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Substituent Effect on the Dissociation Energy of the Si−H Bond: A Density Functional Study

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The bond dissociation energies of a series of substituted silanes have been studied with quantum mechanics density functional calculations. Successive Me, F substitutions strengthen the Si−H bond, while MeO, Cl, Br, SMe, SiH_3, as well as Ph groups weaken the bond. These mostly agree with experimental measurements and previous *ab initio* calculations. The calculated substituent effect can be correlated reasonably well with the calculated Hirshfeld charge and spin density variations on the Si radical center. While radical spin delocalization reduces the bond strength, withdrawing inductive character of the substituents increases the Si−H bond strength. The second-row element substituents have larger radical spin delocalization ability, which is responsible for the greater reduction of the Si−H bond dissociation energy.

Free radical reactions have found wide applications in organic synthesis in recent years, thanks to the successful development of suitable radical reducing agents.[1,2] One such reducing agent is tri-*n*-butyltin.[3] In recent years, tris(trimethylsilyl)silane, $(TMS)_3SiH$, has become a more attractive alternative, primarily due to its powerful reducing ability.[4] Its Si−H bond has been found to be about 11 kcal/mol weaker than that of triethylsilane.[5]

There is an apparent difference in the substituent effect on Si−H and C−H bond dissociation energies. The C−H bond dissociation energy is significantly reduced by conjugating groups such as phenyl (17 kcal/mol) and vinyl (19 kcal/mol) groups, π-donating groups such as OMe (12 kcal/mol), NMe_2 (17 kcal/mol), and F (5 kcal/mol), as well as σ-donor groups such as Me (5 kcal/mol) and $SiMe_3$ (6 kcal/mol).[6,7] On the other hand, the above substituents seem to have little effect on the bond dissociation energy of Si−H (within 2 kcal/mol) except for $SiMe_3$ which reduces the Si−H bond strength by about 3 kcal/mol.[8] Additional anomalies are F_3SiH, $(MeS)_3SiH$,[9] and $(TMS)_3SiH$[5] which are reported to give SiH bond dissociation energies of 100 , 82 , and 79 kcal/mol, respectively, compared to 90 kcal/mol for SiH_4.[10]

This fascinating difference in substituent effect has aroused wide interest,[11−14] and some recent work has been devoted to determining more accurately the Si−H bond dissociation energies of substituted silanes.[15−17] However, a good understanding of the origin of the substituent effect on Si−H bond dissociation energy is still lacking.[11] In the case of C−H bond dissociation energies, discussions are often based on the effect of substituents on the stability of the radicals generated.[18] Since there is no good correlation between the substituent effects and electronegativities of substituents, several groups have used two parameters to rationalize the substituent effects.[19−26] One is the Hammett-type polar substituent parameter σ^X, and the other is radical spin

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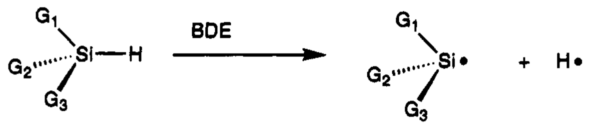
Scheme 1



Mono-substitution ($G_2 = G_3 = H$)
G_1 = H, Me, F, Cl, Br, Ph, SiH_3, OMe, SMe

Disubstitution ($G_3 = H$)
$G_1 = G_2$ = Me, F, Cl, Br, SiH_3

Trisubstitution
$G_1 = G_2 = G_3$ = Me, F, Cl, Br, SiH_3, SMe

delocalization parameter, $\sigma^{\bullet}$. For example, Arnold *et al.* used σ^+ parameters and $\sigma^{\bullet}$ parameters which are derived from C−H hyperfine coupling constants of substituted benzyl radicals to correlate the reactivities of several types of reactions.[19] Jiang *et al.* derived σ_{mb} and $\sigma^{\bullet}$ by their careful studies on the kinetics of the thermal cycloaddition reaction of substituted α,β,β-trifluorostyrenes.[20] These dual-parameter descriptions for substituent effects have been quite helpful in understanding the origin of substituent effects in carbon chemistry.

In this paper, we report a density functional study of the substituent effect on the Si−H bond dissociation energy.[27] We demonstrate that the substituent effect can be quite accurately calculated by the density functional method. We also correlate the calculated relative bond dissociation energies with spin densities and Hirshfeld charges on the Si radical centers, which is important for the understanding of the origin of the substituent effect.

Results

A series of mono-, di-, and trisubstituted silanes (see Scheme 1) have been studied with density functional calculations[28] using the DMol and GAUSSIAN 92/DFT programs.[29,30] In the first stage, the local density approximation of Janak, Moruzzi, and Williams (JMW)[31] was used. Geometries were fully optimized with the DND basis (double numerical with polarization functions on heavy atoms which is equivalent to the 6-31G* basis set). This is referred to as JMW/DND. In the second stage, geometric optimization was carried out with the 6-31G* basis set using BLYP non-local density functional approximation, which uses Becke's 88 non-local exchange functional[32] and Lee-Yang-Parr's nonlocal correlation functional.[33] This is referred to as BLYP/6-31G*. Harmonic vibrational freqnecies of the silanes and silyl radicals were also carried out with the BLYP/6-31G* method. Each species is a true minima without any imaginary frequency. Table 1 summarizes the calculated energies of silanes and silyl radicals with the two methods along with BLYP/6-31G* zero-point energies. Collected in Table 2 are experimental bond dissociation energies, calculated bond dissociation energies corrected with the BLYP/6-31G* ZPE's),[34] calculated substituent effect, as well as calculated Hirshfeld charges and spin densities on the Si radical centers (JMW/DND). Selected bond distances and bond angles of silanes and silyl radicals are given in Table 3. Since the JMW/DND and BLYP/6-31G* give similar geometries, only the JMW/DND geometric parameters are presented.

The BDE for SiH_4 has been studied on numerous occasions. The latest value is 91.5 kcal/mol derived by Seetula *et al.*[10] This is in good agreement with Pople's G1 and G2 calculations which give a value of 91.3 kcal/mol.[35,36] Recent calculations with nonlocal density functional approximation with several high basis sets give somewhat lower values (86.8–87.2 kcal/mol).[37] Our calculations give a value of 89.6 and 87.0 kcal/mol.[38] Since we are most concerned with the substituent effect on the Si−H BDE, the calculated absolute Si−H BDE are less important. It has been shown before by many studies that a systematic error in calculated absolute bond dissociation energies can be cancelled out by isodesmic reaction calculations which give relative bond dissociation energies.[15−17,27] If one likes, one can make a correction for each Si−H BDE based on the most accurate value for SiH_4. This will not affect the relative BDEs.

In general, the calculated substituent effects by the JMW/DND and BLYP/6-31G* are similar. The largest difference between the two methods is 1.5 kcal/mol for Cl_3SiH. The correction of ZPE on the reactions ranges from 5.7 to 6.2 kcal/mol. There is a general agreement between the calculated and experimentally reported substituent effect on the bond dissociation energy.

Our results for consecutive methyl substitutions differ slightly from those of Marshall's MP4/6-31G* results.[15,16] Marshall reported that mono- and dimethyl substitutions slightly reduce the Si−H BDE and trimethyl substitution significantly increases the Si−H BDE by about 3 kcal/mol. Our results indicate that each methyl substituent causes a small increase in the Si−H BDE, similar to Coolidge and Borden's results.[11]

The calculations suggest that consecutive fluoro substitutions increase the Si−H bond strength. In particular, trifluoro substitution increases the Si−H BDE by about 7.4 kcal/mol with the BLYP/6-31G*. This calculated effect is about 3 kcal/mol smaller than the reported experimental value.[8] While Coolidge *et al.* reported a 3.5 kcal/mol increase in the Si−H BDE by a monofluoro substituent,[11] our best value is 1.5 kcal/mol.

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[38] Local density functional method usually gives higher bond dissociation energies than experimental values. However, in the present case, we do not find that.

Table 1. Calculated Energies (au) of Silanes and Silyl Radicals with JMW/DND and BLYP/6-31G*

	JMW/DND		BLYP/6-31G*		ZPE (BLYP/6-31G*) (kcal/mol)	
	silane	silyl radical	silane	silyl radical	silane	silyl radical
SiH_4	−290.687 13	−290.048 44	−291.839 90	−291.196 01	19.06	12.89
$MeSiH_3$	−329.667 69	−329.028 85	−331.139 00	−330.494 76	37.42	31.47
Me_2SiH_2	−368.650 15	−368.010 01	−370.437 97	−369.793 08	55.57	49.65
Me_3SiH	−407.632 73	−406.990 80	−409.736 76	−409.091 27	73.14	67.37
$FSiH_3$	−389.428 74	−388.788 81	−391.134 12	−390.488 08	16.76	10.74
F_2SiH_2	−488.180 84	−487.539 01	−490.441 14	−489.792 20	14.20	7.97
F_3SiH	−586.935 33	−586.286 18	−589.751 18	−589.095 83	11.07	5.10
$ClSiH_3$	−748.895 70	−748.258 72	−751.473 99	−750.832 77	15.99	10.11
Cl_2SiH_2	−1207.108 20	−1206.472 14	−1211.110 48	−1210.471 75	12.55	6.64
Cl_3SiH	−1665.318 76	−1664.683 58	−1670.746 35	−1670.109 13	8.57	2.86
$BrSiH_3$	−2860.742 35	−2860.106 71				
Br_2SiH_2	−5430.801 05	−5430.167 51				
Br_3SiH	−8000.855 71	−8000.226 97				
$PhSiH_3$	−519.776 23	−519.141 62	−522.794 26	−522.155 12	70.53	64.46
$(H_3Si)SiH_3$	−580.231 59	−579.597 36	−582.506 68	−581.867 81	29.61	23.91
$(H_3Si)_2SiH_2$	−869.777 46	−869.147 45	−873.174 77	−872.540 38	41.15	35.03
$(H_3Si)_3SiH$	−1159.325 19	−1158.698 53	−1163.843 59	−1163.213 66	51.03	45.41
$(Me_3Si)SiH_3$	−697.174 67	−696.541 41				
$MeOSiH_3$ (a)	−404.425 82	−403.788 59	−406.368 77	−405.726 96	41.12	34.98
(b)		−403.784 52				
$MeSSiH_3$ (a)	−726.539 37	−725.907 36	−729.327 48	−728.691 22	39.14	33.28
(b)		−725.900 82				
$(MeS)_3SiH$	−1598.254 80	−1597.627 57				

[a] Refers to gauche geometry. [b] Refers to anti geometry.

Table 2. Calculated and Experimental Si−H Bond Dissociation Energies (kcal mol^{-1}) and Hirshfeld Charge and Spin Densities (JMW/DND) on Si Radical Centers

			calcd BDE					
	experimental BDE		JMW/DND		BLYP/6-31G*			
Si−H Bond	ref 8	ref 15	BDE	Δ BDE	BDE	Δ BDE	rel Hirshfeld charge Δ*C*	rel spin density Δ*S*
H_3Si-H	90.4	91.5	89.7	0.0	87.0	0.0	0.000	0.000
$MeSiH_2-H$	89.7	92.7	89.8	0.1	87.4	0.4	−0.056	−0.027
Me_2SiH-H	89.5	93.7	90.6	0.9	87.9	0.9	−0.145	−0.059
Me_3Si-H	90.4	95.1	91.7	2.0	88.4	1.4	−0.253	−0.102
$FSiH_2-H$			90.4	0.8	88.5	1.5	−0.182	−0.030
F_2SiH-H			91.6	2.0	90.1	3.1	−0.343	−0.055
F_3Si-H	100.2		96.2	6.6	94.7	7.4	−0.474	−0.088
$ClSiH_2-H$			88.6	−1.1	85.6	−1.4	−0.102	−0.081
Cl_2SiH-H			88.0	−1.7	84.0	−3.0	−0.179	−0.166
Cl_3Si-H	91.4		87.5	−2.2	83.3	−3.7	−0.232	−0.273
$BrSiH_2-H$			87.7	−1.9			−0.083	−0.101
Br_2SiH-H			86.4	−3.2			−0.139	−0.213
Br_3Si-H			83.4	−6.3			−0.176	−0.356
$PhSiH_2-H$	88.3		87.1	−2.6	84.1	−2.9	−0.083	−0.122
H_3SiSiH_2-H	86.4	88.9[c]	86.9	−2.8	84.3	−2.7	−0.008	−0.077
$(H_3Si)_2SiH-H$			84.2	−5.5	81.1	−6.0	−0.024	−0.129
$(H_3Si)_3Si-H$			82.1	−7.6	80.7	−6.3	−0.033	−0.178
$(Me_3Si)SiH_2-H$			86.3	−3.4			0.042	−0.063
$MeOSiH_2-H$ (a)			88.7	−0.9	85.7	−1.3	−0.103	−0.088
(b)			91.3	1.6			−0.128	−0.011
$MeSSiH_2-H$ (a)			85.5	−4.2	82.5	−4.5	−0.013	−0.170
(b)			89.6	−0.1			−0.050	−0.046
$(MeS)_3Si-H$		82.5[d]	82.5	−7.2			−0.135	−0.388

[a] In gauche geometry. [b] In anti geometry. [c] Refers to ref 16a. [d] Refers to ref 9.

Consecutive chloro substitutions, on the other hand, weaken the Si−H bond. The overall effect is small. Trichloro substitution gives a 3.7 kcal/mol (BLYP/6-31G*) reduction in the Si−H BDE, while a 1.5 kcal/mol increase in the Si−H BDE was reported.[8] Once again, there is a discrepancy of about 5 kcal/mol between experiment and calculation. We hope that this will stimulate further experiments. Consecutive bromo substitutions cause larger reductions in the Si−H BDE. In the case of tribromo substitution, a 6.3 kcal/mol (JMW/DND)[39] weakening of the Si−H BDE is predicted. Unfortunately, no experimental data on this are available for comparison.

In agreement with the experiment, the phenyl group is calculated to reduce the Si−H bond strength by just about 2.9 kcal/mol.[8] The methoxy group causes about 1 kcal/mol Si−H bond weakening. However, methylthio has a much larger effect of about 4.5 kcal/mol. Our estimated Si−H bond dissociation energy for $(MeS)_3SiH$ is about 82.5 kcal/mol, very close to that recently reported by Chatgilialoglu *et al.*[9]

SiH_3 is calculated to reduce the Si−H BDE by 2.8 kcal/mol, quite close to the values deduced by Marshall *et al.* from both experiment and *ab initio* calculations.[17] Additional SiH_3 substituents further weaken the Si−H bond. Our calculated substituent effect for $(H_3Si)_3SiH$ with respect to that of Me_3SiH is about 9.6 kcal/mol. This is close to the 11 kcal/mol Si−H BDE difference between

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(39) The bromosubstitutions were not calculated with the BLYP/6-31G* method because the 6-31G* basis set is not available to the Br atom.

Table 3. Calculated Bond Lengths (Å) and Bond Angles in Substituted Silane and Silane Radicals with JMW/DND

	substituted silane						substituted silane radical					
X_3SiH	H−Si	X−Si	<H−Si−X	<X−Si−X	<H−Si−H	A_{sum}	H−Si	X−Si	<H−Si−X	<X−Si−X	<H−Si−H	A_{sum}
H_3SiH	1.498				109.4	328.2	1.502				110.4	331.2
$MeSiH_3$	1.500	1.869	111.0		107.9	329.9	1.504	1.875	111.8		108.3	331.9
Me_2SiH_2	1.504	1.867	109.7	111.7	106.4	331.1	1.511	1.874	110.0	111.3		331.3
Me_3SiH	1.507	1.870	108.8	110.9		332.7		1.875		110.5		331.5
$FSiH_3$	1.496	1.632	108.4		111.2	328.0	1.508	1.641	106.8		111.1	324.7
F_2SiH_2	1.488	1.617	108.4	107.5	115.8	324.3	1.510	1.627	106.3	106.7		319.3
F_3SiH	1.474	1.600	111.0	107.9		323.7		1.613		107.8		323.4
$ClSiH_3$	1.496	2.066	108.6		110.7	327.9	1.504	2.073	107.6		110.1	325.3
Cl_2SiH_2	1.485	2.058	108.8	110.4	112.5	328.0	1.506	2.068	106.9	109.5		323.3
Cl_3SiH	1.484	2.042	109.6	109.4		328.2		2.064		109.3		327.9
$BrSiH_3$	1.490	2.228	108.5		111.0	328.0	1.506	2.238	107.5		109.8	324.8
Br_2SiH_2	1.488	2.227	108.8	110.5	111.7	328.1	1.511	2.235	106.3	110.4		323.0
Br_3SiH	1.485	2.209	109.0	110.4		331.2		2.237		110.1		330.3
$PhSiH_3$	1.494	1.852	110.6		109.0	330.2	1.497	1.836	112.1		112.0	336.2
$(H_3Si)SiH_3$	1.502	2.321	110.6		108.3	329.5	1.505	2.313	114.7		108.5	337.9
$(H_3Si)_2SiH_2$	1.504	2.323	110.2	107.9	107.9	328.3	1.506	2.312	114.0	113.0		341.0
$(H_3Si)_3SiH$	1.505	2.320	109.4	110.7		332.1		2.316		111.5		334.5
$(Me_3Si)SiH_3$	1.507	2.331	112.2		106.7	331.1	1.508	2.327	117.7		107.9	343.3
$MeOSiH_3$ (a)	1.492[c]	1.660	110.7[c]		107.4[c]	328.0	1.516[c]	1.672	109.0[c]		110.5	323.8
	1.487[d]		106.4[d]		110.9[d]		1.505[d]		104.3[d]			
(b)							1.514	1.669	109.2		108.9	327.3
$MeSSiH_3$ (a)	1.495[c]	2.125	112.4[c]		112.0[c]	326.4	1.510[c]	2.123	110.3[c]		108.5	322.0
	1.491[c]		104.0[d]		110.0[d]		1.500[d]		103.2[d]			
(b)							1.504	2.122	110.7		108.4	329.8
$(MeS)_3SiH$	1.502	2.123	110.3	110.4		331.2		2.135		108.0		324.0

[a] Refers to gauche geometry. [b] Refers to anti geometry. [c] Refers to syn SiH bond. [d] Refers to anti SiH bond.

Me_3SiH and (TMS)SiH reported by Griller *et al.*[5] Our calculations suggest that Me_3Si has a slightly higher ability to reduce the SiH BDE than SiH_3.

The calculated Si−H bond lengths are about 0.02 Å longer than those obtained with HF/6-31G* values.[15,16] The Si−C bonds are about 0.02 shorter and the Si−F bonds are about 0.02−0.03 Å longer compared to the HF/6-31G* values.[15,16,40,41] The calculated bond angles are close to the HF/6-31G* values. Each radical is pyramidal.[41,42]

Several geometric features are worthy of mentioning. (1) Successive methyl and silyl substitutions increase the Si−H bond length, while there is little variation in Si−C and Si−Si bond lengths. (2) Consecutive F, Cl, Br substitutions, on the other hand, reduce both H−Si and Si−X bond lengths, as found previously.[43] This is especially significant for F substitutions. (3) The Si−H and Si−X bonds of the radical species are generally longer than those in the corresponding silanes except for silyl and phenyl substitutions in which the Si−X bonds in the radicals are shorter by about 0.01 Å. The Si−H bond length elongation in the radicals is especially large in difluoro, dichloro, and dibromo substitutions (about 0.02 Å). Comparison with Marshall's HF/6-31G* calculations indicates that the Si−H bond length elongations in the methyl-substituted radicals are too large. We question whether this could be a defect of density functional calculation.[44] (4) The degree of pyramidalization of the radical center can be roughly represented by the summation of the three angles involved in the three Si-attached bonds. These angles along with those of silanes are given in Table 3. Comparison of A_{sum}(radical) with A_{sum}(silane) indicates that there is a small flattening for the formation of methyl-substituted radicals. The flattening becomes larger for the silyl substitutions, especially for the trimethylsilyl substitution which has a difference in A_{sum} of about 13°. This most likely reflects the relief of steric interactions during radical formation. Fluoro, chloro, bromo, methoxy, and methylthio substitutions slightly increase the pyramidalization upon radical formation as indicated by a small reduction in the A_{sum}(radical) compared to A_{sum}(silane).

Discussion

To understand the origin of the substituent effect, we first note that in every case, the spin density on the Si radical is reduced by the presence of substituent, as shown in Table 2. Spin delocalization is larger for the second row element substituents than their corresponding first-row element substituents. Spin delocalization ability is roughly in the following order: SMe > Ph > Br > MeO > Cl ≈ Si > F ≈ Me.

It is known that UHF molecular orbital calculations often give quite poor spin density for carbon radicals due to spin contamination.[6c] However, the calculated $\langle S^2 \rangle$ for silyl radical is quite close to the ideal value of 0.75.[27,41] Although we are not aware of a systematic study of spin density by density functional calculations, the calculated values shown in Table 2 seem to be quite reasonable.

The inductive effects of the substituents are reflected by Hirshfeld charges[45] on the radical centers (with hydrogen summed in). These are roughly proportional to the electronegativities of the substituents. Thus, F, OMe, and Cl cause considerable positive charge on the radical, while silyl groups have little effect. It is interesting that methyl groups also cause considerable positive charge on the radical center. The quality of Hirshfeld charge population analysis was recently discussed by

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(40) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 7363.

(41) Guerra, M. *J. Am. Chem. Soc.* **1993**, *115*, 11926.

(42) Cartledge, F. K.; Piccione, R. V. *Organometallics* **1984**, *3*, 299.

(43) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614.

(44) For a recent systematic comparison of performance between molecular orbital ab initio method and density functional method, see: Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612 and references therein.

(45) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.

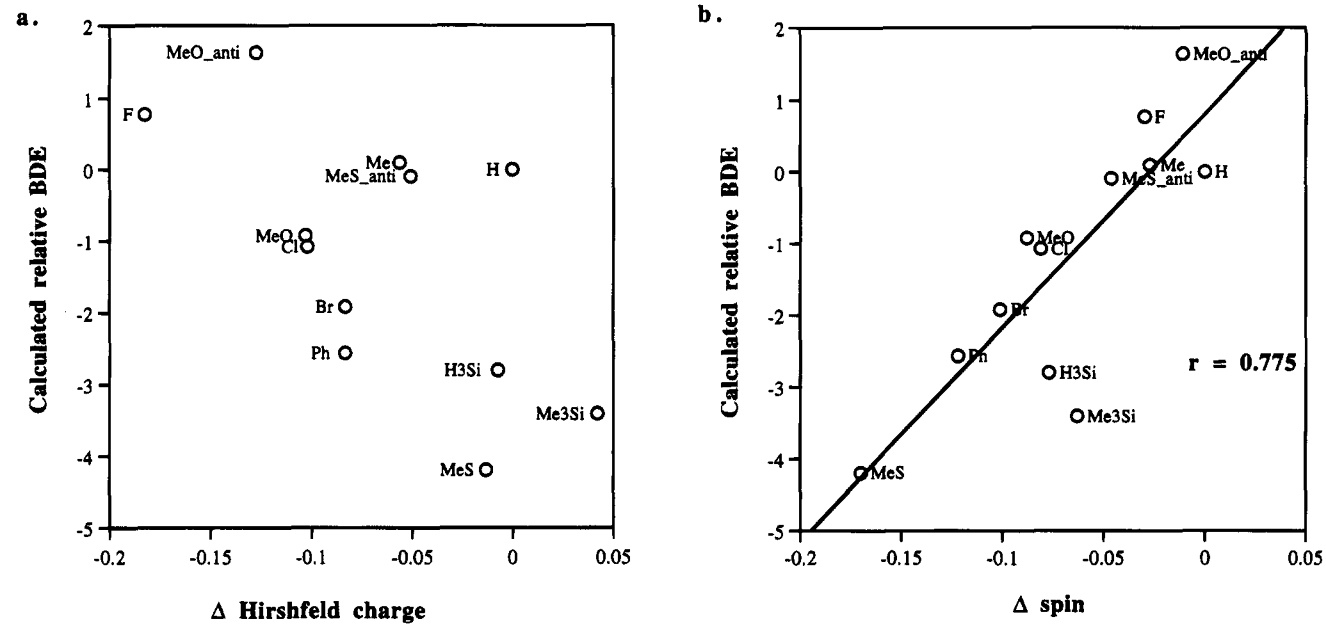


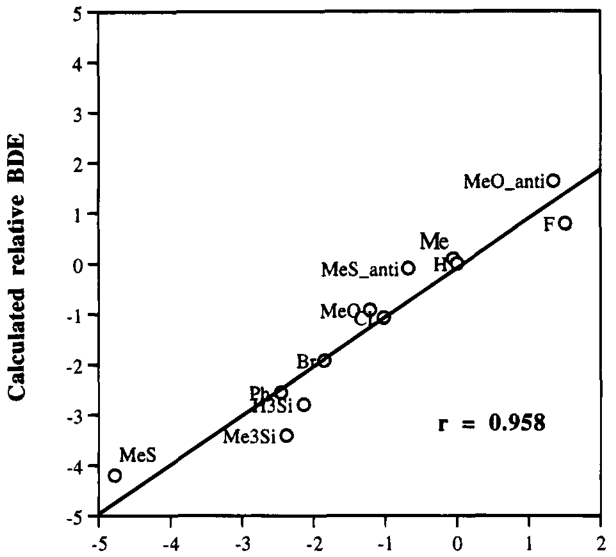
Figure 1. Correlation plot of the calculated relative BDE with the calculated Hirshfeld charge and spin density, respectively, for monosubstituted silanes.

Wiberg *et al.* and Davidson *et al.*[46] In general, the Hirshfeld atomic charges are smaller in magnitude than Mulliken charges, but correlate well with those obtained by other computational methods.[46a]

Figure 1a,b presents calculated substituent effects on the Si–H BDE plotted against spin density and Hirshfeld charge, respectively, for monosubstituted silanes. No correlation is observed. This is understandable since every group is an electron-withdrawing group with respect to Si. Every group causes spin delocalization but some groups cause increased BDE while some others cause decreased BDE.

However, when both spin density and Hirshfeld charge are used as parameters, a good correlation is found for the calculated substituent effect. Figure 2 is the plot of the calculated substituent effect against the estimated substituent effect according to eq 1. The correlation coefficient (r) is 0.958. The largest deviation is for $SiMe_3$ substitution, which is about 1 kcal/mol.

It is fair to say that at least two major factors affect the substituent effect. Spin delocalization, which can be represented by spin density variation, stabilizes the radical. Inductive effect, which is represented by charge variation, stabilizes the radical if the substituent is electron-donating and destabilizes the radical if the substituent is electron-withdrawing. In the present case, each substituent is electron-withdrawing. Thus, the methyl and fluoro substituents have small radical spin delocalization effects and inductive radical destabilization is the dominant effect, causing increased Si–H BDE. The methoxy group causes larger spin delocalization and is less electronegative than the fluoro group, giving an overall small stablization to the silyl radical. Compared to the first-row elements, the second-row elements have larger spin delocalization effects and smaller inductive radical destabilization, and they cause relatively large stabilizations to the silyl radical.



$$\Delta BDE(rel) = 29.11\Delta S - 13.07\Delta C \qquad (1)$$

Figure 2. Correlation plot of the calculated relative BDE with the estimated relative BDE from the correlation equation $\Delta BDE(rel) = 29.11\ \Delta S - 13.07\ \Delta C$ for the monosubstituted silanes.

Although it is convenient to attribute the inductive effect to the relative stabilities of radicals, as we do here, actually the major effect could be on the reactant. For example, the shortening of the Si–H bond by heteroatom substitutions would suggest a strengthening of the Si–H bond, which agrees with the electron-withdrawing inductive effect of these substituents.

We also tested the correlation of the calculated substituent effect with the σ^X and σ^* parameters which were used by Arnold *et al* .[19] and Jiang *et al.*[20] As shown in Figure 3a, Jiang's parameters for seven substituents give a quite good correlation with the calculated Si–H BDEs ($r = 0.940$). Arnold's parameters can only be applied to four substituents, and we find a less satisfactory correlation (0.790) as shown in Figure 3b. We would expect a better correlation if more substituents were included.

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(46) (a) Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504. (b) Davidson, E. R.; Chakravorty, S. *Theor. Chim. Acta* **1992**, *83*, 319.

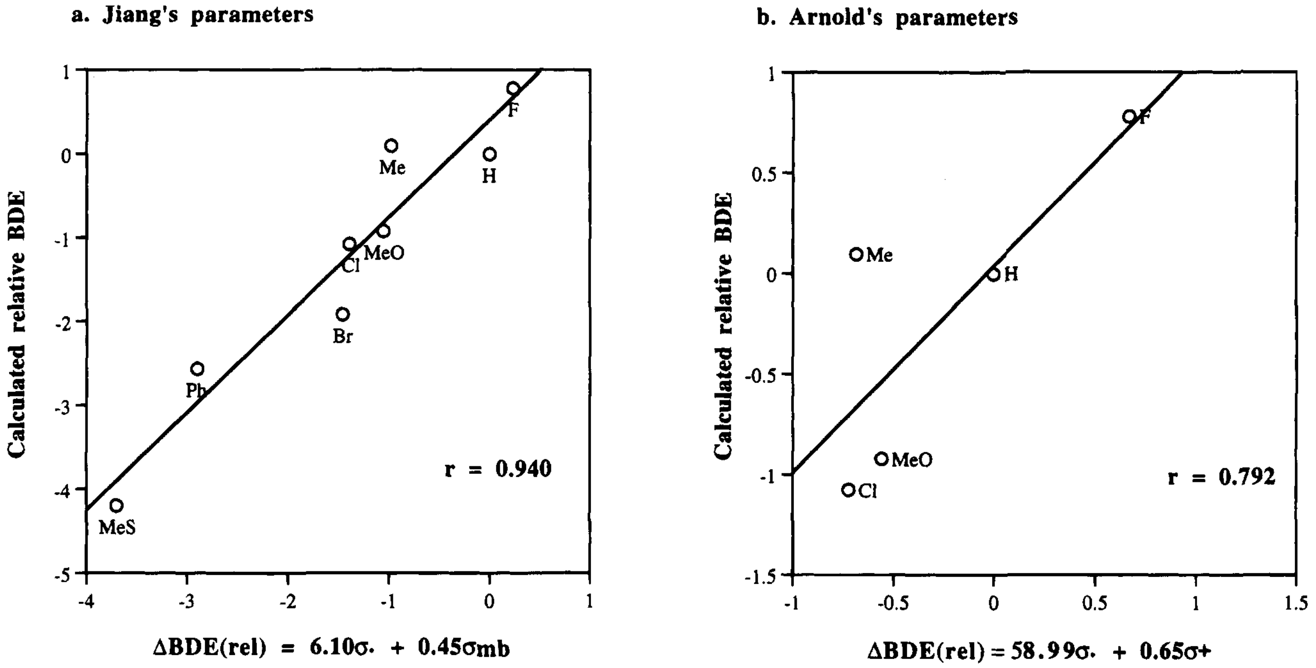


Figure 3. (a) Correlation plot of the calculated relative BDE with Jiang's $\sigma^{\bullet}$ and σ_{mb} estimated by ΔBDE(rel) = 6.10 $\sigma^{\bullet}$ + 0.45 σ_{mb} for the monosubstituted silanes. (b) Correlation plot of the calculated relative BDE with Arnold's $\sigma^{\bullet}$ and σ^{+} estimated by ΔBDE(rel) = 58.99$\sigma^{\bullet}$ + 0.65 σ^{+} for the monosubstituted silanes.

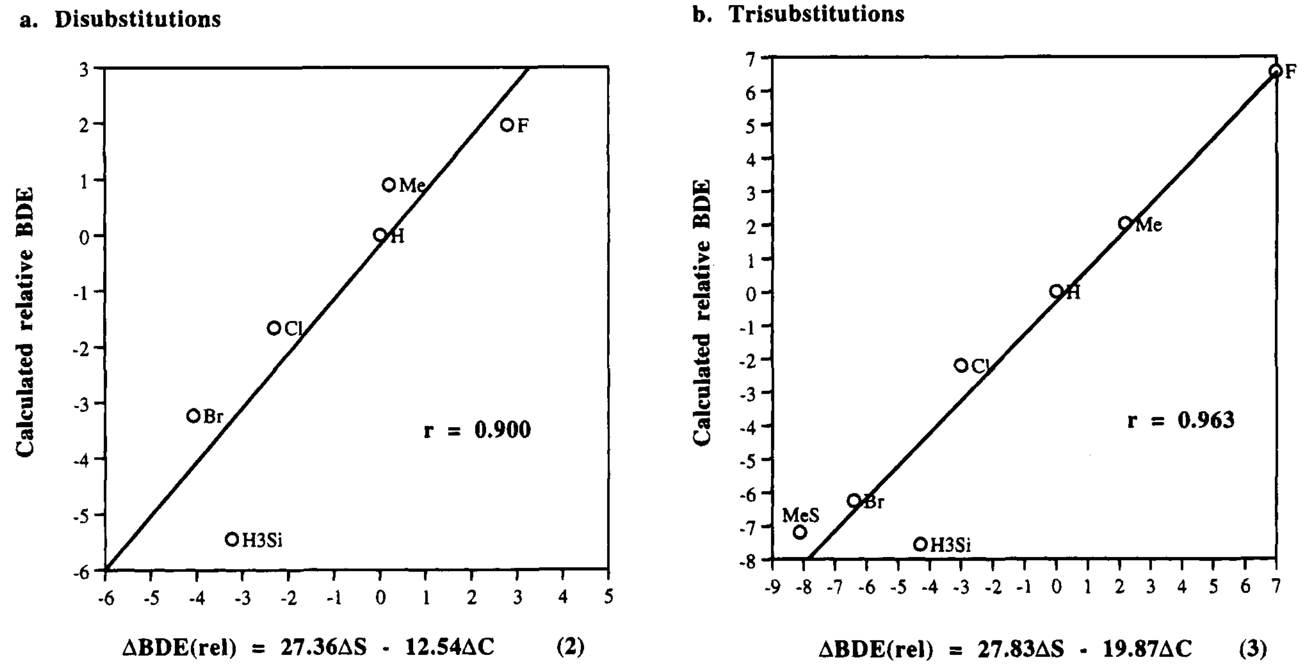
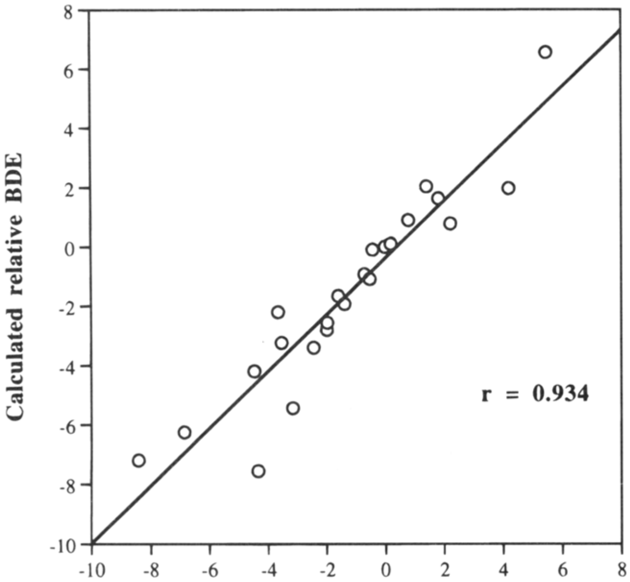


Figure 4. (a) Correlation plot of the calculated relative BDE with the estimated relative BDE from the correlation equation ΔBDE(rel) = 27.36 ΔS − 12.54ΔC for the disubstituted silanes. (b) The correlation plot of the calculated relative BDE with the estimated relative BDE from the correlation equation ΔBDE (rel) = 27.83ΔS − 19.87 ΔC for the trisubstituted silanes.

Figure 4a,b contains plots of calculated substituent effect against estimated substituent effect according to eqs 2 and 3 for disubstitutions and trisubstitutions, respectively. Once again, the calculated substituent effect can be accounted for reasonably well by a spin delocalization effect and an inductive effect. The estimated effect for $(SiH_3)_2SiH_2$ and $(SiH_3)_3SiH$ according to eqs 2 and 3, respectively, are 2.2 and 2.9 kcal/mol smaller than the calculated values. This might be partially caused by the relief of steric interactions between the large silyl groups upon the formation of the silyl radicals. Geometrical changes discussed earlier support this argument. Thus, our calculations seem to support the explanation that the large Si−H bond weakening in $(TMS)_3Si$−H is partially due to the relief of steric interactions.[5] Thus, if the SiH_3 substituent is omitted from Figure 4a,b, r = 0.982 and r = 0.998 are obtained, respectively, for the two panels. It is also noted that the two coefficient constants vary slightly from monosubstitution to trisubstitution (eqs 1−3). The ratio of the two constants becomes smaller with more substituents. This might reflect the Capto-Dative effect which has attracted much attention recently.[47,48]

Figure 5 shows calculated substituent effect plotted



$$\Delta\mathbf{BDE(rel)} = 27.44\Delta S - 16.62\Delta C \qquad (4)$$

Figure 5. Correlation plot of the calculated relative BDE with the estimated relative BDE from the correlation equation ΔBDE(rel) = 27.44ΔS − 16.62 ΔC for all of the substituted silanes.

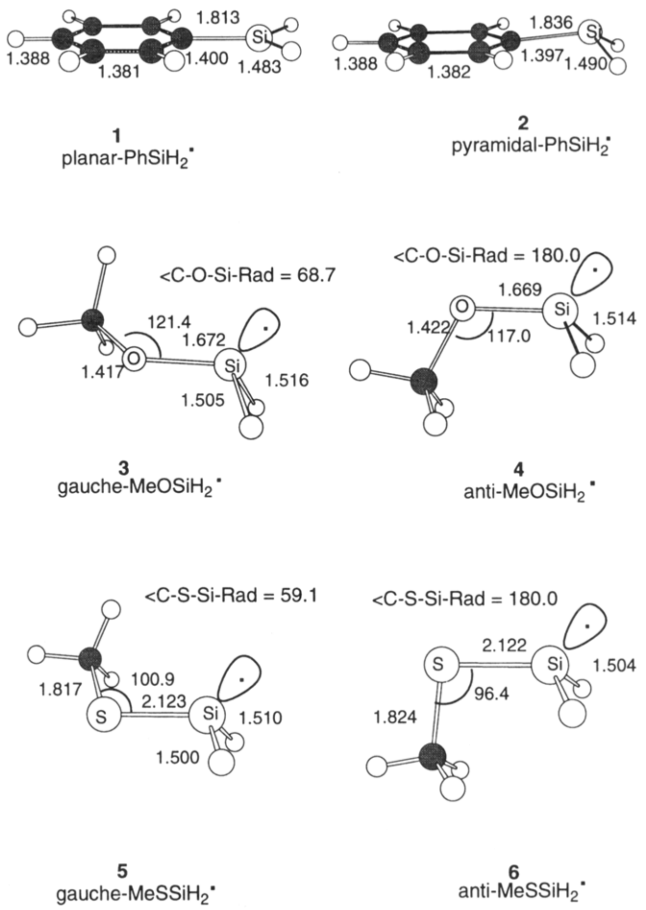


Figure 6. Calculated structures (JMW/DND) of the planar and pyramidal phenylsilyl radical and gauche and anti conformations of the methoxysilyl radical and (methylthio)silyl radical.

against the estimated substituent effect according to eq 4 for all of the substituents. The correlation is reasonably good with $r = 0.934$. Once again, if the silyl substituents are omitted, a better correlation with r = 0.969 is obtained.

In a separate paper, we will report our similar study on the substituent effect on C-H bond dissociation energy.[49] The basic concept can also be applied to the C-H case, where the spin delocalization effect is much larger compared to the Si−H case, while the inductive destabilization is smaller because C is more electronegative than Si. This explains why the substituent effect is much more significant for the C−H BDE.

The smaller spin delocalization effect on silyl radical is partially caused by the large size of the Si radical center compared to C and the pyramidal structure of the Si radical. In the case of the benzyl radical, there is a good spin (or π) delocalization in a planar structure. The spin density at the radical center is reduced to 0.61. For phenylsilyl radical, a pyramidal structure is more stable than a planar structure by about 3 kcal/mol. Since the planar structure of the parent silyl radical (SiH_3) is less stable than the pyramidal structure by about 6 kcal/mol,[40] the additional spin delocalization in structure **1** cannot overcome the barrier for Si radical inversion. The spin density on the Si radical center is 0.88 and 0.84, respectively, in structures **1** and **2**.

The radical spin delocalization by a substituent is often described as the result of 1e and 3e stabilization interactions involving the SOMO of radical center and the LUMO and HOMO of the substituent.[18,40] If this is indeed important, one would expect a shortening of the X−Si bond upon Si−H bond dissociation. This is not observed. In fact, calculations show that the X−Si bond length is generally shorter in silyl radicals. The only exceptions are phenyl substitution and silyl substitutions where the X−Si bond in radical is slightly shorter, which is likely due to the small flattening of the radical center by the substituents.

It has been suggested that the large radical stabilizations by SMe and Me_3Si may be due to the involvement of 3d orbitals of S and Si, which can interact with the radical SOMO.[9] However, previous analysis of molecular orbital coefficients indicates that there is little d orbital contribution.[27,50] Our current calculations indicate that the spin delocalization by the second-row element substituents is mainly due to the 3p orbitals for Cl, S, and Si substitutions and 4p orbitals for Br substitutions.

We prefer a hyperconjugation explanation for the radical spin delocalization effect. Thus, the second-row and third-row element substituents have larger spin delocalization effect than their corresponding first-row element substituents because they are larger in size and

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(47) For geminal effect in radicals, see: (a) Viehe, H. G.; Janousek, Z.; Mereny, R. In *Free radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer: Dordrecht, 1989; pp 1−26. (b) Biekhofer, H.; Hädrich, J.; Pakusch, J.; Beckhaus, H.-D.; Peters, K.; Schnering, H.-G. v. *Ibid.* pp 27−36. (c) Pasto, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 8164. (d) Leroy, G.; Sara, M.; Wilante, C. *THEOCHEM* **1991**, *80*, 303.

(48) (a) For ground state geminal effect, see: Salzner, U.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1992**, *190*, 401, and references therein. (b) Apeloig, Y.; Biton, R.; Abu-Freih, A. *J. Am. Chem. Soc.* **1993**, *115*, 2522. (c) Richard, J. P.; Amyes, T.; Rice, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 2523. (d) Kirmse, W.; Wonner, A.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1992**, *114*, 8828. (e) Wu, Y.-D.; Kirmse, W.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4557.

(49) Wu, Y. D.; Wong, C. L. Manuscript in preparation.

(50) For a discussion on the importance of d-orbital participation in the chemical bonding in hypervalent molecules, see: Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 7363.

can easily accommodate more spin density.[51] This can also be applied to explain the significant gauche conformational preference for the methoxysilyl radical (2.5 kcal/mol) and the (methylthio)silyl radical (4.1 kcal/mol). As shown in Figure 6, the O−Si bond and S−Si bond in gauche conformations are actually slightly longer than those in anti conformations. The gauche methoxy and methylthio have much larger spin delocalization effect (see Table 2). A closer check of spin density on O and S atoms of the gauche conformations indicates that the lone pair which is antiperiplanar to the radical orbital on Si is responsible for the large spin delocalization. This is understandable because it allows minimum spin repulsion.

Summary

We have shown that the density functional method can be used to calculate quite accurately the substituent effect on the Si−H bond dissociation energy. In the cases of trifluoro and trichloro substitutions, we predict a 7 kcal/mol increase for the former and a 3 kcal/mol decrease for the latter in the Si−H bond dissociation energy, which are different from experimental values by about 3−4 kcal/mol. The calculated substituent effect can be correlated reasonably well with the spin density and Hirshfeld charge on the silyl radical, and with Jiang's σ_{mb} and $\sigma^{\bullet}$ parameters, indicating that the substituent effect can be largely accounted for by a radical spin delocalization effect and an inductive effect. The substituent effect for the Si−H BDE is much different from that for C−H BDE because the radical spin delocalization is smaller and the inductive effect is larger for the former. We suggest that radical spin delocalization effect is mainly caused by hyperconjugative interaction and the participation of d-orbitals of a substituent is not important.

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[51] For other hyperconjugation explanations, see: Smith, D. A.; Ulmer, C. W., II *J. Org. Chem.* **1993**, *58*, 4118. Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.