

Radical cations from trialkylsilanes: a computational study of structures and energetics

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Abstract

Radical cations $(R_3SiH)^{+\bullet}$ are shown by AM1 calculations to relax from the geometries of the neutral R_3SiH species by elongation of the Si–H bond when $R = Me$, but to relax by elongation of a single Si–C bond for $R = Et, Me_2CH,$ or Me_3C . This difference in behaviour is related to the form of the HOMO in neutral R_3SiH , of symmetry a_1 in Me_3SiH , but of e symmetry in the other species; this is in turn related to the degree of α -carbon substitution by electron donor groups.

Key words: Silicon; AM1 calculations; Radical cations; Electron spin resonance

1. Introduction

It has recently been shown [1] that the γ -irradiation of the highly-branched alkylsilane $(Me_3C)_3SiH$ as a pure compound leads at 77 K to the production of a primary radical cation $[(Me_3C)_3SiH]^{+\bullet}$. The ESR spectrum showed strong coupling to three equivalent hydrogens, and was interpreted in terms of electron depletion of a single Si–C bond, with the three strongly coupled hydrogens belonging to the same t-butyl group. This observation is in marked contrast to the behaviour of the simpler analogue Me_3SiH where γ -irradiation leads to products consistent with electron depletion of the Si–H bonds, with retention of the three-fold rotational symmetry [2]. Here we present the results of a computational study designed to probe the differences in behaviour of trialkylsilanes and their radical cations, which serves also to support the earlier ESR assignments.

2. Experimental section

2.1. Calculations

All calculations were made by the AM1 method [3] as incorporated in the MOPAC system [4], version 6.0. Published atomic parameters were employed [3,5]. UHF wavefunctions were employed for all open-shell species and all geometric variables were simultaneously optimised unless it is specifically stated otherwise.

2.2. E.S.R. Measurement on $(Me_2CH)_3SiH$ radical cation

For comparison with calculated spin densities in the series $(Et_3SiH)^{+\bullet}$, $[(Me_2CH)_2SiH]^{+\bullet}$ and $[Me_3C_3SiH]^{+\bullet}$, the ESR spectrum of the second member was recorded following γ -radiolysis of $(Me_2CH)_3SiH$ in a $CFCl_3$ matrix at 77 K.

3. Results and discussion

3.1. $(Me_3C)_3SiH$

When freely optimised, the structure of neutral $(Me_3C)_3SiH$ converged to a minimum of precise C_3 symmetry, perturbed from exact C_{3v} symmetry only by

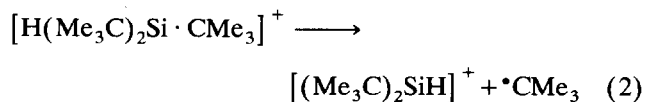
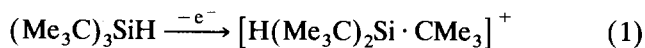
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a geared rotation by *ca.* 15° of the individual Me₃C groups about the Si–C bonds. The local symmetry of the central C₃SiH fragment was however C_{3v} exactly. For this neutral molecule the HOMO is strongly localised in the Si–C bonds, having e symmetry: the a₁ orbital localised in the Si–H bond is the next level, some 0.66 eV more tightly bound than the HOMO.

The symmetry of the HOMO in neutral (Me₃C)₃SiH means that vertical ionisation, as upon direct γ-irradiation or electron exchange, gives rise to a Jahn-Teller sensitive radical cation, expected for local C_{3v} symmetry to distort along one component of a skeletal vibration of e symmetry to give a relaxed geometry of only C_s symmetry. If the full C₃ symmetry is considered, the relaxed cation will after following an e vibration have no symmetry (C₁).

Free optimisation of the radical cation [(Me₃C)₃SiH]^{+•} indeed led to a relaxed geometry of overall C₁ symmetry, with approximate C_s symmetry for the central core, again perturbed by the rotation of the Me₃C groups: another conformer, of precise C_s symmetry, lies only 0.7 kJ mol⁻¹ higher in energy.

The most important structural feature of the radical cation [(Me₃C)₃SiH]^{+•} are: (i) the very long Si–C bond (2.670 Å) to one only of the t-butyl groups (compare calculated values of 1.793 Å for the other two such bonds in the cation, and 1.881 Å in the neutral (Me₃C)₃SiH); (ii) the marked flattening of both the distant Me₃C fragment (mean angle CCC is 118.2°) and of the residual (Me₃C)₂SiH fragment (sum of angles at silicon is 350.7°); (iii) the concentration of the SOMO in the long Si–C bond, with a very strong contribution from the carbon atom. These findings indicated that the relaxed form of the radical cation [(Me₃C)₃SiH]^{+•} has moved well down the reaction channel towards dissociation of a t-butyl radical, eqns. (1) and (2).



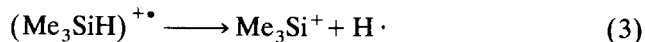
It is instructive to consider the thermodynamics of these processes: the calculated ΔH_f^φ and IP values for neutral (Me₃C)₃SiH (–262.2 kJ mol⁻¹ and 9.94 eV respectively) lead to a ΔH_f^φ for the vertically ionised radical cation of +696.6 kJ mol⁻¹. On the other hand, for the fully relaxed radical cation, the calculated ΔH_f^φ value is +522.2 kJ mol⁻¹ while reaction (2) above is endothermic only by 24.1 kJ mol⁻¹ with no other activation barrier between the relaxed radical cation and its dissociated fragments. These findings are entirely consistent with, and supportive of, the earlier interpretation [1] of the observed ESR changes: the

relaxed but intact radical cation (*cf.* eqn. (1) above) is observed at 77 K, but upon warming to 130 K the entropically-favoured dissociation (eqn. (2)) occurs irreversibly.

Within the relaxed radical cation, the unpaired spin density is concentrated in the distant Me₃C fragment, with in particular very high values (0.0501) on one hydrogen in each of the methyl groups, lying close to the respective CCSi planes. This is consistent with a major hydrogen hyperfine coupling of 43 G arising from three hydrogen atoms [1].

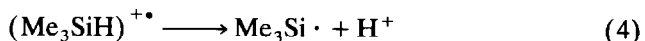
3.2. Me₃SiH

The structure of neutral Me₃SiH optimises, as expected, to exact C_{3v} symmetry. In contrast to (Me₃C)₃SiH however the HOMO is of a₁ symmetry and strongly localised in the Si–H bond: the Si–C orbitals of e symmetry are more tightly bound than the HOMO by 0.23 eV. Accordingly ionisation gives a non Jahn-Teller radical cation, but rather causes electron depletion in the Si–H bond. Optimisation of the structure of [Me₃SiH]^{+•} gave a geometry, still of C_{3v} symmetry but with the Si–H bond elongated, from 1.466 Å in the neutral molecule, to 1.832 Å, and the CSiC angle expanded, from 111.2° in the neutral, to 119.9°, indicative of incipient dissociation in the sense of eqn. (3).



For this process the calculated ΔH^φ value is only +23.2 kJ mol⁻¹.

Experimentally, γ-irradiation of Me₃SiH has been found [2] to produce Me₃Si· radicals, and clearly some highly exothermic proton-trapping step must be coupled to any dissociation of (Me₃SiH)^{+•} which forms Me₃Si· radicals as the calculated ΔH^φ value for reaction (4) is *ca.* +660 kJ mol⁻¹.



In any event there is no evidence, either experimental or computational, for any Si–C bond cleavage in the dissociation of (Me₃SiH)^{+•}, and this directly related to the symmetry of the HOMO in Me₃SiH and of the SOMO in (Me₃SiH)^{+•}.

In neutral Me₃SiH the a₁ (Si–H) orbital is less tightly bound by 0.23 eV than the e (Si–C) pair of orbitals. In both (Me₃C)₃SiH and Et₃SiH (see below) it is the e orbital which is the HOMO (Table 1). While the binding energy of the a₁ orbital changes by only a

TABLE 1. Calculated orbital binding energies in R₃SiH (eV)

	Me ₃ SiH	Et ₃ SiH	(Me ₂ CH) ₃ SiH	(Me ₃ C) ₃ SiH
a ₁ : σ(SiH)	10.95 ^a	10.93	10.68	10.60
e: π(SiC)	11.18	10.47 ^a	10.12 ^a	9.94 ^a

^a HOMO in this system.

little between Me_3SiH and $(\text{Me}_3\text{C})_3\text{SiH}$, the binding energy of the e orbital changes much more. This can be readily understood in terms of the changing electron density at the α -carbon atoms as the degree of methyl substitution increases. With more electron-donating methyl groups at the α -carbon, the orbital energy of the α -carbon orbitals decreases, and so too do the binding energies of the resulting Si–C orbitals, as found. With sufficient methyl substitution, the e (Si–C) orbital will become less tightly bound than the a_1 (Si–H) orbital. A simple test of this idea can be made using the series $\text{Me}_x\text{Et}_{3-x}\text{SiH}$ and $\text{Me}_2(\text{Me}_x\text{H}_{3-x}\text{C})\text{SiH}$: in Me_2EtSiH and MeEt_2SiH , of C_s symmetry the relevant Si–H and Si–C levels are not separated by symmetry but the form of the HOMO is a sufficient indicator. In Me_2EtSiH , with a single α -methyl substituent, the HOMO contains contributors from both Si–H and Si–C, but in both MeEt_2SiH and $\text{Me}_2(\text{Me}_2\text{CH})\text{SiH}$ each with two α -methyl substituents the HOMO of each is unambiguously concentrated in the Si–C bonds. On this analysis therefore, amongst the trialkylsilanes R_3SiH , Me_3SiH is the exception in having its HOMO concentrated in the Si–H bond whereas virtually all others will have the HOMO concentrated in the Si–C bonds, except where electron-withdrawing substituents are present.

3.3. Et_3SiH and $(\text{Me}_2\text{CH})_3\text{SiH}$

As with $(\text{Me}_3\text{C})_3\text{SiH}$, the structure of Et_3SiH when freely optimised converged to a minimum of exact C_3 symmetry, with local C_{3v} symmetry for the C_3SiH core, and a HOMO of e symmetry (Table 1). As expected from this, the radical cation is Jahn-Teller sensitive and its structure optimised to give one long Si–C bond (2.395 Å) with one ethyl group having almost left a nearly planar residual Et_2SiH fragment where the sum of bond angles at silicon is 356.0°. In the distant ethyl group, there is very high spin density at the β -hydrogen in the CCSi plane, calculated as 0.0775: this is consis-

TABLE 2. Comparison of observed hyperfine coupling and calculated spin density at hydrogen in $(\text{R}_3\text{SiH})^{+\bullet}$

	A (^1H)	$\rho[\text{H}(1s)]$
$(\text{Et}_3\text{SiH})^{+\bullet}$	68 G (1H) ^a	0.0775 (1H)
$[(\text{Me}_2\text{CH})_3\text{SiH}]^{+\bullet}$	55 G (2H) ^b	0.0653 (2H)
$[(\text{Me}_3\text{C})_3\text{SiH}]^{+\bullet}$	43 G (3H) ^a	0.0501 (3H)

^a Ref. 1.

^b This work.

tent with the observed [1] strong coupling of 68 G to a single hydrogen (*cf.* Table 2).

In entirely similar fashion $(\text{Me}_2\text{CH})_3\text{SiH}$ optimised to a C_3 structure with an e HOMO, and its radical cation optimised to a structure containing one distant Me_2CH group weakly bound by an Si–C bond of length 2.919 Å to a fragment $(\text{Me}_2\text{CH})_2\text{SiH}$ to which the bond angle-sum at silicon is 351.8°. There is thus a steady increase in the long Si–C bond in $(\text{R}_3\text{SiH})^{+\bullet}$ and a reduction in the flattening of the residual (R_2SiH) as R changes from ethyl to iso-propyl to t-butyl. Within the distant Me_2CH fragment of $[(\text{Me}_2\text{CH})_3\text{SiH}]^{+\bullet}$ there is a high concentration of spin density on two hydrogen atoms, out in each methyl group, again in the maximally extended conformational site: the calculated value of 0.0653 predicts (*cf.* Table 2) an A value of *ca.* 56 G for the hyperfine coupling in this species. This is in very good agreement with the value measured in a CFCl_3 matrix (55 G). Thus there is good accord between the trend of calculated spin densities and the observed hyperfine coupling constants, for the series of extended σ -radical cations $(\text{Et}_3\text{SiH})^{+\bullet}$, $[(\text{Me}_2\text{CH})_3\text{SiH}]^{+\bullet}$ and $[(\text{Me}_3\text{C})_3\text{SiH}]^{+\bullet}$.

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