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.

$$2SiH_3NH_2 \longrightarrow (SiH_3)_2NH + NH_3 \tag{1}$$

$$3(SiH_3)_2NH \longrightarrow 2(SiH_3)_3N + NH_3 \tag{2}$$

$$(SiH_3)_2NH \longrightarrow 1/n(SiH_2NH)_n + SiH_4 \tag{3}$$

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

$$2(C_6H_5)_2NSiH_3 + NH_3 \longrightarrow 2(C_6H_5)_2NH + (SiH_3)_2NH \tag{4}$$

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.

$$4(SiH_3)_2NH + SiH_3I \longrightarrow 3N(SiH_3)_3 + NH_4I \tag{5}$$

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.

Chemistry Department
Westfield College
Hampstead, London, N.W.3.
England

B. J. Aylett
M. J. Hakim

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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 the more rigorous treatments such as that in "Group Theory and Quantum Mechanics" by M. Tinkham (McGraw-Hill Book Co., New York, N. Y., 1964).

The book by Jaffé and Orchin starts with a chapter on symmetry operations, one on point groups, and one on the principles of group theory. The next chapter treats applications to molecular orbital theory, molecular vibrations, and spectroscopic selection rules and polarization. A final chapter is devoted to crystal symmetry. The appendices give the character tables for all common point groups and some other tables concerned with symmetries of molecular vibrations.

This book has many good points. One of the most valuable things is the treatment of space groups and crystal symmetry, a topic neglected in many books including Cotton's. Going along with this is the introduction of both the Schönfliess notation commonly used for molecular properties and the Hermann–Mauguin notation usually used by crystallographers. Stereographic projections are also employed in illustrating point groups and space groups. These factors will make this book a valuable starting point for those whose use of group theory will include applications to the solid state. Another particularly interesting section is the discussion of the relationship between symmetry operations and optical activity. Few errors were noted, and they were minor. The style is clear and understandable.

On the debit side, many inorganic chemists will find this book much less useful than "Chemical Applications of Group Theory" because it lacks the specific applications to hybrid orbitals and ligand field theory treated so well by Cotton. The authors' determination to emphasize the use of group theoretical methods without mathematical complications is perhaps carried too far, as the book lacks even a precise definition of a group, or of terms such as representation or class of operations. Although it is quite true that one can often use group methods without knowing these definitions, it seems unfortunate to this reviewer that they should be omitted from a book of this type.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO
S. J. STRICKLER

BOOKS RECEIVED

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D. M. ADAMS and J. B. RAYNOR. "Advanced Practical Inorganic Chemistry." John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1965. vii + 182 pp. $6.00.

BERTIL ARONSSON, TORSTEN LUNDSTROM, and STIG RUNDQUIST. "Borides, Silicides and Phosphides." John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1965. vii + 120 pp. $4.25.

GEORGE A. OLAH, Editor. "Friedel–Crafts and Related Reactions. Volume IV. Miscellaneous Reactions." John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1965. v + 1191 pp. $45.00.