

Electrostatic model of bond dissociation energies in polyhalogen methanes

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ABSTRACT: Homolytic bond dissociation energy (BDE) for C—H and C—X (X = F, Cl, or Br) bonds in polyhalogen methanes was successfully correlated with a two-parameter model describing the repulsion energy of the bonding electron pair with other electrons and its attraction with nuclei, respectively. BDE values for seven molecules were predicted and compared with those calculated by a DFT method. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: bond cleavage; bond dissociation energy; carbon–halogen bond; dissociative electron transfer; electrostatic interactions; polyhalogen methanes

INTRODUCTION

Polyhalogen methanes and other halogen-containing organic molecules have been extensively investigated as a group of serious environmental pollutants. Some of them in liquid phase are present in the soils and underground waters, some others in gaseous state are constantly released into the atmosphere.¹ Their degradation by biotransformations as well as a number of abiotic processes involving bonds cleavage strongly depends on the C—X bond strengths. In atmospheric chemistry the rate constants for hydrogen atom abstraction in halogenated alkanes were reported to correlate with their C—H bond strengths,^{2–4} whereas their photolytic instability to correlate with strengths of their C—X bonds. On the other hand, the reductive cleavage of C—X bonds is the useful step in organic synthesis providing the chemically clean way to generate reactive species such as radicals.^{5,6} The dissociative electron transfer in homogeneous and electrochemical reactions as well as the kinetics of the bond cleavage in radical anions and the reverse coupling reactions were successfully describe by Savéant in the models^{5,7} designating the homolytic bond dissociation energy, BDE, of a parent molecule as a fundamental factor determining the activation barrier. In view of the above, BDE values are important for understanding the reaction mechanisms and structure-reactivity relationships, essential for attempts to propose some predictive rules. Unfortunately, BDE values have been experimentally determined for only a small number of halogenated molecules⁸ and for

some of them direct measurements are difficult or even impossible. Thermodynamic estimations and earlier accurate theoretical calculations, which needed high-quality levels of theory, were also limited. Fortunately, the continuing development in the use of the density functional theory, DFT, for calculating BDE values has been reached satisfactory results in recent years. It has been achieved not only for C—H and C—X bonds in simple haloalkanes^{9–12} but also for a variety of bonds (including C, H, N, O, S, Si, P and halogen atoms) in larger molecules (e.g., phenyl substituted compounds,^{11,13} phenolic antioxidants as catechins and tocopherols,¹⁴ thiophenols,¹⁵ *p*-substituted anilines,¹⁶ phenylphosphines,¹⁷ substituted toluenes¹⁸). However, for a deeper understanding of variations in BDE values in a series of similar compounds the correlation analysis is still valuable. It can show effects of structural changes in a series of interest on stability of a parent molecule and radicals formed in dissociation, that is, properties which determine BDE values. For molecules containing the benzene ring, substituent effects on BDE values obtained from DFT calculations were successfully described by the Hammett equation^{15–17} and for various substituents the additivity values, Δ BDE, were proposed.¹⁴

In the present study BDE values (taken from the recent compilation⁸) for C—H and C—X (X = F, Cl, and Br) bonds in polysubstituted methanes were described by two-parameter correlations taking into account electrostatic interactions of a bonding electron pair with charges of other atoms. The chose of halomethanes, very simple molecules, allowed to use a very simple electrostatic model and the main purpose of this analysis is to visualize fundamental factors determining variations of BDE values in a series. However, additional support of validity of correlations proposed was obtained by the estimation

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of unknown BDE values for seven molecules and a comparison with those calculated by the DFT method.

RESULTS AND DISCUSSION

Electrostatic model

In general, the homolytic BDE depends on the energy of interactions of the bonding electron pair with all other electrons and nuclei in a molecule. Considering a polysubstituted molecule X-CYY'Y'' (or H-CYY'Y'', where Y denotes hydrogen or halogen atom) it was assumed that the BDE values for a given C—X (or C—H) bond in a series of compounds consist of three additive contributions: (i) the constant dissociation energy of the C—X (or C—H) bond alone, ignoring other atoms; (ii) the sum of the energy of the repulsion of the bonding electron pair with all electrons in all Y atoms binding to the carbon atom; and (iii) the sum of the energy of its attraction with all nuclei of Y atoms. In terms of simple electrostatic interactions with point charges and ignoring small deviations from the tetrahedral symmetry of methane due to a substitution, the second contribution can be given by the sum $\sum Z/d$, where Z is the atomic number, representing charge of electrons in each Y atom and d is the C—Y distance, assumed to be equal to the average bond length between the carbon and the Y atom; the summation includes all Y atoms. Then, in a similar manner the third contribution is given by the sum $\sum Z_{\text{eff}}/d$, where Z_{eff} is the effective charge of the Y nucleus, taking into account its shielding by the inner-shell electrons. Literature values of Z_{eff} ¹⁹ and bond lengths in CH₄ and CH₃X molecules²⁰ were used in further calculations.

Correlation analysis

For a series of $n=11$ substituted methanes the BDE values for C—H bonds, taken from the recent compilation⁸ (recommended values were used when indicated) were correlated with two parameters according to Eqn (1)

$$\text{BDE} = a \sum \frac{Z}{d} + b \sum \frac{Z_{\text{eff}}}{d} + c \quad (1)$$

BDE values used are given in Table 1 (molecules 1–11) and the correlation obtained is plotted in Fig. 1. Three other compounds of known BDE_{C—H} values, containing bromine atoms in a molecule (34–36 in Table 1) deviate strongly from the correlation line, as is shown in Fig. 1. The higher the number of Br atoms in the molecule, the greater the deviation observed and estimated BDEs are lower than experimental values. This behavior indicates that the repulsion with electrons of Br atoms which destabilizes the molecule is actually smaller than those described by the electrostatic model, treating the bromine

atom as a point charge. Thus, for soft bromine and iodine atoms in substituted methane (as well as for greater molecules as haloethanes) it is necessary to take into account the actual electron density distribution, ignored in the simple model under consideration. Nevertheless, results shown in Fig. 1 encouraged us to use for further analysis of Eqn (1) because of its simplicity and a visualization of main electrostatic effects, however, excluding molecules with Y = Br and I atoms.

Statistical parameters of the correlation (1): the multiple (here planar) correlation coefficient R , regression coefficients a , b , and c , the average deviation of experimental points from the correlation line δ , and F -test parameters are given in Table 2. Snedecor F parameter was calculated^{22a} as

$$F = \frac{R^2(n-k-1)}{(1-R^2)k} \quad (2)$$

where n is the size of sample (the number of compounds in the series) and k the number of parameters; $k=2$ for the planar regression. The critical value of $F_{\alpha,2,n-3}$ from statistical tables^{22b} lower than the calculated F value is also given in Table 2. It indicates the significance level α , describing the probability of error due to the rejection of the hypothesis of no correlation. Considering the series with C—H bonds the probability that the correlation obtained is not significant is lower than 0.5%. However, the more important for the examination of the significance of planar correlations is the test F_{imp} which indicates the significance of the addition of the second explanatory parameter to the linear correlation, characterized by the correlation coefficient r and obtained with only one, the better explanatory parameter²³

$$F_{\text{imp}} = \frac{(R^2 - r^2)(n-3)}{(1-R^2)} \quad (3)$$

The F_{imp} value is the quotient of the BDE variation which is explained by two parameters in the planar correlation reduced by the part of variation which was already explained by the first parameter in the linear correlation to the part of the BDE variation which is not explained by the planar correlation. Note, that in a similar manner the significance of the quadratic effect is examined in the parabolic correlation^{22c} for which there is a strong mutual correlation between linear and quadratic parameters. This is also the case for the planar correlation described by Eqn (1), where both parameters, $(\sum Z_{\text{eff}}/d)$ and $(\sum Z/d)$, mutually correlate (giving, e.g., $r=0.873$ for the series with C—H bonds). Nevertheless, the calculated F_{imp} value (Table 2) is greater than the critical value of $F_{\alpha,1,n-3}$ from statistical tables^{22b} for $\alpha=0.005$ which indicates the significance of the addition of the second parameter with the probability 0.5%.

It can be added that the weighted regression, taking into account the experimental errors in BDE values as

Table 1. Bond dissociation energies (in kJ mol⁻¹) at 298 K estimated from Eqn (1), experimental and calculated by DFT method

Molecule ^a	Estimated from Eqn (1)	Experimental from Ref. 8	Calculated from Ref. 12
1 H-CH ₃	431.4	439.3 ± 0.4	443.9 (443.5) ^b
2 H-CHF ₂	436.7	431.8 ± 4.2	427.4 (419.7) ^b
3 H-CH ₂ F	434.0	423.8 ± 4.2	426.2 (420.9) ^b
4 H-CClF ₂	422.2	421.7 ± 8.4	(423.0) ^b
5 H-CCl ₂ F	410.4	410.9 ± 8.4	(407.9) ^b
6 H-CHClF	424.9	421.7 ± 10	(414.2) ^b
7 H-CCl ₃	396.0	392.5 ± 2.5	398.7 (392.9) ^b
8 H-CHCl ₂	407.8	407.1 ± 4.2	408.4 (405.4) ^b
9 H-CH ₂ Cl	419.6	419.0 ± 2.3	420.9 (420.9) ^b
10 H-CHClBr	388.6	393	(405.8) ^b
11 H-CF ₃	439.7	449.4	449.0 (441.0) ^b
12 Cl-CH ₃	357.1	350.2 ± 1.7	352.0 (355.2) ^c
13 Cl-CHCl ₂	314.7	320.5 ± 6.3	311.2
14 Cl-CHFCl	333.9	346.0 ± 13	
15 Cl-CF ₃	350.9	359.0 ± 5.4	362.9
16 Cl-CF ₂ Cl	331.8	319.7 ± 8.4	
17 Cl-CFCl ₂	312.6	301.2 ± 8.4	
18 Cl-CH ₂ Cl	336.0	338.1 ^d	331.0
19 Cl-CCl ₃	293.5	296.6	282.3
20 Cl-CH ₂ F	355.1	354.4 ± 12	
21 Br-CH ₃	292.8	294.1 ± 2.1	294.0 (305.9) ^c
22 Br-CHF ₂	292.5	288.7 ± 8.4	
23 Br-CF ₃	292.4	296.2 ± 1.3	294.3
24 Br-CF ₂ Cl	271.8	269.9 ± 6.3	
25 Br-CCl ₃	230.8	231.4 ± 4.2	
26 F-CF ₃	543.1	542.2 ± 4.2	543.7
27 F-CHF ₂	519.0	533.9 ± 5.9	531.7
28 F-CF ₂ Cl	499.4	489.5 ± 25	
29 F-CH ₂ F	495.0	496.2 ± 8.8	501.9
30 F-CFCl ₂	455.7	460.2 ± 25	
31 F-CHFCl	475.4	462.3 ± 10	
32 F-CH ₂ Cl	451.3	465.3 ± 9.6	
33 F-CH ₃	470.9	460.2 ± 8.4	467.1 (464.8) ^c
34 H-CH ₂ Br	396.8	425.1 ± 4.2	430.1 (423.4) ^b
35 H-CHBr ₂	361.9	417.1 ± 7.5	421.0 (405.8) ^b
36 H-CBr ₃	327.0	401.7 ± 6.7	410.4 (387.4) ^b
		395.2 ± 8.4	

^a The broken bond is indicated.^b From Ref. 9.^c From Ref. 11.^d Value of 338.0 ± 3.3 was reported recently in Ref. 21.

weights, is also statistically significant, for example, for C—H bonds

$$\text{BDE} = -4.1(\pm 0.8) \sum \frac{Z}{d} + 8(\pm 3) \sum \frac{Z_{\text{eff}}}{d} + 430(\pm 5) \quad (4)$$

with the $R = 0.9762$, $\delta = 6.8$, $F = 15.83$ and the addition of the second explanatory parameter cannot be rejected with the probability of 0.5% ($F_{\text{imp}} = 15.58 > F_{0.005, 1, 8} = 14.69$); 95% errors of regression coefficients are given in parentheses. However, errors in BDE values are not known for all compounds (for the above equation unknown errors for two compounds were assumed to be equal to the average error in the series) and thus, the weighted regression was not analyzed for other series.

Similar correlations as given by Eqn (1) for dissociation of C—H bond were analyzed for three

other series concerning C—F, C—Cl and C—Br bonds (Table 1). Unfortunately, the number of BDE values available⁸ for the C—I bond is too small for the planar regression. Statistical parameters obtained are given in Table 2. In all cases acceptable planar correlations were found and the addition of the second explanatory parameter is statistically significant at the level of $\alpha = 0.005$ or 0.025. Moreover, a comparison of results presented in Table 2 indicates reasonable trends. For all series signs of a and b coefficients are opposite and their values are similar for C—H, C—Cl, and C—Br bonds, respectively. The negative sign of the a coefficient indicates that the stronger repulsion with other electrons destabilize the molecule decreasing the BDE value. On the other hand, the reverse behavior is evident for the b coefficient describing the attraction with the positive charge of nuclei. Moreover, the obtained intercepts

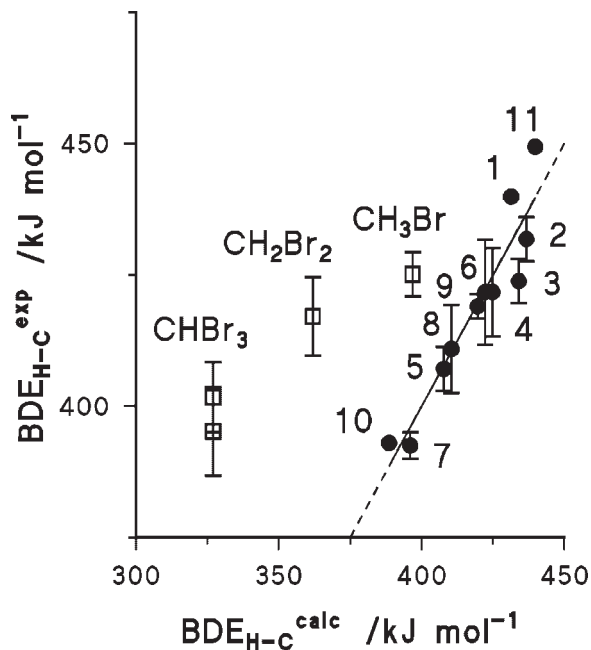


Figure 1. Relationship between experimental⁸ and estimated from Eqn (1) bond dissociation energies of C–H bonds, BDE_{C-H} . Compounds numbering as in Table 1. Open squares: compounds 34–36 not included in the correlation line. Errors in experimental BDE values⁸ are indicated, when available

(i.e., regression coefficients c) correspond to the Pauling's empirical values of bond energy²⁴ equal to 415, 328, and 276 kJ mol^{-1} for C–H, C–Cl, and C–Br bonds, respectively, in full agreement with the assumed model.

Table 2. Parameters of correlation analysis of BDE values according to Eqn (1)

Parameter	Bond			
	C–H	C–F	C–Cl	C–Br
n^a	11	8	9	5
a^b	-4 ± 1	-12 ± 5	-5 ± 3	-6 ± 2
b^b	9 ± 4	32 ± 13	10 ± 7	12 ± 6
c^b	418 ± 16	415 ± 38	344 ± 26	277 ± 26
R^c	0.9435	0.9459	0.9292	0.9940
δ^d	5.6	10.2	8.1	2.6
F^e	32.42	21.27	18.95	82.65
$F_{\alpha,2,n-3}^f$	11.04	18.31	14.54	39.00 ^g
F_{imp}^h	31.94	34.23	11.61	69.31
$F_{\alpha,1,n-3}^i$	14.69	22.78	8.81 ^g	38.51 ^g

^a Number of compounds.

^b Regression coefficients of Eqn (1) with 95% errors calculated using the Student's distribution.

^c Correlation coefficient of Eqn (1).

^d The mean quadratic deviation of BDE values from the correlation line.

^e Values of the F -test calculated from Eqn (2).

^f Critical values of F for 2 and $n-3$ degrees of freedom and the significance level of $\alpha = 0.005$.

^g For the significance level of $\alpha = 0.025$.

^h Values of F_{imp} test calculated from Eqn (3).

ⁱ Critical values of F for 1 and $n-3$ degrees of freedom and the significance level of $\alpha = 0.005$.

Only for the C–F bond the Pauling's bond energy equal to 443 kJ mol^{-1} is much higher, but still within the error of the estimating c value (Table 2). Thus, the electrostatic model proposed looks generally correct.

BDE values estimated from Eqn (1) are given in Table 1 with experimental values⁸ used for correlations. For a comparison literature BDE values calculated by DFT method^{9,11,12} are also given in Table 1. They were obtained at the B3LYP/6-311G(d,p) level with ROB3LYP method for radicals,⁹ at the B3P86/6-31G(d) level,¹¹ and at the B3P86/6-133++G(2df,p) level with an empirical correction increasing the absolute energies of the radicals.¹² Agreement between the presented data for compounds 1–33 is satisfactory.

The plot of all BDE values estimated from Eqn (1) against the experimental data is shown in Fig. 2; it holds with the correlation coefficient of $r = 0.9956$ for 33 compounds. The mean deviation of estimated BDEs from the correlation line $\delta = 7.35$ is acceptable taking into account errors of literature BDE values (given in Table 1), which change in the range from 0.4 to 25.1 with the average value equal to 7.3 kJ mol^{-1} .

It is obvious that an electron density distribution in a molecule is oversimplified in the proposed model, considering many-electron atoms as point charges. For that reason the model cannot be used for larger halogenated alkanes and even, as shown in Fig. 1, for methane substituted by bromine atoms. The correct electron-charge distribution is given by quantum chemical calculations and only such calculations have to be used for predictions of BDE values for larger molecules, as well as to explain intercepts (c coefficients) in Eqn (1).

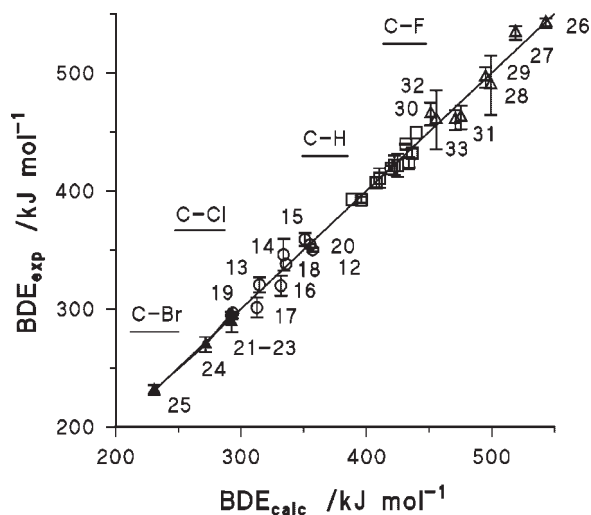


Figure 2. Relationship between experimental⁸ and estimated from Eqn (1) bond dissociation energies, BDE, in polyhalogen methanes. Compounds numbering as in Table 1. Errors in BDE values⁸ are indicated and theoretical line is shown

Table 3. Bond dissociation energies, BDE, estimated from Eqn (1) and calculated by the DFT method

Compound ^a	BDE (kJ mol ⁻¹)	
	Eqn (1)	DFT
Cl-CHF ₂	353 ± 8	333.5
Br-CH ₂ F	293 ± 3	286.0
Br-CFCl ₂	251 ± 3	232.9
Br-CH ₂ Cl	272 ± 3	264.8
Br-CHCl ₂	251 ± 3	236.4
F-CHCl ₂	431 ± 10	439.1
F-CCl ₃	406 ± 10	422.4

^aThe broken bond is indicated.

Nevertheless, for a correct charge distribution the stabilities of reactants and products of a dissociation process depend mainly on the Coulomb interactions in a similar sense as for a covalent bond. The electrostatic model under consideration can show this in a persuasive way, although this aspect is not so obvious in other approaches. In order to support that a regularity described by Eqn (1) for simple haloalkanes is not accidental, unknown BDE values were estimated using coefficients from Table 2. They are given in Table 3 and their errors were assumed to be equal to the δ value for each correlation.

For Br-CH₂Cl the estimated BDE value can be verified by the recently reported²¹ experimental result, BDE = 277.3 ± 3.6 kJ mol⁻¹, obtained employing the threshold photoelectron photoion coincidence technique. For all halides given in Table 3 BDE values were calculated by the DFT method at the B3LYP/6-311G(d,p) level with ROB3LYP method for open shell radicals, as proposed by Chandra and Uchimaru.⁹ Calculations were carried out using Gaussian-03 programs. The obtained values are given in Table 3. Differences between both sets of data are in the range from 1.8% to 7.8% with the mean value of 4.4%.

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