

Photoelectron spectra and molecular properties

CXXII *. The low first ionization energies of the β -trimethylsilyl substituted sulfides $(\text{H}_3\text{C})_3\text{SiH}_2\text{CSCH}_2\text{Si}(\text{CH}_3)_3$ and $((\text{H}_3\text{C})_3\text{Si})_3\text{CSCH}_3$ and their rationalization **

Hans Bock *, Jochen Meuret and Udo Stein

Chemistry Department, University of Frankfurt, Niederurseler Hang, W-6000 Frankfurt (Germany)

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Abstract

The rather low first vertical ionization energies of bis(trimethylsilylmethyl)sulfide, $\text{IE}_1^\nu = 8.04$ eV, and tris(trimethylsilyl)methylmethyl sulfide, $\text{IE}_1^\nu = 7.66$ eV, are compared with those of other alkyl, silylalkyl and silylsulfides and shown further to confirm the small influence of α -trimethylsilyl groups and of the very large donor effect of β -trimethylsilyl substituents in the ground state of radical cations. The overall 2.8 eV (!) lowering of the sulfur π lone pair ionization and of the individual, mostly non-additive, substituent effects, are rationalized in terms of a qualitative approach based on the electron distribution in the ground state of the neutral molecules.

Introduction

Tris(trimethylsilyl)methyl substituents $[(\text{H}_3\text{C})_3\text{Si}]_n\text{H}_{3-n}\text{C}$ are powerful electron donors, especially in the ground state of radical cations [2–4], as exemplified by the first π or lone pair n_E ionization energies of the molecules M listed in Tables 1, 2 and 3.

A survey of the selected [3] first vertical ionization energies, involving comparison of the values for the parent molecules M with those of their H_3C - and $(\text{H}_3\text{C})_3\text{SiH}_2\text{C}$ -persubstituted derivatives (Table 1) as well as effects of progressive trimethylsilylmethyl (Table 2) and β -trimethylsilyl substitution (Table 3), shows how greatly such substitution can lower these energies. For instance, the radical cation ground state of tetrakis(trimethylsilylmethyl)ethylene is stabilized by 3.36 eV

* For part CXXI see ref. 1.

** Herrn Professor Edwin Hengge zum 60. Geburtstag gewidmet.

Table 1

First vertical ionization potentials IE_1^v (eV) of acetylene, ethylene, benzene, ammonia and phosphane and of their persubstituted methyl and trimethylsilylmethyl derivatives

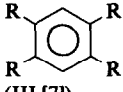
IE^v (eV) (M)	$R-C\equiv C-R$ (I [5])	$\begin{array}{c} R \\ \diagup \\ C \\ \diagdown \\ R \end{array} = \begin{array}{c} R \\ \diagdown \\ C \\ \diagup \\ R \end{array}$ (II [6])	 (III [7])	$N \begin{array}{c} \nearrow R \\ \searrow R \\ \vdots R \end{array}$ (IV [8])	$P \begin{array}{c} \nearrow R \\ \searrow R \\ \vdots R \end{array}$ (V [9])
$R = H$	11.40	10.51	9.24	10.85	10.60
CH_3	9.61	8.31	8.05	8.44	8.60
$CH_2Si(CH_3)_3$	8.85	7.15	7.10	7.66	7.85
Δ	2.55 eV	3.36 eV	2.14 eV	3.19 eV	2.75 eV

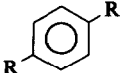
Table 2

First vertical ionization potentials IE_1^v (eV) of acetylene, ethylene, ammonia and trimethylamine and of their successively $(H_3C)_3SiH_2C$ substituted derivatives (with in parenthesis, an adiabatic value determined by RPD mass spectroscopy)

IE^v (eV) (M)	$R_n(C\equiv C)H_{2-n}$ (I [5])	$R_n(C=C)H_{4-n}$ (II [3,6])	R_nNH_{3-n} (IV [8])	$R_nN(CH_3)_{3-n}$ (IV [8])
$R=CH_2Si(CH_3)_3$				
$n = 0$	11.40	10.51	10.85	8.44
1	(9.04)	9.10	9.07	8.20
2	8.85	8.30	8.36	7.86
3	—	—	7.66	7.66
4	—	7.10	—	—

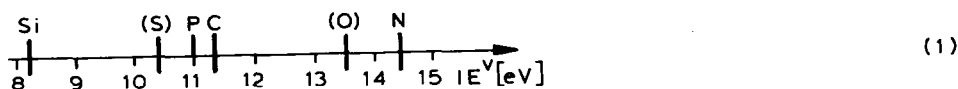
Table 3

First vertical ionization potentials IE_1^v (eV) of butyne-2, toluene, *p*-xylene, and methyl mercaptan and of their successively $(H_3C)_3Si$ substituted derivatives

IE^v (eV) (M)	$R-C\equiv C-R$ (I [10])	 (VI [11])	 (VII [11])	$R-SH$ (VIII [12])
$R=CH_{3-n}(Si(CH_3)_3)_n$				
$n = 0$	9.61	8.84	8.44	9.46
1	—	8.35	7.75	8.96
2	—	8.10	7.40	8.55
3	7.60	8.10	7.4	8.18

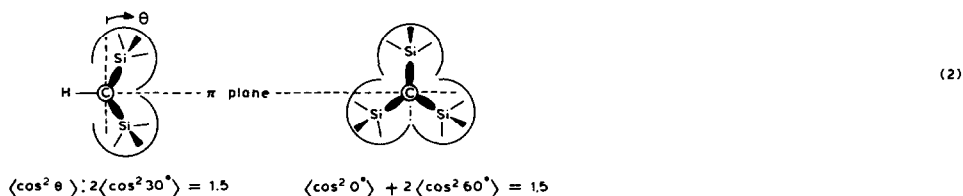
(Table 1: II), and that of $N(CH_2Si(CH_3)_3)_3$ by 3.19 eV (Table 1: IV). The largest difference observed, $\Delta IE_1^v = 3.8$ eV, occurs when both acetylene hydrogens are replaced by two rather bulky $((H_3C)_3Si)_2C$ -groups (Tables 1: I and 3: I) and reflects the advantageous spherical delocalization of the positive charge generated on electron expulsion. As expected, the substituent (second order [13]) perturbations are predominantly non-additive (Tables 2 and 3; the smallest deviations are for $R_nN(H_3C)_{3-n}$ and RSH), suggesting that several, and partly "molecule-specific", factors contribute to the measured differences ΔIE_1^v [2–4]:

(i) The atomic ionization energies of main group elements (brackets denote energetically favorable ns^2np^3 cations) [2,3]:



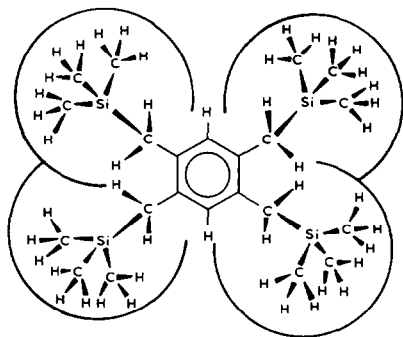
reveal the low effective nuclear potential of silicon.

(ii) That the first ionization potentials of $(R_3Si)_2HC\cdot$ and $(R_3Si)_3C\cdot$ -substituted benzenes (Table 3: VI and VII) are identical is in accord with expected identical angle-dependent CSi bond perturbations $\Sigma d(CSi)\langle \cos^2\theta \rangle$ [11]:



and so can be rationalized in terms of 'hyperconjugative' $\pi \rightarrow \sigma(CSi)$ charge delocalization in the radical cations formed on ionization.

Both inductive (1) and hyperconjugative (2) substituent effects are needed within an additive (first order) perturbation model [7] to satisfactorily account for, e.g., the first ionization potential of 1,2,4,5-tetrakis(trimethylsilylmethyl)benzene (Table 1: III), which is 2.14 eV lower than that of benzene:



$$IE_1^v = 9.24 - \left[\sum_{\mu} (c_{j\mu}^{HMO})^2 (\delta\alpha\{CH_2Si(CH_3)_3\}) + \sum_n \Delta\sigma\{CH_2Si(CH_3)_3\} \right]$$

$$= 9.24 - [4 \cdot \frac{1}{4} \cdot 1.33 + 4 \cdot 0.24]$$

$$= 7.00 \text{ eV}$$

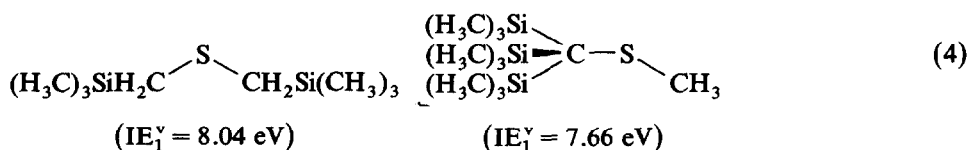
$$IE_1^v = 7.10 \text{ eV}$$

(3)

(iv) The analogous tetra-substituted ethylene derivative [6] (Table 1: II), which has an almost identical first ionization energy of 7.15 eV, can be treated in terms of the same π perturbation model (3: $(c_{\mu}^{\text{HMO}})^2 = 1/2$). In addition, it should be pointed out that owing to steric interaction between the bulky $(\text{H}_3\text{C})_3\text{SiH}_2\text{C}$ groups [2-4] both π systems are tetrahedrally embedded in an almost spherical alkyl cloud, and thus seemingly lose their identity in respect of an optimum spatial charge delocalization.

(v) The lone pair ionizations of the NR_3 and PR_3 derivatives [8,9] (Table 1: IV and V; Table 2: IV) are strongly substituent-dependent. They demonstrate both the effect of decreasing effective nuclear charge $N > P$, and (especially in the case of the rather large differences ΔIE_1^v between the parent hydrogen and methyl compounds) the importance of spatial charge delocalization in the ground state of their radical cations, which are generated vertically within $\sim 10^{-15}$ seconds, and thus in the "frozen" pyramidal structure of the neutral molecules.

All the above arguments used to account for the very large donor effect of β -trimethylsilyl groups, which is useful in both organic synthesis and in the design of novel organosilicon compounds exhibiting interesting molecular properties [13] can be and have been [2,9] further tested. A recent quotation of unpublished results (with our permission) [12] prompts us to report on PE spectroscopic investigations of the title organosilicon sulfur derivatives [14,15]:



and to discuss the reasons for their rather low first vertical ionization energies compared with those for other saturated sulfides [16,17].

Experimental

Bis(trimethylsilylmethyl) sulfide. Following a procedure [18] used for thiophenyl derivatives, 16.3 g (0.1 mole) $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ were dehydrated by heating at 150°C in 100 ml dimethylacetamide until no more water distilled off. The temperature was lowered to 100°C , 25 g (0.2 mole) of $(\text{H}_3\text{C})_3\text{SiCH}_2\text{Cl}$ were added, and the mixture was refluxed for 8 hours. The product (yield 6 g = 25%) was purified by recrystallization from a low-boiling hydrocarbon fraction.

Tris(trimethylsilyl)methyl methyl sulfide. This compound was kindly provided by Professor D. Seebach, and had been made from tris(trimethylsilyl)methyl lithium and dimethyl disulfide [15].

Photoelectron spectra were recorded with a Perkin Elmer PS 16 spectrometer equipped with a heated inlet system at 10^{-2} mbar, and were calibrated against the vertical ionizations $^2\text{P}_{3/2}(\text{Xe}) = 12.13 \text{ eV}$ and $^2\text{P}_{3/2}(\text{Ar}) = 15.76 \text{ eV}$.

MNDO calculations were performed on our VAX 11/750 computer with the program version 4.10, kindly provided by Professor M.J.S. Dewar. For both dimethyl and disilyl sulfide as well as the mixed derivative, the gas phase structures (cf. Eq. 3) are known; for the title compounds use of standard bond lengths and angles, such as $\text{CSC} = 99^\circ$, provides a satisfactory approximation. Bis(trimethyl-

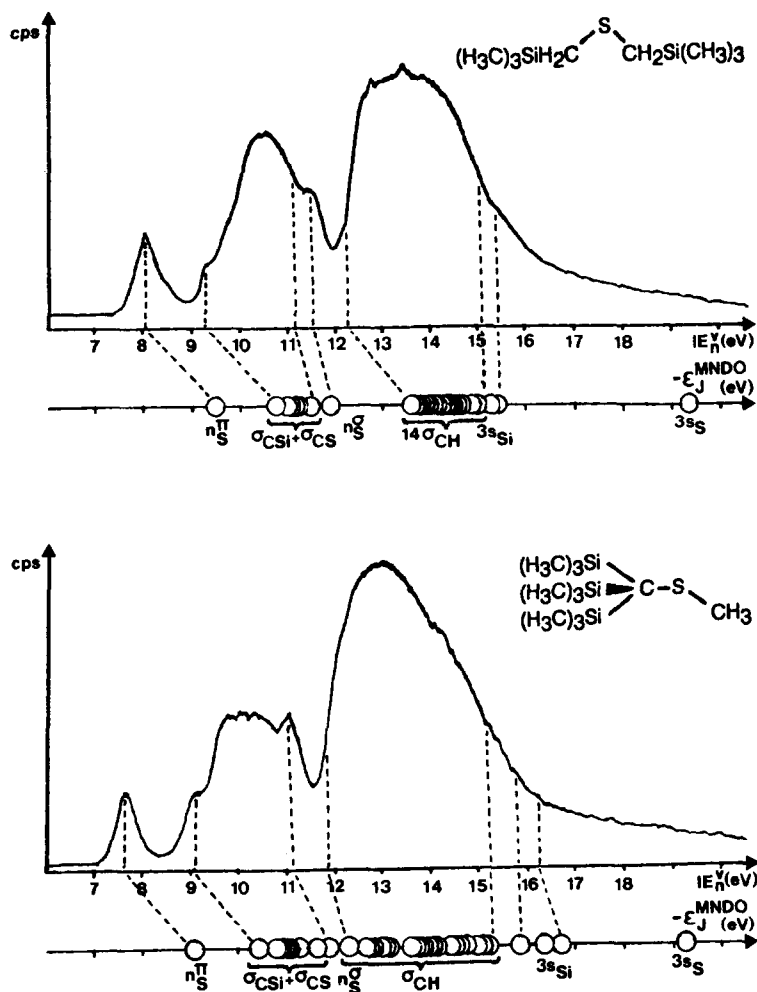


Fig. 1. He(I) photoelectron spectra of bis(trimethylsilylmethyl) and tris(trimethylsilyl)methyl methyl sulfide and their tentative assignment to MNDO eigenvalue patterns.

silylmethyl) sulfide was considered in two conformations, with either Si-C-S-C-Si or H-C-S-C-H as planar central skeletons. No attempt was made to further optimize the geometries generated by use of the Fletcher/Powell/Davidson subroutine of the MNDO program.

Photoelectron spectra

The PE spectroscopic ionization patterns of the β -trimethylsilyl substituted sulfides, $((\text{H}_3\text{C})_3\text{SiH}_2\text{C})_2\text{S}$ and $((\text{H}_3\text{C})_3\text{Si})_3\text{CSCH}_3$, both exhibit isolated low-energy bands (Fig. 1) with maxima $\text{IE}_1^v = 8.03$ eV and 7.66 eV, respectively, which can be straightforwardly [2,3,12,16,17,19–26] assigned to electron expulsion from the sulfur lone pairs n_s , which generates radical cation ground states with predominant n_s contribution.

For the rather large molecules $C_8H_{22}SSi_2$ and $C_{11}H_{30}SSi_3$, according to a useful rule of thumb $\sum_m IE_m^v = (np_E + 1s_H)/2$ [22] and taking account of the element p and hydrogen $1s$ electrons, altogether 23 and 31 valence ionizations, respectively, are expected within the He(I) excitation region. Except for the low-energy band, they overlap to two almost contourless ionization hills (Fig. 1), the assignment of which, by Koopmans correlation $IE_n^v = -\epsilon_j^{SCF}$, to SCF eigenvalues would be a futile exercise owing to the density of states around 10.5 eV and especially around 13 eV. Qualitatively, comparison of the M^{++} states with those of related silicon compounds [3] suggests the following sequence of ionizations as indicated by the respective M^{++} state main contributions: n_S^π at 8.03 eV or 7.66 eV, $\sigma(CSi)$ [3] as well as $\sigma(CS)$ [19] between 9 and 11 eV, the 'in plane' sulfur lone pair n_S^σ at 11 eV to 11.5 eV [19] (Fig. 1: recognizable humps), and the numerous $\sigma(CH)$ as well as higher σ ionizations between 12 and 16 eV.

The above overall assignment is supported by the sequence of MNDO eigenvalues (Fig. 1: $-\epsilon_j^{MNDO}$). They predict for each of the compounds energetically separated M^{++} ground states with a predominant sulfur lone pair n_S^π contribution (MNDO orbital coefficients $S(p_z) = 0.95$ and 0.86 , respectively). The subsequent ionization hills should contain $\sigma(CSi)$ and $\sigma(CS)$ -type radical cation states, and the observed PE spectroscopic humps around 11 eV those corresponding to a delocalized n_S^σ lone pair (MNDO orbital coefficients $S(s + p_{x,y}) = 0.71$ and 0.55 , respectively). The big 'ionization mountains' between 12 and 16 eV should comprise some 14 or 25 predominantly $\sigma(CH)$ ionizations, respectively, each with $3s(Si)$ -type M^{++} states at their high-energy flank. In contrast, the largely $3s(S)$ -type M^{++} states predicted above 19 eV, cannot be detected among the unresolved 'noise' in the PE spectra above 16 eV (Fig. 1).

However, in the context of this rather qualitative assignment based on semiempirical SCF calculations, the limitations imposed by neglecting the Koopmans deviations, i.e. the opposing effects of electron correlation and M^{++} electronic relaxation [27] have to be pointed out. In addition (cf. Experimental Section), no attempts were made to optimize the structures in the calculations on the rather large trimethylsilyl-substituted sulfides, with their 93 and 129 degrees of freedom, respectively.

Discussion of the sulfur π lone pair ionizations

The assignment of the first PE spectroscopic bands of the rather bulky organosilicon sulfides (Fig. 1) to vertical ionizations of the π -type sulfur lone pairs is further substantiated by observation of a linear relationship between $\nu_m^{CT} \text{ (cm}^{-1}\text{)} = 3690 IE^v(n_S) - 11490$ ($SE = 42 \text{ cm}^{-1}$) [19] and the charge transfer excitation energies ν_m^{CT} of the TCNE complexes formed by dialkyl sulfides RSR in H_2CCl_2 solution [19]; the relationship also includes the di(*t*-butyl)-derivative. Overall, including the new entry of 7.66 eV for $(R_3Si)_3CSCH_3$ reported here, the sulfur lone pair ionizations of saturated sulfides starting from H_2S with $IE_1^v = 10.47$ eV span the surprisingly wide range of 2.81 eV (Fig. 2). Reference to the values for selected organosilicon compounds presented in Tables 1, 2 and 3, shows that this is one of the largest substituent perturbations so far observed for β trimethylsilyl groups. For comparison, in $(R_3SiH_2C)_2C=C(CH_2SiR_3)_2$ the 4 R_3SiH_2C groups lower the first π -type ionization by $\Delta IE_1^v = 3.36$ eV, and in the saturated compounds NR_3 or PR_3 ,

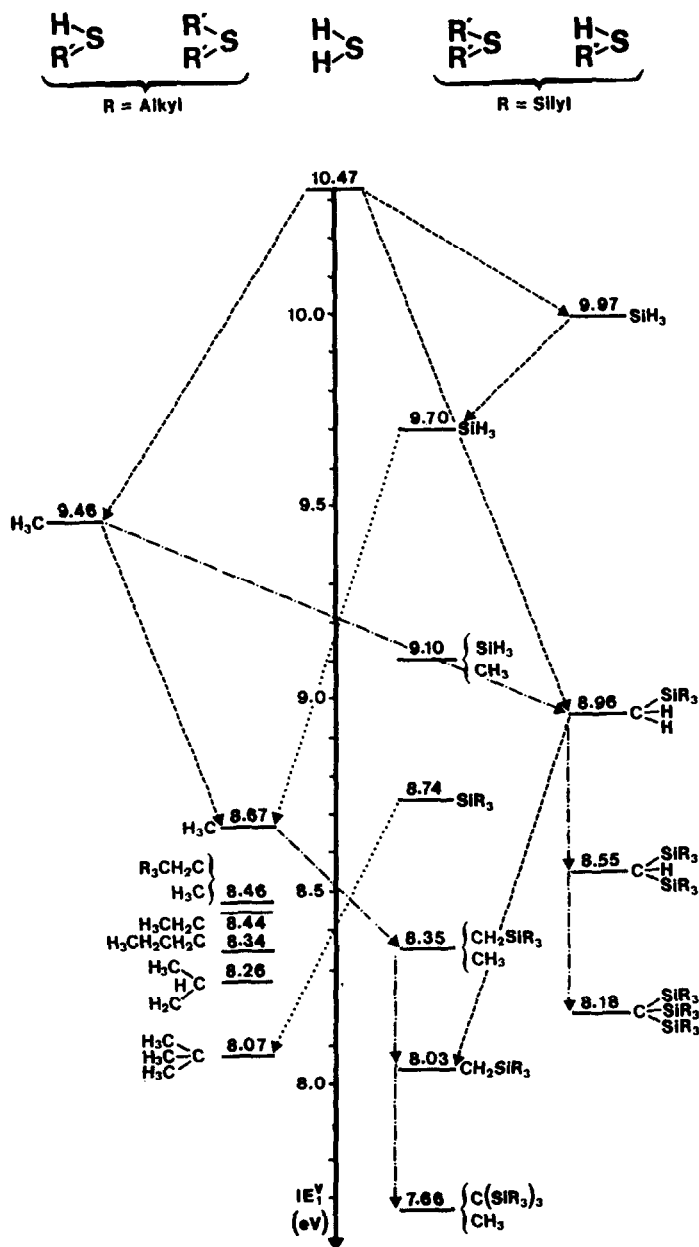
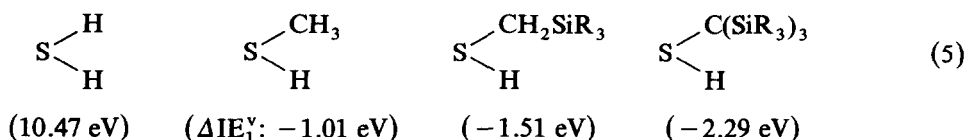


Fig. 2. First vertical ionization energies of H_2S and its alkyl, silyl, trimethylsilyl and trimethylsilylmethyl derivatives (connecting lines: ----- identical mono- and di-substitution; alkyl/silyl comparison; -.-.- β silyl substituent effects).

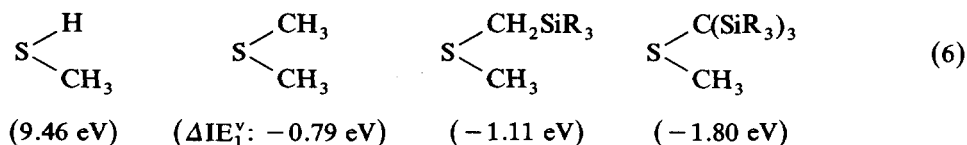
each, with three $\text{R}_3\text{SiH}_2\text{C}$ groups, the lone-pair ionizations are lowered by $\Delta\text{IE}_1^v = 3.19$ or 2.75 eV, respectively (Tables 1 to 3).

Among the various features emerging from a comparison of first vertical RSR ionization energies (Fig. 2), the following deserve special emphasizes:

(i) The effects of β -trimethylsilyl groups are evident already on monosubstitution of H_2S :

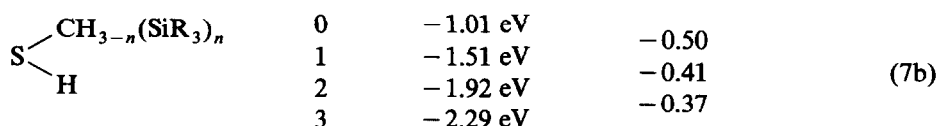
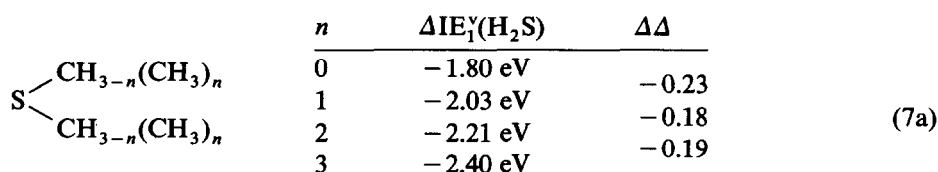


Analogously, relative to $\text{H}_3\text{C-SH}$ the methyl derivatives exhibit similar pronounced, although somewhat smaller, ΔIE_1^γ shifts to lower energies:

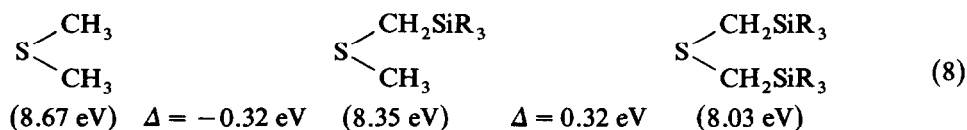


Obviously (cf. (5) and (6)), the first methyl substitution $\text{HS}\text{H} \rightarrow \text{H}_3\text{CS}\text{H}$ already allows the 'out of plane' delocalisation of the positive charge generated on electron expulsion from the π -type sulfur lone pair.

(ii) With respect to the relatively large decrease in ΔIE_1^γ of 1.01 eV caused by the first methylation of H_2S (6), the effects of additional β - CH_3 or SiR_3 substitution are smaller:



Attention is drawn again to the very large lowering of $\Delta\text{IE}_1^\gamma(n_s)$ relative to that for H_2S by a single bulky $(\text{R}_3\text{Si})_3\text{C}$ substituent (7b: -2.29 eV), which is almost as large as that by two *t*-butyl groups (7a: -2.40 eV). Obviously, the second and third substitutions (7a,b: $n = 1 \rightarrow 2$ and $n = 2 \rightarrow 3$) lower the sulfur lone pair ionizations less than the first one (7a,b: $n = 0 \rightarrow 1$), and to approximately the same amount. An (accidental) additivity is observed for the series:

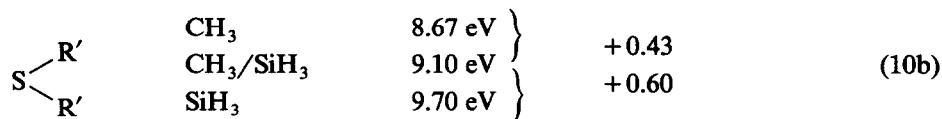
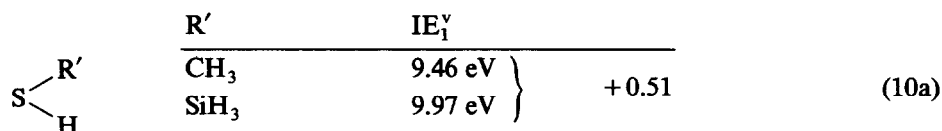


(iii) In general, however, substituent effects are clearly non-additive:

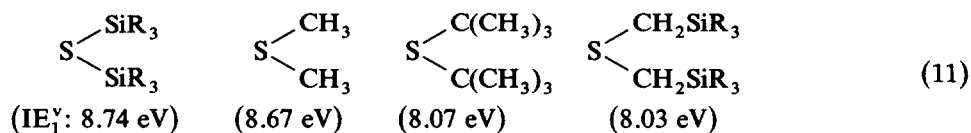
(R')	IE ₁ ^v (CH ₃)	ΔIE ₁ ^v	IE ₁ ^v (CH ₂ SiR ₃)	ΔIE ₁ ^v	(9)
HSH	10.47 eV	-1.01	10.47 eV	-1.51	
R'SH	9.46 eV		8.96 eV		
R'SR'	8.67 eV		8.03 eV		

The mean values, 0.90 eV for CH₃ and 1.22 eV for CH₂SiR₃, nevertheless, demonstrate the special M⁺⁺ ground state stabilization by β trimethylsilyl groups, which exceeds that of β methyl groups (Fig. 2: ΔIE₁^v(CH₂CH₃) = 1.01 eV) by 0.21 eV for every R₃SiH₂C substituent.

(iv) Figure 2 also shows the first vertical ionization potentials for α-SiH₃ and α-SiR₃ substituted sulfides, the n_S^π-type ionization potentials of which increase relative to those of the corresponding alkyl derivatives:



Again, the substituent effects are non-additive (10b). The opposing perturbations of the n_S^π-ionizations by α- and β-trimethyl groups are best illustrated by direct comparison (Fig. 2):



Relative to the value for S(SiR₃)₂, the first vertical ionization energy of which even slightly exceeds that of S(CH₃)₂, that for S(CH₂SiR₃)₂ is lower by 0.71 eV.

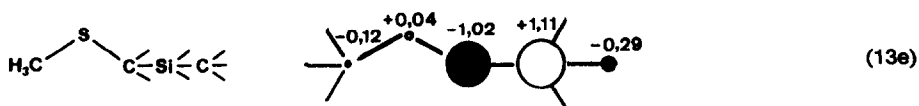
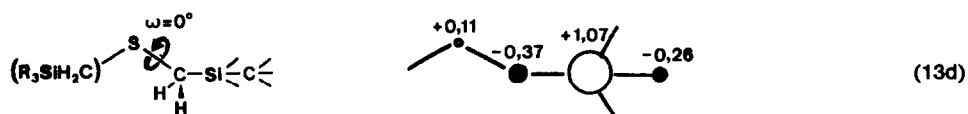
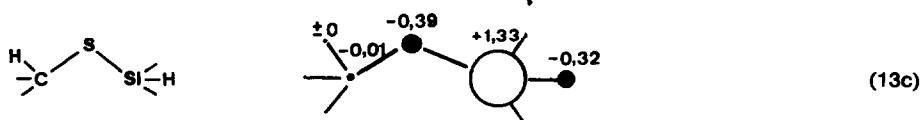
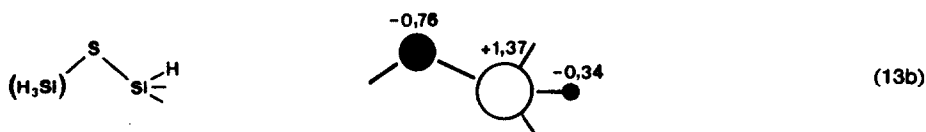
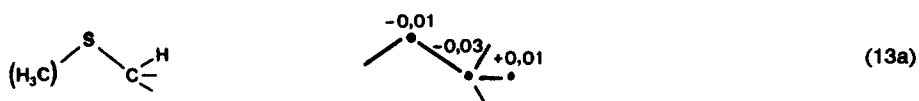
Overall, the first vertical ionization energies of 'saturated' alkyl and silyl sulfides are lowered relative to H₂S by up to 2.8 eV (Figs. 1 and 2) and the substituent effects (Eq. 5–11) in the resulting radical cation ground states are generally non-additive. The positive π-charge generated by electron expulsion from the 'out of plane' sulfur lone pair is increasingly stabilized in the order SiH₃ < Si(CH₃)₃ ~ CH₃ < CH₂Si(CH₃)₃ < C(Si(CH₃)₃)₃ (Fig. 2). How can one rationalize these puzzling PE spectroscopic observations? And especially outside a molecular orbital picture, which, as noted in the above assignment of the PE spectra, is inappropriate for larger radical cations and for the rather small energy differences between many of their states?

In order to demonstrate that the Koopmans' defects [27] $\Delta = (-\epsilon_1^{\text{SCF}} - \text{IE}_1^{\text{v}})$, vary even for chemically closely related molecules and the same quantum chemical SCF procedure, the PE spectroscopically determined first vertical ionization energies of selected silyl, silyl-alkyl and alkyl sulfides are compared with the corresponding MNDO eigenvalues $-\epsilon_1^{\text{MNDO}}$:

R^1SR^2 ($\text{R} = \text{CH}_3$)	$\text{IE}_1^{\text{v}}(\text{eV})$	$-\epsilon_1^{\text{MNDO}}(\text{eV})$	$(-\epsilon_1^{\text{MNDO}} - \text{IE}_1^{\text{v}})(\text{eV})$
$\text{H}_3\text{SiSSiH}_3$	9.70	9.92	0.22
H_3CSSiH_3	9.10	9.75	0.65
H_3CSCH_3	8.67	9.56	0.89
$\text{R}_3\text{SiH}_2\text{CSCH}_2\text{SiR}_3$	8.03	9.46	1.43
($\omega = 60^\circ$)		(9.16)	(1.13)
$\text{H}_3\text{CSC}(\text{SiR}_3)_3$	7.66	9.08	1.42

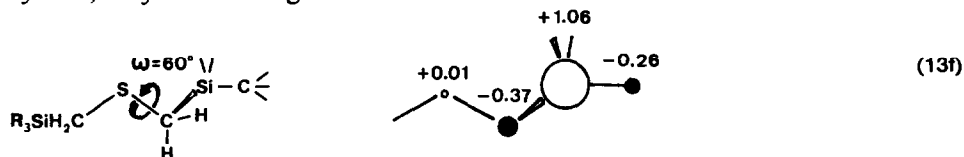
Obviously, the sequence of decreasing ionization energies within the series of differently substituted sulfides is correctly reproduced by the rather reliable semiempirical MNDO procedure (cf. e.g. [28]). The variations in the Koopmans defects [27] are predominantly due to neglect of two factors having opposing effects. First, the radical cations $\text{M}^{+\cdot}$ contain one electron less than the neutral molecules, for which the SCF calculation is performed, which results in an overshoot with respect to the electron correlation energy. Second, the electronic redistribution after ionization within 10^{-15} seconds is not taken into account, although it will stabilize $\text{M}^{+\cdot}$ owing to the delocalization of the generated positive charge and so lower the energy difference between M and $\text{M}^{+\cdot}$.

The MNDO total charges for the individual centers in the ground state of the neutral sulfide derivatives exhibit characteristic differences (Eq. 13a-e).



Thus, the 'equalized' electron distribution calculated for neutral $\text{S}(\text{CH}_3)_2$ contrasts with the highly 'polarized' one for $\text{S}(\text{SiH}_3)_2$, and the considerable difference in effective nuclear charges between C and Si centers (cf. (Eq. 1)) becomes especially obvious for sulfide $\text{H}_3\text{CSC}(\text{Si}(\text{CH}_3)_3)_3$, with its 'record' low first ionization energy.

As expected, the MNDO eigenvalues for trimethylsilylmethyl derivatives such as $\text{S}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_2$ are conformationally dependent (Eq. 12). In respect of the MNDO total charge distribution, however, when the C-Si bonds in the neutral molecule are twisted out of the assumed planar central arrangement (13d: $\omega = 0^\circ$) by 60° , only small changes result:

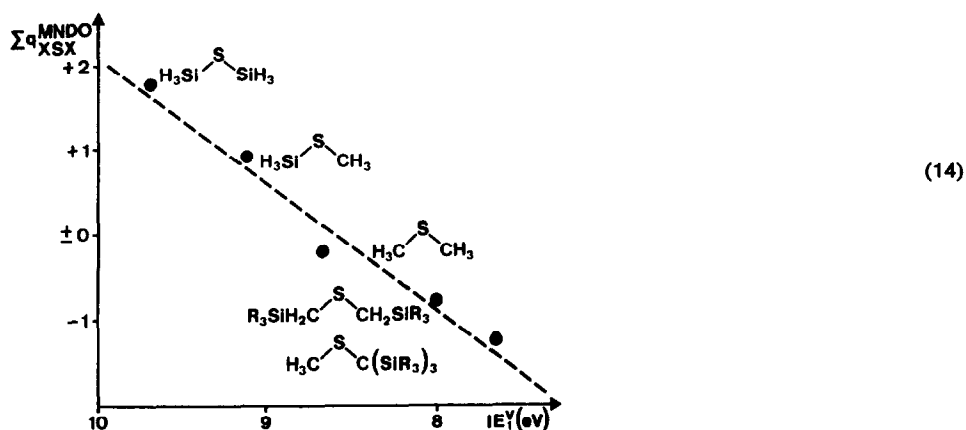


As mentioned in the Introduction, for π and n_E perturbations of radical cations, especially by β - SiR_3 substituents, ESR measurements [2-4] provide a clear-cut justification for using an angle-dependent 'hyperconjugation model' (Eq. 2), in terms of which tris-silylated methyl groups, as in $\text{H}_3\text{CSC}(\text{SiR}_3)_3$, will always exercise a maximum substituent effect.

In the absence of the usual molecular orbital basis for both first order perturbation proportional to the squared coefficients (Eq 3) or for second order interactions between levels of same irreducible representation, how can one rationalize the rather large substituent effects (Figure 2), which are mostly non-additive (cf. Eq. 5-7, 9-11) and, in respect of α - and β - SiR_3 groups, act in opposite directions? As repeatedly pointed out, the widely differing first vertical ionization potentials into radical ground states with predominant sulfur π lone pair contribution do not correlate straightforwardly with either the bulk of the individual groups (Eq. 11) or with the difference in effective nuclear charges (Eq. 1) between sulfur and the adjacent carbon or silicon centers.

On the other hand there is little doubt that the radical cation states, resulting from vertical electron expulsion, $\text{M} \rightarrow \text{M}^{+\cdot} + e^-$, in the gas phase within 10^{-15} seconds, i.e. a period some orders of magnitude before vibrations start to change the 'frozen' M ground state structure to the optimal one for $\text{M}^{+\cdot}$ [2-4,14,27], will be stabilized considerably by delocalization of the generated positive charge. Thus, this molecule-specific 'electronic relaxation' can be considered to be one of the essential factors in lowering the respective ionization energy. If this is so, then a high electron density at centers next to the sulfur lone pair in the ground state of a saturated sulfide should be favorable, and it is not surprising that the lop-sided derivative $\text{H}_3\text{CSC}(\text{Si}(\text{CH}_3)_3)_3$, with three trimethylsilyl groups on the same carbon center, for which the MNDO approximation predicts a charge of -1.02 (13e), exhibits the by far lowest first vertical ionization, 7.66 eV, among all the sulfides investigated (Fig. 2). Next in the sequence is the other title compound $((\text{H}_3\text{C})_3\text{Si})\text{H}_2\text{CS-CH}_2(\text{Si}(\text{CH}_3)_3)_3$, with each $q^{\text{MNDO}} = -0.37$ (13d) on both sides of the central sulfur, unchanged on 'out of plane' twisting by 60° (13f). Also, the ionization sequence can be extended to include both the charge-equilibrated H_3CSCH_3 (13a) and the highly and oppositely polarized $\text{H}_3\text{SiSiSiH}_3$ with $q_{\text{Si}}^{\text{MNDO}} = +1.37$ (13b). Despite some doubts about the crude, and at best qualitative approach, the sums of the MNDO charges XSX , $\sum q_{\text{XSX}}^{\text{MNDO}}$, for sulfur and its adjacent centers X were

found, to our surprise, to show an approximately linear correlation with the PE spectroscopic first ionizations IE_1^v :



It can be seen that the MNDO calculation for the mixed alkyl silyl sulfide H_3CSSiH_3 (Eq. 11) yields an approximate charge distribution (Eq. 13c), which also fits satisfactorily into the correlation (Eq. 14).

Concluding remarks

Starting from the parent species H_2S and including the title compounds, saturated sulfides with alkyl and silyl substituents with their first vertical 'sulfur π lone pair' ionizations span the rather wide range of 2.8 eV. The substituent effects, which increase in the order $H < SiH_3 < Si(CH_3)_3 \sim CH_3 < CH_2Si(CH_3)_3 < C(Si(CH_3)_3)_3$, are mostly non-additive. Because orbital perturbation models break down due to the size of the title compounds and their low symmetry, a broad rationalization is offered for the equivalent radical cation states of the chemically related compounds in terms of the charge distribution around the sulfur center in the ground state of the neutral molecules. This rather qualitative approach, which neglects all other aspects of the complex ionization process and does not account specifically for the change in correlation energies between M and M^{++} , turn out to provide some clues to the charge delocalization in the radical cations generated vertically in the 'frozen' M structure, i.e. to their electronic relaxation before the onset of vibrations.

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