JOC *Article*

Remote Substituent Effects on Bond Dissociation Energies of Para-Substituted Aromatic Silanes

Yu-Hui Cheng, Xin Zhao, Ke-Sheng Song, Lei Liu,*,† and Qing-Xiang Guo

Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China

leiliu@chem.columbia.edu

Received February 4, 2002

UB3LYP/6-31G(d) and ROMP2/6-311++G(d,2p) methods were used to calculate the Si−X bond dissociation energies (BDEs) of a number of para-substituted aromatic silanes (4-Y−C_6H_4−SiH_2X, where X = H, F, Cl, or Li). It was found that the substituent effect on the Si−H BDE of 4-Y−C_6H_4−SiH_3 was small, as the slope (ρ^+) of the BDE−σ_p^+ regression was only 0.09 kJ/mol. In comparison, the substituent effect on the Si−F BDE of 4-Y−C_6H_4−SiH_2F was much stronger, whose ρ^+ value was −2.34 kJ/mol. The substituent effect on the Si−Cl BDE of 4-Y−C_6H_4−SiH_2Cl was also found to be strong with a ρ^+ value of −1.70 kJ/mol. However, the substituent effect on the Si−Li BDE of 4-Y−C_6H_4−SiH_2Li was found to have a large and positive slope (+9.12 kJ/mol) against σ_ρ^-. The origin of the above remarkably different substituent effects on the Si−X BDEs was found to be associated with the ability of the substituent to stabilize or destabilize the starting material (4-Y−C_6H_4−SiH_2X) as well as the product (4-Y−C_6H_4−SiH_2• radical) of the homolysis. Therefore, the direction and magnitude of the effects of Y-substituents on the Z−X BDEs in compounds such as 4-YC_6H_4Z−X should have some important dependence on the polarity of the Z−X bond undergoing homolysis. This conclusion was in agreement with that from earlier studies (for example, *J. Am. Chem. Soc.* **1991**, *113*, 9363). However, it indicated that the proposal from a recent work (*J. Am. Chem. Soc.* **2001**, *123*, 5518) was unfortunately not justified.

1. Introduction

Organotin radicals are widely utilized in organic synthesis, thanks to the successful development of suitable organotin free-radical reducing agents such as tri-*n*-butyltin.[1] However, due to the bad environmental effects of organotin derivatives and the difficulty experienced in the removal of the organotin impurity from the final product, development of alternative reagents is recommended in synthetic organic chemistry. As a consequence, use of organosilyl radicals to replace organotin ones in organic synthesis has been studied recently by a number of groups.[2,3]

Unfortunately, it has been found that unlike organotin radicals, generation of organosilyl radical intermediates is not practically convenient. This fact is clearly related to the Si−X bond dissociation energy (BDE) being greater than the corresponding Sn−X one. For example, the H−Si BDE of H−SiH_3 is measured to be 384.1 kJ/mol, compared to 308.4 kJ/mol found for the H−Sn BDE of H−Sn(n-C_4H_9)$_3$.[4]

Thus, knowledge of the Si−X homolysis is valuable to the study of organosilyl radicals, which has attracted a few researchers to experimentally measure[5] or theoretically calculate[6] the Si−X BDEs. From systematic studies, it was found that there are some apparent differences between the α-substituent effects on the Si−H and C−H BDEs.[7−9] For example, the benzyllic C−H BDE of toluene is 371.1 kJ/mol, which is about 61.1 kJ/mol smaller than the C−H BDE of methane (432.2 kJ/mol). In comparison, the Si−H BDE of Ph−SiH_3 is 369.0 kJ/mol, which is only 15.1 kJ/mol less than that of SiH_4 (384.1 kJ/mol). Therefore, the substituent effect on the Si−H bond strength is considerably less significant than that on the C−H BDE.

In the present paper, we report a theoretical study of the remote substituent effects on the Si−X BDEs of para

---

† Current address: Department of Chemistry, Columbia University, New York, NY 10027.

[1] (a) Neumann, W. P. *Synthesis* **1987**, 665. (b) Curran, D. P. *Synthesis* **1988**, 417. (c) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *24*, 969.

[2] For reviews, see: (a) Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188. (b) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

[3] For a recent example, see: Matsumoto, A.; Ito, Y. *J. Org. Chem.* **2000**, *65*, 5707.

[4] Lide, D. R. *CRC Handbook of Chemistry and Physics*. CRC Press, LLC: Boca Raton, FL, 2001.

[5] (a) Chatgilialoglu, C.; Guerra, M.; Guerrini, A.; Seconi, G.; Clark, K. B.; Griller, D.; Kanabus-Kaminska, J.; Martinho-Simoes, J. *J. Org. Chem.* **1992**, *57*, 2427. (b) Seetula, J. A.; Feng, Y.; Gutman, D.; Seakins, P. W.; Pilling, M. J. *J. Phys. Chem.* **1992**, *95*, 1658. (c) Ding, L.; Marshall, P. *J. Am. Chem. Soc.* **1992**, *114*, 5754. (d) Bullock, W. J.; Walsh, R.; King, K. D. *J. Phys. Chem.* **1994**, *98*, 9551.

[6] (a) Dakternieks, D.; Henry, D. J.; Schiesser C. H. *J. Chem. Soc., Perkin Trans. 2* **1998**, 591. (b) Zhang, Q. Z.; Wang, S. K.; Liu, C. P.; Zhang, J. G.; Wang, M. G.; Gu, Y. S. *Acta Chim. Sin.* **2001**, *59*, 189. (c) Zhang, Q. Z.; Zhang, J. G.; Wang, S. K.; Zhang, M.; Liu, C. P.; Gu, Y. S. *Chin. J. Chem.* **2001**, *19*, 566. (d) Yu, X.; Li, S. M.; Xu, Z. F.; Li, Z. S.; Sun, C. C. *J. Phys. Chem. A* **2001**, *105*, 7072.

[7] Chatgilialoglu, C.; Newcomb, M. *Adv. Organomet. Chem.* **1999**, *44*, 67.

[8] Wu, Y.-D.; Wong, C.-L. *J. Org. Chem.* **1995**, *60*, 821 and references therein.

[9] Schwartz, M.; Berry, R. J. *J. Mol. Struct. (THEOCHEM)* **2001**, *538*, 9.

10.1021/jo020085h CCC: $22.00

substituent phenylsilanes ($Y-C_6H_4-SiH_2-X$, where X = H, F, Cl, or Li). Similar studies on phenylsilanes have not been done before, but we expect to obtain a number of interesting results from the study. First, it is known that the benzyllic C−H BDEs are lowered by both the para electron-withdrawing and electron-donating substituents. By contrast, the O−H and N−H BDEs of phenols and anilines are reduced by the para electron-donating groups but increased by para electron-withdrawing groups.[10,11] Thus, it is then interesting to know the para substituent effect on Si−H BDEs and compare it to the above cases. It should be noted that unlike most other heteroatoms, silicon is less electronegative than carbon.

Another interesting question related to the Si−X BDEs is the effects of the Si−X polarity on the bond strength. For some time, it has been assumed that the direction and magnitude of the effects of Y-substituents on the Z−X BDEs in compounds $4\text{-}YC_6H_4Z-X$ could be correlated with the polarity of the Z−X bond undergoing homolysis.[12] However, very recently, it was proposed that when Y has significant effects on Z−X BDEs it must be due to their stabilization or destabilization of the radical instead of the neutral compound, regardless of the nature of X, Y, and Z.[1313] This argument was thought to be evidenced by the fact that the effects of Y on CH_2-X in $4\text{-}YC_6H_4\text{-}CH_2-X$ (X = H, F, Cl, Br) are roughly equal for each X, despite large changes in the C−X bond polarity. The same argument was also thought to be supported by the fact that changes in O−X BDEs induced by changing Y in YC_6H_4O-X (X = H, CH_3, CH_2Ph) are large and essentially identical.[13] Clearly, it is then interesting to know if the same behaviors could be observed for Si−X BDEs of $YC_6H_4SiH_2-X$.

2. Methods

All calculations were done with Gaussian 98.[14] Substituted silanes and their corresponding radicals were optimized with density function theory (DFT) at the UB3LYP/6-31G(d) method. Frequency calculations at the UB3LYP/6-31G(d) level were also conducted on all the optimized structures, which confirmed that they were real minima without any imaginary frequencies.

Single-point energy calculations were done at UB3LYP/6-31G(d) and ROMP2/6-311++G(d,2p) levels. It should be mentioned that such levels of methods represent a good compromise between the accuracy and CPU cost of the calculation, especially when open-shell species are involved. Higher levels of methods such as CCSD(T), G3, or CBS-Q are not feasible now for a systematic study of a number of disubstituted benzenes, which individually have about 10 heavy atoms. On the other hand, other similar levels of methods such as UMP2 and PMP2 have been shown to be much less reliable than the above methods for the radical species, because the spin contamination suffered by UMP2 and PMP2 may lead to severely erratic calculation results.[15]

Bond dissociation energies were calculated as the enthalpy changes of the following reactions at 298 K. The results were corrected with zero point energies, temperature corrections, and a pressure−volume work term calculated at the UB3LYP/6-31G(d) level scaled by 0.9806.[16]

$$Y-C_6H_4-SiH_2-X \rightarrow Y-C_6H_4-SiH_2\bullet + X\bullet \qquad (1)$$

3. Results and Discussion

3.1. Geometry. In Figure 1 are shown the optimized structures of phenylsilane, phenylfluorosilane, phenylchlorosilane, phenylsilyllithium, and the phenylsilyl radical. According to the structures shown, in all the five species there is almost no C−C bond length alternation in the phenyl ring, as all the C−C bonds are 1.393$\sim$1.411 Å long. The C−H bond lengths are 1.087−1.089 Å, and the Si−H bond lengths are 1.483−1.507 Å.

The C−Si bond length in phenylsilane is 1.879 Å, which is larger than the C−Si bond length in the phenylsilyl radical (1.864 Å) because of the slightly stronger conjugation effect for the silyl radical than that for the $-SiH_3$ group. However, the C−Si bond lengths in phenylfluorosilane (1.861 Å) and phenylchlorosilane (1.864 Å) are slightly shorter than that in phenylsilyl radical. The C−Si bond length in phenylsilyllithium, on the other hand, is 1.913 Å.

3.2. Bond Dissociation Energies. We calculate the Si−X BDEs using UB3LYP/6-31G(d) and ROMP2/6-311++G(d,2p) methods. (Supporting Information) From the results, we find that the Si−F bond is the strongest ($\sim$ 605 kJ/mol), followed by the Si−Cl ($\sim$435 kJ/mol) and then Si−H bond ($\sim$360 kJ/mol). The weakest bond is Si−Li (180 kJ/mol).

The Si−H BDE of phenylsilane is calculated to be 367.8 kJ/mol by the UB3LYP/6-31G(d) method and 357.1 kJ/mol by the ROMP2/6-311++G(d,2p) method. Both of the values are smaller than the experimental value, 369.0 kJ/mol at 298 K.[4] Similar underestimation of BDEs was

---

[10] For reviews, see: (a) Hansch, C.; Gao, H. *Chem. Rev.* **1997**, *97*, 2995. (b) Cherkasov, A. R.; Jonsson, M.; Galkin, V. I.; Cherkasov, R. A. *Usp. Khim.* **2001**, *70*, 3.

[11] For recent examples, see: (a) Fox, T.; Kollman, P. A. *J. Phys. Chem.* **1996**, *100*, 2950. (b) Wu, Y. D.; Wong, C. L.; Chan, K. W. K.; Ji, G. Z.; Jiang, X. K. *J. Org. Chem.* **1996**, *61*, 746. (c) Wu, Y. D.; Lai, D. K. W. *J. Org. Chem.* **1996**, *61*, 7904. (d) Brinck, T.; Haeberlein, M.; Jonsson, M. *J. Am. Chem. Soc.* **1997**, *119*, 4239. (e) Wright, J. S.; Carpenter, D. J.; McKay, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1997**, *119*, 4245. (f) Adams, W.; van Barneveld, C. *J. Am. Chem. Soc.* **1999**, *121*, 10820. (g) Wright, J. S.; Johnson, E. R.; DiLabio. G. A. *J. Am. Chem. Soc.* **2001**, *123*, 1173. (h) Wen, Z.; Li, Z.; Shang, Z.; Cheng, J. *J. Org. Chem.* **2001**, *66*, 1466.

[12] Clark, K. B.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1991**, *113*, 9363.

[13] (a) Pratt, D. A.; Wright, J. S.; Ingold, K. U. *J. Am. Chem. Soc.* **1999**, *121*, 4877. (b) Pratt, D. A.; de Heer, M. I.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 5518.

[14] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

[15] (a) Parkinson, C. J.; Mayer, P. M.; Radom. L. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2305. (b) Henry, D. J.; Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Phys. Chem. A* **2001**, *105*, 6750.

[16] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

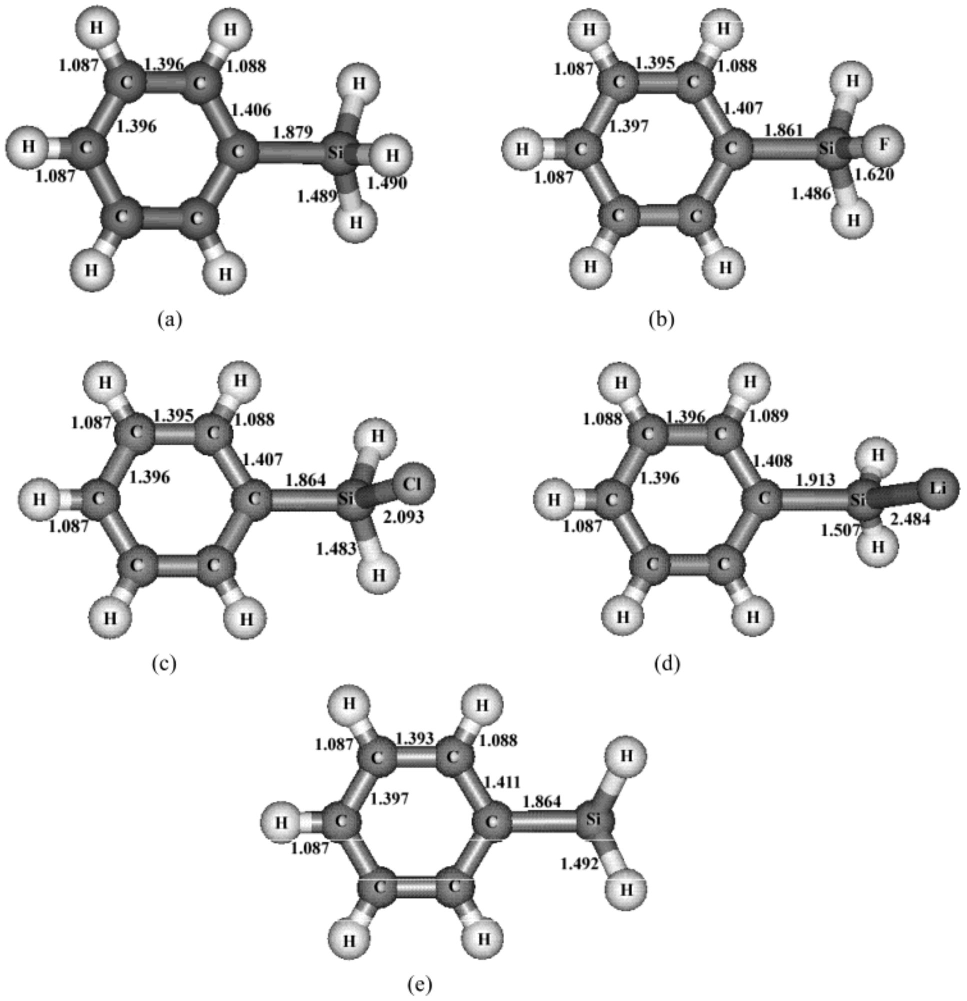

FIGURE 1. UB3LYP/6-31G(d) optimized geometry of (a) phenylsilane, (b) phenylfluorosilane, (c) phenylchlorosilane, (d) phenylsilyllithium, and (e) the phenylsilyl radical.

also found in a number of former studies not only for silyl radicals but also for carbon-, nitrogen-, and oxygen-centered radicals.[8,11,15]

Nevertheless, we are most concerned with the substituent effects on the Si−X BDEs. Therefore, the calculated absolute BDEs are less important. From many studies, it has been shown that the error in the calculated BDEs by a certain theoretical method is usually systematic in nature.[8,11,15] As a consequence, if one calculates the relative bond dissociation energies (ΔBDE) according to the following equation

$$\Delta\text{BDE (Si}-\text{X)}_\text{Y} = \text{BDE (Y}-\text{C}_6\text{H}_4-\text{SiH}_2\text{X)} - \text{BDE (C}_6\text{H}_5-\text{SiH}_2\text{X)} \quad (2)$$

the corresponding results are expected to be fairly accurate.[15,17] If that were true, one could make corrections for a series of Si−X BDEs using only one experimental BDE value and theoretical ΔBDEs.

Because methods such as CBS-Q, UCCSD(T), UQCISD(T), and G3 are too expensive for disubstituted benzenes with over eight heavy atoms, we have only two choices left, namely, UB3LYP and ROMP2, to be used to calculate the ΔBDEs for phenylsilanes. Other similar levels of methods such as UMP2 and PMP2 are known to be highly unreliable for BDE calculations. To test if the UB3LYP and ROMP2 methods are reliable for ΔBDE calculations, we used UB3LYP/6-311++G(d,2p), ROMP2/6-311++G(d,2p), CBS-Q, and G3 methods to calculate the Si−H BDEs of a number of relatively small silanes. The results are summarized in Table 1.

From Table 1, it can be seen that both the UB3LYP and ROMP2 methods underestimate the Si−H BDEs if one uses CBS-Q and G3 as benchmark methods. However, if one performs a linear regression between the UB3LYP (or ROMP2) BDEs and the CBS-Q (or G3) methods, it will be found that the correlations are fairly good with the correlation coefficients larger than 0.95. Therefore, ΔBDEs calculated using UB3LYP and ROMP2 methods are indeed reasonably good.

3.3. Relative Bond Dissociation Energies. According to the above results, we used ROMP2/6-311++G(d,2p) to calculate the ΔBDEs of all the substituted phenylsilanes, phenylfluorosilanes, phenylchlorosilanes, and phenylsilyllithium using eq 2. (Table 2) Since we have UB3LYP/6-31G(d) BDEs in hand, we also list the UB3LYP/6-31G(d) ΔBDEs in Table 2, which can be used to double-check the reliability of the ROMP2 ΔBDEs.

---

[17] Froese, R. D. J.; Morokuma, K. *J. Phys. Chem. A* **1999**, *103*, 4580.

TABLE 1. Si−H BDEs of Relatively Small Compounds X−SiH$_2$−H Calculated at Different Levels of Methods (kJ/mol)[a]

X	UB3LYP/6-311++g(d,2p)	ROMP2/6-311++g(d,2p)	CBS-Q[b]	G3[c]
H	375.7	362.5	386.5	383.6
CH$_3$	378.2	365.9	390.2	387.8
Cl	373.0	367.2	386.4	384.4
F	381.9	373.1	396.6	394.5
NH$_2$	365.3	360.1	381.3	379.3
OH	375.5	368.0	389.9	388.5
SH	364.2	360.4	377.8	376.1

[a] All geometry optimizations were done at the UB3LYP/6-31G(d) level. Final BDEs were corrected with zero point energies calculated at the UB3LYP/6-31G(d) level scaled by 0.9806. [b] Equivalent to the MP2(FC)/6-31g* optimization. [c] Equivalent to the MP2(full)/6-31g(d) optimization.

TABLE 2. Relative Bond Dissociation Energies (kJ/mol) Associated with the Si−X Bond Homolysis Calculated at UB3LYP/6-31G(d)//UB3LYP/6-31G(d) and ROMP2/6-311++G(d,2p)//UB3LYP/6-31G(d) Levels

	Y−C$_6$H$_4$−SiH$_2$−H		Y−C$_6$H$_4$−SiH$_2$−F		Y−C$_6$H$_4$−SiH$_2$−Cl		Y−C$_6$H$_4$−SiH$_2$−Li	
substituent	UB3LYP	ROMP2	UB3LYP	ROMP2	UB3LYP	ROMP2	UB3LYP	ROMP2
N(CH$_3$)$_2$	−2.8	−0.6	0.8	2.1	1.6	2.4	−10.8	−5.5
NH$_2$	−2.1	−0.5	1.1	2.1	1.8	2.1	−6.1	−1.7
OH	−0.8	−0.2	1.0	1.4	1.0	1.6	−4.0	−2.1
OCH$_3$	−0.8	−0.8	0.9	1.3	1.1	1.7	−4.7	−3.5
SCH$_3$	−1.2	−0.8	−0.3	0.3	−0.3	1.0	−1.8	−0.6
CH$_3$	−0.4	−0.5	0.3	0.4	0.4	1.1	−2.2	−1.9
F	0.1	0.1	0.3	0.2	−0.1	0.5	1.4	2.3
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cl	0.0	−0.4	−0.8	−0.6	−1.4	0.1	4.8	3.7
COOH	−1.0	−0.5	−2.9	−2.3	−3.4	−0.7	7.4	6.3
CONH$_2$	−0.6	−0.5	−1.7	−1.2	−2.1	0.0	4.8	4.0
COCH$_3$	−1.1	−0.8	−2.9	−2.3	−3.3	−0.5	6.7	5.6
CF$_3$	0.0	−0.1	−2.0	−3.0	−2.7	−1.0	8.3	8.7
CN	−0.9	−0.4	−3.7	−3.2	−4.6	−1.8	11.9	10.6
CHO	−1.4	−0.8	−3.7	−2.5	−4.4	−1.3	9.1	7.7
NO$_2$	−1.2	−0.2	−4.6	−3.2	−5.7	−1.6	14.4	11.3

From Table 2, it can be seen that for phenylsilanes, the substituent effect on the Si−H BDE is quite small. This fact can be easily seen from the largest absolute ΔBDE value, which is 0.6 kJ/mol found for the NMe$_2$ substituent. In comparison, the absolute ΔBDE for the benzyllic C−H BDE in 4-*N*,*N*-dimethylamino toluene is as large as 9.2 kJ/mol.[11]

Nevertheless, it is interesting to note that for phenylsilanes, except for the F substituent, all the other groups are predicted by ROMP2/6-311++G(d,2p) to have negative ΔBDEs, regardless of whether they are electron donating or electron withdrawing. Similar effects have been seen only for C−H BDEs before. By contrast, for O−H, N−H, and S−H BDEs, electron-donating substituents normally reduce the BDEs, whereas the electron-withdrawing groups increase them.

The above substituent effect can also be shown by the plots of the Si−H ΔBDEs against the substituent σ_ρ^+ and σ_{JJ} constants. (Figures 2) According to these plots, the Si−H BDEs do not have a significant correlation with the substituent σ_ρ^+ constants. This is reflected not only by the small correlation coefficient ($r = 0.24$) but also by the small slope (ρ^+) of the regression (0.09 kJ/mol). It should be mentioned that the UB3LYP/6-31G(d) slope for the Si−H ΔBDEs is 0.57 kJ/mol ($r = 0.54$).

On the other hand, the Si−H BDEs have a significant correlation with the substituent σ_{JJ} constants.[18] The correlation coefficient is fair ($r = -0.70$) for the ROMP2/6-311++G(d,2p) results and very good for the UB3LYP/6-31G(d) results ($r = -0.95$). As the σ_{JJ} constant was considered to reflect the ability of a substituent to stabilize a carbon radical (or to delocalize the spin carried by the carbon radical), the above correlation indicates that the remote substituent effect on the stability of silyl radials is fairly similar to that on carbon radicals.

3.4. Substituent Effects on Si−F, Si−Cl, and Si−Li BDEs. If the para substituent effects on Z−X BDEs of 4-Y−C$_6$H$_4$−Z−X depend only on the ability of the substituent to stabilize or destabilize the 4-Y−C$_6$H$_4$−Z• radical, regardless of the nature of X, Y, and Z, we would expect that the Si−F, Si−Cl, and Si−Li BDEs should show substituent effects similar to that on Si−H BDEs. However, this does not turn out to be true.

In fact, the Si−F BDEs calculated by the ROMP2/6-311++G(d,2p) method display a very strong correlation with the substituent σ_ρ^+ constants ($r = -0.95$) as shown in Figure 2b. More interestingly, the ρ^+ value here is −2.34 kJ/mol, whose negative sign not only differs from that for Si−H BDEs but also contrasts those previously found for the C−H, N−H, O−H, and S−H BDEs in the 4-Y−C$_6$H$_4$−Z−X systems.[11] It should be mentioned that the UB3LYP/6-31G(d) method predicts that the Si−F BDEs should correlate with the substituent σ_ρ^+ constants with a ρ^+ value of −2.20 kJ/mol and a correlation coefficient of −0.86. Therefore, we believe that the observed substituent effects on Si−F BDEs are real.

The Si−Cl BDEs calculated by the ROMP2/6-311++G(d,2p) method display a similar correlation with the substituent σ_ρ^+ constants. The ρ^+ value is −1.70 kJ/mol, and the correlation coefficient is −0.97. The corresponding UB3LYP/6-31G(d) values are $\rho^+ = -2.85$ kJ/mol and $r = -0.91$.

---

(18) Jiang, X. K. *Acc. Chem. Res.* **1997**, *30*, 283.

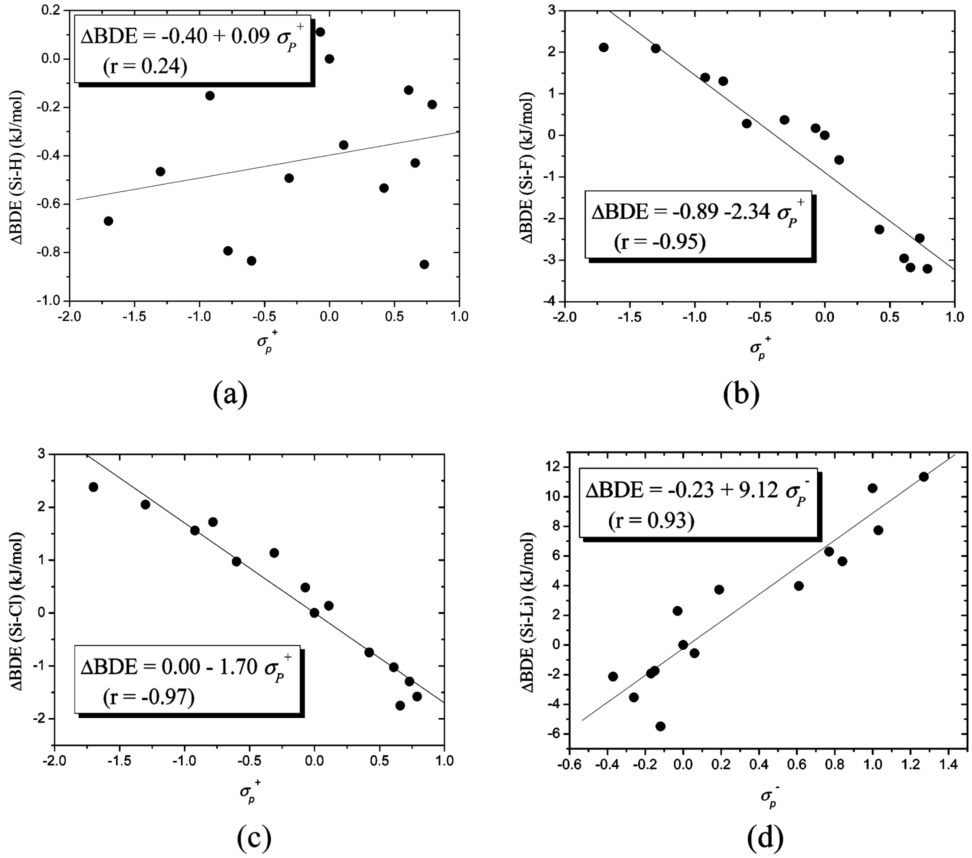

FIGURE 2. Correlation between the Si−X (X = H, F, Cl, or Li) ΔBDEs calculated by the ROMP2/6-311++G(d,2p) method and the substituent σ_ρ^+ constants.

By contrast, the Si−Li BDEs calculated by the ROMP2/6-311++G(d,2p) method exhibit a completely different fashion of substituent effects. In fact, their correlation with the substituent σ_ρ^- constants has a large positive slope (+9.12 kJ/mol) and a correlation coefficient of 0.93. The corresponding UB3LYP/6-31G(d) values are +12.12 kJ/mol and $r = 0.92$.

Compared to the ρ^+ value (0.09 kJ/mol) and correlation coefficient (0.24) of Si−H BDEs, the above results clearly demonstrate that the effects of Y-substituents on the Z−X BDEs in compounds such as 4-YC_6H_4Z−X should have some dependence on the polarity of the Z−X bond undergoing homolysis. Such dependence is able to change not only the significance of the substituent effects but also the sign of the correlation.

3.5. Origin of the Substituent Effects. Clearly, the substituent effects on the Si−X BDEs must be related to their effects on the stabilities of both the starting materials and products of the Si−X homolysis. Therefore, to reveal the origin of the substituent effects on Si−X BDEs, we calculated the energy changes of the following isodesmic reactions (Table 3).

Reaction:

$$\mathrm{Y{-}C_6H_4{-}SiH_2X + C_6H_6 \rightarrow C_6H_5{-}SiH_2X + Y{-}C_6H_5}$$

$$\text{(Reaction 1, X = H; reaction 2, X = F; reaction 3, X = Cl; reaction 4, X = Li; reaction 5, X = }\bullet\text{)} \quad (3)$$

The Hammett regressions results for the energy changes of each reaction are shown by the following equations.

$$\text{Reaction 1:} \quad \Delta E = 0.20 - 1.59\,\sigma_\rho^+\ (r = 0.98) \quad (4)$$

$$\text{Reaction 2:} \quad \Delta E = -0.29 - 4.03\,\sigma_\rho^+\ (r = 0.98) \quad (5)$$

$$\text{Reaction 3:} \quad \Delta E = 0.60 - 3.39\,\sigma_\rho^+\ (r = 0.98) \quad (6)$$

$$\text{Reaction 4:} \quad \Delta E = 1.19 + 7.30\,\sigma_\rho^-\ (r = 0.95) \quad (7)$$

$$\text{Reaction 5:} \quad \Delta E = 0.60 - 1.69\,\sigma_\rho^+\ (r = 0.94) \quad (8)$$

Reaction 1 reflects the substituent effects on the energy to separate the $-SiH_3$ group from the para substituent. According to eq 4, the energy changes of this reaction have a good correlation with the substituent σ_ρ^+ constants. The slope is −1.59 kJ/mol. Therefore, the electron-withdrawing substituents favor the right side of the reaction equation, whereas the electron-donating ones favor the left side. Presumably, the above effects are caused by the fact that the electronegativity of Si (1.8) is smaller than that of hydrogen (2.1). As a result, Si carries some positive charge and separating the $-SiH_3$ group from an electron-withdrawing substituent is energy downhill.

Clearly, if the above theory is correct, replacement of one hydrogen atom in Y−C_6H_4−SiH_3 by a fluorine atom should make the above substituent effects stronger. Indeed, this is true as the slope for reaction 2 is found to

TABLE 3. Energy Changes of Isodesmic Reactions (kJ/mol) Calculated by the ROMP2/6-311++G(d,2p) Method

	reaction				
substituent	1	2	3	4	5
$N(CH_3)_2$	2.9	5.7	5.9	−2.0	3.5
NH_2	2.1	4.7	4.6	0.8	2.6
OH	1.4	3.0	3.1	−0.6	1.6
OCH_3	1.5	3.6	4.1	−1.2	2.3
SCH_3	1.7	2.9	3.5	2.0	2.6
CH_3	0.8	1.7	2.5	−0.6	1.3
F	0.0	0.0	0.3	2.2	−0.1
H	0.0	0.0	0.0	0.0	0.0
Cl	0.4	0.2	0.9	4.5	0.8
COOH	−0.5	−2.3	−0.7	6.3	0.0
$CONH_2$	−0.3	−1.1	0.1	4.1	0.2
$COCH_3$	−0.4	−1.9	−0.1	6.1	0.5
CF_3	−1.0	−3.9	−1.9	7.8	−0.9
CN	−1.0	−3.7	−2.3	10.0	−0.5
CHO	−0.9	−2.6	−1.4	7.7	−0.1
NO_2	−0.9	−3.9	−2.2	10.7	−0.7

be even more negative, i.e., −4.03 kJ/mol. Similarly, chlorination also leads to a larger slope found for reaction 3, i.e., −3.39 kJ/mol.

However, it is conceivable that replacement of one hydrogen atom in $Y-C_6H_4-SiH_3$ by a lithium atom may change the substituent effects, because unlike H, F, or Cl, Li (1.0) has a much smaller electronegativity than Si. As a result, Si in $Y-C_6H_4-SiH_2Li$ carries some negative charge and separating the $-SiH_3$ group from an electron-withdrawing substituent is energetically unfavorable. The net substituent effects should be associated with a positive slope against the substituent σ_ρ^- constants. Indeed this is true as the slope is +7.30 kJ/mol.

At this point, it should be noted that the ΔBDE value for $Y-C_6H_4-SiH_2X$ (X = H, F, Cl, or Li) actually equals the difference between the energy changes of reactions 1−4 and reaction 5. Therefore, as the slopes for reaction 1 and 5 are −1.59 and −1.69 kJ/mol, respectively, the net substituent effects on the Si−H BDEs should have a positive slope of about 0.10 kJ/mol. Indeed, this slope was predicted above to be 0.09 kJ/mol. Thus, the two analyses of substituent effects agree with each other. In addition, as the slopes for reactions 1 and 5 are very close, it is understandable why the $\Delta BDE-\sigma_\rho^+$ correlation for Si−H BDEs is not good ($r = 0.24$).

The slope for reaction 2 is −4.03 kJ/mol, which is significantly more negative than that for reaction 5. Therefore, the net substituent effects on Si−F BDEs should have a negative slope of about −2.34 kJ/mol. Indeed, this value was found above to be −2.34 kJ/mol. Thus, the negative correlation of Si−F BDEs with the substituent σ_ρ^+ constants is caused by the stronger substituent effect on the starting material ($Y-C_6H_4-SiH_2-F$) than that on the product ($Y-C_6H_4-SiH_2\bullet$). Similarly, the slope for the Si−Cl BDEs should be around −1.70 kJ/mol according to reactions 3 and 5 and is found to be −1.70 kJ/mol.

Finally, the slope for reaction 4 is +7.30 kJ/mol, which means that the slope for Si−Li BDEs should be about +9.12 kJ/mol (the slope for reaction 5 is −1.82 if correlated with the substituent σ_ρ^- constants); this value is compared to the value of +9.12 kJ/mol predicted above. Clearly, the major reason for the positive slope of Si−Li BDEs is the stabilization/destabilization effects of the substituents on $Y-C_6H_4-SiH_2Li$ instead of the homolysis product, $Y-C_6H_4-SiH_2\bullet$.

Therefore, all the above analyses demonstrate the importance of the substituent effects on the starting material of the bond homolysis to BDEs. It should be mentioned that some authors prefer to refer to the energy effects for reactions 1−4 as ground effects and those for reaction 5 as radical effects.[11] According to these definitions, we have shown the importance of the ground effects on BDEs. Clearly, although the radical effects play an important role in determining the net substituent effects on BDEs, it is the variation of the ground effects that dictates the change of the pattern of the substituent effects on Z−X BDEs in $4-YC_6H_4Z-X$ when X is changed.

3.6. Alternative Explanation of the Substituent Effects. Since 1996, Nau has established another theory to explain the remote substituent effects on BDEs using Pauling's theory of electronegativity.[19] According to this theory, the conversion of two homonuclear molecules AA and BB to the corresponding heteronuclear species AB is exothermic on account of the additional "ionic resonance energy" E_i of the A−B bond, which is equal to the square of the difference in electronegativity of the atoms forming the bond. The relevant BDE of A−B is thus obtained from the BDEs of the homosymmetric molecules plus E_i (eq 9).

$$\mathrm{BDE\ (A-B) = 0.5BDE\ (A-A) + 0.5BDE\ (B-B) +}\ E_\mathrm{i}\ \mathrm{(A-B)} \quad (9)$$

This simple definition can be directly transferred to the situation in polyatomic molecules, e.g., for benzylic and related bonds XR−Z (eq 10), where the ionic resonance energy contribution to the BDE is now actually a composite (E_i) of E_i for the R−Z bond and the differences in E_i for the remaining bonds in XRZ relative to ZZ and XRRX (eq 11).

$$\mathrm{XR-RX + Z-Z \rightarrow 2XR-Z} \quad (10)$$

$$\mathrm{BDE\ (XR-Z) = 0.5BDE\ (XR-RX) + 0.5BDE\ (Z-Z) + \Sigma\Delta}E_\mathrm{i}\ \mathrm{(XR-Z)} \quad (11)$$

The effects of aryl substituents X on BDEs of benzylic and related bonds are measured relative to the unsubstituted system HR−Z (eq 12), i.e., BDE = BDE (XR−Z) − BDE (HR−Z). Here, the covalent and ionic contributions correspond to the radical stabilization energy (RSE) and the polar ground-state stabilization energy (PSE) of the substituent X (eqs 13 and 14).

$$\mathrm{\Delta BDE = 0.5BDE\ (XR-RX) - 0.5BDE\ (HR-RH) + \Sigma\Delta}E_\mathrm{i}\ \mathrm{(XR-Z) - \Sigma\Delta}E_\mathrm{i}\ \mathrm{(HR-Z)} \quad (12)$$

$$\mathrm{RSE = 0.5BDE\ (XR-RX) - 0.5BDE\ (HR-RH)} \quad (13)$$

$$\mathrm{PSE = -[\Sigma\Delta}E_\mathrm{i}\ \mathrm{(XR-Z) - \Sigma\Delta}E_\mathrm{i}\ \mathrm{(HR-Z)]} \quad (14)$$

Herein, we used this theory and calculated the RSE and PSE using the UB3LYP/6-31G(d) method. For our

---

(19) (a) Nau, W. M. *J. Org. Chem.* **1996**, *61*, 8312. (b) Nau, W. M. *J. Phys. Org. Chem.* **1997**, *10*, 445.

TABLE 4. RSE and PSE (kJ/mol) According to Nau's Theory Calculated at the UB3LYP/6-31G(d) Level

		PSE			
substituent	RSE	$Y-C_6H_4-SiH_2-H$	$Y-C_6H_4-SiH_2-F$	$Y-C_6H_4-SiH_2-Cl$	$Y-C_6H_4-SiH_2-Li$
$N(CH_3)_2$	−4.6	−1.6	−5.3	−6.3	6.4
NH_2	−3.4	−1.2	−4.5	−5.2	5.1
OH	−1.6	−0.7	−2.5	−2.6	2.5
OCH_3	−1.4	−0.6	−2.4	−2.6	3.3
SCH_3	−1.5	−0.3	−1.2	−1.2	0.2
CH_3	−0.7	−0.3	−1.0	−1.2	1.4
F	−0.1	−0.2	−0.4	0.0	−1.7
H	0.0	0.0	0.0	0.0	0.0
Cl	−0.1	0.0	0.8	1.4	−5.0
COOH	−0.6	0.3	2.3	2.7	−8.4
$CONH_2$	−0.6	−0.1	1.1	1.4	−5.8
$COCH_3$	−1.0	0.0	1.9	2.3	−8.1
CF_3	0.1	0.0	2.0	2.7	−8.4
CN	−0.9	−0.1	2.7	3.7	−13.1
CHO	−1.0	0.3	2.7	3.3	−10.4
NO_2	−1.3	−0.3	3.2	4.3	−16.1

systems, we used the following two equations.

$$\mathrm{RSE} = 0.5\mathrm{BDE}\,(Y-C_6H_4-SiH_2-SiH_2-C_6H_4-Y) - 0.5\mathrm{BDE}\,(C_6H_5-SiH_2-SiH_2-C_6H_5) \quad (15)$$

$$\mathrm{PSE} = \mathrm{RSE} - \Delta\mathrm{BDE} \quad (16)$$

The results are listed in Table 4.

We performed the Hammett regressions on the calculation results (eqs 17−21).

$$\mathrm{RSE} = -1.0 + 1.3\,\sigma_\rho^+\ (r = 0.7) \quad (17)$$

$$\mathrm{PSE\ (H)} = -0.2 + 0.6\,\sigma_\rho^+\ (r = 0.8) \quad (18)$$

$$\mathrm{PSE\ (F)} = 0.3 + 3.4\,\sigma_\rho^+\ (r = 0.9) \quad (19)$$

$$\mathrm{PSE\ (Cl)} = 0.6 + 4.1\,\sigma_\rho^+\ (r = 0.99) \quad (20)$$

$$\mathrm{PSE\ (Li)} = 0.3 - 12.0\,\sigma_\rho^-\ (r = 0.95) \quad (21)$$

Clearly, the results indicate that the RSE effects (covalent contributions) are small for Si radicals. Therefore, the total effects are mainly determined by the PSE effects (ionic contributions). Since the PSE effects are quite different for the H, F, Cl, and Li cases, the substituent effects on Si−H, Si−F, Si−Cl, and Si−Li BDEs cannot be the same.

For the H case, the positive slope for PSE indicates that the $X-C_6H_4-SiH_2$ group has a smaller electronegativity value than H. Therefore, an electron-donating group would increase the electronegativity difference, making the Si−H bond more ionic and, thereby, harder to break. On the other hand, an electron-withdrawing group would decrease the electronegativity difference, making the Si−H bond less ionic and, thereby, easier to break. Since F and Cl are more electronegative than H, it is expected that the above effects would be stronger in the F and Cl cases. Indeed, in eqs 19 and 20, the slopes are much larger than that in eq 18.

In comparison, the $X-C_6H_4-SiH_2$ group should have a larger electronegativity value than Li. Therefore, an electron-withdrawing group would increase the electronegativity difference, making the Si−Li bond more ionic and, thereby, harder to break. This is exactly what is observed.

Therefore, the direction of the substituent effects is mainly determined by the sign of the electronegativity difference between the two groups going to break from each other. The magnitude of the substituent effects, on the other hand, is mainly determined by the magnitude of the electronegativity difference between the two groups. The net conclusion drawn from this theory is basically the same as that drawn from Section 3.5.

3.7. Vibration Frequencies. Si−X and C−Si vibration frequencies are experimentally accessible quantities. Thus, we calculated them using the UB3LYP/6-31G(d) method (Supporting Information).

From the results, we find that the C−Si vibration frequency increases in the order $Y-C_6H_4-SiH_2Li$ < $Y-C_6H_4-SiH_2\bullet$ < $Y-C_6H_4-SiH_3$ < $Y-C_6H_4-SiH_2F$ < $Y-C_6H_4-SiH_2Cl$. Such an order can be explained if one considers the ionic bond order of the C−Si bond. Clearly, when more positive charge is carried by the Si atom, the ionic bond order of the C−Si bond will be enhanced and, thereby, its vibration frequency will increase.

The Si−H vibration frequencies are about 2230 cm^{-1}, which are larger than the vibration frequencies of Si−F (∼870 cm^{-1}), Si−Cl (∼540 cm^{-1}), and Si−Li (∼440 cm^{-1}). Clearly, these Si−X vibration frequencies are dependent on the Si−X bond strength, the Si−X bond length, as well as the Si−X effective mass. Although it has been proposed before that the X−Y vibration frequency may correlate with its BDE for certain groups of compounds,[20] we find that such an empirical relationship cannot be well applied for Si−X homolysis. In fact, the best correlation between Si−X BDEs and Si−X vibration frequencies is that found for the Si−F case, where a relatively low correlation coefficient of −0.84 is obtained.

4. Conclusion

In this study, we performed UB3LYP/6-31G(d) and ROMP2/6-311++G(d,2p) calculations on the Si−X bond dissociation energies of a number of para-substituted aromatic silanes ($4\text{-}Y-C_6H_4-SiH_2X$). Our major finding is that the substituent effect on the Si−H BDE of $4\text{-}Y-C_6H_4-SiH_3$, whose slope against the substituent σ_ρ^+ constants is only 0.09 kJ/mol, is not significant. By

---

(20) (a) Zavitsas, A. A.; Chatgilialoglu, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 10645. (b) Finkelshtein, E. I. *J. Phys. Org. Chem.* **2001**, *14*, 543.

contrast, the substituent effect on the Si−F BDE of 4-Y−C_6H_4−SiH_2F, whose slope against the substituent σ_ρ^+ constants is −2.34 kJ/mol, is much stronger. Similarly, the substituent effect on the Si−Cl BDE of 4-Y−C_6H_4−SiH_2Cl has an appreciably negative slope (−1.70 kJ/mol) against the substituent σ_ρ^+ constants. The substituent effect on the Si−Li BDE of 4-Y−C_6H_4−SiH_2Li, on the other hand, is also strong but has a positive slope (+9.12 kJ/mol) against the substituent σ_ρ^- constants.

Therefore, the direction and magnitude of the effects of Y-substituents on the Z−X BDEs in compounds such as 4-YC_6H_4Z−X should have some dependence on the polarity of the Z−X bond undergoing homolysis. Such a conclusion is in agreement with that from earlier studies,[12,19] indicating that the proposal from a recent work[13] is unfortunately not justified.

Acknowledgment. We are grateful for the financial support from NSFC. We are also grateful to Prof. W. M. Nau for his insightful suggestions on the origin of the substituent effects.

Supporting Information Available: Table of bond dissociation energies, Mulliken charges, spin densities, vibration frequencies, and detailed descriptions of the optimized geometry for each of the molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

JO020085H