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Calorimetric Determination of Thermodynamic Parameters for the Dissociations of Acids in Dipolar Aprotic Solvents

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A calorimetric method has been investigated for the determination of the thermodynamic parameters of acid dissociations in dipolar aprotic solvents. For the dissociations of monoprotonated bases BH^+ (B: aniline, pyridine, triethylamine, tributylamine, triethanolamine, 1,3-diphenylguanidine and 1,1,3,3-tetramethylguanidine) in *N,N*-dimethylformamide, dimethyl sulfoxide (DMSO), acetonitrile and propylene carbonate, the solutions of the bases were titrated with small volumes of a "strong acid," trifluoromethanesulfonic acid. In each solvent, there was an approximately linear relation of unit slope between ΔH°_{298} and ΔG°_{298}, showing that the difference in pK_a between different BH^+'s can mainly be attributed to the difference in the enthalpy term. As for the solvent effect on pK_a, however, the entropy term seems to play an important role. A preliminary study has shown that the calorimetric method is also applicable to the dissociations of HX-type weak acids (benzoic and salicylic acids in DMSO, for example), if the dissociation equilibria are not complicated by such reactions as homoconjugation.

Acid-base equilibria in dipolar aprotic solvents have been extensively studied, and fairly abundant data for acid-dissociation constants are available.[1] But the data concerning the thermodynamic parameters of acid dissociations are quite limited, and, in most cases, have been obtained from the effect of temperature on the dissociation constants. To our knowledge, no thermodynamic parameters of acid dissociation in dipolar aprotic solvents have been obtained calorimetrically.

In the present study, we used a calorimetric method to obtain thermodynamic parameters for acid dissociations in dipolar aprotic solvents. The main dissociations investigated were for monoprotonated bases BH^+ (Eq. (1)):

$$BH^+_{solv} \longrightarrow B_{solv} + H^+_{solv}. \quad (1)$$

The reactions which occur when a large amount (100 ml) of a base (B) solution is titrated with small amounts (10—60 μl to keep the heat of dilution negligibly small) of a strong acid (HA) can be considered to consist of the following three steps:

$$HA \longrightarrow (HA)_{solv}, \quad (2)$$

$$(HA)_{solv} \longrightarrow H^+_{solv} + A^-_{solv}, \quad (3)$$

$$H^+_{solv} + B_{solv} \longrightarrow BH^+_{solv}. \quad (4)$$

If we express the heat generated by reactions (2) and (3) by ΔH_1 (kJ mol^{-1}) and that by reactions (2), (3) and (4) by ΔH_T, the heat generated by reaction (4) is equal to $(\Delta H_T - \Delta H_1)$. Thus, the standard enthalpy ΔH°_{298} for the reaction (1) should also be equal to $(\Delta H_T - \Delta H_1)$. Here, ΔH_1 can be obtained by titrating the pure solvent with the "strong acid" HA. In the present study, we used trifluoromethanesulfonic acid as HA. It is one of the strongest acids and a pure, water-free product can be obtained easily. In *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide(DMSO), it actually behaved as a strong acid and reliable values of ΔH_1 could be obtained. In acetonitrile(AN) and propylene carbonate (PC), however, the dissociation of the acid was not complete and only approximate ΔH_1-values could be obtained as will be described later. We also have studied preliminarily on the determination of thermodynamic parameters for the dissociations of HX-type weak acids.

Experimental

Apparatus and Reagents. A multi-purpose calorimeter, model MPC-11, of the Tokyo Riko Co. was used for calorimetric measurements. The cell assembly is shown in Fig. 1. Trifluoromethanesulfonic acid was added with a Gilmont ultra precision 250 μl-microburet S3100A (0.01 μl/div).

DMF, DMSO, and AN were the reagent grade products of Wako Chemicals Co., and PC was a synthetic grade Merck product. They were purified by the methods recommended in Ref. 2). Trifluoromethanesulfonic acid (Wako reagent grade) was purified by a distillation with a semimicro distilling apparatus. All the amines tested were Wako analytical grades. Tributylamine and triethanolamine were distilled under reduced pressures, and other amines were purified by the

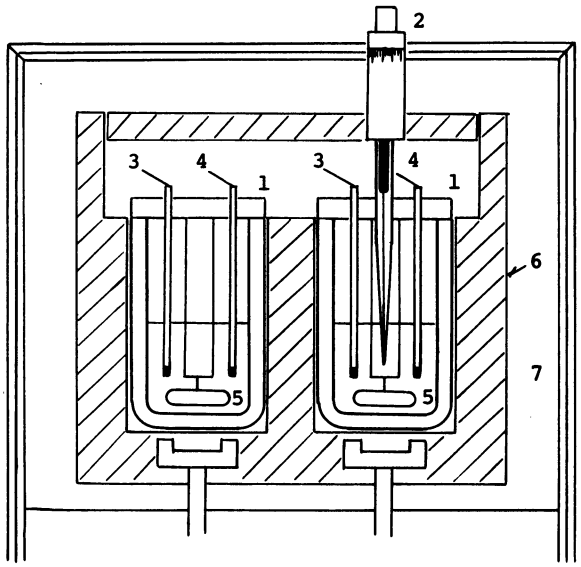

Fig. 1. Cell assembly for calorimetric measurements. 1: Dual cells, 2: microburet, 3: thermistor, 4: heater for calibration, 5: magnetic stirrer, 6: aluminum thermostat bath and 7, air thermostat bath.

methods described in a previous report.[3] Benzoic and salicylic acids (Wako reagent grades) were used as received.

Procedure for Monoprotonated Bases. To the cell was added 100 ml of the solution containing an appropriate amount of the base to be tested (in the case of ΔH_T measurement) or 100 ml of the pure solvent (in the case of ΔH_1 measurement). The cell and the microburet containing trifluoromethanesulfonic acid were set to the calorimeter as shown in Fig. 1 and kept for 2—3 h until they reached a uniform temperature of 25 °C (298 K). The amounts of the bases taken were 100 μl (0.0124 M, 1M=1 mol dm^{-3}) for pyridine, 100 μl (0.0109 M) for aniline, 200 μl (0.0143 M) for triethylamine, 250 μl (0.0105 M) for tributylamine, 200 μl (0.0150 M) for triethanolamine, 150 μl (0.0117 M) for 1,1,3,3-tetramethylguanidine and 211 mg (0.0100 M) for 1,3-diphenylguanidine. The solution in the cell was titrated with six aliquots of the acid, 10.0 μl (1.13×10^{-3} M) each, and, from the temperature changes, the heats corresponding to ΔH_1 and ΔH_T were obtained. The factor to convert temperature change to heat was determined for each solution with an accuracy of ±0.2% by using a built-in heater (accuracy: ±0.1%). During the titrations, the solutions were stirred with a magnetic stirrer at 280 rpm.

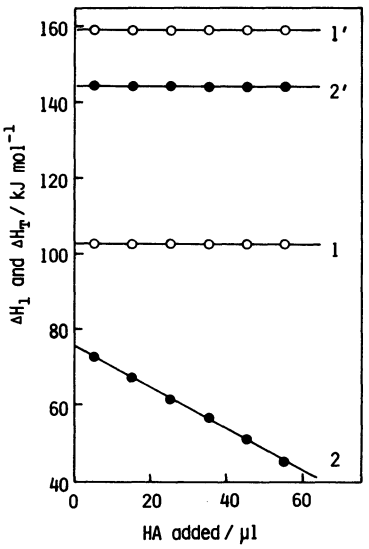

Fig. 2. ΔH_1 and ΔH_T (B=triethanolamine) *vs.* the volume of trifluoromethanesulfonic acid added. Lines 1 and 1′ in DMSO and 2 and 2′ in AN.

Results and Discussion

Thermodynamic Parameters for the Dissociations of Monoprotonated Bases. Measurements of ΔH_1: As described above, trifluoromethanesulfonic acid was added to 100 ml of the pure solvent six times in an aliquot of 10.0 μl (1.13×10^{-3} M) each. For DMF and DMSO, the heat generated each time was almost constant as line 1 in Fig. 2. ΔH_1, obtained from the average of these values, was 112.3±0.3$_2$ kJ mol^{-1} for DMF (n=4, where n is the number of similar measurements) and 102.9±0.3$_1$ kJ mol^{-1} for DMSO (n=6). In PC and AN, the determination of ΔH_1 encountered difficulties due to the incomplete dissociation of the acid. The heat generated by the addition of the acid decreased gradually with the increase of the acid concentration (line 2, Fig. 2). Because the decrease was approximately linear against the amounts of the acid added, we assumed that the value obtained by an extrapolation to zero concentration nearly corresponded to ΔH_1. It was 85.$_4$± 0.9 kJ mol^{-1} for PC (n=5) and 75.$_9$±0.6 kJ mol^{-1} for AN (n=6).

Measurements of ΔH_T: Trifluoromethanesulfonic acid was added to the solution of the base to be tested. The heat generated by each addition of the acid was almost constant (lines 1′ and 2′, Fig. 2) and ΔH_T was obtained as the average of the values. In Table 1 the results of ΔH_T are summarized. Most of the ΔH°_{298} values were obtained by the relation $\Delta H^\circ_{298}=(\Delta H_T-\Delta H_1)$. In DMF and DMSO, however, pK_a for aniline and pyridine were not large enough for the reaction (4) to be quantitative. In those cases, ΔH°_{298} were obtained from $(\Delta H_T-\Delta H_1)$ by correcting for the incompleteness of the reaction.

Thermodynamic Parameters: Thermodynamic parameters for the dissociations of monoprotonated bases are shown in Table 2. The values of ΔG°_{298} were calculated by the relation $\Delta G^\circ_{298}=-RT\ln K_a$. For most of the p$K_a$ we referred to the literature values[3-9], but we determined some of them in this work from the half-neutralization points of the potentiometric titra-

Table 1. Heats (ΔH_T) generated by reactions (2), (3), and (4) at 298 K

Bases	ΔH_T/kJ mol^{-1}			
	DMSO	DMF	PC	AN
Pyridine	129.0±0.9$_1$ (5)	134.6±0.2$_4$ (4)	118.3±0.4$_7$ (5)	120.0±0.2$_9$ (4)
Aniline	134.1±0.7$_5$ (5)	136.9±0.3$_6$ (4)	112.8±0.1$_8$ (4)	114.1±0.1$_8$ (4)
Triethanolamine	159.2±0.2$_9$ (4)	162.1±0.4$_0$ (4)	146.6±0.1$_8$ (4)	144.4±0.3$_8$ (4)
Tributylamine	165.5±0.1$_7$ (5)	167.0±0.4$_9$ (4)	154.4±0.6$_7$ (5)	154.8±0.4$_1$ (4)
1,3-Diphenylguanidine	161.3±0.6$_9$ (5)	166.9±0.1$_3$ (4)	142.5±0.3$_1$ (4)	146.5±0.2$_5$ (4)
Triethylamine	166.6±0.1$_9$ (6)	170.9±0.3$_4$ (4)	155.7±0.4$_6$ (6)	154.8±0.2$_3$ (5)
1,1,3,3-Tetramethylguanidine	190.7±0.3$_7$ (4)	—	—	—

The figures in parentheses show the number of measurements.

TABLE 2. THERMODYNAMIC PARAMETERS FOR THE DISSOCIATIONS OF MONOPROTONATED BASES IN DMSO, DMF, PC, AND AN (298 K)

Bases	$pK_a(BH^+)$	$\Delta G°_{298}$	$\Delta H°_{298}$	$-T\Delta S°_{298}$
		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
		Dimethyl sulfoxide		
Pyridine	3.5[a](3.4[b])	20.0	26.9	−6.9
Aniline	3.7[a](3.6[b])	21.1	31.9	−10.8
Triethanolamine	7.4$_8$[c]	42.7	56.3	−13.6
Tributylamine	8.3[a]	47.4	62.6	−15.2
1,3-Diphenylguanidine	8.6[a]	49.1	58.4	−9.3
Triethylamine	9.0[b]	51.3	63.7	−12.4
1,1,3,3-Tetramethylguanidine	13.2[b]	75.3	87.8	−12.5
		N,N-Dimethylformamide		
Pyridine	3.3[d]	18.8	23.3	−4.5
Aniline	3.6$_6$[e] (4.3$_6$[f])	20.9	25.2	−4.3
Triethanolamine	7.5$_5$[d]	43.1	49.8	−6.7
Tributylamine	8.5$_7$[c]	48.9	54.7	−5.8
1,3-Diphenylguanidine	9.1[f](8.9[d])	51.9	54.6	−2.7
Triethylamine	9.2$_5$[d,f]	52.8	58.6	−5.8
		Propylene carbonate		
Aniline	10.0$_9$[g]	57.6	(27.4)	(30.2)
Pyridine	11.9$_2$[g]	68.0	(32.9)	(35.1)
Triethanolamine	15.8$_7$[c]	90.5	(61.2)	(29.3)
1,3-Diphenylguanidine	16.9$_8$[g]	96.9	(57.1)	(39.8)
Tributylamine	17.5$_2$[c]	99.9	(69.0)	(30.9)
Triethylamine	17.9$_4$[g]	102.3	(70.3)	(32.0)
		Acetonitrile		
Aniline	10.5$_6$[h]	60.2	(38.2)	(22.0)
Pyridine	12.3$_3$[h]	70.3	(44.1)	(26.2)
Triethanolamine	15.9$_3$[c]	90.9	(68.5)	(22.4)
1,3-Diphenylguanidine	17.9$_0$[h]	102.1	(70.6)	(31.5)
Tributylamine	18.0$_9$[h]	103.2	(78.9)	(24.3)
Triethylamine	18.4$_6$[h]	105.3	(78.9)	(26.4)

a) Ref. 4. b) Ref. 5. c) This work. d) Ref. 6. e) Ref. 7. f) Ref. 8. g) Ref. 3. h) Ref. 9. In the calculation of $\Delta G°_{298}$, the pK_a value without parentheses was used. The values of $\Delta H°_{298}$ and $-T\Delta S°_{298}$ in parentheses are somewhat approximate due to the reasons as described in text.

tions of the bases with trifluoromethanesulfonic acid (use of a glass pH-electrode). The pK_a of pyridine/pyridinium ion system was used as the reference.

In Figs. 3 and 4, the values of $\Delta H°_{298}$ and $-T\Delta S°_{298}$ were plotted against $\Delta G°_{298}$. For each solvent, there is an approximately linear relation of unit slope between $\Delta H°_{298}$ and $\Delta G°_{298}$ (though fairly big deviations are observed for 1,3-diphenylguanidine in PC and AN). Thus, for each solvent, the difference in pK_a values between different monoprotonated bases may mainly be attributed to the difference in the enthalpy term. As for the changes in pK_a with solvents (solvent effect on pK_a), however, the results in the figures show that the entropy term also takes a considerable part, though the reason for this has not been elucidated yet.

Thermodynamic Parameters for the Dissociation of Weak Acid HX. In dipolar aprotic solvents, the dissociation equilibria of weak acids of the type HX often become complicated due to such reactions as dimerization and homoconjugation. In the absence of such complicating reactions and when the acid HX is weak enough, the thermodynamic parameters for the dissociation (Eq. (5)) can be obtained by either of the following methods:

$$(HX)_{solv} \longrightarrow H^+_{solv} + X^-_{solv}. \quad (5)$$

i) The solution of R_4NX (tetraalkylammonium salt of X^-) is titrated by a strong acid HA. The thermodynamic parameters should be obtained by the same principle as in the above.

ii) The solution of the weak acid HX is titrated with an appropriate base B. Then, the reactions which occur can be expressed by:

$$B \longrightarrow B_{solv}, \quad (6)$$

$$(HX)_{solv} \longrightarrow H^+_{solv} + X^-_{solv}, \quad (7)$$

$$H^+_{solv} + B_{solv} \longrightarrow BH^+_{solv}. \quad (8)$$

The enthalpy for reaction (8) is known from the above work and that for reaction (6) can easily be determined. Thus, the enthalpy for reaction (7) should be obtained.

iii) The solution of a base B is titrated with the weak acid HX. The reactions which occur can be expressed by $HX \rightarrow (HX)_{solv}$ and Eqs. (7) and (8). Because

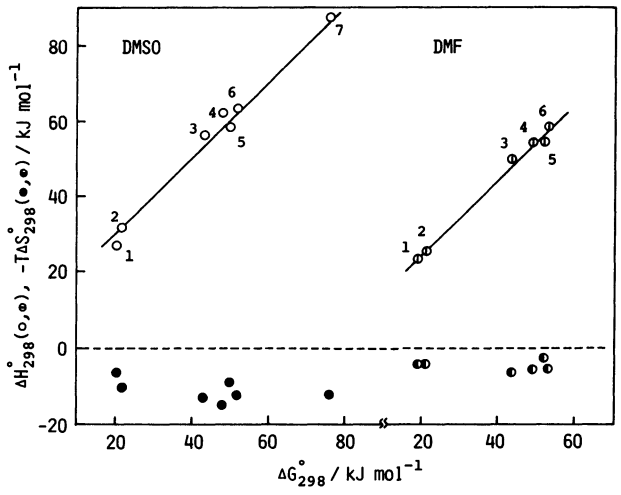

Fig. 3. Relations of ΔH°_{298} and $-T\Delta S^\circ_{298}$ *vs.* ΔG°_{298} in DMSO and DMF.
B: 1 pyridine, 2 aniline, 3 triethanolamine, 4 tributylamine, 5 1,3-diphenylguanidine, 6 triethylamine, and 7 1,1,3,3-tetramethylguanidine.

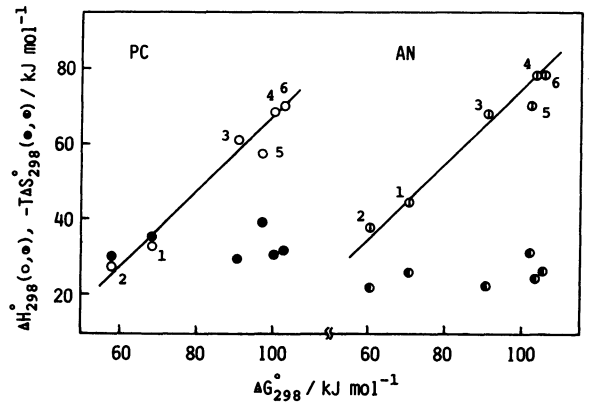

Fig. 4. Relations of ΔH°_{298} and $-T\Delta S^\circ_{298}$ *vs.* ΔG°_{298} in PC and AN (see the caption of Fig. 3).

the enthalpy for reaction (8) is known, that for reaction (7) can be obtained, if the enthalpy for HX→ $(HX)_{solv}$ is obtained separately.

In the present study, method ii) was employed for salicylic and benzoic acids in DMSO. For salicylic acid (pK_a=6.6, ΔG°_{298}=37.7 kJ mol^{-1} [10]), its solution in the cell was titrated with triethylamine ($pK_a(BH^+)$=9.0) and also with tetramethylguanidine (pK_a (BH^+)=13.2[5]). The titration with triethylamine gave ΔH°_{298} of 19.9 kJ mol^{-1} and that with tetramethylguanidine 20.3 kJ mol^{-1}.[11] The average of the two values, 20.1 kJ mol^{-1}, is somewhat larger (but probably more reliable) than 17.1 kJ mol^{-1} which we calculated using literature data of the changes of pK_a with temperature.[10] For benzoic acid (pK_a=10.6, ΔG°_{298}=60.5 kJ mol^{-1} [10]), the titration with tetramethylguanidine gave ΔH°_{298} of 35.6 kJ mol^{-1}[12] which is in good agreement with 35 kJ mol^{-1} obtained from the temperature effect on pK_a.[10]

In the above examples for HX-type weak acids, fair agreements were obtained between calorimetric results and the results from the temperature effect on pK_a. Usually, however, it is rather difficult in dipolar aprotic solvents to determine with enough precisions the temperature effect on pK_a. The calorimetric method as employed in the present work seems to be easier and give more reliable results for dissociations of both BH^+- and HX-type weak acids, if there is a "strong acid" which completely dissociates in the relevant solvents.

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11) ΔH° for reactions (6), (7), and (8) was $-34.1\pm0.2_5$ kJ mol^{-1} (n=3) with triethylamine and $-65.8\pm0.2_0$ kJ mol^{-1} (n=3) with tetramethylguanidine, while ΔH° for reaction (6) was 9.7 kJ mol^{-1} for triethylamine and 1.7 kJ mol^{-1} for tetramethylguanidine.

12) ΔH° of $-50.5\pm0.1_7$ kJ mol^{-1} (n=4) was obtained for reactions (6), (7), and (8) by extrapolation to the tetramethylguanidine concentration of zero.