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METHYL SUBSTITUENT EFFECTS ON THE DISSOCIATION ENERGIES OF Si—X BONDS

YU-RAN LUO AND PHILIP D. PACEY
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

Empirical expressions are obtained for bond dissociation energies (BDEs) of alkylsilanes and their derivatives. It is pointed out that the sensitivity of the BDEs of Si—X bonds to methyl substitution depends on the electronegativity of the substituent X. When X is an atom or group with low or moderate electronegativity, the Si—X BDE is insensitive to methyl substitution, but when X is a halogen atom or OH, the Si—X BDEs increase with increasing methyl substitution.

INTRODUCTION

Thermochemical data on organosilicon compounds have been critically reviewed recently.[1–6] It has been found[1,6–11] that Si—H, Si—C and Si—Si bond dissociation energies (BDEs) do not appear to be sensitive to alkyl substitution, unlike C—H and C—C bonds. In particular, the BDEs of Si—H bonds are uniform: $DH^\circ[\mathrm{H{-}Si(CH_3)_mH_{3-m}}] \approx 90 \pm 2\ \mathrm{kcal\,mol^{-1}}$ (1 kcal = 4·184 kJ) where *m* represents the degree of methyl substitution (= 0, 1, 2 or 3). Carbon—hydrogen bonds strengths, $DH^\circ[\mathrm{H{-}C(CH_3)_mH_{3-m}}]$, have a different pattern; the BDEs are equal to 105·0 ± 0·1, 100·5 ± 0·5, 97·0 ± 0·6 and 94·1 ± 0·7 kcal mol^{-1} for $\mathrm{CH_3{-}H}$, $\mathrm{C_2H_5{-}H}$, $i\text{-}\mathrm{C_3H_7{-}H}$ and $t\text{-}\mathrm{C_4H_9{-}H}$ bonds, respectively.[12] This comparison is fascinating, since the factors which influence carbon—hydrogen bonds are now reasonably well understood. Why is there a lack of a methyl substituent effect for Si—H bonds? Chemists have been puzzled by this problem; some have commented that 'there is hardly any information'[7] and that 'the reasons are not yet clear.'[13]

In this work we studied this problem using a method that extends a previous empirical method.[14–17] It will be predicted that the BDEs of Si—X bonds are insensitive to alkyl substitution when X is an atom or group with low or moderate electronegativity, such as H, $\mathrm{CH_3}$, $\mathrm{SiH_3}$, SH and $\mathrm{NH_2}$, but when X is a halogen atom or a group with high electronegativity, such as OH, the BDEs of Si—X bonds are sensitive to alkyl substitution. Expressions will be derived giving the effect of electronegativity and of methyl substitution on the BDEs.

EMPIRICAL RELATIONS FOR Si—X BOND DISSOCIATION ENERGIES

According to thermochemistry, the difference between $\mathrm{X{-}Si(CH_3)_mH_{3-m}}$ and $\mathrm{X{-}SiH_3}$ bond strengths is dependent on the heats of formation of the relevant compounds and free radicals. That is,

$$\begin{aligned}\Delta DH^\circ[\mathrm{X{-}Si(CH_3)_mH_{3-m}/X{-}SiH_3}] &= \Delta\Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}/SiH_3}] \\ &\quad - \Delta\Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}X/SiH_3X}] \qquad (1)\end{aligned}$$

where

$$\Delta DH^\circ[\mathrm{X{-}Si(CH_3)_mH_{3-m}/X{-}SiH_3}] = DH^\circ[\mathrm{X{-}Si(CH_3)_mH_{3-m}}] - DH^\circ(\mathrm{X{-}SiH_3}) \qquad (2)$$

$$\Delta\Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}X/SiH_3X}] = \Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}X}] - \Delta_f H^\circ(\mathrm{SiH_3X}) \qquad (3)$$

$$\Delta\Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}/SiH_3}] = \Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}}] - \Delta_f H^\circ(\mathrm{SiH_3}) \qquad (4)$$

Thermochemical data on $\mathrm{SiH_3X}$, required in equation (3), have not been determined with high precision and are relatively scarce. Luo and Benson[15–17] took another approach to avoid uncertainties from this source when estimating heats of formation of silicon-containing compounds. Heats of formation of $\mathrm{CH_3X}$ compounds were better known, so they studied the relationships between $\Delta\Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}X/CH_3X}]$ and the covalent potential, V_X.[18] V_X is equal to the number of valence electrons of the bonding atom in group X divided by its covalent radius. This is a new scale of electronegativity, related to Parr and Pearson's absolute theory.[19]

$$\Delta\Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}X/CH_3X}] = \Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}X}] - \Delta_f H^\circ(\mathrm{CH_3X}) \qquad (5)$$

All of the relationships were reported to be linear. The relationships between $\Delta\Delta_f H^\circ[\mathrm{Si(CH_3)_mH_{3-m}X/SiH_3X}]$ and V_X can be determined from $\Delta\Delta_f H^\circ$

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$[\mathrm{Si(CH_3)}_m\mathrm{H}_{3-m}\mathrm{X/CH_3X}]$:

$$\Delta\Delta_f H^\circ\,[\mathrm{Si(CH_3)}_m\mathrm{H}_{3-m}\mathrm{X/SiH_3X}] = \Delta\Delta_f H^\circ\,[\mathrm{Si(CH_3)}_m\mathrm{H}_{3-m}\mathrm{X/CH_3X}] - \Delta\Delta_f H^\circ(\mathrm{SiH_3X/CH_3X}) \quad (6)$$

where

$$\Delta\Delta_f H^\circ(\mathrm{SiH_3X/CH_3X}) = \Delta_f H^\circ(\mathrm{SiH_3X}) - \Delta_f H^\circ(\mathrm{CH_3X}) \quad (7)$$

The first term on the right-hand side of equation (6) was given in equation (4) in Ref. 17 for X = H, CH_3 and SiH_3 and with different parameters for F, Cl, Br, I, OH, SH and NH_2. The need for different parameters was believed to be caused by p–d π-backbonding from lone pairs on the electronegative atoms to vacant d orbitals on Si. The final term in equation (6) was given in equation (4) in Ref. 15 for X = H, F, Cl, Br and I. We have assumed that the same relationships also apply to the polyatomic groups. Combining these terms, we obtain

$$\Delta\Delta_f H^\circ\,[\mathrm{Si(CH_3)}_m\mathrm{H}_{3-m}\mathrm{X/SiH_3X}] = \begin{cases} -16{\cdot}0m + 0{\cdot}9\ \mathrm{kcal\,mol^{-1}} \\ \quad \text{if X} = \mathrm{H} \\ -(15{\cdot}5m + 9{\cdot}8) - (0{\cdot}2m - 1{\cdot}06)V_\mathrm{X} \\ \quad \text{if X} = \text{halogen} \\ -(15{\cdot}5m - 0{\cdot}4) - (0{\cdot}2m - 0{\cdot}1)V_\mathrm{X} \\ \quad \text{if X} = \mathrm{CH_3, SiH_3, OH, SH\ or\ NH_2} \end{cases} \quad (8)$$

Appropriate values of V_X were substituted to obtain the expressions listed in the third column of Table 1. These expressions will be substituted for the last term in equation (1).

Now we examine the other term in equation (1), the effect of methyl substitution on the heats of formation of the radicals. Taking the preferred values for the heats of formation of alkylsilyl radicals,[1,6] the differences, $\Delta\Delta_f H^\circ\,[\mathrm{Si(CH_3)}_m\mathrm{H}_{3-m}/\mathrm{SiH_3}]$, are equal to $-15{\cdot}9 \pm 1{\cdot}4$, $-32{\cdot}1 \pm 1{\cdot}4$ and $-47{\cdot}2 \pm 1{\cdot}4$ kcal mol^{-1} for m = 1, 2 and 3, respectively. By linear regression we obtain an approximate relationship

$$\Delta\Delta_f H^\circ\,[\mathrm{Si(CH_3)}_m\mathrm{H}_{3-m}/\mathrm{SiH_3}] = -0{\cdot}4 - 15{\cdot}7m\ \mathrm{kcal\,mol^{-1}} \quad (9)$$

$$\approx -16m \quad (9a)$$

The differences in the BDEs of Si—X bonds can then be estimated by substituting equation (9) into equation (1). These values are listed in the last three columns of Table 1.

DISCUSSION

As shown in Table 1, replacement of a hydrogen atom by a methyl group lowers the heats of formation of the compounds by amounts between $-16{\cdot}0$ and $-17{\cdot}5$ kcal mol^{-1}. The fact that the average Me-for-H replacement enthalpy in the methylmonosilanes is about $-16{\cdot}0$ ($-15{\cdot}8$ to $-17{\cdot}7$) kcal mol^{-1} has also been noted by Walsh[1,20] and by O'Neal's group.[21] For the methyldisilanes, the average Me-for-H replacement enthalpy is about $-15{\cdot}3$ kcal mol^{-1}.[11] Previous workers, however, did not express the replacement enthalpy as a function of m and V_X and did not use it to correlate the BDEs. The average Me-for-H replacement enthalpies they noted are reproduced by both equation (8) and Table 1 in this work.

Values of BDEs, calculated directly from observed heats of formation, are listed in parentheses in Table 1.

Table 1. Differences in heats of formation of silicon compounds and in the BDEs of Si—X Bonds (kcal mol^{-1})

			$\Delta\mathrm{DH}^\circ\,[\mathrm{X{-}Si(CH_3)}_m\mathrm{H}_{3-m}/\mathrm{X{-}SiH_3}]$[b]		
X	V_X[a]	$\Delta\Delta_f H^\circ\,[\mathrm{Si(CH_3)}_m\mathrm{H}_{3-m}\mathrm{X/SiH_3X}]$	$m = 1$	$m = 2$	$m = 3$
F	9·915	$-17{\cdot}5m + 0{\cdot}7$	0·9	2·2	4·6
OH	8·11	$-17{\cdot}1m + 1{\cdot}2$	0·0	0·9	2·9
Cl	7·04	$-16{\cdot}9m - 2{\cdot}3$	3·3	4·0	5·8 (4·9 ± 3·0)
NH_2	6·67	$-16{\cdot}8m + 1{\cdot}1$	−0·2	0·4	2·1
Br	6·13	$-16{\cdot}7m - 3{\cdot}4$	4·2	4·7	6·3 (7·6 ± 2·9)
SH	5·77	$-16{\cdot}7m + 1{\cdot}0$	−0·2	0·3	1·9
I	5·25	$-16{\cdot}5m - 4{\cdot}3$	4·9	5·2	6·6 (5·2 ± 2·9)
CH_3	5·19	$-16{\cdot}5m + 0{\cdot}9$	−0·3 (−0·3 ± 2·1)	0 (0·0 ± 2·1)	1·4 (1·5 ± 2·0)
SiH_3	3·41	$-16{\cdot}2m + 0{\cdot}8$	−0·5	−0·5	0·6
H	2·70	$-16{\cdot}0m + 0{\cdot}9$	−0·8 (−0·7 ± 1·9)	−1·0 (−1·3 ± 1·9)	−0·1 (0·1 ± 1·9)

[a] From Refs 12 and 14–17.

[b] Values in parentheses were calculated directly from experimental results; see Ref. 17. The other values were obtained from equations (1), (8) and (9).

The heats of formation of these compounds were used in Ref. 17.

From equation (1), the differences between the BDEs, $\Delta DH^\circ[\text{X—Si(CH}_3)_m\text{H}_{3-m}/\text{X—SiH}_3]$, arise from two terms. The first is the difference in the heats of formation of the silicon radicals, which is a function of m, as in equation (9). The second is the difference in the heats of formation of the silicon compounds, which is a function of V_X and m, as shown in the third column of Table 1. The last three columns in Table 1 give the total contribution of these two terms. The results predict that the electronegativity of X has a significant effect on the trend of BDEs with increasing m.

As also shown in Table 1, the differences for X—Si bonds, where X = H, CH_3, SiH_3, SH and NH_2, are predicted to be zero within ±2 kcal mol^{-1}, which is the experimental uncertainty for silicon compounds today. For X = H, SiH_3 and CH_3, the differences are especially small. This reflects the observation that the methyl substitution effects for H—Si, Si—C and Si—Si bonds are negligible within the present experimental uncertainty.

From Table 1, Si—halogen and Si—OH bonds have a stronger dependence on m. The predicted increase in the BDEs of S—X bonds with increasing substitution at the silicon atom is similar to the effect of alkyl substitution at a carbon atom when X = F or OH, which has been investigated by many workers.[12,22-28]

Why do the differences in the BDEs of Si—H bonds approach zero? There are two opposing contributions. The first contribution is the difference in the heats of formation of alkylsilyl radicals, $\Delta\Delta_f H^\circ[\text{Si(CH}_3)_m\text{H}_{3-m}/\text{SiH}_3]$, which are approximately $-16m$, as in equation (9a). Second, the heats of formation of the alkylsilanes are a linear function of m, as shown in Fig. 1.

$$\Delta_f H^\circ[\text{Si(CH}_3)_m\text{H}_{4-m}] = -16{\cdot}0(\pm 0{\cdot}2)m + 0{\cdot}9(\pm 0{\cdot}4)\ \text{kcal mol}^{-1} \quad (10)$$

The correlation coefficient is 0·9998. This is equivalent to the first line in equation (8). Substituting equations (9) and (10) in equation (1), we can see that the differences of the BDEs of H—Si bonds are almost independent of m because the coefficients of m, i.e. 16, almost cancel out.

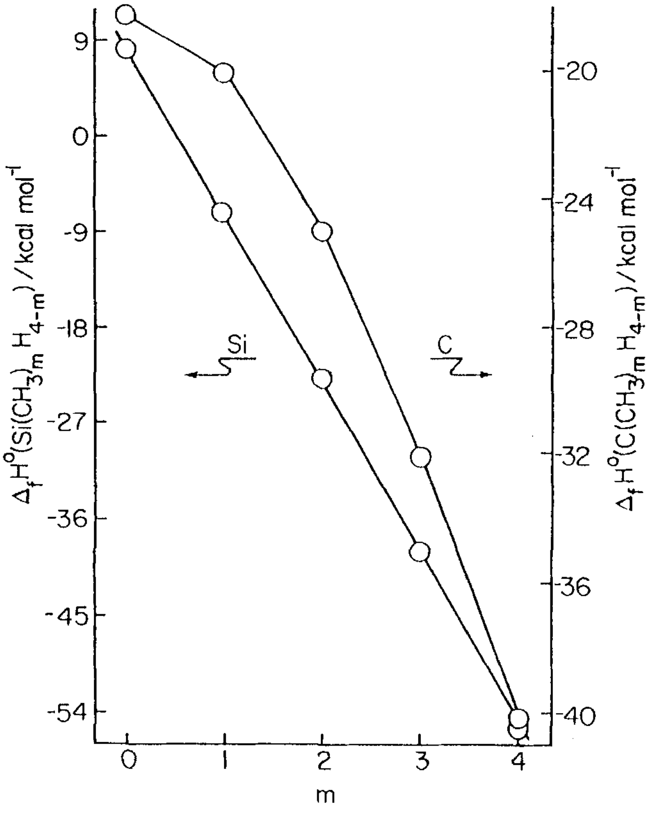

Figure 1. Relationships between $\Delta_f H^\circ[\text{X(CH}_3)_m\text{H}_{4-m}]$ and m, where X = Si and C. For X = Si, the straight line was obtained by least squares. The heats of formation of silanes and hydrocarbons are from Refs 1 and 29, respectively

Heats of formation of hydrocarbons, also shown in Fig. 1, have a non-linear pattern, which was described quantitatively in Refs 30 and 31.

On the basis of similar analyses, we can also interpret the behavior of Si—C and Si—Si BDEs.

Our relationship for the trend in the H—Si BDEs is based on thermochemical information, the electronegativity, V_X, and the degree of substitution by methyl, m. This approach reproduces the uniformity of the BDEs of Si—H and Si—C bonds, and the trends in bond strengths between Si and other atoms.

Our approach is empirical, and is independent of any particular theoretical approach. However, the important role of V_X is consistent with the suggestion of Walsh[6] that inductive effects can explain these observed trends. Coolidge and Borden,[10] based on the results of their *ab initio* calculations, also emphasized the importance of electronegativity. Their scale of electro negativity reversed the order of Si and H compared with the V_X scale, but the differences were so small they should not affect the overall results.

Based on structural information for free alkylsilyl and alkyl radicals, Wetzel *et al.*[8] thought the modest changes in geometry between silanes and the corresponding silyl radicals would result in smaller substituent effects than for alkanes, which change to almost planar radicals. Hyperconjugation in the radicals is another potential explanation, but it has not been accepted, as noted previously by Walsh.[6]

The BDEs of Si—H bonds, of course, may not be uniform when dissociation relieves steric compression in silicon compounds, as pointed out by Kanabus-Kaminska *et al.*[7] and Walsh.[20] A quantitative description of steric compression relief in the bond cleavage of organosilicon compounds has not yet been offered. This problem will be considered quantitatively in a forthcoming paper.

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