9,12 positions.[13,14] These results all indicate that the course of these reactions is determined by the charge distribution of the molecule.

[13] H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

[14] J. A. Potenza and W. N. Lipscomb, *ibid.*, **5**, 1471 (1966).

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Thermodynamic Properties for the Dissociation of Bisulfate Ion and the Partial Molal Heat Capacities of Bisulfuric Acid and Sodium Bisulfate over an Extended Temperature Range[1,2]

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Heat of solution measurements of sodium sulfate in water and dilute aqueous hydrochloric acid solutions were made at several temperatures between 0 and 100° to obtain the thermodynamic properties of the aqueous bisulfate ion. From the temperature dependence of these heats the standard partial molal heat capacities for bisulfuric acid ($H \cdot HSO_4$) and sodium bisulfate were determined. Values of -4142 ± 69 cal mol^{-1} and -22.90 ± 0.20 cal mol^{-1} deg^{-1} were obtained for $\Delta H°$ and $\Delta S°$, respectively, at 25° for the dissociation of the aqueous bisulfate ion. New values of the dissociation constant, K^0, of the bisulfate ion were evaluated from 0 to 150° from the calorimetric data. Previous values of K^0 obtained from equilibrium measurements over this temperature range were analyzed by the third-law method and shown to be in satisfactory agreement with the thermal measurements.

Introduction

The integral heat method of obtaining partial molal heat capacities of pure substances has been described in some preceding papers of this series.[4-7] As used previously, the standard heats of solution of some salt are determined at convenient temperature intervals over a range of temperatures. The temperature dependence of the standard heat of solution can then be calculated as can, ultimately, the partial molal heat capacity of the ions which are formed on dissolution. In this communication we describe the extension of this method to obtain accurate thermal data on a species, the bisulfate ion, which cannot be formed in the pure state, but only in equilibrium amounts and in the presence of other ions. In principle, measurements on HSO_4^-(aq) can be obtained either from dissolving sulfuric acid in water or from dissolving a soluble sulfate salt in dilute solutions of a strong acid. The heat obtained is then due to the sum of the heat of solution and the heat of the association or dissociation of HSO_4^-. A number of considerations led to the choice of allowing sodium sulfate to react with dilute hydrochloric acid solutions, not the least of which was the smaller heat of solution of sodium sulfate compared to sulfuric acid or one of its hydrates. Consequently more of the observed heat is due to the bisulfate ion and not to the solution process.

One hundred and sixty-eight separate heats of solution of solid sodium sulfate have been made in water and dilute solutions of hydrochloric acid at various ionic strengths between 4.34 and 95.00°. From these data and the accepted value of the dissociation constant of HSO_4^-(aq) at 25° it was possible to determine the thermodynamic properties for the dissociation process over an extended interval of temperature. From the temperature dependence of $\Delta H°$ of dissociation and the previously reported[8] heat capacities of Na_2SO_4(aq) and H_2SO_4(aq), the standard partial molal heat capacities of $NaHSO_4$(aq) and $H \cdot HSO_4$(aq) have been obtained. Finally, it has been possible to reexamine the previously obtained thermodynamic functions for the dissociation of HSO_4^-(aq) from extensive equilibrium measurements[9-11] and check their consistency with the thermal data.

Experimental Section

Apparatus.—The submarine-type heat of solution calorimeter (CS-2) which was used to make these measurements has been previously described.[7] The calorie was taken as 4.1840 abs J.

Materials.—The sodium sulfate used to make these calorimetric measurements was prepared from Baker Analyzed reagent grade sodium sulfate in the anhydrous form. The salt was dissolved in

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[1] This communication constitutes paper XII of a series of communications from these laboratories on the thermodynamic properties of high-temperature aqueous solutions.

[2] Supported in part by a grant from the National Science Foundation.

[3] From the Ph.D. thesis of J. M. R., Purdue University, Jan 1969.

[4] C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **83**, 3223 (1961).

[5] J. C. Ahluwahlia and J. W. Cobble, *ibid.*, **86**, 5377 (1964).

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[8] W. L. Gardner, E. C. Jekel, and J. W. Cobble, *J. Phys. Chem.*, **73**, 2017 (1969).

[9] T. F. Young, C. R. Singleterry, and I. M. Klotz (theses of Singleterry and Klotz), University of Chicago, 1940; quoted by R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. Ltd., London, 1959, p 385.

[10] M. H. Lietzke, R. W. Stoughton, and T. F. Young, *J. Phys. Chem.*, **65**, 2247 (1961).

[11] W. L. Marshall and E. V. Jones, *ibid.*, **70**, 4028 (1966).

distilled water which had been passed through an ion-exchange column and was filtered through a medium-porosity filter. The stirred solution was then cooled in an ice bath, the recrystallized salt was filtered and washed, and the process was repeated three times, retaining about half of the salt each time. After drying in a vacuum oven at 85° for 1 day, it was ground finely in a mullite mortar, dried again in a muffle furnace at 150° for another day, and stored in a vacuum oven at 120°. In order to check the consistency of heats of solution made on separately prepared samples of sodium sulfate, two purified sets of samples were made up from different lots of the commercial salt. Two series of measurements, which will be referred to as series I and II, were made at 34.96° on the heats of solution of these materials in water. The data indicated that they were calorimetrically equivalent within experimental error.

Hydrochloric acid solutions were prepared from the Baker Analyzed reagent, which contained 36–37% HCl by weight. A stock solution was prepared by first diluting the concentrated acid to about 0.8 *M* and then accurately determining the concentration by a pH titration, using the standard base THAM. The concentrations of the final hydrochloric acid solutions were prepared by diluting a known volume of the stock solution in a volumetric flask.

Procedure.—The heats of solution measurements made by dissolving sodium sulfate in dilute hydrochloric acid solutions were endothermic at all temperatures. The heats of solution of sodium sulfate in water, however, were exothermic at temperatures >18°. The procedures used to carry out these two types of heat of solution measurements were the same as those used by previous workers in these laboratories.[4,5]

Thermal Data for the Dissociation of the Bisulfate Ion

Thermodynamic properties for the dissociation of bisulfate were obtained from measurements made on two separate series of heats of solution. The first measurements involved the reaction

$$\mathrm{Na_2SO_4(c)} \xrightarrow{\mathrm{aq}} \mathrm{2Na^+(aq) + SO_4{}^{2-}(aq)} \qquad (1)$$

A series of measurements at various concentrations was made on this reaction at each selected temperature and the heat of solution of sodium sulfate was obtained as a function of concentration. The values of ΔH_s obtained were extrapolated to infinite dilution in the usual manner employed in these laboratories[4] by adding a Debye–Hückel term to each ΔH_s value. The quantity obtained, ρ, is given by the equation

$$\rho = \Delta H_s - (\nu/2)|Z_+Z_-|A_{\mathrm{H}}I^{1/2}\alpha = \Delta H_s{}^\circ - 2.303RT^2\frac{\mathrm{d}B}{\mathrm{d}T}\nu_+\nu_-I \qquad (2)$$

where ν is the number of ions formed from each molecule of salt, Z is the ionic charge, I is the ionic strength, A_{H} is the Debye–Hückel limiting slope, $\mathrm{d}B/\mathrm{d}T$ is a constant,[12] and α is expressed in terms of the equation

$$\alpha = (1 + I^{1/2})^{-1} - I^{-3/2}[1 + I^{1/2} - (1 + I^{1/2})^{-1} - 2\ln(1 + I^{1/2})] \qquad (3)$$

A linear extrapolation of ρ *vs.* ionic strength was made to zero concentration using the method of least squares. At infinite dilution, the last term in eq 2 becomes zero and the intercept becomes $\Delta H_s{}^\circ$, the standard heat of solution. The thermal data on this reaction are summarized in an empirical form in Table I.

TABLE I

SUMMARY OF HEATS OF SOLUTION OF SODIUM SULFATE

$$\rho^a = \Delta H_s{}^\circ + (\mathrm{d}\rho/\mathrm{d}I)I$$

Temp, °C	$\Delta H_s{}^\circ$, cal/mol	$10^3\mathrm{d}\rho/\mathrm{d}I$
4.53[b]	1412 ± 19	−1.6 ± 0.2 (10)[c]
15.00	302 ± 13	−1.9 ± 0.2 (8)
24.99	−567 ± 12	−1.0 ± 0.2 (9)
34.96 (I)[d]	−1311 ± 29	0.1 ± 0.2 (14)
34.96 (II)[d]	−1305 ± 15	−0.1 ± 0.2 (11)
60.03	−2896 ± 14	0.6 ± 0.2 (7)
85.17[b]	−4387 ± 20	−0.1 ± 0.2 (9)
95.00[b]	−5054 ± 30	0.4 ± 0.2 (9)

[a] This equation is for ionic strength ≤0.05. [b] Data at these temperatures are from ref 8. [c] Parenthetical values refer to the number of different heats of solution obtained at each temperature. [d] Series I and II refer to different samples of $\mathrm{Na_2SO_4}$ used at the same temperature. The heat data were treated separately for the two samples in all calculations even though $\Delta H_s{}^\circ$ and $(\mathrm{d}\rho/\mathrm{d}I)$ agree within experimental error.

The second series of heat of solution measurements were carried out by dissolving sodium sulfate in dilute hydrochloric acid solutions at 4.34, 15.00, 24.99, 34.96, 60.03, 85.62, and 95.00°. The solution of sodium sulfate in aqueous hydrochloric acid can be considered as taking place in two steps

$$\mathrm{Na_2SO_4(c)} \xrightarrow{\mathrm{aq}} \mathrm{2Na^+(aq) + SO_4{}^{2-}(aq)} \qquad (4a)$$

$$\mathrm{H^+(aq) + SO_4{}^{2-}(aq)} \rightleftarrows \mathrm{HSO_4{}^-(aq)} \qquad (4b)$$

The first step is simply the heat of solution of sodium sulfate (Δh_s). In the second step of the reaction, sulfate ions associate with hydrogen ions to form bisulfate ions, and the heat obtained from this association step will be identified as Δh_r. The problem is to isolate Δh_r from Δh_s in order to obtain the thermodynamic properties for the dissociation of the bisulfate ion.

The calorimeter measured an over-all energy, Δh, when sodium sulfate was dissolved in aqueous hydrochloric acid, and so Δh_r is equal to $\Delta h - \Delta h_s$. For each calorimetric measurement a value of Δh_s, corresponding to the ionic strength of the final calorimetric solution of sodium sulfate in aqueous hydrochloric acid, was subtracted from Δh to give Δh_r. A value of Δh_s was calculated for each measurement in the following way. First a ρ value for $\mathrm{Na_2SO_4}$ was obtained from the relationship summarized in Table I at the ionic strength of the experiment. ΔH_s corresponding to this ionic strength was then obtained from the equation

$$\Delta H_s = \rho + 3A_{\mathrm{H}}I^{1/2}\alpha \qquad (5)$$

The value of ΔH_s so obtained[13] was multiplied by the number of moles of sodium sulfate dissolved finally to obtain Δh_s, which was subtracted from Δh to give Δh_r.

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(12) G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 640.

(13) At two temperatures (4.34 and 85.62°) the measurements on sodium sulfate in aqueous hydrochloric acid were not made at exactly the same temperatures as the measurements on sodium sulfate in water (4.53 and 85.17°). At these temperatures it was necessary to make a small correction to ΔH_s. The corrections were 26 and −29 cal mol^{-1}, respectively.

TABLE II

THERMAL DATA FOR THE DISSOCIATION REACTION $HSO_4^-(aq) \rightleftarrows H^+(aq) + SO_4^{2-}(aq)$

Initial moles of Na_2SO_4 × 10^3	Initial molality × 10^3 Na_2SO_4	Initial molality × 10^3 HCl	Δh, cal	Moles of HSO_4^- × 10^3	$-\Delta H_{diss}$, cal mol^{-1}	$-2A_H I^{1/2}\alpha$, cal mol^{-1}	$-\rho_{diss}$, cal mol^{-1}	$10^3 I$
4.34°								
1.1480	2.726	3.939	2.2505	0.2095	2429	65	2352	10.98
1.1031	2.620	3.939	2.1070	0.2021	2145	64		
0.9064	2.152	7.887	2.0713	0.2886	2401	69	2470	12.97
1.5012	3.565	11.818	3.6649	0.6041	2255	84	2403	18.89
1.2358	2.935	11.818	3.1157	0.5041	2428	81		
1.3442	3.192	11.818	3.3022	0.5453	2279	83		
1.1014	2.616	19.701	3.2314	0.5975	2571	94	2705	25.13
1.2800	3.040	19.701	3.7999	0.6905	2650	95		
0.8037	1.909	27.612	2.5410	0.5074	2562	103	2665	30.93
2.2695	5.390	27.612	7.0373	1.389	2539	112	2651	37.18
3.1681	7.525	27.612	9.5281	1.900	2432	117	2549	41.16
$\Delta H_{diss}° = -2290 \pm 140$[a] cal mol^{-1}								
15.00°								
0.9508	2.260	8.036	1.4470	0.3436	3100	83	3272	13.05
0.9040	2.148	8.036	1.4374	0.3278	3280	82		
1.2554	2.984	8.036	1.9428	0.4440	3229	88	3188	14.52
1.2017	2.856	8.036	1.8219	0.4266	3130	88		
1.1177	2.656	8.036	1.6265	0.3992	2944	86		
0.9623	2.287	12.054	1.8417	0.4454	3250	93	3343	16.80
2.0915	4.971	12.054	3.7307	0.9130	3128	106	3234	22.63
3.0300	7.202	12.054	5.2047	1.258	3115	117	3232	27.68
2.7160	6.456	16.072	5.4453	1.362	3151	118	3269	28.96
2.2602	5.372	20.091	5.1474	1.292	3240	120	3295	30.30
3.0253	7.191	16.072	5.9455	1.498	3109	121		
1.5239	3.622	28.110	4.0990	1.018	3384	128	3512	34.14
2.3500	5.585	28.110	6.1511	1.544	3329	134	3463	37.53
3.5164	8.358	28.110	8.8008	2.253	3232	141	3373	42.47
3.9512	9.391	28.110	9.8522	2.507	3249	143	3392	44.36
4.3877	10.429	28.110	10.7828	2.756	3224	145	3369	46.29
$\Delta H_{diss}° = -3150 \pm 99$[a] cal mol^{-1}								
24.99°								
0.8144	1.939	7.866	0.9820	0.3317	4038	94	4132	12.10
0.9580	2.281	7.866	1.1415	0.3859	4039	96	4135	12.87
1.1426	2.720	7.866	1.3189	0.4538	3993	99	4092	13.86
1.3424	3.196	7.866	1.5393	0.5250	4024	103	4127	14.95
1.8551	4.416	7.866	1.8722	0.6975	3794	112	4158	16.49
0.8991	2.140	11.826	1.5246	0.4588	4152	107		
0.8040	1.914	11.826	1.3914	0.4124	4203	105		
1.7157	4.084	11.826	2.6517	0.8379	4004	118	4122	20.09
1.8183	4.329	11.826	2.7868	0.8830	3997	119	4116	20.61
2.3473	5.588	11.826	3.3275	1.107	3857	125	4144	24.14
1.3609	3.240	19.747	3.0038	0.8603	4118	130		
0.9746	2.320	19.747	2.1508	0.6232	4077	126		
2.2957	5.465	19.747	4.8060	1.410	4038	140	4162	29.56
2.3538	5.604	19.747	4.8714	1.443	4006	140		
$\Delta H_{diss}° = -4120 \pm 110$[a] cal mol^{-1}								
34.96°								
0.3629[b]	0.863	3.941	0.1098	0.1136	4782	78	4860	5.990
0.5267[b]	1.253	7.880	0.6005	0.2500	4843	100	4967	10.57
0.9649[b]	2.297	3.941	0.1829	0.2789	4688	96		
0.7118	1.694	7.890	0.8676	0.3333	5057	105		
0.5910	1.407	7.890	0.6574	0.2793	4792	103		
0.5750	1.369	7.899	0.6842	0.2723	4948	102		
0.9076[b]	2.161	7.877	0.9431	0.4180	4745	109	4883	12.36
0.9314	2.217	7.890	0.9522	0.4286	4704	110		
0.8402	2.000	7.899	0.9493	0.3897	4905	108		
0.8867	2.111	7.871	0.9431	0.4089	4786	109		
0.9578	2.280	7.871	0.9837	0.4392	4729	110		
1.0574[b]	2.517	7.877	1.0861	0.4812	4766	112	4806	13.48
1.1901[b]	2.833	7.877	1.1205	0.5358	4618	115		
1.2031[b]	2.864	11.834	2.0205	0.6730	5003	127	4981	17.05
1.3165[b]	3.134	11.834	1.9492	0.7319	4671	129		
0.9787[b]	2.330	11.834	1.6088	0.5540	4890	124		

TABLE II (*Continued*)

Initial moles of Na_2SO_4 × 10^3	Initial molality × 10^3 Na_2SO_4	Initial molality × 10^3 HCl	Δh, cal	Moles of HSO_4^- × 10^3	$-\Delta H_{diss}$, cal mol^{-1}	$-2A_HI^{1/2}\alpha$, cal mol^{-1}	$-\rho_{diss}$, cal mal^{-1}	10^3I
34.96° (*Continued*)								
1.9760	4.704	19.747	4.1744	1.330	4734	157	4891	27.53
2.1333[b]	5.079	19.732	4.4775	1.428	4735	158	4893	28.17
1.3188[b]	3.139	23.589	3.1905	0.9569	4809	159	4903	28.77
2.3296[b]	5.546	19.676	4.7933	1.549	4701	161		
2.2949	5.464	19.747	4.8184	1.529	4753	161		
2.2860	5.442	19.747	4.7321	1.524	4708	160		
2.4362[b]	5.800	19.708	5.0304	1.615	4722	162	4884	29.42
2.5360	6.038	19.747	5.2460	1.678	4737	162	4899	29.87
$\Delta H_{diss}^\circ = -4922 \pm 100$[a] cal mol^{-1}								
60.03°								
0.9507	2.263	8.040	1.3518	0.5960	6513	152	6655	11.99
1.1243	2.676	8.040	1.5813	0.6952	6567	156	6723	12.76
1.3461	3.204	8.040	1.7516	0.8175	6498	162	6711	13.96
1.4310	3.407	8.040	1.9129	0.8629	6598	164		
1.0053	2.393	16.123	2.5768	0.7875	6590	190	6780	19.55
1.7270	4.111	16.123	4.2003	1.325	6537	200	6737	22.15
2.2010	5.240	20.156	5.9918	1.765	6571	221	6792	27.47
2.2191	5.283	20.156	6.0248	1.779	6565	221	6786	27.54
2.3082	5.495	20.156	6.1913	1.846	6535	222	6757	27.85
2.5429	6.054	32.252	8.4275	2.219	6641	260	6886	39.72
2.4598	5.856	32.252	8.0950	2.148	6611	259		
$\Delta H_{diss}^\circ = -6637 \pm 34$[a] cal mol^{-1}								
85.62°								
1.1373	2.707	3.951	0.6459	0.6652	8179	184	8398	9.546
1.3689	3.259	3.951	0.5603	0.7538	8240	194		
1.1792	2.807	11.854	3.5682	0.9946	8407	236	8600	15.83
1.3525	3.220	11.854	3.9450	1.134	8317	241		
1.4806	3.525	19.728	5.3241	1.338	8393	288	8682	24.02
1.5394	3.665	19.728	5.5312	1.390	8395	288		
1.4449	3.440	27.625	5.6877	1.348	8439	325	8764	31.53
$\Delta H_{diss}^\circ = -8325 \pm 59$[a] cal mol^{-1}								
95.00°[c]								
0.8352	2.010	3.225	0.4342	0.5062	8740	183	8921	6.820
0.8367	2.012	3.225	0.4321	0.5070	8736	183		
1.6756	4.030	6.450	2.7217	1.222	8651	243	8894	12.66
2.0846	5.014	6.450	2.6845	1.448	8561	260	8821	14.53
3.1319	7.532	12.900	8.1729	2.616	8592	319	8908	22.89
3.1182	7.499	12.900	8.1311	2.606	8585	319		
4.1525	9.987	32.250	15.8730	3.928	8696	423	9138	43.33
4.1634	10.013	32.250	16.0621	3.938	8734	423		
$\Delta H_{diss}^\circ = -8808 \pm 66$[a] cal mol^{-1}								

[a] Calculated probable error. [b] In these measurements Δh_s was determined from series I of the heat of solution measurements of sodium sulfate dissolved in water at 34.96°. For the other measurements at 34.96° series II was used (see Table I). [c] Heat of solution measurements on this system at 95.00° were made by Dr. Eugene C. Jekel in these laboratories.

Each value of Δh_r was then converted to ΔH_r, the heat of association in calories per mole, by dividing by the number of moles of bisulfate formed in the reaction

$$\Delta H_r = \Delta h_r/(\text{moles of } HSO_4^-) = -\Delta H_{diss} \qquad (6)$$

In order to determine the ionic strength of each solution and the number of moles of bisulfate ion formed, it is first necessary to know the equilibrium constant, *K*, for the dissociation reaction

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \qquad (7)$$

Assuming that the concentrations of the solutions are sufficiently dilute ($I \simeq 0.005\text{–}0.05$) so that the activity coefficient ratios are nearly equal to 1, K^0 is given by the equation

$$K^0 = [H^+][SO_4^{2-}]/[HSO_4^-] \qquad (8)$$

This assumption has been shown to be valid at these concentrations by Covington, Dobson, and Wynne-Jones,[14] who found that the equilibrium constant changes by only 0.3–0.6% up to an ionic strength of 0.05. The ionic strength of each solution was computed from the relationship

$$I = {}^1/_2 \sum c_iZ_i^2 \qquad (9)$$

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(14) A. K. Covington, J. V. Dobson, and Lord Wynne-Jones, *Trans. Faraday Soc.*, **61**, 2057 (1965).

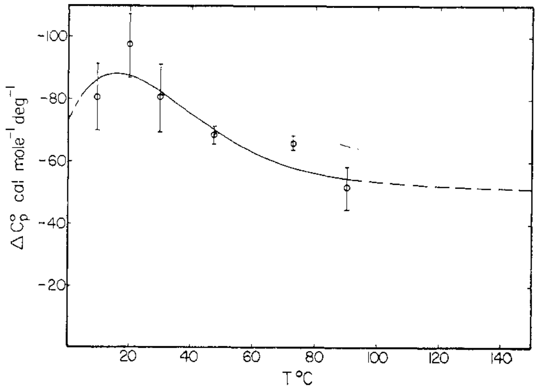

Figure 1.—ΔC_p° (cal mol^{-1} deg^{-1}) for the dissociation of bisulfate ion as a function of temperature.

where c_i is the concentration of an ion and Z_i is the ionic charge.

The dissociation constant K^0 has been repeatedly determined at 25°, and a value of K^0 equal to 0.0103 ± 0.0001 has been generally accepted in the literature.[14-16] However, the values of K^0 at other temperatures between 0 and 100° are less well known. Since it is necessary to know the dissociation constant accurately at each temperature where the heats of solution were made in order to make the thermal calculations, an estimate was used initially for K^0 at all other temperatures. This made it possible to obtain preliminary values for ΔH_{diss} and the ionic strength for each calorimetric measurement. These values of ΔH_{diss} were extrapolated to infinite dilution by adding the Debye–Hückel term to each ΔH_{diss} value in order to obtain the ρ function. In this case, ρ_{diss} is given by the equation

$$\rho_{\text{diss}} = \Delta H_{\text{diss}} - \sum(\nu/2)|Z_+Z_-|A_{\text{H}}I^{1/2}\alpha = \Delta H_{\text{diss}}^\circ - 2.303RT^2(\text{d}B/\text{d}T)\sum\nu_+\nu_-I \quad (10)$$

A plot was made of ρ_{diss} *vs.* ionic strength, and a least-squares linear extrapolation to zero concentration gave $\Delta H_{\text{diss}}^\circ$. The criterion that the slopes of these plots ($\text{d}\rho/\text{d}I$) be a smooth function of temperature was also required. In this way a preliminary value was determined for $\Delta H_{\text{diss}}^\circ$ at each temperature where these measurements were made.

The preliminary values of $\Delta H_{\text{diss}}^\circ$ were based upon estimated dissociation constants at temperatures other than 25°. In order to obtain a better set of dissociation constants a procedure was devised for generating constants consistent with the thermal data of this research and based upon the well-established dissociation constant at 25°.

The free energy change for the dissociation of bisulfate ion to form hydrogen ion and sulfate ion at temperature T can be expressed in terms of the equation

$$\Delta F^\circ_T = \Delta F^\circ_{298^\circ\text{K}} + \int_{298^\circ\text{K}}^{T} \Delta C_p^\circ \text{d}T - T\int_{298^\circ\text{K}}^{T} (\Delta C_p^\circ T)\,\text{d}T - \Delta S^\circ_{298^\circ\text{K}}\Delta T \quad (11)$$

If eq 11 were evaluated, new dissociation constants could be obtained from the equation

$$\Delta F^\circ_T = -RT \ln K^0 \quad (12)$$

and these constants could be used to recalculate the thermal data. Since the dissociation constant at 25° is well known, $\Delta F^\circ_{298^\circ\text{K}}$ was obtained from eq 12 and a preliminary value of $\Delta S^\circ_{298^\circ\text{K}}$ was obtained from the second law. The integral terms in eq 11 were evaluated from the preliminary values of ΔH° ($\Delta H_{\text{diss}}^\circ$) at the several temperatures. Average values of the change in heat capacity, $\Delta \bar{C}_p^\circ|_{T_1}^{T_2}$, were obtained from the equation

$$\Delta \bar{C}_p^\circ|_{T_1}^{T_2} = (\Delta H^\circ_{T_2} - \Delta H^\circ_{T_1})/(T_2 - T_1) \quad (13)$$

A value of $\Delta \bar{C}_p^\circ|_{T_1}^{T_2}$ was obtained for each pair of successive values of ΔH° and $\Delta \bar{C}_p^\circ|_{T_1}^{T_2}$ was taken to be equal to ΔC_p° at a temperature halfway between the two temperatures where the ΔH° values were obtained.

ΔC_p° was plotted as a function of temperature and a smooth curve was drawn through the data points. The integral terms in eq 11 were evaluated graphically and new values of ΔF°_T were used to calculate new K^0 values from eq 12. The newly generated values of K^0 at each temperature were then used to recalculate the thermal data as before and obtain still another set of heats, heat capacities (ΔC_p°), ΔF°_T values, and new dissociation constants. This iterative method of successive approximations was repeated, altering the ΔC_p° *vs.* temperature curve each time, until the dissociation constants obtained from the resulting ΔC_p° curve gave the same values of ΔH_{diss}. A CDC 6500 computer was used in these calculations. Table II gives the final values of ΔH_{diss}, ρ_{diss}, and ΔH° and the final ΔC_p° *vs.* temperature curve is shown in Figure 1. Since the ΔC_p° curve levels off at higher temperatures, an extension of the curve was made up to 150° (dashed line), which permitted the reliable estimation of the dissociation constants up to this temperature.

It was possible to obtain an average third-law value of $\Delta S^\circ_{298^\circ\text{K}}$ based upon ΔS°_T calculated at each temperature from the second law

$$\Delta S^\circ_T = \Delta S^\circ_{298^\circ\text{K}} + \int_{298^\circ\text{K}}^{T} (\Delta C_p^\circ/T)\,\text{d}T \quad (14)$$

A value of $\Delta S^\circ_{298^\circ\text{K}}$ was obtained at each temperature where heats of solution measurements were made. These results were averaged to obtain the "best" value of $\Delta S^\circ_{298^\circ\text{K}}$ used in eq 11. In a similar manner a "best" value of $\Delta H^\circ_{298^\circ\text{K}}$ was obtained by averaging the values determined from the equation

$$\Delta H^\circ_T = \Delta H^\circ_{298^\circ\text{K}} + \int_{298^\circ\text{K}}^{T} \Delta C_p^\circ\,\text{d}T \quad (15)$$

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TABLE III

THERMODYNAMIC FUNCTIONS FOR THE DISSOCIATION PROCESS $HSO_4^-(aq) \rightleftarrows H^+(aq) + SO_4^{2-}(aq)$

t, °C	10^3K^0 [a]	ΔF°,[a] cal mol^{-1}	$-\Delta H^{\circ}$, cal mol^{-1}	$-\Delta S^{\circ}$, cal mol^{-1} deg^{-1}	t(av), °C	$-\Delta C_p^{\circ}$, cal mol^{-1} deg^{-1}	$-\Delta C_p^{\circ}$ (smooth), cal mol^{-1} deg^{-1}	$-\Delta H^{\circ}_{25^{\circ}}$ (calcd), cal mol^{-1}	$-\Delta S^{\circ}_{25^{\circ}}$ (calcd), cal mol^{-1} deg^{-1}
4.34	15.42	2301	2290	16.54			80.1	4073	22.74
					9.67	80.7			
15.00	12.76	2498	3150	19.60			88.1	4022	22.57
					19.99	97.1			
24.99	10.30	2711	4120	22.91			85.2	4120	22.91
					29.97	80.4			
34.96	8.060	2952	4922	25.56			78.7	4106	22.87
					47.49	68.4			
60.03	3.941	3666	6637	30.92			62.8	4056	22.72
					72.83	66.0			
85.62	1.760	4522	8325	35.81			55.1	4258	23.29
					90.31	51.5			
95.00	1.304	4860	8808	37.13			53.9	4230	23.21

$\Delta H^{\circ}_{25^{\circ}}(\text{av}) = -4124 \pm 69^{b}$ cal mol^{-1}

$\Delta S^{\circ}_{25^{\circ}}(\text{av}) = -22.90 \pm 0.20^{b}$ cal mol^{-1} deg^{-1}

[a] Based upon values in column 8 and the average value from column 10. [b] Average error.

The smoothed thermodynamic functions are generated from the smooth ΔC_p° *vs.* T curve and are to be distinguished from the directly determined values (such as ΔH°_T) at each temperature. The ΔF°_T values obtained from eq 11 and the resulting dissociation constants are smoothed values. Table III summarizes the final values of the thermodynamic properties for the dissociation of bisulfate ion.

It must be noted that all of these thermodynamic properties are based upon one independent measurement, the dissociation constant, K^0, at 25°. If the value of K^0 at 25° varies by as much as 3%, however, it can be shown that ΔC_p° will change by about 3 cal mol^{-1} deg^{-1} up to 90°.

It was necessary to make two minor assumptions related to the chemistry which occurs when sodium sulfate dissolves in air-saturated water. The first concerns the fact that some sodium ions and sulfate ions remain in the form of the $NaSO_4^-(aq)$ complex. A value for the dissociation constant of 0.198 for this complex has been reported at 25° in the literature.[17] However, there are not enough thermal data available to obtain an accurate estimate of the heat correction involved. Fortunately, less and less of the complex is formed as the solutions become more dilute and the correction becomes zero at infinite dilution. This means that the extrapolation procedure for the sodium sulfate and sodium sulfate–hydrochloric acid systems automatically removes any effect of the complex.[18]

When water is exposed to the atmosphere, a certain amount of carbon dioxide dissolves, which forms hydrogen ion

$$CO_2(aq) + H_2O(l) \rightleftarrows H^+(aq) + HCO_3^-(aq) \qquad (16)$$

When sodium sulfate dissolved in this water, a small amount of the sulfate ion reacted to form bisulfate. Thermal data for the solubility of CO_2 and the dissociation constant of carbonic acid have been reported,[19] which makes it possible to calculate the heat effect. It was found that a correction of only about 0.6 cal mol^{-1} in $\Delta H_{\text{diss}}^{\circ}$ was required at 25°; a similar calculation at 95° gave a value of about 10 cal mol^{-1}. The effect is small enough to ignore.

Discussion

A large portion of the previous work done on the bisulfate dissociation reaction has been confined to 25° and was reviewed in 1962 by Young and Irish.[15] They examined the values of K^0 at 25° determined by several different methods,[9,10,20–23] including conductance, emf, solubility, and spectroscopic measurements. The values of K^0 ranged from 0.01016 to 0.0106 with a deviation from the average value of less than 1%. Young and Irish proposed a value for K^0 of 0.0103 and this value formed the basis for the thermodynamic determinations in this work.

The values of $\Delta H_{\text{diss}}^{\circ}$ at 25° reported in this survey are more scattered.[9,10,20,22,24–26] The range is from −4.9 to −5.6 kcal mol^{-1}. In this case Young and Irish decided upon a "best" value of −5.21 ± 0.12 kcal mol^{-1} at 25°. This value is not in agreement with the value of −4120 ± 110 cal mol^{-1} and the third-law value of −4124 ± 69 cal mol^{-1} obtained in this research at 25°. In more recent work Marshall and Jones[11] obtained a value of −3850 cal mol^{-1} from

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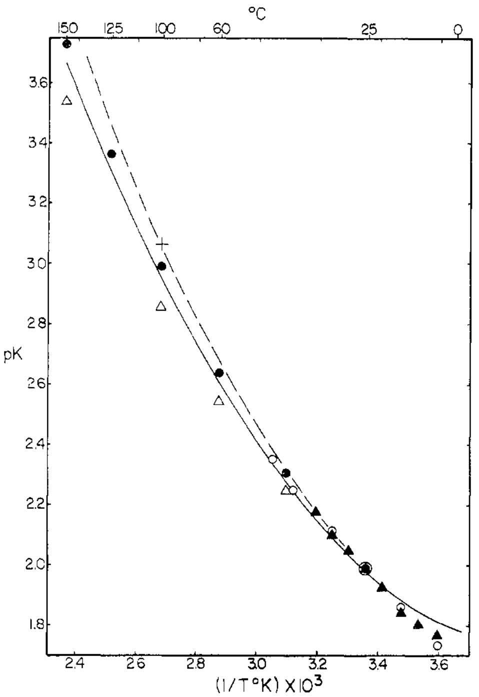

Figure 2.—pK^0 *vs.* $1/T$°K for the dissociation of bisulfate: —, present calorimetric data; △, Marshall and Jones;[11] ●, Lietzke, Stoughton, and Young;[10] ---○, Young, Klotz, and Singleterry;[9] ▲, Davies, Jones, and Monk;[20] +, Ryzhenko.[31]

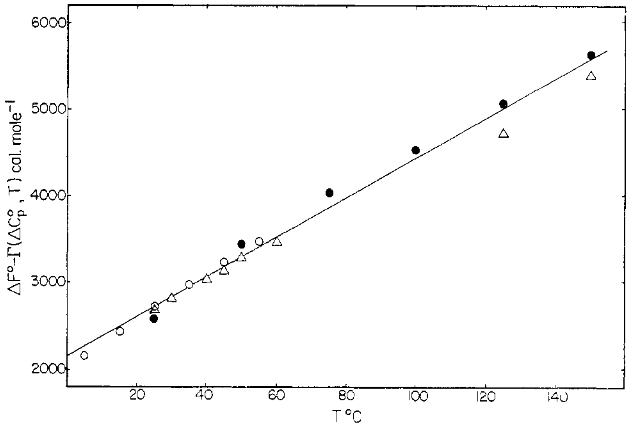

Figure 3.—$\Delta F°$ − $\Gamma(\Delta C_0°,T)$ for the dissociation of bisulfate as a function of temperature: —, required calorimetric slope (ΔS = −22.90 cal mol^{-1} deg^{-1}); ○, Young, Klotz, and Singleterry;[9] △, Marshall and Jones;[11] ●, Lietzke, Stoughton, and Young.[10]

Table IV

Third-Law Values of K^0, the Dissociation Constant for Bisulfuric Acid[a]

Temp, °C	K^0	Temp, °C	K^0	Temp, °C	K^0
0	(0.0166)[b]	50	0.00529	110	(0.000808)
10	0.0140	60	0.00394	120	(0.000583)
20	0.0114	70	0.00290	130	(0.000415)
25[c]	0.0103	80	0.00213	140	(0.000297)
30	0.00912	90	0.00152	150	(0.000218)
40	0.00705	100	(0.00111)		

[a] Based on an entropy of dissociation, $\Delta S°_{25°}$ = −22.90 cal deg^{-1} mol^{-1} (see text). [b] Quantities in parentheses are obtained from extrapolations made to temperatures beyond the experimental data. [c] The value of K^0 at 25° was fixed at 0.0103.

solubility measurements of calcium sulfate in sulfuric acid over an extended range of temperatures (25–350°) and Jekel[27] obtained a preliminary value of −4000 cal mol^{-1} from calorimetric measurements made in these laboratories.

Much of the early work on this system was done by obtaining values of the equilibrium constant at several temperature intervals around 25° and determining $\Delta H_{\mathrm{diss}}°$ at 25° from $\Delta F_{\mathrm{diss}}°$ at 25° and the temperature derivative of $\Delta F_{\mathrm{diss}}°$. The problems of calculating heats from the temperature coefficients of free energy measurements have been discussed elsewhere and these values are subject to larger errors.[28] The most recent evidence, therefore, would seem to indicate a more positive value of $\Delta H_{\mathrm{diss}}°$ than that proposed by Young and Irish.

By extending the smooth $\Delta C_p°$ curve in Figure 1 to 150°, it was possible to obtain K^0 up to this temperature (Table IV). These results are compared with those obtained by others[9–11,20] on the dissociation process between 0 and 150° (Figure 2). Marshall and Jones[11] and Lietzke, Stoughton, and Young[10] have made determinations of the equilibrium constants up to 150° (and higher). The agreement with the present results is satisfactory. The data of Young, Klotz, and Singleterry[9] on the dissociation constants were extended[10] to 150°, using conductance data determined by Noyes[24] and fitted by Young to an empirical equation (dashed line). Their values of pK^0 vary progressively more from the other results as the temperature increases. It can be seen that all values of pK^0 tend toward the same point at 25°.

The third-law method, which has been used previously to analyze results on cell potential measurements,[29–31] can be used to examine the data on the dissociation constants for bisulfate ion. Equation 11 is rearranged to give

$$\Delta F°_T - \Gamma(\Delta C_p°,T) = \Delta F°_{298°\mathrm{K}} - \Delta S°_{298°\mathrm{K}}\Delta T \quad (17)$$

where

$$\Gamma(\Delta C_p°,T) = \int_{298°\mathrm{K}}^{T} \Delta C_p°\, dT - T\int_{298°\mathrm{K}}^{T} (\Delta C_p°/T)\, dT \quad (18)$$

A plot can be made of $\Delta F°_T - \Gamma(\Delta C_p°,T)$ *vs.* T. The third-law analysis requires that all of the points lie on a straight line with a slope equal to $-\Delta S°_{298°\mathrm{K}}$. The equilibrium constants of Young, Klotz, and Singleterry,[9] Marshall and Jones,[11] and Lietzke, Stoughton, and Young[10] have been converted to free energies and $\Gamma(\Delta C_p°,T)$ has been evaluated from the smooth $\Delta C_p°$ values of this research. Table V summarizes the results of these calculations and Figure 3 is the third-law plot of $\Delta F°_T - \Gamma(\Delta C_p°,T)$ *vs.* temperature. The line in

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TABLE V

THIRD-LAW ANALYSIS OF PREVIOUS VALUES FOR THE DISSOCIATION CONSTANT OF BISULFATE ION

Temp, °C	Source	K^0	$\Delta F°$, cal mol^{-1}	$\int_{298°K}^{T} \Delta C_p° \, dT$, cal mol^{-1}	$-T\int_{298°K}^{T} (\Delta C_p°/T) \, dT$, cal mol^{-1}	$\Gamma(\Delta C_p°,T)$, cal mol^{-1}	$\Delta F° - \Gamma(\Delta C_p°,T)$, cal mol^{-1}
5	YKS[a]	0.0185	2205	1722	−1664	58	2147
15	YKS	0.0139	2448	872	−856	16	2432
25	YKS	0.0104	2705	0	0	0	2705
	MJ[b]	0.0103	2711	0	0	0	2711
	LSY[c]	0.0129	2580	0	0	0	2580
30	MJ	0.00942	2810	−412	415	3	2807
35	YKS	0.0077	2980	−815	828	13	2967
40	MJ	0.00725	3066	−1199	1229	30	3036
45	YKS	0.00565	3273	−1515	1616	51	3222
	MJ	0.00666	3168	−1515	1616	51	3117
50	MJ	0.00531	3364	−1921	2000	79	3285
	LSY	0.00423	3510	−1921	2000	79	3431
55	YKS	0.00413	3580	−2258	2371	113	3467
60	MJ	0.00432	3604	−2581	2734	153	3451
75	LSY	0.00200	4300	−3468	3753	285	4015
100	LSY	0.000977	5139	−4845	5463	618	4521
125	MJ	0.000707	5740	−6160	7186	1026	4714
	LSY	0.000463	6074	−6160	7186	1026	5048
150	MJ	0.000275	6894	−7456	8973	1517	5377
	LSY	0.000205	7141	−7456	8973	1517	5624

[a] Data of Young, Klotz, and Singleterry.[9] [b] Data of Marshall and Jones.[11] [c] Data of Lietzke, Stoughton, and Young.[10]

TABLE VI

SMOOTHED HEAT CAPACITY DATA FOR SODIUM BISULFATE AND BISULFURIC ACID[a]

Temp, °C	$\bar{C}_{p_2}°$(NaHSO$_4$), cal mol^{-1} deg^{-1}	$\Delta C_{p_{diss}}°$, cal mol^{-1} deg^{-1}	$\bar{C}_{p_2}°$(H·H·SO$_4$),[b] cal mol^{-1} deg^{-1}	$\bar{C}_{p_2}°$ (H·HSO$_4$), cal mol^{-1} deg^{-1}
0	(−88.5)	(−72.2)	(−176.4)	(−104.2)
10	−0.1	−86.3	−91.5	5.2
20	22.5	−87.6	−75.5	12.1
25	26.6	−85.2	−70.6	14.6
30	27.9	−82.0	−67.1	14.9
40	26.7	−75.3	−63.3	12.0
50	23.0	−68.7	−61.3	7.4
60	18.6	−62.8	−60.8	2.0
70	13.4	−58.6	−63.3	−4.7
80	6.8	−56.1	−69.5	−13.4
90	−3.2	−54.4	−80.6	−26.2
100	(−16.4)	(−53.4)	(−96.8)	(−43.4)
110		(−52.7)		
120		(−52.3)		
130		(−52.0)		
140		(−51.8)		
150		(−51.7)		

[a] Quantities in parentheses are obtained from extrapolations made to temperatures beyond the experimental data. [b] The heat capacities of aqueous sulfuric acid are from ref 8.

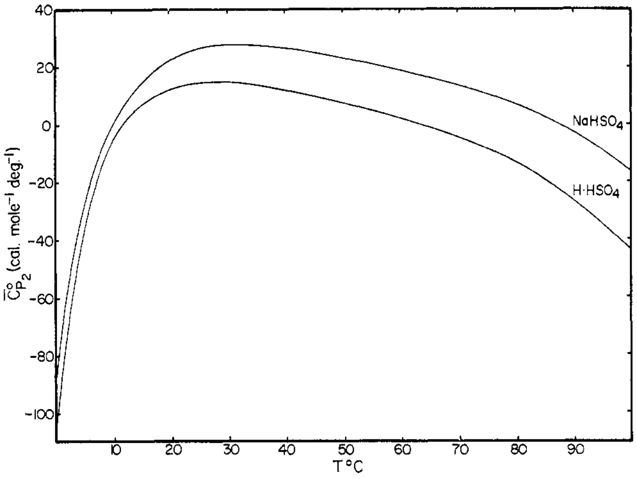

Figure 4.—The partial molal heat capacities of sodium bisulfate and bisulfuric acid as a function of temperature.

Figure 3 represents the theoretical calorimetric slope obtained from this research with $\Delta S°_{298°K} = -22.90 \pm 0.20$ cal mol^{-1} deg^{-1}. All three sets of data are fairly linear except that the point of 25° from the data of Lietzke, Stoughton, and Young[10] lies below the line formed from their other points. This latter slope, however, agrees better with the theoretical slope than the slopes of the other two sets of data. All of the equilibrium data in Figure 3 were treated by the method of least squares to obtain a slope giving $\Delta S°_{298°K} = -22.61$ cal mol^{-1} deg^{-1}, which is in good agreement with the third-law value, -22.90 ± 0.20 cal mol^{-1} deg^{-1}.

We believe that the values of K^0 given in Table IV represent the best available constants at present; they are consistent both with the most extensive thermal data and the directly determined equilibrium constants over extended temperatures.

Partial Molal Heat Capacities of Bisulfuric Acid and Sodium Bisulfate

Having obtained the thermodynamic properties for the dissociation of aqueous bisulfate ion at temperatures between 0 and 100°, the partial molal heat capacities of bisulfuric acid and sodium bisulfate were also calculated over this temperature range. Values of $\Delta C_p°(t)$ were obtained at each temperature from the $\Delta C_p°$ *vs.* *t* curve (Figure 1) and the heat capacities of sulfuric acid were obtained from the values of $\bar{C}_p°_{H \cdot H \cdot SO_4}$ determined recently in these laboratories.[8] By subtracting values of $\Delta C_p°(t)$ from $\bar{C}_p°_{H \cdot H \cdot SO_4}$ at regular temperature intervals, smooth values of the heat capacity for aqueous bisulfuric acid were obtained from 0 to 100°.

Heat capacity data for aqueous sodium bisulfate were also calculated as a function of temperature from the heat capacity of aqueous bisulfuric acid and the difference in the heat capacity of aqueous sodium ion and aqueous hydrogen ion[5]

$$\bar{C}_p{}^\circ{}_{\mathrm{NaHSO_4}}(t) = \bar{C}_p{}^\circ{}_{\mathrm{H\cdot HSO_4}}(t) + \bar{C}_p{}^\circ{}_{\mathrm{Na^+}}(t) - \bar{C}_p{}^\circ{}_{\mathrm{H^+}}(t) \qquad (19)$$

These data are summarized in Table VI and Figure 4.

The Thermodynamic Functions of the Bisulfate Ion

Since the thermodynamic functions of the aqueous sulfate ion are well established,[32] it is now possible to derive similar functions for the bisulfate ion from eq 7 and the data of Tables III, IV, and VI. The revised values for the standard heat and free energy of formation at 25° are −213.20 and −180.68 kcal mol^{-1}, respectively. The standard entropy and heat capacity at 25° are 27.7 and 14.6 cal mol^{-1} deg^{-1}, respectively. The heat of formation and entropy are considerably different from the previously accepted values,[31] but, as discussed, the previous values were based on much less extensive data than in the present analysis.

Acknowledgment.—The authors are indebted to Dr. Eugene C. Jekel for his determination of the heats of solution of sodium sulfate in aqueous hydrochloric acid solutions at 95.00°.

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Nature of the Donor–Acceptor Bond in Acetonitrile–Boron Trihalides. The Structures of the Boron Trifluoride and Boron Trichloride Complexes of Acetonitrile

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The crystal and molecular structure of the boron trichloride complex of acetonitrile has been determined and that of the boron trifluoride complex redetermined. Least-squares refinement of three-dimensional X-ray data led to a conventional R factor on F of 3.9% for the BCl_3 complex (441 nonzero reflections) and 5.6% for the BF_3 complex (382 nonzero reflections). Both complexes crystallize in the space group $D_{2h}{}^{16}$-Pnma of the orthorhombic system with four molecules in unit cells of dimensions a = 8.67 (1), b = 7.32 (1), and c = 10.19 (1) Å for Cl_3BNCCH_3 and a = 7.784 (3), b = 7.177 (3), and c = 8.360 (3) Å for F_3BNCCH_3. The calculated densities of 1.65 g/cm^3 for Cl_3BNCCH_3 and 1.55 g/cm^3 for F_3BNCCH_3 are in reasonable agreement with previously measured densities of 1.60 and 1.59 g/cm^3, respectively. The molecules are required to have symmetry m. The configuration about the boron in each complex is nearly tetrahedral. The B–N bond length in the BCl_3 complex (1.562 (8) Å) is significantly shorter than the B–N bond length in the BF_3 complex (1.630 (4) Å). The X_1–B–N and X_2–B–N bond angles are, respectively, 105.3 (3) and 105.8 (2)° where X = F and 106.9 (3) and 106.7 (4)° where X = Cl. These results are rationalized in terms of a model for donor–boron halide interaction in which the acceptor strength of a boron halide increases with increasing distortion of the BX_3 group. This model also is consistent with thermochemical and spectroscopic data on boron halide complexes.

Introduction

The enthalpy for the reaction of boron halides with Lewis bases is in the order $BF_3 > BCl_3 \gtrsim BBr_3$ (*i.e.*, the BF_3 reaction is the least exothermic).[3] This is the reverse of the order expected from consideration of the inductive effects of the halogens, and the explanation generally offered is that inductive effects are less important than the energy necessary to reorganize the planar free boron halide to the pyramidal form required for complex formation.[3,4] That is, the relative order of ΔH_5 for a series of boron halides with one reference donor, D, is thought to be dominated by ΔH_1 in the thermochemical cycle

$$\begin{tikzcd}
\underset{\text{pyramidal}}{BX_3(g)} & + & D(g) \arrow[r, "\Delta H_3"] & X_3BD(g) \arrow[d, "\Delta H_4"] \\
\underset{\text{planar}}{BX_3(g)} \arrow[u, "\Delta H_1"] & + & D(l) \arrow[u, "\Delta H_2"] \arrow[r, "\Delta H_5"] & X_3BD(\text{s or soln})
\end{tikzcd}$$

where X = F, Cl, or Br. If published estimates of ΔH_1 are employed[4] and ΔH_4 is assumed to be constant for the series of boron halides with one donor, then one finds that the heat of donor–acceptor bond formation, ΔH_3, follows the trend expected from electronegativities. That is, the calculated B–N bond strength decreases from the BF_3 through the BBr_3 complexes.

In addition to the thermochemical work, many spectroscopic studies have been performed on boron halide complexes. These include studies of the

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