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Photoelectron spectrum and reactivity of silylalkyl sulphides. Stabilization of radical cations by the β -silyl effect

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Abstract

The effect of a β -silyl group on sulphur lone pair ionization energies has been re-investigated by use of *ab initio* and semi-empirical MNDO quantum-chemical calculations. The effect of the interaction between n_S and σ_{Si-C}^* orbitals and that of electron reorganization have been shown to be unimportant in the case of silyl-methyl-sulphides. To interpret the observed features of the ionization energies and reactivity, the electron release by the β -silyl group and hyperconjugative interactions have been considered. Stabilization brought about by β -substitution for the ground state of the radical cation is *ca.* 10 kcal mol⁻¹ for alkyl (10.11 kcal mol⁻¹) and silyl (9.48 kcal mol⁻¹) substituents at the MP2 6-31G**//HF 6-31G** level of theory. The effects of the substituents are smaller on the neutral ground state of the molecules (6.80 and 0.50 kcal mol⁻¹ for methyl and silyl groups, respectively) at the same level of theory. The observed low ionization energy of the β -silyl-substituted sulphides must be attributed to differences in the stabilization of the neutral ground states of the silyl- and alkyl-substituted derivatives rather than to the stabilization of the radical cationic ground state in the case of compounds of the type R₃SiCH₂SH.

1. Introduction

Maroshina *et al.* [1] recently investigated the photoelectron spectra of hexaethyldisilathiane and several bis(triethylsilylalkyl) sulphides and also the absorption spectra of the charge transfer complexes formed from these compounds and tetracyanoethylene. Comparison of the ionization energies (IEs) of the sulphur lone pairs (n_S) in the (Et₃Si(CH₂)_m)₂S series ($m = 0, 1, 2, 3$) revealed that the lowest IE value is that for (Et₃SiCH₂)₂S ($m = 1$), whereas in the case of the alkyl derivatives, the n_S ionization energy decreases monotonically with increasing length of the alkyl chain as indicated by the IE values reported previously by Bock *et al.* [2]. The special effect of a silicon atom in a β -position (with respect to sulphur) was attributed to interaction between the n_S and σ_{Si-C}^* levels. Such an interaction would, however, increase the IE rather than lower it, as assumed by Maroshina *et al.* [1].

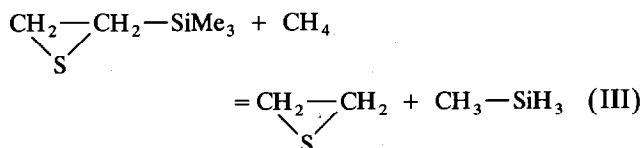
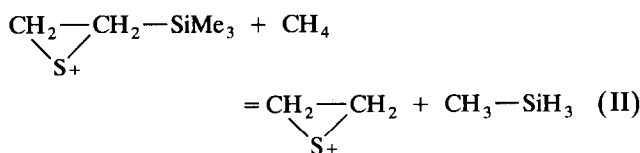
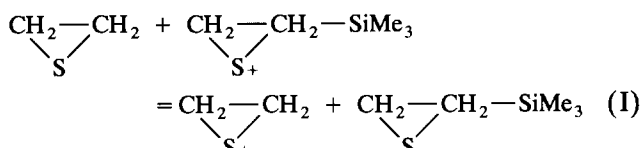
The effect of the β -silyl substituent as an extremely strong electron donor on π and n ionization energies

has also been investigated by Bock *et al.* (for a review see ref. 3). The low ionization energies observed for β -silyl-substituted compounds were attributed to the stabilization of the cation by delocalization to the neighbouring carbon atom of the positive charge generated by electron expulsion. In a report that appeared a few months before that of Maroshina *et al.* [1], Bock *et al.*, considering the low first IE of β -trimethylsilyl-sulphides, criticised use of Koopman's theorem, since the difference between the measured and MNDO calculated Koopmans' ionization energies varied throughout the series of the investigated compounds [4]. In their interpretation, which was based on general considerations not on quantum-chemical calculations, the reorganization effect during the ionization was responsible for the observed low IE for the β -silylated compound [4].

The β -silyl effect on sulphur lone pair ionization energies has also been studied by Block *et al.* [5] who examined the photoelectron and Penning ionization spectra of 2- and 3-substituted thiiranes. The lowering of the n_S IE relative to that for thiirane was attributed to stabilization of the radical cation by the β -silyl group. The difference in the ionization energies, how-

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ever, corresponds to the electron-transfer isodesmic reaction (I). Apeloig *et al.*, who investigated the stabilizing effect of the thio group on carbenium ions, have pointed out that contrasting results can be observed for different isodesmic reactions owing to differences in ground state stabilization [6]. (Another possible isodesmic reaction in the case of the thiiranes investigated by Block *et al.* [5] would be reaction (II); ground state stabilization can be given by reaction (III).)



Consequently great care should be taken in selecting the appropriate isodesmic reaction when the stabilization of the radical cationic state is under consideration.

Conflicting views about the nature of the β -silyl substituent effect prompted us to re-investigate the photoelectron spectrum of alkyl-, silyl- and alkylsilyl sulphides using *ab initio* and semi-empirical quantum-chemical calculations.

The lowering of the π - and non-bonding IE values by β -silyl substituents is well known. Early explanations were based on inductive effects and (d-p) π interaction [7]. Hyperconjugation with the σ Si-C bonding (but not with the σ^* Si-C antibonding) orbital was considered as an alternative [8].

It has also been established that the ground state conformation of allylsilanes is determined by a hyperconjugative interaction; *i.e.* the π -system and the β -silyl group are in a *gauche* and not a *cis* disposition [9].

The β -silyl effect on sulphur and on its radical cation have not previously been studied by means of *ab initio* quantum-chemical calculations, but this effect has been thoroughly investigated for carbocations and carbon radicals [10–20]. In the case of carbocations, significant stabilization (20–30 kcal mol⁻¹) [13–16,19] was revealed by thermodynamic measurements [13–15], quantum-chemical calculations [15,16,19] and kinetic studies of solvolysis [19], but the effect of the β -silyl group on radicals was judged to be much smaller (*ca.* 2 kcal mol⁻¹) [19,20] from *ab initio* calculations. (The stabilization of carbocations has also been assessed by

use of isodesmic reactions of type (I) [13,15] and type (II) [16].)

The observed stabilization of carbocations has been attributed in recent publications to hyperconjugative interaction, although the possible importance of inductive effects could not be completely ruled out [11]. Another possible explanation of the observed carbocation stabilization is the formation of a bridged species [11,16,19,20] (so-called nonvertical stabilization (see [11] and refs. cited therein) since significant movement of nuclei is involved in the process). For a recent review of the β -silyl effect on carbocations see ref. 11.

The aim of the present work was to investigate the role of inductive and hyperconjugative (considering both $\sigma_{\text{Si-C}}$ and $\sigma_{\text{Si-C}}^*$ orbitals) effects as well as that of electronic relaxation and nonvertical stabilization in order to throw light on the relationship between the low ionization energy and stabilization of the β -silylated radical-cation ground state.

2. Calculations

Quantum-chemical calculations were carried out by use of the GAMESS program [21] for HF (ROHF) geometry optimization and frequency calculations. The basis set was of the split valence 6-31G** type [22]. (For silicon, Gordon's basis [23] was used.) Second-derivative calculations at the optimum structures ensured that a real minimum was located on the potential energy surface, since no imaginary value appeared among the calculated harmonic frequencies. MP2 6-31G**//HF 6-31G** (PUMP2 6-31G**//ROHF 6-31G**) calculations at the derived HF (ROHF) optimum geometries were carried out by use of the GAUSSIAN 90 package [24]. In the UHF procedure, the S^2 values were less than 0.76 for the doublet states. Spin contaminations were projected out, resulting in S^2 values of less than 0.7501.

Vertical ionization energies were taken as the energy differences between the ion and the neutral molecule at the optimum geometry of the neutral molecule, and adiabatic ionization energies were taken as the energy differences between the ion and the neutral molecule (both at their optimum geometries). Reorganization energies of the radical cations were obtained at the ROHF 6-31G** level of theory at the optimum geometry for the neutral species. The energy of the vertically relaxed cation was obtained by use of the converged SCF wavefunction. The nonrelaxed energy was obtained by using the wavefunction of the neutral species (fed in as an initial guess). The corresponding energy was that of the first SCF cycle.

Semi-empirical calculations were carried out by the MNDO method [25] with geometry optimization. For

TABLE 1. Measured and calculated n_S IE values of $R_3Si(CH_2)_mSX$ compounds (in eV)

	Measured	ϵ_{MNDO}^d
$m = 0$	8.49 ^a	10.48 ^e
$m = 1$	7.95 ^b	10.26 ^c 10.00 ^f
$m = 2$	8.05 ^b	10.35 ^e 10.36 ^f
$m = 3$	8.10 ^b	10.31 ^e
CH_3SR	8.71 ^a	10.33
H_2S	10.48 ^c	10.65

^a Ref. 2, R = Me. ^b Ref. 1, R = Et, X = $Et_3Si(CH_2)_m$. ^c Ref. 28. ^d X = H, R = H. ^e *b* type conformer. ^f *a* type conformer.

silicon, the “old” parameters [26] were used, since it has been reported [27] that results obtained in this way are closer to those from the *ab initio* approach.

3. Results and discussion

Koopmans' ionization energies calculated by the MNDO method for $m = 0-3$ in $SiH_3(CH_2)_mSH$ are listed in Table 1 together with the values observed by Maroshina *et al.* for the ethyl-substituted derivatives [1]. In the case of the alkylsilyl compounds, two different geometrical arrangements were considered, as shown in Fig. 1. Whereas for the type *b* conformer no $n_S-\sigma_{Si-C}^*$ interaction is possible for symmetry reasons, in the type *a* arrangement, the n_S orbital might interact with the σ_{Si-C} and σ_{Si-C}^* orbitals. The variations in both the measured and calculated IE values show the same trend (similar to that observed by Bock *et al.* [4] for the methyl-substituted derivatives) indicating, that as usual the MNDO method using Koopmans' theorem provides a reasonably good basis for the assignment of the photoelectron spectrum. For the compound having a silyl group β to the sulphur atom ($m = 1$), the analysis of the linear coefficients in the HOMO reveals that there is no Si-C antibonding contribution in this orbital for either the *a* or *b* conformer, and so the assumption made by Maroshina *et al.* [1] must be rejected. It should be pointed out, that there is no difference between ionization energies of the *a* and *b* type conformers in the case of the β -silylated derivative, for which the type *a* conformer has a considerably

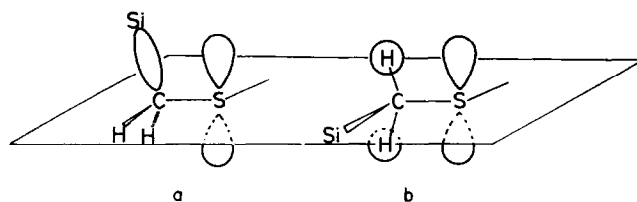


Fig. 1. Two possible arrangements of the Si-C-S moiety.

lower first ionization energy as a result of the hyperconjugative interaction between the n_S and σ_{Si-C} (but not σ_{Si-C}^*) levels. According to the MNDO calculations, the lowest ionization energy in the whole series is that of the β -silyl derivative, not only for the type *a* conformer but also for the type *b* conformer and so the inductive effect of the β -silyl group must be partly responsible for the observed low ionization energy.

Although a good qualitative description of the observed ionization energies was given by using the MNDO method and Koopmans' theorem, we decided to study the problem at a higher level of theory. The calculated ionization energies for RSH compounds (R = H, CH_3 , SiH_3 , CH_3CH_2 and SiH_3CH_2) are listed in Table 2. While the calculated 6-31G** Koopmans ionization energies are in excellent agreement with the available ionization energies, ΔSCF ionization energies are, as usual, lower than the observed values. When some of the correlation energy was taken into account by single point MP2 (MP2 6-31G**//HF 6-31G**) calculations the calculated values were much closer to the experimental ones ($\Delta MP2$ values in Table 2). The vertical and adiabatic ionization energies are close to one another for the alkyl derivatives, in accord with the narrow bands observed in the photoelectron spectra [28]. The largest deviation is observed in the case of SiH_3SH (0.26 and 0.33 eV at the $\Delta MP2$ and ΔSCF levels, respectively), and this is consistent with the relative broadness of the corresponding band in the photoelectron spectrum [29]. The difference between the adiabatic and vertical ionization energies is again considerable in the case of SiH_3CH_2SH (0.24 and 0.16 eV at the $\Delta MP2$ and ΔSCF levels, respectively) indi-

TABLE 2. 6-31G** ionization energies of $H_3Si(CH_2)_mSH$ and related compounds (in eV)

	$-\epsilon_{HOMO}$	$\Delta SCF(ad.)$	$\Delta SCF(vert.)$	$\Delta MP2(ad.)$	$\Delta MP2(vert.)$	Obs.
H_2S	10.44	9.39	9.39	9.96	9.97	10.48 ^a
CH_3SH	9.68	8.48	8.51	9.09	9.11 ^c	9.44 ^b
CH_3CH_2SH	9.62	8.31	8.36	8.95	8.98	9.36 ^a
SiH_3SH	10.22	8.65	8.98	9.35	9.61	9.97 ^b
SiH_3CH_2SH	9.58	8.18	8.34	8.71	8.95	

^a Ref. 28. ^b Ref. 29. ^c At the MP3 6-31G**//HF 6-31G* + ZPE level of theory 9.0 eV was obtained [30].

TABLE 3. Reorganization energies calculated at the ROHF 6-31G** level of theory (in eV)

HSH	CH ₃ SH	SiH ₃ SH	CH ₃ CH ₂ SH	SiH ₃ CH ₂ SH
1.05	1.17	1.24	1.26	1.24

cating that the β -silyl stabilization cannot be regarded as an entirely vertical process for the investigated radical cations.

Inspection of the *ab initio* optimized geometries (Fig. 2) leads to a similar conclusion. Ionization results in small changes in the R-S-H angles, S-H and C-S bond lengths. (According to Yates *et al.* [31] MP2 6-31G* optimum geometries are close to those derived by HF 6-31G* in the case of CH₃SH and its radical cation. Our equilibrium structures are similar to those obtained previously with similar basis sets for CH₃SH and CH₃CH₂SH [6,31,32].) In the case of SiH₃SH, however, a significant increase (0.168 Å) in the Si-S bond length is predicted upon ionization of one electron from the sulphur lone pair. For SiH₃CH₂SH, again a considerable change in the equilibrium geometry is predicted by the calculations. The S-C bond length is decreased by 0.060 Å, while the Si-C bond length is increased by 0.088 Å. Both effects are in accord with the increased hyperconjugative interaction in the ionic state (see below).

The optimum geometry of SiH₃CH₂SH, both in the neutral and radical cationic ground states was found to be of type *a*, given rise to hyperconjugative interactions between n_s and Si-C levels. (The energy difference between the type *a* and *b* conformers was 1.24 kcal

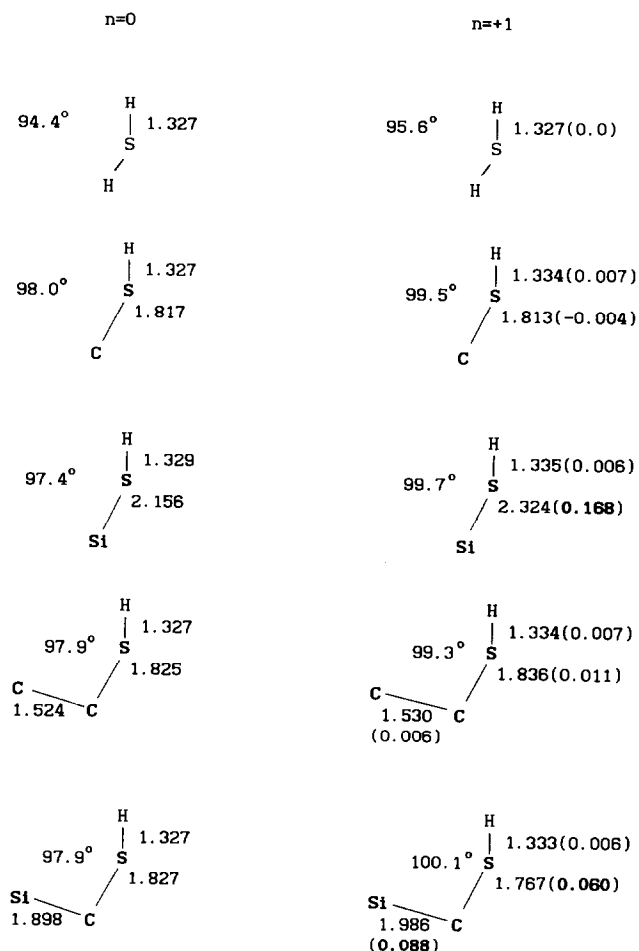


Fig. 2. HF 6-31G** geometries of the investigated compounds in Å and degrees, $n=0$ refers to the neutral and $n=1$ to the radical cationic ground state.

TABLE 4. Charge distributions for the compounds investigated. The numbering of the carbon atoms starts from the sulphur atom ^a

	δ_S	δ_{C_1}	δ_{C_2}	δ_{C_3}	δ_{Si}
SiH ₃ SH	{ -0.30 / +0.25 -0.28	-	-	-	+0.60 / +0.67 +0.62
SiH ₃ CH ₂ SH	{ -0.01 / +0.62 -0.08	-0.61 / -0.74 -0.19	-	-	+0.65 / +0.70 +0.61
SiH ₃ CH ₂ CH ₂ SH	-0.12	+0.01	-0.19	-	+0.62
SiH ₃ CH ₂ CH ₂ CH ₂ SH	-0.11	-0.01	0.00	-0.18	+0.61
CH ₃ SH	{ -0.02 / +0.67 -0.11	-0.49 / -0.60 +0.03	-	-	-
CH ₃ CH ₂ SH	{ -0.02 / +0.66 -0.11	-0.37 / -0.49 -0.02	-0.33 / -0.37 0.02	-	-
H ₂ S	{ -0.13 / +0.63 -0.09	-	-	-	-

^a Bold letters represent *ab initio* Mulliken charges separated by / for the neutral molecule and ion, respectively. Lowdin analysis gives somewhat smaller values, but the trends are the same. MNDO charges of the neutral molecules are given in normal letters. MNDO data in Table 2 refer to *b* type conformers. Partial charges for the *a* type conformers, however, do not deviate more than 0.01 from the above values.

mol⁻¹ according to the MNDO calculations.) The Si–S distance (3.122 and 3.142 Å for the neutral and ion, respectively) stays nearly constant upon ionization, and so there is no indication of a stable bridged structure in the radical cationic ground state. (Such structures were calculated to be minima on the potential energy surface in the case of carbocations.)

To investigate Bock's suggestion that the reorganization energy is a possible cause of the large β -silyl stabilization, ROHF reorganization energies were calculated for the radical cation ground state (Table 3). From the data, it is clear that this effect is very similar for all the molecules investigated, and no significant increase is observed in the case of the β -silylated derivative.

The assumed large reorganization energy was considered by Bock *et al.* to be the result of delocalization of the positive charge generated by the electron expulsion [4]. When the charge distributions in the neutral and corresponding ionic species are compared, however, (Table 4) it can be seen that α -carbon atoms become more *negative* upon ionization. The changes in the partial charges for both sulphur and α -carbon are similar for each compound investigated, and so the charge delocalization in the case of the β -silylated compound is similar to that for the other alkyl-substituted sulphides.

Charge distributions in the neutral ground state are in agreement with earlier assessments by Bock *et al.* [4] in the case of the β -silyl-derivative; *i.e.* the carbon atom in the α -position with respect to sulphur is more negative for this compound than for the other derivatives. This polarizing effect of α -silyl groups is well known [33], and is also reflected in the chemical behaviour [34]. The observed variations in the reactivities of (alkylsilyl) sulphides [35] attributed by Maroshina *et al.* [1] to interaction between n_s and σ_{Si-C}^* orbitals in the case of the β -silylated compound must instead be attributed to change in the S–C bond polarity (Table 4).

In order to investigate the β -silyl stabilization of the ground state of the radical cation and neutral molecule, the following isodesmic reactions were considered, where E = C, Si; $n = 0, 1$ (neutral and cationic ground states, respectively).



Stabilization of the cationic ground state (Table 5) is about 10 kcal mol⁻¹ for both methyl and silyl groups in the β -position at the highest level of theory used in this study. This value lies between that for stabilization by the β -silyl group in carbocations (*ca.* 30 kcal mol⁻¹) and that in carbon radicals (*ca.* 2 kcal mol⁻¹) [16]. The stabilization effect exerted on the neutral ground state

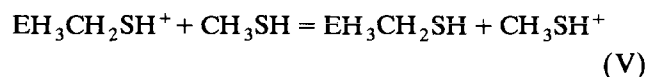
TABLE 5. Energies of the isodesmic reactions investigated in kcal mol⁻¹: $EH_3CH_2SH^{n+} + CH_4 = EH_3CH_3 + CH_3SH^{n+}$

E	n^a	MP2 6-31G**	HF 6-31G**
		//HF 6-31G**	//HF 6-31G**
C	0	6.80	4.76
C	1	10.11	8.71
Si	0	0.50	-1.24
Si	1	9.48	5.79

^a $n = 0$ refers to the neutral and $n = 1$ to the cationic ground state.

by a β -methyl group is considerably larger than that of a β -silyl group (Table 5). (In the latter case, no stabilization is observed.) The observed stabilizations are in accord with hyperconjugative interaction between Si–C and half-filled n_s orbitals. Indications of such hyperconjugative interaction in the case of β -methyl substituted radicals were reported recently by von Schleyer *et al.* [36].

Energies of the electron-transfer reaction (V) (E = C, Si) can be



obtained as energy differences in the values for $n = 0$ and $n = 1$ in reaction (IV). The energy of this reaction (8.98 and 3.31 kcal mol⁻¹ for the β -silyl and β -methyl groups, respectively) provides the ionization energy difference between EH_3CH_2SH and CH_3SH , and is often referred to as the stabilization of the cationic ground state (*cf.* refs. 3–5). The difference between those energies and those in Table 5 must be attributed to ground state stabilization of the neutral species by the β -substituent (reaction (IV); $n = 0$). Thus the observed low ionization energy of the β -silyl substituted sulphides must be attributed not only to the considerable stabilization of the ground state of the radical cation but to the difference in stabilization of the neutral species by β -alkyl and β -silyl groups.

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