A New Approach of Evaluating Bond Dissociation Energy from Eigenvalue of Bonding Orbital-Connection Matrix for C−C and C−H Bonds in Alkane

Chenzhong Cao* and Hua Yuan

Department of Chemistry, Xiangtan Normal University, Xiangtan, 411201, People's Republic of China

Received September 5, 2002

A new bonding orbital-connection matrix was constructed, in which the diagonal elements were assigned the chemical potentials E_1 and E_2 of two radicals $R_i\bullet$ and $R_j\bullet$ obtained by cutting the interested bond, and the off-diagonal elements, representing bonding connections, were assigned values 1. The eigenvalues X_{1CC} and X_{1CH} of the bonding orbital-connection matrix were obtained for C−C and C−H bonds, respectively. Also a steric effect parameter S_{ij} was proposed for C−C bond. Using X_{1CC}, X_{1CH}, and S_{ij} as bond descriptors, good correlations with the Bond Dissociation Energies (BDEs) of the C−C and C−H bonds were obtained for alkanes. The result shows that the eigenvalue of bonding orbital-connection matrix is a good descriptor for expressing the relative bond energies of C−C and C−H bonds in alkane. This work provides a new physical insight and a principally novel general approach to the evaluation of the bond dissociation energies of carbon−carbon (C−C) and carbon−hydrogen (C−H) bonds in alkane. Also it builds a simple bridge linking the adjacent matrix of radicals $R_i\bullet$ and $R_j\bullet$ with the BDE of R_i-R_j and R_i-H. Furthermore, the Heat of Atomization (HA) and Heat of Formation in Gas (HFG^0) of alkane can be estimated well with the parameters X_{1CC}, X_{1CH}, and S_{ij}.

1. INTRODUCTION

The bond dissociation energy (BDE) is a fundamental factor influencing chemical reactivity and is of paramount importance in radical processes. It has also been shown that the BDE can influence reactivity in polar processes. On the other hand, because BDE is related to the heat of formation of a compound, it is widely used for estimation of heats of formation for organic compounds. This method is the so-called bond additivity.[1,2] 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 energies.[1−17] Quantum chemical calculations have also proven to be a very useful tool for the determination of bond dissociation energies,[18] even in relatively large molecules.[19] Experimental determining of BDEs is tedious and time-consuming. Semiempirical quantum chemical calculation needs a time-consuming parametrization,[18] and the application of high-level ab initio quantum chemical theory is very expensive.[18] Thus, an estimation scheme is very valuable. A number of empirical methods for estimations of heats of formation of molecules and radicals (and thereby also for estimation of homolytic bond dissociation energies) have been put forward.[1,15−17] The most famous of these methods is probably the empirical scheme by Benson and co-workers.[1] Recently, some new estimation methods have also been investigated.[15−17]

In this work, we develop a novel semiempirical method for estimation of C−C and C−H bond dissociation energies (BDE) in alkanes. The approach is based on the eigenvalue of bonding orbital-connection matrix for carbon−carbon

(C−C) and carbon−hydrogen (C−H) bonds in alkane and does not need complicated calculation.

2. METHOD

Pauling[20,13] ever proposed that the relation between the heteropolar bond energy D_{AB} and the homopolar terms D_{AA} and D_{BB} is

$$D_{AB} = \frac{1}{2}(D_{AA} + D_{BB}) + k(\Delta\chi)^2 \qquad (1)$$

where k is an empirical constant (96.5 kJ/mol) and $\Delta\chi$ is the difference in electronegativity between the atoms A and B. However, it has been shown[13] that eq 2, with $k = 134$ kJ/mol, gives better results than eq 1:

$$D_{AB} = (D_{AA}D_{BB})^{1/2} + k|\Delta\chi| \qquad (2)$$

Equation 2 implies if A and B are the same kind of atom, the D_{AB} will be a constant. That is to say all C−C bonds in alkane have the same BDE and so do the C−H bonds. As we know, not all C−H or C−C bonds have the same BDE, and the BDE is actually related to its chemical environment. To resolve this problem, Smith suggested[13] that the carbon−carbon bond energy $D(C_i-C_j)$ is variable according to eq 3

$$D(C_i-C_j) = D°(C-C) - aq_iq_j \qquad (3)$$

where i and j indicate adjacent singly bonded carbon atoms having fractional charges q_i and q_j, and a is an empirical constant, $D°(C-C)$ is taken as 358.6 kJ/mol. Equation 3 shows that the carbon−carbon (C_i-C_j) bond-energy is enhanced by the fractional charges on themselves. From the principle of electronegativity equalization, Smith[13] further changes eq 3 to eq 4

* Corresponding author phone: 00086-0732-8291336; fax: 00086-0732-8291001; e-mail: czcao@xtnu.edu.cn.
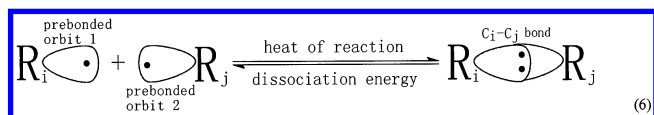
EVALUATING BOND DISSOCIATION ENERGY

J. Chem. Inf. Comput. Sci., Vol. 43, No. 2, 2003 **601**

$$D(C_i - C_j) = D°(C-C) + k|\Delta\chi| \qquad (4)$$

where k is an empirical constant and $\Delta\chi$ is the difference in electronegativity between the groups linked by the carbon–carbon (C_i–C_j) bond. Equation 4 appears to be inconsistent with eq 2, but it is an extension of eq 2 and gives a new meaning of carbon–carbon bond-energy relating to its environment.

It is known that the electronegativity χ of any chemical species (an atom or a molecule) is the negative of its chemical potential,[21,22] μ, obtained from density functional theory as in eq 5

$$\chi = -\mu = -(\partial E/\partial N)_v \qquad (5)$$

where E is the exact Hohenberg and Kohn energy functional for an N-electron system characterized by an external potential v. Based on eqs 4 and 5, we think that the carbon–carbon (C_i–C_j) bond-energy perhaps relates to the energies of "prebonded" atomic orbitals that form the C_i–C_j bond. Suppose the alkyl radical $R_i\bullet$ links with $R_j\bullet$ to form R_i–R_j (C_i–C_j) bond, its heat of reaction is equal to its dissociation energy. If the chemical potentials (or energy level) of orbitals

1 and 2 in eq 6 are in low (large electronegativity), the formed carbon–carbon bond will be strong, in other words, its bond dissociation energy will be large. Otherwise, the bond will be weak and its bond dissociation energy will be small. The chemical potentials of orbitals 1 and 2 can be expressed by the ionization potentials of alkyl radical $R_i\bullet$ and $R_j\bullet$, respectively. It should be noted that, up to now, only a few ionization potential values of alkyl radicals have been measured, so it is necessary to develop a method for estimating their ionization potentials. Our previous work[23] has shown that the ionization potentials of monosubstituted alkanes have relation with the polarizabilities of their alkyl groups. Here, we also find a linear correlation between the ionization potentials of alkyl radicals and their polarizability effect index (PEI)[24] when their ionization potentials are measured by a same method such as photoionization and electron impact (see eq 7 and Table 1). For examples, photoionization(the third column values of Table 1)[25] of alkyl radicals has the correlation

$$Ip(eV) = 18.092(\pm0.911) - 8.358(\pm0.787)PEI(R_i) \quad (7a)$$

$$r = 0.9913, s = 0.16, F = 112.79, n = 4$$

Electron impact ionization (the fourth column values of Table 1)[25] of alkyl radicals has the correlation

$$Ip(eV) = 15.554(\pm0.535) - 5.724(\pm0.403)PEI(R_i) \quad (7b)$$

$$r = 0.9902, s = 0.09, F = 202.08, n = 6$$

It can be seen from Table 1 that there are different ionization potential values in different measured condition for an alkyl radical.

Further, we calculated the highest occupied molecular orbital(HOMO) energies(E_{HOMO}) of $H_3C\bullet$, $MeH_2C\bullet$, $EtH_2C\bullet$,

Table 1. Ionization Potential for Some Alkyl Radicals

no.	radical	PEI(R_i)[a]	Ip_{exp} (Ip_{calc}) (eV)[b]	Ip_{exp} (Ip_{calc}) (eV)[c]
1	$H_3C\bullet$	1	9.83 (9.73)	
2	$MeH_2C\bullet$	1.1405	8.4 (8.56)	
3	$EtH_2C\bullet$	1.1887	8.1 (8.16)	
4	$PrCH_2\bullet$	1.2122		8.64 ± 0.05 (8.61)
5	$i\text{-}PrCH_2\bullet$	1.2368		8.35 ± 0.05 (8.47)
6	$Me_2CH\bullet$	1.2810	7.5 (7.38)	
7	$MeEtCH\bullet$	1.3292		7.93 ± 0.05 (7.94)
8	$Me_3C\bullet$	1.4215		7.42 ± 0.07 (7.42)
9	$EtMe_2C\bullet$	1.4696		7.12 ± 0.1 (7.14)
10	$Me_3CH_2C\bullet$	1.2849		8.33 ± 0.1 (8.20)
			method: photoionization	method: electron impact

[a] PEI of radical, calculation based on ref 24. [b] The Ip_{exp} is measured by photoionization, taken from ref 25. The Ip_{calc} is calculated by eq 7a. [c] The Ip_{exp} is measured by electron impact, taken from ref 25. The Ip_{calc} is calculated by eq 7b.

and $PrCH_2\bullet$ by semiempirical quantum chemistry method AM1(using MOPAC program packages in SYBL 6.7 of Tripos, Inc.) and got the values of −13.7962, −11.9448, −11.3913, and −11.2204 (eV), respectively. The obtained correlation between E_{HOMO} and PEI(R_i) is

$$E_{HOMO}(eV) = -26.1568(\pm0.6127) + 12.3914(\pm0.5382)PEI(R_i) \quad (7c)$$

$$r = 0.9981, s = 0.0886, F = 529.93, n = 4$$

Equations 7a, 7b, and 7c all show a same change rule that the chemical potentials (or energy level) of orbitals 1 and 2 in eq 6 can be expressed by $E_1 = a + bPEI(R_i)$ and $E_2 = a + bPEI(R_j)$, respectively. To relate the bond dissociation energies (BDEs) of carbon–carbon (C_i–C_j) bonds to the chemical potentials (or energy level) of orbitals 1 and 2, we construct an adjacency matrix for each carbon–carbon (C_i–C_j) bond and assign the E_1 and E_2 as the diagonal elements of the matrix. The off-diagonal elements, representing bonding connections, are assigned values 1. Thus the constructed connection-matrix (CM_{ij}) (see eq 8) of bond R_i–R_j (C_i–C_j) is similar to Hückel molecular orbital (HMO) method.[26]

$$CM_{ij} = \begin{bmatrix} E_1 & 1 \\ 1 & E_2 \end{bmatrix} = \begin{bmatrix} a + bPEI(R_i) & 1 \\ 1 & a + bPEI(R_j) \end{bmatrix} \quad (8)$$

The number 1 in CM_{ij} indicates the alkyl radical $R_i\bullet$ linked with $R_j\bullet$. Here let the eigenvalues of connection-matrix (CM_{ij}) be $^OX_{1CC}$, $^OX_{2CC}$ (and $^OX_{1CC} < ^OX_{2CC}$ which is similar to the HOMO and LUMO of Hückel molecular orbital method). It can be found (see the next section of this paper) that the bond energies $D(C_i$–$C_j)$ (or BDE of bond C_i–C_j) have a linear correlation with the eigenvalues.

For the calculation convenience, we further modify the connection-matrix (CM_{ij}) into another form, which is named as modified connection-matrix ($CM_{ij,m}$) (see eq 9), and assign its eigenvalues X_{1CC} and $X_{2CC}(X_{1CC} < X_{2CC})$.

$$CM_{ij,m} = \begin{bmatrix} PEI(R_i) & 1 \\ 1 & PEI(R_j) \end{bmatrix} \quad (9)$$

Table 2. Polarizability Effect Index Increment $\Delta PEI(l)$[24] of the lth Carbon Atom.

lth carbon atom	$\Delta PEI(l)$	lth carbon atom	$\Delta PEI(l)$
1	1.0000	6	0.0090
2	0.1405	7	0.0064
3	0.0481	8	0.0047
4	0.0235	9	0.0037
5	0.0138	10	0.0022

Because a and b in expressions of E_1 and E_2 are constants, it can be demonstrated that there are linear correlation between the $^OX_{1CC}$ or $^OX_{2CC}$ of CM_{ij} and the X_{1CC} or X_{2CC} of $CM_{ij,m}$ respectively. That is

$$^OX_{1CC} = a_1 + b_1X_{1CC} \tag{10a}$$

$$^OX_{2CC} = a_2 + b_2X_{2CC} \tag{10b}$$

Thus this paper employs the eigenvalues X_{1CC} and X_{2CC} of modified connection-matrix ($CM_{ij,m}$), instead of $^OX_{1CC}$ and $^OX_{2CC}$, to calculate the BDEs of carbon−carbon (C_i−C_j) bond in alkanes (all the eigenvalues in this paper are obtained by computer). Some calculation examples of eigenvalues X_{1CC} and X_{2CC} are listed in Table 3. The calculation procedure can be briefly divided into three steps.

First Step. Cut an interested carbon−carbon (C_i−C_j) bond into two alkyl radicals R_i and R_j. Then calculate their polarizability effect index $PEI(R_i)$ and $PEI(R_j)$ according to the method in the literature,[24] respectively. That is $PEI(R_i)$ $= \sum\Delta PEI(l)$, in which $\Delta PEI(l)$ is the contribution of the lth carbon atom in alkyl radical to the $PEI(R_i)$, for example, 2-methylbutyl radical ($\bullet CH_2CH(CH_3)CH_2CH_3$), taking the radical carbon atom as the beginning one (first one), the next carbon atoms are the second one, and the next next carbon atoms are the third one, and so on (see Figure 1). Using the $\Delta PEI(l)$ values of Table 2, we can obtain its $PEI(R_i)$:

$$PEI(R_i) = \Delta PEI(1) + \Delta PEI(2) + 2\Delta PEI(3) + \Delta PEI(4)$$
$$= 1.0000 + 0.1405 + 2(0.0481) + 0.0235 = 1.2602$$

Second Step. Use the $PEI(R_i)$ and $PEI(R_j)$ values of radical R_i and R_j to construct the modified connection-matrix (see the $CM_{ij,m}$ of Table 3).

Third Step. Solve the modified connection-matrix $CM_{ij,m}$ and get the eigenvalues (see the X_{1CC} and X_{2CC} of Table 3).

For the carbon−hydrogen bond R_i−H (or C_i−H), we can use the chemical potentials of orbital 1 in alkyl radical $R_i\bullet$ and hydrogen atomic orbital, E_1 and E_H, to construct the connection-matrix (CM_{iH}) (see eq 11).

$$CM_{iH} = \begin{bmatrix} E_1 & 1 \\ 1 & E_H \end{bmatrix} = \begin{bmatrix} a + bPEI(R_i) & 1 \\ 1 & E_H^0 + bPEI(H) \end{bmatrix} \tag{11}$$

Because the electron in hydrogen atomic orbital connects with only a proton, its $PEI(H) = 0$, that is $E_H = E_H^0 + 0 =$ constant (the ionization potential of hydrogen atom) in eq 11. In accordance with eq 9, we obtain the modified connection-matrix ($CM_{iH,m}$) of bond R_i−H (C_i−H) as follows.

$$CM_{iH,m} = \begin{bmatrix} PEI(R_i) & 1 \\ 1 & 0 \end{bmatrix} \tag{12}$$

If let the eigenvalues of connection-matrix (CM_{iH}) be $^OX_{1CH}$, $^OX_{2CH}$ (here $^OX_{1CH} < {}^OX_{2CH}$) and the eigenvalues of modified connection-matrix ($CM_{iH,m}$) be X_{1CH}, X_{2CH}, there are also linear correlations between X_{1CH}, X_{2CH} and $^OX_{1CH}$, $^OX_{2CH}$, respectively. That is

$$^OX_{1CH} = a_{1H} + b_{1H}X_{1CH} \tag{13a}$$

$$^OX_{2CH} = a_{2H} + b_{2H}{}^OX_{2CH} \tag{13b}$$

Thus the eigenvalues X_{1CH} and X_{2CH} of modified connection-matrix ($CM_{iH,m}$), instead of $^OX_{1CH}$ and $^OX_{2CH}$, are used to calculate the BDEs of carbon−hydrogen (C_i−H) bond in alkanes. Some calculation examples of eigenvalues are listed in Table 4.

3. CORRELATION BETWEEN EIGENVALUES AND BDE FOR C_i−C_j AND C_i−H BONDS

BDE for C_i−C_j Bond. Here we suppose that the BDE of C_i−C_j bond has a linear relation with $^OX_{1CC}$ or $^OX_{2CC}$.

$$BDE(C_i-C_j) = A + B^OX_{1CC} \tag{14a}$$

or

$$BDE(C_i-C_j) = A + B^OX_{2CC} \tag{14b}$$

From eqs 10a and 10b, we can lead to eqs 15a and 15b.

$$BDE(C_i-C_j) = A + B(a_1 + b_1X_{1CC}) =$$
$$A_1 + B_1X_{1CC} \tag{15a}$$

$$BDE(C_i-C_j) = A + B(a_2 + b_2X_{1CC}) =$$
$$A_2 + B_2X_{2CC} \tag{15b}$$

where A, B, A_1, B_1, A_2, and B_2 all are coefficients of regression equations. Taking some measured BDEs[12,16] of C_i−C_j as data set (listed in Table 5), we make a regression analysis with their eigenvalues X_{1CC} and X_{2CC}, respectively, and obtain the following correlation expressions.

$$BDE(C_i-C_j)(kJ/mol) = 378.741(\pm 5.032) -$$
$$210.237(\pm 15.169)X_{1CC} \tag{16}$$

$$r = 0.9872, s = 5.22, F = 192.08, n = 7$$

$$BDE(C_i-C_j)(kJ/mol) = 793.501(\pm 43.444) -$$
$$207.206(\pm 18.766)X_{2CC} \tag{17}$$

$$r = 0.9801, s = 6.50, F = 121.92, n = 7$$

Equations 16 and 17 show that there are indeed good linear correlations between the BDE and X_{1CC} or X_{2CC}. The correlation of eq 16 is better than that of eq 17, so we take eq 16 as the basic model to correlate the BDE of C_i−C_j bond. However the lager standard deviation of eq 16 also reminds us of the steric effect in the alkanes[1,2,7,8] and the influence of steric effect on the BDE of C_i−C_j bond. Thus, for eq 16, we can expect an improved result if a steric term is added in. This paper proposes a simple steric effect parameter, S_{ij} $= (V_iV_j)^2$, and employs it to scale the steric effect on the BDE of C_i−C_j bond (V_i and V_j are the vertex degrees of C_i and C_j, which is the number of carbon atoms linked to C_i

EVALUATING BOND DISSOCIATION ENERGY

J. Chem. Inf. Comput. Sci., Vol. 43, No. 2, 2003 **603**

Table 3. Some Calculation Examples of Eigenvalues X_{1CC} and X_{2CC}

C_i-C_j bond	first step		second step $CM_{ij,m}$	third step	
	R_i	R_j		X_{1CC}	X_{2CC}
CH_3-CH_3	$PEI(R_i)$ $H_3C\bullet$ 1.0000	$PEI(R_j)$ $H_3C\bullet$ 1.0000	$\begin{bmatrix} 1.0000 & 1 \\ 1 & 1.0000 \end{bmatrix}$	0.0000	2.0000
$CH_3-CH_2CH_3$	$H_3C\bullet$ 1.0000	$H_3CH_2C\bullet$ 1.1405	$\begin{bmatrix} 1.0000 & 1 \\ 1 & 1.1405 \end{bmatrix}$	0.0678	2.0727
$(CH_3)_2CH-CH_2CH_3$	$(CH_3)_2CH\bullet$ 1.2810	$H_3CH_2C\bullet$ 1.1405	$\begin{bmatrix} 1.2810 & 1 \\ 1 & 1.1405 \end{bmatrix}$	0.2083	2.2132
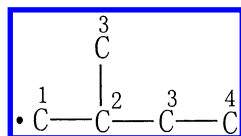
Figure 1. The 2-methylbutyl radical and carbon atom ordinal.

Table 4. Some Calculation Examples of Eigenvalues X_{1CH} and X_{2CH}

C_i-H bond	R_i	H	$CM_{iH,m}$	X_{1CH}	X_{2CH}
CH_3-H	$H_3C\bullet$	H	$\begin{bmatrix} 1.0000 & 1 \\ 1 & 1.0 \end{bmatrix}$	−0.6180	1.6180
CH_3CH_2-H	$H_3CH_2C\bullet$	H	$\begin{bmatrix} 1.1405 & 1 \\ 1 & 0 \end{bmatrix}$	−0.5809	1.7214
$(CH_3)_2CH-H$	$(CH_3)_2CH\bullet$	H	$\begin{bmatrix} 1.2810 & 1 \\ 1 & 0 \end{bmatrix}$	−0.5470	1.8280

and C_j, respectively). That is to say the more the carbon atoms linking to the given carbon atom, the more crowded the space around the given one. For a pair of carbon atoms in a carbon−carbon bond, the more crowded space will lead to the more nonbonding interaction among the adjacent groups and raises the inner energy of the bond rapidly. For example, CH_3-CH_3, $V_i = V_j = 1$, $S_{ij} = (1 \times 1)^2 = 1$; $(CH_3)_2CH-CH_2CH_3$, $V_i = 3$, $V_j = 2$, $S_{ij} = (3 \times 2)^2 = 36$. Using the two variables X_{1CC} and S_{ij}, we obtained the following regression equation.

$$BDE(C_i-C_j)(kJ/mol) = 376.160(\pm 1.777) - 162.718(\pm 9.270)X_{1CC} - 0.100(\pm 0.016)S_{ij} \quad (18)$$

$$r = 0.9988, s = 1.79, F = 833.73, n = 7$$

Compared to eq 16, the correlation of eq 18 is much better and the standard deviation s is much less. The calculated BDEs of C_i-C_j bond by eq 18 are also listed in Table 5.

BDE for C_i-H Bond. As did in the correlation of BDE for C_i-C_j bond, we carry out correlations between some measured BDEs[15] and X_{1CH} or X_{2CH} for C_i-H bonds. The obtained regression equations are as follows:

$$BDE(C_i-H)(kJ/mol) = 244.560(\pm 14.038) - 311.043(\pm 25.365)X_{1CH} \quad (19)$$

$$r = 0.9806, s = 2.43, F = 150.38, n = 8$$

$$BDE(C_i-H)(kJ/mol) = 590.935(\pm 16.938) - 96.072(\pm 9.306)X_{2CH} \quad (20)$$

$$r = 0.9730, s = 2.86, F = 106.58, n = 8$$

Both eqs 19 and 20 show that there are good correlations between BDE of C_i-H and X_{1CH} or X_{2CH}. The correlation of eq 19 is better than that of eq 20, hence this paper employs eq 19 to evaluate the BDE of C_i-H bond. Here, the steric effect does not need to be considered because of the very small volume of hydrogen atom. The calculated BDEs of C_i-H bonds by eq 19 are listed in Table 6.

The correlation between the eigenvalues of connection-matrix and the bond dissociation energy may be understood as follows. Based on quantum chemistry, a bond combined by two lower energy atom orbitals will be in lower energy level[26] or has higher BDE. In fact, it is true. For examples, the energy ordering of carbon atomic hybrid orbitals is $sp < sp^2 < sp^3$ (the ionization potential ordering is $sp > sp^2 > sp^3$), the carbon−carbon bond dissociation energy ordering is $C(sp)-C(sp) > C(sp^2)-C(sp^2) > C(sp^3)-C(sp^3)$, and the carbon−hydrogen bond dissociation energy ordering is also $C(sp)-H > C(sp^2)-H > C(sp^3)-H$. As stated in the above section, the PEI-values for alkyl radicals are linearly correlated to the ionization potentials, so eqs 16, 17, 19, and 20 mean that the eigenvalues of a connection-matrix containing the ionization potentials would also be linearly related to the bond dissociation energies. According to the LCAO-MO approximation, the molecular orbitals are linear combinations of the two atomic orbitals. That is a linear combination of the two atomic orbitals will lead to a secular determinant and result in two molecular orbitals,[26] a bonding orbital with lower energy and an antibonding orbital with higher energy. The BDE is better related to the energy of its bonding orbital. Each connection-matrix (similar to a secular determinant) yields two eigenvalues, which are something corresponding to the energies of two molecular orbitals formed by two atomic orbitals. Perhaps, the smaller value (the first eigenvalue) is related to the energy of the bonding orbital and the larger value (the second eigenvalue) is related to the energy of the antibonding orbital. Therefore the first eigenvalue gives a somewhat better correlation with the BDE than the second eigenvalue.

4. DISCUSSION

Evaluation of BDE of C−H and C−C Bonds in Alkane. Equation 18 shows a good correlation between the BDE and parameters X_{1CC} and S_{ij} of carbon−carbon (C_i-C_j) bond. Equation 19 indicates a good correlation between the BDE and X_{1CH} of carbon−hydrogen (C_i-H) bond. Therefore eqs 18 and 19 can be directly employed to evaluate the relative BDE of carbon−carbon (C_i-C_j) bond and carbon−hydrogen (C_i-H) bond for an assigned alkane molecule. Take 2,2,5-trimethylheptane (Figure 2) for example. Cutting the C_1-H

Table 5. Bond Dissociation Energies (BDEs) of the C_i–C_j Bonds in Alkane (in kJ/mol)

no.	R_i–R_j(C_i–C_j)	X_{1CC}	X_{2CC}	S_{ij}	BDE(C_i–C_j)$_{exp}$	BDE(C_i–C_j)$_{calc}$[d]
1	H_3C–CH_3	0.0000	2.0000	1	376.0 ± 2.1[a]	376.06
2	Me_2HC–CMe_3	0.3488	2.3538	144	305.2[b]	305.00
3	Me_3C–CMe_3	0.4215	2.4215	256	282.4[c]	281.96
4	MeH_2C–$CEtMe_2$	0.2916	2.3186	64	322.59[b]	322.31
5	Me_2HC–$CEtMe_2$	0.3709	2.3798	144	298.32[b]	301.40
6	$EtMeHC$–$CHEtMe$	0.3292	2.3292	81	315.05[b]	314.49
7	$EtMeHC$–CMe_3	0.3743	2.3764	144	302.5[b]	300.85

[a] Taken from ref 12(a). [b] Taken from ref 16. [c] Taken from ref 12(b). [d] Calculated by eq 18.

Table 6. Bond Dissociation Energies (BDE) of the C_i–H Bonds in Alkanes (in kJ/mol)

no.	R_i–H(C_i–H)	X_{1CH}	X_{2CH}	BDE-(C_i–H)$_{exp}$[a]	BDE-(C_i–H)$_{calc}$[b]
1	CH_3–H	−0.6180	1.6180	438.9	436.78
2	$MeCH_2$–H	−0.5809	1.7214	423	425.24
3	$MeCH_2CH_2$–H	−0.5689	1.7576	420	421.51
4	Me_2CH–H	−0.5470	1.8280	412.5	414.70
5	$EtMeCH$–H	−0.5363	1.8653	410.9	411.37
6	Me_3C–H	−0.5161	1.9377	403.8	405.09
7	Me_3CCH_2–H	−0.5461	1.8310	418	414.42
8	$EtMe_2C$-H	−0.5061	1.9758	404	401.98

[a] Taken from ref 15. [b] Calculated by eq 19.

```
        C8
        |
C1–C2–C3–C4–C5–C6–C7
    |        |
    C9       C10
```
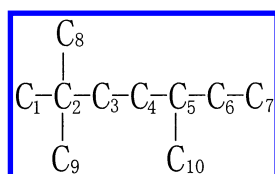
Figure 2. Molecule 2,2,5-trimethylheptane (non-hydrogen atom).

bond, we can get 2,2,5-trimethylheptyl •$CH_2CMe_2CH_2CH_2$-$CHMeCH_2CH_3$ (its PEI = 1.3466) and a hydrogen atom H. Then construct its modified connection-matrix ($CM_{1H,m}$) by means of eq 12. The modified connection-matrix ($CM_{1H,m}$) of C_1–H bond for 2,2,5-trimethylheptane is

$$CM_{1H,m} = \begin{bmatrix} 1.3466 & 1 \\ 1 & 0 \end{bmatrix} \quad (21)$$

By solving the matrix $CM_{1H,m}$ (eq 21), the eigenvalue X_{1CH} (−0.5322) is obtained.

When cutting the C_3–C_4 bond, we can get 2,2-dimethyl-propyl •$CH_2CMe_2CH_3$ (its PEI = 1.2849) and 2-methylbutyl •$CH_2CHMeCH_2CH_3$ (its PEI = 1.2603) and further construct its modified connection-matrix ($CM_{34,m}$) by means of eq 9. The modified connection-matrix ($CM_{34,m}$) of C_3–C_4 bond for 2,2,5-trimethylheptane is

$$CM_{34,m} = \begin{bmatrix} 1.2849 & 1 \\ 1 & 1.2603 \end{bmatrix} \quad (22)$$

From eq 22, the eigenvalue X_{1CC}, 0.2725 is calculated.

Using the similar steps as above, we get different X_{1CH} value for different C_i–H bond and different X_{1CC} value for different C_i–C_j bond of 2,2,5-trimethylheptane molecule. These eigenvalues (X_1) together with the steric effect parameter S_{ij} values of C_i–C_j bonds all are listed in Table 7.

Based on eqs 19 and 18, we evaluate BDE of each C–H and C–C bond for the 2,2,5-trimethylheptane molecule with

Table 7. Eigenvalues X_1 for C_i–C_j and C_i–H and S_{ij} Values for C_i–C_j in 2,2,5-Trimethylheptane

bond	X_1[a]	S_{ij}	BDE$_{exp}$[b] (kJ/mol)	BDE$_{calc}$[c] (kJ/mol)
C_1–H	−0.5322		410.0	409.56
C_3–H	−0.4932		397.5	397.47
C_4–H	−0.4962			398.40
C_5–H	−0.4839		384.9	394.59
C_6–H	−0.5119			403.27
C_7–H	−0.5478			414.40
C_{10}–H	−0.5372			411.11
C_1–C_2	0.2304	16	342.3	337.07
C_2–C_3	0.3318	64	325.1	315.76
C_3–C_4	0.2725	16	342.3	330.22
C_4–C_5	0.2936	36	336.4	324.78
C_5–C_6	0.2593	36		330.36
C_6–C_7	0.1393	4	354.8	353.09
C_5–C_{10}	0.1970	9	352.3	343.20

[a] For C_i–H bond, $X_1 = X_{1CH}$. For C_i–C_j bond, $X_1 = X_{1CC}$. [b] Taken from ref 17. [c] For C_i–H bond, calculated by eq 19. For C_i–C_j bond, calculated by eq 18.
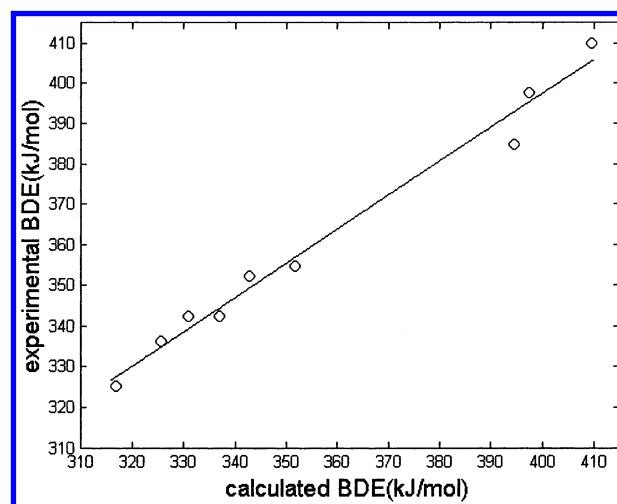
Figure 3. The plot of calculated BDE vs experimental BDE of C–H and C–C bond for 2,2,5-trimethylheptane.

their X_{1CH} and X_{1CC} values, respectively. The calculated results are listed in Table 7, and the plot of calculated BDE versus experimental BDE is shown by Figure 3, which illustrates that even small changes in the BDE of C–H and C–C bonds can be reproduced and the calculated BDE order is in good accordance with the experimental ones. We also noted that there are several discrepancies more than 10 kJ/mol, which cannot be addressed better.

Evaluation of Heats of Atomization for Alkanes. For an alkane molecule, its heat of atomization (HA) must be related to the bond dissociation energies of C–H and C–C bonds, which consist in the molecule. Of course it cannot be the simple sum of the bond dissociation energies of C–H
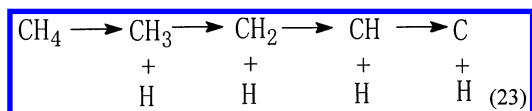
Table 8. Experimental and Estimated Heats of Atomization for 45 Alkanes

no.	alkanes[a]	$\sum X_{1CC}$	$\sum X_{1CH}$	N_{C-C}	N_{C-H}	$\sum S_{ij}$	$HA_{exp}{}^{b}$ (kJ/mol)	$HA_{calc}{}^{c}$ (kJ/mol)
1	1	0.0000	−2.472	0	4	0	1663.1	1660.14
2	3	0.1356	−4.5074	2	8	8	4000.45	4002.43
3	4	0.3203	−5.5244	3	10	24	5176.18	5178.07
4	2m3	0.3921	−5.5327	3	10	27	5184.56	5184.04
5	5	0.5296	−6.5340	4	12	40	6349.91	6352.44
6	2m4	0.6219	−6.5407	4	12	58	6357.95	6357.78
7	22mm3	0.7552	−6.5532	4	12	64	6369.46	6367.86
8	6	0.7533	−7.5404	5	14	56	7524.10	7526.45
9	2m5	0.8540	−7.5453	5	14	74	7531.22	7531.59
10	3m5	0.8753	−7.5440	5	14	89	7528.54	7531.09
11	22mm4	1.0264	−7.5706	5	14	116	7542.48	7545.16
12	23mm4	0.9654	−7.5496	5	14	117	7534.69	7535.22
13	7	0.9866	−8.5424	6	16	72	8698.16	8699.46
14	2m6	1.0914	−8.5469	6	16	90	8705.32	8704.66
15	3m6	1.1214	−8.5434	6	16	105	8702.68	8703.85
16	22mm5	1.2794	−8.5515	6	16	132	8716.54	8712.14
17	23mm5	1.2403	−8.5454	6	16	148	8709.63	8707.08
18	24mm5	1.1998	−8.5486	6	16	108	8712.39	8709.11
19	33mm5	1.3200	−8.5480	6	16	168	8711.94	8710.30
20	3e5	1.1517	−8.5400	6	16	120	8700.04	8703.09
21	223mmm4	1.4076	−8.5526	6	16	210	8715.20	8712.97
22	8	1.2266	−9.5424	7	18	88	9872.22	9872.13
23	2m7	1.3335	−9.5454	7	18	106	9879.26	9876.94
24	3m7	1.3679	−9.5414	7	18	121	9876.41	9876.17
25	4m7	1.3765	−9.5392	7	18	121	9875.87	9875.86
26	22mm6	1.5296	−9.5480	7	18	148	9888.51	9884.14
27	23mm6	1.499	−9.5407	7	18	164	9877.71	9879.09
28	24mm6	1.4798	−9.5432	7	18	139	9883.19	9880.82
29	25mm6	1.4418	−9.5482	7	18	124	9886.42	9881.75
30	33mm6	1.5865	−9.5405	7	18	184	9883.90	9881.76
31	34mm6	1.5284	−9.5370	7	18	179	9876.77	9878.18
32	3e6	1.4112	−9.535	7	18	136	9874.65	9875.04
33	223mmm5	1.7023	−9.5556	7	18	241	9883.90	9888.16
34	224mmm5	1.6445	−9.5487	7	18	166	9887.92	9888.57
35	233mmm5	1.7215	−9.5399	7	18	262	9880.22	9882.36
36	234mmm5	1.6247	−9.5409	7	18	207	9881.22	9882.05
37	2m3e5	1.5374	−9.5357	7	18	179	9874.99	9878.19
38	3m3e5	1.6351	−9.5358	7	18	220	9878.75	9879.92
39	2233mmmm4	1.8843	−9.5454	7	18	352	9889.68	9885.42
40	9	1.4718	−10.5392	8	20	104	11046.24	11043.99
41	2233mmmm5	2.2165	−10.5260	8	20	404	11054.45	11053.47
42	2234mmmm5	2.1053	−10.5301	8	20	300	11054.20	11057.07
43	2244 mmmm	2.1076	−10.5398	8	20	224	11059.18	11065.93
44	2334mmmm5	2.1414	−10.5252	8	20	356	11053.45	11053.10
45	33ee5	1.9716	−10.5152	8	20	272	11049.17	11047.77

[a] m, methyl; e, ethyl; for example, 3m3e5 represents 3-methyl-3-ethylpentane. [b] All but for methane were taken from ref 27. The HA of methane is taken from ref 11. [c] Calculated by eq 26.

and C−C bonds calculated by the above approaches. For example, methane CH_4 has four C−H bonds, and its process of atomization can be considered as the following:

Step by step:

$$CH_4 \longrightarrow CH_3 \longrightarrow CH_2 \longrightarrow CH \longrightarrow C$$
$$+ \qquad + \qquad + \qquad +$$
$$H \qquad H \qquad H \qquad H \quad (23)$$

Or simultaneous:

$$CH_4 \rightarrow C + 4H \qquad (24)$$

If eq 23 is employed to calculate its heat of atomization (HA), the HA will be the sum of the BDEs of the $H-CH_3$, $H-CH_2$, $H-CH$, and $H-C$ bonds. In this case, the approach of this work cannot be used for calculating the HA. When eq 24 is employed to estimate the heat of atomization (HA), the HA may be considered as the sum of the BDEs of four quasi-$H-CH_3$ bonds, whose BDE is not just equal to the BDE of a real $H-CH_3$ bond but is proportional to the BDE of a real $H-CH_3$ bond. From the view of simultaneous process, alkane with formula C_nH_{2n+2} can be considered as consisting of n-1 quasi-C_i-C_j and 2n+2 quasi-C_i-H bonds. Because that the BDE of C_i-C_j and C_i-H bond can be calculated by eqs 18 and 19, respectively, here we propose a model eq 25 to evaluate the HA of alkane.

$$HA = d_1 N_{C-C} + d_2 \sum X_{1CC} + d_3 \sum S_{ij} + d_4 N_{C-H} + d_5 \sum X_{1CH} \quad (25)$$

Here d_i is the regression coefficients, N_{C-C} and N_{C-H} are the number of C−C and C−H bonds, which equal n-1 and 2n+2, respectively. In the right of eq 25, the first term together with the second term express the contribution of C−C bonds to the HA. The third term is the contribution of the steric effect to the HA, and the fourth term together with the fifth term indicate the contribution of C−H bonds to the HA. Using eq 25 and the experimental HA[b] (see

Table 9. Estimated Enthalpy of Formation in Gas (HFG⁰) of Some Alkanes

no.	alkanes	no. of C	no. of H	$\text{HFG}^0_{\exp}{}^a$ (kJ/mol)	$\text{HFG}^0_{\text{calc}}{}^b$ (kJ/mol)	$\text{HFG}^0_{\text{calc}}{}^c$ (kJ/mol)
1	1	1	4	74.85(74.4)	71.47	72.25
2	2	2	6	84.68(83.8)	85.48	84.61
3	3	3	8	103.85(104.7)	108.40	106.20
4	4	4	10	126.15(125.7)	131.37	128.02
5	2m3	4	10	134.52(134.2)	137.34	134.13
6	5	5	12	146.44(146.9)	153.07	148.73
7	2m4	5	12	154.47(153.6)	158.40	154.20
8	22mm3	5	12	168.49(168.0)	168.49	164.58
9	6	6	14	167.19(166.9)	174.40	169.16
10	2m5	6	14	174.31(174.6)	179.53	174.49
11	3m5	6	14	171.63(171.9)	179.03	173.99
12	22mm4	6	14	185.56(185.9)	193.11	188.14
13	23mm4	6	14	177.78(178.1)	183.16	178.21
14	7	7	16	187.82	194.73	188.67
15	2m6	7	16	194.97	199.93	194.08
16	3m6	7	16	192.30	199.12	193.33
17	22mm5	7	16	206.23	207.41	201.91
18	23mm5	7	16	195.18	202.35	196.70
19	24mm5	7	16	202.09	204.38	198.78
20	3 mm5	7	16	201.54	205.57	200.05
21	3e5	7	16	189.70	198.35	192.62
22	223mmm4	7	16	204.85	208.24	202.73
23	8	8	18	208.45	214.72	207.89
24	2m7	8	18	215.48	219.53	212.93
25	3m7	8	18	212.63	218.76	212.24
26	4m7	8	18	212.09	218.45	211.98
27	22mm6	8	18	224.72	226.73	220.54
28	23mm6	8	18	214.05	221.68	215.37
29	2 mm6	8	18	219.41	223.41	217.15
30	25mm6	8	18	222.63	224.34	217.97
31	33mm6	8	18	220.12	224.36	218.23
32	34mm6	8	18	213.01	220.78	214.52
33	3e6	8	18	210.87	217.63	211.24
34	223mmm5	8	18	220.12	230.75	224.54
35	224mmm5	8	18	224.14	231.16	225.25
36	233mmm5	8	18	216.44	224.95	218.85
37	234mmm5	8	18	217.44	224.64	218.52
38	2m3e5	8	18	211.21	220.78	214.57
39	3m3e5	8	18	214.97	222.51	216.40
40	2233mmmm4	8	18	225.89	228.02	221.91
41	9	9	20	228.20	233.91	226.35
42	2233mmmm5	9	20	238.78	243.39	236.84
43	2234mmmm5	9	20	237.69	246.99	240.60
44	2244mmmm5	9	20	243.34	255.85	249.78
45	2334mmmm5	9	20	237.11	243.02	236.49
46	33ee5	9	20	233.51	237.69	231.16

a Taken from ref 27. The values enclosed in parentheses are taken from ref 13 and not be used for regression analysis in eq 29. *b* Calculated by eq 28. *c* Calculated by eq 29.

Table 8),[27] we obtained the multiple regression equation as follows.

$$\begin{aligned}
\text{HA (kJ/mol)} = {} & 410.338(\pm7.966)N_{\text{C-C}} + \\
& 47.946(\pm5.446)\sum X_{1\text{CC}} - 0.0729(\pm0.0155)\sum S_{ij} + \\
& 210.575(\pm20.198)N_{\text{C-H}} - 330.841(\pm32.251)\sum X_{1\text{CH}}
\end{aligned}$$

$$r = 0.999999, \ s = 2.64, \ F = 5106213, \ n = 45$$

There is an excellent correlation in eq 26, whose correlation coefficient r is 0.999999, and the standard deviation s is only 2.64(kJ/mol). The largest absolute error between the experimental and the calculated HA is 6.75 kJ/mol. S. S. Liu and co-workers[27] estimated the HA of alkanes in Table 8 with molecular electronegative distance
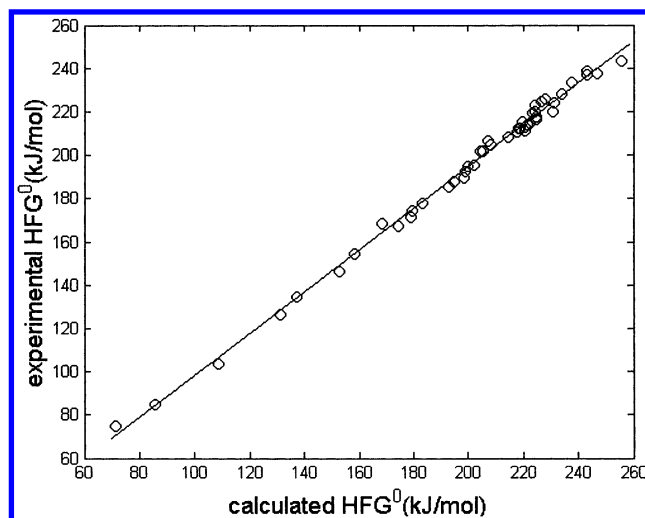

Figure 4. The plot of calculated HFG⁰ by eq 28 vs experimental HFG⁰ for alkanes (HFG⁰$_{\exp}$ = 1.784 + 0.964HFG⁰$_{\text{calc}}$ r = 0.9979, s = 2.58, F = 10476.65, n = 46).

vector (MEDV) (10 variables) and got a result $r = 0.9998$, $s = 29.98$. The result of this paper is much better than that of the literature.[27] Furthermore, eq 26 has less parameters and clearer physical meaning. In Liu's work,[27] all of $-\text{CH}_3$ groups in alkane molecule are treated as the same, and their chemical environments are ignored. So are the groups $>\text{CH2}$, $-\text{CH}<$, and $>\text{C}<$. In this paper, each group is treated as one related to chemical environment, and every group is distinguishable. Further, the steric effect inside alkane molecule on the HA is taken into account in this paper but not in Liu's work.[27] Thus this method has better precision than earlier approaches for estimating HA of alkanes.

According to the relation[1,2,13] between the heat of atomization (HA) and the enthalpy of formation in gas (HFG⁰) for alkanes

$$\text{HA} = n\text{HA}^0(\text{C, g}) + (2n + 2)\text{HA}^0(\text{H, g}) + \text{HFG}^0 \quad (27)$$

we can directly calculate the enthalpy of formation in gas (HFG⁰) if we have worked out their heat of atomization (HA).

In eq 27, n is the number of carbon atom in alkane, the HA^0 (C, g) and HA^0 (H, g) are enthalpies of formation of carbon and hydrogen atoms (which equal 716.68 kJ/mol for carbon and 217.998 kJ/mol for hydrogen),[28] respectively. From which, we can express the HFG⁰ as eq 28.

$$\text{HFG}^0 \text{ (kJ/mol)} = \text{HA} - 716.68n - 217.998(2n + 2) \quad (28)$$

Where HA can be calculated by eq 26. Thus combining eqs 26 and 28, we can conveniently evaluate the enthalpy of formation in gas (HFG⁰) of alkanes with the eigenvalues of modified connection-matrix of the C–C and C–H bonds. Taking decane ($\text{C}_{10}\text{H}_{22}$), for example, we obtained its parameters $N_{\text{C-H}} = 9$, $\sum X_{1\text{CC}} = 1.7204$, $\sum S_{ij} = 120$, $N_{\text{C-H}} = 22$, and $\sum X_{1\text{CH}} = -11.5348$, respectively, and then calculated its HA = 12215.61 kJ/mol with eq 26. Thus we can directly compute its enthalpy of formation in gas (HFG⁰) by eq 28, that is HFG⁰ (kJ/mol) = 12215.61 − 716.68 × 10 − 217.998 × 22 = 252.85 kJ/mol. This calculated value is close to its

EVALUATING BOND DISSOCIATION ENERGY

J. Chem. Inf. Comput. Sci., Vol. 43, No. 2, 2003 **607**

Table 10. Experimental HFG^0 and Calculated HFG^0 by AM1 for Some Alkanes

alkane	HFG$^0_{exp}$[a] (kJ/mol)	HFG$^0_{AM1}$[b] (kJ/mol)	alkane	HFG$^0_{exp}$[a] (kJ/mol)	HFG$^0_{AM1}$[b] (kJ/mol)
1	74.85	36.72	3m5	171.63	169.54
2	84.68	67.63	22mm4	185.56	157.46
3	103.85	101.51	23mm4	177.78	162.45
4	126.15	130.22	7	187.82	216.16
2m3	134.52	122.88	8	208.45	244.81
5	146.44	158.87	2m7	215.48	233.35
2m4	154.47	147.61	224mmm5	224.14	199.06
22mm3	168.49	137.06	2233mmmm4	225.89	170.34
6	167.19	187.51	9	228.2	273.46
2m5	174.31	176.11			

[a] Taken from ref 27. [b] Calculated by semiempirical quantum mechanical method (AM1).

experimental one (249.66 kJ/mol).[8,17] Some evaluated examples are listed in Table 9.

The estimated HFG^0 (the sixth column in Table 9) by eq 28 is somewhat larger than the experimental value, but it is very close to the experimental one. Figure 4 shows the plot of the calculated HFG^0 versus experimental HFG^0 for alkanes. By comparison, we finished the calculation of the HFG^0 for some alkanes with semiempirical quantum chemistry method AM1 (using MOPAC program packages in SYBL 6.7 of Tripos, Inc.). The obtained results (see Table 10) are in less agreement with the experimental values. We can say that eq 28 is a good expression for estimating the HFG^0 of alkane.

When we make a multiregression between the experimental HFG^0 of alkanes in Table 9 and their parameters Nc-c, $\sum X_{1CC}$, $\sum S_{ij}$, N_{C-H}, and $\sum X_{1CH}$ directly, we obtain eq 29:

$$HFG^0 \text{ (kJ/mol)} = 47.512(\pm 7.322)Nc\text{-}c +$$
$$51.367(\pm 5.410)\sum X_{1CC} - 0.0785(\pm 0.0154)\sum S_{ij} -$$
$$179.626(\pm 18.919)N_{C-H} - 319.885(\pm 30.305)\sum X_{1CH}$$
$$(29)$$

$$r = 0.9980, \ s = 2.62, \ F = 2032.55, \ n = 46$$

Equation 29 shows that there is still a good correlation between the experimental HFG^0 and the parameters Nc-c, $\sum X_{1CC}$, $\sum S_{ij}$, N_{C-H}, and $\sum X_{1CH}$, and its standard deviation (s = 2.62 kJ/mol) is equal to that of eq 26 as well as equal to that of eq 28 (see Figure 4). The calculated HFG^0 values by eq 29 (average error is 2.03 kJ/mol) are closer to the experimental ones than those obtained by eq 28 (compare the sixth and seventh column of Table 9).

From the discussion above, it can be seen that there are good correlations between the Bond Dissociation Energy (BDE) and the eigenvalue of bonding orbital-connection matrix for C−C and C−H bonds in alkane. The eigenvalue of bonding orbital-connection matrix is a good descriptor for expressing the relative bond energy of C−C and C−H bonds in alkane. This work provides a new physical insight and a principally novel general approach to the evaluation of the bond dissociation energies of carbon−carbon (C−C) and carbon−hydrogen (C−H) bonds in alkane. Also it builds a simple bridge linking the adjacent matrix of radicals R$_i$• and R$_j$• with the BDE of R$_i$−R$_j$ and R$_i$−H and perhaps opens a new perspective for the application of topological theory method.

REFERENCES AND NOTES

(1) Cohen, N.; Benson, S. W. Estimation of Heats of Formation of Organic Compounds by Additivity Methods. *Chem. Rev.* **1993**, *93*, 2419−2438.

(2) Smith, D. W. Additivity bond-energy scheme with geminal H−H terms Applications to the enthalpies of formation of alkane derivatives. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2037−2041.

(3) Hellmann, S.; Beckhaus, H.-D.; Rüchardt, C. Zusammenhänge zwischen thermischer Stabilität und Spannung nichtsymmetrisch hochverzweigter Kohlenwasserstoffe. *Chem. Ber.* **1983**, *116*, 2238−2249.

(4) Kratt G.; Beckhaus, H.-D.; Rüchardt, C. Thermolyse symm. Tetraalkyldiarylethane und Resonanzstbilisierung der α, α-Dialkylbenzylradikale. *Chem. Ber.* **1984**, *117*, 1748−1764.

(5) Barbe, W.; Beckhaus, H.-D.; Rüchardt, C. Die thermische Stabilität tetrasubstituierter Bernsteinsäuredinitrile. *Chem. Ber.* **1983**, *116*, 1042−1057.

(6) Barbe, W.; Beckhaus, H.-D.; Rüchardt, C. Die thermische Stabilität 2,2-disubstituierter Malononitrile. *Chem. Ber.* **1983**, *116*, 1058−1069.

(7) Somayajulu, G. R.and Zwolinski, B. J. Generalized Treatment of Alkanes. *Trans. Faraday Soc.* **1966**, *62*, 2327−2340.

(8) Somayajulu, G. R.; Zwolinski, B. J. Generalized Treatment of Alkanes Part 2. *Trans. Faraday Soc.* **1972**, *68*, 1971−1987.

(9) Seetula, J. A.; Slagle I. R. Kinetics and thermochemistry of the R+HBr=RH+Br(R=n-C$_3$H$_7$, iosC_3H$_7$, n-C$_4$H$_9$, iosC$_4$H$_9$, sec-C$_4$H$_9$, or tert-C$_4$H$_9$) equilibrium. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1709−1719.

(10) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang X. Bond Dissociation Energies in DMSO Related to the Gas Phase. *J. Am. Chem. Soc.* **1991**, *113*, 9790−9795.

(11) Laurencelle, N.; Pacey, P. D. Simple Electrostatic Model for Enthalpies of Formation of Singly Substituted Alkanes. *J. Am. Chem. Soc.* **1993**, *115*, 625−631.

(12) (a) *CRC Handbook of Chemistry and Physics*, 81st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 2000−2001; pp 9−65. (b) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw−Hill, Inc.: New York, 1999; pp 4.42−4.43.

(13) Smith, D. W. Group electronegativities from electronegativity equilibration Applications to organic thermochemistry. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 201−205.

(14) DeTuri, V. F.; Ervin K. M. Competitive Threshold Collision-Induced Dissociation: Gas-Phase Acidities and Bond Dissociation Energies for a series of Alcohols. *J. Phys. Chem. A* **1999**, *103*, 6911−6920.

(15) Cherkasov, A. and Jonsson, M. A New Method for Estimation of Homolytic C−H Bond dissociation Enthalpies. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 1222−1226.

(16) Hiob, R.; Karelson M. Quantitative Relationship between Rate Constants of the Gas-Phase Homolysis of C−X Bonds and Molecular Descriptors *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 1062−1071.

(17) Gasteiger, J.; Marsili, M.; Hutchings, M. G.; Saller, H.; Löw, P.; Röse, P.; Rafeiner, K. Models for the Representation of knowledge about Chemical Reactions. *J. Chem. Inf. Comput. Sci.* **1990**, *30*, 467−476.

(18) Mizukami, F.; Tasi, G. Scaled Effective One-Electron Method Based on G2 Theory: Results for Aliphatic Alkane Molecules. *J. Chem. Inf. Comput. Sci.* **1998**, *38*, 632−638 (also see the references herein).

(19) Froese R. D. J.; Morokuma, K. IMOMO-G2MS Approaches to Accurate Calculation of Bond Dissociation Energies of Large molecules. *J. Phys. Chem. A* **1999**, *103*, 4580−4586.

(20) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; p 93.

(21) Mortier, W. J.; Ghosh, S. K.; Shankar, S. Electonegativity Equalization Method for Calculation of Atomic Charge in Molecules. *J. Am. Chem. Soc.* **1986**, *108*, 4315−4320.

(22) Parr, R. G.; Bartolotti, L. J. On the Geometric Mean Principle for Electronegativity Equalization, *J. Am. Chem. Soc.* **1982**, *104*, 3801−3803.

(23) Cao, C.; Yuan H.; Liu, S.; Zeng R. On Molecular Polarizability: 3. Relationship to the Ionization Potential of Haloalkanes, Amines,

Alcohols, and Ethers. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 1010−1014.

(24) Cao C.; Li, Z. Molecular polarizability I: relationship to water solubility of alkanes and alcohols. *J. Chem. Inf. Comput. Sci.* **1998**, *38*, 1−7.

(25) Weast R. C. *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL, 1989−1990.

(26) (a) Isaacs, N. *Physical organic chemistry*, 2nd ed.; Addison-Wesley Longman Limited: London, 1995; Chapter 1. (b) McQuarrie, D. A. Quantum Chemistry, University Science books: CA, U.S.A., 1983; Chapter 9.

(27) Liu, S. S.; Cai, S.; Cao, C.; Li, Z. Molecular Electronegative Distance Vector (MEDV) Related to 15 Properties of Alkanes. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 1337−1348.

(28) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: 1999; section 6, Table 6.3.