Correspondence

The Preparation and Some Properties of Disilylamine

Sir:

In the course of their studies on the reaction of chlorosilane with ammonia, Stock and Somieski[1] noted that high yields of trisilylamine could be obtained only when chlorosilane was in excess. With excess ammonia, there was some evidence for the formation of partly silylated products; these were unstable, however, and could not be isolated. Stock and Somieski suggested that decomposition might occur in the following ways, which were consistent with the volatile products they observed.

$$2SiH_3NH_2 \longrightarrow (SiH_3)_2NH + NH_3 \qquad (1)$$

$$3(SiH_3)_2NH \longrightarrow 2(SiH_3)_3N + NH_3 \qquad (2)$$

$$(SiH_3)_2NH \longrightarrow 1/n(SiH_2NH)_n + SiH_4 \qquad (3)$$

The conception of the reaction as a stepwise process (*via* mono- and disilylamine) has been discussed by MacDiarmid,[2] Stone,[3] and Ebsworth.[4] Stone points out that the silane observed may well be formed by an ammonia-catalyzed disproportionation of trisilylamine, similar to that discussed by Schaeffer and Wells,[5] rather than by the decomposition of a hypothetical intermediate. Also, Ebsworth is doubtful whether disilylamine, if formed, would be basic enough to react with a halosilane.[6]

We have now isolated pure disilylamine by the amine exchange

$$2(C_6H_5)_2NSiH_3 + NH_3 \longrightarrow 2(C_6H_5)_2NH + (SiH_3)_2NH \qquad (4)$$

using a deficit of ammonia. Reaction proceeded smoothly at −46° either in toluene solution or in the absence of a solvent. No monosilylamine could be detected.

The compound is a volatile liquid [m.p. −132°; b.p. (extrapolated) 36°]. *Anal.* Calcd. for $(SiH_3)_2NH$: H (Si–H), 7.8; NH_3, 22.0; Si, 72.7; mol. wt., 77.2. Found: H (Si–H), 7.6; NH_3, 21.7; Si, 73.4; mol. wt., 77.3. Vapor pressure data given in Table I yield the equation: $\log P$ (mm.) $= 6.832 - 1220/T$. The value of the entropy of vaporization (18.0 cal. mole^{-1} deg.$^{-1}$) does not suggest that association is significant.

TABLE I

T, °C.	−96	−84.5	−64.2	−44.5	−23.0
P, mm.	1.0	2.4	8.7	28.9	94.5

Although the compound was unaffected by heating to 150° for 3 hr. in the gas phase, it decomposed in the liquid phase to give, after 72 hr. at 0°, over 80% of the trisilylamine demanded by eq. 2. Likewise, disilylamine and excess ammonia did not react in the gas phase at room temperature, but interaction at about −130° for 1 min. destroyed all the disilylamine and yielded silane and a little ammonia. There was evidence of complex formation at low temperatures between disilylamine and trimethylborane, but the Lewis acid iodosilane reacted with disilylamine to give 87% of the trisilylamine calculated from eq. 5.

$$4(SiH_3)_2NH + SiH_3I \longrightarrow 3N(SiH_3)_3 + NH_4I \qquad (5)$$

Thus disilylamine alone decomposes by one of Stock's routes (eq. 2) while, with ammonia, it decomposes by the other (eq. 3). Under his reaction conditions, ammonia was always present to some extent. Both these reactions proceed only in a condensed phase. Any doubt[4] that disilylamine is capable of reacting with iodosilane has been removed; if the reaction mechanism does indeed involve electron donation by nitrogen as a preliminary step, the observed interaction with trimethylborane makes such donation entirely credible.

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[1] A. Stock and K. Somieski, *Ber.*, **54**, 740 (1921).

[2] A. G. MacDiarmid, *Advan. Inorg. Chem. Radiochem.*, **3**, 207 (1961).

[3] F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Englewood Cliffs, N. J., 1962.

[4] E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, Oxford, 1963.

[5] R. Schaeffer, L. Ross, M. Thompson, and R. Wells, Office of Naval Research Technical Report NONR-908(4), Aug. 1961; R. Wells, *Dissertation Abstr.*, **23**, 1921 (1962).

[6] Trisilylamine does not interact even with iodosilane.

Book Review

Symmetry in Chemistry. By HANS H. JAFFÉ and MILTON ORCHIN. John Wiley and Sons, 605 Third Ave., New York, N. Y. 1965. v + 191 pp. 15 × 22 cm. Hardback, $5.50; paperback, $3.95.

The past few years have seen a great increase in the number of chemists making use of symmetry arguments in treating chemical systems, and there has been a corresponding increase in available sources for learning group theory. This book is similar in scope to "Chemical Applications of Group Theory" by F. A. Cotton (Interscience Publishers, New York, N. Y., 1963), and comparisons between them are inevitable. They are designed to bridge the gap between the briefer and more specialized treatments in books on spectroscopy, quantum chemistry, etc., and