Physical Chemistry

Quantum-chemical calculations of the dissociation energy of the C—H bond in hydrocarbons, alcohols, and ethers

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The dissociation energy of the C—H bonds in hydrocarbons, alcohols, and ethers were calculated by semiempirical MNDO, AM1, and PM3 methods. The average error of calculations of the D(C—H) values by using various quantum-chemical methods is 1.3 kcal mol^{-1}.

Key words: hydrocarbons; alcohols; ethers; quantum-chemical calculations; the energy of the bond dissociation.

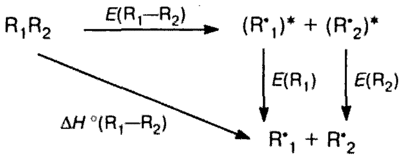
The use of quantum-chemical methods to calculate the enthalpy of formation of molecules and radicals ($\Delta_f H^\circ$) and the dissociation energy of bonds (D) in organic compounds appears very appealing if one takes into account the difficulty (and even the impossibility in some cases) of experimental determination of these values.

In many cases, the accuracy of the $\Delta_f H^\circ$ calculations even for particles with closed electron shells is inadequate.[1,2] Previously we reported[3] that the dissociation energies of the bonds in alkanes (and, therefore, the $\Delta_f H^\circ$ in alkyl radicals) can be calculated with satisfactory accuracy by using the MNDO method. In this work, the results of calculations of D(C—H) in alkanes, aliphatic alcohols, and ethers by semiempirical MNDO,[4] AM1,[5] and PM3 [6] methods are reported.

Calculations of the dissociation energy

The homolytic cleavage of a chemical bond can be considered[7] to occur in two stages: a) proper homolysis, after which the radical retains the geometry it had in the molecule, and b) stabilization of the radical, *i.e.*, its transformation to its most stable form (for instance, the planar form for the $^{\cdot}CH_3$ radical). Let us imagine the process of the homolysis of the compound $R_1—R_2$ by scheme 1.[8]

Scheme 1



Here, according to the terminology used,[8] $\Delta H^\circ(R_1—R_2)$ is the dissociation enthalpy of the bond, $E(R_1—R_2)$ is the term of the bond enthalpy, and $E(R_1)$ and $E(R_2)$ are the energies of relaxation (or reorganiza-

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2858—2861, December, 1996.

1066-5285/96/4512-2709 $15.00

tion) of the fragments. There are several approaches to determining these values,[9—11] which show that E(R) can be reasonably high (for instance,[9] E(PhO) = −24.0 kcal mol^{-1}).

The values of E, $\Delta H°$ and E(R) are related by a simple relationship (1).

$$\Delta H°(R_1-R_2) = E(R_1-R_2) + E(R_1) + E(R_2) \qquad (1)$$

On the basis of an analysis of the energetic characteristics of the chemical bond one can conclude[8] that the dissociation energy (or the bond strength) D, determined experimentally, is better described by the enthalpy term E than by the dissociation enthalpy of the bond $\Delta H°$. Therefore, one needs to calculate $\Delta_f H°$ of the radicals R_1 and R_2 using the geometric characteristics of the R_1-R_2 molecule (*i.e.*, before relaxation (reorganization)) in the quantum-chemical calculations of the dissociation energy of the bond.

The strength of the C—H bond is determined from Eq. (2).

$$D(\mathrm{R-H}) = \Delta_f H°(\mathrm{R}^{\cdot}) + \Delta_f H°(\mathrm{H}^{\cdot}) - \Delta_f H°(\mathrm{RH}) \qquad (2)$$

The use of this equation with $\Delta_f H°$ values calculated by the MNDO, AM1, and PM3 methods for molecules and radicals with fully optimized geometry[12] leads to considerable deviations from experimental data. In our opinion, the reason for those deviations is that, in addition to the parametrization errors of the semiempirical approximation, the enthalpy $\Delta H°$ calculated using this approach[12] differs from D (see above) by the relaxation energy of the radical $\mathrm{R}^{\cdot}$ (E(R) of the H atom is zero).

Taking this into account, we calculated the dissociation energy of the C—H bond as follows: the $\Delta_f H°$ of the RH molecule was calculated with full optimization of its geometry, then $\Delta_f H°$ of the $\mathrm{R}^{\cdot}$ radical with the geometric characteristics it has in the starting molecule was calculated. The obtained values were substituted into Eq. (2), taking[13] $\Delta_f H°(\mathrm{H}^{\cdot})$ to be 52.1 kcal mol^{-1}. In the case of a carbon atom with nonequivalent C—H-bonds, the value of D(C—H) was calculated as the arithmetic mean. For instance, in the case of cyclohexane the calculated dissociation energy of the C—H bonds is equal to half the sum of the D(C—H) values for the axial and equatorial hydrogen atoms.

Results and Discussion

Using the procedure described above, the dissociation energies of the C—H bonds in hydrocarbons, alcohols, and ethers were calculated. The results of the calculations using the three semiempirical methods are listed in Table 1. The experimental values of $\Delta_f H°(\mathrm{R}^{\cdot})$[14—18] and $\Delta_f H°$(RH)[19,20] were used for comparison; a critical selection of the values of $\Delta_f H°(\mathrm{R}^{\cdot})$ was made. Nevertheless, some of the calculated enthalpies of formation of radicals $\mathrm{R}^{\cdot}$ appear to be insufficiently accurate.

For this reason, the strengths of the *sec*-C—H bonds in pentane (position 2) and hexane were not used in the statistical data processing. The enthalpies of formation of oxygen-containing C-centered radicals are not readily available in the literature; therefore, a statistically justified critical selection of the "best" values of $\Delta_f H°(\mathrm{R}^{\cdot})$ is impossible. We considered two sets of experimental enthalpies $\Delta_f H°(\mathrm{R}^{\cdot})$,[17,18] which in some instances considerably differed from each other.

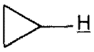
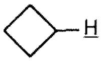
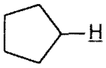
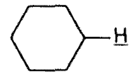
As a whole, good agreement between the calculated and experimental values of D(C—H) is observed. Thus, all the calculation methods adequately reflect the tendency for D(C—H) to decrease on going from a primary to a tertiary bond. However, the AM1 method systematically overestimates D(C—H) in alkanes. Thus, although the calculated values for the primary and tertiary C—H bonds are in good agreement with the experimental values (the average absolute errors of the calculations are 1.3 and 2.0 kcal mol^{-1}, respectively), for *sec*-C—H bonds the use of this method is unsuitable as the calculation error for acyclic alkanes is 3.4 and that for cyclic alkanes is 6.0 kcal mol^{-1}. On the other hand, the MNDO method tends to somewhat underestimate the values of D(C—H). The dissociation energies of the primary and secondary C—H bonds are calculated with high accuracy; however, in the case of tertiary and cyclic hydrocarbons the error is larger (3—4 kcal mol^{-1}). According to Table 1, the average absolute error for all the C—H bonds is 1.3 kcal mol^{-1} if the PM3 method is used.

In oxygen-containing compounds, the strength of the cleaved bond increases as the distance between this bond and the heteroatom increases (see Table 1 for the α- and β-C—H bonds in *n*-propyl alcohol), which explains the activation of the α-position in alcohols and ethers in the reactions of radical oxidation.[21] The calculated dissociation energies of bonds distant from the oxygen atom are in much better agreement with the published data.[17] It is likely that the experimental[18] values of D(β-C—H) and D(γ-C—H) are underestimated.

The choice of the calculation procedure plays an important role in the reliable determination of D(C—H) in oxygen-containing compounds. The dissociation energies of the C—H bonds in alcohols are better reproduced by the AM1 method. This is likely due to the fact that its parametrization more precisely reflects the structure and the distribution of the electron density in alcohols and, as a consequence, allows one to more reliably describe systems containing hydrogen bonds.[5] In contrast to this, what little data there is on the strengths of the C—H bonds in ethers show that the AM1 method is unsuitable in this case, whereas the MNDO and PM3 methods allow one to make calculations with an accuracy of ~1.2 kcal mol^{-1}.

The proposed method can be used to estimate the enthalpy of formation of radicals. The dissociation energy of the bond is calculated as described above, and

Table 1. The dissociation energies of the C—H bonds in hydrocarbons, alcohols, and ethers (kcal mol^{-1})

Compound	D^*_{exp}	$\Delta D = D_{exp} - D_{calc}$		
		MNDO	AM1	PM3
Hydrocarbons Primary C—H bonds				
$C\underline{H}_4$	104.8 [14]	2.0	1.4	1.7
$CH_3—C\underline{H}_3$	100.3 [14]	0.8	−0.6	2.1
$CH_3—CH_2—C\underline{H}_3$	99.6 [15]	0.3	−1.6	0.8
$CH_3—CH_2—CH_2—C\underline{H}_3$	100.3 [14]	0.9	−0.9	1.5
$(C\underline{H}_3)_3CH$	100.3 [14]	1.3	−1.3	1.1
$C\underline{H}_3—(CH_2)_3—CH_3$	100.1 [14]	0.8	−1.4	1.3
$(C\underline{H}_3)_4C$	99.8 [14]	1.3	−2.1	0.3
$C\underline{H}_3—(CH_2)_4—CH_3$	100.1 [14]	0.9	−1.1	1.3
Average error		1.0	1.3	1.3
Secondary C—H bonds				
$CH_3—C\underline{H}_2—CH_3$	96.9 [16]	1.7	−1.1	2.8
$CH_3—CH_2—C\underline{H}_2—CH_3$	94.8 [17]	−0.2	−3.4	0.2
$CH_3—C\underline{H}_2—C_3H_7$**	99.1 [14]	4.2	0.9	4.5
$C_2H_5—C\underline{H}_2—C_2H_5$	94.2 [17]	−0.5	−4.3	−0.8
$CH_3—C\underline{H}_2—$*iso*-C_3H_7	94.3 [17]	0.3	−4.1	−0.6
$CH_3—C\underline{H}_2—C_4H_9$**	99.1 [14]	4.4	0.8	4.1
$CH_3—C\underline{H}_2—$*tert*-C_4H_9	94.0 [17]	0.8	−4.1	−1.0
Average error		0.7	3.4	1.1
Tertiary C—H bonds				
$(CH_3)_3C\underline{H}$	93.8 [15]	3.7	−1.7	2.1
$(CH_3)_2C\underline{H}—C_2H_5$	95.5 [14]	5.5	−0.4	3.3
$(CH_3)_2C\underline{H}—C_3H_7$	94.6 [14]	5.0	−1.4	2.6
$(CH_3)_2C\underline{H}—$*iso*-C_3H_7	92.4 [17]	2.7	−3.5	−0.1
$(CH_3)_2C\underline{H}—$*tert*-C_4H_9	92.1 [17]	4.6	−2.8	0.3
Average error		4.3	2.0	1.7
Cyclic hydrocarbons, secondary C—H bonds				
	104.4 [17]	−4.1	−3.9	0.8
	96.7 [17]	−5.0	−6.8	−2.6
	94.9 [17]	−2.1	−8.6	0.1
	94.5 [17]	−1.2	−4.5	−0.9
Average error		3.1	6.0	1.1
Average error over all hydrocarbons		2.1	2.8	1.3
Alcohols				
$C\underline{H}_3OH$	96.0 [17]	2.1	−1.7	3.6
$C\underline{H}_3CH_2OH$	100.8 [17]	0.8	−2.2	1.0
	94.8 [18]	−5.2	−8.2	−5.0
$CH_3C\underline{H}_2OH$	92.5 [17]	4.1	−0.6	2.0
	93.8 [18]	5.4	0.7	3.3
$C\underline{H}_3CH_2CH_2OH$	100.3 [17]	−0.2	−1.1	1.5
	97.1 [18]	−3.4	−4.3	−1.7
$CH_3C\underline{H}_2CH_2OH$	98.0 [17]	2.0	−2.0	2.6
	94.3 [18]	−1.7	−5.7	−1.1
$CH_3CH_2C\underline{H}_2OH$	91.8 [17]	3.6	−1.6	0.9
$(C\underline{H}_3)_2CHOH$	94.3 [18]	−5.4	−8.7	−5.9
$CH_3C\underline{H}(OH)CH_3$	90.6 [17]	−2.8	−1.2	4.9
	91.7 [18]	−1.7	−0.1	6.0
$(C\underline{H}_3)_3COH$	91.6 [18]	−7.5	−11.2	−8.7
$HOC\underline{H}_2CH_2OH$	95.0 [17]	5.6	−0.1	6.1
	92.1 [18]	2.7	−3.0	3.2
Average error over experimental data[17]		2.7	1.3	2.8
Average error over experimental data[18]		4.1	5.2	4.4
Ethers				
$C\underline{H}_3OCH_3$	93.3 [17]	−1.1	−5.8	−2.2
$C\underline{H}_3OCH_2CH_3$	93.0 [17]	−1.4	−6.0	−1.3
	93.2 [18]	−1.2	−5.8	−1.1
$CH_3OC\underline{H}_2CH_3$	90.0 [17]	0.6	−4.8	1.0
$CH_3OCH_2C\underline{H}_3$	99.8 [17]	−0.4	12.4	0.0
Average error over experimental data[17]		0.9	7.3	1.1
Average error over experimental data[18]		1.2	5.8	1.1
Average error over all compounds***		2.2	2.8	1.8

* Calculated from the experimental values of $\Delta_f H^\circ(R^\cdot)$[9–13] and $\Delta_f H^\circ$(RH).[14–15] ** The experimental value of *D*(C—H) for this compound was excluded from the calculations of the average absolute error. *** The literature data[17] were used for the oxygen containing compounds.

the value of $\Delta_f H^\circ$(RH) is taken from a handbook or is calculated by using one of the approximate methods (for instance, the Benson additive scheme[22]). The error of the estimate of $\Delta_f H^\circ(R^\cdot)$ is equal to the calculation error of *D*(C—H), which is comparable with the experimental errors of determining the enthalpy of formation of radicals.

Example of the calculation of $\Delta_f H^\circ((CH_3)_2CHCH_2CH_2^\cdot)$. To determine the dissociation energy of the bond, let us use, for instance, the MNDO method. According to this method, $D((CH_3)_2CHCH_2CH_2—H) = 99.0$ kcal mol^{-1}, the enthalpy of formation of 2-methylbutane[15] is −36.7 kcal mol^{-1}, and hence, $\Delta_f H^\circ((CH_3)_2CHCH_2CH_2^\cdot) =$ 10.2 kcal mol^{-1}. The experimental value of $\Delta_f H^\circ$ is not available, $\Delta_f H^\circ = 12.2$ kcal mol^{-1} according to the Benson method of group additivity,[14,22] the Orlov and Lebedev approach in the framework of the compact scheme[23,24] leads to 7.6 kcal mol^{-1}, while the second approximation[25] gives 7.7 kcal mol^{-1}.

As can be seen from a comparison of the experimental and the calculated data, the proposed procedure allows one to calculate the dissociation energy of the bonds with a high degree of accuracy, despite the fact that the error of determination of $\Delta_f H^\circ$ of the starting RH and R$^\cdot$ can be considerable. The reason for this apparent contradiction is likely as follows.

As is known,[26] a considerable amount of the error in nonempirical quantum-chemical calculations of $\Delta_f H^\circ$ is due to the neglect of the electron correlation. In the case of semiempirical methods, the attempt to fit adequate parameters usually leads to systematic calculation errors in the geometric characteristics and in $\Delta_f H^\circ$. For example, the MNDO method reproduces the geometry and $\Delta_f H^\circ$ of peroxides, four-membered cycles, and structures containing *tert*-butyl fragments worse than it reproduces those of other organic compounds.[27] If one estimates the dissociation energy of the bond instead of $\Delta_f H^\circ$, and one of the radicals is an atom with zero energy of relaxation (reorganization), then a nearly isostructural molecule and a "large" radical will have similar systematic errors. The latter cancel each other out in calculations of D (Eq. (2)).

For example, the *tert*-butylhydroperoxide molecule, $(CH_3)_3COOH$, contains two "bad" fragments simultaneously: the *tert*-butyl group and the peroxide group, which causes unsatisfactory reproduction of $\Delta_f H^\circ$. The calculated (AM1 method) enthalpies of formation of the $(CH_3)_3COOH$ molecule and the $(CH_3)_3COO\cdot$ radical are -44.4 and -10.3 kcal mol^{-1}, respectively, while the experimental enthalpies are -58.8 ± 1.2 [20] and -25.2 ± 3.0 [18] kcal mol^{-1}, *i.e.*, in both cases $\Delta\Delta_f H^\circ$ exceeds 14 kcal mol^{-1}. Nevertheless, the dissociation energy calculated from Eq. (2) ($D((CH_3)_3COO{-}H) = 86.2$ kcal mol^{-1}) is in good agreement with the experimental value ($D = 85.8$ kcal mol^{-1}).[28]

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Received January 24, 1996;
in revised form July 8, 1996