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The *E*, *C*, and *T* Interpretation of Bond Dissociation Energies and Anion–Neutral Molecule Interactions

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Abstract: Gas-phase enthalpies for anions bonding to neutral acids and enthalpies of dissociation are incorporated into the *E* and *C* model with excellent results. In addition to predicting and interpreting enthalpies, the resulting parameters for anions and radicals provide reactivity scales that can be used to interpret physicochemical properties. Significant chemical insights result from the fit of the data to the *ECT* model. The predicted HSAB basicity order of the anions is not obtained in the gas phase and is shown to result for displacement reactions in water because the hydrogen bonding of water to the anions levels the strength and the electrostatic contribution to their basicity. The parameters from the bond energy fit follow trends with literature estimates of ionic and covalent character. The partial charges in molecules from ab initio calculations are reproduced by trends in the bond energy parameters. It is concluded that no scale of electronegativity, substituted into a difference function, can correlate bond energies to their known accuracy. This new model concludes that polarity is a consequence of the product of the transmittance of the atom at the positive end of the dipole and the receptance of the atom forming the negative end. The electron transfer is further driven by the stabilization of the bond from ionic interactions. One-parameter physicochemical correlations with electronegativity will only be successful under a very limited set of specified conditions. No improvement in the electronegativity parameters will change these conclusions. Differences in electronegativities for atoms (modified herein with more recent data, and those calculated for radicals as described) should mainly be used in the qualitative way that Pauling intended to predict the ionicity of bonds.

Introduction

In recent reports,[1] the *E* and *C* acidity and basicity scale for predicting enthalpies of solution-phase neutral molecule, adduct formation reactions[2]

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

was extended to the calculations of enthalpies of binding neutral bases to gas-phase cations:

$$A^+(g) + B(g) \rightarrow AB^+(g) \qquad (2)$$

In the gas-phase interaction of cations, a considerable contribution to the measured enthalpy results from the transfer of electron density from the base to the cation in addition to the covalent, C_AC_B, and electrostatic, E_AE_B, contributions. This transfer contribution is discussed in the quantum mechanical description of the chemical bond by Kutzelnigg.[3] In the extension of eq 1 to cation–base systems, the transfer energy is accommodated by adding an R_AT_B term:

$$-\Delta H = E_A E_B + C_A C_B + R_A T_B \qquad (3)$$

Here R_A, *the receptance*, identifies the Lewis acid (i.e. the cation) as the receptor of the transferred electron density. The *transmittance*, T_B, determines the extent of the transfer from the base and the product represents the enthalpic stabilization (kcal mol^{-1}) that accompanies the electron transfer into the cation from the base. If one views R_A, as being related to the enthalpic stabilization of the cation per increment of electron density transferred to it, T_B relates to the ease of removing electron density from the base in the presence of the cation.

Electron affinity, EA, and ionization energy, IE, refer to isolated species in the gas phase. In contrast, R_A corresponds to a modified electron affinity of A^+ and T_B relates to a modified ionization energy of *B*. In other words, the receptance and transmittance correspond to modifications in the one-center nuclear–electron attractions from having a neighbor at a bonding distance. In the reported[2] molecular Lewis acid–molecular Lewis base adduct formation correlations, the quantity R_AT_B is defined as zero and any small enthalpic contribution that may exist from a small transfer effect is accommodated in the *E* and *C* parameters. This is not possible with extensive electron transfer.

In this article, extension of this model to gas-phase enthalpy data for the bonding of anions to neutral molecules, $-\Delta H_{A-B^-}$

$$B^-(g) + A(g) \rightarrow AB^-(g) \qquad (4)$$

and to the correlation of bond strengths in molecules, $-\Delta H_D$

$$A^\bullet(g) + B^\bullet(g) \rightarrow AB(g) \qquad (5)$$

is reported.

The successful correlation leads to a quantitative basicity scale for anions and a quantitative reactivity scale for atoms and radicals. The parameters, enable one to predict enthalpies and provide the same chemical insights into these systems as has resulted in the area of donor–acceptor and gas-phase cation–neutral base chemistry.[1,2] This is a significant accomplishment in view of the difficulty in measuring these enthalpies and the underlying fundamental importance of bond strengths in understanding chemical reactivity.

Approach

The approach involves using a pseudo-linearization, least-squares minimization method[4] on literature[5,6] enthalpy data to find the best parameters to fit the enthalpy changes to eq 3. By analogy to fixing reported[2] E_B and C_B parameters in the cation–molecular base fit,[1] known[2] E_A and C_A parameters for molecular acids were fixed in the A–B$^-$ system. The systems are limited in quantity and in the type of acid employed. Thus, even with the known[2] E_A and C_A parameters fixed, a shallow minimum results in the data fit. The analogous situation is discussed[2,7] for molecular acids and bases. An acceptable minimum can be obtained when information from the combined dissociation energy and A–B$^-$ data

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set is used simultaneously. The complication in doing this involves determining which parameters are common to the two different systems.

When an atom, A, reacts with another atom, B, to form a molecule, AB, in which A is the positive end of a polar bond, we shall refer to A as the *catimer*. We expect the same C_A number to apply to both the catimer $A^{\delta+}$ of $A^{\delta+}B^{\delta-}$ and the cation A^+ of AB^+. The range of partial charges on A in most compounds of both systems is limited to 0.3 ± 0.3. Thus, the factors determining the energy of the covalent bonding of A^+ and $A^{\delta+}$ (the energy of the A orbital and its overlap tendencies) should be similar. An atom, B, that reacts to form the negative end of the dipole will be called an *animer*. The charge ranges discussed above also apply to the animer and the corresponding ion, B^- of $A-B^-$. The same C_B value should apply to the tendency of B^- to undergo covalent bonding with a molecular acid and for atomic B to undergo reaction to form $A^{\delta+}B^{\delta-}$.

When similar constraints are placed on both the E_A and E_B parameters, the data are not fit very well. This is expected because of the different functional form for the electrostatic interaction[8] in the four types of systems (neutral adduct formation, eqs 2, 4, and 5). Even the empirical covalent constraints may have to be relaxed as more extensive data become available. The philosophy is not to introduce any more parameters than the mathematical analysis of the data justifies.

The transfer term in the AB^+ fit involves transfer of electron density to the cation from a molecular base (eq 2). The cation behaving as a receptor is expected to involve a different parameter than those for atoms of the same element when it is a catimer and behaves as a transmitter. Transfer of electron density from the catimer A occurs in the opposite direction of that for the cation A^+ reacting with molecular bases.

The above discussion can be summarized by writing the following expressions for fitting gas-phase anion–neutral acid enthalpies, $-\Delta H_{(A-B^-)}$, and bond energies, $-\Delta H_D$

$$-\Delta H_{(A-B^-)} = E_A E_B + C_A C_B + R_A T_B \qquad (6)$$

$$-\Delta H_D = E_{ca} E_{an} + C_A C_B + T_{ca} R_{an} \qquad (7)$$

It should be emphasized that E_{ca}, T_{ca}, E_{an}, and R_{an} are parameters for combinations of atoms or radicals reacting to form ionic or polar molecules in which the polarity is such as to make E_{ca} and T_{ca} correspond to the atom with partial positive charge, i.e. the catimer, and E_{an} and R_{an} to the atom or radical with partial negative charge, i.e. the animer. One cannot use the animer E_{an}, C_B, or R_{an} values for an iodine atom to describe the reaction to form ICl but will need the catimer parameters E_{ca}, C_A, and T_{ca} for iodine. To describe covalent molecules like H_2 or C_2H_6 we will need to combine catimer with animer parameters for the like atoms or radicals bonded. The only major constraint imposed on the data fit involves setting the $C_A C_B$ product of H_2 at 88 kcal mol^{-1} in accord with the valence bond calculation of covalency.[9]

Table I. Parameters for Enthalpies of Dissociation for Catimers (Positive End of Dipole) and Animers (Negative End of Dipole)

catimer[a]	E_{cat}	C_A	T_{cat}
H	8.05	13.03	0.06
Li	6.52	1.45	31.46
K	5.54	0.30	30.67
CH_3	4.90	12.61	1.97
Mg	10.33	0.88	2.29
Al	9.41	4.20	21.04
Mn	3.59	2.70	25.16
$(^5\eta\text{-}C_5CH_3)IrP(CH_3)_3$	3.83	7.37	16.51
Ag*	1.61	3.21	27.45
Hg*	2.12	0.63	0.21
Tl	6.01	1.84	20.39
Ba*	10.85	0.15	14.92
Na*	3.83	1.03	30.01
Rb*	5.93	0.14	29.58
Cu	3.62	6.52	18.90
CH_3CH_2	5.55	11.42	0.55
$C_6H_5CH_2$	3.56	11.55	0.20
CH_3CO*	7.13	8.00	0.20
C_6H_5	8.11	7.59	5.72
Ni	5.02	5.01	18.54
$MoCp(CO)_3$	2.09	7.10	14.08
Cr*	5.89	1.72	20.20
Zn*	4.26	0.10	10.73
I	3.48	6.18	1.93
Br*	1.76	10.01	1.76
Cl*	0.74	13.69	1.04
J_{CH_3}	−1.56	8.87	−2.42

animer[a]	E_{an}	C_B	R_{an}
F	10.00	4.28	2.03
Cl	6.72	3.76	2.10
Br	5.67	3.21	1.87
I	4.03	2.97	1.76
CN*	4.82	6.52	8.02
OH	7.32	4.60	1.62
H	2.23	6.60	0.97
NH_2*	5.29	4.82	0.39
CH_3	4.26	5.42	0.03
CF_3	3.76	5.84	3.69
CCl_3*	3.64	5.10	2.70

[a] Tentative values which were constrained to fit because of a limited data set or large errors in the reported data are indicated with an asterisk.

Results and Discussion

The parameters used in eq 7 to calculate enthalpies in the $-\Delta H_D$ fit are listed in Table I. The parameters to be used in eq 6 for $-\Delta H_{(A-B^-)}$ fit are listed in Table II. Of the 55 enthalpies solved for 30 unknowns in the limited (involving acids with known E_A and C_A parameters) $A-B^-$ data set none of the calculated enthalpies miss the experimental by more than 0.8 kcal mol^{-1}. This is an excellent fit. Upon expansion of the $A-B^-$ data set to 92 enthalpies solved for 50 unknowns, only five enthalpies calculated from the parameters miss experimental by more than 1.1 kcal mol^{-1}. Two misses ($B(C_2H_5)_3Cl^-$ and $Fe(CO)_5OCH_3^-$) are attributed to steric effects in the adduct. The other three all involve Cl^- and could result from errors in reported values by a single investigator or some unknown electronic effect.

The bond energy, $-\Delta H_D$, fit contains 173 data points (enthalpies and coupling constants,[10] vide infra) and 107 unknowns. Considering our model to be accurate to 1 kcal mol^{-1}, very few systems miss the experimental error range by more than 1 kcal mol^{-1}. Of these, two misses are attributed to steric effects (CF_3I and CCl_3Br), four misses are attributed to bond weakening from lone pair–lone pair repulsion (BrF, BrOH, ClF, ClOH), and two misses are attributed to π-bond stabilization (AlF and AlOH). This leaves only four unaccounted misses (KH, NaCl, CuI, and HgCl)

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[8] Since covalency depends upon energy match and overlap considerations, it is reasonable to expect the same C parameters to fit the neutral adducts, cation–neutral base, and anion–neutral acid systems. The electrostatic parameters are more complex, for the E parameters must have a distance function in them. For a dipole–dipole interaction the energy is given by $e^2/(r_A + r_B)^3$. E_A must contain contributions from $e/r_1{}^3$ and E_B from $e/r_2{}^3$ so E_A times E_B gives $e^2/(r_1r_2)^3$ where $(r_1r_2)^3$ approximates $(r_A + r_B)^3$. For a cation–neutral base interaction the ion–dipole energy is given by $e^2/(r_A + r_B)^2$. Using the neutral base parameters, the neutral distance function in E_B is given by $1/r_1{}^3$ and the cation E_A would have a $1/r_2$ distance function with $(r_1{}^3r_2)$ giving the right units for the $(r_A + r_B)^2$ term. The r_2 value will adjust to accommodate $r_1{}^3$ in fitting $1/(r_A + r_B)^2$. The ionic interaction energy has a $1/(r_A + r_B)$ distance function and would be given by $1/r_1$ times $1/r_2$ or $1/r_1r_2$ giving the distance units to approximate $1/(r_A + r_B)$. Thus, if we force the neutral base E parameter $(1/r^3)$ on the system the cation E_A will have to accommodate this with its $1/r_2$ value. The anion will behave in a corresponding fashion with a $1/r_1$ to fit the anion neutrals. These r_1 and r_2 values will not be those needed to fit the $1/(r_A + r_B)$ function for the electrostatic interaction so a new E parameter, E_{cat}, is needed. If one considers the transfer term it is clear that different values are needed for atoms and ions. The energy involved in removing fractional electron density from a hydrogen atom behaving as a catimer is very different from that involved when a neutral base transfers electron density to a proton.

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Table II. Anion–Neutral Fit[a] for Acids and Bases

acid	E_A	C_A	R_A
$\mathit{H_2O}$	1.54	0.13	0.20
$\mathit{SO_2}$	0.56	1.52	0.85
HF^b	2.03	0.30	0.47
HCN^b	1.77	0.50	0.54
$\mathit{CH_3OH}$	1.25	0.75	0.39
$\mathrm{H_2S}^b$	0.77	1.46	0.56
HCl^b	3.69	0.74	0.55
$\mathit{C_6H_5OH}$	2.27	1.07	0.39
$\mathit{(CH_3)_3COH}$	1.36	0.51	0.48
$\mathit{HCCl_3}$	1.49	0.46	0.45
$\mathrm{CH_3CO_2H}^b$	1.72	0.86	0.63
$\mathit{CF_3CH_2OH}$	2.07	1.06	0.38
$\mathit{C_2H_5OH}$	1.34	0.69	0.41
i-$\mathit{C_3H_7OH}$	1.14	0.90	0.46
$\mathrm{PF_3}^b$	0.61	0.36	0.87
$\mathrm{B(OCH_3)_3}^b$	0.54	1.22	0.84
$\mathrm{AsF_3}^b$	1.48	1.14	0.78
$\mathit{C_4H_4NH}$	1.38	0.68	0.48
$\mathrm{Fe(CO)_5}^b$	0.10	0.27	1.00
$\mathrm{CHF_3}^b$	1.32	0.91	0.27
$\mathrm{B(C_2H_5)_3}^b$	1.70	2.71	0.61
base	E_B	C_B	T_B
F^-	9.73	4.28	37.40
Cl^{-b}	7.50	3.76	12.30
Br^{-b}	6.74	3.21	5.86
I^-	5.48	2.97	6.26
CN^-	7.23	6.52	9.20
OH^{-b}	10.43	4.60	50.73
$\mathit{CH_3O}^{-b}$	10.03	4.42	33.77

[a] Acids and anions in italics were employed in the fit of the limited data set. [b] Tentative parameters from limited data.

out of 178 enthalpies. The agreement of the model with experiment is excellent, and at our present level of information, the bonding in these systems is fully consistent with the *ECT* description of the interaction. We shall now proceed to discuss the insights provided by these results.

Anion–Neutral Fit. As a result of this fit, parameters for four new neutral acids and tentative parameters for eleven others are added to our correlation. This enables us to predict over 1000 enthalpies of interaction for these acids with neutral bases and anions in the correlation. Seven new anionic bases (two tentative) have also been added leading to predictions of about 410 enthalpies for binding these anions with acids in the correlation.

The parameters describing the anions lead to some new insights concerning the coordination chemistry of the halides and cyanide. Fluoride is a stronger Lewis base than any other halide. If σ bonding considerations dominate, i.e. there are no unusual repulsive or π effects, fluoride will bind strongest of all the halides to *all* acids because its values of *E*, *C*, and *T* are *all* larger than those of any other halide. This result is in contrast to HSAB predictions which would label F^- hard and I^- soft and predict stronger binding of iodide to soft acids. The failure of HSAB considerations to work on gas-phase adduct-formation data has been previously noted by Larson and McMahon.[5a]

The trend in *E* for the halides parallels the charge/size ratio with that of cyanide being comparable to chloride. Cyanide is the most covalent anion. In plots of the adduct formation enthalpies of two different acids binding to a series of anions, deviations from linearity for $A-CN^-$ systems are attributed to[4a] nitrogen binding in some instances and carbon in others. Since one set of *ECT* parameters fits all the CN^- enthalpies, the same atom is the donor site in all adducts studied. In view of the large *C* value, this donor atom is most probably carbon and the reported[4a] cyanide deviations in the ΔH plots are attributed to variations in the covalent bond contribution[2,7] toward the two different acids plotted. The tendency to undergo covalent bonding in the halides follows the order $F^- > Cl^- > Br^- > I^-$. This is not the order expected on the basis of the anion–acid, HOMO–LUMO energy match estimated from the electron affinities. Overlap considerations also make important contributions to the tendency to undergo covalent bonding. In terms of describing the nature of the interaction, the C/E ratios of the halides are very similar with fluoride being slightly more electrostatic and iodide slightly more covalent.

The trend in the T_B values is inversely proportional to the size of the anions with the tentative value for bromide (only four enthalpies have been measured) deviating slightly. The relation of larger T_B values with smaller size parallels the stabilization expected in the gas phase when the smaller anion can be relieved of some of its excess negative charge. The large T_B value for fluoride does not necessarily imply that it transfers more electron density to acids than the other halides but could result because more stabilization results per unit of electron density transferred. It is the combined contribution of the extent of transfer and the stabilization resulting per unit of electron density transferred that determines the energy of stabilization from electron transfer, R_AT_B. The largest R_A value and the largest C_A/E_A ratio of the well-defined systems are obtained for the acid SO_2 which accepts electron density into a valence shell, low-energy LUMO.

In comparing gas-phase and solution chemistry, we have demonstrated[1b] the necessity of both finding the appropriate model compounds to describe the acid–base chemistry and utilizing the appropriate model reaction. Enthalpy differences in the identical reaction in the two media can then be attributed to solvation. By using this approach, the long-standing anomalies of gas-phase vs solution alkyl amine basicities and of the relative toluene and methanol acidities disappeared.[1b] In a similar fashion, we can increase our understanding of the coordination chemistry of cyanide and the halides in solution. First consider the gas-phase displacement of water from a hydrogen-bonded anion by a covalent acid, e.g. SO_2

$$(H_2O)_n\text{–}B^-(g) + SO_2(g) \rightarrow SO_2\text{–}B^-(g) + (H_2O)_n(g) \quad (8)$$

Enthalpies for this model reaction will give a simplified acid–base component of the complex energetics of the same reaction of the anions in aqueous solution. Since gas-phase studies show that the acidity and basicity of water changes appreciably as the extent of aggregation increases, the parameters for aggregated water in nonpolar solvents[2] are used in this discussion instead of those for gaseous water monomer. Using the reported[2] $E_A = 2.7$ and $C_A = 0.45$ for a water cluster and assuming $R_A = 0.5$, the enthalpy change for various anions binding to water (eq 4 with A equal to water) is calculated and listed in the column $\Delta H_{(H_2O)_n}$ of Table III. Note that the enthalpy contributions for the anions bonding to this water cluster in the gas phase show that fluoride is clearly the strongest base. It is also clearly the strongest base toward the more covalent acid SO_2. Thus, the adduct formation reaction toward both SO_2 and water gives the following donor order: $F^- > CN^- \sim Cl^- > Br^- \sim I^-$. The enthalpy change for the model reaction in eq 8 is given by the third column of numbers. The positive enthalpies for the displacement of water (eq 8) show that the anions are bound stronger to the water cluster than to SO_2.

Table III. Calculated Enthalpy Change for Reactions of B^-

anion B^-	$\Delta H_{(SO_2)}$	$\Delta H_{(H_2O)_n}{}^a$	ΔH_{calc}(eq 6)	ΔH_{calc}(g) $C_A/E_A = 3.5^b$	ΔH_{calc}(disp) $C_A/E_A = 3.5$
F^-	−43.9	−46.9	+3.0	−43.4	+3.5
Cl^-	−20.6	−28.2	+7.4	−26.9	+1.3
Br^-	−13.8	−22.4	+8.6	−20.8	+1.6
I^-	−12.9	−19.2	+6.3	−19.0	+0.2
CN^-	−22.0	−27.0	+5.0	−34.6	−7.6

[a] $E = 2.7$ and $C = 0.45$ from ref 2 and $R = 0.5$ for a water cluster from analogy to alcohols. [b] T assumed equal to 0.5.

However, using the gas-phase enthalpy of the displacement reaction as a criterion for a donor order of these anions toward SO_2 would lead to the order $F^- > CN^- > I^- > Cl^- > Br^-$. The displacement reaction converts CN^- to a basicity almost equal to that of F^-, bromide becomes the weakest base, and chloride becomes a weaker base than iodide. Thus, the acid–base chemistry of the aqueous solution displacement reaction, not solvation, scrambles the gas-phase order.

Instead of SO_2, consider coordination of these anions to a more covalent acid whose $E_A = 1$ and $C_A = 3.5$ with $R = 0.5$. The ΔH (column 6) for binding to this more covalent acid (eq 8) still shows fluoride to be the strongest donor with cyanide next and the same order of anion basicity as that toward $(H_2O)_n$ for the remaining anions. However, the displacement enthalpies for the analogue to eq 8 (listed in the last column of Table III) now gives rise to a gas-phase donor order toward this new acid of $CN^- > I^- > Cl^- - Br^- > F^-$. Note, the specific Lewis acid–base, hydrogen-bonding interactions of water with these anions "levels" the electrostatic contribution of the acid being coordinated and emphasizes its covalent properties. Varying basicity orders result for these anions toward different acids in the aqueous displacement reaction depending upon the C/E ratio of the acid. The order toward the covalent acid ($C/E = 3.5$), the so-called soft order, is not manifested in the adduct formation reaction. It is not observed until the water-displacement reaction, which factors out a large portion of the electrostatic contribution, is considered. Thus, the HSAB concept works in polar solvents because some of the strength and a sizable component of the electrostatic interaction is factored out in the displacement reaction. HSAB does not apply to and should not be offered as an explanation of coordinate bond strengths or bond energies, vide infra. Furthermore, the model must be carefully examined when used in solvents other than water. For example, one can replace water in eq 8 by a solvent molecule with a larger C/E ratio (e.g. 3.5) to "level" the covalent contribution. Under these conditions, F^- reacts stronger than CN^- with covalent (soft) solutes (e.g. SO_2). The fourth column of numbers can be subtracted from the first to give the enthalpy for displacing the anions from a soft solvent by SO_2. Cyanide becomes the weakest base toward the soft acid, SO_2.

Chemistry in solution is a complicated phenomenon with nonspecific solvation and entropy effects making contributions. In the case of the basicity of the anions treated here and in the interpretation of the amine basicities,[1b] acid–base displacement enthalpies of the model gas-phase reaction dominate the trends and produce the observed solution orders. Clearly, understanding coordination chemistry in polar, coordinating solvents involves considering the acid–base chemistry of the appropriate model gas-phase *displacement* reaction. It is misleading to compare solution displacement chemistry to simple gas-phase adduct-formation reactions and attribute the difference to solvation for the reasons illustrated above.

The detailed insights illustrated by the above discussion indicate the advantages of an *ECT* analysis compared to "explaining" differences in solution and gas-phase thermodynamic data with the term solvation or "explaining" trends in the coordination chemistry of acids and bases in solution with the term HSAB. Clearly much interesting chemistry is missed when these terms are accepted as an explanation.

In the design of further experiments in this area, the *ECT* analysis indicates that if data are obtained on one aromatic or aliphatic alcohol, very little further information for characterizing the basicity of an anion is obtained by studying more hydrogen-bonding acids. Such experiments should only be carried out for the purpose of characterizing alcohols.

Bond Energy Fit. The calculated and experimental bond enthalpies show excellent agreement. The reported parameters permit the calculation of the bond energy for 308 systems, 140 of which have not been measured. Except for NH_2 and CCl_3, the animer parameters are well-defined. Though the bond energies of cyanides are limited in number, its C_B parameter is defined with the aid of the substantial data available from the A–B⁻ system. Several catimers have poorly defined parameters because of limited data. The similarity of the F, Cl, Br, I, and OH animers in terms of both R_{an} and C_B/E_B makes it impossible to determine accurate parameters for a catimer from a data set limited to the enthalpies of dissociation of these animers. The most reliable catimer parameters are those determined from accurate enthalpies for bonding to H, CH_3, CN, and at least two halogen animers. Tentative parameters can be used to predict fairly reliable enthalpies of interaction with animers or catimers whose C/E ratio is similar to those used to define the parameters, but may give incorrect predictions for interactions with atoms whose E, C, and T ratios differ from those studied. Tentative parameters may also behave poorly in the correlation of physicochemical properties. As more and better data become available all the reported parameters are subject to change.

(a) **Insights from the Bond Energy Fit.** The electron transfer that occurs in the bond energy systems is different than that in the cation–molecular base or anion–molecular acid systems. In the former, cations gained electron density, and in the latter, anions lost electron density. In the dissociation energy fit, T and R correspond to the electron transfer that occurs when atoms react to form molecules. Catimers give up electron density and animers gain electron density. In this system, receptance refers to the enthalpic demand for electron density by the animer and transmittance to the ease with which electrons are transferred by the catimer to meet this demand. In systems that form ionic products, the transfer term is seen to comprise about 50–60% of the total energy of interaction. This parallels the very extensive amount of electron transfer that occurs. The 103 kcal mol⁻¹ enthalpy of reaction of potassium and chlorine atoms is broken up into $R_{an}T_{cat} = 65$, $C_AC_B = 1$, and $E_{an}E_{cat} = 37$ kcal mol⁻¹.

The T parameters from the fit are not expected to correlate with ionization energies because the proximity of the charged animer formed as a consequence of the transfer modifies the energy required to remove electron density from the catimer. The ionization energy describes an isolated gaseous atom. In a similar way, the proximity of the charged catimer modifies the electron affinity of the animer leading to the quantity described as receptance. As electron density is transferred when two atoms are brought together, the proximity of the animer and catimer facilitates transfer through the electrostatic, covalent, and transfer terms until a minimum energy is attained for the system. At the energy minimum, the transmittance of the partially positive catimer becomes equal to the receptance of the partially negative animer and further electron transfer from the catimer to the animer is endothermic. Recall that the electron affinity of any atom is not exothermic enough to remove an electron from even the most electropositive element. Thus, it is the proximity of the two atoms that leads to electron transfer and causes the $R_{an}T_{cat}$ term to be exothermic.

The trend in C values for the alkali metals varies from 1.45 for Li to 0.1 for Rb as expected for the trend in ionic character. The H, alkyl, I, Br, and Cl catimers all have appreciable covalent bonding with C ranging from 6.2 to 14. The electrostatic contribution to the bonding in a molecule is given by $E_{cat}E_{an}/-\Delta H$. The trends are those expected on the basis of energy match of the bonding orbitals of these catimers with the animers. The electrostatic contribution to the bonding of CH_3F calculated with the above formula from the parameters in Table I is 45%. In the past, the electrostatic counterpart was defined as everything that is not covalent, i.e.

$$\left(1 - \frac{C_AC_B}{\Delta H}\right)100$$

This gives a value of 50% electrostatic bonding in CH_3F. Both agree well with a reported[11] fractional polarity of 47% for this molecule.

The extent of electron transfer (polarity) cannot be gauged directly from the magnitude of $T_{ca}R_{an}$ which reflects the stabilization accompanying transfer. Extensive transfer can accompany a small $T_{cat}R_{an}$ value if the stabilization of the system that results from the accompanying increase in ionic and covalent bonding

Table IV. Estimate of Percent Ionic Character

	$([EE + TT]/-\Delta H_{calc})100$	Pauling[a] dipole moment	NQR studies[11,12]
LiCl	95	69.3	
NaCl	96	70.9	
KCl	99	74.2	99
RbCl	99	74.2	
LiF	95	90.0	
LiBr	95	62.2	
LiI	95	50.2	
LiH	83	30.9	
HF	59	54.2	
HCl	53	20.6	47
HBr	52	13.6	
HI	46	5.2	
HOH	50	39.0	
HCH_3	33	<1	
CH_3F	50	50.2	
CH_3Cl	44	17.1	21
CH_3Br	44	10.1	18
CH_3I	38	3.4	15
CH_3OH	40	34.5	
BrCN	26		10
ICN	45		5
HCN	32		25
BrF	33		47
ICl	54		25

[a] Pauling, L. *The Nature of Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, NY, 1948; p 69.

increases with transfer. Many molecules that contain the hydrogen catimer are seen to have small $T_{cat}R_{an}$ products but large ionic contributions. This results because hydrogen with a large ionization energy has a low transmittance leading to a small energy gain in the $T_{cat}R_{an}$ product as electron density is transferred from the catimer. However, the small size of the proton leads to a large ionic contribution which increases the extent of electron transfer above that manifested by the magnitude of the *energy* given with the $T_{cat}R_{an}$ term.

In order to determine the direction of the polarity of a molecule with *ECT*, e.g. $H^{\delta+}-X^{\delta-}$ vs $H^{\delta-}-X^{\delta+}$, the parameters can be used to calculate the energies of formation of the two polarities using the appropriate animers and catimers. The most stable combination will lead to the correct polarity. For HI, for example, the energy to form $H^{\delta+}-I^{\delta-}$ is calculated to be 71 kcal mol^{-1} and that for $H^{\delta-}-I^{\delta+}$ is 50 kcal mol^{-1}. For IBr, the energies for $I^{\delta+}-Br^{\delta-}$ and $I^{\delta-}-Br^{\delta+}$ are calculated to be 43 and 40 kcal mol^{-1}, respectively. For $H^{\delta+}-{}^{\delta-}CH_3$ and $H^{\delta-}-{}^{\delta+}CH_3$ the energies are 105 and 96 kcal mol^{-1}.

In the classification of molecules as ionic, polar covalent, or covalent, the quantity $C_AC_B/-\Delta H$ is utilized. Values equal to or greater than 0.7 are covalent, those from less than 0.7 to 0.2 are polar covalent, and those less than 0.2 are ionic. Application of this recipe to the compounds formed from the various combinations of animers and catimers produces results consistent with accepted descriptions of molecules.

The *ECT* model is in good agreement with generally accepted trends in ionicity. The comparison of ionic character in a bond is afforded by the ratio of $(E_AE_B + T_AT_B)/-\Delta H$ and values for representative compounds are given in Table IV as the percent ionic character. The ionic character in CH_3X and HX compounds is seen to increase slightly in the order $I^- < Cl^- - Br^- < F^-$. There is no direct measure of ionic character to use as a standard. Pauling's values based on dipole moment and the values based on the Townes–Dailey interpretation of nuclear quadrupole resonance spectroscopy[12,13] are given in Table IV. Pauling's values make bonds more covalent than either *ECT* or NQR. The methyl series is less covalent from *ECT* than from either Pauling or NQR. The trends of ionicity are in good general agreement in all three estimates. The conclusion to be drawn is that the parameters from the data fit show trends that are consistent with the qualitative ideas concerning the covalent–electrostatic nature of bonding. In view of the loose definition of these terms and the wide ranges in other estimates, *ECT* provides as good a quantitative break up of the bond energy as is available.

The systems $CH_3C(O)F$, $CH_3C(O)OH$ and $CH_3C(O)NH_2$ were omitted from the ΔH_D fit because of the possible contributions to the $CH_3C(O)$-X bond energy from π-bonding. Using the parameters of Table I in Equation (7), one calculates 106, 89, and 76 kcal mol^{-1} for the bond energy of these systems compared to experimental values of 119, 106, and 99 kcal mol^{-1}. The deviations (13, 17 and 23 kcal mol^{-1}) support an increased enthalpy contribution from multiple bonding in the expected order F < OH < NH_2. It is also of interest to note that the barrier to C-N bond rotation (breaking the π-bond) in N, N-dimethyl formamide is around[14] 18 kcal mol^{-1}. These exceptions to the fit and the reasonable estimate of the π-bond contribution in amides again support the contention that the parameters contain fundamental bonding information.

(b) *ECT* in the Interpretation of Physicochemical Data. The *ECT* parameters not only have use in predicting and interpreting bond energies but can be used as a reference scale to determine if various physicochemical properties, ΔX, are dominated by the same electronic factors that determine σ bond energies.[2] The use of *ECT* parameters in the analysis of a physicochemical property, involves substituting $\Delta\chi$ for ΔH in eq 7 to produce eq 9. A series

$$\Delta\chi = \text{“}E_{cat}\text{”}E_{an} + \text{“}C_A\text{”}C_B + \text{“}T_{cat}\text{”}R_{an} \qquad (9)$$

of measured properties for an acid, as the base is varied, lead to a series of simultaneous equations (one for each measurement). Substituting reported E_{an}, C_B, and R_{an} parameters for known bases allows one to solve for the best fit values of “E_{cat}”, “C_A”, and “T_{cat}”. The quotes indicate units to give the correct $\Delta\chi$ units for the product terms in a system in which the catimer is held constant. Since three unknowns need to be defined in eq 9, as many animers as possible should be studied. When only a limited number of animers can be investigated, correlations can be attempted in which chemical insight is used to select one or two terms of eq 9 and the interpretation appropriately qualified. If an animer property is studied as the catimer is varied, known catimer values are substituted into eq 9 and the animer values “E_{an}”, “C_B”, and “R_{an}” determined. This type of application can be illustrated with the *ECT* fit of the ^{13}C–H NMR coupling constant, *J*, of CH_3X derivatives. A coupling constant change with electronegativity is predicted[10] with the isovalent hybridization concept. A more electronegative X group causes carbon to use more p orbital in the bond to X and more s orbital in the bond to hydrogen leading to an increase in *J*. The failure to obtain a linear relationship when $J\ ^{13}CH_3$ is plotted versus electronegativity has been attributed[10] to the importance of overlap considerations which work in the opposite direction of the electronegativity. Better overlap of carbon with fluorine than with the larger iodine atom causes carbon to use a more effective bonding hybrid with more s orbital to bond fluorine. This leads to more p character and less s character in the C–H bond and a smaller $J_{^{13}CH_3}$ for CH_3F than CH_3I.

Table VII contains the results of an *ECT* analysis of this data. The correlation employs ΔJ_{CH}, which equals 166.7 – $J_{^{13}CH_3}$, where 166.7 is the J_{CH_3} calculated from $J_{^{13}CH_3} = 500\rho$ for an sp^2 hybrid bond to hydrogen. Thus, larger J_{CH_3} values correspond to smaller ΔJ values. The importance of the *C* term in the *ECT* fit and the opposite sign of *C* compared to *E* and *T* are consistent with the literature interpretation of coupling constant trends. As overlap improves, covalency becomes more important and carbon uses more s character to bond X decreasing J_{CH} or increasing ΔJ_{CH}. Accordingly, “*C*” is positive. As the bond becomes more ionic, more transfer occurs and more p character is used in the bond

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(12) Townes, C. H.; Dailey, B. P. *J. Chem. Phys.* **1949**, *17*, 782. Dailey, B. P. *J. Chem. Phys.* **1960**, *33*, 1641. Whitehead, M. A.; Jaffe, H. H. *Trans. Faraday Soc.* **1961**, *57*, 1854.

(13) Smith, J. A. S., Ed. *Advances in Nuclear Quadrupole Resonance*; Heyden and Sons Ltd.: London; Vol. 1, 1974; Vol. 2, 1975; Vol. 3, 1977.

(14) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

to X, increasing J_{CH} or decreasing ΔJ_{CH}. Accordingly, "E" and "T" are negative.

The interpretation of some chlorine quadrupole coupling constant data was carried out in a similar fashion. The quantity Δe^2Qq was calculated by subtracting the measured values of various compounds from the e^2Qq values of Cl_2. The more ionic the bond, the larger ΔeQq^2 will be. The fit was then carried out using C_{cat}, E_{cat}, and T_{cat} for the various atoms bonded to chlorine. Literature interpretations of these data invoke a complex set of variables to interpret the data including ionic character in the bond as well as s, p, and d orbital participation.[12,13] A much simpler interpretation is obtained by carrying out an *ECT* analysis with C_A, E_{cat}, and T_{cat} parameters of the attached groups. Values of "E_{an}" = 2.91, "C_B" = 0.08, and "T_{an}" = 1.30 result with the interpretation dominated by the E and T contribution. The discrepancies between the calculated and experimental values are about the same as differences in reported values of the quadrupole coupling constants and the magnitude of differences in the gaseous and solid states.[13] The physical picture is one in which transfer and electrostatic bonding drive the electron transfer making the bonding more ionic and decreasing the measured e^2Qq value of chlorine and increasing Δe^2Qq. The covalent contributions are of the order of magnitude of the error in the fit. The literature interpretations[12,13] are much more involved because of omission of the transfer term and because systems in which chlorine is the catimer are combined with those in which it is an animer. Extension of this *ECT* interpretation to other nuclei cannot be assumed, but must be similarly evaluated to determine if the same electronic factors influencing bond energies are determining the spectroscopic trends.

(c) *ECT* and Electronegativity. Since the heat of dissociation was used[15] to establish Pauling's electronegativity scale, *EN*, it is relevant to consider the relationship of *ECT* and *EN*. Electronegativity was originally defined by Pauling[15] as "the power of an atom *in a molecule* to attract electrons to itself". Since it is the property of an atom in a molecule, it obviously differs from the electron affinity or the ionization energy.

A large number of papers have followed[16] which attempted to improve upon Pauling's parameters. Most of these use spectroscopic properties (including ionization energies) of isolated atoms in the gas phase to calculate electronegativities. These approaches can be challenged, because the ionization energy and spectroscopic transitions of a gas-phase atom are modified extensively by having another atom in close proximity. As mentioned earlier, the electron affinity of the most electronegative atom is not exothermic enough to remove an electron from the most electropositive atom. Thus, in the course of atoms combining, the formation of the bond is the factor causing electron transfer. It is surprising that the properties of isolated atoms work as well as they do in reproducing the Pauling electronegativity values derived from the behavior of atoms in molecules.

A major problem is encountered with the electronegativity concept upon extending it to chemical reactivity and bond strengths. One can view the Pauling approach to electronegativities as fitting the observed heats of dissociation to the equation

$$-\Delta H_D = (D_{AA} + D_{BB})/2 + (\chi_A - \chi_B)^2 \qquad (10)$$

A limited data set was selected[17] consisting of atoms whose E, C, and T parameters differ. Two approaches were used to fit the limited data set in Table V to eq 10. In the first case, Pauling's electronegatives (χ_A and χ_B) were substituted into eq 10 and $-\Delta H_D$ calculated. The calculated enthalpies are compared to experimental values in Table V. In the second case, a computer least-squares fit of the enthalpy data was carried out to find the best set of χ values to fit the enthalpies to eq 10 with χ_F set equal to 4.0. The calculated enthalpies using these "best fit electronegativities" are also compared to experimental values in Table V. Since even the best fit χ values do not fit the enthalpies as well as they are known or as well as *ECT* (eq 7, see Table V), we can conclude that there is no set of electronegativities that can be substituted into eq 10 to do any better. Equation 10 as a description of bond energies is vastly inferior to eq 7. The electronegativity model cannot predict the $(\chi_A - \chi_B)^2$ term, i.e. the ionicity in the bond, any better than the bond energy and thus provides a crude measure of relative ionicities. A very important conclusion can be drawn from the results in Table V. *The fundamental view of ionicity and bond stabilization from ionic contributions should not involve an electronegativity difference function but should use the product function, receptance times transmittance.* This is the main difference between *ECT* and *EN*. When two atoms combine the direction of electron flow determines which atom is the catimer and which the animer and accordingly whether transmitter or receptor properties are appropriate. Electron density is transferred until the transfer energy for more electron flow becomes more positive than the corresponding stabilization that would result from a more ionic bond.

In attempts to make electronegativity work other difference functions have and will be proposed. They should be first screened with the data in Table V. Many functions work on a data set limited to halides.[17]

Of course, any equation with three terms will fit data better than one with two terms. However, in this case, neither eq 10 nor the two-term E and C equation (eq 1) can fit the data to the accuracy with which it is known. Thus, the mathematical analysis of the data shows that an electrostatic–covalent model needs the additional transfer contribution to explain bond strengths in a quantitative or qualitative way.

With the above objections to electronegativity applications, we must consider the question, why are electronegativity correlations sometimes successful? The answer to case, question is found in a previous article[18] that discusses the conditions whereby two-parameter scales (e.g. the E_B and C_B base scale) can be converted to one-parameter scales (e.g. $R_{0.n.}$) that work for any system whose C/E ratio is a constant, 0.n. Electronegativity can be viewed as a one parameter scale. The reported Pauling electronegativity values, χ_p, for the halides and hydroxide can be fit to the equation

$$\chi_p = 0.182E_{an} + 1.04R_{an} \qquad (11)$$

The electronegativities calculated by substituting E_{an} and R_{an} from Table I into eq 11 are 3.9 (4.0) for F, 3.4 (3.2) for Cl, 3.0 (3.0) for Br, 2.6 (2.7) for I, and 3.0 (2.3–3.9) for OH^-, with the reported values in parentheses. Thus, any physicochemical property that correlates with these Pauling electronegativities has contributions from transfer and ionic bonding considerations combined in the electronegativity parameters being employed. The catimer ratio of E/R in eq 11 is about 0.2 with $C = 0$. When the above atoms are used in the correlation of a physicochemical property with an E/R ratio of 0.2 and $C \sim 0$, the property will plot up linearly with the one-parameter electronegativity scale. The limited conditions whereby this type of one-parameter application is acceptable and pitfalls in inappropriate use have been described.[18] We continue to maintain that there is no one-parameter scale to universally describe bonding, and physicochemical properties related to it. A full *ECT* analysis is always preferred to any one-parameter analysis.

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(15) Pauling, C. *The Nature of the Chemical Bonds*, 2nd ed.; Cornell University Press: Ithaca, NY, 1948; p 58.

(16) (a) See for example: Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 7821; **1935**, *3*, 573. (b) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264. (c) Sanderson, R. T. *J. Chem. Educ.* **1954**, *31*, 238. (d) Iczkowski, R. P.; Margrave, J. C. *J. Am. Chem. Soc.* **1961**, *83*, 3547. (e) Hinze, J.; Whitehead, M. A.; Jaffe, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148. (f) Bergman, D.; Hinze, J. Electronegativity and Charge Distribution. In *Structure and Bonding*; Sen, K. D., Jorgensen, C. K., Eds.; Springer-Verlag: New York, 1987; Vol. 66. (g) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34, 223. (h) Nagle, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4741.

(17) It is essential in testing any bonding model to employ atoms for which the ratios of the covalent, electrostatic, and transfer parameters are different. Many functions will reproduce the bond energies of the halides because they differ mainly in the magnitude of the interaction and not in the relative importance of transfer, electrostatic, and bonding terms. The data set in Table V is recommended as a first test to evaluate new models for interpreting bond energies.

(18) Drago, R. S. *Inorg. Chem.* **1990**, *29*, 1379.

Table V. Comparison of Enthalpies Calculated with the *ECT* and Electronegativity Models

M–X	expt[a]	*ECT*	electronegativity best fit[b]	electronegativity Pauling
H–CH_3	104.8 (0.1)	104.8	99.5	99.7
H–F	136.3 (0.1)	136.4	137.4	143.8
H–Cl	103.2 (0.1)	103.2	101.9	102.3
H–Br	87.6 (0.1)	87.6	93.4	88.5
H–I	71.3 (0.1)	71.3	80.6	75.1
CH_3–F	108.0 (1)	106.9	102.3	106.7
CH_3–Cl	85.0 (–)	84.5	80.2	80.3
CH_3–Br	70.0 (1)	71.9	72.9	70.1
CH_3–I	57.0 (1)	60.7	64.1	62.3
F–Cl	61.2 (0.1)	68.1[c]	60.8	63.3
F–Br	59.8 (0.2)	64.1[c]	57.0	65.9
F–I	64.9 (lt)	65.2	61.5	77.2
Cl–Br	52.0 (0.2)	53.2	52.3	53.1
Cl–I	50.5 (0.1)	50.7	49.1	53.1
Br–I	42.8 (0.1)	43.2	42.5	43.5
Na–H	44.4 (–)	44.5	88.6	98.4
Na–F	124.0 (–)	103.6	207.5	242.5
Na–Cl	98.5 (2)	92.7	134.2	152.9
Na–Br	78.0 (3)	81.1	122.8	127.4
Na–I	72.7 (2)	71.4	98.9	96.5
Li–H	56.9 (0.001)	54.6	66.3	67.2
Li–F	138.5 (5)	135.2	208.8	239.4
Li–Cl	112.0 (3)	115.3	136.3	151.8
Li–Br	100.1 (5)	100.4	124.9	126.7
Li–I	82.5 (3)	86.0	101.2	96.5

[a] Error limits are reported in parentheses. (lt) = lower limit; (–) no error reported. [b] The Pauling and best fit (in parentheses) χ values are 2.2 (2.30) for H, 2.34 (2.69) for CH_3, 4.0 (4.0) for F, 3.16 (3.25) for Cl, 2.96 (3.19) for Br, 2.66 (2.97) for I, 0.93 (1.21) for Na, and 0.98 (1.23) for Li. [c] Larger than normal lone pair–lone pair repulsions are anticipated.

Table VI. Prediction of ab Initio Charges (δ) with *ECT*

atom-δ	bonded atom	δ ab initio[a]	δ *ECT*	BPI[13]	BPI(*ECT*)
H[b]	CH_3	0.17	0.21[b]	0.03	0.15[g]
	NH_2	0.33	0.26[b]	0.14	0.19[g]
	OH	0.43	0.37[b]	0.27	0.26[g]
	F	0.52	0.51[b]	0.44	0.44[g]
	CN	0.32	0.31[b]	0.17	0.19[g]
	Cl	0.24	0.35[b]		0.24[g]
CH_3	F	0.41	0.35[c]	0.18	0.15[h]
	OH	0.29	0.25[c]	0.09	0.11[h]
	NH_2	0.17	0.24[c]	0.04	0.08[h]
	Cl	0.10	0.17[c]		0.10[h]
	CN			0.05	0.05[h]
Li	H	0.17	0.17[d]	0.42	0.40[i]
	OH	0.61	0.52[d]	0.49	0.56[i]
	F	0.64	0.70[d]	0.73	0.68[i]
	Cl	0.48	0.50[d]		0.73[i]
F[c]	H	0.52	0.54[e]	0.44	0.39[j]
	Li	0.68	0.75[e]	0.73	0.73[j]
	CH_3	0.41	0.35[e]	0.18	0.27[j]
	Cl	0.36	0.06[e]		
	Na	0.70	0.60[e]		
Cl[d]	H	0.24	0.18[f]		
	Li	0.48	0.61[f]		
	CH_3	0.10	0.14[f]		
	Na	0.66	0.53[f]		

[a] Hehre, W. S.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab-initio Molecular Orbital Theory*; Wiley: New York, 1988; pp 337–40. [b] Calculated with $\delta = 0.049E_{an} + 0.008R_{an}$. [c] Calculated with $\delta = 0.052E_{an} - 0.085R_{an}$. [d] Calculated with $\delta = 0.062E_{an} + 0.038R_{an}$. [e] Calculated with $\delta = E_{cat}0.067 + T_{cat}0.011$. [f] Calculated with $\delta = E_{cat}0.022 + T_{cat}0.015$. [g] Calculated with BPI = $0.035E_{an} + 0.003R_{an}$. [h] Calculated with BPI = $0.015E_{an} + 0.002R_{an}$. [i] Calculated with BPI = $0.349R_{an}$. [j] Calculated with BPI = $E_{cat}0.049 + T_{cat}0.013$.

Table VII. Correlation of ^{13}C–H Coupling Constants of CH_3X Compounds with the *ECT* Model and Chlorine Quadrupole Coupling Constants

(A) CH_3X Coupling Constants

CH_3–X	$\Delta J_{^{13}CH_3}$(exptl)[a]	$\Delta J_{^{13}CH_3}$(calc)[b]
–OH	26 ± 1	25.4
–F	18 ± 1	17.5
–Cl	17 ± 1	17.8
–Br	15 ± 1	15.1
–I	16 ± 1	15.8
–CH_3	41 ± 1	41.3
–CN	31 ± 1	30.9
–NH_2	34 ± 1	33.6
–CF_3[c]	37 ± 1	37.0
–CCl_3	33 ± 1	33.0

(B) Cl Quadrupole Coupling Constants

X–Cl	Δe^2Qq(meas)	Δe^2Qq(calc)[d]
BrCl[e]	2.70	8.2
ICl	13.2	13.2
TlCl[e]	46.5	44.1
CH_3Cl	21.4	17.9
ClCl[e]	0.0	1.4
C_2H_5Cl[e]	21.4	17.8
HCl	20.4	24.6
KCl	54.5	56.0
RbCl[e]	54.5	55.7
CH_3COCl[e]	19.1	21.7

[a] $\Delta J_{^{13}CH_3} = 167 - J_{^{13}CH_3X}$. [b] Calculated using "$E_{J(CH_3)}$" = −1.56; "$C_{J(CH_3)}$ = 8.87; "$T_{J(CH_3)}$" = −2.42. [c] Unpublished data meausred by F. Weigert, E. I. DuPont. $\delta^{13}C(CH_3)$ = 20.6, $\delta^{13}C(CF_3)$ = 126.2, J_{CCF} = 32.0, J_{CF} = 272.4, and J_{C-CH} = 6.7. [d] Δe^2Qq(meas) (MHz) = e^2Qq(Cl_2) (54.4) − e^2Qq(XCl) calculated using "E_{an}" = 2.91, "C_B" = 0.08, "T_{an}" = 1.30 for Cl. [e] Tentative parameters, given a weight of 0.4 vs 0.2 for known systems.

It is now widely recognized that electronegativities of atoms in radicals vary with substituent and hybridization.[14e,f,g,16f] The considerable variation in reported[19] values of group electronegativities derived from physicochemical measurements suggests that an assignment of electronegativities from these measurements is not viable. Variation can result when different physicochemical criteria, $\Delta\chi$, are employed because different linear combinations of E_{an}, C_B, and T_{an} (see eq 9) are contributing to the measured property used to derive the group electronegativity. For one-parameter electronegativity correlations, electronegativities of radicals should be calculated[20] with eq 11 using our reported E_B and R_{an} parameters.

(d) Physical Significance of the *ECT* Parameters. The *ECT* model provides a view of ionicity and bond polarity that involves a product function, transmittance times receptance. The stabilization energy from this term combines with the gain in stabilization from ionic bonding to drive the electron transfer and determine the bond polarity. In order to determine if the *ECT* parameters have physical significance in terms of the model proposed, the *ECT* parameters are compared to theoretical estimates of bond polarity. The problems associated with determining charges on atoms and polarity in a molecule have been discussed recently by Allen.[11] A bond polarity index, BPI_{AB}, is described as a new measure of bond polarity. We decided to try to fit both the Mulliken charges and BPI_{AB} to eq 9. With charge and polarity being semiquantitative, a correlation with reported estimates that parallels the reported trends[11] would be acceptable.

Atomic charges obtained from ab initio calculations employing a 6-31G* basis set and the Mulliken charge partitioning scheme were used for $\Delta\chi$ in eq 9. To determine if the animer parameters show trends that determine partial charges, the catimer charges, δ^+, are used as $\Delta\chi$. The charges fit the equation

$$\delta^+_{cat} = E_\delta E_{an} + T_\delta R_{an} \qquad (12)$$

The parameters E_δ and T_δ are characteristic of the catimer and determine the E_{an} and R_{an} contributions to the catimer partial charge. It is gratifying that the value of C_δ of the $C_\delta C_{an}$ term is found to be near zero as expected, and it was subsequently omitted

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(19) Huheey, J. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978; p 171.

(20) Electronegativities calculated with eq 11 lead to H 1.4, CH_3 0.8, CCl_3 3.5, CF_3 4.5, CN 9.2.

in the fit to eq 12. The results of fitting the charges for hydrogen and lithium are given in Table VI where they are compared to the ab initio values. The partial positive charges on the catimers parallel our reported animer parameters. For hydrogen, for example, the E_δ value is 0.049 and T_δ is 0.008 leading to 0.49 and 0.02 contributions from $E_\delta E_{an}$ and $T_\delta R_{an}$, respectively, to the formal charge of HF. The respective contributions of $E_\delta E_{an}$ and $T_\delta R_{an}$ to LiF are 0.44 and 0.35. These results suggest that the energy gained from electrostatic bonding is an important factor in driving the electron transfer and determining the polarity.

The charges on fluorine and chlorine animers, δ^-_{an}, were fit to the equation

$$-\delta^-_{an} = E_{cat}E_\delta + T_{cat}R_\delta \tag{13}$$

where E_δ and R_δ are properties of the animer that determine the contribution the catimer *E* and *T* parameters make to the charge on the animer. The results in Table VI again show that the trends in animer charges parallel those of the catimer parameters. The ionic interaction makes an important contribution to the extent of electron transfer that occurs when atoms interact. The trends in charges for both the catimers and animers are identical with the ab initio results supporting the idea that the parameters from the enthalpy fit not only fit enthalpies but also contain fundamental information concerning the bonding interaction. Equation 12 is expected to predict charges for the other animers in Table II binding to H. Equation 13 can predict charges for the other catimers given in Table II bonding to fluorine. The data sets for chlorine and lithium are limited and the parameters tentative.

In view of shortcomings in the Mulliken population analysis, correlations were attempted next with bond polarity indexes described by Allen.[11c] The BPI_{AB} values, as the criterion of polarity, were substituted into eqs 12 and 13 in place of δ. The best fit of these data is indicated in the BPI-*ECT* column. We conclude that the *ECT* model employing a product function for the transfer term not only predicts enthalpies but also leads to parameters that have meaning consistent with the best theoretical estimates of polarity available. Again, the trends parallel the reported BPI values and have substantial contributions from the electrostatic term.

With *ECT* we have a direct, quantitative, quantum chemistry based[3,21] interpretation of bond strengths. Our analysis has shown that three independent terms are needed. Two will not work and eq 10 gives poor results. The resulting parameters predict the enthalpies of 173 known systems and the trends have meaning in terms of the best theoretical estimates of polarity available. These direct connections to observable and calculated molecular properties constitute the main advantage of the *ECT* model over the chemical hardness approach[22] to reactivity. Bond strengths are of fundamental significance in understanding chemical reactivity. Models and parameters that cannot be substituted into an equation that correlates these quantities are of little use in furthering our understanding of reactivity. The determination of *E*, *C*, *T*, and *R* parameters on the simple systems reported here should encourage quantum mechanical investigations aimed at furthering our understanding of the *ECT* approach and calculating the parameters from theory.

Procedure

The least-squares fitting procedure for determining the parameters from reported enthalpies has been described previously.[1] The bond dissociation energies reported previously[6a] were updated.[6b-e] The weighting scheme for the anion–molecular acid fit assigns a value of 0.2 for data from molecular acid–base systems, 1 for anion–molecular acid enthalpies, and 2 for enthalpies that are reported[5] estimates of interaction. The dissociation energies are weighted according to reported errors. A weight of 1 is assigned if the error is less than 1 $kcal^{-1}$, 2 for errors of 1–1.9 kcal mol^{-1}, 3 for errors of 2–2.9 kcal mol^{-1}, 4.5 for errors of 3–4.9 kcal mol^{-1}, 7.5 for errors of 5–9.9 kcal mol^{-1}, and 10 for errors greater than 10 kcal mol^{-1}. Since many of the ions besides methyl have similar covalent–electrostatic contributions, the methyl weights were assigned lower values than those described above to compensate. In nine instances, where deviations from the fit and from expected trends in the enthalpies suggested that errors or unusual steric or electronic effects may exist, large weights were assigned. The contribution a particular enthalpy makes to the fit is given by $1/(\text{weight})^2$.

A limited data set (indicated in Table I) of anion–molecular acid enthalpies with acids whose E_A and C_A values are known was solved for the unknown parameters in eq 6. The resulting C_B values for the anions are used with our reported[1] C_A values for cations to solve the heat of dissociation data for the unknown parameters in eq 7. Since the C_B values from the limited data, B^-–A fit are tentative, they are entered into the $-\Delta H_D$ fit as enthalpies toward a hypothetical acid, C-acid, with $E = 0$, $C = 1$, and $T = 0$. This technique provides a means of changing these C_B values during the least-squares minimization of the $-\Delta H_D$ data if a better fit of the dissociation energies results. By iterating back and forth between the two data sets, the best combined parameters are found. Two constraints were placed on the enthalpy of formation data set. The C_B value of the animer hydrogen (δ^-) was fixed to give an 86 kcal mol^{-1} C_AC_B contribution to the H_2 enthalpy leaving 18 kcal mol^{-1} to be divided up among the electrostatic and transfer contributions. This constraint corresponds to the valence bond calculation of the covalent contribution to the bond strength of the H_2 molecule.[9] The C_B value for chloride was weighted heavily to make HCl 50% covalent, a value from gas-phase NQR studies. The value of R_{an} for chlorine was set at 2.1 to set the scale for dividing up the $R_{an}T_{cat}$ product. The E_{an} value of fluorine was set at 10 to break up the $E_{cat}E_{an}$ product. These assignments in no way influence the fit and have the same effect as our setting $E_A = 2$ and $C_A = 0.5$ for I_2 in the molecular acid–base fit. The data set for the enthalpies of dissociation is given in Table M1, supplementary material.

In the first fit of the enthalpies of dissociation, negative parameters resulted for a few of the systems for which a limited amount of data are available. It is to be emphasized that negative parameters for bond dissociation energies are meaningless in our model and result because of errors in the limited set of data for the system involved. In the next fit, the negative parameters were constrained to a small positive value with C-base or C-acid etc. The tentative C_A parameters from the cation-base fit were also entered as E-base. After several iterations in which the calculated C-base etc. values were reentered as experimental values in the next fit, these constrained values changed only slightly. It was also noted that the spectroscopic $J_{^{13}C-H}$ values for CH_3–X compounds[10] in which X is an animer are well fit by the animer parameters. Since this is a quantity clearly related to bond strength and bond type, these values were added to the bond energy fit. The final iteration is reported as the final fit in Table M1.

The resulting C_B parameters from the heat of dissociation fit were used in the fit of the limited A–B^- data set. The excellent fit is shown in Table M2. The acid parameters and C_B values from the small A–B^- data set were held fixed and enthalpies for A–B^- systems involving acids or anions with a limited amount of data were added to the fit. Most of these new systems are poorly defined and some gave negative numbers in the data fit. Accordingly, the *C*/*E* ratio for these systems was estimated by analogy to like systems and entered as a constraint. A *C*/*E* ratio of *k* establishes that $C = kE$ which is then substituted into eq 3 to yield: $-\Delta H = E_A(E_B + kC_B) + R_AT_B$. The calculated values of $(E_B + kC_B)$, which we will call k_n, for both CN^- and F^-, were entered as k_n (i.e. $E_B = k_nC = 0$) values into the fit along with the $-\Delta H$ value for the particular anion interacting with the acid. This procedure allows k_n to be adjusted if a better fit of the enthalpy data would result. The parameters from this fit are listed in Table II and the actual fit is given in Table M3, supplementary material. Any acids or bases whose final parameters are influenced by estimates are labeled tentative in tables I and II.

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Supplementary Material Available: Tables giving the dissociation energy fit, the anion–neutral fit, and the extended anion–neutral fit (24 pages). Ordering information is given on any current masthead page.

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