrograde or guaranteed reagent of Nakarai Chemicals Co. They were fractionally distilled with a column of about 30 theoretical plates, and their purity was checked by gas chromatography.

The concentration of HF in sample solution was

determined after mixing in the following manner. The sample solution in the outlet and inlet tubes which did not take part in the mixing was removed by a thin Teflon feeding tube and this space was dried with nitrogen gas. The diaphragm was pulled down again. Then about $10\ cm^3$ of the sample solution, the HF concentration of which is to be determined, was transferred from the mixing vessel to a $100\ cm^3$ polyethylene flask containing $80\ cm^3$ of water through a thin Teflon feeding tube by the pressure of nitrogen gas. After shaking the flask for an adequate time, the HF dissolved in cyclohexane solution was extracted into water. The concentration of HF in dilute aqueous solution was then determined by photomeric method with La-alizarin complexone.

2.4 Calculation of ΔH_c

The enthalpy change due to complex formation ΔH is given by

$$\Delta H = Q_{obs} - Q_{dil}(HF) - Q_{dil}(ether) \qquad (1)$$

where Q_{obs}, $Q_{dil}(HF)$ and $Q_{dil}(ether)$ are observed heat, heat of dilution of HF and heat of dilution of diethyl ether, respectively. Since $Q_{dil}(HF)$ and $Q_{dil}(ether)$ were negligibly small in the concentration range used in the present measurements, ΔH becomes equal to Q_{obs}. Then the molar enthalpy of hydrogen bond formation ΔH_c is given by

$$\Delta H_c = (Q_{obs}/C_t)(1/V) \qquad (2)$$

where C_t is total concentration in M of HF and

V is the volume in liter of calorimeter.

In eq. (2), it was assumed that (1) HF exists as a monomer before mixing, that (2) only 1:1 complex is formed in mixture, and that (3) there exists no free monomer HF in solution after mixing. The validity of the first assumption may be confirmed by the experimental evidence that, in the HF concentration range used, no self-association band of HF was observed on the infrared spectra in carbon tetrachloride solution. Thus $Q_{dil}(HF)$ is surely negligibly small. As for the second assumption, the formation of complexes other than 1:1 complex between HF monomer and acceptor is not conceivable under the condition that the amount of acceptor is about thirty times as much as that of HF. In the present measurement, total concentration of diethyl ether was constant at $6.470 \times 10^{-2}\ M$ and that of HF was $2-3 \times 10^{-3}\ M$. Possible error in ΔH_c arised from the third assumption will be discussed in later section.

3. RESULTS AND DISCUSSION

3.1 Excess Enthalpy of Chlorobenzene with Benzene

The performance of the calorimeter was examined by measuring excess enthalpies for the system of chlorobenzene(1) + benzene(2) at 298.15 K. Examples of the measurements at x_1 = 0.3445 are shown in Table 1. The values of heat evolved in four runs agrees well with each other within ±0.07 J. The agreement with the data reported recently by Tanaka and Benson[9] is also

Table 1.　Enthalpy of Mixing of Chlorobenzene + Benzene Solution at 298.15 K.

Molar composition of solution			
C_6H_5Cl (1)	C_6H_6 (2)		x_1
0.4854 mol	0.9235 mol		0.3445
Heat evolved		$-\Delta H$/J mol^{-1}	
Present work	Run 1	5.31	$(+1.5\%)^a$
	Run 2	5.40	$(+3.0\%)^a$
	Run 3	5.28	$(+0.8\%)^a$
	Run 4	5.21	$(-0.5\%)^a$
	Average	5.30 ± 0.07	$(+1.2\%)^a$
Literature value^b		5.23 ± 0.03	

a) Percentage deviation from the value calculated from the data given in reference 9.　b) Reference 9.

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complex formation of HF with diethyl ether has been given by

$$K_1 = \frac{C_t - C'}{C'(B_t - C_t + C')} \qquad (3)$$

where B_t is the total concentration of the acceptor and C' is the apparent concentration of HF monomer in inert solvent. In the case of CCl_4 as solvent, however, another equilibrium exists for the specific interaction between HF and CCl_4.

$$K_2 = C_c/C_f \qquad (4)$$

where C_c is the concentration of HF which is forming a weak bonded complex with the solvent CCl_4 and C_f is the concentration of truly free HF. Accordingly C' is given by

$$C' = C_c + C_f . \qquad (5)$$

Neglecting physical interaction between HF and solvent, the true equilibrium constant may be expressed by

$$\begin{aligned} K_3 &= \frac{C_t - C_c - C_f}{C_f(B_t - C_t + C_c + C_f)} \\ &= \frac{C_t - C'}{C_f(B_t - C_t + C')} \\ &= K_1(C'/C_f) = K_1(K_2 + 1). \end{aligned} \qquad (6)$$

Whichever solvent may be used, K_3 is considered to be a constant.

Since no specific interaction except for non-specific and physical one exists between HF and cyclohexane, K_3 may be regarded as the equilibrium constant in cyclohexane solution. Though very difficult to evaluate, K_2 should be always positive and hence K_3 will be larger than K_1, which was estimated to be 928 M^{-1}.[5] One may use tentatively this value for K_3 as the lower limiting value. Since B_t and C_t in the present case are 6.470×10^{-2} M and 3.33×10^{-3} M, respectively, free monomer HF concentration can be estimated to be 5.69×10^{-5} M. Then systematic error in ΔH_c caused by employing C_t instead of $C_t - C_c - C_f$ is estimated to be -1.7%. Since K_3 is actually larger than 928 M^{-1} and C_f is smaller than the value estimated the above, it will become still smaller. This can be further supported by the linear relation between Q_{obs} and C_t shown in Figure 3.
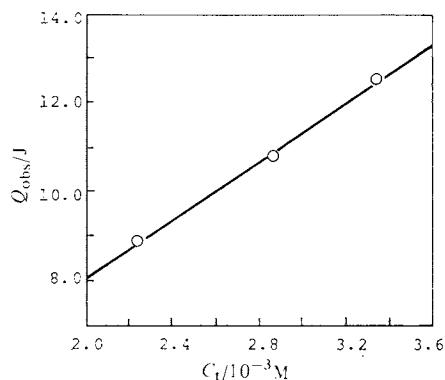

Fig. 3. Plots of the observed heat evolved, Q_{obs}, against total HF concentration, C_t.

In conclusion, we could construct a new calorimeter which is capable of measuring mixing enthalpies for highly reactive samples. The present calorimeter and its operation established are sufficiently well applicable for determining ΔH_c for HF hydrogen bonding complex.

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