Notes

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The Synthesis of Germylsilane from Silane and Germane in a Silent Electric Discharge[1a]

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It recently has been shown that both silane, SiH_4, and germane, GeH_4, may be converted to mixtures of higher silanes and germanes, respectively, when subjected to an ozonizer type of electric discharge.[2,3]

In the present investigation it has been found that when an approximately equimolar mixture of SiH_4 and GeH_4 is subjected to such a discharge under identical conditions to those used for SiH_4 alone, the new compound, germylsilane, H_3GeSiH_3, is produced in good yields. It appears that other hydrides of the general type $Ge_xSi_{y-x}H_{2y+2}$, which contain silicon–germanium bonds, also are formed in this reaction.

The structure H_3GeSiH_3 is confirmed by the fact that the mass spectrum of the compound shows a strong peak for the parent molecule-ion, $(H_3GeSiH_3)^+$, and for the fragments, GeH_3^+ and SiH_3^+, formed by cleavage of the silicon–germanium bond. In pure samples no $(H_3GeGeH_3)^+$ or $(H_3SiSiH_3)^+$ fragments were observed, thus indicating the absence of possible H_3GeGeH_3 or H_3SiSiH_3 impurities. Germylsilane undergoes no decomposition during manipulations at room temperature.

It is of interest to note that the mean of the boiling points of H_3SiSiH_3 and H_3GeGeH_3, 7.7°, is almost identical with the observed boiling point, 7.0°, of H_3GeSiH_3. This suggests that the germylsilane molecule must possess only a very small polarity and that intermolecular attractive forces between molecules are very similar in type to those between disilane and digermane molecules, respectively. This is consistent with the fact that the electronegativity values of silicon and germanium are, for practical purposes, almost identical.[4] It is more surprising to find that the mean of the melting points of H_3SiSiH_3 and H_3GeGeH_3, −120.8°, is almost identical with the observed melting point, −119.7°, of H_3GeSiH_3.

A few compounds containing a silicon–germanium bond have been reported previously, but all of these have had organic groups attached to the silicon and/or germanium atoms.[5] The attached organic groups, particularly if bulky, might be expected to modify certain chemical and physical properties of the bond. The absence of such groups in H_3GeSiH_3 shuld make this molecule particularly valuable for studies involving the physical and chemical properties of the Ge–Si bond.

Germylsilane is of interest since it is a parent member of the series of compounds of $RSiH_3$. These compounds and examples of derivatives are shown below.

R	Parent compound ($RSiH_3$)	Derivatives
CH_3	H_3CSiH_3	H_3CSiH_2I,[6] etc.[7]
SiH_3	H_3SiSiH_3	H_3SiSiH_2I,[8] etc.[7]
GeH_3	H_3GeSiH_3	Possibly H_3GeSiH_2I, etc.

Compounds of the above types already have assisted, and should continue to assist, in contributing to an understanding of the nature of the linkage formed between elements of group IV.

Experimental

All work was carried out in a Pyrex glass vacuum system using the apparatus, techniques, and instruments previously described for the electric discharge experiments with SiH_4.[2] The mass spectra were observed on a Consolidated Electrodynamics Model No. 21–130 mass spectrometer. Germane was prepared by the reduction, with $NaBH_4$,[9] of an aqueous solution of GeO_2[10] dissolved in HBr. GeH_4 (44.7 mmoles) and SiH_4 (47.5 mmoles) were subjected to a silent electric discharge for a total of 28 hr. The minimum pressure observed in the system on the downstroke of the automatic Toepler pump was 9.05 cm. and the maximum pressure on the upstroke was 20.30 cm. The Toepler pump was adjusted to cycle approximately 500 cc. of gas per min. Hydrogen was removed from the system periodically. Two traps immersed in −134° baths were used to remove the products from the system constantly as they were formed.

The condensate in the −134° trap was passed through a trap held at −78° and then into a trap immersed in liquid nitrogen. The material which condensed in the −78° trap appeared to consist of higher silanes and germanes together with hydrides containing Ge–Si bonds. The condensate in the liquid nitrogen trap was distilled through a low temperature distillation column held at approximately −115° to separate H_3GeSiH_3 from Si_2H_6 and Ge_2H_6. Germylsilane (0.90 mmole; mol. wt. found, 106.6, calcd., 106.74; m.p. −119.7 ± 0.2°) was obtained as a middle

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(2) E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.*, **1**, 432 (1962).

(3) J. E. Drake and W. L. Jolly, *Proc. Chem. Soc.*, 379 (1961).

(4) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 93; R. S. Drago, *J. Inorg. Nucl. Chem.*, **15**, 237 (1960); E. G. Rochow and A. L. Allred, *ibid.*, **20**, 167 (1961).

(5) C. A. Kraus and W. K. Nelson, *J. Am. Chem. Soc.*, **56**, 195 (1934); H. Gilman and C. W. Gerow, *ibid.*, **77**, 4675, 5509 (1955); **78**, 5823 (1956); J. G. Milligan and C. A. Kraus, *ibid.*, **72**, 5297 (1950).

(6) H. J. Emeléus, M. Onyszchuk, and W. Kuchen, *Z. anorg. allgem. Chem.*, **283**, 74 (1956).

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

(8) L. G. L. Ward and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **82**, 2151 (1960).

(9) Sample of GeO_2 kindly donated by Germanium Information Center, Midwest Research Institute, Kansas City 10, Mo.

(10) T. S. Piper and M. K. Wilson, *J. Inorg. Nucl. Chem.*, **4**, 22 (1957).

TABLE I

VAPOR PRESSURES OF GERMYLSILANE

Temp., °C.	P_{mm}, obsd.	P_{mm}, calcd.	Temp., °C.	P_{mm}, obsd.	P_{mm}, calcd.
−83.4	4.6	4.5	−45.2	65.1	65.2
−79.1	6.6	6.5	−41.7	79.5	79.6
−78.1[a]	7.0	7.0	−39.9	87.7	87.7
−64.0	19.8	19.9	−39.3	90.9	90.6
52.6	41.7	41.9	−37.1	102.1	102.5
49.5	50.6	50.6	−36.3	106.2	106.7
−49.3[a]	51.1	51.0	−35.9	109.1	109.0
−49.3	51.3	51.0	−23.3	207.6	207.0
−46.3	61.3	61.2	−196[a]	0.0	0.0

[a] Values observed as the temperatures were decreased at the conclusion of the measurements. The infrared spectrum of the whole sample, after the measurements were completed, was identical with that of the starting materials.

fraction. Vapor pressures in the range -83.4 to $-23.3°$ were determined by means of a mercury manometer and are represented by the equation: $\log P_{\mathrm{mm}} = (-1307.06/T) + 7.54701$. The extrapolated boiling point is 7.0°. The molar heat of vaporization is 6.00 kcal. mole^{-1} and the Trouton constant is 21.3 cal. deg.$^{-1}$ mole^{-1}.

The reproducibility of the vapor pressures when the sample was cooled at the conclusion of the experiment, together with the fact that no hydrogen (which would exert a pressure at $-196°$) was formed during the determinations, indicates that no thermal decomposition of the compound had occurred. This conclusion is supported by the fact that the infrared spectrum of the sample was unchanged after the vapor pressures had been measured.

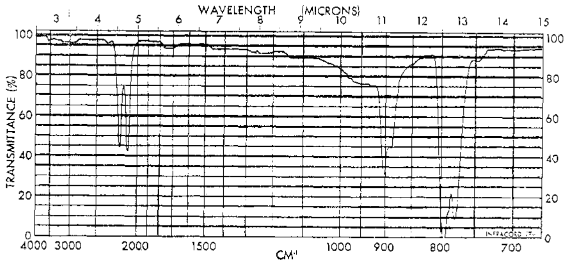

Figure 1.

The infrared spectrum of gaseous H_3GeSiH_3, observed at a pressure of 4.0 mm., is given in Fig. 1. The absorption maxima are: 2180 cm.$^{-1}$, m (Si–H); 2100 cm.$^{-1}$, m (Ge–H); 903 cm.$^{-1}$, m; 888 cm.$^{-1}$, sh, m; 796 cm.$^{-1}$, vs; 788 cm.$^{-1}$, sh, s; 778 cm.$^{-1}$, s.

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Composition and Stability of the Chelate between Uranium(VI) and Sulfodichlorohydroxydimethyl Fuchson Dicarboxylic Acid (Trisodium Salt)

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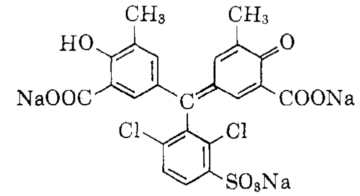
The trisodium salt of sulfodichlorohydroxydimethyl fuchson dicarboxylic acid (Chrome Azurol S)



forms colored complexes in aqueous solution with many metal ions and has widely been used in analytical chemistry,[1] though detailed data on the nature of the complexes produced are not available. In the present communication, detailed studies on the composition and stability of the uranyl Chrome Azurol S chelate are reported.

Experimental

Materials.—Standard solutions were prepared by dissolving uranyl sulfate (BDH L.R.) in double distilled water. Solutions of the trisodium salt of Chrome Azurol S (color index 723) in double distilled water were used and standardized by determining their sulfur content. In view of the strong complexing nature of carbonate with uranyl ions, care was taken to exclude carbon dioxide.

Instruments. Absorbance Measurements.—Measurements of absorbance were carried out with a Unicam SP 500 spectrophotometer, using matched glass cells (10-mm.) supplied with the instrument. At wave lengths of 625 mμ or below, the blue ultrasensitive phototube was used and above 625 mμ, the red sensitive phototube. The phototube circuit was kept at maximum sensitivity. The slit width corresponds to very nominal band widths and ranges between 0.030 and 0.080 mm. All absorbance readings were noted against distilled water blanks.

pH Measurements.—The hydrogen ion concentration of the solutions was measured with a Leeds and Northrup direct reading pH indicator, standardized by the buffer solution supplied with the instrument.

Electrical Conductance Measurements.—The measurements of electrical conductance were performed with a Leeds and Northrup Kohlrausch slidewire with an audiofrequency oscillator in the circuit using a dip type measuring cell having a cell constant of 0.580.

All experiments were performed at 30°. The total volume of all the mixtures prepared for the measurements was kept at 50 ml. The individual solutions and mixtures were adjusted to pH 5.0 by addition of HCl or NaOH and stored at 30 ± 0.01°, for about 1 hr. before use. Added electrolytes in the solution produced coagulation of the lake, hence constant ionic strength could not be attained.

Procedure.—Three different methods: (i) the method of continuous variations[2] (using absorbance as well as electrical conductance measurements), (ii) the mole ratio method,[3] and (iii) the slope ratio method[4] (both using absorbance measurements) were employed to establish the composition of the chelate.

A series of mixtures is prepared for the mole ratio method, containing a constant amount of the metallic ion but with increasing ratios of the metal to the reagent (or *vice versa*). When

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[1] (a) H. H. Willard and C. A. Horton, *Anal. Chem.*, **22**, 1190 (1950); (b) M. Theis, *Z. anal. Chem.*, **144**, 106, 192, 275 (1955); (c) A. Musil and M. Theis, *ibid.*, **144**, 427 (1955); (d) J. S. Fritz and M. O. Fulda, *Anal. Chem.*, **26**, 1206 (1954); (e) M. Malát and M. Tenerova, *Chem. Listy*, **51** (11), 2135 (1957); (f) T. Matsuo, *Bunseki Kagaku*, **7**, 557 (1958); (g) S. P. Sangal and A. K. Dey, *Z. anal. Chem.*, **178**, 415 (1961); (h) D. Ravinson and J. H. Harley, *Anal. Chem.*, **25**, 794 (1953); (i) B. J. MacNulty and L. D. Woolard, *Anal. Chim. Acta*, **14**, 452 (1956); (j) L. Silverman and M. E. Shideler, U. S. At. Energy Comm. NAA-SR 2686, 1958; *Anal. Chem.*, **31**, 152 (1959).

[2] P. Job, *Compt. rend.*, **180**, 928 (1925); *Ann. Chim.*, (10) **9**, 113 (1928).

[3] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

[4] A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).