Journal of Organometallic Chemistry, 294 (1985) 151–161
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ELECTRONIC TRANSITIONS OF POLYSILANES AND THEIR PHOTOCHEMISTRY

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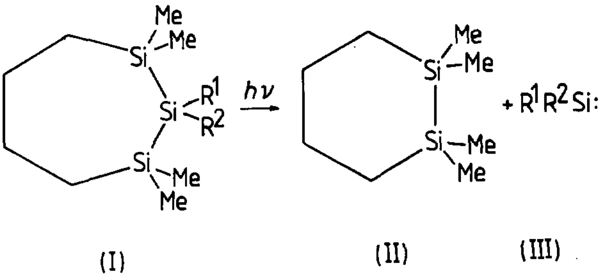
(Received April, 22nd, 1985)

Summary

The photolytic fragmentation of trisilane to disilane and silylene has been studied by means of a pseudopotential method. The lower-lying electronically excited states in several of the silanes have been calculated and analysed with respect to their Rydberg character, with the inclusion of *d* orbitals. The effect of methylation on the stability of the silicon–silicon bond, as well as on the above photochemical model reaction, is discussed. An orbital correlation diagram with defined energy levels is presented.

Introduction

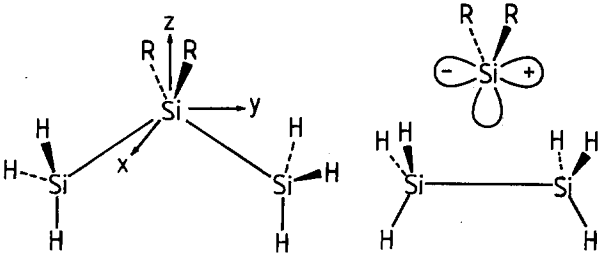
This investigation was prompted by a communication with the same title by Ramsey [1], in which the author ingeniously deduced the nature of the first excited state of a cyclic trisilane (I) from the orbital correlation diagram between I and the products of its photolysis, the ring-contracted disilane (II) and the extruded silylene (III). When only σ and σ* orbitals were included in the diagram, the photochemical



reaction was found to be "allowed". However, when the *d* orbitals of silicon were also included, and it was assumed that their most strongly bonding combination was singly-occupied in the lowest excited state, the photochemical reaction was "forbidden". Since the photolysis is known to occur readily [2], Ramsey concluded that the long wavelength transition is indeed $\sigma \rightarrow \sigma^{\star}$, and does not involve the *d* orbitals of silicon.

While we would certainly not wish to discourage the use of orbital symmetry arguments, several points should be kept in mind: (a) A reaction that is "forbidden" in total symmetry, here C_{2v}, may become "allowed" under the influence of a relatively facile symmetry-lowering displacement, so the geometry and energetics of such possible displacements should be considered in detail [3,4]. (b) The possibility of reactive intersystem crossing should also be allowed for [5]. (c) All occupied orbitals, especially those singly occupied, must be properly identified.

In this communication we describe a computational study of the excited states of the model compounds IV: $H_3SiSiR_2SiH_3$ (IVa: $R = H$; IVb; $R = CH_3$). A complete all-electron ab initio computation would be prohibitive, even for our simplest model, IVa, but considerable economies can be made by using the method of local pseudopotentials, which avoids the useless calculation of the many core electrons. The present investigation employs a modification of this method, which has been applied successfully to the hydrides of silicon and their methyl analogs [6]. In this modification, the ordinarily used Gaussian orbitals are transformed into silicon valence atomic orbitals, a feature which facilitates the discussion of molecular orbitals in conventional terms and the construction of an orbital correlation diagram for the model fragmentation reaction.



(IV)

(IVa) R=H ; (IVb) R=CH_3

The computational method

The local pseudo-potential employed has been described in detail [6]; the corresponding atomic pseudo-orbitals for the silicon atom are those in Table V of that reference. The ground-state silicon 3*s* and 3*p* pseudo-AOs have no radial nodes; it is this factor, rather than the reduced number of electrons, which is the main source of computational economy. All of the electrons of the carbon atoms are taken into account, using the well known 3-21 G basis set; the basis set for hydrogen is that described in ref. 6. Altogether, the valence electrons of silicon and all of the electrons of carbon and hydrogen are treated in an ab initio manner, using the SCF procedure.

The following geometric data were used. Trisilane: SiSi 233 pm, SiSiSi 118.4°, SiH 149 pm, SiSiH 112.7°; disilane: SiSi 235 pm, SiH 148 pm, SiSiH 110.4°; silylene ($^1A_1$): SiH 152 pm, HSiH 92°; ($^1B_2$): SiH 147 pm, HSiH 123°. The additional parameters for dimethylated trisilane are SiC 187 pm, CSiC 118.4°; the corresponding data for dimethylsilylene are ($^1A_1$): SiC 195 pm, CSiC 99.6°; ($^1B_2$): SiC 200 pm, CSiC 120°.

The calculation of excited states was performed by the method of improved virtual orbitals (IVO) (for references see [6]), but important modifications were made in the method in order to obtain more reliable excitation energies, as well as to reduce computer time. The main advantage of the IVO method is the generation of a set of singly excited orbitals for a variety of singlet and triplet states. Accordingly, an excitation energy can be simply expressed as the difference between two orbital energies, the uncertainty in the calculated excitation energies being that of the Koopmans approximation. One modification of the computational method [7], is concerned with the reduction of the Koopmans error.

A further modification [6], which has already been mentioned, increases the economy of computation. Before starting the SCF calculation, the Gaussians comprising the silicon valence basis set are transformed to valence pseudo-AOs. The use of atomic orbitals enables us to make a clear distinction between ground-state and excited states basis functions. Specifically, there is no need to use the same complete basis set, say ($3s$, $3p$, $4s$, $4p$, $3d$), for the ground- *and* excited states when we know that the ground-state is almost unaffected by the inclusion of $4s$, $4p$ and $3d$ AOs. Thus, only the $3s$ and $3p$ orbitals of silicon are used for the SCF calculation of the ground-state, whereas the excited states require the extended basis set. The projection technique, described by Huzinaga and Hirao [8], enables us to extend the excited state basis set without wasting computer time on a time-consuming SCF calculation of the ground-state.

The description of the excited orbitals

The electronically excited orbitals of a molecule in a given nuclear arrangement fall roughly into two groups: First, the valence MOs, which can be constructed from the AOs that are occupied in the ground-states of the contributing atoms; and second, the Rydberg MOs, which are diffuse orbitals enveloping the entire molecule. It is evident from the schematic correlation diagrams at the top of Fig. 1 that whereas the energy of a bonding SiH orbital is too low for it to interact to any appreciable extent with excited AOs of silicon, the corresponding SiH antibonding MO may well be energetically comparable to one or more of them. In such a case, Rydberg character will offer an energetic advantage to the relevant excited state, since an excited antibonding valence MO can be stabilized by mixing into it an atomic orbital with higher principal quantum number, making it more diffuse. For example, the lowest-lying excited orbital (a_1) of silane is more nearly a $4s$ Rydberg orbital than a conventional SiH antibonding valence orbital, as indicated in Fig. 1 by a shift of the nodal surface from within the SiH bond to well beyond it. The ensuing stabilization can be substantial, so the construction of an antibonding MO out of valence AOs alone, with neglect of the contribution of Rydberg AOs, may lead to an error of several eV in its energy.

In molecules containing first row atoms, the valence orbitals can be easily

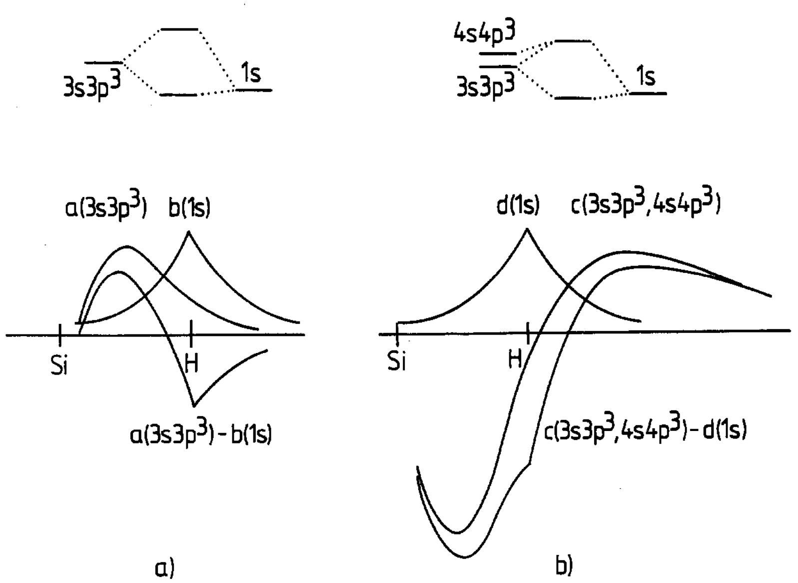


Fig. 1. The stabilization of an SiH-antibonding valence MO of silane by Rydberg character. (a) Its composition out of an Si valence $3s3p^3$ hybrid and an H $1s$ AO ($|a| \approx |b|$). The nodal surface intersects the SiH bond. (b) Its composition after the admixture of a $4s4p^3$ hybrid ($|c| \gg |d|$). The nodal surface lies beyond the bond.

distinguished from the Rydberg orbitals, because AOs with the principal quantum numbers 2 and 3 are widely different in size, and are therefore unable to combine effectively. In the case of second row atoms, however, the small energy gap between the AOs with the principal quantum numbers 3 and 4 leads us to expect that an excited orbital will show Rydberg as well as valence character. The $3d$ orbitals play an intermediate role: Although unoccupied in the atomic ground states, these AOs have the same principal quantum number as those from which the valence MOs are constructed by LCAO. The $3s$, $3p$, $3d$, $4s$ and $4p$ AOs are all sufficiently similar, as regards both energy and size, to combine with each other in various excited MOs.

(1) The minimal basis set (3s, 3p)

When the minimal basis set is used for the description of the orbitals which are doubly occupied in the ground state of trisilapropane, as well as of those which are singly occupied in its excited states, all of the resulting excited orbitals are forced to be of the valence type. As can be seen in Fig. 2a, only two of them lie below the ionization limit. In the lowest excited MO (b_1), the three silicon atoms are π-bonded, the plane containing them serving as the nodal plane. Antibonding character is manifest between six hydrogen atoms and the corresponding adjacent silicon atoms. The linear expansion coefficients for the central SiH_2 group predominate over those for the terminal SiH_3 groups by a factor of two. The next excited MO, which lies very close to the former, has a_1 symmetry, and is antibonding with respect to both Si–Si bonds as well as to the two Si–H bonds which lie in the SiSiSi plane. The third excited MO (a_2), antibonding in four Si–H fragments, already lies slightly above the

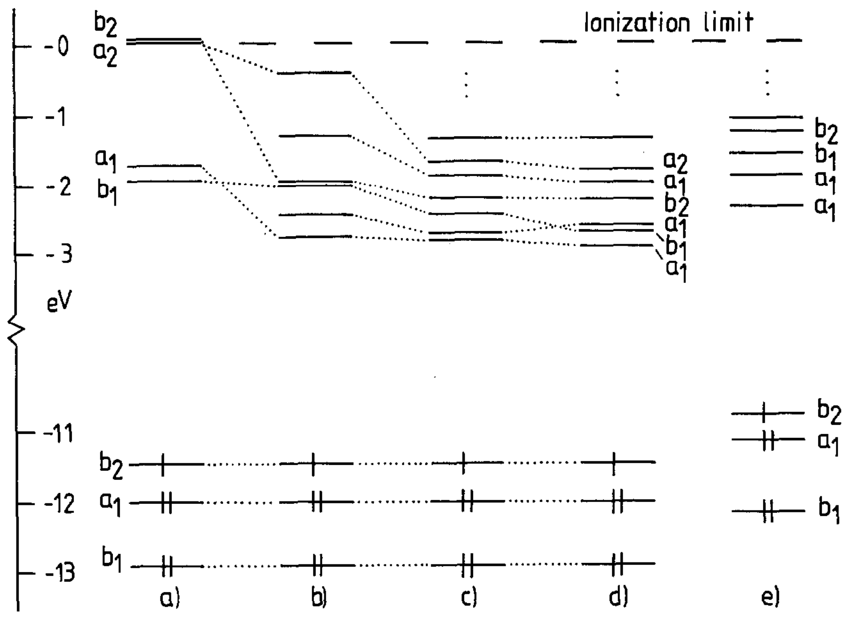


Fig. 2. The energy of orbitals which are doubly occupied in the ground-state and of singly excited orbitals under the condition of a singly occupied HOMO (in an open-shell singlet), calculated with different extended atomic silicon basis sets: (a) IVa (3*s*, 3*p*); (b) IVa (3*s*, 3*p*)+(4*s*, 4*p*); (c) IVa (3*s*, 3*p*)+(4*s*, 4*p*, 3*d*); (d) IVa (3*s*, 3*p*)+(4*s*, 4*p*, 2×3*d*); (e) IVb (3*s*, 3*p*)+(4*s*, 4*p*).

ionization limit. The fourth (b_2), lying just above it, shows two antibonding Si–Si interactions, as well as two antibonding Si–H contributions.

(2) The intermediate basis set (3s, 3p) + (4s, 4p)

Extending the valence basis set for the description of the excited MOs by including the silicon 4*s* and 4*p* atomic pseudo-orbitals lowers the energy of several of them by 1–2 eV, whereas others remain almost unchanged. In addition, new MOs are generated which are represented mainly by atomic orbitals of the principal quantum number 4 (Fig. 2b).

The lowest excited MO now has a_1 symmetry; its energy having decreased by 1 eV. It is predominantly a combination, with approximately equal weights, of the 3*s* and 4*s* AOs of the silicon atoms. This MO is stabilized by its decreased antibonding nature with respect to the SiH bonds, as well as by its diffuseness in the Si–Si antibonding region (Fig. 1). The second MO, which is only slightly higher in energy than the former, also has a_1 symmetry. This MO does not appear when the minimal basis set is used, because it is an almost pure 4*s* AO located at the central silicon atom. The third orbital is the valence b_1 MO, which is nearly unaffected by the inclusion of the additional basis functions and so remains unchanged in energy. The next MO, which has b_2 symmetry, behaves quite differently. This Si–Si antibonding $3p_y$–$3s$ MO is stabilized to the extent of 2 eV by bonding between the 4*s* AOs on the terminal silicon atoms and the $3p_y$ AO of the central silicon atom. There are several other excited MOs; these need not be discussed, except for the ninth which has a_2 symmetry. Within the minimal basis set, this MO could only be a combination of

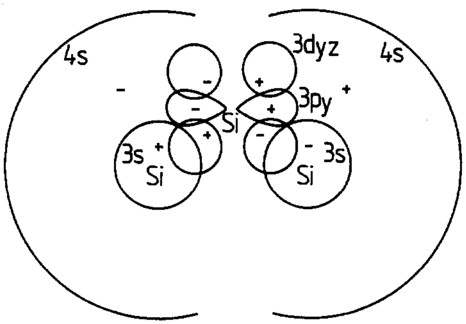


Fig. 3. The stabilization of the SiSi $3s$–$3p_y$ antibonding b_2 MO by the admixture of $4s$ (Section (2)) and of $3d_{yz}$ (Section (3)) in trisilane.

$3p_x$ AOs, but now it has been converted to a $4p_x$ MO. As a result of its larger extension, it is stabilized by decreased SiH antibonding, but only to a relatively minor extent.

(3) The extended basis set (3s, 3p) + (4s, 4p, 3d)

The much discussed involvement of d orbitals in excited MOs deserves special discussion. The $3d$ AOs have no radial nodes, in contrast to the $4s$ and $4p$ pseudo-AOs, each of which has one. Thus, one exponential parameter is sufficient for the description of the radial behaviour of the $3d$ AOs, provided that their size is assumed to be the same in all of the excited MOs. Several of the excited MOs which were discussed in the preceding section are almost unchanged by their inclusion, but others are stabilized to the substantial extent of more than 1 eV, as a result of the combination of $3d$ with $4s$ and/or $4p$, as well as by bonding with the hydrogen AOs.

The lowest excited MO is still the a_1, which contains an insignificant d-contribution and is consequently unchanged in energy (Fig. 2c). The second is the Rydberg orbital previously discussed. The predominance of the $4s$ AO on the central silicon atom is increased, because the required slight ovoid distortion is now accomplished entirely by an admixture of $d_{y^2-z^2}$, leading to a stabilization of 0.3 eV. The third excited MO is again the b_1 orbital; upon the addition of $3d$ AOs to the extended basis set, it increases its "Rydberg character" *, and thus lowers its energy by 0.4 eV. The fourth MO (b_2) is stabilized by an interesting effect: The $3p_y$ AO, contaminated with d_{yz}, on the central silicon atom is bent away from the terminal silicon atoms, as can be seen in Fig. 3. Thus the antibonding character of $3p_y$–$3s$ is reduced but the bonding character of $3p_y$–$4s$ is scarcely affected by this interaction, because of the diffuseness of the $4s$ AOs. The most interesting of the higher MOs is the sixth, which has a_2 symmetry. It is stabilized by 1.2 eV when d AOs are included, the main contribution coming from the d_{xy} AO on the central silicon atom, which takes up an antibonding relation to the $4p_x$ AOs on the terminal silicon atoms in order to stabilize four Si–H antibonding regions. The comparatively small

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* As suggested by Sandorfy [9], we here use the term "Rydberg character" more loosely, to describe the effect of including any AO, whether or not of higher principal quantum number, which makes an excited MO more diffuse.

contribution of d_{xy} on the terminal silicon atoms shows that d–d bonding in the Si–Si bonds is negligibly weak.

(4) The variable size of the d orbitals

One general result of the calculations described in the preceding section was seen to be the varying importance of diffuse $4s$, $4p$ and $3d$ AOs, relative to the combinations of $3s$ and $3p$ AOs with those of the hydrogen atoms. A further general result is the widely varying ratio between the expansion coefficients of $3s$ and $4s$ as well as those of $3p$ and $4p$ in different excited MOs. Consequently, the assignment of a common size to the d AOs in different MOs may lead to a poor description of the effect of d orbitals. When d orbitals are used as polarization functions in doubly-occupied ground-state MOs, the radial exponent for silicon is commonly assigned a value between 0.35 and 0.45. On the other hand, the value of the radial exponent for an excited d AO on a free silicon atom is found to be 0.03. Both of these boundary values can be exceeded when polar bonds are involved.

In extending the d-AO basis set, we rely on the experience that, whereas the d orbitals of the central silicon atom contribute significantly to the lower excited MOs, the effect of those of the terminal silicon atoms is negligibly small. Thus, the use of two d sets with the radial exponents of 0.03 and 0.10 is only justified on the central silicon atom. The $4s$ and $4p$ AOs are used as described in the preceding section.

The lowest excited MO is still the a_1 orbital. Even when two d sets are included, the d contribution to this MO is small; it is, therefore, only slightly stabilized with respect to its representation in the preceding section. The second excited MO is now that with b_1 symmetry. This was described as a $3p$–$4p$ valence-Rydberg combination, containing a slight d contribution (section (3)). This MO makes better use of the d-AO contraction, losing its $4p$ character and becoming a $3p$–$3d$ combination with roughly equal weights; its stabilization energy is 0.3 eV with respect to the energy cited in section (3). The other lower-lying excited MOs, such as a_1, b_2 and a_2, make no essential use of the additional contracted d-AOs and are therefore stabilized by no more than 1–2 kcal/mol (Fig. 2d).

The variable size of d orbitals is reminiscent of the nephelauxetic effect in transition metal complexes, i.e. the increasing size of d orbitals when going from a free metal cation to a complex [10]. The effect of the variable size of d orbitals in different excited molecular orbitals can be regarded as a nephelelattotic effect *: The size of a d orbital in an MO decreases below that in the free atom, in order to combine optimally with the valence AOs of the adjacent atoms.

The effect of methylation of trisilane

The experience gained by the calculations on trisilane, with the increasingly large basis sets reported in the preceding section, can be summarized as follows: (a) The basis set ($3s$, $3p$)+($4s$, $4p$) is sufficient for the assignment of the lowest excited states; (b) The singly-occupied orbitals of the excited states are localized, for the most part, on the central silicon atom. Therefore, in investigating the effect of methylation on the nature of the excited states of permethylated trisilane, we felt

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* From: nephele = cloud, elattoun = to reduce.

justified in restricting our calculations to the dimethylated trisilane (IVb), in which only the two hydrogen atoms at the central silicon atom are replaced by two methyl groups.

Methylation destabilizes the doubly-occupied orbitals by 0.7 eV and the singly-occupied excited orbitals by about 0.5 eV, so that the excitation energies are decreased by 0.2 eV (Fig. 2e). The shape and energetic ordering of the excited orbitals are almost the same as those of trisilane (IVa). The experimentally determined Si–Si bond dissociation energies [11] in Si_2H_5–SiH_3 (297 kJ/mol), SiH_3–SiH_2 (201 kJ/mol) and SiH_3–SiH_3 (309 kJ/mol) provide a value of 188 kJ/mol) for the ground-state decomposition energy of trisilane to disilane and silylene. This is in good agreement with the calculated value, corrected for zero-point vibrational energy as described below, of 192 kJ/mol (Fig. 4). Methylation is now recognized to increase the Si–Si bond energy in polysilanes [11]. This feature is reproduced in our calculations, the decomposition energy increasing by 21 kJ/mol on going from IVa to IVb.

The effect of methylation of silicon hydrides can quickly be summarized: The bond energy of the silicon–silicon bond is increased and the transition energies are decreased, but both effects are slight. Its overall effect is hardly sufficient to account for the observed differences in reactivity between silanes and permethylsilanes, which must therefore be ascribed to kinetic factors, perhaps steric hindrance to attack by external reagents.

The excitation energies and the orbital symmetry analysis

The lowest electronic transition energy for the dimethylated trisilane using the $(3s, 3p)+(4s, 4p)$ silicon basis set, was calculated to be 8.4 eV. The quasi-continuum of states which starts at this energy is much denser than suggested by Fig. 2, which includes only those states in which an electron has been promoted from the HOMO (b_2). A second singlet ladder exists, in which the excitation is from the totally symmetric SiSi bonding orbital (a_1) lying just below the HOMO. These states are shifted upwards by only 0.4 eV with respect to those shown in Fig. 2.

In order to obtain a more realistic energy for the onset of the quasi-continuum, two corrections to the calculated transition energy were made. The first is the zero-point energy correction. Several molecular parameters in the reactant molecule are absent in its photolysis fragments. These are: one SiSi bond, one SiSiSi angle, and four CSiSi angles. Fundamental frequencies of 400, 200, and 200 cm^{-1}, respectively, were assumed for the vibrations associated with these degrees of freedom, leading to a zero-point correction of 0.1 eV. A second correction takes into account the fact that electronic transitions can occur between the classical turning points. The steep descent of the excited state energy surface, which is schematically depicted in Fig. 4, reduces the onset of the transitions drastically. The resultant value, 7.1 eV, is in reasonable agreement with the observed value of 6.5 eV for permethylated silanes [12].

The correlation diagram for the photolytic fragmentation of trisilane, with the energies adjusted as described above, is shown in Fig. 5. The vertical deactivation energy of $^1B_2$ silylene is 0.6 eV; the corresponding value for dimethylsilylene is 1.2 eV. All in all, Fig. 5 should provide an adequate basis for the qualitative description of the photolysis of permethylated trisilanes as well. It resembles Ramsey's [1]

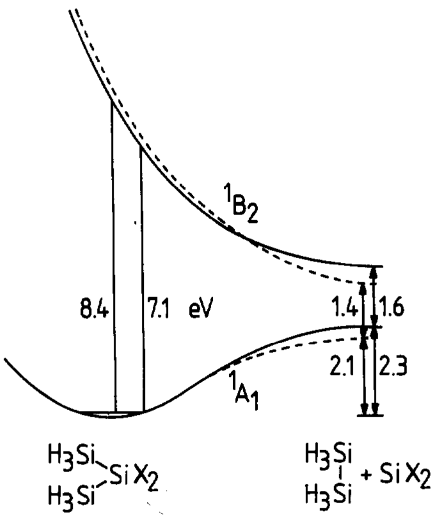

Fig. 4. A schematic representation of the energy surface for the ground- and lowest excited singlet states for the fragmentation of trisilane to disilane and silylene. X = H: dotted lines; X = CH_3: solid lines (1 eV = 96.4 kJ/mol).

correlation diagram *, in that the photolysis is "allowed" on the open-shell singlet surface. His conclusion that *d* orbitals are not involved in the low-lying excited states is also borne out. However, the singly occupied a_1 orbital of trisilane, which correlates with the lone-pair orbital of sylilene, is not the σ^* valence orbital, as he supposed, but a diffuse, loosely bonding, orbital with a large 4*s* component. Furthermore, the lowest excited orbital of disilane is a $4s(a_1')$ MO, and not the $\sigma^*(a_1'')$ valence MO, which would correlate with a b_2 MO of trisilane; the lowest such orbital of disilane is the fourth one up, 0.5 eV above the lowest excited MO, and composed mainly of the 4*s* AOs of the silicon atoms.

As indicated in Fig. 5, the lowest vertical excitation energies in trisilane and disilane are nearly identical, and much lower than that of the first member of the series, SiH_4, 10.2 eV. Since the latter molecule has no SiSi bond, the excitation must come from an SiH bonding orbital, at considerably greater energetic cost.

It is noteworthy that the energetic ordering of the singly occupied orbitals of silylene is reversed in the triplet: $3p_y(b_2) < n(a_1)$. The energetic separation of 0.5 eV is decreased to zero in the case of dimethylsilylene. A further point, of direct relevance to the reaction under study, is the expectation that the photochemical reaction in the parent system should stay on the singlet surface, since reactive intersystem crossing to $^3SiH_2$ would require a totally symmetric spin–orbit coupling term, which does not exist in C_{2v} [5] **. Direct crossing to the ground-state singlet

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* Our axis convention differs from that adopted by Ramsey [1], so the symmetry labels b_1 and b_2 are interchanged.

** This restriction might, however, be relaxed by spin-vibronic coupling in the case of methylated reactants.

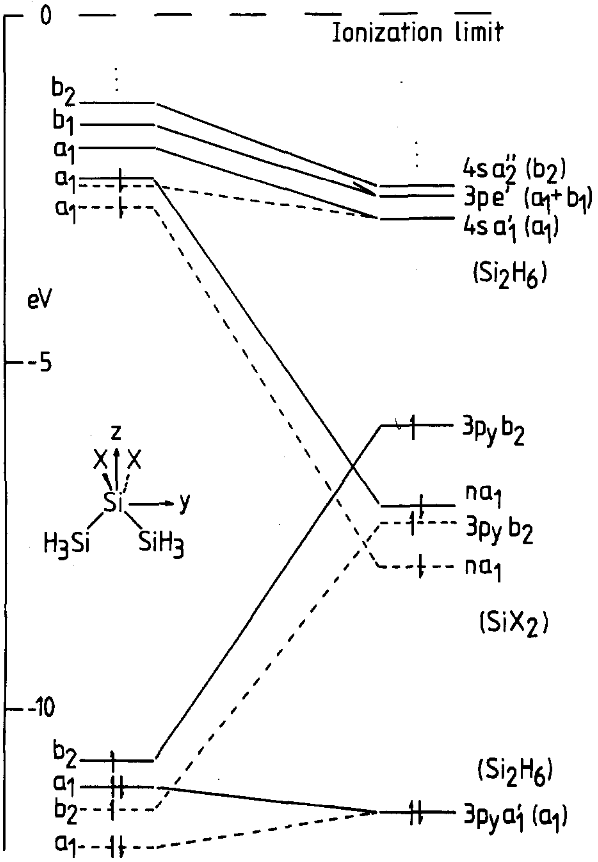

Fig. 5. The orbital correlation diagram (C_{2v}) for the photolytic fragmentation of trisilane to disilane and silylene ($^1B_2$). X = H: dotted lines; X = CH_3: solid lines. The orbitals of disilane are labelled in D_{3h} (eclipsed conformation); their irreducible representations in the subgroup C_{2v} are given in parenthesis.

should also be difficult, particularly in cyclic molecules like I, because of the necessity for an energetically costly in-plane (b_2) distortion [3b,5].

Acknowledgements

The authors thank Professors E. Hengge and R. West for stimulating discussions and correspondence. We are indebted to the Fonds zur Förderung der wissenschaftlichen Forschung (Project 4917) and to the Fund for the Promotion of Research at the Technion for financial support. The computer time made available by the Rechenzentrum der Universität Graz (UNIVAC 1100/81) is gratefully acknowledged.

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