Conclusion

The most important conclusion to be drawn from this work is that with the observation of a low-lying antibonding σ^* orbital it is possible to understand the silyl, germyl, and stannyl substituent effects upon π systems without appealing to a model which involves electron delocalization onto the metal d orbitals. This is consistent with a number of theoretical studies which find that the inclusion of d orbitals in the description of π systems with substituents containing group 4A atoms does not improve the agreement between the computations and PES and other experimental observations.[16,20,22] The trends in the energies of unfilled π^* orbitals of substituted benzenes as inferred from the measurement of electron attachment energies can be explained on the basis of hyperconjugative interactions between the π^* orbitals and a low-lying σ^* orbital. This conclusion is at odds with ESR studies of the *p*-disubstituted benzenes; however, the calculations performed to explain the ESR results explicitly exclude hyperconjugative interactions by treating the substituent simply as a heteroatom.[4]

Acknowledgment. We wish to thank the National Science Foundation (Grant No. CHE-81-21125) for support of this work, and Dr. W. Kaim of the University of Frankfurt for the aforementioned compounds.

Registry No. 1, 71-43-2; **2**, 1012-72-2; **3**, 13183-70-5; **4**, 21364-16-9; **5**, 1012-73-3; **6**, 463-82-1; **7**, 75-76-3; **8**, 865-52-1; **9**, 594-27-4.

---

[22] Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998.

Negative Ions: Effect of α- vs. β-Silyl Substitution on the Negative Ion States of π Systems

Judith C. Giordan*

Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20742.

Received September 29, 1982

Abstract: To elucidate the effects of α- vs. β-silyl substituents on the π-electronic properties of unsaturated hydrocarbons, the gas-phase electron affinities of tetramethylsilane (TMS) (**1**), 3,3-dimethyl-1-butene (**4**), vinyltrimethylsilane (**5**), propyne (**7**), 3,3-dimethyl-1-butyne (**8**), (trimethylsilyl)acetylene (**9**), 1-butene (**10**), 4,4-dimethyl-1-pentene (**11**), allyltrimethylsilane (**12**), and silane (**13**) were determined by electron transmission spectroscopy. The trends in the energies obtained for the silylated compounds are proposed to arise from hyperconjugative interactions between low-lying, silicon-substitutent-based unoccupied molecular orbitals and occupied π-type orbitals.

The dual donor–acceptor effect of silyl substitutents on various properties of π systems has long been an intriguing topic. Ionization energies, as determined by photoelectron and mass spectroscopies,[1-3] ESR spectra,[4] characteristic vibrational frequencies,[5] NMR signals,[6] and theoretical molecular orbital energies[7] have been determined over the years for various series of unsaturated alkyl- and silyl-substitued compounds and the data interpreted in terms of the difference in electronegativity of carbon vs. silicon and π-electron back donation from carbon to low-lying unoccupied orbitals on silicon. In particular, the trends in the energies of the occupied orbitals of these systems, as obtained from ionization potential data using Koopmans' theorem,[8] have been instrumental in elucidating the silization effects. However, a thorough description of the electronic properties also requires information on the energies of the low-lying, unoccupied orbitals. This can be obtained from electron transmission spectroscopy (ETS).[9,10] The conjugate experiment to photoelectron spectroscopy (PES), ETS measures the energy of a negative ion state resulting from temporary capture of an electron into an unoccupied orbital while PES measures the energy required to remove an electron from an occupied orbital. Although the technique of ETS has been used to study atoms and di- and triatomics[10,11] as well as properties of π^* orbitals in unsaturated hydrocarbons,[9,12a] it has only recently been applied to systems containing transition metals[13] and selected silicon compounds.[14] We report here the application of this technique to an investigation of the effect of α- vs. β-silyl substitution on the energies of the unoccupied orbitals of unsaturated hydrocarbons.

Experimental Section

Electron transmission spectroscopy is a technique for measuring the energy of a temporary negative ion formed by electron capture into an unoccupied orbital of a molecule. The experiment involves the measurement of the transparency of a gas to an electron beam as a function

---

[*] Polaroid Corporation, Waltham, MA 02254.

[1] (a) Mollère, P.; Bock, H.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1972**, *46*, 89, and references therein. (b) Bieri, G.; Brogli, F.; Heilbronner, E.; Kloster-Jensen, E. *J. Elec. Spec. Rel. Phen.* **1972/73**, *1*, 67. (c) Bock, H; Seidl, H. *J. Chem. Soc. B* **1968**, 1158. (d) Ensslin, W.; Bock, H.; Becker, G. *J. Am. Chem. Soc.*, **1974**, *96*, 2757.

[2] Kaim, W.; Tesmann, H.; Bock, H. *Chem. Ber.* **1980**, 3221, and references therein.

[3] Weidner, U.; Schweig, A. *J. Organomet. Chem.* **1972**, *39*, 261, and references therein.

[4] (a) Sipe, J. S., Jr.; West R. *J. Organomet. Chem.* **1974**, *70*, 353, 367. (b) Evans, G. E.; Jerome, B.; Rees, N. H. *J. Chem. Soc. Perkins Trans. 2* **1973**, *2*, 2091. (c) Allred, A. L.; Bush, W. *J. Am. Chem. Soc.* **1968**, *90*, 3352. (d) Allred, A. L.; Curtis, M. D. *Ibid.* **1965**, *87*, 2554. (e) Bedford, J. A.; Bolton, J. R.; Carrington, A.; Prince, R. H. *Trans. Faraday Soc.* **1962**, *59*, 53.

[5] West, R.; Kraihanzel, C. S. *Inorg. Chem.* **1962**, *1*, 967.

[6] (a) Kraihanzel, C. S.; Losee, M. L. *J. Organomet. Chem.* **1967**, *10*, 427. (b) Simonnin, M. P. *Bull. Soc. Chim. Fr.* **1966**, 1774.

[7] (a) Toman, J. J.; Frost, A. A.; Toplol, S. *Theor. Chim. Acta* **1981**, *58*, 285. (b) Maksic, Z. B.; Rupnik, K.; Mileusnic, N. *J. Organomet. Chem.* **1981**, *219*, 21. (c) Horn, M.; Morrell, J. N. *Ibid.* **1974**, *70*, 51. (d) Bernardi, F.; Guerra, M.; Pedulli, G. F.; *Tetrahedron*, **1978**, *34*, 2141. (e) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998.

[8] Koopmans, T. *Physica*, **1934**, *1*, 104.

[9] Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 344.

[10] Schulz, G. J. *Rev. Mod. Phys.* **1973**, *45*, 379, 423.

[11] Sanche, L.; Schulz, G. J. *J. Phys. Chem.* **1973**, *58*, 479.

[12] (a) Giordan, J. C.; McMillan, M. R.; Moore, J. H.; Staley, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 4870. (b) Staley, S. W.; Giordan, J. C.; Moore, J. H. *Ibid.* **1981**, *103*, 3638. (c) Staley, S. W.; Bjorke, M. D.; Giordan, J. C.; McMillan, M. R.; Moore, J. H. *Ibid.* **1981**, *103*, 7057.

[13] Giordan, J. C.; Moore, J. H.; Tossell, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 6632. Giordan, J. C.; Moore, J. H.; Tossell, J. A.; Weber, J. *Ibid.* **1983**, *105*, 3431. Modelli, A.; Foffani, A.; Guerra, M.; Jones, D.; DiStefano, G. *Chem. Phys. Lett.* **1983**, *99*, 58.

[14] Modelli, A.; Jones,·D.; DiStefano, G. *Chem. Phys. Lett.*, **1982**, *86*(4), 434.

0002-7863/83/1505-6544$01.50/0

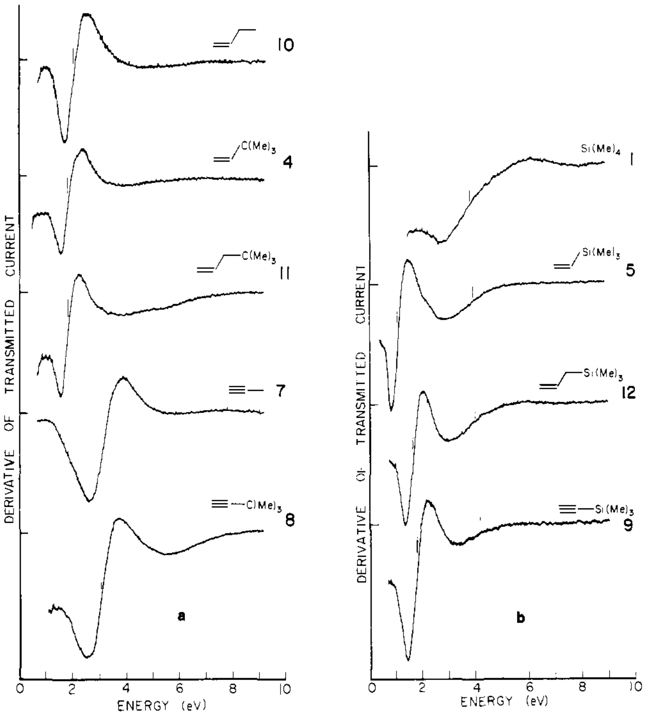

Figure 1. (a) Derivative electron transmission spectra of methyl- and *tert*-butyl-subsituted unsaturated compunds. Attachment energies are indicated by a tick. Each spectrum was calibrated against that of nitrogen (see ref 12a). (b) Derivative electron transmission spectra of trimethylsilyl-substituted unsaturated compounds. A tick indicates the attachment energies. Each spectrum was calibrated against that of nitrogen (see ref 12a).

of energy. The transparency depends in an inverse fashion upon the electron-scattering cross section. Temporary negative ion formation occurs with large cross section only over a narrow energy range. Since the negative ion promptly decays by giving up the trapped electron, the formation and decay process appears as a sharp fluctuation in the electron-scattering cross section. The process, as well as the corresponding feature in the transmission vs. electron energy spectrum, is referred to as a "resonance".

The electron spectrometer[15] consists of an electron source followed by an electron monochromator, a gas cell, and an electron collector. In practice the first derivative of the transmitted current as a function of energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance.[16] The energy associated with a resonance is known as an "attachment energy" (AE) and, with respect to the derivative spectrum, is defined as the point vertically midway between the minimum and maximum which charcterize the resonance. For the present purposes an attachment energy may be identified with the negative of the corresponding electron affinity (EA).[12] All samples were obtained from commercial sources and used without further purification.

Results

Figures 1a and b contain the derivative electron transmission spectra of tetramethylsilane (**1**), 3,3-dimethyl-1-butene (**4**), vinyltrimethylsilane (**5**), propyne (**7**), 3,3-dimethyl-1-butyne (**8**), (trimethylsilyl)acetylene (**9**), 1-butene (**10**), 4,4-dimethyl-1-pentene (**11**), and allyltrimethylsilane (**12**). A correlation diagram giving the attachment energies and ionization potentials of the aforementioned compounds, as well as ethylene (**2**), propene (**3**), and acetylene (**6**), is presented in Figure 2. As seen from Figures 1a and b, the spectrum of each unsaturated compound displays a resonance in the range between approximately 1 and 3 eV arising from the temporary capture of an electron into an antibonding orbital whose character is predominantly that of $\pi_2{}^*$ of the unsaturated moiety. It is noteworthy that for the silylated compounds, **5**, **9**, and **12**, there is also a second broad resonance to higher energy.

Discussion

The silylated hydrocarbons, vinyltrimethylsilane (**5**), (trimethylsilyl)acetylene (**9**), and allyltrimethylsilane (**12**) are in broad use in synthetic reactions and polymer systems. They were chosen for study due to their ease of availability and because previous PES results indicate that these compounds comprise a representative series to demonstrate the effects of α- vs. β-silyl substitution on simple unsaturated hydrocarbons. To contrast perturbations to the unsaturated moiety arising from carbon vs. silicon substitution, the carbon analogues **4**, **8**, and **11**, respectively, were also investigated.

In order to discuss the trends observed in the energies of the unoccupied orbitals of **1**–**12**, it is important to understand the arguments used to describe the PES data on these molecules. The general effect of replacing carbon by silicon in such unsaturated systems has been extensively investigated and may be discussed for the occupied orbitals by referring to Figure 2. In each case, the highest occupied molecular orbital (HOMO) is assigned as a bonding π orbital (π_1).

For α-substituted ethylenes or acetylenes the introduction of a methyl or silyl group produces a destabilization of π_1 due to (1) the positive inductive effect of the substituent and (2) the antibonding hyperconjugative interaction between the unsaturated system and the trimethyl silyl or alkyl group. (It has become commonplace to refer to orbitals as physical entities and thus this paper uses such language as "the orbital becomes more stable" to mean "the orbital eigenvalue decreases", although it is imprecise in a rigorous treatment. It is hoped that the reader is familiar with this terminology.) Since the valence state ionization potentials (VSIP's) of carbon are higher than those of silicon (C 2s, 19.54 eV; C 2p, 11.20 eV; Si 3s, 14.76 eV; Si 3p, 7.90 eV),[17] the inductive donor effect of $-Si(Me)_3$ would be expected to exceed that of $-C(Me)_3$. In addition, these lower VSIP's of silicon result in a more effective mixing between the $\sigma_{Si(Me)_3}$ than the $\sigma_{C(Me_3)_3}$ orbitals with the hydrocarbon π orbitals. However, it has been proposed that these destabilizing interactions are mitigated for the silylated molecules by Si $\leftarrow$ C_π back donation from the occupied π hydrocarbon orbital (π_1) to a low-lying, primarily silicon-based, unoccupied orbital resulting in net stabilization of π_1 in α-silylated compared to α-methylated compounds.[1a]

This hypothesis had been substantiated by various calculations which could reportedly better reproduce the PES experimental data when d functions on the silicon were included,[7c,18] thus indicating that silicon d orbitals aligned along the Si–C bond were responsible for the stabilization of the hydrocarbon π orbitals.[1,3] However, recent calculations on compounds containing alkyl and silyl substituents α to π systems indicate that d orbitals on silicon are not required for interpreting various experimental results. The data are adequately explained by hyperconjugation between SiC $\sigma_\pi{}^*$ orbitals and the π system.[7d,e]

The net destabilization of π_1 observed upon β-silyl substitution (Figure 2) has been attributed to overriding inductive and hyperconjugative interactions between the occupied substituent orbitals and the π system which cannot be countered by the stabilizing influence of Si $\leftarrow$ C_π back donation due to the insulating methylene group.

Negative Ion States—Alkyl Substituents. Upon methyl substitution of ethylene or acetylene, the energy of the $\pi_2{}^*$ orbital is destabilized with respect to the parent compound (Figure 2). This has been noted in previous ETS studies on substituted ethylenes[19] and butadienes[12b] and is attributed to the antibonding

---

[15] Stamatovic, A.; Schulz, G. J. *Rev. Sci. Instrum.* **1970**, *41*, 423. McMillan, M. R.; Moore, J. H. *Ibid.* **1980**, *51*, 944.

[16] Sanche, L.; Schulz, G. J. *Phys. Rev.* **1972**, *45*, 1672.

[17] Cusachs, L.; Corrington, J. in "Sigma Molecular Orbital Theory", Sinanoglu, O., Wiberg, K., Ed.; Yale University Press: New Haven, 1970; p 256.

[18] See Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, and also Huheey, J. "Inorganic Chemistry", Harper and Row: New York, 1973; p 309 ff. Mitchell, K. A.; *Chem. Rev.* **1969**, *69*, 157. Dyatkima, M. E.; Klimenko, N. M. *Zh. Struct. Khim.* **1973**, *14*, 173. Kwart, H.; King, K. G. "*d*-Orbitals in the Chemistry of Silicon, Sulfur and Phosphorus"; Springer-Verlag: New York, 1977.

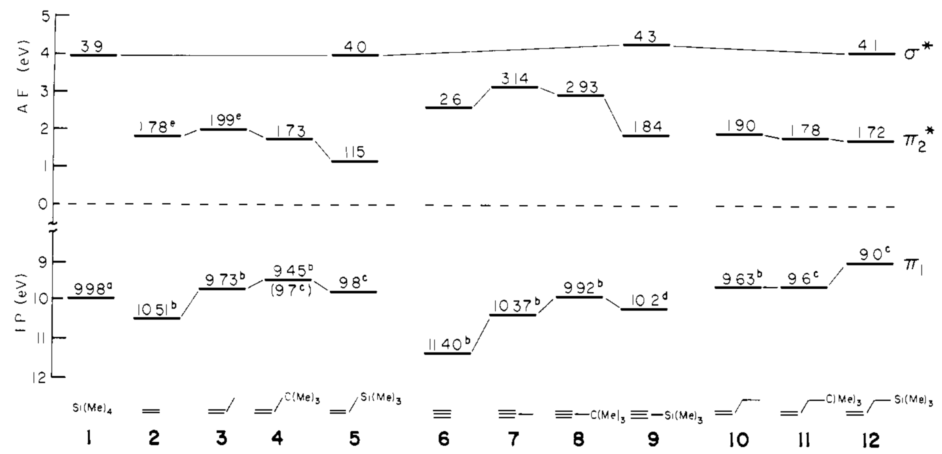

Figure 2. Correlation diagram giving attachment energies and ionization potentials of **1**–**12** (a, ref 22; b, ref 23; c, ref 3; d, ref 1b; e, ref 19). The uncertainty in the attachment energies reported to two decimal places is 0.05 eV. The uncertainty in the attachment energies reported to one place is 0.1 eV.

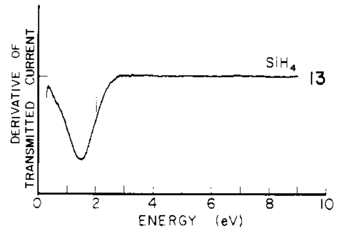

Figure 3. Derivative electron transmission spectrum of silane (**13**).

interaction between the highest occupied substituent orbital and the π^* orbital of the unsaturated system. Upon replacing the methyl group with a *tert*-butyl group, a stabilization of 0.2 eV for π_2^* in both **4** and **8** is noted. This has been observed previously upon *tert*-butyl substitution[14,20a] and may be attributed to (1) the bonding interaction between the unoccupied *tert*-butyl orbitals and π_2^* of the alkene or alkyne and (2) the possibility of stabilizing, through-space interactions between the *tert*-butyl group and the π system. Since the energy of a $\sigma_{t\text{-butyl}}^*$ orbital (6.1 eV)[20b] is lower than that of a $\sigma_{CH_3}^*$, mixing between the $\sigma_{t\text{-butyl}}^*$ and π_2^* is expected to be important.

Replacement of an α-hydrogen with a methyl group in **3** to form **10** results in stabilization of π_2^* with respect to propene (**3**). This may be attributed to stabilizing, through-space methyl interactions as noted for *cis*-1,3-pentadiene[12b] or isoprene.[20] Further substitution of methyl groups for β-hydrogens to form **11** results in increased stabilization of π_2^* as was also observed for the acetylenes on going from **7** to **8**.

Negative Ion States—Silyl Substitution. α-Silyl Substitution. Upon α-silyl substitution, π_2^* of **5** of **9** are stabilized not only with respect to their carbon analogue **4** and **8**, but also in relation to the parent compounds, ethylene (**2**) and acetylene (**6**), respectively. The stabilization of the acetylene derivative, **9**, with respect to acetylene (**6**) is greater than for the substituted ethylene, **5**. In discussing the results of the PES data for silylated acetylenes, this additional stabilization was attributed to the availability of two π systems in **6** for interaction with an unoccupied substituent orbital, while for ethylene (**2**) there is only one.[1c] The same is presumed to be true here.

β-Silyl Substitution. In allyl trimethyl silane (**12**), β-silyl substitution also causes a lowering of π_2^*, in direct contrast to the PES data (Figure 2). For the occupied orbitals, a net destabilization of π_1 was noted and attributed to the inability of the unoccupied d orbital on silicon to interact with the π center due to the intervening methylene group. The silicon and π centers were considered to be too far apart to mix. However, the stabilization of π_2^* of **12** with respect to **11** indicates that there is indeed a low-lying unoccupied orbital associated with the silyl group which, regardless of the distance between the π center and the silicon, can interact resulting in a lowering in energy of π_2^* in **12**. The greater stabilization of π_2^* in **5** compared to **12** may simply reflect the larger number of Si–C σ^* orbitals in **5** compared to **12**.

Our results imply that net stabilization of π_2^* in both α- and β-silyated species is due to hyperconjugation between the unoccupied orbitals associated with the Si–C bond, designated π_π^*, and the π center and not to silicon d-orbital participation.[7d,e] The presence of this low-lying σ_π^* orbital is manifested in a resonance near 4 eV in each of the silyl-substituted compounds (**5**, **9**, and **12**) as well as in tetramethylsilane (**1**). Indeed, if this resonance were due to the insertion of an electron into an unoccupied silicon d orbital, then substitution of hydrogens for methyl groups would be expected to have a small effect on the energy. Consider, however, the ETS spectrum of SiH_4 (**13**) (Figure 3). The energy of the resonance of 2.04 eV! This substantial stabilization indicates that the orbital giving rise to the resonance in SiH_4 and $Si(Me)_4$ is not a silicon d orbital but a substitutent-dependent silicon σ_π^* orbital. Work is currently underway to further elucidate the nature of this low-lying orbital as well as the anomolous shape of the associated resonance.[21]

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-81-21125) for funding this work, and Professor John Moore for his invaluable assistance and advice.

Registry No. 1, 75-76-3; **4**, 558-37-2; **5**, 754-05-2; **7**, 74-99-7; **8**, 917-92-0; **9**, 1066-54-2; **10**, 106-98-9; **11**, 762-62-9; **12**, 762-72-1.

---

(19) Jordan, K. D.; Burrow, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 6882.

(20) (a) Giordan, J. C. Doctoral Dissertation, University of Maryland, 1980. (b) Giordan, J. C.; Moore, J. H.,to be published.

(21) Preliminary calculations indicate that many new channels open up at energies above that of the σ^* resonance causing the scattering cross section to hold up at a more or less constant value from 2 eV up at least 10 eV.

(22) Hess, G. G.; Lampe, F. W.; Sommer, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 5327.

(23) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta*, **1977**, *60*, 2213.