

(1) The ir spectra of samples with the new modification were identical with the spectrum of $H_2B(NH_3)_2BH_4$ prepared according to the literature.¹⁷ It is not surprising that differences in crystal structure do not show up in the spectra because the ir absorptions are fairly broad whereas these differences should amount to less than 10 cm^{-1} .

(2) The compound could be dissolved in liquid ammonia and recovered without any apparent sign of decomposition, such as hydrogen evolution. If the solvent was pumped off at -83° , the literature modification was formed. Ir spectra of the substance before dissolution and after removal of ammonia were identical.

(3) An ether-insoluble sample of 0.316 g gave 3.91 units of $H_2/H_2B(NH_3)_2BH_4$ upon hydrolysis with glacial acetic acid and dilute HCl. After pumping off all volatile material, the residue showed the X-ray patterns of boric acid and of $H_2B(NH_3)_2Cl$ reported by Schultz and Parry.¹⁸

The unstable modification of $H_2B(NH_3)_2BH_4$ is shown by the following d values (in Å): 5.03 (w), 4.74 (m), 4.62 (m), 4.37 (vs), 4.19 (w), 4.00 (m), 3.75 (w), 3.63 (m), 3.52 (w), 3.44 (m), 3.41 (s), 3.13 (m), 3.04 (w), 2.99 (w), 2.92 (m), 2.83 (m), 2.71 (w), 2.66 (w), 2.37 (w).

Reaction of Diborane with Ammonia in Liquid Ammonia.—The procedure described in ref 17 was used except that a -96° trap was taken to freeze out impurities from the diborane-nitrogen gas stream and no fritted cylinder was used. This tended to plug. After removal of ammonia the solid residue was extracted with diethyl ether stirring the suspension for 1 hr at

(17) S. G. Shore, K. W. Boedekker, and J. A. Patton, *Inorg. Syn.*, **9**, 4 (1967).

(18) D. R. Schultz and R. W. Parry, *J. Amer. Chem. Soc.*, **80**, 4 (1958).

room temperature. In two experiments 0.009 g of H_3BNH_3 was isolated from 0.246 g of crude product and 0.045 g of H_3BNH_3 from 0.779 g, corresponding to 4 and 5.8% yields of H_3BNH_3 . The samples were again characterized by ir spectra and X-ray powder patterns. Further extraction with diethyl ether produced no more H_3BNH_3 which proves that H_3BNH_3 was not formed by decomposition of $H_2B(NH_3)_2BH_4$ in the ether slurry.

$H_2B(NH_3)_2BH_4$ precipitated even from liquid ammonia in the form of either the literature modification or the new modification, or a mixture of both. Rapid removal of solvent at temperatures above -78° gave the new modification; slow removal from a cooling bath at -83° produced the one already reported.

Attempted Reaction of Ammonia-Borane with Sodium Borohydride.—A 1.15-mmol sample of H_3BNH_3 was dissolved in 20 ml of monoglyme and 3.34 mmol of $NaBH_4$ was added. At room temperature no trace of hydrogen was formed within 8 hr. After heating the solution at 60° for 12 hr, monoglyme was pumped off. A 1.04-mmol amount of H_3BNH_3 (=91%) was recovered by extraction with diethyl ether.

Attempted Reaction of Ammonia-Borane with Ammonium Chloride.—The reaction of 0.88 mmol of H_3BNH_3 with an equimolar amount of dry NH_4Cl was investigated with monoglyme and liquid ammonia as solvents. No hydrogen was produced within 10 days at room temperature in either solvent. The X-ray powder patterns of the nonvolatile residues contained only the reflections of the starting materials.

Acknowledgment.—I am very grateful to Doz. Dr. E. Schnell and Mr. W. Strele, both of this institute, for patiently recording and discussing numerous X-ray powder patterns.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE BERKELEY LABORATORY, BERKELEY, CALIFORNIA 94720

The Prediction of Gas-Phase Lewis Acid-Base Dissociation Heats with an Empirical Four-Parameter Equation

By WILLIAM L. JOLLY,* JOHN D. ILLIGE, AND MARSHALL H. MENDELSON

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The Drago-Wayland four-parameter equation for predicting Lewis acid-base dissociation heats has been extended to gaseous compounds, most of which are considered as adducts of cationic acids and anionic bases. By use of the empirically evaluated parameters for 14 acids and 12 bases, the heats of 105 different dissociations are reproduced with an average error of ± 3.9 kcal/mol. The method gives poor results for adducts in which the dissociated bonds are either weakened by lone-pair repulsions or affected by unusual π -bonding effects.

In 1952, Mulliken¹ showed theoretically that the dissociation energy of a Lewis acid-base adduct can be partitioned into a "no-bond" part and a "dative" or covalent part. In 1954, Edwards² showed that the free energies (or logarithms of equilibrium constants) of Lewis acid-base reactions can be reproduced by the two-term four-parameter equation

$$\log \frac{K}{K_0} = \alpha E_n + \beta H$$

where K is the equilibrium constant for the reaction of a base with a particular acid and K_0 is the constant for the corresponding reaction of a reference base. The parameters α and β are empirical constants characteristic of the acid, and E_n and H are independent parameters for the base. More recently, Drago and

Wayland³ used a similar equation to reproduce the heats of dissociation of Lewis acid-base adducts

$$\Delta H = E_A E_B + C_A C_B \quad (1)$$

Two empirical parameters, E_A and C_A , were assigned to each acid, and two empirical parameters, E_B and C_B , were assigned to each base. The $E_A E_B$ term was interpreted as a measure of electrostatic interaction energy, and the $C_A C_B$ term was interpreted as a measure of covalent bond energy. By application of eq 1 to reactions of neutral acids and bases in the gas state or in poorly solvating solvents (for which the dissociation heats ranged from 0.5 to 18.0 kcal/mol), it was possible to correlate the dissociation heats with an average error of approximately ± 0.1 kcal/mol.

Dissociation heats are available for an extensive set of gaseous compounds, not considered by Drago and

(1) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

(2) J. O. Edwards, *ibid.*, **76**, 1540 (1954); **78**, 1819 (1956).

(3) R. S. Drago and B. B. Wayland, *ibid.*, **87**, 3571 (1965).

Wayland, which may be considered as Lewis acid-base adducts. Most of these compounds are adducts of cationic acids and anionic bases. These acids and bases and their corresponding E and C parameters⁴ are listed in Tables I and II. The E and C parameters were

TABLE I
ACID PARAMETERS

Acid	E_A	Std error	C_A	Std error
F ⁺	2.705	0.094	4.618	0.221
Cl ⁺	1.675	0.052	3.794	0.180
Br ⁺	1.552	0.047	3.231	0.150
I ⁺	1.366	0.047	2.688	0.136
CN ⁺	2.537	0.103	3.367	0.250
OH ⁺	1.817	0.090	3.852	0.224
H ⁺	2.413	0.054	3.157	0.1775
CH ₃ ⁺	1.611	0.044	2.534	0.122
C ₆ H ₅ ⁺	1.539	0.045	2.513	0.124
NO ₂ ⁺	1.052	0.057	3.082	0.236
NO ⁺	1.051	0.117	2.305	0.257
Li ⁺	1.228	0.077	0.940	0.237
Na ⁺	1.010	0.074	0.957	0.215
O	-1.175	0.979	3.620	1.713

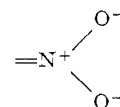
TABLE II
BASE PARAMETERS

Acid	E_B	Std error	C_B	Std error
F ⁻	134	...	15	...
Cl ⁻	105.80	5.87	21.07	3.37
Br ⁻	92.86	6.23	28.30	3.73
I ⁻	80	...	37	...
CN ⁻	93.43	8.44	40.70	5.05
OH ⁻	120.25	7.22	31.93	4.08
H ⁻	86.82	11.96	63.51	7.12
CH ₃ ⁻	95.27	9.03	51.66	5.44
C ₆ H ₅ ⁻	92.08	8.58	47.95	5.16
-NO ₂ ⁻	65.14	7.09	36.89	4.13
NH ₂ ⁻	99.55	26.02	47.08	18.36
CO	0.83	16	35.16	11.37

evaluated by a least-squares fit to the dissociation heats given in Table III. Table III contains 105 heats, of which 78 are independent and of which 22 would be sufficient to determine the E and C parameters for the 26 acids and bases in Tables I and II. Inasmuch as the parameters are "overdetermined," the deviations between the experimental and calculated heats are a measure of the adequacy of eq 1 for predicting heats of dissociation. The weighted⁵ average error in Table III is ± 3.9 kcal/mol; because many of the heats of formation of the adducts are uncertain by more than this amount, we take this average error as an endorsement of eq 1. The heats in Table III range from 61 to 519 kcal/mol; the average *percentage* error is comparable to that found by Drago and Wayland for much weaker adducts.

Several acid-base combinations for which the dissociation heats are known have been omitted from Table III because of anticipated abnormal weaknesses in the adduct bonds. Adducts which dissociate by the cleavage of bonds between nitrogen, oxygen, or

fluorine atoms with lone-pair electrons have been omitted because of the expected lone pair-lone pair repulsions.^{6,7} The H⁺ + H⁻ combination has been omitted because, in H₂, proton-proton repulsion prevents good overlap of the two 1s orbitals, whereas, in the bonds of hydrogen to other elements which use orbitals having considerable p character, good overlap of the hydrogen 1s orbital is achieved.⁷ The NO₂⁺ + NO₂⁻ combination has been omitted because the -NO₂ group in N₂O₄, unlike most -NO₂ groups, cannot have a resonance contribution of the type



In Table IV, the experimental dissociation heats for these adducts may be compared with the heats calculated using the parameters from Tables I and II. As expected, most of the experimental values are smaller than the calculated values. We did not anticipate that, in the cases of NO⁺ + F⁻ and NO⁺ + OH⁻, the reverse would be true. Perhaps these adducts are sufficiently stabilized by contributions from the resonance structures ⁺F=NO⁻ and HO+=NO⁻ to more than overcome the destabilizing effects of lone pair-lone pair repulsion. Of course, deviations between the experimental and calculated values are not necessarily indicative of either abnormal bonding or experimental error. For example, in the case of Cl⁺ + Cl⁻ (for which there is no obvious reason to expect either significant experimental error or extraordinarily strong bonding) the experimental heat exceeds the calculated heat by 12.9 kcal/mol.

Calculations

The E_B and C_B parameters of F⁻ and I⁻ were assigned arbitrary fixed values in order to ensure the existence of just one set of E and C parameters for the acids and bases.⁸ The fixed values were chosen with $E_{F^-} > E_{I^-}$ to suggest relatively greater electrostatic interaction for fluorides and with $C_{I^-} > C_{F^-}$ to suggest relatively greater covalent interaction for iodides. (However these interpretations are not necessarily meaningful and are not justified by the success of the method.) The Fortran computer program ORGLS was used to adjust the parameters to obtain a least-squares fit to the set of experimental heats.⁹

Table III includes thermal data for 37 adducts of the following acids and bases: F⁺, F⁻, Cl⁺, Cl⁻, Br⁺, Br⁻, I⁺, I⁻, CN⁺, CN⁻, OH⁺, OH⁻, H⁺, H⁻, CH₃⁺, CH₃⁻, C₆H₅⁺, C₆H₅⁻, NO₂⁺, NO₂⁻. For each of these adducts, heats are given for dissociations into two different pairs of acids and bases. For example, ClF can

(6) C. A. Coulson, "Valence," Oxford University Press, London, 1952, pp 178-179; R. S. Mulliken, *J. Amer. Chem. Soc.*, **77**, 884 (1955); F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed. Interscience, New York, N. Y., 1966, p 379.

(7) W. L. Jolly, *Inorg. Chem.*, **3**, 459 (1964).

(8) Four parameters must be arbitrarily specified to obtain a single least-squares set of E and C values. If fewer than four parameters are arbitrarily specified, an infinite number of solutions are possible. Drago and Wayland³ in effect fixed four parameters by setting $E_A = C_A = 1.00$ for iodine and $E_B = \nu\mu$ and $C_B = \alpha R_D$ for a set of amines. Although the choice of arbitrary parameters affects the resulting values of the other parameters, it in no way affects the fit of the experimental and calculated values.

(9) W. R. Busing and H. A. Levy, "ORGLS, a General Fortran Least Squares Program," Report ORNL-TM-271, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 1962.

(4) No attempt was made to make the E and C parameters consistent with those reported by Drago and Wayland.³ By combining their data, our data, and a few data not included in Table III into one large matrix, it would be possible to derive a common set of parameters, but the overlap between the two main sets of data would be so poor that the predicted dissociation heat of an adduct of an acid from one set and a base from the other set would be extremely unreliable.

(5) See the Calculations section for a discussion of the method of weighting the data based on their redundancy.

TABLE III
 EXPERIMENTAL AND CALCULATED DISSOCIATION HEATS FOR GASEOUS LEWIS ACID-BASE ADDUCTS

Acid	Base	Heat, kcal/mol		Wt. ^a g	Ref ^b	Acid	Base	Heat, kcal/mol		Wt. ^a g	Ref ^b
		Exptl	Calcd					Exptl	Calcd		
F ⁺	Cl ⁻	375	383.4	0.635	<i>c</i>	H ⁺	F ⁻	366	370.6	0.635	
	Br ⁻	387	381.8	0.635			Cl ⁻	329	321.7	0.635	
	I ⁻	397	387.3	0.635			Br ⁻	319	313.4	0.635	
	H ⁻	519	528.1	0.635			I ⁻	313	309.8	0.635	
	CH ₃ ⁻	495	496.2	0.635	<i>d</i>		CN ⁻	352	353.9	0.635	<i>f</i>
	C ₆ H ₅ ⁻	469	470.5	0.635	<i>d</i>		OH ⁻	390	390.9	0.635	
Cl ⁺	-NO ₂ ⁻	357	346.5	0.635	<i>d, e</i>	CH ₃ ⁻	391	392.9	0.635	<i>d</i>	
	F ⁻	277	281.3	0.635	<i>c</i>	C ₆ H ₅ ⁻	368	373.5	0.635	<i>d</i>	
	Cl ⁻	270	257.1	1.000		NH ₂ ⁻	390	388.8	1.000	<i>d</i>	
	Br ⁻	269	262.8	0.635		CO	119	113.0	1.000		
	I ⁻	278	274.3	0.635		CH ₃ ⁺	F ⁻	262	253.9	0.635	
	CN ⁻	314	310.9	0.635	<i>f</i>	Cl ⁻	220	223.8	0.635		
	OH ⁻	317	322.5	0.635	<i>g</i>	Br ⁻	212	221.3	0.635		
	H ⁻	384	386.3	0.635		I ⁻	210	222.7	0.635		
	CH ₃ ⁻	355	355.5	0.635	<i>d</i>	CN ⁻	257	253.7	0.635	<i>f</i>	
	C ₆ H ₅ ⁻	338	336.1	0.635	<i>d</i>	OH ⁻	274	274.7	0.635		
	-NO ₂ ⁻	243	249.0	0.635	<i>d, g</i>	H ⁻	311	300.8	0.635		
Br ⁺	F ⁻	257	256.4	0.635		CH ₃ ⁻	287	284.4	1.000	<i>d</i>	
	Cl ⁻	237	232.2	0.635		C ₆ H ₅ ⁻	270	269.9	0.635	<i>d</i>	
	Br ⁻	237	235.5	1.000		-NO ₂ ⁻	199	198.4	0.635	<i>d, g</i>	
	I ⁻	243	243.7	0.635		NH ₂ ⁻	278	279.7	1.000	<i>d</i>	
	CN ⁻	274	276.5	0.635	<i>f</i>	CO	82	90.5	1.000		
	OH ⁻	285	289.8	0.635	<i>g</i>	C ₆ H ₅ ⁺	F ⁻	246	243.9	0.635	
	H ⁻	342	339.9	0.635		Cl ⁻	213	215.7	0.635		
	CH ₃ ⁻	315	314.7	0.635	<i>d</i>	Br ⁻	205	214.0	0.635		
	C ₆ H ₅ ⁻	298	297.8	0.635	<i>d</i>	I ⁻	201	216.1	0.635		
	F ⁻	225	223.4	0.635		CN ⁻	250	246.0	0.635		
	Cl ⁻	204	201.2	0.635		OH ⁻	274	265.3	0.635		
I ⁺	Br ⁻	201	202.9	0.635		H ⁻	298	293.2	0.635		
	I ⁻	205	208.7	1.000		CH ₃ ⁻	280	276.4	0.635	<i>d</i>	
	CN ⁻	231	237.0	0.635	<i>f</i>	C ₆ H ₅ ⁻	267	262.2	1.000	<i>d</i>	
	H ⁻	294	289.3	0.635		-NO ₂ ⁻	187	192.9	0.635	<i>d</i>	
	CH ₃ ⁻	271	269.0	0.635	<i>d</i>	NH ₂ ⁻	273	271.5	1.000	<i>d</i>	
	C ₆ H ₅ ⁻	252	254.7	0.635		NO ₂ ⁺	F ⁻	187	187.1	0.635	<i>e</i>
	Cl ⁻	338	339.3	0.635		Cl ⁻	171	176.2	0.635	<i>g</i>	
	Br ⁻	330	330.8	0.635		OH ⁻	231	224.9	0.635		
	I ⁻	329	327.5	0.635		CH ₃ ⁻	262	259.4	0.635	<i>d, g</i>	
	CN ⁻	374	374.0	1.000	<i>f</i>	C ₆ H ₅ ⁻	240	244.6	0.635	<i>d</i>	
	H ⁻	431	434.1	0.635		NO ⁺	Cl ⁻	164	159.7	1.000	
CN ⁺	CH ₃ ⁻	416	415.6	0.635	<i>d</i>	Br ⁻	159	162.8	1.000		
	C ₆ H ₅ ⁻	399	395.0	0.635	<i>d</i>	H ⁻	244	237.6	1.000		
	NH ₂ ⁻	410	411.0	1.000	<i>d, h</i>	CH ₃ ⁻	227	219.2	1.000	<i>d</i>	
	Cl ⁻	275	273.3	0.635	<i>g</i>	-NO ₂ ⁻	132	153.5	1.000	<i>d</i>	
	Br ⁻	275	277.7	0.635	<i>g</i>	F ⁻	178	178.6	1.000	<i>i</i>	
	H ⁻	403	402.4	0.635		Cl ⁻	148	149.7	1.000	<i>i</i>	
	CH ₃ ⁻	367	372.1	0.635	<i>d</i>	Br ⁻	142	140.6	1.000	<i>i</i>	
	C ₆ H ₅ ⁻	357	352.0	0.635	<i>d</i>	I ⁻	137	133.0	1.000	<i>i</i>	
	-NO ₂ ⁻	261	260.4	0.635	<i>d</i>	H ⁻	164	166.3	1.000		
						Na ⁺	F ⁻	148	149.7	1.000	<i>i</i>
						Cl ⁻	128	127.0	1.000	<i>i</i>	
					Br ⁻	122	120.9	1.000	<i>i</i>		
					I ⁻	118	116.2	1.000	<i>i</i>		
					H ⁻	147	148.5	1.000	<i>i</i>		
					O	H ⁻	126	127.9	1.000		
						CH ₃ ⁻	74	75.0	1.000	<i>d</i>	
						-NO ₂ ⁻	61	57.0	1.000	<i>d, j</i>	
						CO	127	126.3	1.000		

^a See footnote 5. ^b When no reference is cited, the source of data is Document No. NSRDS-NBS 26, National Standard Reference Data System, U. S. National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., June 1969. ^c U. S. National Bureau of Standards Report 10074, U. S. Government Printing Office, Washington, D. C., July 1, 1969. ^d G. R. Freeman, *Radiat. Res. Rev.*, 1, 1 (1968). ^e "JANAF Thermochemical Data," The Dow Chemical Co., Midland, Mich., 1969. ^f J. Berkowitz, W. A. Chupka, and T. A. Walter, *J. Chem. Phys.*, 50, 1497 (1969). ^g S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965). ^h J. D. Salley and J. B. Gray, *J. Amer. Chem. Soc.*, 70, 2650 (1948); "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 6, 2nd ed, Interscience, New York, N. Y., p 560. ⁱ G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, "Thermodynamics," 2nd ed, McGraw-Hill, New York, N. Y., 1961. ^j T. C. Waddington, *Advan. Inorg. Chem. Radiochem.*, 1, 157 (1959); H. F. Cordes and N. R. Fetter, *J. Phys. Chem.*, 62, 1340 (1958).

be dissociated into either Cl⁺ + F⁻ or F⁺ + Cl⁻. If heats were available for only one of each pair of dissociations, the heats for all the remaining 37 dissociations could be calculated by use of just 10 supplementary heats, *i.e.*, the heats for the ionization processes F⁻ → F⁺ + 2e⁻, Cl⁻ → Cl⁺ + 2e⁻, etc. Thus 27 of the

total of 74 dissociation heats are redundant. In other words, 27 of the heats are calculable from the other 47 heats. To account for this redundancy, we have weighted each of the 74 heats in this category by the factor ⁴⁷/₇₄, or 0.635.

A matrix (in which the columns correspond to various

TABLE IV
EXPERIMENTAL AND CALCULATED DISSOCIATION HEATS
FOR ADDUCTS EXPECTED TO BE ABNORMALLY WEAK

Acid	Base	— ΔH , kcal/mol—		Ref ^a
		Exptl	Calcd	
F ⁺	F ⁻	356	431.7	
OH ⁺	OH ⁻	311	341.5	
OH ⁺	NH ₂ ⁻	333	362.2	<i>b</i>
NO ⁺	F ⁻	185	175.4	<i>c</i>
NO ⁺	OH ⁻	220	200.0	<i>c</i>
H ⁺	H ⁻	399	410.0	
NO ₂ ⁺	NO ₂ ⁻	148	182.2	<i>b</i>

^a See footnote *b*, Table III. ^b See ref *d* and *g*, Table III. ^c D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat Bur. Stand. (U. S.), Tech. Note*, No. 270-3 (1968).

bases and the rows to various acids) of dissociation heats which can be correlated by eq 1 has the property that all minor determinants of order greater than 2 are zero. This property affords a very convenient method for quickly determining whether or not a given matrix of heats can be satisfactorily correlated by eq 1.

All the parameters in Tables I and II are positive except the E_A value for atomic oxygen. Two questions arise regarding this fact. (1) By a suitable choice of the arbitrarily fixed parameters, can all the parameters be made positive? (2) What is the significance of a negative parameter? It can be shown that, for our set of parameters, the answer to the first question is no. An infinite number of sets of parameters giving an equally good fit can be derived by application of the transformation equations

$$\begin{aligned} E_A' &= aE_A + bC_A \\ C_A' &= cE_A + dC_A \\ E_B' &= (dE_B - cC_B)[1/(ad - bc)] \\ C_B' &= (aC_B - bE_B)[1/(ad - bc)] \end{aligned}$$

where $ad - bc \neq 0$. If we specify that $E_A' > 0$, $E_B' > 0$, $C_A' > 0$, and $C_B' > 0$ for all the species in the set and that $E_A < 0$ for one particular acid, it can be shown that one of the following two relations must hold for the species

$$\begin{aligned} \frac{C_B}{E_B} &> -\frac{E_A}{C_A} \\ \frac{C_A(X)}{|E_A(X)|} &> \frac{E_B}{C_B} \end{aligned}$$

where $C_A(X)$ and $E_A(X)$ refer to the particular acid. If neither of these relations holds for all the species, the parameters cannot all be positive. Such is the case for our data.

The second question, regarding the significance of the negative parameters, is more difficult to answer. A negative E_A value probably is acceptable whenever it is to be combined with a positive E_B value, but we doubt that combination of a negative E_A value with a negative E_B value is meaningful. Probably it is impossible to apply eq 1 to both ion-ion and neutral-neutral acid-base adducts with a common set of parameters. This limitation of eq 1 may be a consequence of the fact that in ion-ion adducts the ionic contribution to bonding is a "no-bond" contribution (*e.g.*, Na⁺Cl⁻) and the nonionic contribution is covalent (*e.g.*, Na-Cl), whereas in neutral-neutral adducts the ionic contribution is covalent (*e.g.*, H₃N⁺-B⁻Cl₃) and the nonionic contribution is a "no-bond" contribution (*e.g.*, H₃N BCl₃).

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E and *C* Parameters for Ionic Interactions

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In this article we report an extension of our *E* and *C* equation, used to correlate enthalpies of interaction of neutral acids and bases to ionic Lewis acid-base reactions of the type $M^+(g) + X^-(g) \rightarrow MX(g)$. E_A , E_B , C_A , and C_B parameters are reported for the ions and the trends in these values are reasonable in terms of the earlier qualitative suggestions of the meaning of these parameters. In some instances, new insights into the important factors affecting bond energies are provided. The $C_A C_B$ products give reasonable estimates of the covalent bond energy contributions to the M-X bond. Parameters are evaluated from 93 enthalpies and can be used to predict and correlate the enthalpies for over 180 interactions. Deviations between predicted and calculated enthalpies are observed for systems with substantial contributions to the measured enthalpies from lone pair-lone pair repulsions or π bonding.

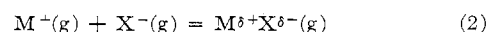
Introduction

We have spent considerable effort correlating enthalpies of neutral donor-acceptor interactions and in this regard have introduced a four-parameter equation (eq 1) which successfully calculates enthalpies for a wide variety of adducts.^{1,2} Soon after our initial success,

$$-\Delta H = E_A E_B + C_A C_B \quad (1)$$

(1) R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, **87**, 3571 (1965).
(2) R. S. Drago, G. C. Vogel, and T. E. Needham, *ibid.*, **94**, 6014 (1972).

we realized that the Lewis acid-base reactions which are described by eq 2 and which can be calculated from



literature data should be amenable to a similar treatment. Of special interest to us was the fact that these enthalpies would have no contributions from condensed phases or solvation effects. The enthalpies for this reaction can be calculated for any compound MX for