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Extraordinary β-silyl effects on C–H, N–H, and O–H bond dissociation energies

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Abstract

Composite ab initio G3 calculations show that most of the β substituents have very little effects (less than 2 kcal/mol) on the C–H, N–H, and O–H bond dissociation energies (BDEs). However, β-silyl groups are found to be able to dramatically reduce the C–H, N–H, and O–H BDEs by ca. 3, 6, and 10 kcal/mol, respectively. Natural bond orbital analysis suggests that the extraordinary β-silyl effect is caused by the strong hyperconjugation interaction between the σ_{Si-C} bonding orbital and the half-filled p-orbital of the radical center.

Keywords: Bond dissociation energy; β-Silyl effect; Composite ab initio methods; Hyperconjugation

Homolytic bond dissociation energy (BDE) is defined as the enthalpy change of the reaction $X\text{–}Y \rightarrow X^{\cdot} + Y^{\cdot}$ in the gas phase at 298 K [1]. Its magnitude is primarily determined by the atoms involved in the bond undergoing homolysis. Nevertheless, as chemists often need to compare the reactivities of a group of compounds that differ only in the substitution, it is also important to learn the effect of substituents on BDEs [2]. Up to now two types of substituent effects have been studied in depth. One of them is the remote substituent effect, which is produced by the *para* and *meta* substituents in the aromatic systems. The other one is the α-substituent effect, which is produced by the substituent located at the α position relative to the radical center.

In the present study, we become interested in the β-substituent effects on C–H, N–H, and O–H BDEs (see Scheme 1). This type of substituent effect on BDEs has not been thoroughly investigated in the past. However, because the carbon-, nitrogen-, or oxygen-centered radicals with β substituents are widespread in organic chemistry, we think it is necessary and valuable to conduct a systematic research about the β-substituent effects on BDEs. Thus, we calculate the C–H, N–H, and O–H BDEs of alkanes, amines, and alcohols with 18 different β-substituents, utilizing the composite ab initio G3 method [3] (see Table 1). It has been established in our previous studies that the G3 method can predict the BDEs within ca. 2 kcal/mol of the experimental values [4]. By comparing the available experimental data with the theoretical values in Table 1, we can also see that the G3 BDEs are indeed within 2 kcal/mol of the experimental BDEs.

The results show that most of the β-substituents do not exert any significant effect on the C–H, N–H, or O–H BDEs, because the BDEs of the substituted molecules are different from the BDE of the unsubstituted case only by less than 2 kcal/mol. This finding is not unanticipated because the β-substituent is separated from the radical center by a saturated sp^3 carbon. Thus, neither the induction nor the resonance effect is anticipated to be strong for a β-substituent. At this point, we are very surprised to find out that a β-$SiMe_3$ group can dramatically reduce the C–H, N–H, and O–H BDEs by 2.8, 5.8, and 9.5 kcal/mol, respectively. Such magnitudes of BDE reduction amount to about 3, 6, and 10% of the respective bonding strengths, making β-$SiMe_3$ an extraordinary group compared to all the other β-substituents.

To confirm the above observations, we utilize several other theoretical methods including UB3LYP/6-311++G(2df,p), RMP2/6-311++G(d,p), UQCISD(T)/6-31G(d),

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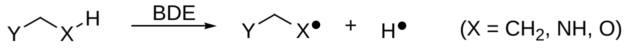

Y= H, NMe$_2$, NH$_2$, OMe, OH, Et, Me, F, Cl, CHO, COMe, CONH$_2$, CN, NO$_2$, CF$_3$, CH=CH$_2$, CCH, SiMe$_3$

Scheme 1.

Table 1
G3 bond dissociation energies for the compounds possessing a β-substituent (kcal/mol)

Y	YCH$_2$CH$_2$–**H**	YCH$_2$NH–**H**	YCH$_2$O–**H**
H	101.2 (100.5±0.3)	99.6 (101.6±2.0)	105.1 (104.2±0.9)
NMe$_2$	101.3 (100.9±0.5)	100.8	103.7
NH$_2$	101.7	100.1	102.5
OMe	102.8	102.6	105.4
OH	102.0 (101.3)	102.5	105.6
Et	101.0	99.2	105.3 (105.9±2.0)
Me	101.9	99.7	105.3 (104.6±0.8)
F	103.1 (103.6±2.0)	104.3	105.1
Cl	101.6 (101.1±0.6)	101.2	106.2
CHO	101.8	100.9	106.2
COMe	101.1	101.2	105.6
CONH$_2$	102.0	99.8	105.6
CN	102.8	102.5	105.9
NO$_2$	103.0	103.8	108.9
CF$_3$	102.7	101.6	106.2
CH=CH$_2$	102.3	100.5	106.2
CCH	103.3	101.3	106.6
SiMe$_3$	**98.4**	**93.8**	**95.6**

Available experimental BDEs [5] are shown in the brackets.

and CBS-Q to calculate the C–H, N–H, and O–H BDEs in the present of β-SiH$_3$ and β-SiMe$_3$ substituents (see Table 2). According to the results shown in Table 2, although the UB3LYP/6-311++G(2df,p), RMP2/6-311++G(d,p), and UQCISD(T)/6-31G(d) methods systematically underestimate the BDEs, they confirm that the β-SiH$_3$ and β-SiMe$_3$ substituents dramatically decrease the C–H, N–H, and O–H BDEs [6]. Furthermore, the results from the CBS-Q method are almost identical to those from the G3 method. It is worth noting that all the theoretical methods demonstrate that the β-CH$_3$ and β-CMe$_3$ groups exert very little influence on the C–H, N–H, and O–H BDEs. Therefore, all the theoretical methods predict the extraordinary β-silyl effects on BDEs.

Having confirmed the above findings, we next attempt to pinpoint the mechanism for the extraordinary β-silyl effects on C–H, N–H, and O–H BDEs. Thus, we carry out natural bond orbital (NBO) analysis [7] on the SiH$_3$–CH$_2$X$^\cdot$ (X=CH$_2$, NH, and O) radicals and their carbon counterparts, the CH$_3$–CH$_2$X$^\cdot$ radicals. Our focus is given to the hyperconjugation interactions between the filled orbitals on the β substituent and the half-filled p orbital of the radical center. The energies of these hyperconjugation interactions can be calculated by deletion of the off-diagonal Fock matrix elements between the interacting orbitals and from the second order perturbation approach, i.e.

$$E(2) = q_i \frac{\langle i|F|j\rangle^2}{\varepsilon_j - \varepsilon_i} = q_i \frac{F_{ij}^2}{\varepsilon_j - \varepsilon_i} \qquad (1)$$

where $\langle i|F|j\rangle$, or F_{ij} is the Fock matrix element between the i and j NBO orbitals, ε_i and ε_j are the energies of i and j NBOs, and q_i is the population of the donor orbital.

The NBO analysis reveals a strong hyperconjugation interaction between the $\sigma_{\text{Si–C}}$ bonding orbital and the half-filled p orbital of the radical center (Fig. 1). For SiH$_3$–CH$_2$CH$_2^\cdot$, SiH$_3$–CH$_2$NH$^\cdot$, and SiH$_3$–CH$_2$O$^\cdot$, the energies of this type of hyperconjugation interactions are 10.2, 14.8, and 28.5 kcal/mol, respectively. In comparison with these significant numbers, the energies for the hyperconjugation interactions between the $\sigma_{\text{C–C}}$ bonding orbital and the half-filled p orbital of the radical center are 1.2, 0.0, and 0.0 kcal/mol for CH$_3$–CH$_2$CH$_2^\cdot$, CH$_3$–CH$_2$NH$^\cdot$, and CH$_3$–CH$_2$O$^\cdot$.

Table 2
Theoretical C–H, N–H, and O–H BDEs in the presence of β-CH$_3$, β-CMe$_3$, β-SiH$_3$, or β-SiMe$_3$ substituents

	UB3LYP/6-311++G(2df,p)	RMP2/6-311++G(d,p)	UQCISD(T)/6-31G(d)	CBS-Q	G3
CH$_3$–CH$_2$–**H**	98.1	97.4	93.3	101.7	101.2
CH$_3$–CH$_2$CH$_2$–**H**	98.3	97.9	93.8	102.0	101.5
Me$_3$C–CH$_2$CH$_2$–**H**	97.6	97.4	92.9	101.4	100.7
SiH$_3$–CH$_2$CH$_2$–**H**	95.6	95.4	91.4	99.2	98.9
Me$_3$Si–CH$_2$CH$_2$–**H**	95.0	94.9	90.9	98.6	98.4
CH$_3$–NH–**H**	95.6	98.1	87.0	100.1	99.6
CH$_3$–CH$_2$NH–**H**	95.3	98.0	87.2	100.0	99.6
Me$_3$C–CH$_2$NH–**H**	94.5	97.2	86.1	101.0	100.6
SiH$_3$–CH$_2$NH–**H**	91.4	94.2	84.0	95.6	95.6
Me$_3$Si–CH$_2$NH–**H**	89.5	92.7	82.6	93.5	93.8
CH$_3$–O–**H**	99.0	105.3	89.5	105.6	105.1
CH$_3$–CH$_2$O–**H**	98.8	105.8	89.4	105.9	105.3
Me$_3$C–CH$_2$O–**H**	97.8	105.3	88.5	106.3	104.8
SiH$_3$–CH$_2$O–**H**	91.1	99.0	83.9	97.7	97.8
Me$_3$Si–CH$_2$O–**H**	88.6	97.2	81.9	95.1	95.6