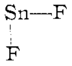
0.59 mm/sec, compares with the value 0.22 mm/sec observed in this laboratory for the corresponding acetylacetonate complex; this indicates a greater electron release by the sulfur than by the oxygen atom to tin. Two infrared absorptions by $SnF_2(2\text{-SpyO})_2$ attributed to the Sn–F stretching vibrations occur at 550 and 535 cm^{-1}, indicating *cis*



$$\begin{array}{l}\mathrm{Sn{-}F}\\ \;|\\ \mathrm{F}\end{array}$$

bonds. A strong absorption at 293 cm^{-1} by the dichloride is attributed to a Sn–Cl stretching vibration; absorption by the organic ligand below 280 cm^{-1} may obscure any other Sn–Cl absorption.

Absorption by $(C_6H_5)_2Sn(NCS)(2\text{-SpyO})$ at 2040 cm^{-1}, compared to 2100 cm^{-1} for polymeric $(C_6H_5)_2Sn(NCS)_2$ and 2040–2020 cm^{-1} for monomeric octahedral isothiocyanates,[3] suggests that NCS bridging does not occur in the solid and that tin is five-coordinate in this compound. The large quadrupole splitting, 2.60 mm/sec, compares with 2.48 mm/sec for the corresponding oxinate,[3] for which dipole moment data indicate a configuration in which the CSnC bond angle is close to 90°.

The quadrupole splitting obtained for $Sn(2\text{-SpyO})_4$ with a palladium–tin source, 0.5 mm/sec, and the large half-width of the spectrum obtained with a barium stannate source, 1.92 mm/sec, indicate quadrupole interaction and suggest that there is not simply a tetrahedral arrangement of sulfur atoms about the tin. Strong absorption at 355 cm^{-1} in the infrared spectrum indicates the presence of oxygen–tin bonds, and the single absorption in the 1200-cm^{-1} region, at 1205 cm^{-1}, is evidence that all four oxygen atoms are bonded to tin. The spectrum resembles those of the other 2-pyridinethiol 1-oxide complexes more closely than the spectra of N-substituted pyridine thiones,[6] suggesting that dangling C═S groups are not present and that tin has a coordination number of 8 in $Sn(2\text{-SpyO})_4$. Eight-coordination is indicated for tin in bis(phthalocyanino)tin(IV), and in $Sn(ox)_4$,[7] but it has not been suggested previously for complexes containing tin–sulfur bonds.

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Contribution from the Department of Chemistry,
Washington University, Saint Louis, Missouri 63130

Preparation of Trisilane by the Schlesinger Method[1]

By Peter P. Gaspar, Carl A. Levy, and Gerald M. Adair

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Reduction of silicon tetrachloride, $SiCl_4$, and hexachlorodisilane, Si_2Cl_6, with lithium aluminum hydride in ether has been the most widely used laboratory method for the preparation of small quantities of silane, SiH_4, and disilane, Si_2H_6, ever since its introduction by Schlesinger and coworkers in 1947.[2] Yields of disilane as high as 87% have been reported[2] despite warnings that considerable cleavage of silicon–silicon bonds can occur in the reduction of hexachlorodisilane.[3] The need for a small sample of trisilane, combined with a healthy respect for the dangers involved in the fractionation of a large quantity of mixed silanes,[4] prompted the successful attempt at the reduction of octachlorotrisilane, Si_3Cl_8, with lithium aluminum hydride. Thus an extension of the Schlesinger method to the preparation of higher silanes, long thought possible,[5] has been realized.

Octachlorotrisilane was obtained by fractional distillation of a mixture of chlorosilanes prepared by passage of a slow stream of gaseous chlorine through a heated tube containing calcium silicide, $CaSi_2$.[6]

Reduction of octachlorotrisilane to trisilane was carried out by addition of solid lithium aluminum hydride *in vacuo* to a solution of octachlorotrisilane in di-*n*-butyl ether. The reducing agent was added in small portions, and after a few minutes stirring the trisilane together with some solvent was removed from the reaction mixture by expansion into the vacuum manifold. The rapid removal of the product from contact with reducing agent seems responsible for the high yields (60 ± 10%) obtained.

The preparation of higher silanes by this method is entirely feasible and is under active investigation.

Experimental Section

Octachlorotrisilane.—The method of Schumb and Gamble was used.[6] Calcium silicide was used in the form of 10–20-mm irregular pieces. If the pieces are too small or if powdered material is included, much lower yields are obtained because the liquid chlorosilanes retained by absorption on the solids suffer pyrolysis to elementary silicon, unreactive at the temperature employed.

Trisilane.—In a dry, 100-ml, three-necked, round-bottom flask were placed 65 ml of di-*n*-butyl ether (freshly distilled from sodium), 7.55 g (20.5 mmol) of octachlorotrisilane, and a small Teflon-coated magnetic stirring bar. This reaction flask was attached *via* a ground joint and vacuum stopcock to a vacuum manifold capable of attaining low pressures of 10^{-4} Torr. On one neck of the reaction flask was mounted a bent addition tube containing 2.00 g (52.6 mmol) of lithium aluminum hydride.

The liquid phase was frozen with a liquid nitrogen bath, and then the flask was opened to the vacuum manifold and evacuated to less than 1 Torr. With the manifold isolated from the pump, the mixture of octachlorotrisilane in butyl ether was allowed to melt. The freeze–evacuate–thaw cycle was repeated twice in order to thoroughly degas the ether solution. After the last melting, the flask was surrounded by a water–ice bath and rapid magnetic stirring of the liquid phase was begun.

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(1) Financial support from the United States Atomic Energy Commission is gratefully acknowledged. This is AEC Report No. COO-1713-15.

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

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With the flask open to the vacuum manifold (volume *ca.* 300 ml) but isolated from the pump, *ca.* one-tenth of the lithium aluminum hydride was added to the reaction mixture by twisting the addition tube. Immediate signs of reaction included release of gas bubbles at the surface of the liquid. Eventually a milky suspension of metal halides was formed. After 10 min *ca.* 20 Torr vapor pressure was indicated by a mercury manometer attached to the manifold. The reaction flask was then isolated from the manifold, and the manifold was opened to a previously evacuated 1-l. gas storage bulb whose bottom was immersed in liquid nitrogen. Then the storage bulb was isolated from the manifold which was again opened to the reaction flask. After several such cycles, each lasting 5–10 min, both reaction and storage flasks were simultaneously opened to the manifold for *ca.* 1 min, allowing a small amount of solvent to distil from the reaction flask to the storage flask. Both flasks were then isolated, and *ca.* 8 Torr of noncondensable gas (presumably hydrogen) was exhausted from the vacuum manifold and the storage flask.

This procedure was followed for each of the *ca.* 10 portions of lithium aluminum hydride, which were added over a 3-hr period. Finally *ca.* 10 ml of a mixture of di-*n*-butyl ether and trisilane was obtained in the storage bulb. The reaction flask was frozen in liquid nitrogen, removed from the vacuum manifold after admission of dry nitrogen, and allowed to thaw out of doors, without incident.

Final purification of the product was accomplished by slowly evaporating the trisilane–butyl ether mixture through a cold trap maintained at −50° in a diacetone–alcohol slush bath into a vacuum manifold to which a liquid nitrogen cooled storage bulb was attached. The butyl ether was retained in the cold trap. Finally 255 Torr of gas was obtained in a 1.2-l. volume at 30°. Vapor chromatographic analysis of the purified product on an 18-ft by 0.25-in. column consisting of 60:20:10 (by weight) diethyl phthalate–silicone oil DC710–diatomaceous earth (ABS Anakrom, Analabs, Inc.) with a 44-cm^3/min helium flow rate indicated that the purified product consisted of 75% trisilane, 10% disilane, and 14% silane, with retention times at ambient temperature of 41, 10, and 5 min, respectively. This composition indicates a yield of 12.2 mmol of trisilane, 60% based on octachlorotrisilane. While these figures are taken from one experiment, the preparation has been carried out four times with similar results.

TABLE I

MASS SPECTRUM OF TRISILANE (70 eV)[a]

m/e	Rel intens	*m/e*	Rel intens	*m/e*	Rel intens
94	0.5	86	4.6	58	56.6
93	1.1	85	12.7	57	22.9
92	4.8	84	10.7	56	13.9
91	5.4	63	0.6	42[b]	8.4[b]
90	5.9	62	6.0	30	3.0
89	4.3	61	18.1	29	1.8
88	4.9	60	100	28	8.8
87	3.6	59	20.5	27	7.2

[a] Every observable peak in the spectrum with *m/e* >20 is given. [b] The *m/e* 42 peak belongs to an impurity.

Positive identification of trisilane was based on its mass spectrum (Table I), taken on a sample purified by vapor chromatography using the conditions given. The spectrum, taken on a Varian M66 cycloidal mass spectrometer with an ionizing electron energy of 70 eV, compares favorably with a spectrum in the literature[7] taken on a Nier-type sector mass spectrometer employing 90-eV ionizing electrons. A parent ion mass of 92 was confirmed by lowering the energy of the ionizing electrons.

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CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION,
OAK RIDGE NATIONAL LABORATORY,
OAK RIDGE, TENNESSEE 37830

Transference Numbers and Mobilities in Molten Mixtures of Beryllium Fluoride and Lithium Fluoride[1]

BY K. A. ROMBERGER AND J. BRAUNSTEIN

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Transference numbers in molten salt mixtures, unlike the so-called transference numbers of pure fused salts, are unambiguous properties, and are required to interpret electrical conductance measurements in terms of the relative mobilities of the ionic constituents. The correlation and interpretation of ionic transport properties in molten mixtures of beryllium fluoride with alkali fluorides are of interest because of their extreme variations with composition, which reflect the breakdown of the network-type structure of beryllium fluoride on addition of alkali fluorides. These systems may be considered as weakened analogs of silica–alkaline earth oxide systems, but analogies may be drawn also to the breakdown of the hydrogen-bonded water structure by ionic solutes. (A central atom—Si, Be, or O—is tetrahedrally coordinated by O, F, or H in SiO_2, BeF_2, or H_2O. Addition of solute ultimately breaks up the Si–O–Si, Be–F–Be, or H–O–H bridges.) Information on the transport properties is important also in the development of electroanalytical methods and electrolytic separation processes for the molten salt reactor program.[2]

Behl and Egan[3] and Behl[4] have reported transference numbers in the molten systems LiCl–$CdCl_2$, LiCl–$PbCl_2$, KCl–$PbCl_2$, KCl–$CaCl_2$, KCl–$MgCl_2$, and KCl–NaCl, evaluated from the emf of cells such as

$$Cl_2(g)\text{–}C|KCl(l)\Big|\Big|\begin{matrix}KCl\\ MCl_n\end{matrix}\Big|\,C\text{–}Cl_2(g) \qquad (A)$$

and data on the activities of one of the components of the mixture. In KCl–NaCl the transference numbers of potassium and sodium ions, relative to chloride, are equal to their ion fractions over the entire range of concentration ($0.0 < x_{NaCl} < 0.1$). In the other systems the transference numbers deviated from the ion fractions, but the departures were generally less than 20%. There was no evidence of inordinately low mobilities to suggest strong anionic complexes, although the mobilities of the alkali ions were higher than those of the divalent cations.

In this note we report measurements of the emf of concentration cells

$$Be\Big|\begin{matrix}LiF\\ BeF_2\end{matrix}\ \Big\vdots\ \begin{matrix}LiF\\ BeF_2\end{matrix}\Big|\,Be \qquad (B)$$

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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