

A New Method for Estimation of Homolytic C–H Bond Dissociation Enthalpies

Artem Cherkasov^{*,1} and Mats Jonsson^{*,†}

Department of Chemistry, Nuclear Chemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

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In this work we have quantitatively analyzed substituent effects on the homolytic bond dissociation enthalpy of 79 different compounds using a method based on discrete distance dependent atomic contributions to a molecular property. The resulting empirical relationship can be used to predict C–H bond dissociation enthalpies (within ± 10 kJ mol⁻¹) for molecules where resonance contributions and captodative stabilization are insignificant. For species where captodative stabilization of the corresponding C-centered radical is possible, the method clearly overestimates the C–H bond dissociation enthalpy.

INTRODUCTION

The homolytic bond dissociation enthalpy, BDE, (reaction 1 and eq 2), is one of the most fundamental properties in



$$\text{BDE}(\text{X-Y}) = \Delta H_f(\text{X}^\bullet) + \Delta H_f(\text{Y}^\bullet) - \Delta H_f(\text{X-Y}) \quad (2)$$

chemistry in general and in the chemistry of free radicals in particular. X–H bond dissociation enthalpies are very important for the understanding of hydrogen abstraction reactions which, in turn, are of major importance in a number of natural and technical processes, as well as in organic synthesis.

For almost a century, the nature of chemical bonds has fascinated chemists and the extensive work performed in this field has resulted in a number of methods for experimental determination or estimation of bond dissociation enthalpies.^{2–4} In recent years, quantum chemical calculations have also proven to be a very useful tool for the determination of bond dissociation enthalpies, even in relatively large molecules. Furthermore, a number of empirical methods for estimations of heats of formation of molecules and radicals (and thereby also for estimations of homolytic bond dissociation enthalpies) have been put forward. The most famous of these methods is probably the empirical scheme by Benson and co-workers.⁵ Recently, a similar additive bond-energy scheme was developed by Smith.⁶

In this paper, we present a new empirical approach for estimation of C–H bond dissociation enthalpies. The approach, which is based on discrete distance dependent atomic contributions to a molecular property, has been used successfully for estimations of ionization potentials and electron affinities of C-, N-, O- and S-centered radicals^{7,8} and for estimations of ionization potentials and gas basicities of amines.⁹

METHOD

In the present method, experimental data are fitted to eq 3 by multiparametric regression analysis.

$$Y - Y^\circ = \sum_{i=1}^n \frac{e_i}{r_{\text{rc}-i}^2} \quad (3)$$

In eq 3, Y is a physicochemical property or the logarithm of a rate or equilibrium constant for a given substance and Y° is the value for the corresponding unsubstituted reference compound, e_i is an empirical atomic parameter for a given type of atom in a given valence state (derived from the multiparametric regression analysis) and $r_{\text{rc}-i}$ is the direct distance between the substituent atom i and a reference atom denoted the reaction center, rc. The choice of reaction center is usually relatively simple. For the radicals studied previously, the radical center, i.e., the atom at which the unpaired electron is localized, was chosen as the reaction center, and in the present case it is natural to choose the carbon atom involved in the C–H bond of interest. For simplicity, the interatomic distances, r , were determined by using the Hyperchem software package (optimization method MM+), allowing simple estimation of the standard geometries of the corresponding hydrocarbons. The accuracy of this procedure would probably be improved if optimized radical structures were used; however, this would make the approach more difficult and time-consuming and thereby less attractive. To avoid confusion with the atomic parameters used for ionization potentials and electron affinities of free radicals, we have used dh_i instead of e_i in this study (eq 4).

$$\text{BDE}(\text{R}_3\text{C-H}) - \text{BDE}(\text{H}_3\text{C-H}) = \sum_{i=1}^n \frac{dh_i}{r_{\text{rc}-i}^2} \quad (4)$$

The method has its origin in theoretical models for inductive and steric effects in which the effects of separate atoms can be treated as purely additive taking the inverse squared distance dependence into account.^{10,11} These methods have been extensively described in the literature; however, a short summary is provided below.

The steric effect of a substituent attached to a given reaction center has been described simply as mechanical shielding of the reaction center by the atoms of the substituent:

[†] Phone: +46 8 790 9123. E-mail: matsj@nuchem.kth.se.

Table 1. Experimental and Estimated C–H Bond Dissociation Enthalpies

no.	substance	BDE_{exp} (kJ mol ⁻¹)	BDE_{est} (kJ mol ⁻¹)	$BDE_{exp} - BDE_{est}$ (kJ mol ⁻¹)	no.	substance	BDE_{exp} (kJ mol ⁻¹)	BDE_{est} (kJ mol ⁻¹)	$BDE_{exp} - BDE_{est}$ (kJ mol ⁻¹)
1	H ₃ C–H	438.9 ¹²	429.7	9.2	48	CHF ₂ –H	431.8 ²³	437.9	-6.1
2	CH ₃ CH ₂ –H	423 ¹²	420.7	2.3	49	CHFCI–H	421.7 ²⁴	424.4	-2.7
3	HCC–CH ₂ –H	374 ¹³	365.6	8.4	50	CF ₂ Cl–H	421.3 ²⁵	428.4	-7.1
4	CH ₃ CH ₂ CH ₂ –H	420 ¹⁴	416.7	3.3	51	CFCl ₂ –H	413.8 ²⁴	415.0	-1.2
5	(CH ₃) ₂ CH–H	412.5 ¹²	411.6	0.9	52	CH ₂ Cl–H	421.7 ²⁴	420.3	1.4
6	CH ₃ CC–CH ₂ –H	364.8 ¹³	364.1	0.7	53	CHCl ₂ –H	411.7 ²⁴	410.9	0.8
7	CH ₃ CH=CH–CH ₂ –H	358.2 ¹³	349.0	9.2	54	CCl ₃ –H	392.5 ²⁶	401.5	-9.0
8	CH ₂ =CH(CH ₃)-CH ₂ -H	358.2 ^{15,16}	347.1	11.1	55	CH ₂ Br–H	425.1 ²⁴	421.4	3.7
9	(CH ₃)(C ₂ H ₅)CH–H	410.9 ¹²	414.8	-3.9	56	CHBr ₂ –H	417.2 ²⁴	413.1	4.1
10	(CH ₃) ₃ C–H	403.8 ¹²	402.6	1.2	57	CBr ₃ –H	401.7 ¹³	404.9	-3.2
11	NCCCH ₂ –H	392.9 ¹²	386.0	6.9	58	CH ₂ I–H	431 ¹³	430.5	0.5
12	CH ₃ NHCH ₂ –H	386 ¹⁷	396.5	-10.5	59	CHI ₂ –H	431 ¹³	431.3	-0.3
13	(CH ₃) ₂ NCH ₂ –H	387 ¹⁷	392.2	-5.2	60	CH ₃ CF ₂ –H	416.3 ¹³	428.8	-12.5
14	CHOCH ₂ –H	394.6 ¹²	404.6	-10.0	61	C ₂ F ₅ –H	429.7 ¹³	432.3	-2.6
15	C ₆ H ₅ CH ₂ –H	370.3 ¹²	381.9	-11.6	62	CF ₃ CHCl–H	425.9 ¹³	414.8	11.1
16	C ₆ H ₅ C(CH ₃)CH–H	357.3 ¹³	372.8	-15.5	63	CHCl ₂ CCl ₂ –H	393 ¹³	393.1	-0.1
17	C ₆ H ₅ C(CH ₃) ₂ –H	353.1 ¹³	363.8	-10.7	64	C ₂ Cl ₅ –H	397 ¹³	388.7	8.3
18	NCCCH(CH ₃)-H	376.1 ¹³	377.0	-0.9	65	CF ₃ CClBr–H	404.2 ¹³	406.5	-2.3
19	NCC(CH ₃) ₂ –H	361.9 ¹³	367.9	-6.0	66	C ₃ F ₇ –H	435 ¹³	429.2	5.8
20	HSCH ₂ –H	392.9 ¹²	390.4	2.5	67	(CF ₃) ₂ CF–H	433.5 ²⁷	422.7	10.8
21	CH ₃ SCH ₂ –H	384.9 ¹⁸	387.4	-2.5	68	(CH ₃) ₃ SiCH ₂ –H	415.1 ²⁸	415.1	0
22	F ₃ C–H	446.4 ¹³	441.9	4.5	69	C ₂ H ₅ COCH(CH ₃)-H	383.7 ²²	390.3	-6.6
23	CH ₂ =CHCH ₂ –H	361.9 ¹²	350.7	11.2	70	HO ₂ CCH ₂ –H	407 ^{29,30}	394.9	12.1
24	CHCC(CH ₃)H–H	347.7 ¹³	356.6	-8.9	71	NH ₂ CH ₂ –H	388 ¹⁷	400.8	-12.8
25	cyclo-C ₄ H ₈	403.8 ¹³	407.5	-3.7	72	NH ₂ C(CH ₃) ₂ -H	388 ¹⁷	386.4	1.6
26	CH ₂ =CHCH(CH ₃)-H	345.2 ¹³	341.7	3.5	73	NH ₂ CH(CH ₃)-H	384 ¹⁷	395.4	-11.4
27	CH ₂ =CH–CH=CH–CH ₂ –H	347 ¹³	335.8	11.2	74	NHC ₅ H ₁₀ (α-NH)	385 ¹⁷	381.2	3.8
28	(CH ₂ =CH) ₂ CH–H	319.7 ^{13,19}	330.0	-10.3	75	HN–([C ₂ H ₄] ₂)-NH	385 ¹⁷	374.3	10.7
29	CH ₃ –CC–CH(CH ₃)-H	365.3 ¹³	355.1	10.2	76	O–([C ₂ H ₄] ₂)-NH (α-NH)	389 ¹⁷	374.5	14.5
30	CHCC(CH ₃) ₂ –H	338.9 ¹³	347.6	-8.7	77	C ₄ H ₈ –NH (α-NH)	377 ¹⁷	383.8	-6.8
31	CH ₂ =CHC(CH ₃) ₂ –H	323 ¹³	332.6	-9.6	78	(C ₂ H ₅) ₂ N–CH(CH ₃)-H	381 ¹⁷	379.5	1.5
32	cyclo-C ₅ H ₁₀	403.5 ¹⁴	404.1	-0.6	79	(C ₄ H ₉)-N–CH(C ₃ H ₇)-H	381 ¹⁷	370.2	10.8
33	(CH ₃) ₃ CCH ₂ –H	418 ¹³	408.8	9.2	80	Scheme 1	325 ³¹	342.2	-17.2
34	C ₂ H ₅ C(CH ₃) ₂ –H	404 ²⁰	398.6	5.4	81	Scheme 1	340 ³¹	355.4	-15.4
35	CH ₃ –CC–C(CH ₃) ₂ –H	344.3 ¹³	346.0	-1.7	82	Scheme 1	348 ³²	364.5	-16.5
36	(CH ₃) ₂ CC(CH ₃)CH ₂ –H	326.4 ¹³	342.1	-15.7	83	Scheme 1	344.3 ³³	355.5	-11.2
37	CH ₂ =C(CH ₃)C(CH ₃) ₂ –H	319.2 ¹³	329.0	-9.8	84	Scheme 1	315.1 ³⁴	349.4	-34.3
38	(C ₆ H ₅) ₂ CH–H	340.6 ²¹	334.1	6.5	85	Scheme 1	324.3 ³⁴	340.3	-16.1
39	(C ₆ H ₅) ₂ C(CH ₃)-H	339 ¹³	325.0	14.0	86	Scheme 1	343.5 ³⁴	314.4	29.1
40	CH ₃ COCH ₂ –H	411.3 ¹³	401.0	10.3	87	Scheme 1	351.9 ³⁴	342.0	9.8
41	CH ₃ COCH(CH ₃)-H	386.2 ¹³	392.0	-5.8	88	Scheme 1	330.5 ³⁴	354.4	-23.9
42	CH ₃ OCH ₂ –H	389 ¹³	396.1	-7.1	89	Scheme 1	322.2 ³⁴	363.6	-41.4
43	C ₂ H ₅ OCH(CH ₃)-H	383.7 ²²	382.8	0.9	90	Scheme 1	326.4 ³⁴	358.3	-31.9
44	HOCH ₂ –H	401.9 ¹²	400.6	1.3	91	Scheme 1	331 ³⁰	365.9	-34.9
45	HOCH(CH ₃)-H	389 ¹³	391.6	-2.6	92	Scheme 1	317.4 ³³	356.9	-39.5
46	HOC(CH ₃) ₂ –H	381 ¹³	382.6	-1.6	93	Scheme 1	327.2 ³³	346.5	-19.3
47	CFH ₂ –H	423.8 ²³	433.8	-10.0	94	Scheme 1	327.8 ³³	342.5	-14.7

$$R'_S = \sum_{i=1}^n \frac{R_i^2}{4r_{rc-i}^2} \quad (5)$$

where n is the number of substituent atoms, R_i is the covalent radius of the i th atom, r_{rc-i} is the direct distance from the i th atom to the reaction center, and R'_S reflects the specific surface of the reaction center screened by the atoms of the substituents.

The inductive interaction of substituents with the reaction center has also been interpreted in terms of additive summation of atomic contributions to the overall interaction:

$$\sigma^* = \sum_{i=1}^n \frac{\sigma_{A_i}}{r_{rc-i}^2} \quad (6)$$

where σ_A is an overall empirical atomic value, depending on the chemical nature and valence state of the substituting atom and on the nature of the reaction center. There is a correlation between the overall empirical atomic values, σ_A ,

and the difference in electronegativity of the i th atom and the reaction center, $\Delta\chi_{i-rc}$, and the squared covalent radius.

$$\sigma_A = 7.84\Delta\chi_{i-rc}R_i^2 \quad (7)$$

The method based on eq 3 is a purely empirical tool providing no physical insight into the mechanisms underlying the observed substituent effects. The parameters derived from eq 3 could, however, be analyzed in terms of possible steric and inductive contributions in accordance with the theories mentioned above. To separate the inductive and steric contributions properly, we would need the electronegativity for the reaction center. Unfortunately, these values are not always available, but instead of trying to find correlations between e and $\Delta\chi R^2$ and R^2 , according to eqs 5–7 we can try to find correlations between e and χR^2 and R^2 .

$$e_i = A\chi R_i^2 + BR_i^2 \quad (8)$$

The term B may then contain the inductive electronegativity for the radical atom and a constant describing the pure

Table 2. Empirical Atomic Parameters

atom	dh_i	atom	dh_i
H	-2.7 ± 0.9	O	-63 ± 9
C _{sp3}	-23 ± 3	S	-132 ± 21
C _{sp2}	-135 ± 6	F	3 ± 2
C _{sp}	-108 ± 6	Cl	-36 ± 4
C _{ar}	-52 ± 3	Br	-38 ± 8
N _{sp}	33 ± 38	I	-7 ± 18
N	-65 ± 7	Si	-24 ± 32
O _{sp2}	178 ± 25		

sterical contribution (if any), thus, eq 8 describes both the inductive and steric contribution as described by eqs 5–7. However, it will not be possible to separate these two terms.

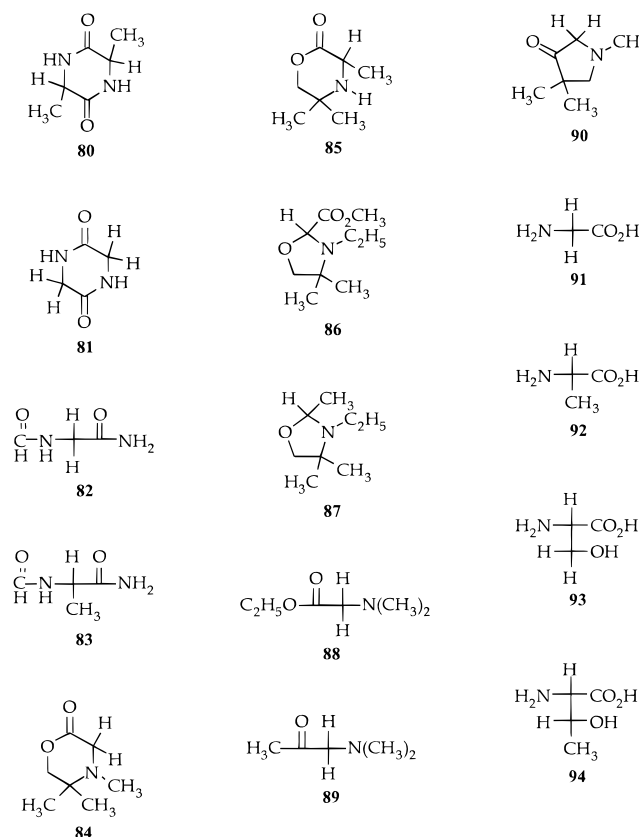
RESULTS AND DISCUSSION

Using the approach previously described, i.e., by multiparametric regression analysis of experimental data in accordance with eq 4, we analyzed the substituent effects on the C–H bond dissociation enthalpies of 79 hydrocarbons. The experimental numbers as well as the estimated numbers are given in Table 1. The empirical parameters, dh_i , derived from the regression analysis are given in Table 2.

The statistical parameters for the regression are $R^2 = 0.94$, std dev = 8.6, and $F = 63.6$. As can be seen in Table 1, the discrepancies between the experimental values and the corresponding estimated values for the first 79 entries are rarely more than 10 kJ mol⁻¹. There are some exceptions though, where the discrepancy is up to 15 kJ mol⁻¹. The estimations with deviations of more than 10 kJ mol⁻¹ from the experimental values can be divided into four categories: (1) N-containing substituents, (2) C_{sp2}-containing substituents, (3) C_{ar}-containing substituents, and (4) C_{sp}-containing substituents. There could in principle be two methodological reasons for these deviations. First, the method does not account for resonance contributions, and second, the effect of a given substituent atom is assumed to be unaffected by the substituents attached to it; e.g., C_{sp2} is assumed to have the same effect when it belongs to a carbonyl group as when it is part of a C–C double bond. This can explain the deviations in categories 1–4.

Due to the additive nature of the empirical method employed in this work, we have not included substances where captodative effects (nonadditive, synergistic, effects of electron-donating and electron-withdrawing groups) on the C–H bond dissociation enthalpies are expected to be significant, i.e., the α -C–H bonds in peptides and peptide-like substances. Nevertheless, to demonstrate the captodative effect, we have used the parameters derived from the regression analysis to estimate the C–H bond dissociation enthalpies also for these compounds (entries 80–94, see Scheme 1 for structures). It should be noted that entry 87 is not expected to be affected by captodative stabilization of the corresponding radical.

Here, the C–H bond dissociation enthalpies are clearly overestimated (with the exception of entries 86 and 87), which can be attributed to captodative stabilization of the radical formed upon C–H homolysis. This can be seen in Figure 1 where the estimated C–H bond dissociation enthalpies are plotted against the corresponding experimental numbers. The C–H bonds affected by captodative stabiliza-

Scheme 1

tion are clearly separated from the C–H bonds where captodative stabilization is absent.

Physical Assessment of Substituent Effects. Attempts to analyze the physical meaning of the substituent effects in terms of eq 8 failed. Thus, the effects cannot be accounted for by inductive and steric contributions solely. Nevertheless, some interesting information concerning the effects of α -substitution can be obtained if the substituent effect of a given atom is compared to the strength of the corresponding CH₃–X bond, where X is the atom of interest. The CH₃–X bond dissociation enthalpies for some of the atoms used in this study are given in Table 3 along with the corresponding empirical atomic parameters, dh_i . The values for C_{sp}, C_{sp2}, and C_{ar} are excluded due to the resonance contributions which cannot be accounted for in this method, O_{sp2} and N_{sp} are excluded since they do not bind directly (α) to sp³ carbon, and Si and I are excluded since the corresponding empirical atomic parameters are only based on data from one and two substances, respectively.

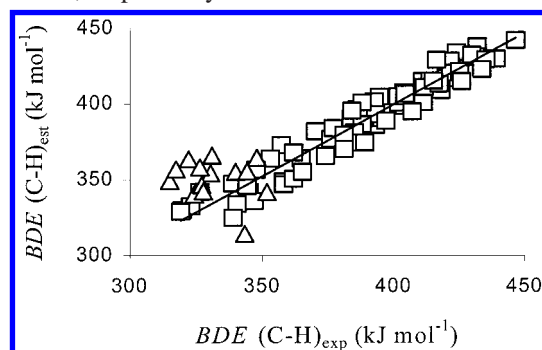
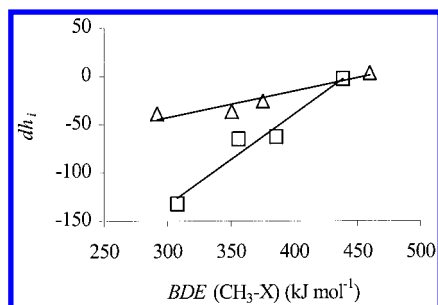


Figure 1. Estimated C–H bond dissociation enthalpies plotted against the corresponding experimental numbers. (Squares represent entries 1–79 in Table 1 and triangles represent entries 80–94).

Table 3. C–X Bond Dissociation Enthalpies and Empirical Atomic Parameters

atom	BDE(H ₃ C–X) (kJ mol ^{–1})	dh _i
H	438.56 ¹²	–2.7
C _{sp} ³	375.22 ³⁵	–25.7
N	356 ³⁶	–65
O	385.7 ³⁵	–62.7
F	459.69 ³⁵	3.3
Cl	350.7 ³⁵	–36.3
Br	291.8 ³⁵	–38.6
S	307.8 ³⁵	–132

**Figure 2.** Empirical atomic parameters derived from the multilinear regression plotted against the CH₃–X bond dissociation enthalpy for the corresponding atom, X.

In Figure 2, the empirical atomic parameters are plotted against the corresponding CH₃–X bond dissociation enthalpies. From this plot, we can see that this set of data can be fitted to two straight lines. The line with the smallest slope fits the data for H, C_{sp}³, F, Cl, and Br, and the line with the largest slope fits the data for H, N, O, and S. The reason for including H in both sets of data is that it is the reference point used in the method. The rationale for separating data into two sets is that N, O, and S contain lone-pair electrons while the other atoms do not.

The finding that the CH₃–X bond dissociation enthalpy for a given substituent atom seems to reflect the α -substituent effect on the C–H bond dissociation enthalpy is quite interesting. The linear trend implies that the strength of the C–X bond in the radical is linearly related to the strength of the C–X bond in the parent molecule. Consequently, for strongly bonded α -substituents, the difference in C–X bond dissociation enthalpy in absolute numbers between the molecule, CH₃X, and the radical, CH₂X[•], is larger than for more loosely bonded substituents. For the data set including H, N, O, and S, the reducing factor for the C–X bond in the radical compared to the parent molecule is smaller, which could be explained in terms of an additional radical stabilization due to spin-delocalization on the heteroatoms.

It should be noted that the effects of N-, O- and S-substituent atoms also deviate from the general trends found for the ionization potential and electron affinity of C-centered radicals. In these cases, the main contribution to the substituent effect was interpreted as purely inductive and the extra contribution from N-, O- and S-substituents was attributed to the presence of lone-pair electrons.^{7,8}

CONCLUSIONS

A relatively simple approach based on discrete distance dependent atomic contributions to a molecular property can be used with reasonable accuracy for prediction of C–H bond dissociation enthalpies in molecules where resonance

and captodative effects are absent. The atomic substituent constants obtained from the multiparametric regression of experimental data are to some extent related to the corresponding CH₃–X bond dissociation enthalpies, where X is the substituent atom.

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