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Effects of α- and β-Silicon Atoms on the Free Energies of C–H Homolysis and Heterolysis

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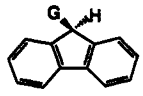
Among the most fascinating of all carbocations are those in which silicon is in the vicinity of the electron-deficient carbon atom.[1] Specifically, the presence of silicon adjacent to (α) or one atom removed from (β) a developing carbocation center has been shown to result in marked changes in the solvolytic reactivities of appropriately substituted substrates. For example, when dissolved in aqueous ethanol, $(H_3C)_3Si(CH_3)_2C{-}Br$ solvolyzed ca. 38 000 times slower than $(H_3C)_3C(CH_3)_2C{-}Br$.[2] Conversely, when dissolved in trifluoroethanol, 2-(trimethylsilyl)cyclohexyl trifluoroacetate solvolyzed ca. 10^9 times faster than cyclohexyl trifluoroacetate.[3] Contained in this communication are the first experimentally-derived thermodynamic data that enable comparisons of the effects of α- and β-$Si(CH_3)_3$ moieties on the free energies of C–H homolysis and C–H heterolysis, for variously substituted fluorenes dissolved in dimethyl sulfoxide (DMSO). Analyses of these data indicate that replacement of a 9-H atom in fluorene with the β-silicon-containing 9-(trimethylsilyl)methyl moiety reduces the 9C–H heterolysis free energy by 16 kcal/mol. This and other comparisons provide a thermodynamic-based experimental foundation for the importance of $Si^+/C{=}C$ hyperconjugation as it pertains to solution-phase carbocation stabilization.

It has been shown that insertion of selected acid–base[4] and redox data into thermochemical cycles[5] (as in eqs 1[6] and 2[7]) results in accurate (±1–2 kcal/mol) determinations of relative and absolute free energies of homolysis[6] [$\Delta G^\circ_{\rm hom}$(R–H)] and

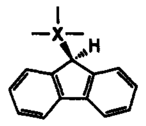
$$\Delta G^\circ_{\rm hom}(\mathrm{R{-}H}) = 1.36\ \mathrm{p}K_a(\mathrm{R{-}H}) + 23.1[E_{\rm NHE}(\mathrm{R^-/R^\bullet})] + 57.2\ \mathrm{kcal/mol} \quad (1)$$

$$\Delta G^\circ_{\rm het}(\mathrm{R{-}H}) = 1.36\ \mathrm{p}K_a(\mathrm{R{-}H}) + 23.1[E_{\rm NHE}[(\mathrm{R^-/R^\bullet}) + (\mathrm{R^\bullet/R^+})]] + 69.9\ \mathrm{kcal/mol} \quad (2)$$

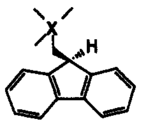
heterolysis[7] [$\Delta G^\circ_{\rm het}$(R–H)] for several classes of reactions.[8] We have therefore endeavored to collect the pK_a(R–H), $E_{\rm NHE}(R^-/R^\bullet)$, and $E_{\rm NHE}(R^\bullet/R^+)$ data that enable determination of the $\Delta G^\circ_{\rm hom}$(R–H) and $\Delta G^\circ_{\rm het}$(R–H) values for fluorenes **1**–**3** (Table 1). This study was undertaken in efforts to examine the effects of α-$Si(CH_3)_3$ (as in **2b**) and β-$Si(CH_3)_3$ (as in **3b**) substituents on the thermodynamic stabilities of solution phase anions, radicals, and cations derived from **1**–**3**. The instability of the 12-π-electron fluorenium cation [$pK_{R^+} = -14.0$[9]] acts to minimize any masking of the stabilizing effects resulting from reduced-demand-associated phenomena.[10]



1a G=H
1b G=—CH₃



2a X=C
2b X=Si



3a X=C
3b X=Si

Consider the acidity data first. The DMSO pK_a's for 9*H*-fluorene (**1a**) and 9-(trimethylsilyl)fluorene (**2b**) (22.6 and 21.7, respectively) as well as 9-methylfluorene (**1b**) and 9-[(trimethylsilyl)methyl]fluorene (**3b**) (22.3 and 21.4, respectively) suggest that the presence of α-$Si(CH_3)_3$ and β-$Si(CH_3)_3$ substituents has minor stabilizing effects on the anionic fluorenide moieties. While these results are consistent with the notion of an enhanced electron-accepting ability for silicon atoms[11] (relative to hydrogen), the magnitude of the differences ($\Delta\ pK_a = 0.9$) demands cautious interpretation. Furthermore, 9-neopentylfluorene (**3a**, $pK_a = 20.3$) is slightly *more* acidic than its β-silicon analogue, 9-[(trimethylsilyl)methyl]fluorene (**3b**, $pK_a = 21.4$).[12a] That the presence of silicon results in an acid-weakening effect is not surprising in light of published aqueous pK_a's for $(CH_3)_3CCH_2CO_2H$ (pK_a = 5.0) and $(CH_3)_3SiCH_2CO_2H$ (pK_a = 5.2).[13]

Inspection of the $\Delta G^\circ_{\rm hom}$(C–H) data in Table 1 reveals that the free energies of homolysis for the 9C–H bonds in 9*H*-fluorene (**1a**), 9-*tert*-butylfluorene (**2a**), and 9-(trimethylsilyl)fluorene (**2b**) are nearly equal (76, 76, and 75 kcal/mol, respectively). Therefore, relative to hydrogen (as in **1a**) or its carbon analogue *tert*-butyl (as in **2a**), the α-Si(CH3)3 substituent (as in **2b**) has a negligible effect on 9C–H bond homolysis. Published gas-phase homolytic (enthalpic) C–H BDEs for $(CH_3)_3CCH_2{-}H$ and $(CH_3)_3SiCH_2{-}H$ (99[14] and 100[15] kcal/mol, respectively) provide support for the general assertion that an α-$Si(CH_3)_3$ substituent provides little stabilization to carbon-centered radicals. Evidently, $C^\bullet/Si{=}C$ hyperconjugation is of little value as it pertains to radical stabilization as measured by $\Delta G^\circ_{\rm hom}$(C–H) values as well as gas-phase BDEs.

$\Delta G^\circ_{\rm hom}$(C–H) values for 9-methylfluorene (**1b**), 9-neopentylfluorene (**3a**), and 9-[(trimethylsilyl)methyl]fluorene (**3b**) are 72, 70, and 69 kcal/mol, respectively. Analyses of these data indicate that, *relative to hydrogen* (as in 9*H*-fluorene, **1a**), a (trimethylsilyl)methyl substituent [as in **3b**; i.e., one containing a β-$Si(CH_3)_3$ moiety] results in a substantial weakening of the 9C–H bond (7 kcal/mol). However, the 7 kcal/mol bond-weakening effect ascribed to the β-$Si(CH_3)_3$ moiety in **3b** is nearly equal to the 6 kcal/mol perturbation provided by the *neo*-pentyl substituent in 9-neopentylfluorene (**3a**). $\Delta G^\circ_{\rm hom}$(R–H) data for **3a** and **3b** therefore suggest that the degree of stabilization afforded the fluorenyl radical derived from **3b** *via* $Si^\bullet/C{=}C$ hyperconjugation is not substantially greater than any stabilization provided to **3a** *via* $C^\bullet/C{=}C$ hyperconjugation.

Further inspection of Table 1 reveals that the $\Delta G^\circ_{\rm het}$(R–H) values for 9*H*-fluorene (**1a**), 9-methylfluorene (**1b**), 9-*tert*-

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Table 1. Dimethyl Sulfoxide Solution Acidity, Redox, and Free Energy Data for 9-Substituted Fluorenes **1–3** and Their Respective Conjugate Ions and Radicals

fluorene substrate[a]	pK_a(C–H)[b]	$E_{NHE}(R^-/R^\bullet)$[b,c] (V)	$E_{NHE}(R^\bullet/R^+)$[c,d] (V)	$\Delta G^\circ_{(hom)}$(R–H)[e] (kcal/mol)	$\Delta G^\circ_{(het)}$(R–H)[f] (kcal/mol)
9*H*-fluorene (**1a**)	22.6	–0.53	0.70 (0.87)	76	105
9-methylfluorene (**1b**)	22.3	–0.69	0.56	72	97
9-*tert*-butylfluorene (**2a**)	24.4	–0.62	0.63 (0.79)	76	103
9-(trimethylsilyl)fluorene (**2b**)	21.7	–0.52	0.66	75	103
9-neopentylfluorene (**3a**)	20.3	–0.65	0.54	70	95
9-[(trimethylsilyl)methyl]fluorene (**3b**)	21.4[g]	–0.75[h]	0.30	69	89

[a] **1a** is commercially available, and **1b**, **2a**,**b** and **3a** were synthesized using published procedures.[8a] 9-[(Trimethylsilyl)methyl]fluorene (**3b**) appears to be a new compound and was prepared by allowing the lithium salt of fluorene to react with (iodomethyl)trimethylsilane (1 equiv). After recrystallization from EtOH, **3b** was obtained in 37% yield (mp 78–79 °C): ^{1}H NMR ($CDCl_3$) δ 7.2–7.8 (m, 8H, aryl protons), 4.2 (t, 1H), 1.5 (d, 2H), 0.5 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 149.0, 140.7, 126.8, 126.7, 124.6, 119.7, 44.1, 19.9, –0.4. Anal. Calcd for **3b** ($C_{17}H_{20}Si$): C, 80.89; H, 7.99. Found: C, 80.79; H, 8.00. [b] Literature values[4,8a] except where noted. [c] Irreversible peak potentials in which $E_{NHE} = E_{ferrocene/ferrocenium} + 0.54$ V.[7] [d] Collected using photomodulated voltammetric (PMV) apparatus similar to that described previously.[17] Values in parentheses were collected using acetonitrile as solvent.[7] [e] Determined using eq 1,[6] estimated uncertainty ±1–2 kcal/mol. [f] Determined using eq 7, estimated uncertainty ±1–2 kcal/mol. [g] Obtained using previously described indicator method.[4] [h] Electrochemical conditions described previously.[18]

butylfluorene (**2a**), 9-(trimethylsilyl)fluorene (**2b**), and 9-neopentylfluorene (**3a**) are 105, 97, 105, 103, and 95 kcal/mol, respectively. The α-$Si(CH_3)_3$ and α-$C(CH_3)_3$ substituents therefore have near-equal effects on the free energies of 9C–H heterolysis. However, the data suggest that the α-CH3 substituent present in 9-methylfluorene (**1b**) provides more stabilization to the fluorenium cation (6 kcal/mol) than does α-$Si(CH_3)_3$. These observations are in agreement with computational- and kinetic-based studies from which it has been deduced that an α-CH3 substituent stabilizes the 2-adamantyl carbocation 6–8 kcal/mol more than an α-$Si(CH_3)_3$ substituent.[16] Hyperconjugation-based arguments (i.e., that $R^+/C{=}C$ provides greater stabilization than $R^+/Si{=}C$ hyperconjugation) are generally invoked when rationalizing these and similar results. On the other hand, it has been asserted[16] that an α-$Si(CH_3)_3$ substituent stabilizes the 2-adamantyl carbocation 12–14 kcal/mol more than hydrogen, results that are in conflict with our observations that the ΔG°_{het}(R–H) values for 9*H*-fluorene (**1a**) and 9-(trimethylsilyl)fluorene (**2b**) are 105 and 103 kcal/mol, respectively. Perhaps steric interactions between hydrogen atoms of the trimethylsilyl substituent and the 1- and 8-hydrogen atoms of the fluorene ring minimize the degree of substantial cation stabilization realized *via* $C^+/Si{=}C$ hyperconjugation.

Finally, the ΔG°_{het}(R–H) value for a β-silylated fluorene, 9-[(trimethylsilyl)methyl]fluorene (**3b**), is also listed in Table 1. Comparisons of the ΔG°_{het}(R–H) values for **3b** (89 kcal/mol) and 9*H*-fluorene (**1a**, 105 kcal/mol) suggest that replacement of a 9-H atom in **1a** with the $CH_2Si(CH_3)_3$ moiety (as in **3b**) weakens the 9C–H bond by 16 kcal/mol. Other appropriate comparisons are between the ΔG°_{het}(R–H) values for **3b**, 9-methylfluorene (**1b**), and 9-neopentylfluorene (**3a**) (89, 97, and 95 kcal/mol, respectively), since the cations derived from **3b**, **1b**, and **3a** are tertiary. Such a comparison reveals that the β-silicon atom present in **3b** results in an additional 6–8 kcal/mol stabilization (when compared to **3a** and **1b**). The *thermodynamic solution phase* ΔG°_{het}(R–H) data for **1–3** are therefore in qualitative agreement with results from kinetic evaluations of solution-phase reactions thought to involve β-silyl carbocations, as well as computational and experimental investigations of the effects of β-silicon atoms on gas phase carbocation stabilities.[16] The data provide confirmation of the importance of $Si^+/C{=}C$ hyperconjugation as it pertains to carbocation stabilization. We are continuing our studies of the effects of silicon and other heteroatoms on the stabilities of organic reactive intermediates.

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