Tetrahedron Letters No. 52, pp 4647 - 4650, 1977. Pergamon Press. Printed in Great Britain.

A THEORETICAL INVESTIGATION OF α-SUBSTITUTED SILICENIUM IONS.

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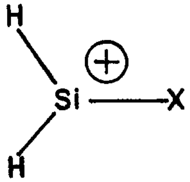
(Received in UK 24 October 1977; accepted for publication 3 November 1977)

Carbenium ions have been studied extensively for over fifty years and a wealth of information is available regarding their energies, structure and reactions.[1] In contrast, the analogous trivalent positively charged silicon cations (silicenium ions) have been elusive chemical species. Numerous experimental attempts to observe R_3Si^+ ions in solution all have failed, even under conditions where analogous carbenium ions are long-lived.[2] These failures do not necessarily indicate a lack of thermodynamic stability for trivalent silicon cations. Indeed, silicenium ions are readily observed in the gas phase under electron impact[3] and ion cyclotron resonance (ICR) conditions.[4a] The photoionization study by Beauchamp and Murphy[4b] involving a rather limited range of substituents, provides the most reliable experimental data of silicenium ion stabilities currently available. Silicenium ions also have received little attention computationally; the parent H_3Si^+ is the only cation which has been studied by _ab initio_ methods.[5]

This paucity of information regarding the most fundamental properties of silicenium ions prompts our interest in exploring such species theoretically. This communication concentrates on the stabilities of α-substituted silicenium ions (1). By varying X systematically along the whole series of first short period substituents, Li, BeH, BH_2, CH_3, NH_2, OH and F, it is possible to analyze quantitatively the importance of the various properties of the α-substituents (such as σ-inductive effects, lone pair π-donation and hyperconjugation) in stabilizing Si^+ centers. We recently reported an analogous study of α-substituted methyl, ethyl and vinyl cations which provides a revealing comparison.[6]



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Calculations were carried out using the *ab initio* SCF-MO Gaussian 70 series of programs.[7a] Each structure of **1** and of the corresponding saturated silane H_3SiX was fully optimized using the RHF/STO-3G method.[7b] The optimized geometries and energies of **1** are reported in Table 1.

Table 1. Optimized Structures [a] and Calculated Energies (RHF/STO-3G) of α-Substituted Silicenium Cations (**1**).

Substituent (X = YH_n)	Bond lengths, A° $Si^+ - Y$	 $Si^+ - H$	 $Y - H$	Bond angles, deg $< HSiY$	 $< SiYH$	Energy, hartrees
H	1.436[b]	1.436[b]	—	120.0	—	-287.08706
Li	2.484	1.436	—	127.9	—	-293.92745
BeH	2.187	1.436	1.293	124.1	180.0	-301.55120
Planar BH_2[c]	2.025	1.435	1.161	123.2	117.9	-312.03751
Perpendicular BH_2[d]	1.977	1.436	1.162	122.7	118.3	-312.04790
CH_3	1.845[e]	1.435	1.087	121.5	110.8	-325.70112
Perpendicular HN_2[d]	1.670	1.436	1.015	121.1	123.3	-341.43186
Planar NH_2[c]	1.620	1.429	1.021	117.5	124.0	-341.48471
OH[f]	1.584	1.431[g]	0.984	h	118.1	-360.97548
F	1.561	1.435	—	117.0	—	-384.57109

[a] Assuming C_{2v} symmetry for the YSi^+H_2 groups in **1**. [b] D_{3h} symmetry. [c] The YH_2 group and YSi^+ atoms in **1** lie in the same plane. [d] The YH_2 and the SiH_2^+ groups define two perpendicular planes. [e] Structure with C_s symmetry. [f] Assuming C_s symmetry. The $HOSiH^+$ dihedral angles are 0° and 180°. [g] For the Si-H bond trans to the O-H bond and 1.434 A° for the bond cis to the O-H bond. [h] $< HSiO = 114.5°$ for HSiOH trans and $< HSiO = 120.2°$ for HSiOH cis.

The stabilities of the α-substituted silicenium cations **1** are compared with that of the parent H_3Si^+ cations by means of the isodesmic reaction (eq. 1) and the results are summarized in Table 2. Table 2 includes also the calculated energies of the analogous reaction (eq. 2) which similarly compares the stabilities of α-substituted methyl cations with that of the parent methyl cation.

$$SiH_2X^+ + SiH_4 \longrightarrow SiH_3^+ + SiH_3X \qquad (1)$$

$$CH_2X^+ + CH_4 \longrightarrow CH_3^+ + CH_3X \qquad (2)$$

The following conclusions emerge from the data in Table 2. (a) Relative to hydrogen all the substituents examined (with the possible exception of fluorine[8]) stabilize the Si^+ center. (b) The substituents examined are all more effective in stabilizing carbenium ions than in stabilizing silicenium ions. This is most pronounced for substituents which are good π - donors such as NH_2 and OH. Thus the stabilization of the methyl cation by an amino substituent is 93.8 kcal/mole, but only 38.3 kcal/mole for the silyl cation. This contrast in the behavior of π-donors towards silicenium and carbenium ions is further exemplified in the calculated rotation barriers around the C-N bond, i.e. 72.3 and 33.2 kcal/mole in $H_2NCH_2^+$ and $H_2NSiH_2^+$ respectively. The main reason for the stronger stabilization of the methyl cation by π-donors is probably the lower energy of a 2p orbital compared with a 3p orbital, giving rise to a stronger interaction between the empty cationic orbital and for example, the nitrogen lone pair in the aminomethyl cation. This is reflected in a reduced π-electron transfer from the amino group to the cationic center; the population of the cationic 3p orbital on silicon in $H_2NSiH_2^+$ is 0.377 electrons, considerably lower than the population of the $2p(c^+)$ orbital in $H_2NCH_2^+$ (0.576 electrons). (c) A direct comparison of the stabilities of α-substituted silyl and methyl cations is provided by equation 3 (Table 2).

$$SiH_2X^+ + CH_3X \longrightarrow CH_2X^+ + SiH_3X \qquad (3)$$

The parent silyl cation is more stable than the parent methyl cation by 73.5 kcal/mole (the experimental estimate is 50 kcal/mole.[4b]) This is not unexpected as silicon is a larger and more electropositive atom than carbon and can therefore accomodate better a positive charge. The stability gap between the Si^+ and the C^+ families is however reduced upon substitution particularly by π-donors. Thus, $H_2NSiH_2^+$ is more stable than $H_2NCH_2^+$ by only 18.0 kcal/mole, and $(NH_2)_2CH^+$ might as well be more stable than $(H_2N)_2SiH^+$. It should be noted that this order of stability is true for hydride as the reference base; different results might be obtained when fluoride is used as the reference base.[4]

Table 2. Calculated Energies [a] (RHF/STO-3G) for Equations 1, 2 and 3.[b]

Substituent	Equation 1[c,d]	Equation 2[e]	Equation 3[c-e]
H	0.0	0.0	73.5
Li	56.8	91.3	39.0
BeH	15.6	26.7	62.2
Planar BH_2	9.9	12.0	71.4
Perpendicular BH_2	16.4	30.7	59.2
CH_3	12.7	30.9	55.3
Perpendicular NH_2	5.1	12.9	65.8
Planar NH_2	38.3	93.8	18.0
OH	21.2	66.0	28.7
F	6.2	32.1	47.7

[a] In kcal/mole. [b] The monosubstituted silanes and the monosubstituted methanes are taken in their most stable conformations using fully optimized geometries (RHF/STO-3G). [c] Using the energies in Table 1 for the silicenium cations. [d] Energies for the monosubstituted silanes are taken from ref. 9, or were calculated in this study. Full details will be presented.[10] [e] From ref. 6.

It is appropriate to comment on the reliability of the calculations. We use rather a limited minimal basis set (STO-3G), since the presumably more reliable extended basis set (44-31G) is not available for silicon.[9] Our previous experience, however, indicates that for equation 2 the STO-3G and 4-31G stabilization energies are similar except for X=Li, OH and F where the RHF/STO-3G stabilization energies are higher.[6] The inclusion of d-orbitals on silicon (e.g. by use of the STO-3G* basis set)[9] is not expected to change the results considerably especially for cations where the silicon has a lower lying partially empty 3p orbital. Experimental data of silicenium ions stabilities is unfortunately too limited to allow calibration of our calculations, but we note the qualitative agreement. Thus, in agreement with the results in Table 2 Beauchamp found that in silicenium ions a methyl substituent is more stabilizing than fluorine and that C^+ is stabilized more effectively than Si^+ by both CH_3 and F substituents.[4] We therefore believe that our main conclusions will hold when we use more elaborate basis sets, and can be used to predict the trend of stabilities of silicenium ions in the gas phase. We are extending our studies to polysubstituted silicenium ions and to other substituents such as PH_3, SH, vinyl, phenyl, and cyclopropyl.

Acknowledgement: We thank J.L. Beauchamp for communicating his results prior to publication, and J.A. Pople for his interest in this work. Discussions with J.B. Collins, S.A. Godleski, W.J. Hehre, G. Klopman, K. Mislow, and G.A. Olah were stimulating.

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