Ser. C, **266**, 507 (1968).
(8) J. Heicklen, *J. Phys. Chem.*, **70**, 477 (1966).
(9) F. Gozzo and G. Camaggi, *Chim. Ind. (Milan)*, **50**, 197 (1968).
(10) T. Johnston and J. Heicklen, *J. Chem. Phys.*, **47**, 475 (1967).

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Vacuum-Ultraviolet Photolysis of $C_2(CH_3)_6$, $Si_2(CH_3)_6$, and $(CH_3)_3CSi(CH_3)_3$. Evidence for an Unsaturated Silicon-Carbon Linkage

Sir:

We have initiated studies on the vacuum-ultraviolet photochemistry of gas phase peralkylated silanes and their hydrocarbon analogues. While at this point only relative yields of fragments containing 17 atoms or less are available, the paucity of data of this type and the current interest in silicon-containing reactive intermediates prompt us to communicate our preliminary results.

Hexamethyldisilane, hexamethylethane, and *tert*-butyltrimethylsilane[1] were photolyzed using a xenon resonance lamp (147 nm) under a variety of conditions. Each of the three compounds was photolyzed as a pure gas at its vapor pressure (approximately 10 Torr in each case) and in the presence of 10% oxygen. Additionally, hexamethylethane was photolyzed as part of a mixture (containing O_2 and CF_4) over the range of pressures 1-760 Torr. All photolyses were terminated after $\leq 0.1\%$ conversion of parent to product.

Table I summarizes product yields in each experiment. In samples in which oxygen was added, products whose yield decreased to zero or near zero are interpreted as arising from bimolecular reactions involving at least one free radical intermediate.[2] Products remaining in scavenged systems are interpreted as arising from unimolecular reactions, either as direct products of the photolysis or as secondary decomposition products from species containing excess internal energy.

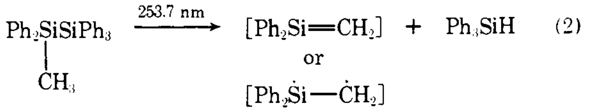
Our primary motivation in this work was to compare the probability of developing a silicon-carbon double bond or its equivalent relative to that of forming a carbon-carbon double bond under similar conditions.

In the vacuum-ultraviolet photolysis of alkanes containing more than one kind of hydrogen, the elimination of alkanes by the transfer of a primary hydrogen, particularly via a four-centered transition state as compared to a three-center transition state, is of low probability.[3] Nonetheless, it can be seen from Table I that the production of isobutane from hexamethylethane is of considerable importance. The addition of oxygen to remove radical sources of isobutane leaves a significant yield of this hydrogen transfer product. Apparently the removal of other reaction pathways and the large number of equivalent hydrogens available for transfer enhances the importance of this reaction as an exit path from the excited state of hexamethylethane.

The only similar reactions reported for the photochemistry of silicon containing compounds are:

$$CH_3SiH_3 \xrightarrow[\text{or 123 nm}]{\text{147 nm}} [\dot{C}H_2\dot{S}iH_2] + H_2 \qquad (1)$$

and



$$\underset{\displaystyle CH_3}{\overset{}{Ph_2Si}}SiPh_3 \xrightarrow{\text{253.7 nm}} \begin{matrix}[Ph_2Si{=}CH_2] \\ \text{or} \\ [Ph_2\dot{S}i{-}\dot{C}H_2]\end{matrix} + Ph_3SiH \qquad (2)$$

In their discussion of reaction 1, Obi, et al., refer to $[CH_2SiH_2]$ as a diradical rather than assigning olefinic character to the species.[4] The reactive intermediate produced from pentaphenylmethyldisilane on the other hand, was described as a silicon-carbon double bond or its equivalent which then undergoes rapid addition to methanol-d_1.[5]

The photolysis of hexamethyldisilane in the presence of oxygen clearly establishes the importance of a hydrogen transfer reaction, as trimethylsilane is the most important stable fragmentation product. The absence of the silicon analogue to isobutene is not surprising in view of its demonstrated high reactivity.[6] While our work does not allow us to comment on the electronic configuration of the "unsaturated" carbon-silicon moiety, it does allow for a comparison of the probability of its production relative to the formation of a carbon-carbon double bond.

Photolyzing *tert*-butyltrimethylsilane provides an opportunity to form an unsaturated cofragment, isobutene, when hydrogen transfer occurs to form trimethylsilane. This is formally the reverse of the well-known hydrosilation reaction.[7] At the same time there is an opportunity to form isobutane, a process observed to give an unsaturated cofragment in the photolysis of hexamethylethane, in such a way that the cofragment contains silicon. These two possibilities may be represented as:

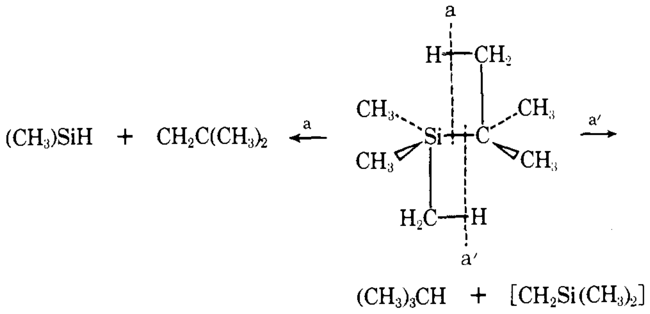


Table I. Relative Quantum Yields of Several Fragments Produced by the Photolysis of $C_2(CH_3)_6$, $Si_2(CH_3)_6$, and $(CH_3)_3CSi(CH_3)_3$

Product/system	$C_2(CH_3)_6$[a]	$C_2(CH_3)_6 + O_2$	$Si_2(CH_3)_6$	$Si_2(CH_3)_6 + O_2$	$(CH_3)_3CSi(CH_3)_3$	$CH_3CSi(CH_3)_3 + O_2$
CH_4	0.46	0.47	0.12	0.21	0.55	0.61
C_2H_6	0.50	—	0.28	—	0.4	0.04
C_3H_6	0.61	1.2	—	—	0.09	0.08
i-C_4H_{10}	1.0	1.0	—	—	1.0	1.0
$(CH_3)_3SiH$	—	—	1.0	1.0	0.6	0.48
i-C_4H_8	2.0	3.3	—	—	1.3	1.04
neo-C_5H_{10}	0.4	—	—	—	0.18	—
$Si(CH_3)_4$	—	—	0.33	—	0.10	—
Yields given relative to:	i-C_4H_{10}	i-C_4H_{10}	$(CH_3)_3SiH$	$(CH_3)_3SiH$	i-C_4H_{10}	i-C_4H_{10}

[a] Traces of C_2H_4, C_2H_2, C_3H_8, and C_3H_4 were also observed, yields $<0.10 \times i$-C_4H_{10}.

The relative probabilities of reaction (a) to reaction (a′) should be given directly by the ratio of trimethylsilane to isobutane obtained when *tert*-butyltrimethylsilane is photolyzed in the presence of oxygen. No alternative intramolecular mechanism for the formation of either product appears possible. Table I shows that the yield of isobutane is approximately twice that of trimethylsilane. This strongly suggests that reaction (a′) predominates over reaction (a).

While the driving force for the production of Si-C unsaturation is not probed directly by our experiments, there is clear evidence that this species must be the single most important even electron product in the photolysis of $(CH_3)_3SiC(CH_3)_3$. i-C_4H_{10}, the saturated cofragment of $(CH_3)_2SiCH_2$, is produced in yield equal to that of i-C_4H_8, and in other examples where the ratio of saturation to unsaturation can be compared (Table I) the unsaturated product yield is equal to two-three times that of its saturated cofragment. Thus, we conclude that the failure to isolate $(CH_3)_2SiCH_2$ must be due to its reactivity rather than some intrinsic barrier to its formation.

Similar conclusions have been reached based on pyrolysis studies.[8,9]

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References and Notes

(1) (a) Hexamethyldisilane (Petrarch) and hexamethylethane (Aldrich) were obtained commercially and used without further purification. *tert*-Butyltrimethylsilane[1b] was prepared in 90% yield by the reaction of methylmagnesium bromide on *tert*-butyldimethylchlorosilane. The sample used for photolysis was purified by preparative gas chromatography. (b) L. J. Taylor, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 981 (1947).
(2) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, N.Y., 1966, p 598.
(3) P. Ausloos and S. G. Lias in "Chemical Spectroscopy and Photochemistry in the Vacuum-Ultraviolet", Sandorfy, Ausloos, Robin, Ed., D. Reidel Publishing Co., Boston, Mass., 1974, p 465.
(4) K. Obi, A. Clement, H. E. Gunning, and O. P. Strausz, *J. Am. Chem. Soc.*, **91**, 1622 (1969).
(5) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Am. Chem. Soc.*, **94**, 7926 (1972).
(6) R. D. Bush, C. M. Golino, G. D. Homer, and L. H. Sommer, *J. Organomet. Chem.*, **80**, 37 (1974).
(7) E. A. V. Ebsworth in "Bond to Carbon", Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968.
(8) R. Walsh, *J. Organomet. Chem.*, **38**, 245 (1972).
(9) R. A. Jackson, *Chem. Soc., Spec. Pub.*, **No. 24**, 295 (1970).

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Theoretical Model for the 4-Fe Active Sites in Oxidized Ferredoxin and Reduced "High-Potential" Proteins. Electronic Structure of the Analogue $[Fe_4S^*_4(SCH_3)_4]^{2-}$

Sir:

Active sites of the 1-, 2-, and 4-Fe types are now established in Fe-S redox proteins[1,2] and synthetic analogues for each have been characterized.[3,4] For the 4-Fe sites $[Fe_4S^*_4(S\text{-}Cys)_4]$ in ferredoxin (Fd) and high-potential (HP) proteins, whose structures are known,[2,5,6] the protein-analogue stereochemical[7] and electronic[8] correlation $Fd_{red} \equiv HP_{ox} \equiv [Fe_4S^*_4(SR)_4]^{2-}$ is well established. Electronic structures of these clusters have previously been described by a qualitative symmetry-factored MO model[7a,9] Here we present preliminary electronic structural results for the simplest known analogue,[7a] $[Fe_4S^*_4(SCH_3)_4]^{2-}$, obtained by the recently developed SCF-Xα-SW method.[10,11]

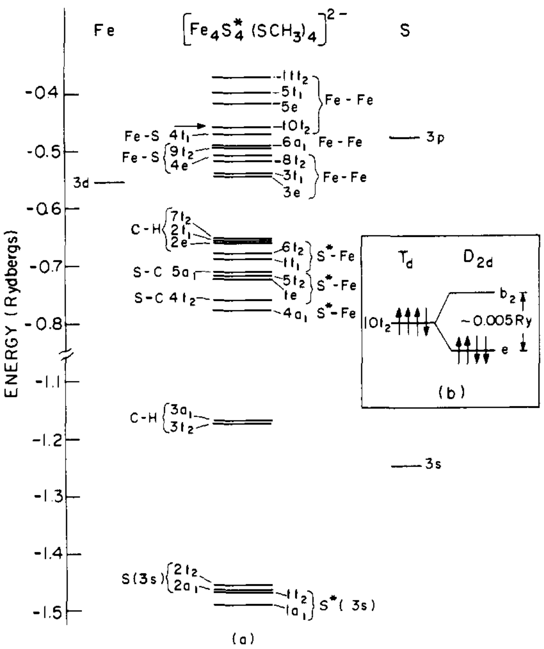

Figure 1. (a) SCF-Xα-SW orbital energies of $[Fe_4S^*_4(SCH_3)_4]^{2-}$ in T_d symmetry and (b) splitting of highest occupied orbital ($10t_2$) in D_{2d} symmetry. Fe and S free-atom energy levels obtained by SCF-Xα method.

In the present model overall perfect T_d analogue symmetry was imposed (Fe-S*, 2.27; Fe-S, 2.25; S-C, 1.83;[7] and C-H, 1.12 Å) and the actual D_{2d} $Fe_4S^*_4S_4$ cluster symmetry[7] considered a perturbation. The energies of the highest occupied and first few unoccupied orbitals are shown in Figure 1a,[12] from which emerge the following points. (1) The number and character of occupied orbitals suggest that each Fe atom has the effective fractional valence state $Fe^{2.5+}$; discrete integral valence states are not spectroscopically detectable in $[Fe_4S^*_4(SR)_4]^{2-}$.[13] (2) The electronic inequivalence of S* and S atoms is emphasized by the findings that the charge localized in sulfur atomic regions averages 54.3 and 36.7% in the S*-Fe and Fe-S orbitals, respectively, a behavior attributable to the influence of the electropositive metal in the structural fragments $S^*\text{-}Fe_3$ and Fe-S-C. (3) The band of levels between −0.55 and −0.35 Ry corresponds to orbitals ("Fe-Fe") predominantly Fe 3d-like in character and orbitals ("Fe-S") with almost equal amounts of Fe-3d and S-3p character. However, the Fe-Fe levels are not purely metallic in nature, as compared with the orbitals of an isolated tetrahedral Fe_4 cluster having the same Fe-Fe interatomic distance. The Fe-Fe orbitals in $[Fe_4S^*_4(SCH_3)_4]^{2-}$ have S 3p-like components ranging from only 3% S and 1% S* in the most metallic occupied bonding orbital (3e) to as much as 25% S and 12% S* in the least metallic unoccupied antibonding orbital (5e). Therefore, the Fe-S interactions are quite covalent. This is in contrast to earlier SCF-Xα-SW calculations for the simpler prototype cluster, $[Fe_4S^*_4(SH)_4]^{2-}$, which gave results suggesting an almost purely metallic 3d-like band of levels separated in energy well above two bands of almost pure S (3p) and S* (3p) character.[14] However, these earlier results are unphysical because Fe-Fe antibonding orbitals holding 12 electrons were occupied in place of two S*-Fe bonding orbitals of t_2 symmetry, whose nearly degenerate eigenvalues were inadvertently missed in the computational procedure. Recent (unpublished) calculations for $[Fe_4S^*_4(SH)_4]^{2-}$, with the proper occupancy, are qualita-