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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. Mendelsohn

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 following 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 equation 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 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 parameters,⁴ are listed in Tables I and II. The E and C parameters were 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 equation 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 equation 1. The heats in Table III range from 61 to 519

Table I

Acid Parameters

Acid	E_A	C_A
F^+	2.705	4.618
Cl^+	1.675	3.794
Br^+	1.552	3.231
I^+	1.366	2.688
CN^+	2.537	3.367
OH^+	1.817	3.852
H^+	2.413	3.157
CH_3^+	1.611	2.534
$C_6H_5^+$	1.539	2.513
NO_2^+	1.052	3.082
NO^+	1.051	2.305
Li^+	1.228	0.940
Na^+	1.010	0.957
O	-1.175	3.620

Table II

Base Parameters

Base	E_B	C_B
F^-	134	15
Cl^-	105.80	21.07
Br^-	92.86	28.30
I^-	80	37
CN^-	93.43	40.70
OH^-	120.25	31.93
H^-	86.82	63.51
CH_3^-	95.27	51.66
$C_6H_5^-$	92.08	47.95
$-NO_2^-$	65.14	36.89
NH_2^-	99.55	47.08
CO	0.83	35.16

Table III

Experimental and Calculated Dissociation Heats for
Gaseous Lewis Acid-Base Adducts

Acid	Base	Exptl.	Calcd.	Weight ^a	Ref. ^b
F ⁺	Cl ⁻	375	383.4	0.635	c
	Br ⁻	387	381.8	0.635	
	I ⁻	397	387.3	0.635	
	H ⁻	519	528.1	0.635	
	CH ₃ ⁻	495	496.2	0.635	d
	C ₆ H ₅ ⁻	469	470.5	0.635	d
	-NO ₂ ⁻	357	346.5	0.635	d,e
Cl ⁺	F ⁻	277	281.3	0.635	c
	Cl ⁻	270	257.1	1.000	
	Br ⁻	269	262.8	0.635	
	I ⁻	278	274.3	0.635	
	CN ⁻	314	310.9	0.635	f
	OH ⁻	317	322.5	0.635	g
	H ⁻	384	386.3	0.635	
	CH ₃ ⁻	355	355.5	0.635	d
	C ₆ H ₅ ⁻	338	336.1	0.635	d
	-NO ₂ ⁻	243	249.0	0.635	d,g

Br ⁺	F ⁻	257	256.4	0.635	
	Cl ⁻	237	232.2	0.635	
	Br ⁻	237	235.5	1.000	
	I ⁻	243	243.7	0.635	
	CN ⁻	274	276.5	0.635	f
	OH ⁻	285	289.8	0.635	g
	H ⁻	342	339.9	0.635	
	CH ₃ ⁻	315	314.7	0.635	d
	C ₆ H ₅ ⁻	298	297.8	0.635	d
I ⁺	F ⁻	225	223.4	0.635	
	Cl ⁻	204	201.2	0.635	
	Br ⁻	201	202.9	0.635	
	I ⁻	205	208.7	1.000	
	CN ⁻	231	237.0	0.635	f
	H ⁻	294	289.3	0.635	
	CH ₃ ⁻	271	269.0	0.635	d
	C ₆ H ₅ ⁻	252	254.7	0.635	
CN ⁺	Cl ⁻	338	339.3	0.635	
	Br ⁻	330	330.8	0.635	
	I ⁻	329	327.5	0.635	
	CN ⁻	374	374.0	1.000	f
	H ⁻	431	434.1	0.635	
	CH ₃ ⁻	416	415.6	0.635	d
	C ₆ H ₅ ⁻	399	395.0	0.635	d
	NH ₂ ⁻	410	411.0	1.000	d,h

OH ⁺	Cl ⁻	275	273.3	0.635	g
	Br ⁻	275	277.7	0.635	g
	H ⁻	403	402.4	0.635	
	CH ₃ ⁻	367	372.1	0.635	d
	C ₆ H ₅ ⁻	357	352.0	0.635	d
	-NO ₂ ⁻	261	260.4	0.635	d
H ⁺	F ⁻	366	370.6	0.635	
	Cl ⁻	329	321.7	0.635	
	Br ⁻	319	313.4	0.635	
	I ⁻	313	309.8	0.635	
	CN ⁻	352	353.9	0.635	f
	OH ⁻	390	390.9	0.635	
	CH ₃ ⁻	391	392.9	0.635	d
	C ₆ H ₅ ⁻	368	373.5	0.635	d
	NH ₂ ⁻	390	388.8	1.000	d
CO	119	113.0	1.000		
CH ₃ ⁺	F ⁻	262	253.9	0.635	
	Cl ⁻	220	223.8	0.635	
	Br ⁻	212	221.3	0.635	
	I ⁻	210	222.7	0.635	
	CN ⁻	257	253.7	0.635	f
	OH ⁻	274	274.7	0.635	
	H ⁻	311	300.8	0.635	

	CH_3^-	287	284.4	1.000	d
	C_6H_5^-	270	269.9	0.635	d
	$-\text{NO}_2^-$	199	198.4	0.635	d,g
	NH_2^-	278	279.7	1.000	d
	CO	82	90.5	1.000	
C_6H_5^+	F^-	246	243.9	0.635	
	Cl^-	213	215.7	0.635	
	Br^-	205	214.0	0.635	
	I^-	201	216.1	0.635	
	CN^-	250	246.0	0.635	f
	OH^-	274	265.3	0.635	
	H^-	298	293.2	0.635	
	CH_3^-	280	276.4	0.635	d
	C_6H_5^-	267	262.2	1.000	d
	$-\text{NO}_2^-$	187	192.9	0.635	d
	NH_2^-	273	271.5	1.000	d
NO_2^+	F^-	187	187.1	0.635	e
	Cl^-	171	176.2	0.635	g
	OH^-	231	224.9	0.635	
	CH_3^-	262	259.4	0.635	d,g
	C_6H_5^-	240	244.6	0.635	d

NO ⁺	Cl ⁻	164	159.7	1.000	
	Br ⁻	159	162.8	1.000	
	H ⁻	244	237.6	1.000	
	CH ₃ ⁻	227	219.2	1.000	d
	-NO ₂ ⁻	132	153.5	1.000	d
Li ⁺	F ⁻	178	178.6	1.000	i
	Cl ⁻	148	149.7	1.000	i
	Br ⁻	142	140.6	1.000	i
	I ⁻	137	133.0	1.000	i
	H ⁻	164	166.3	1.000	
Na ⁺	F ⁻	148	149.7	1.000	i
	Cl ⁻	128	127.0	1.000	i
	Br ⁻	122	120.9	1.000	i
	I ⁻	118	116.2	1.000	i
	H ⁻	147	148.5	1.000	i
O	H ⁻	126	127.9	1.000	
	CH ₃ ⁻	74	75.0	1.000	d
	-NO ₂ ⁻	61	57.0	1.000	d,j
	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, Washington, D.C., June 1969.

- ^c U.S. National Bureau of Standards Report 10074, July 1, 1969.
- ^d G. R. Freeman, Radiation Res. Rev., 1, 1 (1968).
- ^e JANAF Thermochemical Data, The Dow Chemical Co., Midland, Michigan, 1969.
- ^f J. Berkowitz, W. A. Chupka, and T. A. Walter, J. Chem. Phys., 50, 1497 (1969).
- ^g S. W. Benson, J. Chem. Education 42, 502 (1965).
- ^h J. D. Salley and J. B. Gray, J. Amer. Chem. Soc., 70, 2650 (1948);
Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., Vol. 6,
Interscience, N. Y., p. 560.
- ⁱ G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, "Thermodynamics,"
2nd ed., McGraw-Hill, 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).

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 H_2 , 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 $NO_2^+ + NO_2^-$ combination has been omitted because the $-NO_2$ group in N_2O_4 , unlike most $-NO_2$ groups, cannot have a resonance contribution of the type $=N^+ \begin{matrix} O^- \\ \diagdown \\ O^- \end{matrix}$. 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 $^+F=N-O^-$ and $H-O^+=N-O^-$ 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.

Table IV

Experimental and Calculated Dissociation Heats
for Adducts Expected to be Abnormally Weak

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

^a See footnote b, Table III.

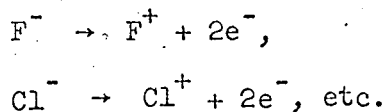
^b See Refs. d and g, Table III.

^c U.S. National Bureau of Standards Technical Note 270-3.

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. 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 OR GLS was used to adjust the parameters to obtain a least-squares fit to the set of experimental heats.⁸

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^- , CH_3^+ , CH_3^- , $C_6H_5^+$, $C_6H_5^-$, NO_2^+ , NO_2^- . For each of these adducts, heats are given for dissociations into two different pairs of acids and bases. For example, ClF can 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



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 bases and the rows to various acids) of dissociation heats which can be correlated by equation 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 equation 1.

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References

- (1) R. S. Mulliken, J. Amer. Chem. Soc., 74, 811 (1952).
- (2) J. O. Edwards, J. Amer. Chem. Soc., 76, 1540 (1954); J. Amer. Chem. Soc., 78, 1819 (1956).
- (3) R. S. Drago and B. B. Wayland, J. Amer. Chem. Soc., 87, 3571 (1965).
- (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.
- (6) C. A. Coulson, "Valence," Oxford, 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, 1966, p. 379.
- (7) W. L. Jolly, Inorg. Chem., 3, 459 (1964).
- (8) W. R. Busing and H. A. Levy, Oak Ridge National Laboratory Report ORNL-TM-271, June, 1962, "OR GLS, A General Fortran Least Squares Program."

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