

coupling of electronic and nuclear motions, and other nuclear dynamic effects can be assumed to be negligible. It should be emphasized that the same fundamental basis governs the operation of both sets of symmetry rules and in this respect the two sets of rules are fundamentally similar.

The examples, given in section IV, show that Wigner–Witmer and Woodward–Hoffmann rules give equivalent results to the extent that *total* orbital symmetry can be useful but that the Woodward–Hoffmann rules can often provide a further distinction between possible reaction paths by considering *individual* orbital symmetries as well. The examples include cases where total symmetry is sufficient to analyze a reaction and

also cases where an examination of individual symmetries is required.

The hierarchy of symmetry control rests on the occurrence of energy barriers of different heights being encountered, along various reaction coordinates, corresponding to the degree of concordance or discordance of symmetry species from reactant to product wave function structures. The possible experimental observation of “forbidden” processes^{23,29–33} presages the need to emphasize that these different barrier heights do not control the reaction destiny in an absolute sense but only affect the various probabilities of reaction along different paths. However, for many purposes,¹⁴ this degree of reaction control is quite important.

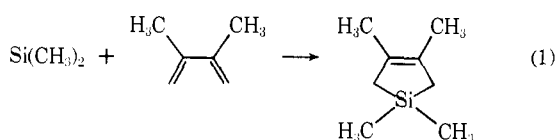
Ground Electronic State of Silylene¹

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Abstract: Silylene-³¹Si adds to 1,3-butadiene to give silacyclopent-3-ene-³¹Si. Studies using nitric oxide as a scavenger demonstrate that the reacting silylene is present as 80% triplet and 20% singlet, while studies using neon as a moderator prove that the ground electronic state of silylene is a singlet.

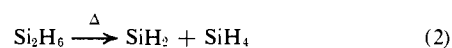
The chemistry of silylene and its derivatives has been the subject of several recent review articles.^{3–5} Ever since dimethylsilylene was formed by the reduction of dimethyldichlorosilane and trapped through the Si–H insertion process in the pioneering work of Skell and Goldstein,⁶ numerous investigations on reactions of various substituted silylenes have been performed.^{3–5} One such investigation which pertains to our study is the addition of dimethylsilylene to 2,3-dimethyl-1,3-butadiene.⁷



It was further established that conjugated dienes were more reactive toward dimethylsilylene than molecules with only one double bond.⁴ While studies such as these have provided a considerable amount of information about substituted silylenes, the knowledge about unsubstituted silylene, SiH₂, itself is rather limited.

Silylene has been successfully produced by two different methods: (i) the nuclear recoil technique which

was developed by Gaspar and coworkers,^{8–12} and (ii) the decomposition studies stemming from the pyrolysis and photolysis of compounds such as SiH₄ and Si₂H₆.^{13–17}



The only well-established silylene reaction to date is the insertion of SiH₂ into Si–H bonds.^{8,9,11–16}



The possible insertion of silylene into other types of bonds such as Si–Si bonds has also been suggested.^{11,15} On the other hand, it has been demonstrated that SiH₂ is inert toward C–H, C–C, and Si–C bonds.^{3–5} The predicted products from the silylene addition to olefins are substituted silacyclopropanes which have never been detected experimentally.^{9,18} Their absence can be explained by the instability of such highly

(8) P. P. Gaspar, B. D. Pate, and W. C. Eckelman, *J. Amer. Chem. Soc.*, **88**, 3878 (1966).

(9) P. P. Gaspar, S. A. Bock, and W. C. Eckelman, *J. Amer. Chem. Soc.*, **90**, 6914 (1968).

(10) P. P. Gaspar, S. A. Bock, and C. A. Levy, *Chem. Commun.*, 1317 (1968).

(11) P. P. Gaspar and P. Markusch, *Chem. Commun.*, 1331 (1970).

(12) P. P. Gaspar, P. Markusch, J. D. Holten III, and J. J. Frost, *J. Phys. Chem.*, **76**, 1352 (1972).

(13) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **87**, 179 (1965).

(14) J. H. Purnell and R. Walsh, *Proc. Roy. Soc., Ser. A*, **293**, 543 (1966).

(15) M. Bowrey and J. H. Purnell, *J. Amer. Chem. Soc.*, **92**, 2594 (1970).

(16) P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *Inorg. Chem.*, **9**, 1068 (1970).

(17) I. DuBois, G. Herzberg, and R. D. Verma, *J. Chem. Phys.*, **47**, 4262 (1967).

(18) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

(1) Preliminary information concerning this work was reported in, G. P. Gennaro, Y.-Y. Su, O. F. Zeck, S. H. Daniel, and Y.-N. Tang, *J. Chem. Soc., Chem. Commun.*, 637 (1973).

(2) Address correspondence to this author.

(3) I. M. T. Davidson, *Quart. Rev., Chem. Soc.*, **25**, 111 (1971).

(4) W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

(5) P. P. Gaspar and B. J. Herold in “Carbene Chemistry,” 2nd ed, W. Kirmse, Ed., Academic Press, New York, N. Y., 1971.

(6) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

(7) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968).

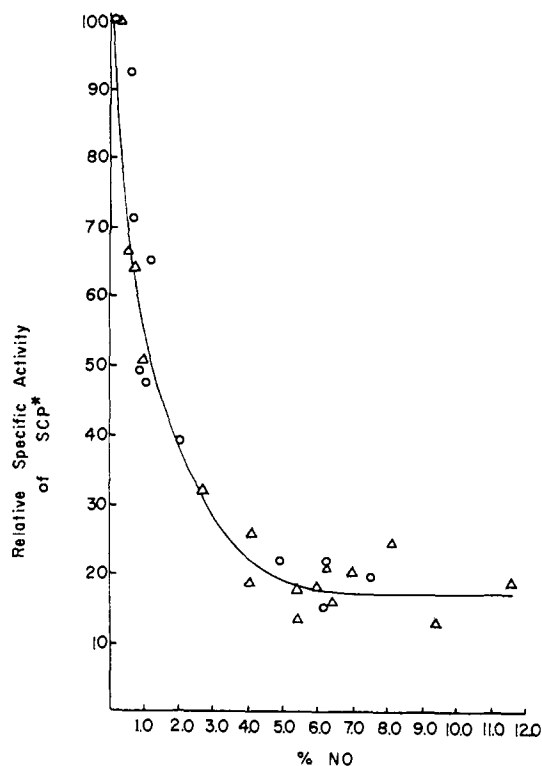


Figure 1. Dependence of SCP* specific yields on nitric oxide concentration (O and Δ represent cyclotron and reactor irradiations, respectively).

strained three-member rings with respect to isomerization to give straight chain compounds, as hinted by Skell and Goldstein's study on dimethylsilylene addition reactions.¹⁸

Just as the carbene chemists experienced the problems of determining the ground electronic state of CH_2 a decade ago, one of the major problems facing the silylene chemist today is what the ground state of silylene is. An early hypothesis citing a triplet ground state based purely on analogy with the CH_2 system is definitely too speculative.¹⁴ On the other hand, semi-empirical calculations done by Jordan have shown that the $^1\text{A}_1$ singlet is the ground state of silylene while the $^3\text{B}_1$ triplet state is much higher in energy.¹⁹ The spectrum of singlet SiH_2 has been studied using flash photolysis, but no conclusion could be drawn as to the ground state of silylene.¹⁷ Experimental results showing that silylene- d_2 inserts into the Si-H bonds of methylsilane without scrambling point to the fact that singlet silylene- d_2 results from the pyrolysis of disilane- d_6 but do not show whether this singlet species is in its ground electronic state.¹⁶ However, for substituted silylenes, Skell and Goldstein have definitely established that the ground state of dimethylsilylene is a singlet.⁶

The purpose of the present work is threefold: (i) to report the formation of silacyclopent-3-ene- ^{31}Si (SCP*) from the reaction of $^{31}\text{SiH}_2$ with 1,3-butadiene as the first confirmed olefin addition reaction of silylene, (ii) to report that the reacting $^{31}\text{SiH}_2$ present in the PH_3 -butadiene system consists of 80% triplet and 20% singlet, and (iii) to establish that silylene has a singlet ground electronic state. The nuclear recoil method has been employed here for the $^{31}\text{SiH}_2$ formation to achieve the above goals.

(19) P. C. Jordan, *J. Chem. Phys.*, **44**, 3400 (1966).

Experimental Section

Sample Preparation and Storage. The general procedure used in this study was the same as that used in other typical nuclear recoil experiments.²⁰ Phosphine and 1,3-butadiene along with other desired additives such as nitric oxide (a scavenger) and neon (a moderator) were sealed in standard Pyrex or Pyrex 1720 bulbs, using standard high-vacuum techniques. Neutron irradiations were performed only on freshly prepared samples. Preliminary results showed that samples containing nitric oxide which had been prepared several days prior to irradiation and stored at room temperature gave the same SCP* yields as those of nonscavenged samples. However, freshly prepared samples showed a definite nitric oxide effect as indicated by Figure 1. Therefore, the above preliminary results show that nitric oxide was chemically removed during storage. We have not made a study of the rate at which nitric oxide reacts with these other components, but such effects were minimized here because all data reported were obtained from samples that were prepared less than 24 hr prior to irradiation and stored in the dark at 0° until the actual time of irradiation.

Irradiation. Silicon-31 from the $^{31}\text{P}(n,p)^{31}\text{Si}$ nuclear transformation⁹ was formed using fast neutrons from two different sources. (i) A 16 or 20 MeV deuteron beam from the Texas A & M University cyclotron was focussed on a beryllium target initiating the nuclear transformation, $^9\text{Be}(d,n)^{10}\text{B}$. (ii) We have also succeeded in producing recoil ^{31}Si atoms by using fast neutrons from a Triga nuclear reactor at the Texas A & M University Nuclear Science Center. This is possible because the threshold energy for the $^{31}\text{P}(n,p)^{31}\text{Si}$ transformation is only 2 MeV.²¹ Although the energy spectrum of the reactor neutrons is unknown, our experiments show that the reactor facility is at least as efficient as the cyclotron in producing ^{31}Si activity.

A rotisserie holding six sample bulbs placed directly behind the beryllium target was employed for cyclotron irradiations. An internal cadmium-lined boron sample rotisserie which removed thermal neutrons and held four samples was used in connection with the reactor irradiations. Typical cyclotron irradiations involved beam currents (on target) of $50 \mu\text{A}$ for 60–90 min. Reactor irradiations typically lasted for 10 min while exposing the outside of the rotisserie to a thermal neutron flux of approximately 2×10^{11} neutrons/($\text{cm}^2 \text{ sec}$). As shown in Figures 1 and 2, the results obtained were independent of whether the cyclotron or the nuclear reactor was used as the fast neutron source.

Sample Analysis. Identification of SCP* was confirmed by co-injection of authentic samples²² of silacyclopent-3-ene (SCP) on four different gas chromatographic columns. These columns were: (i) a 30-ft 20% silicone fluid (SF-96) column operated at 80° , (ii) a 25-ft 10% tri-*o*-tolylphosphate column operated at 55° , (iii) a 5 or 10-ft 35% dimethylsulfolane (DMS) column operated at 75° . Chromosorb P (45–60 mesh) was used as a solid support for all of the above columns.

Only the DMS and SF-96 columns were used for obtaining quantitative data. The major products obtained from fast neutron irradiations of phosphine-butadiene mixtures were silacyclopent-3-ene- ^{31}Si and an unidentifiable component (A). It was desired to show that an isomer of SCP*, silacyclopent-2-ene- ^{31}Si , was not a reaction product. The DMS column was used for this purpose. Analysis of the reaction products on DMS showed that SCP* was eluted first with component A appearing at the end of the SCP* activity peak. Silacyclopent-2-ene was eluted afterwards and clearly separated from these two products, but no activity was associated with the mass peak of an authentic sample of this compound. After establishing the absence of this potential product, successive experiments were performed on the SF-96 column which clearly separated peak A and SCP* (silacyclopent-2-ene and SCP have the same retention times on SF-96). Due to the fact that SCP* yields were the only ones required in evaluating the ground electronic state of silylene, we have ascribed quantitative values to this product without presently concerning ourselves with the identity of peak A. However, Gaspar and coworkers have tentatively identified it as silacyclopenta-2,4-diene- ^{31}Si .²²

(20) J. K. Lee, E. K. C. Lee, B. Musgrave, Y.-N. Tang, J. W. Root, and F. S. Rowland, *Anal. Chem.*, **34**, 741 (1962).

(21) J. A. Grundl, R. L. Henkel, and B. L. Perkins, *Phys. Rev.*, **109**, 425 (1958).

(22) T. H. Chao, S. L. Moore, and J. Laane, *J. Organometal. Chem.*, **33**, 157 (1971).

(23) P. P. Gaspar, R.-J. Hwang, and W. C. Eckelman, *J. Chem. Soc., Chem. Commun.*, 242 (1974).

The absolute yield measurements were obtained by simultaneously irradiating two samples each of a 1:1 phosphine-silane mixture and a 3:1 phosphine-butadiene mixture under normalized neutron flux conditions. The yield of SCP* from the butadiene samples as measured on the SF-96 column was compared to the $^{31}\text{SiH}_4$ yield from the silane samples as measured on a 50 ft triisobutylene column at 0°.

Mass peaks were measured using thermal conductivity response. The radioactivity was assayed with a gas proportional counter of 85 ml active volume. There was no noticeable quenching of the internal counter by the compounds used in connection with this research.

Chemicals. Phosphine (>99.0%), 1,3-butadiene (>99.5%), silane (>99.9%), nitric oxide (>99.0%), and neon (>99.99%) were all obtained from Matheson and used without further purification except for degassing.

Data Treatment. All the data presented in Figures 1 and 2 are expressed in terms of relative specific activity (RSA). Specific activity is defined as the observed activity of the peak in question per unit PV of phosphorus precursor where PV is expressed in Torr-milliliters. The arbitrary standard used for normalizing the SCP* specific activities to give the RSA values was a sample containing 75% phosphine and 25% butadiene. The RSA value chosen for this standard was 100. A secondary standard which comprised phosphine and butadiene in a 3:1 ratio together with approximately 5% nitric oxide was also frequently used in the sets of NO-scavenged samples. This was possible because, as shown in Figure 1, a sample containing 5% NO lies in the plateau region of the graph. A factor of 5 was used to normalize the secondary standard (since well-scavenged samples exhibit 20% of the unscavenged SCP* activity).

All RSA values presented in Figures 1 and 2 are expressed relative to the primary standard. Experimentally, the primary standard was employed for the sample sets used in the scavenger studies (Figure 1) and the unscavenged, moderator studies (Figure 2) while the secondary standard was used solely in connection with the scavenged, moderated studies (Figure 2). Sometimes in order to check the reproducibility, either two primary standards or a primary and a secondary standard were included in a set of irradiated samples.

The data points in Figure 1 and those for the unscavenged Ne-moderated samples in Figure 2 exhibited much higher SCP* yields than the NO-scavenged, Ne-moderated samples shown in Figure 2. The errors associated with the RSA values of the SCP* yields in the former series were usually low with the maximum errors being in the range of 5%. The NO-scavenged, Ne-moderated samples, however, exhibited a much larger experimental uncertainty. In order to give a realistic representation of the limits of uncertainty, error bars have been drawn in Figure 2 for the *normalized* RSA values associated with this less accurate series.

Results

Identification of Silacyclopent-3-ene- ^{31}Si . The identification of SCP* by coinjection of SCP on four different columns should be confirmatory. The authentic SCP sample was prepared using the method described by Chao, *et al.*,²² and confirmed by its infrared spectrum.

Quantitatively, the actual number of counts observed for this product was usually in the 10^3 to 10^5 range and the calculated specific activities were always very reproducible. In Table I, two typical sets of experiments for testing the reproducibility of SCP* specific activities are given. Actually, ten sets of such experiments consisting of a total of 30 samples have been performed and the observed fluctuation was usually within 5%.

Absolute Yield Measurement. No direct measurement of the absolute yield of SCP* has been attempted. However, this value has been indirectly evaluated by using the known $^{31}\text{SiH}_4$ absolute yield from the PH_3 - SiH_4 system (13%, as obtained by Gaspar and co-workers²³) as a comparison standard. In each set of the experiments evaluating the absolute yield, the specific activities of SCP* and $^{31}\text{SiH}_4$ were first ob-

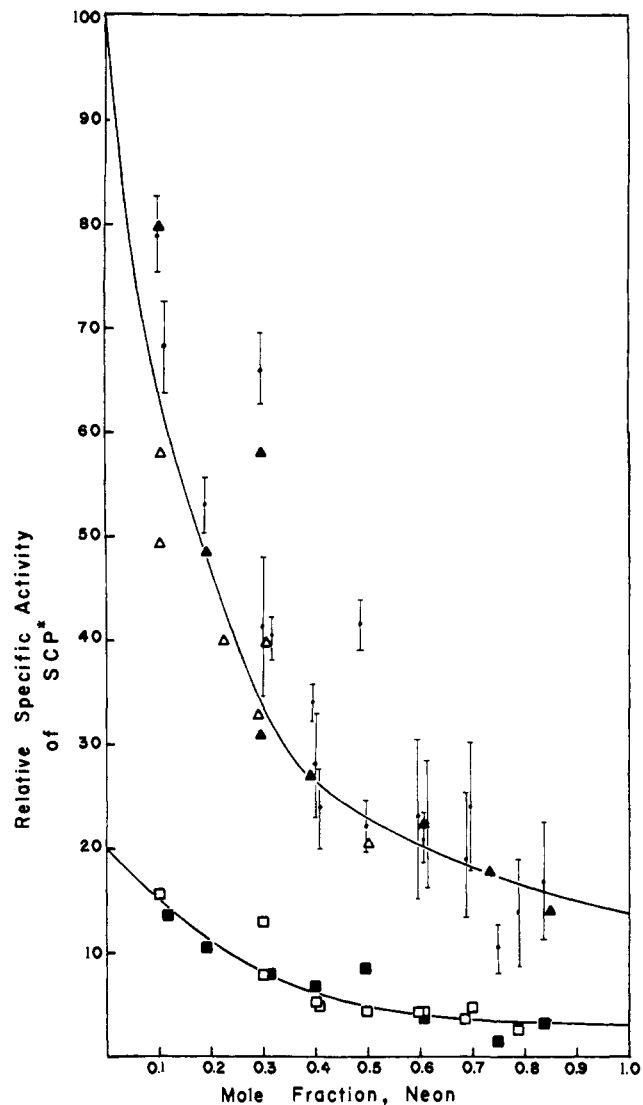


Figure 2. Relative specific activity of SCP* vs. mole fraction of neon. Δ and \blacktriangle : unscavenged, Ne-moderated systems, cyclotron and reactor irradiations, respectively. \square and \blacksquare : NO-scavenged, Ne-moderated systems, cyclotron and reactor irradiations, respectively. The points with error bars represent data points from the NO-scavenged, Ne-moderated systems normalized to the unscavenged, Ne-moderated system.

Table I. Typical Data Showing SCP* Reproducibility

Data set	PH_3 , Torr	C_4H_6 , Torr	A/PV, counts/(Torr ml)	Norm ^a SCP* yield	Source of neutrons
1	598	206	9.33	110.7	Cyclotron
1	588	206	8.22	97.6	Cyclotron
1	592	206	8.42	99.9	Cyclotron
1	600	206	7.73	91.8	Cyclotron
2	626	202	65.3	107.8	Reactor
2	626	202	61.8	102.0	Reactor
2	634	202	54.7	90.3	Reactor

^a Based on the average of the set being 100.

tained. The ratio of these two quantities was calculated after correcting for the difference in flow rate of the gas chromatographic systems. Then the 13% value²³ for $^{31}\text{SiH}_4$ was employed in the evaluation of the SCP* absolute yields.

Three sets of experiments have been performed. In one of the sets, 10 Torr of SCP carrier was added to the

PH₃-butadiene system before irradiation to ensure the preservation of SCP*. The results obtained for the sets with and without SCP carrier were 4.9, 3.4, and 3.8%, respectively, with the highest value attributable to the SCP-addition sample. The overall average, 4.0%, agrees well with the 4.5% value obtained by Gaspar and coworkers.²³

Scavenger and Moderator Studies. Three series of experiments have been performed to study the variation of SCP* specific activity with: (i) varying amounts of NO as a scavenger; (ii) varying amounts of Ne as a moderator; and (iii) varying amounts of Ne together with a constant 5% NO. Case i is shown in Figure 1 while both cases ii and iii are presented in Figure 2.

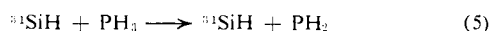
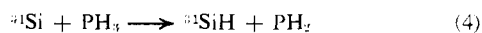
Figure 1 resembles a typical scavenger curve in that the SCP* specific activities decrease rapidly in the 0–4% NO region and remain essentially constant thereafter. Such behavior shows that NO is an efficient scavenger for this system. The plateau value attained for the specific activity is 20% of the original unscavenged value. The fact that this scavenger curve does not show as sharp a decrease as that of some other species such as triplet CH₂ is probably due to the efficient competition between butadiene and NO for triplet ³¹SiH₂ species.

The two curves in Figure 2 indicate that with or without a scavenger the SCP* precursors are highly energetic, but the reactivity of these species is diminished by transfer of their excitation energy through intermolecular collisions. It is noteworthy that the two curves shown in Figure 2 are different in general shape from the typical moderator curves observed for univalent hot atoms such as recoil tritium or halogen atoms. However, in the formation of SCP*, moderation of the multivalent reaction precursors may occur at several different stages, and a much more pronounced moderator effect is actually anticipated. The curves in Figure 2 show that with the addition of 50% Ne there is already enough moderation to eliminate about 75% of the SCP* yield.

Discussion

Formation of Silacyclopent-3-ene-³¹Si. A plausible reaction scheme for the formation of SCP* is proposed below and will be corroborated either immediately or in later sections.

Hot silicon atoms resulting from the nuclear transmutation, ³¹P(n,p)³¹Si, originally possess a recoil energy of 0.6 MeV.⁹ This kinetic energy is transferred to the molecules present in the system by collisions and is eventually degraded to the chemical reaction range whereupon the following H-abstraction reactions may take place.



The corresponding H abstraction from 1,3-butadiene should be negligible due to its much higher *D*(CH) value in comparison with the *D*(PH) value in PH₃.^{24–26}

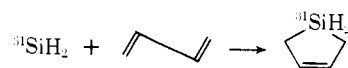
In the presence of butadiene, ³¹SiH₂ undergoes an

(24) F. E. Saalfeld and H. J. Svec, *Inorg. Chem.*, **3**, 1442 (1969). The *D*(PH₂H) value cited here is 90.3 kcal/mol.

(25) T. McAllister and F. P. Lossing, *J. Phys. Chem.*, **73**, 2996 (1969). The *D*(PH₂H) value cited here is 83.9 kcal/mol.

(26) The CH bond in molecules similar to butadiene (e.g., ethylene) has bond dissociation energies of 104 kcal/mol.

apparent 1,4-addition reaction to give SCP* as a final product.



Possibility of ³¹Si⁺ as SCP* Precursor. Silicon-31 produced by the nuclear recoil method initially is ionic, but as predicted by the adiabatic principle,^{27–29} these ions are neutralized before reaching energies where chemical reactions may occur.⁹ However, due to the low ionization potential of silicon atoms (IP = 8.15 eV),³⁰ reionization of neutral silicon-31 atoms may take place below the adiabatic region by collision of neutral silicon atoms with other molecules.³¹ For the reasons stated below, we do not believe that silicon ions contribute significantly to the SCP* yield in our PH₃-butadiene system. (1) The formation of ³¹SiSi₂H₈ in 7% absolute yield (*vs.* 61% absolute yield for products derived from neutral ³¹Si atom reactions)²³ from a PH₃(IP = 10.0 eV)–SiH₄(IP = 12.2 eV) mixture was attributed to ion–molecule reactions involving ³¹Si⁺, chiefly because its yield was decreased by the addition of triethylamine, a compound of very low ionization potential.³¹ However, ³¹SiSi₂H₈ may also be *partially* formed by a diinsertion mechanism of ³¹Si atoms as proposed in one of Gaspar's earlier works¹¹ and corroborated by Skell and Owen's thermally vaporized Si atom studies.³² Therefore, the 7% value can at most be treated as an upper limit for the contribution of ³¹Si⁺ in the PH₃–SiH₄ system. In our PH₃(IP = 10.0 eV)–butadiene(IP = 9.0 eV) system the contribution of ³¹Si⁺ reactions should be very minor compared to that of neutral ³¹Si atom reactions. Due to the lower ionization potential of butadiene,³⁰ this ionic contribution is likely to be much less than the 7% value quoted above. Any major product such as SCP* should therefore be primarily due to the reactions of neutral ³¹Si species. (2) As shown in Figure 2 the SCP* specific yield decreased sharply with the addition of Ne(IP = 21.5 eV)³⁰ to the PH₃-butadiene system. If ³¹Si⁺ were a precursor of SCP*, the efficient ion–molecule reactions for its formation should not show such a large moderator dependence. (3) One possible suggestion to explain the results observed in Figure 1 is that NO(IP = 9.3 eV)³⁰ effectively removes products arising from ³¹Si⁺ while those from neutral ³¹Si atom reactions are preserved. This is definitely not the case because in both the nonscavenged and NO-scavenged samples there are always significant quantities of butadiene which actually has a lower ionization potential than NO.

Consideration of ³¹Si, ³¹SiH, and ³¹SiH₂ as Direct SCP* Precursors. Since ³¹Si⁺ is unlikely to be involved in the SCP* formation process, the remaining possibilities include neutral species such as ³¹Si, ³¹SiH, or ³¹SiH₂. In fact all three have been included in our proposed mechanism as SCP* precursors. The only remaining

(27) R. Wolfgang, *Progr. React. Kinet.*, **3**, 63 (1965).

(28) M. A. El Sayed, P. J. Estrup, and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

(29) H. S. Massey and E. H. Burhop, "Electronic and Ionic Impact Phenomena," Clarendon, Oxford, 1952, p 441.

(30) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

(31) G. W. Stewart, J. M. S. Hénis, and P. P. Gaspar, *J. Chem. Phys.*, **58**, 890 (1973).

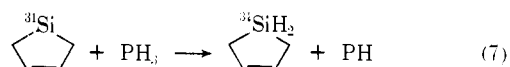
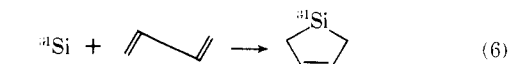
(32) P. S. Skell and P. W. Owen, *J. Amer. Chem. Soc.*, **94**, 5434 (1972).

question is whether H abstraction by the ^{31}Si -containing species precedes addition to butadiene or vice versa for the eventual formation of SCP*. In other words can SCP* be formed by assuming the addition of ^{31}Si or ^{31}SiH to butadiene as the initial steps? Mechanisms such as this are possible, but we believe that $^{31}\text{SiH}_2$ is actually the direct precursor.

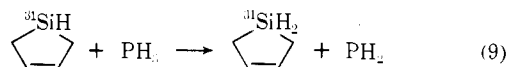
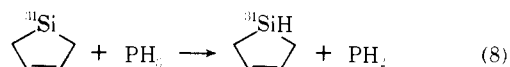
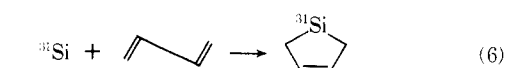
Supporting evidence favoring $^{31}\text{SiH}_2$ as the direct precursor can be derived from information in the literature.^{8,9,11,12,23} (1) In other recoil ^{31}Si systems involving molecules with labile hydrogen (such as SiH_4), the product spectrum is consistent with mechanisms involving $^{31}\text{SiH}_2$ as the direct precursor.^{8,9,11,12,23} This lends support to the occurrence of reactions 4 and 5 since the labile hydrogen in PH_3 should be readily abstractable.^{8,9} (2) The addition of SiH_2 to butadiene (equivalent to that shown in eq 6) has actually been observed in the copolyolysis of disilane and butadiene giving SCP as the major product.²³

Other plausible mechanisms for the formation of SCP* proceeding through the direct interaction of ^{31}Si or ^{31}SiH with butadiene are presented in mechanisms A–C.

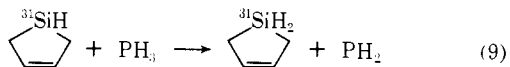
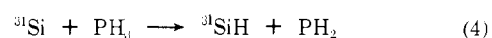
Mechanism A



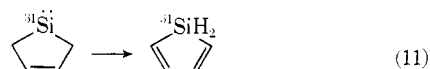
Mechanism B



Mechanism C



Evidence against the above mechanisms is as follows: (1) The addition of ^{31}Si atoms to butadiene as shown in (6) definitely takes place. However, it is more likely to be followed by an intramolecular rearrangement (reaction 11) rather than the H-abstraction reactions (reactions 7

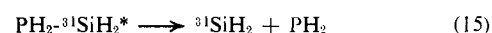
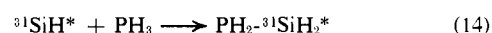
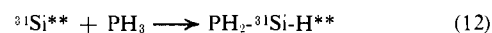


and 8) because the former reaction is probably much faster than the latter two which require intermolecular collisions. In fact silacyclopenta-2,4-diene- ^{31}Si has been tentatively identified as a major product from the PH_3 -butadiene system.²³ (2) Further evidence against mechanism A is that the simultaneous abstraction of two hydrogen atoms as shown in (7) is a less likely

process.¹² Gaspar, *et al.*, have previously shown that $^{31}\text{SiH}_2$ was still formed in systems where molecules with only one labile hydrogen were present.¹² (3) In mechanism C the H abstraction by ^{31}Si in eq 4 to give ^{31}SiH should take place readily and so should the addition of ^{31}SiH to butadiene. However, the silacyclopent-3-enyl- ^{31}Si radical formed from reaction 10 may not necessarily undergo the H-abstraction reaction as shown in (9). Butadiene is known to be an efficient scavenger for free radicals.³³ As a result, unless the silacyclopent-3-enyl- ^{31}Si radical is energetic enough to undergo immediate H abstraction, it will probably be removed from further reaction by other molecules of butadiene to form polymeric species.

Other evidence against these three mechanisms will be presented in later sections.

Energetic Precursors of SCP*. The major deduction from the Ne-moderated results as shown in Figure 2 is that very energetic precursors must be involved in the formation of SCP*. Due to the fact that collision with bath molecules at room temperature can only degrade the energy of a hot species rather than energize it, it is most likely that the energetic species involved in the formation of SCP* are the initial precursors such as ^{31}Si or ^{31}SiH . A plausible mechanism for $^{31}\text{SiH}_2$ formation including energetic considerations is shown in eq 12–15. The major feature of this mechanism (*i.e.*,



the apparent H abstraction actually consisting of an insertion-decomposition sequence) is in accord with what has been proposed by Gaspar, *et al.*¹² It is surely possible that rather than reaction sequence 14 and 15,³⁴ ^{31}SiH may directly abstract H atoms from PH_3 . It is interesting to note that the above mechanism is parallel to reactions responsible for the formation of $\text{H}-^{11}\text{C}\equiv\text{C}-\text{H}$ in recoil ^{11}C systems.³⁵ This mechanism also explains why SiH_2 reactions have not been observed in thermal Si-atom systems.³⁵

Further evidence showing that it is $^{31}\text{SiH}_2$ rather than ^{31}Si or ^{31}SiH which reacts directly with butadiene can be derived from a combination of the above mechanism together with information obtained from a composition variation study for the PH_3 -butadiene system. It has been shown that when the mole fraction of butadiene decreases from 0.3 to 0.03, the specific yield of SCP* remains roughly the same.^{1,23} This means that even if the species which directly adds to butadiene can only collide with butadiene molecules once in every 30 collisions, the SCP* yield will still remain constant. This implies that the reacting species must be thermal rather than energetic. Since energetic precursors *must* be involved in SCP* formation, the butadiene addition reaction should therefore be occurring at the latter stages of the reaction sequence. In other words the nonenergetic species which adds to butadiene is most likely to be $^{31}\text{SiH}_2$ rather than the presumably more energetic ^{31}Si or ^{31}SiH .

(33) G. P. Gennaro and Y.-N. Tang, *J. Inorg. Nucl. Chem.*, **36**, 259 (1974).

(34) J. Nicholas, C. MacKay, and R. Wolfgang, *J. Amer. Chem. Soc.*, **88**, 1065 (1966).

(35) C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965).

Singlet and Triplet Silylene. Nitric oxide effectively removes species having unpaired electrons. Although the mechanism for scavenging of silicon-containing species by nitric oxide may be different from that of other types of free radicals (the silicon atom shows an affinity for the oxygen atom rather than the nitrogen atom of NO^{13,36}), there is no evidence indicating that NO is not an effective scavenger of silicon-containing radicals.

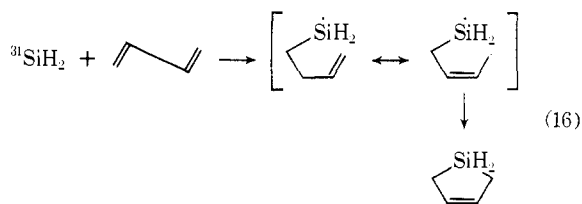
In a manner analogous to carbene, ³¹SiH₂ may exist as either a singlet or a triplet. The triplet species should be scavenged by NO while the singlet species should be inert to it.³⁷ With this in mind, the results presented in the NO scavenger curve in Figure 1 definitely imply that the reacting silylene in the present system is 80% triplet and 20% singlet.

It is conceivable that the species actually being scavenged by NO are ³¹Si atoms or ³¹SiH radicals rather than triplet ³¹SiH₂. The ³¹Si atom has a triplet ground state (³P) with two unpaired electrons while the ³¹SiH radical must contain at least one unpaired electron. Evidence against scavenging of ³¹Si or ³¹SiH is shown by the consistent plateau region observed in the NO-scavenged curve beyond the 4% NO range. If these species were actually being scavenged to a significant extent, there is no reason why such a plateau region should be attained. Instead we should observe a continuous decrease in SCP* yields with increasing amounts of NO until eventually a zero yield is reached.

The reason why ³¹SiH₂ rather than ³¹Si or ³¹SiH is subjected to scavenging by nitric oxide can be explained by the supposition that ³¹SiH₂ is formed by some very efficient reactions. As previously discussed, we know that energetic precursors such as ³¹Si atoms and ³¹SiH radicals are actually involved in the formation of SCP*. If these energetic species abstract hydrogen atoms with an efficiency close to the collision frequency, a 4% concentration of NO will not remove a significant number of these species even though they are susceptible to scavenging.

Mechanism for SCP* Formation. Both the singlet and triplet ³¹SiH₂ in the reaction mixture add to butadiene to yield SCP* as the common product. However, the mechanism for these addition processes may be quite different.

Triplet ³¹SiH₂ may be expected to undergo a real 1,4 addition to butadiene through a biradical intermediate analogous to the 1,4 addition of triplet CH₂.³⁸



The lifetime of this biradical intermediate is unknown. However, if it is as long as 10⁻⁸ sec, it could be the one actually being scavenged by NO rather than its precursor, the triplet ³¹SiH₂. Even if this were true, the same con-

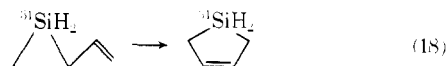
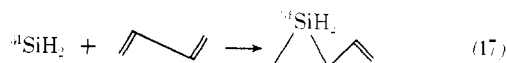
(36) E. A. V. Ebsworth, "Volatile Silicon Compounds," Macmillan, New York, N. Y., 1963.

(37) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496, 6427 (1956); **81**, 3383 (1959).

(38) V. Franzen, *Chem. Ber.*, **95**, 571 (1962).

clusion that 80% of the reacting ³¹SiH₂ is triplet would still be reached.

In a manner similar to other systems, the apparent 1,4 addition of singlet ³¹SiH₂ to butadiene may actually be a 1,2 addition giving an unstable vinylsilacyclopropane-³¹Si (reaction 17) followed by isomerization to SCP* (reaction 18).^{7,39} The isomerization of (18) is



likely to be fast and therefore unaffected by the presence of a scavenger. The absence of a NO effect has also been noted in the vinylcyclopropane isomerization to cyclopentene.⁴⁰ Unfortunately the above analogy between the isomerization of vinylsilacyclopropane-³¹Si and that of its hydrocarbon counterpart cannot be directly verified by experiment. It is feasible that some of the vinylsilacyclopropane-³¹Si actually converts to a biradical with a longer lifetime and may thus be susceptible to scavenging. If this were the case, the product from reaction of singlet ³¹SiH₂ with butadiene would also be partially scavenged by NO.

The Singlet Ground State of Silylene. One of the major questions of interest in silylene chemistry is whether silylene has a singlet or triplet ground electronic state. Similar questions for most other simple divalent species have already been answered. For example, the ground state of CH₂ has been established as a triplet while that of CF₂, CHF, or other halocarbenes has been determined to be a singlet.⁴¹⁻⁴⁴

The general technique used to ascertain the ground state of a divalent species is one where an efficient moderator is added to the system. In the straightforward case where the precursors of the divalent species are not sensitive to the moderator, the continuous addition of a moderator to an unscavenged system will yield a horizontal line (indicating no change of yield with respect to moderator concentration) no matter whether the ground state of the species is a singlet or a triplet. The critical test comes from a well-scavenged system where all the triplet species are subject to immediate removal. In this case, if the ground state of the divalent species is a singlet, no moderator-initiated electronic state conversion should be observed, and as a result an invariant horizontal line is again expected for the moderator curve. On the other hand, if the ground state is a triplet, the remaining singlet in such a system will be converted to triplet by moderating collisions and therefore subject to scavenging. As a result, decreasing product yields should be expected with increasing moderation. Thus from the observed change of the moderation curve, the ground state for such a divalent species could be determined.

The situation described herein is complicated by the fact that besides converting ³¹SiH₂ to its ground elec-

(39) Y.-N. Tang, G. P. Gennaro, and Y. Y. Su, *J. Amer. Chem. Soc.*, **94**, 4355 (1972).

(40) C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962).

(41) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1971.

(42) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961); *Can. J. Phys.*, **39**, 1511 (1961).

(43) C. W. Mathews, *Can. J. Phys.*, **45**, 2355 (1967).

(44) Y.-N. Tang and F. S. Rowland, *J. Amer. Chem. Soc.*, **89**, 6420 (1967).

tronic state a moderator will also decrease the total number of $^3\text{SiH}_2$ species available in the system by moderating the energy of its precursors (this conclusion was abstracted from the results of Figure 2). However, even with such a complication, the ground state of $^3\text{SiH}_2$ can still be evaluated with a similar line of reasoning. First, we have to assume that the precursors of singlet and triplet $^3\text{SiH}_2$ exhibit the same moderator effect. This is a reasonable assumption because the two electronic states of $^3\text{SiH}_2$ probably even come from the same precursors. With this assumption, let us examine the situation where $^3\text{SiH}_2$ has a singlet ground state. In both the unscavenged and well-scavenged systems, a moderator will decrease the SCP* yields because the energy of the $^3\text{SiH}_2$ precursors will be dissipated somewhat before they react. In the absence of any other effect the two moderation curves in the unscavenged and well-scavenged systems should show the same slope and variation. Since singlet $^3\text{SiH}_2$ with a singlet ground state will not be converted to any additional scavengeable species by moderation, the normalized moderation curve for the well-scavenged system should actually coincide with that expected from the unscavenged system.

Next let us examine the situation where $^3\text{SiH}_2$ has a triplet ground state. For the unscavenged system, a certain moderation curve is expected because of the energy degradation of the $^3\text{SiH}_2$ precursors. However, in the well-scavenged system, an *additional* decrease in the SCP* yields is also expected. This is due to the expected conversion of singlet $^3\text{SiH}_2$ to its triplet ground state and the assumed efficient removal of these species by NO. This means that the moderator curve for the well-scavenged systems should descend much more sharply in comparison with that for the unscavenged samples.

In Figure 2, we have normalized the SCP* specific yields in the well-scavenged system in order to compare

the observed yields with the moderation curve obtained from the unscavenged system. This was done by making the two reference points (0% moderation) of the two systems coincide. It is obvious from the figure that the slope and shape of the two moderation curves are nearly identical. This implies that the ground electronic state of $^3\text{SiH}_2$ is a singlet.

The singlet ground state of silylene ($^1\text{A}_1$) predicted by semiempirical calculations¹⁹ is supposedly bent with a bond angle of 95° , while the first excited triplet state ($^3\text{B}_1$) is expected to have a bond angle of 138° . The energy separation between these two electronic states has been calculated as 46 kcal/mol.¹⁹ The bond angle of singlet silylene ($^1\text{A}_1$) in accordance with theoretical calculations was confirmed spectroscopically by DuBois, Herzberg, and Verma¹⁷ to be 92.1° . The agreement of structural parameters, as predicted by Jordan, with the actual experimental values is excellent and shows the semiempirical valence bond method of calculation to be highly accurate here.

However, the major success of Jordan's calculations lies in his correct prediction that the ground state of silylene is a singlet. We believe that the present work is the first experimental confirmation of his prediction. Although DuBois, *et al.*, were able to spectroscopically obtain valuable structural and energetic information about the singlet states of silylene, they caution that from their experimental findings, "It is not possible to say whether the lower state of the observed bands, $^1\text{A}_1$, is the ground electronic state or whether, as in CH_2 , a $^3\Sigma_g$ is the ground state."¹⁷

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