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REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS*

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ABSTRACT

Progress in two areas important to attaining the goals of this research program are briefly reviewed: a. characterization of the major product-forming intermediate in the reactions of recoiling silicon atoms; b. time-resolved laser flash spectroscopic studies of the generation and reactions of silicon radicals.

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A major achievement of the past year has been the demonstration that vibrationally relaxed ground-state singlet silylene $^3\text{SiH}_2$ is the dominant product-forming intermediate in the reactions of recoiling silicon atoms in mixtures of phosphine and silane.

In 1978 we reported that silane is nine times as reactive as butadiene toward the intermediate in the recoil reaction system that gives the products expected from silylene:¹

Since the indirect estimate made for the relative reactivity of silane and butadiene toward SiH_2 at 385°C following chemical generation of silylene was 1.2, these results cast doubt on the intermediacy of the ground singlet state, and indeed a prominent role has been attributed to triplet silylene in recoil reactions.²

More recently we found that the relative reactivity of silane and methylsilane toward the product forming intermediate in recoil reactions is in reasonable agreement³ with the high temperature ratio found in a chemical experiment by Paquin and Ring,⁴ but did not display the temperature dependence found in the chemical experiments.⁵

$$\frac{k_{\text{SiH}_3\text{Me}}}{k_{\text{SiH}_4}} = 1.3$$

We have now independently carried out the thermal generation of SiH_2 in the presence of silane-methylsilane mixtures in the temperature range 385 to 460°C using a flow pyrolysis system and have found a relative reactivity in excellent agreement with the recoil results, and invariant to temperature change.⁶

$$\frac{k_{\text{SiH}_3\text{Me}}}{k_{\text{SiH}_4}} = 1.35 \pm 0.03$$

In addition we studied the reactions of thermally generated SiH_2 with silane-butadiene mixtures in the range from 376 to 470°C and found a steady increase in the relative reactivity of silane and butadiene with decreasing temperature. A reasonable Arrhenius plot was obtained which extrapolated to a relative reactivity at room temperature of 13 ± 4 , again in excellent agreement with room temperature recoil experiments.

Both these results strongly suggest that the important product-forming intermediate in the recoil system is ground state singlet SiH_2 , since its relative reactivity toward three substrates is within experimental error the same as for thermally generated singlet silylene. The temperature dependence of the relative reactivity is also in agreement for the thermal and recoil experiments. Thus the discrepancies noted earlier^{1,3,5} were due to uncertainties in experiments on thermally generated SiH_2 ⁴ and to the temperature dependence of the rate constant for addition of SiH_2 to 1,3-butadiene.

The agreement of the relative reactivity of nucleogenic silylene toward silane-butadiene mixtures with the relative reactivity of chemically generated SiH_2 extrapolated to room temperature suggests that the nucleogenic species is vibrationally as well as electronically relaxed before reaction.

Since we had previously found that neither moderators nor radical scavengers cause a variation in the relative reactivity of the species now firmly established as nucleogenic $^3\text{SiH}_2$, it seems likely that triplet $^3\text{SiH}_2$ is not important in the reaction systems studied.

Another important development in the past year has been the detection in solution for the first time by optical spectroscopy of an intermediate in the

photolysis of organosilicon compounds.

We have detected a transient with an absorption maximum at 435 nm and a lifetime of ca. one microsecond in the 265 nm laser flash photolysis of 2-phenylheptamethyltrisilane in cyclohexane. The object of the experiment was to generate phenylmethylsilylene⁷ and to measure the kinetics of its reactions. Phenylmethylsilylene has been found in a matrix isolation steady state photolysis to absorb at λ_{max} ca. 480 nm⁸ and we have detected a shoulder at this wavelength. It is very likely that the absorber at 437 nm is a silyl radical. It is nevertheless clear that a new and fruitful era in the investigation of reactive silicon and germanium species has been ushered in by these laser photolysis experiments. The time evolution of the absorption in cyclohexane solution is shown in Figure 1. In the presence of ethanol, the reactive species with $\lambda_{\text{max}} = 435$ nm decays with a half-life of ca. 5 nanoseconds, as determined using a picosecond laser flash system. Thus, whatever the structure of this species turns out to be, it is highly reactive.

STATEMENT OF EFFORT

During the preceding twelve months the Principal Investigator devoted approximately 25% of his time during the academic year to this project. A total of four weeks in July and August were spent in England and Wales. The rest of the summer was spent in the laboratory in St. Louis.

PUBLICATIONS

In the past twelve months six papers were published:

1. COO-1713-81, Peter P. Gaspar and J. W. Root, "Kinetics, Mechanism and Hot

- Atom Chemistry," Radiochemica Acta, 28, 191(1981).
2. COO-1713-88, Peter P. Gaspar, "Advances in Silylene Chemistry 1977 to 1979," Reactive Intermediates, vol. 2, M. Jones, Jr. and R.A. Moss eds., Wiley, N.Y., 1981, Chapter 9, pp. 335-385.
  3. COO-1713-92, Peter P. Gaspar, "Recoil Chemistry and Mechanistic Studies with Polyvalent Atoms," Short-Lived Radionuclides in Chemistry and Biology, J.W. Root and K.A. Krohn, eds., ACS Advances in Chemistry Series, No. 197, Washington, 1981, Chapter 1, pp. 3-31.
  4. COO-1713-98, Peter P. Gaspar, Yue-Shen Chen, Adam P. Helfer, Stanislaw Konieczny, Eric C.-l. Ma and Siu Hong Mo, "1-Silacyclopent-3-en-1-ylidene, A Cyclic Silylene From the Reactions of Silicon Atoms, and A Silicon Atom Synthone," J. Am. Chem. Soc., 103, 7344(1981).
  5. COO-1713-101, Eric Ching-lin Ma, Ken Kobayashi, Morris Barzilai and Peter P. Gaspar, "Stereochemistry of Dimethylgermylene Addition to E,E-and E,Z-2,4-Hexadienes in the Gas Phase," J. Organometal. Chem., 224, C13(1982).
  6. COO-1713-102, Siu-Hong Mo, J. Dewey Holten III, Stanislaw Konieczny, Eric C.-l. Ma, and Peter P. Gaspar, "Silylene Rearrangements in the Reactions of Recoiling Silicon Atoms with Trimethylsilane," J. Am. Chem. Soc., 104, 1424(1982).

Three papers are in the press:

1. COO-1713-107, Yue-Shen Chen and Peter P. Gaspar, "Octakis(trimethylsilyl)cyclotetrasilane. A Stable Cyclotetrasilane from a Silylene Precursor," Organometallics, in the press.
2. COO-1713-108, Peter P. Gaspar, "The Formation of the Carbon-Silicon Bond from Silicon Halides," chapter in Inorganic Reactions and Methods, J.J. Zuckerman, ed., Verlag Chemie, in the press.
3. COO-1713-109, Peter P. Gaspar, "The Formation of the Carbon-Silicon Bond from Silicon Alkoxides, Silicon Carboxylates, or Siloxanes," chapter in

Inorganic Reactions and Methods, J.J. Zuckerman, ed., Verlag Chemie, in the press.

Two doctoral dissertations have been completed in the past twelve months:

1. COO-1713-104, Yue-Shen Chen, "The Chemistry of Silylsilylenes. Generation of Reactions of Bis(trimethylsilyl)silylene and Methoxytrimethylsilylsilylene," August 1981.
2. COO-1713-106, Eric Ching-lin Ma, "The Generation of Dimethylgermylene and Its Reactions," May 1982.

In addition the Principal Investigator delivered a plenary lecture at the 11th International Hot Atom Chemistry Symposium at Davis, California, June 27-July 2, 1982: COO-1713-99, "Recent Results in Mechanistic Studies Employing Polyvalent Atoms." From June 22 to June 26 the Principal Investigator was an invited participant in the NSF-sponsored joint Japan-USA Workshop on the Future of Nuclear and Radiochemistry in Irvine, California.

References

1. R.-J. Hwang and P.P. Gaspar, J. Am. Chem. Soc., **100**, 6626(1978); COO-1713-73.
2. O.F. Zeck, Y.-Y. Su, S.P. Gennaro, and Y.-N. Tang, J. Am. Chem. Soc., **96**, 5967(1974).
3. S.-H. Mo, J.D. Holten III, and P.P. Gaspar, "Reactions of Recoiling Silicon Atoms with the Methylsilanes H_nSiMe_{4-n} ," paper presented at the 10th International Hot Atom Chemistry Symposium, Loughborough, Sept. 1979; COO-1713-79.
4. D.P. Paquin and M.A. Ring, J. Am. Chem. Soc., **99**, 1793(1977).
5. P.P. Gaspar, J.D. Holten III, and S. Konieczny, "Reactions of Recoiling Silicon Atoms with the Methylsilanes H_nSi_{4-n} and the Temperature Dependence of Some Silylene Reactions," paper contributed to the XV Organosilicon

Symposium, Duke University, March 1981; COO-1713-94.

6. S. Konieczny and P.P. Gaspar, to be published; results presented by P.P. Gaspar in "Recent Results in Mechanistic Studies Employing Polyvalent Atoms" at the 11th International Hot Atom Chemistry Symposium, Davis, California, July 2, 1982; COO-1713-99.
7. M. Ishikawa, F. Ohi, and M. Kumada, Tetrahedron Lett., 645(1975).
8. Private communication from Professor Robert West.

Figure 1