Journal of Organometallic Chemistry, 67 (1974) C67—C71

Preliminary communication

ELECTRONIC TRANSITIONS OF POLYSILANES AND THEIR PHOTOCHEMISTRY

BRIAN G. RAMSEY

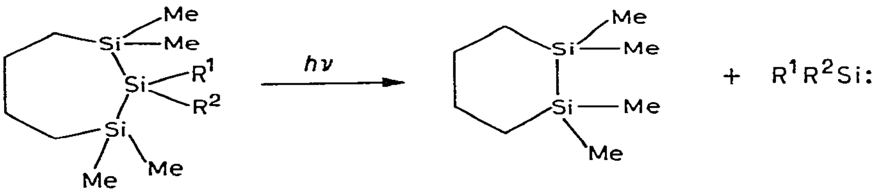
Department of Chemistry, California State University, San Francisco, Calif. 94132 (U.S.A.)

(Received November 1st, 1973)

Summary

Application of Woodward—Hoffmann selection rules to the photolysis of polysilanes requires that the electron transition be assigned to $\sigma \rightarrow \sigma^*$ rather than previously suggested $\sigma \rightarrow \pi(3d$ or $4p)$.

A simple but important relationship exists between the assignment of the first electronic transition in polysilanes and their photolysis products. Both linear and nonlinear [1], cyclic polysilanes [2] and the cyclic trisilanes such as I, photolyze to yield divalent silicon intermediates R_2Si:. This photochemical reaction is exemplified by eq. 1 for the photolysis of I [3].



(1)

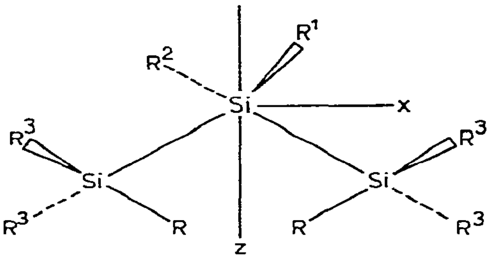
(I) (II) (III)

Permethylated polysilanes, $Me[SiMe_2]_nMe$, in their UV spectra exhibit an intense transition which rapidly moves from 192 nm ($n = 2$) to longer wavelengths as n increases [4], for example λ_{max} 250 nm (ϵ 18400) ($n = 5$). Similar transitions have been observed in the spectra of polygermanes [5], polystannanes [6], and diplumbanes [7].

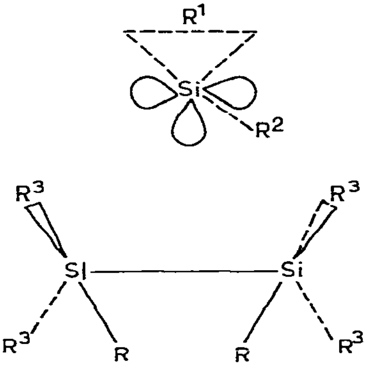
Based on a linear correlation of transition energy with simple Hückel π orbital energies, we and others originally suggested [8] that these polysilane (as well as analogous polygermane and -stannane) transitions were $\sigma(\text{Si—Si}) \rightarrow \pi$ in which the electron was promoted from a Si—Si bond σ orbital to vacant

π orbitals expressed as linear combinations of Si 3d (or 4p) atomic orbitals. More recent measurements of the ionization potentials of a series of polysilanes by Pitt [9], and Bock and Ensslin [10] now suggest σ(Si—Si) → σ^* (Si—Si) as an equally satisfactory assignment, in which σ and σ^* may be expressed as a linear combination of localized Si—Si bond orbitals. Molecular orbital calculations assuming a $\sigma \rightarrow \sigma^*$ transition and based on the Sandorfy C method have also appeared [6]. Obviously, the nature of the 1st UV transition in catenated Group IV metalloids is of widespread interest and controversy.

If we at this point consider a trisilane with local C_{2v} symmetry such as IV, the $\sigma \rightarrow \pi$ transition has the symmetry assignment ${}^1A_1 \rightarrow {}^1A_2$ or ${}^1A_1 \rightarrow {}^1B_2$ whereas the $\sigma \rightarrow \sigma^*$ transition is ${}^1A_1 \rightarrow {}^1B_1$.



(IV)



(V)

If we further make the reasonable assumption that the photochemical reaction of IV proceeds to V with concerted formation of the new Si—Si bond and the divalent silicon, and therefore with conservation of orbital symmetry, the Woodward—Hoffmann selection rules may be applied [11].

In Fig. 1, we see the consequence of assuming a $\sigma \rightarrow \sigma^*$ transition in the construction of a molecular orbital correlation diagram from a linear combination of bonding and antibonding Si—Si σ orbitals for the photolysis of IV (or reaction 1). We note that the excited state half filled orbitals a_1 and b_1 of the trisilane correlate smoothly with the sp^2 (a_1) and p_x (b_1) orbitals of the silene, R^1R^2Si:. Since in this simple orbital approach the a_1 orbital decrease in energy is comparable to the b_1 orbital increase in energy, we would expect that the rearrangement of the ${}^1B_1$ excited state of I to the lowest excited state ${}^1B_1$ of the silene III, and ground state of II, to be an energetically favorable process with a low activation energy barrier. Note that if the photochemical reaction proceeds through a triplet state, the silane I triplet state ${}^3B_1$ then correlates directly with the ground state of the triplet silene, ${}^3B_1$. Thus the initial assumption of a $\sigma \rightarrow \sigma^*$ transition in I is compatable with the observed photochemistry.

In Fig. 2, a Woodward—Hoffmann diagram is constructed for a photochemical reaction proceeding through a $\sigma \rightarrow \pi d$ excited state. There are two sets of d orbitals (d_{xy} and d_{yz}) which might be used on the basis of symmetry alone

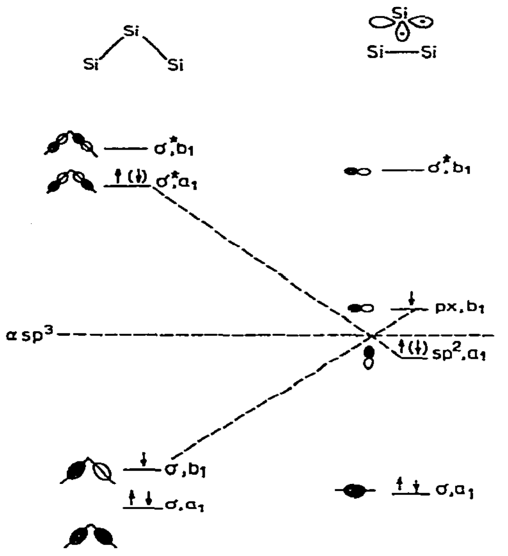


Fig. 1. A simple molecular orbital correlation diagram for reaction 1 based on the assumption that the lowest energy vacant orbitals of the polysilane are σ^*.

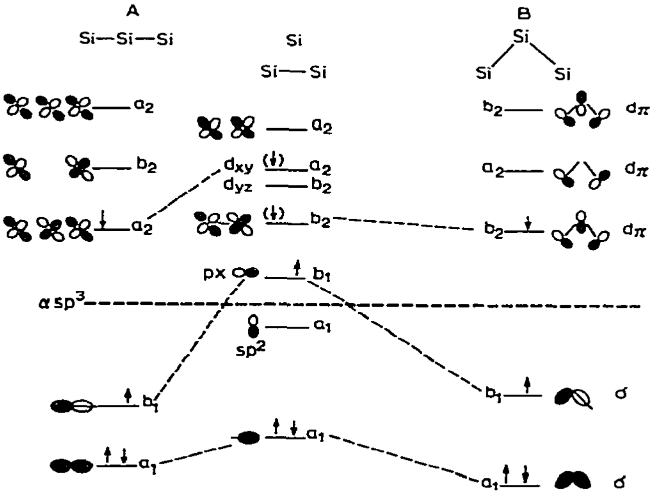


Fig. 2. A simple molecular orbital correlation diagram for reaction 1 based on the assumption that the lowest energy vacant orbitals of the polysilane are d_π (or p_π). A and B are linear combinations of Si d orbitals for limiting cases of linear and bent molecules. B is shown in a bird's eye view.

to construct "π" out of plane delocalized orbitals. These are shown in Fig. 2 on the basis of limiting geometries for linear and bent (bird's eye view) molecules. Here we realize that regardless of whether in a $\sigma \rightarrow \pi d$ excited state the electron is promoted to an orbital of b_2 or a_2 symmetry, the energy of the orbital containing the promoted electron increases during the rearrangement to disilane and silene. It is clear then that a photochemical reaction such as (I) proceeding through rearrangement of a $\sigma \rightarrow \pi$ excited state ($^1B_2$ or $^1A_2$) must be, by several electron volts, an extremely unfavorable process energetically. In fact in the case of a $^1B_2$ excited state a $[(R_3Si\dot{-}SiR_3)^{(1)}R_2Si^{\dot{+}}]$ complex intermediate would be predicted which would require a subsequent electron transfer reaction to produce $R_3SiSi_3R + R_2Si$:.

On the basis of these applications of the Woodward—Hoffmann rules, the ease with which reaction (1) takes place requires the assignment of the long wavelength polysilane transitions to σ(Si=Si)$\rightarrow \sigma^*$(Si—Si) as opposed to a $\sigma \rightarrow \pi$ assignment. Of course if the $\sigma \rightarrow \sigma^*$ assignment is accepted "a priori" Fig. 1 provides a mechanistic interpretation of the photochemical reaction.

Application of Woodward—Hoffmann rules in an analogous manner to molecular orbitals generated from localized σ bonding and antibonding orbitals, and from Si 3*d* (or 4*p*) atomic orbitals for the cyclic system $(Me_2Si)_n$ (n = 4, 5, or 6) and for $(Me_3Si)_4Si$ also produces completely analogous correlation diagrams, with the same conclusions, i.e. that the reactions must proceed through σ^* excited state. Thus, photolysis of $(Me_3Si)_4Si$ is predicted to yield $(Me_3Si)_2Si$:, and the reported [2] failure of cyclo-$(Me_2Si)_4$ to yield Me_2Si: and cyclo-$(Me_2Si)_3$ should be attributed to the instability of cyclohexamethyltrisilane rather than any inherent symmetry restrictions on the reaction. Indeed, the observation [2] of small amounts of $H[Si(Me)_2]_2H$ from the photolysis of cyclo-$[(Me)_2Si]_4$ suggests formation of cyclo-$[(Me)_2Si]_3$ which then opens to $\cdot SiMe_2SiMe_2SiMe_2\cdot$.

The questions of whether the first ionization of alkanes is from a C—C orbital of essentially σ symmetry or from C—H orbitals of π symmetry and along with it the assignment of the first UV transition in saturated alkanes also have not been resolved [12]. The failure of alkanes to undergo a photochemical reaction analogous to that of the silenes, to form carbenes R_2C:, would seem to support assignment of the 1st UV absorption maxima in the spectra of alkanes to a transition originating from delocalized C-H_2 orbitals of π symmetry, since the photochemical reaction to form carbenes analogous to (I) is then prohibited by arguments such as those applied to the $\sigma \rightarrow \pi$ transition of silanes in Fig. 2. If the first alkane transition originates from the C—C σ framework, $\sigma \rightarrow \sigma^*$, there would appear to be no reason not to observe alkane photolysis, on vacuum UV irradiation, with R_2C: carbene formation.

To summarize, the application of Woodward—Hoffmann symmetry selection rules to the photolysis of polysilanes to form divalent silicon intermediates (silenes), R_2Si:, requires that these reactions proceed through σ^* excited states*, and supports the assignment of the controversial long wavelength transition in polysilanes, polygermanes, and polystannanes to $\sigma \rightarrow \sigma^*$ rather than $\sigma \rightarrow \pi$. We believe this to be the first time the Woodward—Hoffmann rules have been applied to the photochemistry of organometalloids, and the first time the results of a photochemical reaction have been utilized to support the assignment of an electronic transition.

---

*The possibility or even probability that the σ^* orbitals in the excited states may include important contributions from appropriate symmetry orbitals derived from in plane Si d_{xz} orbitals is not to be excluded.

References

1 M. Ishikawa and M. Kumada, Chem. Commun.,(1971) 489; J. Organometal. Chem., 42 (1972) 333.
2 M. Ishikawa and M. Kumada, J. Organometal. Chem., 42 (1972) 325.
3 H. Sakurai, Y. Kobayashi and N. Nakadaira, J. Amer. Chem. Soc., 93 (1971) 5272.
4 (a) H. Gilman and P.J. Morris, J. Organometal. Chem., 6 (1966) 102.
(b) M. Kumada and K. Tamao, Advan. Organometal. Chem., 6 (1966) 1 and leading references.
5 W. Drenth, J.G. Noltes, E.J. Bulten and H.M.J. Creemers, J. Organometal. Chem., 17 (1969) 173.
6 P.P. Shorygin, V.A. Petukhov, U.M. Nefedov, S.P. Kolisnikov and V.I. Shiryaev, Teor. Exp. Khim. Akad. Nauk. UKr. SSR, 2 (1966) 190.
7 W. Drenth, L.C. Willemsens, G.J.M. Van der Kerk and J.A. Vliegenthart, J. Organometal. Chem., 2 (1964) 279.
8 (a) B.G. Ramsey, Electronic Transitions in Organometalloids, Academic Press, New York, N.Y., 1969.
(b) C.G. Pitt, L.L. Jones and B.G. Ramsey, J. Amer. Chem. Soc., 89 (1967) 5471.
9 C.G. Pitt, M.M. Bursey and P.F. Rogerson, J. Amer. Chem. Soc., 92 (1970) 519.
10 H. Bock and W. Ensslin, Angew. Chem. Intern. Ed., 10 (1971) 404.
11 (a) R.B. Woodward and R. Hoffmann, J. Amer. Chem. Soc., 87 (1965) 395; 87 (1965) 2046; 87 (1965) 2511.
(b) R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Academic Press, 1970.
12 (a) J.N. Murrell and W. Schmidt, Faraday Trans II, (1972) 1709.
(b) W.A. Lathan, L.A. Curtis and J.A. Pople, Mol. Phys., 22 (1971) 1081.
(c) A.D. Baker, D. Belteridge, N.R. Kemp and R.E. Kirby, J. Mol. Struc., 8 (1971) 75.
(d) B. Naragan, Mol. Phys., 23 (1972) 281.