pressure mercury lamps, no products resulting from the addition of solvent to **1** were evident.

Interesting spectroscopic parallels evolve if one considers that the absorption band for ^{1}**1p*** appears in a region where the diphenylmethyl (DPM) cation and anion exhibit strong absorption bands.[12] In contrast, DPM• exhibits a weak absorption band at 520 nm and a strong band at 330 nm.[13] If the similarities among the spectra of ^{1}**1p***, DPM$^+$, and DPM$^-$ are manifestations of the zwitterionic nature of ^{1}**1p***, ^{1}**p*** of stilbene, for example, should exhibit an absorption maximum near 360 nm where the benzyl cation and anion[14] absorb light rather than near 320 nm where the benzyl radical[15] absorbs light. This trend is consistent with the absorption spectra of ^{3}**p*** of **1**,[6a] 1,1-diphenylethylene,[6a] and stilbene,[16] states best described in terms of a biradical. The absorption maximum for each of these triplet states is at a wavelength less than 350 nm. While lifetimes of 3 ± 2 and 10 ± 3 ps have been reported for ^{1}**p*** of stilbene[17] and 1,1'-bi-indanylidene,[18] respectively, in hexane, no information about the wavelengths of the absorption maxima is, to our knowledge, available.

Additional investigations are underway which probe solvent effects on electronically excited aryl-substituted alkenes.

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Ab Initio Calculations of the Effects of Substituents on the Stabilization of Silyl Radicals versus Methyl Radicals

Michael B. Coolidge and Weston Thatcher Borden*

Department of Chemistry, University of Washington
Seattle, Washington 98195

The ability of substituents to stabilize carbon-centered radicals has been demonstrated by both experimental and computational investigations.[1] In contrast, Walsh's experimental studies have shown that aryl and alkyl substituents provide little or no stabilization for silyl-centered radicals.[2] However, Walsh did find that an SiH$_3$ substituent reduces the Si-H bond dissociation energy (BDE) from 90.3 kcal/mol in SiH$_4$ to 86.3 kcal/mol in H$_3$SiSiH$_3$. Subsequently, Griller and co-workers have shown that the effect of silyl substituents on the Si-H BDE is approximately additive; the three trimethylsilyl substituents on silicon in [(CH$_3$)$_3$Si]$_3$SiH reduce the BDE to 79.0 kcal/mol.[3] Nevertheless, despite the fact

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Table I. MP4SDTQ/6-31G* Energies of the Reaction in Eq 1 and of the Radicals Involved[a]

X	ΔE for eq 1[b] (kcal/mol)		$-E$ of X-AH$_2$• (hartrees)	
	A = C	A = Si	A = C	A = Si
H	0	0	39.6891	290.6957
Li	9.4	12.0	46.5326	297.5804
BeH	9.0	8.0	54.3612	305.3689
BH$_2$	12.4	12.2	65.0355	316.0356
BH$_2$[c]	2.7	0.8	65.0200	316.0175
CH$_3$	3.3	-0.8	78.8720	329.8878
NH$_2$	12.2	0.9	94.8915	345.9258
NH$_2$[c]	3.7	-2.5	94.8780	345.9204
OH	8.6	-0.8	114.7214	365.7776
F	4.4	-3.5	138.7018	389.7816
SiH$_3$	4.4	2.9	329.8663	580.8773

[a] See footnote 8. [b] ΔE is positive when the BDE of X-AH$_3$ is smaller than the BDE of AH$_4$. [c] Twisted 90° about the X-A bond from the equilibrium geometry.

that silyl substituents are substantially better than alkyl substituents at stabilizing silyl-centered radicals, Walsh found that silyl substituents are only marginally more effective than alkyl substituents at stabilizing carbon-centered radicals.[2]

In order to understand the difference between carbon- and silicon-centered radicals in their response to substituents, we have performed ab initio calculations of the energy of the reaction in eq 1. Equation 1 measures the effect of a substituent, X, on

$$X\text{-}AH_2\text{•} + AH_4 \rightarrow X\text{-}AH_3 + AH_3\text{•} \qquad (1)$$

altering the A-H BDE from that in methane (A = C)[1,4] or in silane (A = Si), and it permits cancellation of errors in the absolute A-H BDEs that are computed.

Geometries of the radicals were optimized with the 6-31G* basis set[5] and UHF wave functions.[6] Energies, with electron correlation included at the MP4SDTQ[7] level, were computed at the UHF optimized geometries and are given in Table I, along with the energies derived[8] for the reaction in eq 1. Calculations were performed with the GAUSSIAN 82 package of programs.[9]

The results in Table I show that electropositive substituents with low-lying empty orbitals (Li, BeH, and BH$_2$) are radical stabilizing for both carbon- and silicon-centered radicals, as evidenced by the fact that these substituents, X, cause the BDE for X-AH$_3$ to be less than that for AH$_4$. The calculations with the empty orbital on the BH$_2$ group twisted 90° from conjugation with the singly occupied orbital on AH$_2$ indicate that delocalization of the odd electron into the empty p orbital on boron has a stabilizing effect in both carbon- and silicon-centered radicals. From the energy differences between the two geometries, this type of electron delocalization is found to be responsible for stabilizing H$_2$B-CH$_2$• by 9.7 kcal/mol and H$_2$B-SiH$_2$• by 11.3 kcal/mol.

Despite the fact that π bonds to silicon are usually weaker than π bonds to carbon[10] and that silyl radicals are more pyramidalized

(4) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; pp 347-51.

(5) This is a split-valence basis set with polarization functions on the non-hydrogen atoms. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 212. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(6) UHF optimized 6-31G* geometries and energies are available as Supplementary Material. Ordering information is given on any current masthead page.

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(8) MP4SDTQ/6-31G* energies for molecules with even numbers of electrons were taken from Luke et al. (Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 260).

(9) Binkley, J. S.; Frisch, M. J.; Raghavachari, M.; Fluder, E.; Seeger, R.; Pople, J. A. Carnegie-Mellon University.

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than their carbon-centered counterparts,[11] electron delocalization is calculated to have a slightly greater stabilizing effect in H_2B-SiH_2• than in H_2B-CH_2•. Presumably, the lower electronegativity of silicon compared to carbon is responsible for making delocalization of the odd electron into the empty BH_2 orbital more important in H_2B-SiH_2• than in H_2B-CH_2•.

For substituents that have unshared electron pairs, the greater electronegativity of carbon, compared to silicon, should favor electron donation into the singly occupied orbital on carbon. This effect, coupled with the weaker π bonds formed by silicon and the more highly pyramidalized geometry of silyl radicals, should cause electron donor substituents to be much less stabilizing for silyl-centered radicals than for carbon-centered radicals. This expectation is born out by the results in Table I, which show H_2N, OH, and F substituents all reduce the C–H BDE of X–CH_3 from that in methane. In contrast, all but the least electronegative of these groups, H_2N, actually increase the Si–H BDE of X–SiH_3 to a value above that in SiH_4.[12] The 3.5 kcal/mol greater BDE predicted for F–SiH_3 is slightly more than one third of the 9.8 kcal/mol greater BDE found experimentally for F_3SiH.[2]

Donation of a lone pair of electrons on the substituent is stabilizing for both X–CH_2• and X–SiH_2•, as shown for X = NH_2 by the increase in energy in both radicals on rotation by 90° about the bond to the amino group.[13] That electron pair donation is more important for stabilizing carbon-centered radicals is evidenced by the fact that the energy increase of 8.5 kcal/mol on 90° rotation about the C–N bond in H_2N–CH_2• is considerably larger than the increase of 3.3 kcal/mol on 90° rotation about the N–Si bond in H_2N–SiH_2•.

Since delocalization of a lone pair on the substituent group, X, in X–SiH_2• is apparently stabilizing, albeit by a significantly smaller amount than in X–CH_2•, the calculated increase in the BDE on going from SiH_4 to X–SiH_3 for X = OH and F must have another origin. Inspection of the data in Table I suggests that the BDE in X–SiH_3 generally increases with the electronegativity of X.[12,14] This is revealed more clearly when the very strong electron delocalizing ability of BH_2 is factored out by using the energy for the H_2B–SiH_2• radical with the empty p orbital on boron orthogonal to the singly occupied orbital on silicon.

If, for A = Si, the energetic favorability of the reaction in eq 1 were controlled exclusively by the electronegativity of X, the energy of this reaction would be negative for substituents that are more electronegative than hydrogen. This is, in fact, the case for X = NH_2, when the amino group is twisted 90° about the Si–N bond in order to reduce the stabilizing effect of nitrogen lone pair donation. Since carbon is also slightly more electronegative than hydrogen, it is not surprising that the methyl group in CH_3–SiH_3 too is calculated to cause the Si–H BDE to be larger than that in SiH_4. However, the increase in the BDE is computed to be quite small (0.8 kcal/mol), which is consistent with the experimental fact that alkyl substituents are found to have very little effect on Si–H BDEs.[2,3]

The calculated lowering of the Si–H BDE by a silyl substituent can be largely attributed to the fact that silicon is less electronegative than hydrogen. The computed 2.9 kcal/mol reduction of the Si–H BDE on going from SiH_4 to H_3Si–SiH_3 is slightly less than the 4.0 kcal/mol measured by Walsh and co-workers.[2] Consistent with the experimental results of Griller and co-workers,[3] we calculate the effects of additional silyl substituents to be nearly additive, since the three SiH_3 substituents in $(SiH_3)_3SiH$ are computed to lower the Si–H BDE by 8.2 kcal/mol from that in SiH_4.[15]

In contrast to the case with a silicon-centered radical, both CH_3 and SiH_3 substituents are calculated to stabilize a carbon-centered radical. SiH_3 is predicted to be a slightly more stabilizing substituent than CH_3, in agreement with Walsh's experimental results.[2] However, the computed difference of 1.1 kcal/mol between the stabilizing effects of SiH_3 and CH_3 substituents on a carbon-centered radical is significantly smaller than the calculated difference of 3.7 kcal/mol between the opposite effects of these two substituents on a silicon-centered radical.

Supplementary Material Available: UHF optimized 6-31G* geometries and energies for the radicals listed in Table I with bond lengths in Å, angles in deg, and energies in hartrees (5 pages). Ordering information is given on any current masthead page.

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(15) Since for X = SiH_3 and A = Si the energy calculated for the reaction in eq 1 is essentially the same at both the SCF/UHF and MP4SDTQ levels of theory, the calculations on the stabilizing effect of three SiH_3 substituents were performed at the former level of theory.

Study of Energy Transfer from Upper Triplet States in Solution with Two-Laser Two-Photon Excitation[1]

W. G. McGimpsey and J. C. Scaiano*

Division of Chemistry
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6
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Recent work from our laboratory has shown that upper triplet states, generated by photoexcitation of the first excited triplet, are readily quenched by aromatic substrates, in particular benzene.[2,3] Thus, excitation of triplet benzophenone in benzene in its visible absorption band (λ_{max} 525 nm)[4] results in the repopulation of ground-state benzophenone. Among the various mechanisms which could explain this result (energy transfer, electron transfer, or ring addition), we have favored energy transfer, although no definitive proof supporting this preference was available from our earlier results.[2] This quenching process appears to be general for a wide variety of aromatics and ketones, and while our reported results deal only with benzophenone[2] and 1,2-di-1-naphthylethane[3] in benzene, preliminary work in our laboratory has provided numerous examples showing similar behavior.[5]

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(11) The effect of silyl radical pyramidalization on the π bond strengths of molecules containing doubly bonded silicon has been discussed: Hrovat, D. A.; Sun, H.; Borden, W. T. *Theochem.*, in press. Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5275. Although the SiH_2 group is planar at the optimized geometry of H_2B–SiH_2•, the SiH_2 group is pyramidalized at the 90° twisted geometry. At the latter geometry a planar SiH_2 group is computed to be 5.4 kcal/mol higher in energy. This may be taken as the cost of silyl radical pyramidalization on the electron delocalization energy in H_2B–SiH_2•, since the delocalization energy for a planar silyl radical would be larger by this amount.
(12) Very electronegative substituents, for instance, NH_3^+ and three fluorines, are found to increase C–H BDEs too.[1] A simple explanation of this effect is that an electronegative substituent, X, increases the amount of s character in the A–H bonds of X–AH_3, which results in an increase in the A–H BDE [Bent, H. A. *Chem. Rev.* **1961**, *61*, 275].
(13) When both groups in H_2N–AH_2• are pyramidalized, the energy maximum on rotation about the N–A bond occurs near but not at this geometry.
(14) Substituent electronegativities have been calculated to have the same type of effect on the energies required to dissociate two Si–H bonds to form triplet silylenes: Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270.

(1) Issued as NRCC 28639.
(2) McGimpsey, W. G.; Scaiano, J. C. *Chem. Phys. Lett.* **1987**, *138*, 13.
(3) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511–517.
(4) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data 15* **1986**, 1.
(5) In particular, the compounds referred to in this report all exhibit quenching behavior in benzene, i.e., 2-acetylphenanthrene, 2-acetylnaphthalene, dibenzosuberenone, and *p*-terphenyl. It is now recognized that this quenching process is also *partially* responsible for the observed bleaching of the triplet states of benzil[6] and 1,3-di-1-naphthyl-2-propanone[7] in benzene. Upper state quenching occurs concurrently with the reluctant Type I cleavage on which we reported earlier.[6,7]