Correspondence

The Mechanism of Catalyzed Disilane Decompositions

Sir:

Alkali metal salt catalyzed decompositions of disilanes into silanes and silicon–hydrogen polymers in 1,2-dimethoxyethane have been examined in some detail.[1-3] We had proposed that these decompositions followed a mechanism involving silene[2]

$$Si_2H_6 \longrightarrow SiH_2 + SiH_4 \qquad (1)$$

$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8\text{, etc.} \qquad (2)$$

In an effort to substantiate this mechanism, we have obtained results which shed considerable information on the disilane decompositions.

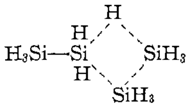
The catalytic decompositions can be envisioned as a "unimolecular process" to yield two silyl radicals or a silene radical and silane or as a concerted "bimolecular process." We have obtained results which appear to eliminate the "unimolecular processes" and are consistent with a concerted mechanism.

The lithium chloride catalyzed decomposition of disilane in 1,2-dimethoxyethane was examined in the presence of a 2:1 excess of either methylsilane or trimethylsilane. In both reactions, the disilane was completely converted to silane and a polymer while the alkylsilane was recovered unreacted.

We have demonstrated that in the gas phase, singlet silene inserts preferentially into methyl- or dimethylsilane in competition with disilane.[4] Therefore if singlet silene were formed in our solution reaction, it should have inserted into methylsilane forming methyldisilane which is inert toward lithium chloride catalytic decomposition.[3]

Triplet silene and silyl radicals should react by hydrogen abstraction reactions. For silane and disilane, the activation energies for the hydrogen abstraction by methyl radicals are 6.99 and 5.63 kcal/mol, respectively.[5] With the use of the weighted average for the silicon–hydrogen stretching frequencies in silane, methylsilane, disilane, and trimethylsilane (2182, 2167, 2159, and 2125 cm^{-1}),[6] we can estimate that the activation energies for the above reaction with methylsilane and trimethylsilane should be about 6 and 4.5 kcal/mol, respectively. Thus, one would expect that the reactions of silyl radicals (or triplet silene biradicals) with methylsilane, trimethylsilane, and disilane should proceed at similar rates. The fact that the catalyzed disilane reaction was not effected by the presence of a 2:1 excess of the alkylsilanes strongly suggests that silyl or triplet silene radicals were not produced in the catalytic decomposition of disilane.

By the elimination of the "unimolecular processes" we are left with a concerted mechanism which is very similar to that proposed by Urry[7] for the amine-catalyzed decomposition of hexachlorodisilane. For the disilane reaction, the activated complex (without the catalyst) would be



which could be classified as an SNi-Si reaction[8] and is consistent with other reactions for silicon–hydrogen bonds.[8]

This mechanism is also consistent with our observations of the following lithium chloride catalyzed reactions in 1,2-dimethoxyethane: (1) The reaction between disilane and methylsilane should involve only hydrogen atom exchange and thus should appear as no reaction. (2) The reaction between disilane-d_6 and methylsilane should result in hydrogen–deuterium exchange. This was the case as the products were silane-d_4, silane-d_3, disilane-d_5, and a deuterated methylsilane. (3) The reaction between disilane and silane-d_4 yielded deuterated disilanes and hydrogenated silanes.[2] A control reaction between silane and silane-d_4 did not result in hydrogen exchange[2] and solvent interaction was also eliminated as a route to hydrogen exchange.[2]

Acknowledgment.—The authors are indebted to the Army Research Office (Durham) for financial support.

---

(1) R. C. Kennedy, L. P. Freeman, A. P. Fox, and M. A. Ring, *J. Inorg. Nucl. Chem.*, **28**, 1373 (1966).

(2) J. A. Morrison and M. A. Ring, *Inorg. Chem.*, **6**, 100 (1967).

(3) W. M. Ingle, E. A. Groschwitz, and M. A. Ring, *ibid.*, **6**, 1429 (1967).

(4) P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *ibid.*, in press.

(5) O. P. Strausz, E. Jakubowski, H. S. Sandu, and H. E. Gunning, *J. Chem. Phys.*, **51**, 522 (1969).

(6) R. P. Hollandsworth and M. A. Ring, *Inorg. Chem.*, **7**, 1635 (1968).

(7) G. Urry, *J. Inorg. Nucl. Chem.*, **26**, 409 (1964).

(8) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

DEPARTMENT OF CHEMISTRY
SAN DIEGO STATE COLLEGE
SAN DIEGO, CALIFORNIA 92115

M. A. RING
R. B. BAIRD
PETER ESTACIO

RECEIVED NOVEMBER 10, 1969