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The Interrelationship of Bond Dissociation Energies and Contributing Bond Energies

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Abstract: The difference between the energy of dissociation of a chemical bond, which breaks a molecule into two fragments, and the contributing bond energy, which is the contribution that that same bond makes to the total atomization energy of the molecule, is the energy of reorganization of any polyatomic fragments formed by the dissociation. A recently developed quantitative theory of polar covalence allows the first simple and accurate calculation of contributing bond energy. This theory is reviewed in brief detail herein, in order to clarify its use in this present study of 76 dissociations of bonds in common molecules. Depending on the kind of data available, it is possible to determine quantitatively the reorganizational energy from the bond dissociation energy and the contributing bond energy or the bond dissociation energy from the contributing bond energy and the reorganizational energy. Reorganizational energies of radicals incapable of rearrangement to form stable molecules present very interesting problems of interpretation for future investigation.

The attractive interactions that hold the atoms of a molecule together are conventionally regarded as somewhat arbitrarily divisible into separate attractions, one between each pair of adjacent atoms. These attractions are known as chemical bonds. The energy required to cause homolytic fission of a chemical bond, or conversely, that is released when such a bond is formed, may be called the bond energy. It has long been recognized that for all but diatomic molecules, the bond energy required to break the molecule into two fragments, at least one of them containing more than one atom, is not the same as the energy assigned to that bond as its contribution to the total atomization energy of the molecule. This paper deals with that difference.

For example, the total atomization energy of gaseous water is 221.6 kcal mol^{-1}. There being no basis for assuming other than exact equivalence between the two O–H bonds in the molecule, the bond energy is obtained as 110.8 kcal mol^{-1} simply by dividing the total atomization energy by the number of bonds. On the other hand, the reaction, $H_2O \rightarrow H + OH$, requires 119.2 kcal mol^{-1}, thus causing the remaining O–H bond to be only $221.6 - 119.2 = 102.4$ kcal mol^{-1}. The value of 110.8 is commonly called the "average bond energy", to indicate how it was obtained. The separate values, 119.2 and 102.4, are called "bond dissociation energies". The purpose of this paper is to attempt to shed new light on the relationship between average bond energies and bond dissociation energies, in a quantitative manner wherever possible.

The term "average bond energy" is unsatisfactory because the energy is roughly applicable to molecules containing more than one kind of bond, wherein averaging would be inappropriate. I suggest substitution of the term, "contributing bond energy", meaning, that part of the total atomization energy which may be considered to be contributed by that particular bond. In other words, the total atomization energy is the sum of all the individual contributing bond energies of the molecule. (The total atomization energy is also, of course, the sum of all the successive bond dissociation energies.)

It is generally and logically assumed that any difference between a contributing bond energy, CBE, and a bond dissociation energy, BDE, for the same bond must arise from reorganization within the fragments formed by the dissociation process. However, this has been mainly a qualitative concept, and a study of recent literature discloses that the distinction is not well understood nor always clearly recognized. Recently developed techniques can provide a clearer and more quantitative insight, as described herein.

For diatomic molecules, there is, of course, no distinction between CBE and BDE. For more complex molecules, the only kind of bond energy susceptible to "direct" experimental measurement is the BDE. In addition, for molecules in which all the chemical bonds are exactly alike, a CBE can easily be determined by dividing the total experimental atomization energy by the number of bonds per molecule, but, for molecules containing unlike bonds, it was necessary until a few years ago to assume, only approximately and not always correctly, that the total atomization energy of the molecule could be represented by summing "standard" bond energies empirically determined, usually as "average bond energies", or by combining such data with energy differences.

That such a scheme works at all is somewhat fortuitous, as will be explained later. However, it is hardly dependable, because of various factors not always recognized, that cause seemingly identical bonds to differ in different environments. Some of the difficulties are illustrated by the following examples. (1) The average bond energy in CCl_4 is lower than would otherwise be expected because of significant bond weakening believed to result from the crowding of the chlorine atoms around the carbon atom; it would therefore be inappropriate to use for something like CH_3Cl. (2) The C═O bond in carbon dioxide is significantly stronger than the C═O bond in a carbonyl derivative of a

Table I. Electronegativities: Pauling and Modified (Pauling, upper, Modified, lower value)

Li	Be		B	C	N	O	F
1.0	1.5		2.0	2.5	3.0	3.5	4.0
0.74	1.99[a]		2.93	3.79	4.49	5.21	5.75
Na	Mg		Al	Si	P	S	Cl
0.9	1.2		1.5	1.8	2.1	2.5	3.0
0.70	1.56		2.22	2.84	3.43	4.12	4.93
K	Ca	Zn	Ga	Ge	As	Se	Br
0.8	1.0	1.6	1.6	1.8	2.0	2.4	2.8
0.42	1.22	2.98	3.28	3.59	3.90	4.21	4.53
Rb	Sr	Cd	In	Sn	Sb	Te	I
0.8	1.0	1.7	1.7	1.8	1.9	2.1	2.5
0.36	1.06	2.59	2.84	3.09	3.34	3.59	3.84
Cs	Ba	Hg	Tl	Pb	Bi		
0.7	0.9	1.9	1.8	1.8	1.9		
0.28	0.78	2.93	1.89 (I)	2.38 (II)	3.16		
			3.02 (III)	3.08 (IV)			

[a] Tentative revision from 2.39.

hydrocarbon although both appear to be represented accurately as normal double bonds. (3) The C—OH bond in an alcohol is about 25-30 kcal mol^{-1} weaker than in a -COOH group, for reasons unpredictable without additional knowledge. The inadequacy of "standard" bond energies is also amply illustrated by the data of Table II, wherein C-H energies are shown to vary, in nine examples, from 94.6 to 99.1; three N-H from 90.1-93.7; nine O-H from 110.6-114.0; two N-N from 31.9-40.0; three P-O from 106.6-120.6, three C-Cl from 82.4-87.3 kcal mol^{-1}, etc. Clearly, reliable reorganizational energies cannot be obtained by use of "standard" bond energies.

The need for such empirical bond energies has fortunately been removed by the recent development of a simple theory of polar covalence which has been successfully applied to the calculation of bond energies.[1] The book describing this theory in detail deals exclusively with contributing bond energies because their relationship to bond dissociation energies was not understood at the time of writing. The present work is based on the concepts and methods of this book, reporting for the first time here how the extension of these ideas leads to a better understanding of bond dissociation energy and therefore of bonding in general. For the convenience of chemists not yet familiar with this reference, the principal features of the new theory and methods will be presented briefly herein. The interested reader is urged to consult the original work[1] for further information.

Polar Covalent Bond Energy. Pauling[2] imagined a polar covalent bond as a nonpolar bond of heteronuclear type in which an additional "ionic" energy, originating from initial electronegativity differences, supplements the total nonpolar covalent energy. He assumed that the nonpolar covalent energy of a heteronuclear bond would be an average of the homonuclear energies of the two atoms and expressed some preference for the geometric mean. The difference between the experimental bond energy and this average was called "ionic" energy and used in the derivation of his well-known electronegativity values.

The methods more recently developed[1] follow Pauling's ideas in a qualitative manner but suggest an important modification of the concept of ionic energy as supplementary. Let us assume two extremes of bond type. In one, the bonding electrons are evenly shared between the two atoms. This, of course, is the covalent extreme. In the ionic extreme, the bonding electrons are monopolized by one of the atoms, causing it to possess unit negative charge and leaving the other atom with unit positive charge. It seems logically inconceivable that the bond could retain its full nonpolar covalent energy, involving the even sharing of the bonding electrons, and, at the same time, or even part of the same time, exhibit any degree of the ionic condition. If the bond is to have any ionic nature at all, this must be at the expense of some of the covalent character. In other words, the ionic energy is not *supplementary* to the total covalent energy. It must *replace a part* of the total covalent energy, so that the residual covalent energy is now less than that of a purely covalent bond. The ionic energy is inherently always larger than that portion of the covalent energy which it replaces. This is why the total bond energy, as a sum of covalent and ionic contributions, is always made greater by ionicity.

This modification of the concept of ionic character in the bonding, which gives greater weight to the ionic contribution and less weight to the covalent contribution than did the concept of Pauling, also calls for an appropriate modification of the electronegativity scale. The modified scale is compared with the more familiar Pauling scale in Table I. It is the modified values that must be used in the bond energy calculations to be described below.

The Calculation of Polar Covalent Bond Energy. A polar covalent bond is treated as a blend of covalence and ionicity. Its total energy, E, is simply the weighted sum of a covalent contribution and an ionic contribution.

$$E = t_cE_c + t_iE_i$$

The nonpolar covalent bond energy, E_c, is easily calculated as the geometric mean of the two homonuclear single covalent bond energies. However, bond energy is closely related to bond length, R_0. A polar covalent bond commonly differs in length from the sum of the nonpolar covalent radii, R_c, being usually shorter. Therefore a correction of covalent bond energy must be made by multiplying it by the factor, R_c/R_0. For the bond A-B

$$E_c = \frac{R_c}{R_0}(E_{A-A}E_{B-B})^{1/2}$$

The ionic bond energy is simply the electrostatic energy between unit electronic opposite charges separated by the bond length

$$E_i = \frac{332}{R_0}$$

The factor, 332, converts the energy per ion pair to kilocalories per mole, when R_0 is in angstrom units.

Of the most vital importance in the calculation of total bond energy for a polar covalent bond is the correct evaluation of the weighting, or blending, coefficients, t_c and t_i. The ionic blending coefficient, t_i, is simply the numerical average of the partial charges on the two atoms

$$t_i = \frac{\delta_A - \delta_B}{2}$$

Since the actual bond is considered to be the sum of the two components, the sum, $t_c + t_i = 1.00$.

The successful calculation of the energies of hundreds of polar covalent bonds thus depends on the validity of the partial charge values. The fundamental principle upon which the concept of partial charge is based is the principle of electronegativity equalization, first published in 1951.[3] This principle is based on the simple concept that electronegativity, being a measure of electron-attracting power, must diminish as negative charge is acquired and increase as negative charge is withdrawn, from a neutral atom. The principle may be stated: when two or more atoms initially different in electronegativity unite to form a compound, they adjust toward an equal, intermediate electronegativity in the compound. A corollary states that the electronegativity in the compound is the geometric mean of the electronegativities of all the component atoms before combination. The mechanism by which electronegativity becomes equalized is uneven sharing of the bonding electrons. As a simple example, in a heteronuclear diatomic molecule, the initially more electronegative atom acquires more than half share of the bonding electrons, thus acquiring a partial negative charge and leaving the other atom with a partial positive charge. The most satisfactory qualitative concept of the meaning of electronegativity was developed by Allred and Rochow:[4] electronegativity is proportional to the coulombic force between an atomic nucleus and an outermost electron, or a foreign electron accommodated within an outermost vacancy. Taking into account the other electrons, this means the force between the *effective* nuclear charge of an atom and an electron at the distance of the covalent radius. Acquisition of partial negative charge means increasing the average electron population around the atomic nucleus. This increases the screening of the nucleus and through increased interelectronic repulsions causes expansion of the electronic sphere with consequent increase in the covalent radius. Thus the effective nuclear charge is reduced and also forced to act over a greater distance, both of which decrease the attractive force which is the electronegativity.

Simultaneously, acquisition of partial negative charge by one atom means electron withdrawal from the other atom, leaving a partial positive charge and decreasing the average electron population around its nucleus. Thus the remaining electronic cloud may be drawn in more closely to the nucleus, and the shielding of the nucleus diminishes, so that the effective nuclear charge not only is greater but also can act over a shorter distance. Both effects increase the force proportional to the electronegativity.

These adjustments in electronegativity must cease when, by virtue of uneven sharing of the bonding electrons, the atoms become equal in electronegativity. The magnitude of the partial charges resulting from such equalization has been estimated on the basis of two assumptions: (1) that the electronegativity of an atom is a linear function of its partial charge, and (2) that the ionicity of NaF is 75%. Both assumptions appear to be confirmed by an abundance of indirect experimental evidence.[1] From these assumptions it has been possible to calculate how much change in electronegativity corresponds to the acquisition of unit charge by each kind of atom for which the electronegativity is known. This change is 2.08 times the square root of the atomic electronegativity. The partial charge is then defined as the ratio of the actual electronegativity change undergone by an atom in becoming part of the compound, to the change corresponding to acquisition of unit electronic charge. Thus the ionic blending coefficient is easily determined.

The approximate validity of empirical "standard" bond energies can now be explained. Any bond in a molecule is affected by the nature of the whole molecule. However, partial charges are nearly compensatory, in that while one becomes more negative, the other becomes less positive, thus maintaining their average, t_i, roughly constant. Therefore the energy of a bond between two particular atoms usually does not change very much unless the bond environment changes rather drastically. However, it can change radically, and the assumption of constancy is not warranted.

It is worth noting here that the homonuclear single covalent bond energy may be thought of as proportional to the coulombic energy of interaction between a bonding electron pair at the distance of the covalent radius, and the effective nuclear charge. It follows that the homonuclear single covalent bond energy, E, and the electronegativity, S, being coulombic energy and force, must be interrelated: $E = CrS$ where C is a proportionality constant related to the type of electronic structure and r is the covalent radius. This relationship exists, but only for the modified electronegativity scale of Table I. Where very accurate homonuclear bond energies are known from experiment, this relationship permits minor correction of electronegativity. The chief importance of this relationship is that it demonstrates that electronegativity is not merely useful in describing heteronuclear bonds, but also it is vital in homonuclear bonding.

Potassium Chloride Molecule. An Example. Both theory and practice can be better understood by means of a simple example. A gas molecule of KCl is selected to illustrate a highly polar bond with no special complications. An atom of potassium is relatively large and diffuse, consistent with having a relatively low effective nuclear charge and only a single outermost electron. Although potassium is largely monatomic in the vapor state, a small concentration of K_2 molecules can be detected. Both bond length and energy have been determined experimentally, as 3.92 Å and 13.2 kcal mol^{-1}. The former corresponds to a nonpolar covalent radius of 1.96 Å. The electronegativity is only 0.42, as expected where a low effective nuclear charge must operate over a relatively large distance. The chlorine molecule, Cl_2, is of course well known. From measurements, the covalent radius of chlorine atom is 0.99 Å, and the homonuclear single covalent bond energy is 58.2 kcal mol^{-1}. In the chlorine atom, the effective nuclear charge is much larger and it operates over a shorter distance, so that the electronegativity is much higher, 4.93. The observed univalence is of course the result of seven outermost electrons, allowing only one outermost half-filled orbital for bonding.

Prediction of a 1:1 combination of potassium and chlorine atoms poses no problem. The initially higher electronegativity of the chlorine atom ensures that the bonding electrons will spend more than half time more closely associated with the chlorine nucleus than with the potassium nucleus. This will impart a partial negative charge to the chlorine, and leave the potassium partially positive. The increase in electron population around the chlorine nucleus will increase the screening of the nucleus, and force expansion of the cloud. Thus the chlorine atom will become larger but less electronegative, since a lower effective nuclear charge must operate over a larger distance. The decrease in electron population around the potassium nucleus will decrease the screening of the nucleus and permit contraction of the cloud owing to reduced repulsions among electrons. Thus the effective nuclear charge will increase and operate over a shorter distance, causing an increase in electronegativity. These adjustments will be complete at the point where the electronegativities have become equal.

The electronegativity within the KCl gas molecule is the geometric mean of the initial electronegativities, which is the square root of the product, 0.42×4.93, or 1.44. In joining the chlorine, the potassium atom thus becomes more electronegative by $1.44 - 0.42 = 1.02$. The change corresponding to unit charge on potassium, 2.08 times the square root of 0.42, is 1.35. By definition, the partial charge on potassium in KCl is therefore $1.02/1.35 = 0.76$. Similarly, the electronegativity of chlorine in KCl has been reduced by $4.93 - 1.44 = 3.49$. Had the chlorine atom become chloride ion, the decrease would have been 2.08 times the square root of 4.93, or 4.62. Hence the partial charge on chlorine, in KCl, is $-3.49/4.62 = -0.76$. Clearly, for this molecule, the ionic blending coefficient t_i is 0.76. (As will be demonstrated presently, the identical value can be obtained from the bond energies, without any dependence whatever on the concepts of electronegativity, equalization, or partial charge.)

These partial charges are equivalent to stating that the average electron populations are now, 18.24 around the potassium nucleus and 17.76 around the chlorine nucleus. As is usually observed for polar bonds, the bond length, R_0, in gaseous KCl is found to be only 2.67 Å, compared to the nonpolar covalent radius sum, R_c, of 2.95 Å. Thus the radial expansion of the chlorine has been exceeded by the radial contraction of the potassium. The author is currently developing a linear relationship between partial charge and reciprocal radius which permits the calculation of the radii of the individual charged atoms, such that their sum represents the bond length.

$$\frac{1}{r} = \frac{1}{r_c} + \delta\left[\Delta\left(\frac{1}{r}\right)\right]$$

In this equation, r is the radius of a combined atom having charge δ, and $\Delta(1/r)$ is the positive difference between $1/r_c$, the reciprocal covalent radius, and $1/r_i$, the reciprocal radius corresponding to unit charge (determined empirically). For potassium, $1/r = 0.510 + 0.587\ \delta$. When δ is 0.76, r is 1.04 Å. For chlorine, $1/r = 1.010 + 0.521\ \delta$, and r is 1.63 Å. The sum is 2.67 Å, equal to the experimental bond length.

Thus the model of polar covalence permits quantitative accounting for bond length. While the chlorine radius increases from 0.99 to 1.63, or by 0.64 Å, the potassium radius decreases from 1.96 to 1.04, or by 0.92 Å, for a net bond shortening of 0.28 Å. The experimental shortening is here 0.28 Å. This method has thus far been successfully applied to more than 120 binary compounds of hydrogen or halogen, covering a complete range in bond polarity.

Since surely all the particles of both atoms must interact, it is of course an oversimplification to assume that the individual atoms retain their individuality so completely. Nevertheless, the inertness of M8 atoms such as argon demonstrates quite clearly that electrons of one atom cannot become significantly attracted to the nucleus of another atom unless the second atom has low energy orbital vacancies into which electrons of the first might be accommodated. This makes it reasonable to neglect the other interactions and concentrate only on the two bonding electrons in the molecule and their effects on the total electronic clouds.

The calculation of the bond energy in the KCl gas molecule may now be completed. If the bond were completely nonpolar, but of the observed bond length, the energy would be

$$E_c = \frac{2.95(13.2 \times 58.2)^{1/2}}{2.67} = 30.8 \text{ kcal mol}^{-1}$$

On the other hand, if the bond were completely polar but of the same length, the energy would be

$$E_i = \frac{332}{2.67} = 124.2 \text{ kcal mol}^{-1}$$

Since the ionic blending coefficient, t_i, is the average of the partial charges, or 0.76, the covalent blending coefficient is $1.00 - 0.76 = 0.24$. The actual calculated total bond energy for the polar bond is then

$$E = t_cE_c + t_iE_i = 0.24 \times 30.8 + 0.76 \times 124.2 = 7.4 + 94.5 = 101.9 \text{ kcal mol}^{-1}$$

The experimental value is 101.6 kcal mol^{-1}.

The only quantity required for this calculation which is not obtained experimentally is the blending coefficient, t_i, derived from electronegativities. This value could also have been obtained from the experimental bond energy and the bond energy equations, by the simple relationship,

$$t_i = \frac{E - E_c}{E_i - E_c} = \frac{101.6 - 30.8}{124.2 - 30.8} = 0.76$$

It is important to realize that this derivation of t_i is completely independent of any assumptions about electronegativity, equalization, or partial charge. It depends only on the validity of the experimental bond energy and the model or polar covalence. Hundreds of similar examples provide convincing support for the entire system of concepts and procedures.

In summary, from a knowledge of the atomic structure, covalent radius, electronegativity, and homonuclear single covalent bond energy of each kind of atom, it is possible to predict the molecular formula and structure of the compound, to calculate the electronegativity within the molecule and the partial charges on the atoms that result from the initial electronegativity difference, to estimate the effect of charge on atomic radius and thus to estimate reasonably accurately the length of the polar bond, and to calculate accurately both the covalent and ionic contributions to the energy of the bond such that their sum equals the experimental bond energy. (In the example of KCl, the condensation of gaseous molecules to a stable nonmolecular solid could also have been predicted, the energy of condensation and thus the atomization energy of the solid could have been calculated quantitatively, and reasonable predictions could have been made concerning the physical and chemical properties of the compound, based on a knowledge of the nature of its bonding and the condition of the atoms in the combination.)

It is this method of calculating contributing bond energies that has made possible the following study of bond dissociation energies. The following modifications may be involved where appropriate. (1) When the partial charge on hydrogen is positive, the homonuclear bond energy of hydrogen must be corrected by a factor which is equal to 1.00 minus the partial charge. (2) If the bond is multiple, then the calculated total energy must be increased by a multiplicity factor (e.g., 1.50 for a double bond). (3) Homonuclear single covalent bond energies of groups M5, M6, and M7 of the periodic table are subject to weakening effects presumed to be caused by nonbonding lone pair electrons. Such effects are reduced not only when bond multiplicity occurs but also in single bonds under certain circumstances detailed in the original reference.[1]

Procedure and Results

In the following work, it was assumed that the sum of the calculated contributing bond energies of all the bonds in the molecule should equal the experimental atomization energy. The consistent existence of such equality was taken as justification for considering each individual calculated bond energy to be essentially correct. Wherever agreement between calculated and experimental atomization energies was somewhat less than nearly perfect (seldom by more than 1-2%), it was deemed appropriate to "correct" the desired calculated bond energy by the factor, experimental/calculated atomization energy.

Data for this study are taken from published compilations,[5-9] and all energies are enthalpies at 25°.

Three kinds of situations were encountered in this study, which included 76 bond dissociations in common molecules. If a fragment from bond rupture was an individual atom, no reorganizational energy was involved. If the fragment was a free radical, however, then the liberated bonding orbital might or might not become absorbed into the total bonding of the fragment. If the radical was capable of reorganizing to form a stable molecule, then this occurred and it was relatively simple to account fully and quantitatively for the experimentally observed BDE, or even to predict it. If the radical was incapable of such reorganization, the effect of liberating a bonding orbital might be zero, exothermic, or endothermic, and the problem of interpretation could not so easily be solved.

There are two ways of defining and calculating the reor-

Table II. Contributing Bond Energies, Reorganizational Energies, and Bond Dissociation Energies (kcal mol^{-1})

	CBE calcd	E_R calcd I	E_R calcd II	BDE calcd (CBE + av E_R)	BDE exptl		CBE calcd	E_R calcd I	E_R calcd II	BDE calcd (CBE + av E_R)	BDE exptl
H–CH_3	99.1	4.1	3.8	103.1	103.2	OC–O	192.1	−64.8	−65.2	127.0	127.3
H–C_2H_5	98.7	−0.7	−1.4	97.6	98.0	OSi–O	152.2	−40.2	−40.2	112.0	112.0
H–C_6H_5	97.3	7	6	104	104	F_3P–O	119.4	5.5	5.5	124.9	124.9
H–$CH_2C_6H_5$	98.7	−14	−14	85	85	Cl_3P–O	120.6	−0.7	−0.7	119.9	119.9
H–CH_2OH	98.7	−7	−6	92	92	Br_3P–O	106.6	12.4	12.4	119.0	119.0
H–CHO	94.6	−18.6	−18.6	76.0	76.0	OCl_2S–O	95.5	0.3	0.3	95.8	95.8
H–$C(O)CH_3$	96.2	−8	−8	88	88	CH_3O–CH_3	82.2	−2.2	−4.5		
H–CH_2COCH_3	98.7	−7	−7	92	92				2.4	80	80
H–$C(O)C_6H_5$	96.7	−23	−23	74	74	C_2H_5O–C_2H_5	81.6	−2.6	−5.9		
H–NH_2	93.4	10.7	10.7	104.1	104.1				3.5	79	79
H–$NHCH_3$	93.7	−2	−2	92	92	C_2H_5–ONO	79.1	−21.4	−5.2		
H–$N(CH_3)_2$	90.1	−4	−5	86	86				−16.2	57.7	57.7
H–OH	111.8	7.4	9.4	120.2	119.2	HO–OH	32.9	18.3	9.1		
H–OOH	111.5	−21.8	−21.9	89.6	89.7				9.1	51.1	51.2
H–OBO	114.4	0.2	−0.5	114.3	114.6	Li–OH	145.0	−39.4	−39.4	105.6	105.6
H–OCH_3	112.6	−10	−10	103	102	Na–OH	123.6	−39.2	−39.4	84.3	84.4
H–OC_2H_5	113.8	−12	−12	102	102	OB–OH	121.9	27.7	15.6		
H–$OC(O)CH_3$	113.6	−2	−2	112	112				12.0	149.5	149.6,
H–$OC(O)C_2H_5$	114.0	−4	−5	109	110						142
H–ONO	110.6	−31.4	−31.7	79.0	79.2,	CH_3–OH	80.7	9.9	−0.3		
					77				10.2	90.6	90.6
H–OF	110.8	8.4	8.4	119.2	119.2	C_2H_5–OH	81.1	9.2	−2.3		
H–SH	87.8	3.3	3.2	91.1	91.1				11.4	90.2	90.3
H–SCH_3	86.6	1.4	1.7	88	88	HC(O)–OH	108.6	−16.7	−25.9		
HC≡CH	188.3	42	20.0						9.2	91.9	91.9,
			20.0	229	230						96 ± 3
$H_2C{=}CH_2$	144.3	31	15.6			$CH_3C(O)$–OH	110.2	−0.7	−11.9		
			15.6	175	175				11.2	109.5	109.5
H_3C–CH_3	83.2	3.4	1.7			ON–OH	51.0	−0.9	−9.5		
			1.7	86.6	86.6				8.2	49.7	50.1
H_5C_2–C_2H_5	83.2	−2.6	−1.3			O_2N–OH	52.8	−3.7	−14.4		
			−1.3	80.6	80.6				11.1	49.5	49.5
H_3C–CHO	84.1	−15.2	0			F–OH	45.9	8.4	8.4	54.3	54.3
			−15.2	68.9	68.9	CH_3–SH	70.4	−0.1	−2.1		
H_5C_2–CHO	83.2	−16.8	−1.0						2.0	70.3	70.3
			−13.1	67.7	66.4	C_2H_5–SH	71.4	−1.3	−4.6		
$CH_3C(O)$–CH_3	84.7	−3.6	−9.6						3.3	70.1	70.1
			3.2	80	81	$CH_3S(O)_2$–CH_3	73.4	−12.8	−16.4		
H_3C–NH_2	71.4	9.5	−1.7						4.3	60.9	60.6
			11.2	80.9	80.9	OB–F	150.9	19.0	19.0	169.9	169.9
H_5C_2–NH_2	72.4	5.2	−0.5			$CH_3C(O)$–F	101.4	−1.8	−1.8	99.6	99.6
			4.6	76.5	77.6	F_2N–F	66.7	−7.2	−7.2	59.5	59.5
CH_3NH–CH_3	72.5	0.5	−0.5			FO–F	48.0	4.3	7.4	53.9	52.3
			1.7	73	73	OB–Cl	105.4	17.7	17.7	123.1	123.1
$(CH_3)_2N$–CH_3	72.5	−3.5	−2.8			Cl_2Al–Cl	102.5	−12.7	−10.2	91.0	89.8
			0.3	70	69	CH_3–Cl	82.4	−0.5	−0.5	81.9	81.9
H_2N–NH_2	40.0	19.2	9.6			C_2H_5–Cl	82.8	−3.6	−1.5	80.2	79.2
			9.6	59.2	59.2	$CH_3C(O)$–Cl	87.3	−9.5	−4.5	80	78
F_2N–NF_2	31.9	−12.0	−6.0			ClO–Cl	49.3	−15.1	−15.1	34.2	34.2
			−6.0	19.9	19.9	CH_3–Br	69.3	−1.0	−1.0	68.3	68.3
FB–O	207.1	−31.7	−31.7	175.4	175.4	C_2H_5–Br	69.5	−4.8	−4.8	64.7	64.7
ClB–O	205.8	−22.5	−22.5	183.3	183.3,	$CH_3C(O)$–Br	70.9	−2.2	−2.2	69	69
					168 ± 8	CH_3–I	54.5	−0.7	−0.7	53.8	53.8
						C_2H_5–I	53.8	−1.5	−1.5	52.3	52.3

ganizational energy of a fragment formed by dissociation of a bond. Method I is to subtract the calculated CBE from the experimental or calculated BDE.

$$E_R = (\text{BDE}) - (\text{CBE})$$

This assumes, of course, that only one of the two fragments is polyatomic. If both are polyatomic, the energy difference is the sum of two reorganizational energies, E_R, which cannot be separately evaluated by this method.

Method II of evaluating E_R is independent of both BDE and CBE, of the dissociated bond. The energy of reorganization of the radical is the difference between the atomization energy of the radical and the sum of the bond energies calculated for the same atoms in the original molecule. This requires, of course, that the atomization energy of the radical be known from experiment. If the radical forms an independent stable molecule, then of course its atomization energy can be calculated, if not known experimentally, as the sum of the calculated contributing bond energies in the molecule. This method can be used to obtain the separate E_R values when the dissociation of the bond forms two different polyatomic radicals. Unfortunately, the methods for contributing bond energy calculation in molecules may be less reliable or inapplicable to bonds in radicals.

The evaluation of E_R may be illustrated by the example of gaseous water. The experimental atomization energy is 221.6 kcal mol^{-1}, corresponding to an average bond energy of 110.8 kcal mol^{-1}, the CBE of an O-H bond in water. The experimental BDE for the reaction, $H_2O \rightarrow H + OH$, is 119.2 kcal mol^{-1}. Thus the value of the reorganizational energy of the hydroxyl radical, for this particular dissociation, is 119.2 − 110.8 = 8.4 kcal mol^{-1}. This is the experimental value of E_R. It means that the above dissociation is made more difficult than expected from the CBE of 110.8, by 8.4 kcal mol^{-1}, because that part of the BDE must be employed in weakening the remaining O–H bond. The calculated CBE in water is 111.8 kcal mol^{-1}. Subtracting this from the experimental BDE of 119.2 gives 7.4 for the calculated E_R by method I. The experimental atomization energy of the hydroxyl radical is 102.4 kcal mol^{-1}, which therefore is the experimental bond energy in O–H. Subtraction from the calculated value of 111.8 kcal mol^{-1} in water gives a calculated E_R of 9.4 kcal mol^{-1} by method II.

The method of calculating bond energy in molecules, applied to the OH molecule, gives 105.0 kcal mol^{-1}, but this of course does not take into account the unknown effect of releasing to the oxygen a bonding orbital with its electron. Evidently the effect results in a weakening of the O–H bond by 105.0 − 102.4 = 2.6 kcal mol^{-1}, in this example.

Table II summarizes the results of the study of 76 bond dissociations, giving the calculated contributing bond energy for the bond dissociated, the values of E_R calculated by both methods I and II, and the value of the bond dissociation energy which would be obtained by addition of the average of the two E_R values to the calculated CBE. The experimental BDE is also tabulated, to show the consistency of the interrelationships.

Discussion and Conclusions

All studies directed toward the theoretical interpretation of thermochemical data are somewhat handicapped by uncertainties in the reliability of some of the experimental data. Within the limits of such reliability, however, one can derive a simple and plausible understanding of the differences between contributing bond energy and bond dissociation energy and thus a better understanding of the latter.

For example, it is now clearly demonstrated that dissociation of hydrogen peroxide into two hydroxyl fragments by breaking the O–O bond requires 51.2 kcal mol^{-1}, despite the O–O CBE of only 32.9 kcal mol^{-1}, because each O–H bond must simultaneously be weakened by 9.2 kcal mol^{-1}. There is no justification for calling the O–O BDE of H_2O_2 the "oxygen–oxygen single bond energy" as though it were a standard value.

A more striking example is provided by the alkali metal hydroxides, in which the condition of the O–H bond is very different from that in water, acids, or alcohols. The partial charge on hydrogen in LiOH is calculated as −0.30. As observed in binary hydrides,[1] highly negative hydrogen appears so highly polarized as to negate any ionicity contribution to its bond energy. Therefore the bond energy is as if the O–H bond were nonpolar, only 63.2 kcal mol^{-1}. The highly polar Li–O bond has a calculated CBE of 145.3 kcal mol^{-1}, making a total calculated atomization energy of 208.5 kcal mol^{-1}, agreeing with the experimental value of 208.

The experimental BDE for the Li–OH bond of gaseous lithium hydroxide is only 105.6 kcal mol^{-1}, compared to the calculated CBE of 145.3. The difference, −39.7 kcal mol^{-1}, is the calculated value of E_R. Alternatively, we may merely note that the O–H bond energy increases from the calculated 63.2 in LiOH to the experimental 102.4 in OH radical. The difference, also a calculation of E_R, is −39.2 kcal mol^{-1}.

Other experimental data needed to support this example were not available, but it was possible to estimate a bond length in Na–OH by adding to the Li–OH length, the experimental difference between bond lengths in gaseous NaCl and LiCl. Then an Na–O energy of 123.6 kcal mol^{-1} was calculated, and the same O–H energy as in LiOH, 63.2, was assumed. The calculated atomization energy is thus 186.8 kcal mol^{-1} for gaseous NaOH. The BDE for Na–OH is then 186.8 − 102.4 = 84.4 kcal mol^{-1}. Although this does not agree closely with an earlier thermochemical estimate of 93, it gives a value of 123.6 − 84.4 = 39.2 kcal mol^{-1}, in agreement with the value of E_R found for OH in LiOH.

It may be concluded from this work that the dissociation of a chemical bond requires quantitatively the contributing bond energy, corrected by the energy of reorganization of the polyatomic fragments formed by the dissociation. The bond dissociation energy may readily be predicted from the knowledge of the contributing bond energies of the undissociated molecule and the atomization energies of the fragments. If the atomization energy of a fragment is unavailable experimentally, it can easily be calculated if it rearranges to a normal molecule.

What is needed next is a quantitative theory of reorganizational energy. We need to learn the fundamental reasons for the observed or calculated reorganizational energies, so that we can understand their exact origin. As but one of many examples to be recognized in Table II, we should be curious as to why the dissociation of an atom of hydrogen weakens the residual bonding in a phenyl radical by about 7 kcal mol^{-1} but strengthens the bonding in a benzyl radical by about 14 kcal mol^{-1}. The empirical reorganizational energies of Table II should serve as a useful basis for a fundamental study, to which the calculation of contributing bond energies can be a valuable tool and asset.

References and Notes

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