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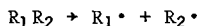
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Résumé. La dissociation d'un lien, $R_1R_2 \rightarrow R_1\cdot + R_2\cdot$, est décrite en tenant compte que dans la molécule les fragments R_1 et R_2 ne sont pas habituellement électriquement neutres à titre individuel, tandis que les radicaux correspondants le sont certainement. On déduit une équation pour l'énergie de neutralisation de charge, ENC, décrivant la neutralisation de R_1 par R_2 . Il en découle une formule pour l'énergie de dissociation, $D^* = \epsilon + ENC + \Delta E_{nl} + RE(R_1) + RE(R_2)$, où ϵ est l'énergie de lien (qui dépend des charges) et ΔE_{nl} est un terme d'interaction entre atomes non liés, les derniers deux termes étant chacun l'énergie de réorganisation d'un fragment neutre devenant un radical. Cette formule est générale. Elle se réduit à $D^* = \epsilon$ pour les molécules diatomiques. Pour un lien à l'"intérieur" d'une molécule (i.e., un lien entre groupes polyatomiques) on obtient $D^* \approx \epsilon + RE(R_1) + RE(R_2)$. Les liens périphériques (e.g., C-X avec X = H, Cl, Br, I) sont décrits par $D^* \approx \text{constante} + RE$. Finalement, les liens impliquant l'"extérieur" d'une molécule (p. ex. les liaisons hydrogène) sont décrits par $D^* = ENC + \Delta E_{nl}$. Bien que les "liens" de ce dernier type puissent être relativement faibles, tout transfert de charge accompagnant leur formation peut déclencher d'importantes modifications dans l'"intérieur" des partenaires liés, se reflétant dans leur réactivité. C'est dans ce contexte que des analyses de populations électroniques et le calcul des énergies de lien qui en dépendent peuvent s'avérer utiles.

Abstract. The problem of bond dissociation, $R_1R_2 \rightarrow R_1\cdot + R_2\cdot$, is addressed from the view point that the fragments, R_1 and R_2 , may not be individually electroneutral in the host molecule, whereas the corresponding radicals certainly are. An expression is derived for the charge neutralization energy, CNE, accounting for the neutralization of R_1 by R_2 . This leads to a new formula for the dissociation energy, $D^* = \epsilon + CNE + \Delta E_{nb} + RE(R_1) + RE(R_2)$, where ϵ is the charge-dependent bond energy, ΔE_{nb} is a small nonbonded contribution and the last two terms are reorganizational energies which measure the relaxation of an electroneutral fragment to yield the final product. This new formula is general. For diatomics it reduces to $D^* = \epsilon$. For a bond in the "interior" of a molecule (i.e. a bond linking sufficiently large groups), the appropriate expression is $D^* \approx \epsilon + RE(R_1) + RE(R_2)$. Peripheral bonds (e.g., C-X with X = H, Cl, Br, I) are described by $D^* \approx \text{constant} + RE$. Finally, bonds involving the "exterior" of a molecule (e.g., hydrogen bonds) are described by $D^* = CNE + \Delta E_{nb}$. Even though the latter "bonds" may be relatively weak, any charge imbalance resulting from their formation is capable of inducing significant modifications in the "interior" of the bonded partners and thus can affect their reactivities. This is where detailed charge analyses and the calculation of charge-dependent bond energies can prove valuable.

INTRODUCTION

The concept of the chemical bond and the energetic aspects governing its dissociation are fundamental to chemistry. The first thing that comes to mind is a cleavage of a molecule into fragments, e.g.,



This process involves the breaking of a chemical bond, in the usual sense of this term. It is one of the topics examined here. In addition, with no change in philosophy, we include in this study the cleavage of other types of bonds, e.g., hydrogen bonds or the bond(s) linking an adsorbate to a substrate. In principle, any dissociation $AB \rightarrow A + B$ is addressed, thus stretching the use of the term "bond cleavage" beyond current practice. As a result, the distinction between recognizable bonded and nonbonded interactions may occasionally become blurred, causing problems of semantics, not of physics.

With this generalization in mind, we must now make a clear distinction between i) the intrinsic energy of a bond (or, simply, bond energy) measuring its contribution to the thermochemical stability of the unperturbed reactant and ii) the bond dissociation energy, i.e., the energy actually required to break that bond. The former, of course, is exclusively viewed as a property of the reactant whereas the latter depends on both the reactant and the final products. Thermochemistry gives access to dissociation energies, but the mental isolation of a bond and its energy is only a matter for theory. Our discussion centers on the relationship between dissociation and intrinsic theoretical (as opposed to empirical) bond energies in order to learn how much of the physics governing dissociation processes can be extracted from a theoretical description of the reactant, thus going beyond a mere consideration of its ground-state bond energies.

Our approach accounts for the important fact that the molecular fragments R_1 and R_2 may not be individually electroneutral while they are part of the host molecule R_1R_2 , whereas each product resulting from the cleavage of the R_1 - R_2 bond is certainly electroneutral. The novelty lies in the straightforward application of this electroneutrality constraint. The emphasis is on the fundamental concepts involved and on an, admittedly incomplete, assessment of future possible developments and applications of the novel views revealed by the present theory.

ENERGY PARTITIONING OF A MOLECULE

It is convenient to begin with molecules where the discrimination between bonded and nonbonded interactions can be made in accord with common practice. Generalizations are made where appropriate. Here we consider all chemical species (isolated molecules or plurimolecular aggregates), before and after cleavage, in their hypothetical vibrationless state, at 0 K. This is not to say that vibrational energies are unimportant, quite on the contrary. The fact is that vibrational, translational and rotational energies are not fairly partitionable among chemical bonds and should, therefore, be treated as separate problems.

The thermochemical measure for what holds the atoms together in a molecule is offered by the difference

$$\Delta E_a^* = \text{energy of all the isolated ground-state atoms} \\ \text{minus the ground-state energy of the molecule}$$

which is the energy required for breaking up that molecule into its constituent atoms. The atomization energy, ΔE_a^* , includes the annihilation of all interactions between atom pairs which are not chemically bonded to one another in the conventional sense, ΔE_{nb} , and the destruction of all chemical bonds ij . The latter are represented by their intrinsic bond energies ϵ_{ij} . Thus

$$\Delta E_a^* = \sum_{i < j} \epsilon_{ij} + \Delta E_{nb} \quad (1)$$

It turns out for "normal" molecules that nonbonded interactions are minor, so that the study of ΔE_a^* essentially reduces to a consideration of bond energies^{1,2}.

The energies associated with the individual bonds depend markedly on the electronic charges carried by the bond-forming atoms, e.g., in a range of ~ 15 kcal mol⁻¹ for CC single bonds. Such charge-dependent bond energies have been successfully used in numerous energy calculations, eq. 1, yielding results well within experimental uncertainties¹⁻³. At this stage, the important point to be kept in mind is that the molecular environment determines the equilibrium charge densities at the individual atoms in a molecule and, hence, the energies of the bonds formed by these atoms. Similarly, the nonbonded contribution, ΔE_{nb} , also depends (albeit slightly) on the distribution of electronic charge in a molecule. Briefly, ΔE_a^* depends both on the total number of electrons of the species under consideration and its detailed charge density profile.

Two important results follow directly from an energy balance made for a reactant R_1R_2 whose atomization energy is $\Delta E_a^*(R_1R_2)$. First we consider the cleavage $R_1R_2 \rightarrow R_1 + R_2$ and the atomization energies of the products R_1 and R_2 , which are $\Delta E_a^*(R_1)$ and $\Delta E_a^*(R_2)$, respectively. The dissociation of the bond linking R_1 and R_2 to one another involves the dissociation energy

$$D^*(R_1-R_2) = \Delta E_a^*(R_1R_2) - \Delta E_a^*(R_1) - \Delta E_a^*(R_2) \quad (2)$$

This definition is general. It covers both typical "strong" chemical bonds and "weaker" ones (e.g., hydrogen bonds), in which case the very definition of chemical bond must be understood in a broader sense.

Alternatively, the following partitioning of $\Delta E_a^*(R_1R_2)$ can be made by reference to eq. 1. The molecule is R_1R_2 . Here we consider all the bonds occurring in R_1 (except the one linking R_1 to R_2) and the nonbonded interactions confined within R_1 . The sum of all these contributions gives $\Delta E_a^*(R_1^{mol})$. This is the part of $\Delta E_a^*(R_1R_2)$ which is associated with the group of atoms R_1 as it exists in that particular molecule R_1R_2 . We proceed similarly with R_2 and obtain $\Delta E_a^*(R_2^{mol})$. The sum $\Delta E_a^*(R_1^{mol}) + \Delta E_a^*(R_2^{mol})$ thus collects the energies of all the bonds found in the molecule except one, that linking R_1 to R_2 , which is $\epsilon(R_1-R_2)$, and all the nonbonded interactions except those occurring between the atoms of R_1 and those of R_2 , i.e., $\Delta E_{nb}(R_1 \cdots R_2)$. The energy balance satisfying eq. 1 is

$$\Delta E_a^*(R_1R_2) = \Delta E_a^*(R_1^{mol}) + \Delta E_a^*(R_2^{mol}) + \epsilon(R_1-R_2) + \Delta E_{nb}(R_1 \cdots R_2) \quad (3)$$

When R_1 and R_2 are identical in the molecule (as in CH_3-CH_3 , for example, but not in $HOH \cdots OH_2$), each of these groups is necessarily electroneutral. Electroneutral groups in a molecule, taken exactly as in $R-R$, are identified by the superscript zero. Under these circumstances, it follows from eq. 3 that

$$\Delta E_a^*(R^0) = \frac{1}{2}[\Delta E_a^*(RR) - \epsilon(R-R) - \Delta E_{nb}(R \cdots R)] \quad (4)$$

which is a useful formula in applications requiring the knowledge of $\Delta E_a^*(R^0)$.

The energy formulas 2 and 3 are straightforward representations of first-principle energy balances. No assumption is involved other than that related to the validity of partitioning the molecular energy into bonded and nonbonded contributions. Eq. 2 features the dissociation energy, $D^*(R_1-R_2)$, and eq. 3 the corresponding intrinsic bond energy, $\epsilon(R_1-R_2)$. Now we examine how these bond terms are related to one another.

THEORY

In order to facilitate the discussion, we start with an example, namely the dissociation of a molecule R_1R_2 into radicals $R_1\cdot$ and $R_2\cdot$ and show at a later stage that this demonstration suffers from no loss in generality.

TABLE 1. Net charges (me) and $\Delta E_a^*(R^{mol})$ energies (kcal mol⁻¹) of methyl, ethyl and isopropyl groups in selected host molecules

R	Host molecule	Net charge	$\Delta E_a^*(R^{mol})$
CH ₃	CH ₄	9.05	314.53
	CH ₃ COCH ₃	3.60	318.45
	CH ₃ CH ₃	0.00	320.34
	CH ₃ C ₂ H ₅	-2.65	322.15
	CH ₃ iC ₃ H ₇	-5.02	323.80
	CH ₃ OCH ₃	-10.47	327.50
C ₂ H ₅	C ₂ H ₅ COC ₂ H ₅	33.6	591.5
	C ₂ H ₅ CH ₃	2.65	610.81
	C ₂ H ₅ C ₂ H ₅	0.00	612.78
	C ₂ H ₅ OC ₂ H ₅	-2.59	615.09
iC ₃ H ₇	iC ₃ H ₇ COiC ₃ H ₇	50.3	875.0
	iC ₃ H ₇ CH ₃	5.02	903.63
	iC ₃ H ₇ OiC ₃ H ₇	3.55	904.50
	iC ₃ H ₇ iC ₃ H ₇	0.00	906.67

The charge analyses are from Ref. 2. The $\Delta E_a^*(R^{mol})$ energies were derived from eq. 1, by means of bond-by-bond calculations of the charge-dependent bond energies and using Del Re's approximation for the nonbonded interactions, as explained elsewhere^{1,2}. Atomization energies of the host molecules, calculated in precisely the same manner, agree within ~ 0.2 kcal mol⁻¹ (average deviation) with their experimental counterparts^{1,2}.

Our central argument rests on a simple but crucial observation concerning any dissociation $R_1R_2 \rightarrow R_1\cdot + R_2\cdot$. The individual fragments (R_1 and R_2) are in general not electroneutral while they are part of the unperturbed host molecule whereas the corresponding radicals certainly satisfy electroneutrality. This, of course, is not a new idea. The novelty lies in the inclusion of this charge re-neutralization in the energy oriented study of a dissociation process. The requirement that electroneutrality constraints should be satisfied is clearly a sound one.

A few simple examples illustrate what we mean (Table 1). They indicate i) to what extent molecular fragments depart from exact electroneutrality and ii) the corresponding response in $\Delta E_a^*(R^{mol})$ energy. This response is significant, even for a relatively small charge imbalance. A fragment increases its thermochemical stability when it gains electronic charge from its environment. $\Delta E_a^*(R^{mol})$ becomes larger. Now we can apply what we have learned from these examples.

We develop our strategy with the help of the examples worked out for the methyl groups. They differ in energy from one another, and we know by how much. Therefore, it suffices to know how any one of them differs from the radical CH₃[•] in order to gain the same information for the other CH₃ groups. A convenient reference is the electroneutral CH₃ of ethane, a choice which permits the association of energy changes with charge neutralization - hence the term CNE = charge neutralization energy. The methyl group of CH₄, for example, is electron deficient by 9.05 me^{1,2}. When recovering that charge, its energy decreases by CNE = -5.81 kcal mol⁻¹ (meaning that $\Delta E_a^*(CH_3)$ increases by that amount). Similarly, when the CH₃ of propane restores its electroneutrality by losing its excess electronic charge, 2.65 me, its energy increases by CNE = 1.81 kcal mol⁻¹. Note that these CNE results include all the effects of geometry changes because they are derived from $\Delta E_a^*(R^{mol})$ energies satisfying eqs. 1, 3 and 4 which hold for molecules at equilibrium geometry and charge density.

The generalization to any group R is straightforward. CNE is a useful concept which permits us to relate any R in a molecule, described by $\Delta E_a^*(R^{mol})$, to the corresponding electroneutral R° , described by $\Delta E_a^*(R^\circ)$. In order to learn how any R (embedded in its host molecule) differs in energy from the radical R^\bullet , it suffices to know once and for all how R° differs from R^\bullet , i.e., the reorganizational energy

$$RE = \Delta E_a^*(R^\circ) - \Delta E_a^*(R^\bullet) \quad (5)$$

The selection of $\Delta E_a^*(R^\circ)$ as a reference is only one of the possible choices. It is arbitrary but convenient because it is the only one agreeing with the idea that it makes sense to first get the number of electrons right, then relax everything else. Having now secured this idea, there is an easy way of exploiting it.

Two radicals are formed in any dissociation $R_1R_2 \rightarrow R_1^\bullet + R_2^\bullet$. For the problem at hand, it is more convenient to consider them jointly rather than proceeding via calculations of the individual CNE contributions, i.e., $\Delta E_a^*(R_1^{mol}) - \Delta E_a^*(R_1^\circ)$ and $\Delta E_a^*(R_2^{mol}) - \Delta E_a^*(R_2^\circ)$. The sum $\Delta E_a^*(R_1^{mol}) + \Delta E_a^*(R_2^{mol})$ differs (in principle) from that of the corresponding electroneutral fragments, $\Delta E_a^*(R_1^\circ) + \Delta E_a^*(R_2^\circ)$. The difference between these sums is CNE, i.e.,

$$\Delta E_a^*(R_1^{mol}) + \Delta E_a^*(R_2^{mol}) = \Delta E_a^*(R_1^\circ) + \Delta E_a^*(R_2^\circ) + CNE \quad (6)$$

Using the energy balance, eq. 3, it follows that

$$CNE = \Delta E_a^*(R_1R_2) - \epsilon(R_1-R_2) - \Delta E_{nb}(R_1 \cdots R_2) - \Delta E_a^*(R_1^\circ) - \Delta E_a^*(R_2^\circ) \quad (7)$$

Equation 7 expresses the important fact that CNE energies depend exclusively on molecular ground-state properties. The atomization energy $\Delta E_a^*(R_1R_2)$ can be obtained from thermochemistry or from calculations. However, the bond energy, $\epsilon(R_1-R_2)$, can only be obtained from theory, as well as $\Delta E_a^*(R_1^\circ)$, $\Delta E_a^*(R_2^\circ)$ (eq. 4) and the less important nonbonded contribution, $\Delta E_{nb}(R_1 \cdots R_2)$. This makes CNE a theoretical quantity. This does not mean that CNE is not a very real quantity. It is a simple reflection of the fact that molecular fragments which are not individually electroneutral in the host molecule must restore their correct numbers of electrons when dissociation occurs.

Equation 7 is important in another way: it is the key equation for the description of bond dissociation energies. Indeed, using the definition of $D^*(R_1-R_2)$, eq. 2, and that of reorganizational energy, eq. 5, it follows from eq. 7 that

$$D^*(R_1-R_2) = \epsilon(R_1-R_2) + CNE + \Delta E_{nb}(R_1 \cdots R_2) + RE(R_1) + RE(R_2) \quad (8)$$

This new energy formula is general and suffers from no approximations in that all the appropriate bonded and nonbonded contributions are taken care of. It is seen that CNE, eq. 7, should not be regarded as just a correction term. Quite on the contrary, this particular form of electroneutrality constraint, eq. 7, is all that is required for deducing the relationship between bond dissociation and intrinsic bond energies. Eq. 8 is exact.

DISCUSSION

The energy formula for $D^*(R_1-R_2)$ contains energy terms, namely $\epsilon(R_1-R_2)$, CNE and $\Delta E_{nb}(R_1 \cdots R_2)$, which depend only on the reactant. However, this formula also contains information about the products, in the form of their reorganizational energies. In other words, there is no way dissociation energies could be predicted exclusively in terms of the reactant's ground-state properties. Though unfortunate, this point must be clear in our minds.

TABLE 2. Selected CNE, CC, CO and CH bond energies, kcal mol⁻¹

R ₁	R ₂	$\epsilon(R_1-R_2)$	CNE
CH ₃	C ₂ H ₅	71.14	-0.16
CH ₃	iC ₃ H ₇	72.42	0.43
C ₂ H ₅	iC ₃ H ₇	73.23	0.36
C ₂ H ₅	tC ₄ H ₉	73.63	0.31
CH ₃ O	CH ₃	71.18	1.88
C ₂ H ₅ O	C ₂ H ₅	79.78	1.00
iC ₃ H ₇ O	iC ₃ H ₇	86.20	-0.38
CH ₃	H	104.86	-5.81
C ₂ H ₅	H	106.81	-9.01
iC ₃ H ₇	H	108.72	-11.08
tC ₄ H ₉	H	110.89	-12.50
cC ₆ H ₁₁	Hequat	109.28	-11.50
CH ₂ :CH	H	105.72	-3.11
CH ₃ CH:CH	H	106.0	-3.9
CH ₂ :C(CH ₃)	H	109.9	-7.1
C ₆ H ₅	H	113.54	-10.97

The results for the hydrocarbons are from Ref. 4 and were obtained from charge-dependent bond energies, for use in eq. 1. The CNE results follow from eq. 7, with nonbonded terms evaluated⁴ by means of Del Re's approximation. The same approach was followed for the ethers, using the charges of Ref. 2. Additional results obtained for the CH₃O, C₂H₅O, C₃H₇O, iC₃H₇O, C₄H₉O and sC₄H₉O alkoxy groups indicate that any of these dissociate from a CH₃ group with CNE + $\Delta E_{nb} \approx 2$ kcal mol⁻¹. Regularities are also observed for dissociations from other alkyl groups, namely CNE + ΔE_{nb} values of ~ 0.7 - 1.0 (C₂H₅, C₃H₇), ~ 0.6 (C₄H₉) and ~ 0 kcal mol⁻¹ (iC₃H₇).

The merits of eq. 8 are revealed by a survey of the leading terms governing bond dissociations when the cleavage occurs i) in the "interior" of the molecule, ii) in its peripheral region or iii) when it concerns "exterior" bonds formed by a molecule, such as hydrogen bonds. (Only dissociations yielding electroneutral products are considered because the formation of ions, $AB \rightarrow A^+ + B^-$, can be treated along the same lines, with final corrections involving the ionization potential of A and the electron affinity of B.) The applicability of eq. 8 to any dissociation process also merits our attention.

Let us first examine the dissociation of diatomic molecules. They have zero nonbonded energy. Eq. 5 gives $RE = \Delta E_a^*(R^\circ)$. It follows from eqs. 1 and 7 that $CNE + RE(R_1) + RE(R_2) = 0$. Finally, eq. 8 yields the well-known result $D^*(R_1-R_2) = \epsilon(R_1-R_2)$. CNE, eq. 6, accounts for the fact that any charge imbalance affects the chemical bonds and the nonbonded terms making up the energies of the fragments. For that reason it concerns only polyatomic fragments. In writing $CNE = 0$ for heteronuclear diatomic molecules, it is understood that the charge neutralization accompanying their cleavage is part of $\epsilon(R_1-R_2)$. On the other hand, eqs. 4 and 5 yield $\Delta E_a^*(R^\circ) = 0$ and $RE = 0$. The following point is now easy to verify. Application of eqs. 5 and 8 to the calculation of step-wise dissociations consisting in an atom-by-atom removal of all the atoms of a polyatomic molecule, with dissociation energies D_1^* , D_2^* , ..., D_i^* , gives $\sum_i D_i^* = \Delta E_a^*$. The energy balance is correct.

Now we proceed with the backbone of organic chemistry, the hydrocarbons. In the dissociation of carbon-carbon bonds, the mutual charge neutralization by alkyl groups results in an important cancellation of the individual CNE terms associated with this neutralization. Briefly, one group loses electronic charge, its ΔE_a^* decreases, the other gains that charge and its ΔE_a^* increases. The net effect is usually small (Table 2) and nonbonded interactions play a minor role (≤ 0.22 kcal mol⁻¹)⁴. As a consequence, we can approximate eq. 8 as follows

TABLE 3. $\epsilon(\text{C-X}) + \text{CNE} + \Delta E_{\text{nb}}$ and dissociation energies for X = H, Cl, Br, I bonded to alkyl groups, kcal mol⁻¹

R	X	$\epsilon(\text{C-X}) + \text{CNE} + \Delta E_{\text{nb}}$	D*(C-X)
CH ₃	H	99.00	111.42
C ₂ H ₅	H	97.76	107.81
C ₃ H ₇	H	98.22	107.41
iC ₃ H ₇	H	97.62	104.61
tC ₄ H ₉	H	98.41	100.86
CH ₃	Cl	74.5	86.9
C ₂ H ₅	Cl	76.0	86.1
C ₃ H ₇	Cl	76.2	85.4
C ₄ H ₉	Cl	75.3	84.2
CH ₃	Br	60.4	72.8
C ₂ H ₅	Br	62.5	72.5
C ₃ H ₇	Br	63.0	72.2
C ₄ H ₉	Br	63.1	72.0
CH ₃	I	46.3	58.7
C ₂ H ₅	I	47.7	57.8
C ₃ H ₇	I	48.1	57.3

The results for the hydrocarbons are taken from Ref. 4. They were deduced from theory.³ For the halogenated hydrocarbons, we have used experimental enthalpies of formation and vibrational analyses¹⁰ for the calculation^{1,2} of ΔE_a^* . The D*(C-X) values were obtained from eq. 2, using the atomization energies described earlier⁴ for the alkyl radicals. The $\epsilon(\text{C-X}) + \text{CNE} + \Delta E_{\text{nb}}$ values were deduced from eq. 7, using the theoretical $\Delta E_a^*(R^\circ)$ results given in Ref. 4.

$$D^*(R_1-R_2) \approx \epsilon(R_1-R_2) + RE(R_1) + RE(R_2) \quad (9)$$

Numerical calculations and comparisons with experiment fully confirm the validity of this approximation⁴. A similar behavior is observed for the cleavage of ether carbon-oxygen bonds. The CNE contributions (Table 2) are somewhat larger than those accompanying the cleavage of CC bonds, but tend to decrease with the size of the groups engaged in the CO bonds. These examples confirm general expectations. The electron loss by one group weakens its bonds, an effect which is largely counteracted by the bond strengthening in the group gaining that electronic charge. As a result, it appears that the dissociation of chemical bonds embedded between sufficiently large molecular fragments involves relatively minor CNE + ΔE_{nb} contributions, as compared to the important structure related changes affecting $\epsilon(R_1-R_2)$ energies. Our approximation, eq. 9, typically represents a bond in the "interior" of a molecule⁵.

In contrast, bond dissociations occurring at the edge of a molecule are accompanied by important CNE contributions. Abstraction of an electroneutral atom which carried a partial charge while part of the host molecule affects only the bond energies of the polyatomic fragment left behind, because the abstracted atom forms no bonds and, hence, cannot compensate for the bond energy changes induced in the other fragment. Any cleavage of a CH bond involves a significant CNE energy (Table 2). On the other hand, the individual CH bonds also differ considerably from one another, depending on what is attached to H. The remarkable feature is that $\epsilon(\text{C-H}) + \text{CNE} + \Delta E_{\text{nb}}$ is nearly constant⁴ (Table 3), averaging 98.40 or 102.65 kcal mol⁻¹ for C(sp³)-H and C(sp²)-H bonds, respectively. CNE disguises CH bonds in such a way that, when viewed from the perspective of dissociation energies, all CH bonds involving the same type of C are perceived as if they were equal in energy, to a good approximation, i.e., (from eq. 8) $D^*(\text{C-H}) \approx \text{constant} + RE$. Similar situations also prevail for C-Cl, C-Br and C-I bonds. Hence, contrasting with the cleavage of a chemical bond well embedded in a molecule,

which is sensitive to any change affecting its intrinsic energy, the cleavage of peripheral bonds is essentially described by the approximation (from eq. 8)

$$D^*(C-X) \approx \text{constant} + RE \quad (X = H, C\ell, Br, I) \quad (10)$$

meaning that $D^*(C-X)$ is primarily determined by the type of bond (CH or $CC\ell$, etc.) and RE. Structure related modifications of intrinsic C-X bond energies, though occasionally large, have little say in the abstraction of an atom from a molecule⁷. (Other types of bonds, e.g. O-X and N-X, are currently under investigation.)

Our approach has revealed fundamental differences between the "interior" of a molecule, eq. 9, and its peripheral bonds, eq. 10. Now it appears interesting to explore processes involving the "exterior" of a molecule, such as the formation of hydrogen bonds or its adsorption onto a surface. This is done on a tentative basis, with the intent of generating new views on old problems - an attempt primarily justified by the fact that eq. 8 is an exact description of any dissociation process.

When two ground-state molecules, A and B, associate without loss of their chemical identities (as in $HOH \cdots OH_2$), some charge transfer is generally to be expected in AB. The CNE part accompanying the dissociation $AB \rightarrow A + B$ is given by eq. 6. The $\Delta E_a^*(R^\circ)$'s are now simply the atomization energies of A and B and we have zero reorganizational energies. The linkage between A and B should certainly not be considered as a "normal" chemical bond. More appropriately, it should be included in the computation of $\Delta E_{nb}(A \cdots B)$ although it may differ from a "usual" nonbonded interaction. $\Delta E_{nb}(A \cdots B)$ is a sum of pair-wise (intermolecular) interactions between the atoms of A and those of B and it is a matter of taste whether or not we single out any particular interaction, e.g., that between the O and H atoms forming the hydrogen "bond" $HOH \cdots OH_2$. The form of eq. 8 describing the cleavage of a molecular association is thus

$$D^*(A \cdots B) = CNE + \Delta E_{nb}(A \cdots B) \quad (11)$$

Equation 11 discriminates, in a way, between intramolecular (CNE) and intermolecular contributions to $D^*(A \cdots B)$. It would be instructive to learn about their relative importance in light of this equation, e.g., via calculations of CNE by means of eq. 6.

The following point merits special attention. As a consequence of a charge transfer in AB, the electronic properties of the moieties A and B are altered, thus affecting the energies of their bonds. Modifications occurring in the "interior" of A, where A is relatively large, are described by eq. 9. Any change in bond energy dictates a similar change in dissociation energy, $\Delta D^* \approx \Delta \epsilon$. (For example^{1,2}, the addition of 1 me to each C atom forming a CC bond increases $\epsilon(C-C)$ and, hence, $D^*(C-C)$ by $\sim 1.0 \text{ kcal mol}^{-1}$. The corresponding change for a CO bond is $\sim 1.2 \text{ kcal mol}^{-1}$.) It takes little to modify dissociation energies in a significant manner. Therefore, in an assessment of the chemistry triggered by molecular associations, one should not confine the discussion to the "bond" $A \cdots B$ described by eq. 11, but, perhaps more importantly, also consider that perturbations induced by charge transfer can be crucial. They are capable of modifying bond dissociation energies and, hence, the reactivity of the species engaged in these associations. This is where eq. 9 and the calculation of charge-dependent bond energies can prove valuable, e.g., in the study of solvent effects.

In short, the response of the "interior" properties of a molecule to modifications of its environment is now amenable to quantitative explorations because of our energy partitioning permitting the study of local properties, namely bond energies, in terms of local charge densities. The present approach hopefully opens new horizons and paves the way to a better insight into the complex problems accompanying "weak" interactions.

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