Organometallics 1988, *7*, 2215–2220

Ab Initio Study of 2-Silaallyl Cation and Anion. Some Attributes of Silicon-Containing π-Conjugated Systems

Andrzej Rajca*,[1] and Andrew Streitwieser*

Department of Chemistry, University of California, Berkeley, California 94720

Received April 20, 1988

2-Silaallyl cation and anion, closed-shell $^1A_1$ states, have been examined by using ab initio single determinantal restricted Hartree–Fock wave functions. Integrated projected electron populations (IPP) indicate significant polarization of both σ and π SiC bonds. The anion shows greater charge alternation (Si, +2.6; CH_2, −1.4) than the cation (Si, +2.6; CH_2, −0.4). Such charge alternation dominates allylic resonance conjugation. The cation is more susceptible to breaking the allylic C_{2v} symmetry as indicated by the smaller diagonal force constant for the SiC bond (0.28 au) than for the anion (0.33 au). The cation possesses a low-lying triplet state (UMP3/6-31G**//6-31G*, 1.5 kcal mol^{-1} above the MP3/6-31G**//6-31G* $^1A_1$ singlet after ZPVE correction at the HF/3-21G* level). The rotational barrier for the cation (25.6 kcal mol^{-1}) is larger than the barrier for the anion (15.5 kcal mol^{-1}) and is reflected in the mininum IPPs along the SiC bond axis for the bonding allylic π-MO. The remarkable CSiC angles, 107.0° for the cation and 135.3° for the anion, are explained in terms of 1,3-HOMO interactions and Coulomb repulsion between the terminal methylene groups.

Introduction

The 2-silaallyl system, CH_2SiHCH_2, provides insight into conjugation of silicon–carbon compounds while the essential symmetry of the all-carbon counterpart is preserved. Recently, silicon-containing π-conjugated systems and the silicon–carbon double bond have attracted enhanced attention among experimental and theoretical chemists.[2] Allyl represents the simplest of all conjugated systems and has been the focus of experimental and theoretical chemists. Ellison[3] and Schleyer[4] have disputed the magnitude of the CCC angle in allyl anion, and the results of ab initio calculations have been useful in the interpretation of experiment.[4] A methyl-substituted 2-silaallyl anion has recently been generated by proton abstraction from dimethylsilene; however, no structural data are available.[5]

The perturbation of the allylic resonance with an electropositive element such as silicon, without change in molecular symmetry, may provide valuable insight into the resonance conjugation itself and its relation to the phenomenon of charge alternation.[6] The present work finds further stimulus from the calculations of Feller, Davidson, and Borden[7] and their discussion of resonance in formyloxy and $O(CH_2)_2{}^+$ radicals. Ideas of topological charge stabilization are also relevant to our study.[8]

We report that ab initio calculations show that the allylic resonance is weakened in 2-silaallyl ions compared to the all-carbon allyl ions. 2-Silaallyl cation (**1**) in its $^1A_1$ state is bent (CSiC, 107.0°) more than allyl cation (**3**) (118.1°),[9] but 2-silaallyl anion (**2**) (CSiC, 135.3°) has a greater allylic angle than allyl anion (**4**) (132.2°).[4] For comparison, the CSiC angle in 2-silapropene is 125.4° (3-21G*). 1,3-Orbital interactions, Coulomb repulsions, and d orbitals on silicon may have roles in these variations of geometry.

Calculational Methods

Calculations were carried out for $^1A_1$ states ($b_1^2a_2^0b_1^0$ and $b_1^2a_2^2b_1^0$ π-configurations for the cations and anions, respectively) and $^3B_2$ states ($b_1^1a_2^1b_1^0$ and $b_1^2a_2^1b_1^1$ π-configurations for the cations and anions, respectively) by using single determinant wave functions. RHF/3-21G* (with d functions on all heavy centers) and RHF/6-31G* levels of theory were employed for the $^1A_1$ states and UHF/3-21G* and UHF/6-31G* for the $^3B_2$ states of the cations.[10] The basis sets for the anions (3-21+G* and 6-31+G*) were supplemented with sp-diffuse functions (exponent of 0.0438) at the carbons.[11] Single point calculations for 2-silaallyl cation were done with the 6-31G** basis set which includes p functions on hydrogens (exponent of 1.0).[12] Møller–Plesset (MP) perturbation theory up to third-order with the RHF and UHF reference for the closed- and open-shell states, respectively, was employed to study electron correlation effects.[13] This level of theory should also be sufficient for the C_s symmetric 90° twisted 2-silaallyl ions as it is for the allyl (CH_2CHCH_2) ions.[11b,14] Calculations were run on a VAX 11/750 using GAUSSIAN82[15] and a modified version[16a] of

---

[1] Miller Institute Fellow, 1985–1987. Permanent address: Department of Chemistry, Kansas State University, Manhattan, KS 66506.

[2] (a) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* 1984, *106*, 6863. (b) Schmidt, M. W.; Gordon, M. S.; Dupuis, M. *J. Am. Chem. Soc.* 1985, *107*, 2585. (c) Truong, T.; Gordon, M. S.; Boudjouk, P. *Organometallics* 1984, *3*, 484. (d) Baldridge, K. K.; Gordon, M. S. *J. Organomet. Chem.* 1984, *271*, 369. (e) Schlegel, H. B.; Coleman, B.; Jones, M., Jr. *J. Am. Chem. Soc.* 1978, *100*, 6499.

[3] Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* 1984, *106*, 7734.

[4] Schleyer, P. v. R. *J. Am. Chem. Soc.* 1985, *107*, 4793.

[5] Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J. *Organometallics* 1986, *5*, 2050.

[6] Klein, J. *Tetrahedron* 1983, *39*, 2733.

[7] (a) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* 1984, *106*, 2513. (b) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* 1983, *105*, 3347. (c) Tachibana, A.; Koizumi, M.; Okazaki, I.; Teramae, H.; Yamabe, T. *Theor. Chim. Acta* 1987, *71*, 7.

[8] Gimarc, M. G.; Ott, J. J. *J. Am. Chem. Soc.* 1986, *108*, 4298. Ott, J. J.; Gimarc, M. G. *J. Am. Chem. Soc.* 1986, *108*, 4303 and references therein.

[9] *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Carnegie-Mellon University: Pittsburgh, PA, 1983.

[10] (a) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* 1982, *104*, 2797. (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* 1980, *102*, 939. (c) 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. (d) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* 1972, *56*, 2257. (e) Dill, J. D.; Pople, J. A. *J. Chem. Phys.* 1975, *62*, 2921.

[11] (a) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* 1982, *3*, 363. (b) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1981, *103*, 5609.

[12] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* 1973, *28*, 213.

[13] (a) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* 1976, *S10*, 1. (b) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* 1978, *14*, 91.

[14] Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1981, *103*, 5649 and references therein.

0276-7333/88/2307-2215$01.50/0

Table I. Selected Optimized Geometrical Parameters for 2-Silaallyl Cation (1) and Anion (2) and Allyl Cation (3) and Anion (4) at the HF/6-31G* Level (Cations) and HF/6-31+G* Level (Anions)

	1-^1A_1	1-^3B_2	2-^1A_1	$3\text{-}^1A_1{}^b$	$4\text{-}^1A_1{}^b$
CSi (C_1C_2)[a]	1.774	1.805	1.741	1.373	1.388
C_1C_3	2.849	3.172	3.221	2.355	2.538
CSiC (CCC)	107.0	123.0	135.3	118.1	132.2

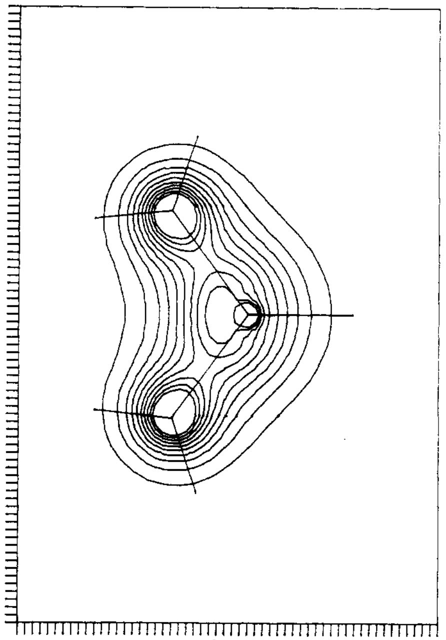
[a] All distances are in angstroms and all angles in degrees. [b] Reference 9 for 3 and ref 4 for 4.

GAUSSIAN80.[16b] Harmonic vibrational frequencies and zero-point energies were obtained from analytical second derivatives.[17]

Projected electron density functions, which are obtained by integration of electron density along the coordinate axis perpendicular to the molecular plane, were calculated by using the program PROJ.[18] The numerical "integrated projected electron populations", IPP, integrations were carried out for regions bounded by minima in the projected density functions.[19] The minimum density demarkations of such projected functions are approximations to the "zero-flux" boundaries of Bader;[20] the projection boundaries are vertical curtains compared to the curved zero-flux surfaces. Accordingly, the derived integrated populations are only approximations to the three-dimensional integrations over Bader "basins"; however, they are expected to be qualitatively correct and are faster to compute. IPP values may differ significantly from the integrated electron populations of Bader's ATOMS (atoms topologically observed in molecules)[21] when the demarkation surfaces involve regions of substantial electron density but the differences are small when only regions of low electron density are involved.[22] Bonds to silicon are in the latter category, and IPP values have been shown to be satisfactory for such bonds.[23] The use of projection functions also facilitates comparison of σ- and π-bonding.

Results and Discussion

The geometry optimizations and subsequent harmonic vibrational frequency calculations at the RHF/3-21G* (cation) and RHF/3-21G* (anion) levels of theory yield C_{2v}-symmetric structures as local minima (all frequencies are real) on the $^1A_1$ potential energy surfaces for both 2-silaallyl cation (1) and anion (2). The anion is, of course, more susceptible to pyramidalization (579.5 (a_2) and 584.0 (b_1) cm^{-1}) than the cation (1131.0 (a_2) and 1044.1 (b_1) cm^{-1}). Subsequent geometry reoptimizations with the larger 6-31G* (cation) and 6-31+G* (anion) basis sets afford similar geometries (Table I). The following discussion pertains to the $^1A_1$ states unless otherwise indicated.


A

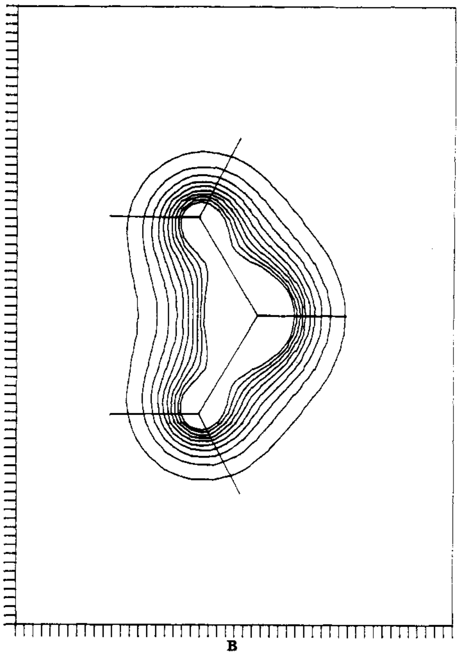

B

Figure 1. Projected electron density of the lowest π-allyl orbital with contour levels from 0.01 to 0.1 by 0.01 e au^{-2}: (A) 2-silaallyl cation at the 3-21G* level; (B) allyl cation at the 6-31G* level.

Allylic Conjugation. Allyl vs 2-Silaallyl and 2-Silaallyl Cation and Anion. The integrated projection populations (IPP, Table III) of 1 and 2 show silicon to have a high positive charge that is much the same in both cation and anion. The attached hydrogen is anionic and also of comparable magnitude in both species. These integrated charges are similar to those in other silicon compounds.[23] The CH_2 groups in *both* silaallyl ions are negatively charged as a result of σ-electron donation by the electropositive silicon, but the terminal groups are much more negatively charged in the anion than in the cation as expected. Note that the Mulliken charges are generally much lower in magnitude; this general effect undoubtedly arises from known deficiencies of the Mulliken method.[22,24] The

---

(15) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon University, 1985.

(16) (a) Kollman, P., unpublished results. (b) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

(17) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1979**, *S13*, 225.

(18) Collins, J. B.; Streitwieser, A., Jr.; McKelvey, J. M. *Comput. Chem.* **1979**, *3*, 79.

(19) McDowell, R. S.; Grier, D. L.; Streitwieser, A., Jr. *Comput. Chem.* **1985**, *9*, 165.

(20) Bader, R. F. W. *Acc. Chem. Res.* **1975**, *8*, 34; **1985**, *18*, 9. Bader, R. F. W.; MacDougall, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 6788. Biegler-Koenig, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317.

(21) Bader, R. F. W., personal communication.

(22) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.*, submitted for publication.

(23) Gronert, S.; Glaser, R.; Streitwieser, A. *J. Am. Chem. Soc.*, submitted for publication.

(24) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; Sections. 2.8, 6.6.2.

present IPP values incorporate known effects of local atomic polarizations.[22,25]

Inspection of the integrated projected electron populations (IPP) for the lowest π-allyl orbital (MO 15) of the cation and anion shows a significant depletion also of the π-electron density at silicon (Figure 1). Moreover, the minimum in the projected electron density function along the allylic bond for this MO 15 is considerably less for the 2-silaallyl system than the all-carbon allyl cation (**3**) and anion (**4**) (Table III). Consequently, silicon–carbon π-overlap is expected to be weaker than the analogous carbon–carbon π-overlap. Indeed, the twisting by 90° of one methylene group in the anion **2** costs only 15.5 kcal mol^{-1} (RHF/3-21+G*)[26]—appreciably less than for allyl anion (22.2 kcal mol^{-1}, MP2/4-31+G//4-31+G).[11b] This behavior is analogous to the relative barriers for rotation of 37 kcal mol^{-1} in silaethylene and 65 kcal mol^{-1} in ethylene.[2b] The proton affinity of anion **2** (382.2 kcal mol^{-1}, RHF/3-21+G*) is less than for the all-carbon analogue **4** (405.5 kcal mol^{-1}, RHF/4-31+G, and 391 kcal mol^{-1}, MP2/4-31+G//4-31+G with 8 kcal mol^{-1} correction for the zero-point vibrational energy).[11b] This result fits a recent experimental finding that dimethylsilene is more acidic than isobutene.[5]

Comparison of the minimum in the projected electron density function along the SiC bond axis ($P_{\min}$) for the bonding allylic MO of the cation (**1**, $P_{\min} = 0.0741$ e au^{-2}) and the anion (**2**, $P_{\min} = 0.0623$ e au^{-2}) indicates stronger Si–C π-overlap for **1**, despite the fact that the SiC bond is longer for **1** than for **2** (Tables I and III). But the larger $P_{\min}$ for the cation has its origin, at least partially, in the additional polarization of the π-electron density located around the silicon into the CSiC triangle (after projection onto the CSiC plane, Figure 1). Nevertheless, the twisting by 90° of one methylene group in **1** raises the energy by 25.6 kcal mol^{-1} after geometry optimization within the C_s symmetry and planar CH$_2$ constraints (RHF/3-21G*). This is more than the 15.5 kcal mol^{-1} for the anion. Therefore, a qualitative link seems to exist between the $P_{\min}$ and the rotational barrier, at least at this level of theory. Furthermore, the harmonic vibrational frequencies for disrotatory twistings of the CH$_2$ groups are 666.7 (a$_2$) cm^{-1} for **1** and 346.7 (a$_2$) cm^{-1} for **2**, showing a qualitative correlation with the rotational barriers and $P_{\min}$.[27]

Feller, Davidson, and Borden's[7] approach to elucidate the importance of allylic resonance using the second-order Jahn–Teller (JT) effect as a criterion actually predicts **2** to be destined for resonance stabilization rather than **1**. Their approach makes use of the relative energy of the "nonbonding" a$_2$ π-MO compared to the bonding and antibonding b$_1$ allyl π-MOs. The replacement of the central carbon with the less electronegative silicon in the allyl system destabilizes both b$_1$ orbitals with respect to the nonbonding a$_2$ allylic orbital compared to the all-carbon system. Therefore, the excited b$_1{}^1$a$_2{}^1$b$_1{}^0$ and b$_1{}^2$a$_2{}^1$b$_1{}^1$ π-configurations (both b$_2$ symmetric) for **1** and **2**, respectively, should be separated from the lowest π-configuration by a relatively small and large, respectively, energy gap. With the assumption of similar vibronic coupling constants for these particular transitions, the second-order Jahn–Teller effect implies a smaller force constant corresponding to the CSiC antisymmetric stretch (b$_2$ = b$_1$ × a$_2$) for **1** compared to **2**—as is, in fact, indicated by the corresponding harmonic vibrational frequencies (799.3 (b$_2$) cm^{-1} for **1** and 1073.6 (b$_2$) cm^{-1} for **2**) and diagonal force constants for the SiC bonds (0.2809 au for **1** and 0.3347 au for **2**).[28] But the small force constant in **1** may be just a classical Coulomb (point charge) effect—**1** has much less charge alternation (Si, +2.6; CH$_2$, −0.4) than **2** (Si, +2.6; CH$_2$, −1.4) according to the total IPPs (Table III). The thought that this could be the case is fostered by the SiC force constant for the triplet state **1**-^{3}B$_2$ (vide infra) that is 0.283 au, *larger* than for the singlet. The very same Coulomb interactions could be responsible for the somewhat longer SiC bond in **1** compared to **2** (Table I).

An alternative explanation for the weakness of allylic resonance in the cation **1** compared to the anion **2** could be based on the rule of topological charge stabilization.[8] The IPP values for the central CH group (Table III) for allyl cation (**3**) and allyl anion (**4**) show that this group is more negative in the cation **3** than in the anion **4**. This phenomenon is also shown in the Mulliken populations for C-2. This result undoubtedly stems primarily from polarization effects. Nevertheless, on the basis of this charge distribution replacement of C-2 with the more electropositive silicon should destabilize the cation **1** relative to the anion **2**. Such polarization effects are even more pronounced in Y-conjugated π-systems (2π- and 6π-electron analogues of trimethylenemethane), further suggesting that π-overlap is not an important factor in resonance stabilization in small molecules.[29]

Triplet States. For the cation **1**, the triplet state (^{3}B$_2$), which is well described by an UHF single configuration (the π-part is b$_1{}^1$a$_2{}^1$b$_1{}^0$, $S(S + 1) = 2.014$) is 21.8 kcal mol^{-1} below the RHF singlet (3-21G*, **1**-^{1}A$_1$ geometry). At the UHF/6-31G* level of theory this difference is also 21.8 kcal mol^{-1} and upon geometry optimization with the C_{2v} symmetry constraint the triplet ($S(S + 1) = 2.014$) drops to 27.4 kcal mol^{-1} below the singlet. The SiC bond lengthens to 1.805 Å, and the CSiC angle opens to 123.0° (Table I). All harmonic vibrational frequencies are real, indicating a local minimum on the potential energy surface for the **1**-^{3}B$_2$ state (3-21G*). Single-point calculations with the 6-31G** basis set for the ^{1}A$_1$ and ^{3}B$_2$ states give the singlet–triplet gaps at the HF, MP2, and MP3 levels as −27.25, 7.05, and 2.66 kcal mol^{-1}, respectively (Table II). The zero-point vibrational energies (RHF/3-21G*) for the singlet and the triplet are 38.67 and 37.37 kcal mol^{-1}, respectively and, at this level of theory, are expected to be too large by about 10%.[30] Thus, our best estimate is that

---

(25) Bader, R. F. W.; Larouche, A.; Gatti, C.; Carroll, M. T.; MacDougall, P. J.; Wiberg, K. B. *J. Chem. Phys.* **1987**, *87*, 1142. Slee, T.; Larouche, A.; Bader, R. F. W. *J. Phys. Chem.*, submitted for publication.

(26) The twisted anion was optimized within the constraints of C_s symmetry and planar CH$_2$ groups. The relaxation of the latter and inclusion electron correlation effects should lower the estimated barrier height for rotation.

(27) On the relation between the curvature (and the third derivatives) for some normal coordinates at a minimum in the potential energy surface with the barriers for bond breaking, see: Bader, R. F. W. *Can. J. Chem.* **1962**, *40*, 1164; *Mol. Phys.* **1960**, *3*, 137; Salem, L. *Chem. Phys. Lett.* **1969**, *3*, 99.

(28) (a) The force constant consists of two terms: $k = k^f + k^r$. The k^f term, sometimes called the classical force constant, corresponds to nuclear motion within a fixed electronic density. The other term, k^r, which describes relaxation of the electronic density upon displacement of nuclei, is relevant to the second-order JT. The force constants, k, which we calculate, are qualitatively related to k^r for **1** and **2** assuming that the k^f's for **1** and **2** are similar. This assumption is justified by the fact that we compare modes involving almost the same set of internal valency coordinates; the similar geometries of **1** and **2** lead to similar contributions of nuclear repulsion to k^f. Moreover, we do not expect that the somewhat different electronic distributions for **1** and **2** could cause such disparate values for k^f's as calculated for k's. On the other hand, k^r for **1** vs **2** should be very different because of the low-lying excited state for **1**; transition densities $\pi \rightarrow \pi^*$ for **1** and **2** are expected to be similar. (b) See ref 7c.

(29) Rajca, A.; Lee, K. H. *J. Am. Chem. Soc.*, to be submitted for publication.

Table II. Total (au) and Relative Energies (kcal mol^{-1}) for 2-Silaallyl Ions (RHF for $^1A_1$ States and UHF for the $^3B_2$ State)

	1		1-perp[a]
	$^1A_1$	$^3B_2$	$^1A'$
3-21G*	−365.376762 (0.0)	−365.420272 (−27.3)	−365.335887
6-31G*	−367.173908 (0.0)	−367.217510 (−27.4)	
6-31G**[b]	−367.183177 (0.0)	−367.226610 (−27.3)	
MP2/6-31G**[b]	−367.537713 (0.0)	−367.526480 (+7.1)	
MP3/6-31G**[b]	−367.569131 (0.0)	−367.564885 (+2.7)	
MP3/6-31G**[b,c]	(0.0)	(+1.5)	
	2		**2-perp**[a]
	$^1A_1$	$^3B_2$[d]	$^1A'$
3-21+G*	−365.685015 (0.0)	−365.570802 (+71.7)	−365.660261
6-31+G*	−367.475278		

[a] C_s symmetric structures with one planar methylene group twisted by 90°. [b] 6-31G* optimized geometry. [c] Corrected with zero-point vibrational energies (ZPVE) calculated at the HF/3-21G* level and scaled by 0.9.[30] Uncorrected ZPVEs (kcal mol^{-1}) are 1-$^1A_1$, 38.67; 1-$^3B_2$, 37.37; 2-$^1A_1$, 37.01. [d] At the geometry of the $^1A_1$ state; for the cation 1 the $^3B_2$ state calculated at the geometry of the $^1A_1$ state is still 21.8 kcal mol^{-1} below the $^1A_1$ state (HF/3-21G*).

the triplet is only 1.5 kcal mol^{-1} above the singlet (Table II). This raises a possibility of nearly degenerate $^1A_1$ and $^3B_2$ states. Note that both π-electrons are uncoupled in the $^3B_2$ state; there is little π-allylic bonding, which underscores the weakness of allylic resonance in 1. The level of calculation employed here should be reliable as to the conclusion that the singlet and the triplet states are close in energy. We note that in carbene, which is biased toward the triplet even more than our cation, a similar level of theory (MP3) overestimates the stability of the triplet by ca. 5 kcal mol^{-1} compared to the experimental value and more adequate CI calculations with a two-configuration reference for the singlet and a one-configuration reference for the triplet.[31] Thus, presumably in 2-silaallyl cation the $^3B_2$ state is somewhat more than 1.5 kcal mol^{-1} above $^1A_1$ state.

For the anion 2, the triplet state ($^3B_2$, UHF/3-21+G*) that arises from promotion of one electron from the nonbonding allylic MO (a_2) to the antibonding allylic MO (b_1) is 71.7 kcal mol^{-1} above the singlet of 2 at the geometry of the singlet.

CSiC Angles. Despite the fact that the C_1C_3 distances for 1 and 2 are longer than in the corresponding all-carbon compounds (SiC bonds are longer than CC bonds), the significant redistribution of the π-electron density toward the terminal carbons may lead to a stronger 1,3-orbital interaction in the 2-silaallyls. Such an interaction for the HOMO of the cation 1 would result in homoaromatic stabilization and a decrease of the CSiC angle in a manner similar to the cation 3.[4,32] An antihomoaromatic interaction for the antisymmetric HOMO of the anion 2 should cause an increase of the CSiC angle—as in allyl anion.[2,4] In fact, the Mulliken overlap population between the p_y ($p\pi$) basis functions at the terminal carbons are nearly identical and positive for cations 1 and 3. The same holds for the anions 2 and 4 except for the negative sign. This result suggests that the 1,3-HOMO interactions in the 2-silaallyl systems are similar to their all-carbon counterparts.

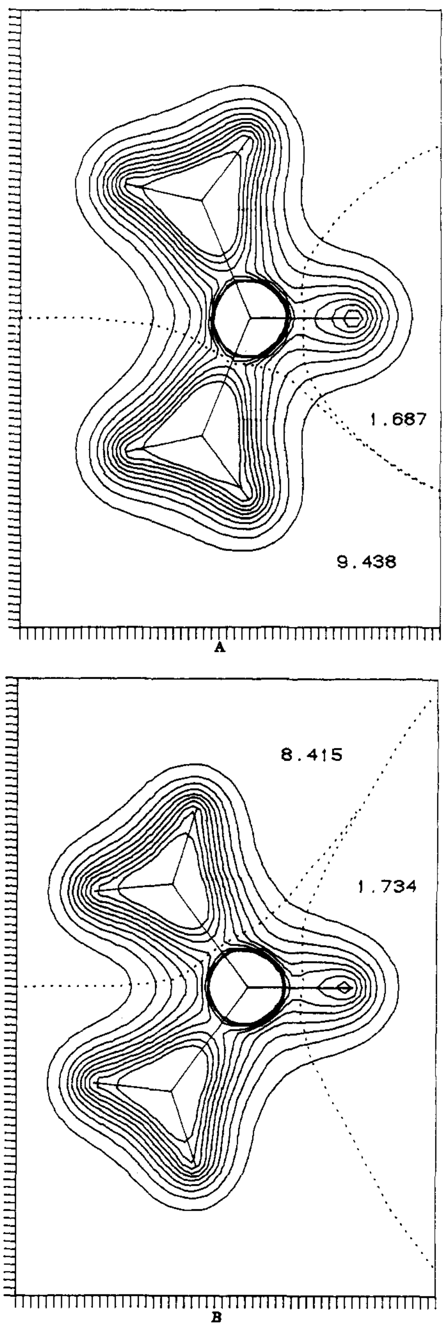


Figure 2. Projected total electron density with contour levels from 0.02 to 0.2 by 0.02 e au^{-2}. The dotted lines indicated lines of demarkation for integration of electron density about H-2 and CH_2: (A) 2-silaallyl anion at the 3-21+G* level; (B) 2-silaallyl cation at the 3-21G* level.

In order to explain the extreme values for the allylic angles in 2-silaallyls, we consider additionally the Coulomb repulsions between the methylene groups and the influence of d orbitals on silicon. The total IPPs as well as the Mulliken populations indicate a highly polarized σ-framework with positively charged silicon in both 1 and 2 (Figure 2). More importantly, the overall charge associated with the methylene groups is smaller in 2-silaallyl cation (1) than in its carbon counterpart 3. The opposite

---

(30) (a) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum. Chem.* **1981**, *S15*, 269. (b) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 4. (c) Reference 10a.

(31) McKellar A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251 and references therein.

(32) (a) Boerth, D. W.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 750. (b) See ref 7b. (c) Cremaschi, P.; Morosi, G.; Simonetta, M. *J. Mol. Struct.* **1982**, *85*, 397.

Table III. Net Charges and Minimum Projected Electron Densities

	1		2		3		4	
	P^a	M^b	P	M	P	M	P	M
Si (C-2)	+2.572	+0.594	+2.562	+0.884		−0.226		+0.249
H-2	−0.735	+0.016	−0.687	−0.210		+0.311		+0.127
C-1		−0.406		−1.157		+0.162		−0.953
CH_2	−0.415	+0.195	−1.438	−0.837	+0.584	+0.457	−0.451	−0.688
$P_{min}{}^c$	0.0741		0.0623		0.112		0.101	

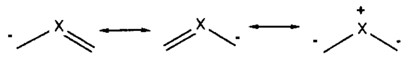
[a] Total net charge from IPP: 3-21G*, 3-21+G*, 6-31G*, and 6-31+G* for 1, 2, 3, and 4, respectively. [b] Total net charge from Mulliken populations; 6-31G* for cations and 6-31+G* for anions. [c] Minimum of the projected electron density (e au^{-2}) along the allylic bond for the lowest π-allyl MO.

is true for the anions (Table III). Hence, the variations of Coulomb repulsion should add to the extreme values for the CSiC angles.

d Orbitals on silicon are not populated enough to induce large variations of the CSiC angle. Nevertheless, their contributions to the HOMO's in 1 and 2 do change the CSiC angle in the observed directions; that is, the differences of IPPs obtained with and without d orbitals on silicon in the HOMOs show the following: for 1, bonding character on the endo side and antibonding on the exo side (d_{yz}); for 2, bonding character on the exo side (d_{xy}) as illustrated by Figure 3. These contributions, however, have only a minor effect on the geometry; e.g., geometry optimization for the cation 1 gives a CSiC angle of 108.2° using a basis set lacking d orbitals (3-21G).

Conclusions

Allylic conjugation normally implies the important contribution of resonance structures such as **5a** and **5b** for a general allylic anion. The charge alternation structure, such as **5c**, involves Coulombic stabilization rather than π-overlap, is normally not discussed but does play an important role even in all-carbon allylic systems. In the 2-silaallyl system charge alternation dominates normal allylic resonance. This conclusion is in line with recent discussions of allylic resonance in nitrous acid[33] and carboxylate ion[34] and in cases of Y conjugation.[29]



5a 5b 5c

1 is more prone to breaking of allylic resonance conjugation than 2 as indicated by the existence of a low-lying triplet state and small force constant for the SiC bond in 1. Double occupancy of the nonbonding allylic MO, which is a LUMO in 1, has two major consequences for 2: (i) no low-energy excited state is available; (ii) the charge alternation, which is favorable from the viewpoint of electronegativity differences, dramatically increases. Hence, the closed-shell $^1A_1$ "allyl-like" state is definitely the ground state with a strong preference for the C_{2v} symmetry. The result (ii) leads, however, to a decrease of π-overlap and, therefore, to the relatively small rotational barrier.

The strong polarization of silicon–carbon bonds, although weakening π-overlap, leads to significant 1,3-carbon–carbon interactions despite their large spatial separation. These interactions together with Coulomb repulsions and, to a lesser degree, the effects of d orbitals on silicon are characteristics of conjugation in the closed-shell 2-silaallyl system and, most probably, in other silicon-containing π-systems as well.

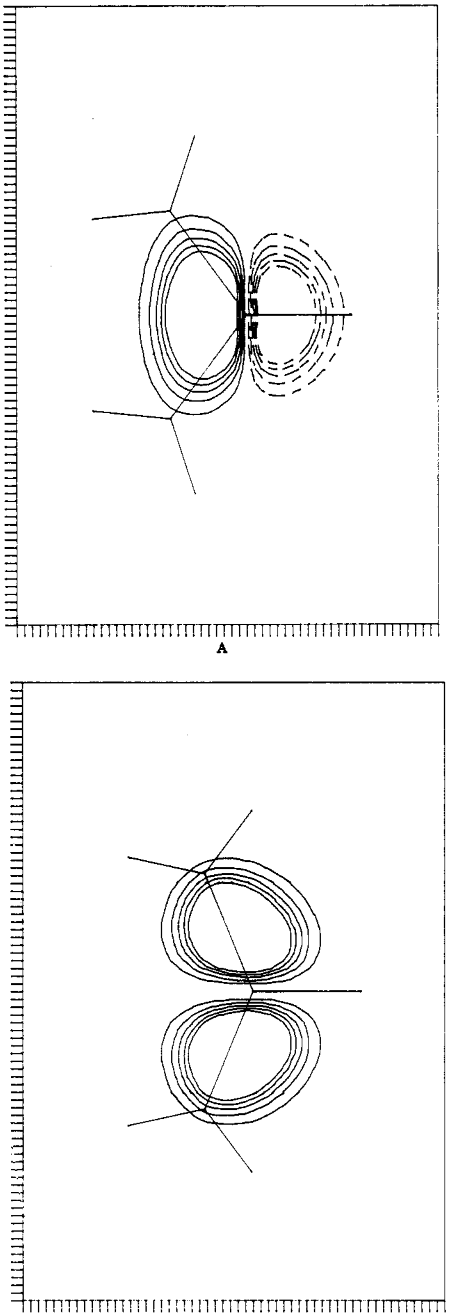


Figure 3. Projected electron density of the difference between the HOMO with and without d orbitals on silicon with contour levels from −0.005 to +0.005 by 0.001 e au^{-2}: (A) 2-silaallyl cation at the 3-21G* level; (B) 2-silaallyl anion at the 3-21+G* level.

Finally, topological charge destabilization may provide

---

(33) Thomas, T. D. *J. Am. Chem. Soc.*, in press. Wiberg, K. B. *J. Am. Chem. Soc.*, in press.

(34) Siggel, M. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 4360. Siggel, M. R.; Thomas, T. D.; Streitwieser, A., Jr. *J. Mol. Struct. Theochem.* **1988**, *165*, 309; *J. Am. Chem. Soc.*, in press.

an entry to ground-state triplet molecules.

Acknowledgment. This work was supported in part by AFOSR Grant No. 82-0114 and grants by the National Science Foundation.

Registry No. 1, 116076-59-6; 2, 116076-60-9.

Supplementary Material Available: Tables of bond lengths and bond angles (4 pages). Ordering information is given on any current masthead page.

Substituent Effects upon the Kinetics of Hydrogen Transfer from Triorganotin Hydrides to the 5-Hexen-1-yl Radical

Philip W. Pike, Vernon Gilliatt, Michael Ridenour, and James W. Hershberger*

Chemistry Department, Hughes Laboratories, Miami University, Oxford, Ohio 45056

Received April 21, 1988

Steric and electronic substituent effects were probed for the hydrogen atom transfer reaction of a series of triorganotin hydrides with the 5-hexen-1-yl radical. Rate data were obtained for tributyltin hydride (**1**), triisopropyltin hydride (**2**), tri-*tert*-butyltin hydride (**3**), trineopentyltin hydride (**4**), trimesityltin hydride (**5**), and dibutylethoxytin hydride (**6**). Arrhenius parameters are reported for the reactions of **1–4** and **6**; the reaction of **5** was studied only at 50 °C. For compounds **1–4**, the activation energy, E_a, decreased monotonically with increasing alkyl size from 3.9 ± 0.1 to 3.1 ± 0.1 kcal mol^{-1}. The preexponential factor, expressed as log A, decreased monotonically from 9.4 ± 0.1 to 8.8 ± 0.1. The effect of the ethoxy substituent, **6**, relative to an *n*-butyl substituent, **1**, upon the activation energy was negligible (4.2 ± 0.2 versus 3.9 ± 0.1 kcal mol^{-1}, respectively), but the preexponential factor, log A, increased from 9.4 ± 0.1 to 10.0 ± 0.1. The activation data for **1–4** are interpreted in terms of the steric requirements of the alkyl groups appended to tin. The lack of a significant substituent effect upon E_a by the ethoxy group is reflective of a nonpolarized transition state for the hydrogen atom transfer reaction.

Introduction

Since Ingold and co-workers[1] reported the Arrhenius parameters for the cyclization of the 5-hexen-1-yl radical, the rearrangement has been useful as a "clock" for reactions involving free radical intermediates.[2] The reduction reaction of 6-halo-1-hexene is particularly well suited for the kinetic study of the hydrogen atom transfer from a metal hydride to a carbon-centered free radical. This has been demonstrated by Ingold and co-workers for the determination of the rate of hydrogen abstraction from tributylgermanium hydride.[3] Reactions 1–4 pertain to a generalized application of the method under free radical chain conditions. When the initial concentration of the metal hydride greatly exceeds that of the 5-hexen-1-yl substrate, the value of K_H is given by eq 5.[3]

$$M^{\bullet} + CH_2{=}CHCH_2CH_2CH_2CH_2X \xrightarrow{k_x} MX + CH_2{=}CHCH_2CH_2CH_2CH_2^{\bullet} \quad (1)$$

$$CH_2{=}CHCH_2CH_2CH_2CH_2^{\bullet} + M{-}H \xrightarrow{k_H} CH_2{=}CHCH_2CH_2CH_3 + M^{\bullet} \quad (2)$$

$$CH_2{=}CHCH_2CH_2CH_2CH_2^{\bullet} \xrightarrow{k_c} c\text{-}C_5H_9CH_2^{\bullet} \quad (3)$$

$$c\text{-}C_5H_9CH_2 + M{-}H \xrightarrow{k_H'} c\text{-}C_5H_9CH_3 + M^{\bullet} \quad (4)$$

$$k_H = \frac{k_c}{[M{-}H]_0}\,\frac{[\text{1-hexene}]}{[\text{methylcyclopentane}]} \quad (5)$$

Table I. Reaction of *n*-Undecyl Iodide with Triorganotin Hydrides[a]

hydride	recovered n-$C_{11}H_{23}I$,[b] %	yield n-$C_{11}H_{24}$,[b] %
1	4	98
2	<1	97
3	<1	98
4	2	95
5	11	91
6	<1	98

[a] Triorganotin hydride (0.100 mmol), 1-iodoundecane (0.100 mmol) and AIBN (0.01 mmol) in 5 mL of benzene, refluxed 8 h under a nitrogen atmosphere. [b] Determined by GLC with *n*-dodecane as an added integration standard. Precision is ca. ±3%.

We have evaluated the kinetic parameters for the abstraction of hydrogen atom by 5-hexen-1-yl by triorganotin hydrides **1–6**. The kinetic parameters for **1** have been

$(CH_3CH_2CH_2CH_2)_3SnH$

1

$[(CH_3)_2CH]_3SnH$

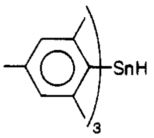
2

$[(CH_3)_3C]_3SnH$

3

$[(CH_3)_3CCH_2]_3SnH$

4



5

$(CH_3CH_2CH_2CH_2)_2(CH_3CH_2O)SnH$

6

previously determined by Ingold.[1a,4] Compounds **2–6** have not been previously studied in this regard. Compounds **1–4** and, arguably, **5**, differ primarily in the steric requirements of the organic ligands appended to tin. Compound **6** bears an alkoxy ligand, which exerts a significantly different electronic effect than do alkyl ligands.

---

[1] (a) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981,** *103,* 7739. (b) Clarkson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968,** *90,* 7047. (c) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974,** *96,* 6355. (d) Schmid, P.; Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* **1979,** *11,* 333.

[2] (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980,** *13,* 317. (b) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo P., Ed.; Academic: New York, 1980; Vol. 1, Chapter 4.

[3] Lusztyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1983,** *105,* 3578.

[4] The actual rate measurement was for the reaction of ethyl radical with tri-*n*-butyltin hydride. This was taken by the authors of ref 1a as equivalent to rate of 5-hexen-1-yl with the hydride. This information, in turn, was used to calcualte the activation parameters for the 5-hexen-1-yl cyclization.

0276-7333/88/2307-2220$01.50/0