the polar resonance form must make an appreciable contribution to the over-all structure of the molecule.

Bates and Hobbs claim that the low basicity of the amide group is due mainly to dipole interaction. Since dipole interaction opposes a coplanar configuration, it is logical to conclude that if this effect is stronger than the resonance effect, the structure they have assumed for their calculations would not exist.

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The Infrared Spectrum of Disulfur Decafluoride

By D. Edelson

Disulfur decafluoride, S_2F_{10}, is one of the fluorides of sulfur formed when sulfur is heated in a fluorine atmosphere; its properties have been described by Denbigh and Whytlaw-Gray.[1] It may be obtained as a by-product in the production of sulfur hexafluoride and is frequently present in the latter as impurity. In this work the infrared spectrum of this compound is reported as a means of comparing its structure to that of SF_6 of which it may be considered a dimer.

Measurements[2] were made on a double-beam spectrophotometer using a four-inch cell with potassium bromide windows. A sodium chloride prism was used to cover the range 2.5–15 μ, and a potassium bromide prism for 15–22 μ. The spectrum was measured at two pressures, 4 mm. and 37 mm. Results are shown in Fig. 1. The bands and their intensities are given in Table I.

Table I

Infrared Bands of S_2F_{10} (Cm.$^{-1}$)

vs, very strong; s, strong; m, medium; w, weak; vw, very weak

544	s	1182	w
576	s	1206	w
605	w	1242	m
683	m	1256	s
733	w	1299	w
827	vs	1323	w
890	s	1404	w
917	s	1497	s
940	vs	1550	w
988	m	1629	w
1107	vw	1736	w
1130	vw		

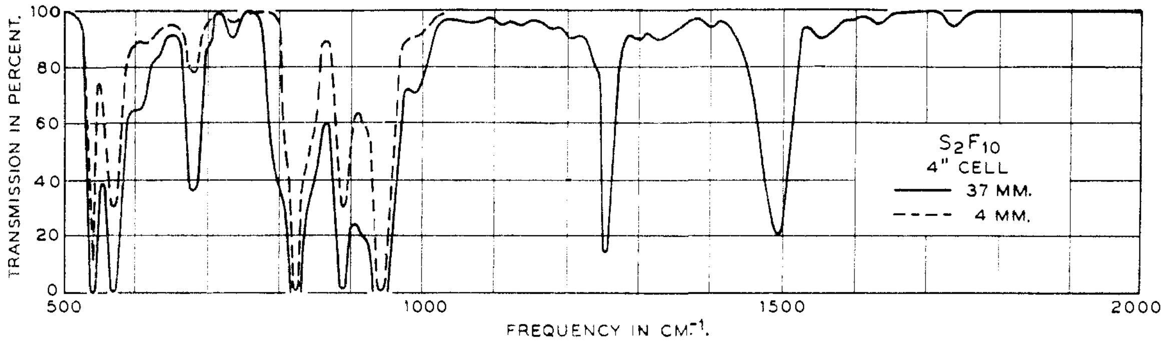

Fig. 1.—The infrared spectrum of S_2F_{10}.

S_2F_{10} may be assumed to consist of two half-octahedra of five fluorine atoms about a central sulfur atom, in analogy with the structure of SF_6, joined by a S–S bond. Although the fundamentals cannot be definitely assigned without further knowledge of the extent of rotation about the S–S bond,[3] and without the Raman spectrum, some tentative assignment may be made by a comparison with the spectrum of SF_6. The vibration of the plane of four fluorine atoms with respect to the central sulfur atom in SF_6 is given by the F_{1u} fundamental[4] at 940 cm.$^{-1}$; the corresponding vibration in S_2F_{10} may be assigned to the very strong band at 940 cm.$^{-1}$. This band in S_2F_{10} is considerably stronger than that in SF_6, undoubtedly because there are twice as many vibrating groups per molecule.

It is questionable whether a S–S vibration should be expected to appear in the infrared; if this may be assumed, however, the bands at 544 or 576 cm.$^{-1}$ may be attributed to this in comparison with the value 512 cm.$^{-1}$ reported by Venkateswaran[5] for this frequency in S_2Cl_2.

The assistance of Mr. K. H. Storks and Mrs. M. H. Read in the experimental work is gratefully acknowledged.

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[1] K. G. Denbigh and R. Whytlaw-Gray, *J. Chem. Soc.*, 1346 (1934).

[2] The sample used in these experiments was obtained through the courtesy of the Pennsylvania Salt Mfg. Co., Chestnut Hill, Phila., Pa.

[3] Note Added in Proof: S. H. Bauer, in a paper presented at the 120th meeting of the American Chemical Society at New York, September 6, 1951, Symposium on Bond Strengths, reported the existence of some hindered rotation despite an abnormally long S–S bond distance.

[4] R. T. Lagemann and E. A. Jones, *J. Chem. Phys.*, **19**, 534 (1951).

[5] S. Venkateswaran, *Ind. J. Phys.*, **6**, 275 (1931).

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Silicon Disulfide and Silicon Diselenide[1a]

By Henry Gabriel[1b] and C. Alvarez-Tostado

The fact that silicon and the sulfur family elements react to form binary compounds has been known since the discovery of these elements and

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[1a] Extract from a dissertation prepared under the direction of Prof. Alvarez-Tostado and submitted to the Dept. of Chemistry of Stanford University by Henry Gabriel in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

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the reaction was described by Wöhler and Berzelius.[2] Although silicon disulfide has been prepared by various methods and extensively investigated, silicon diselenide has never been prepared pure and described. An attempt to prepare the latter by a reaction between hydrogen selenide and silicon resulted in evidence of compound formation but the material was apparently impure.[3]

When Sabatier[4] first investigated a large number of metal sulfides, he prepared silicon disulfide and measured its heat of reaction with water. By the use of the Hess law he determined the heat of formation of this compound from amorphous silicon as 40.4 kcal./fw. and from crystalline silicon as 31.7 kcal./fw. No redetermination of the heat of hydrolysis of silicon disulfide has been carried out but by using more modern values for the other reactions, the value could change slightly. However, there is a wide divergence in the reference literature for the heat of formation of this compound. Lange's Handbook[5] gives 32.02 kcal., Mellor[6] gives 10.4 kcal. as the value reportedly obtained by Sabatier, while the International Critical Tables[7] give a value for a "yellow" silicon disulfide, which, according to Sabatier's original article[4] was an impure mixture of varying composition. It was the purpose of this investigation to resolve this disagreement and to obtain similar information about silicon diselenide.

Experimental

(1) **The Preparation and Purification of Silicon Disulfide and Silicon Diselenide.**—The preparation of the two compounds was based on the observation of Berzelius that silicon and sulfur combine directly at elevated temperatures.[2] One mole of iron-free crystalline silicon and two and a half moles of sulfur were ground together in a mortar. Portions of this mixture were introduced into an 8 inch Pyrex glass test-tube, containing Pyrex glass wool, in such a manner that the mixture was distributed on the fibers of the wool and not in a compact mass at the bottom. The tube was filled about one third full and constricted in order to facilitate sealing. The material was then spot heated with a glass-blowing torch, care being taken that the spot did not blow out. Just about at the softening temperature of the glass, a violent reaction was observed with incandescence spreading through the entire mixture when it was properly distributed. Whenever the reaction was only local, the tube was spot-heated until the entire quantity of material had exhibited this incandescence. The excess sulfur vaporized and burned at the top of the tube. The tube was then sealed until needed for purification. The omission of glass wool inhibited the reaction completely, at least at the temperature below the softening point of the Pyrex glass. The apparent catalytic effect of the glass wool should be noted.[8]

Silicon diselenide was prepared in the same manner as described above. However, the reaction between silicon and selenium is not very evident and it was necessary to bring the entire content of the tube to a temperature of about 650°. Again the catalytic action of Pyrex glass wool was in evidence.

The purification was carried out by means of a Lindberg Tube Furnace, using a $^3/_4$ inch inside diameter Vitroseal combustion tube connected to a high vacuum pump system. The crude material, including the walls of the test-tube which were often covered with active material was crushed and placed into a large porcelain boat. This was placed in the combustion tube and the open end closed by means of a rubber stopper sealed in with commercial gasket cement. The gasket cement produced a satisfactory seal and made the removal of the stopper at the end of the run quite easy. The air was exhausted from the system and the oven allowed to reach a temperature from 900–1150°, which was maintained for about two hours. The vacuum was maintained at less than 0.1 mm. during the entire time and while the tube was cooling back to room temperature. It was essential to allow the material to return to room temperature as immediate decomposition of the compounds took place when they were permitted to come into contact with air at an elevated temperature.

The white crystalline, very porous silicon disulfide which collected in the cooler portion of the tube was removed and immediately sealed into glass vials (sulfur analysis 69.7%, theory 69.6%; hydrolysis and ignition to silica, 0.1221 g. yielded 0.0794 g. of silica, theory 0.0796 g.).

The purified silicon diselenide was also a white, crystalline solid (selenium analysis: 83.9%, theory 84.91%; hydrolysis and ignition to silica, 0.1490 g. yielded 0.0507 g. SiO_2; theory 0.0481 g.).

(2) **Density of Silicon Disulfide and Silicon Diselenide.**—Since the density of silicon disulfide had not been reported previously in the literature, it was measured by means of immersion in dry, thiophene-free benzene. A pycnometer, having a capacity of 10 cc., and closed by a thermometer fitted ground-glass stopper, was used. The average of three determinations at 25° was 1.875 ± 0.01 g./cc. A similar determination for silicon diselenide gave an average value of 2.63 ± 0.05 g./cc. The relatively large uncertainty factor is due to the fact that even sealed silicon diselenide will react with the enclosed oxygen so that it is almost impossible to maintain a purity of more than 98%.

(3) **Heat of Hydrolysis and Heat of Formation of Silicon Disulfide and Silicon Diselenide.**—In order to settle the difference in the values given in the various reference works, the measurement of the heat of reaction of silicon disulfide, and subsequently that of silicon diselenide, was carried out in 6 *M* sodium hydroxide. In this manner the formation of gaseous hydrogen sulfide and selenide would be minimized and the precipitation of hydrated silica could be suppressed in favor of the formation of sodium metasilicate.

The heats of reaction were measured in a small calorimeter employing a five junction thermocouple thermometer balanced by a potentiometer circuit. These measurements were complicated by the fact that both compounds tend to decompose on exposure to moisture of the air, the characteristic odor of hydrogen sulfide and hydrogen selenide becoming noticeable immediately upon breaking of the sealed vials in which the material was kept. Four determinations made on fresh material analyzing 99+% SiS_2, gave 45.38, 46.57, 45.92, 46.38 kcal./fw. for an average of 46.1 kcal./fw. A similar series of determinations on silicon diselenide gave an average value of 391.3 cal./g. and 72.8 kcal./fw. It was noted that whenever two successive determinations of the heat of hydrolysis were made using silicon diselenide from the same vial, the value dropped 4–5 kcal. although remainders were kept only for short periods in tightly stoppered weighing bottles and in a desiccator containing magnesium perchlorate.

The heat of formation of silicon disulfide was calculated from the following reaction, using heat of formation, values from the Handbook of Chemistry and Physics, 32d Edition, except for the value of Na_2SiO_3(aq), as explained below.

$$\begin{array}{llll} SiS_2 & +\ 6NaOH\ (aq.) & \longrightarrow & Na_2SiO_3\ (aq.) \\ -x & -\ 6(112.04) & & +\ 362.25 \end{array}$$

$$\begin{array}{llll} +\ 2Na_2S\ (aq.) & +\ 3H_2O & +\ 46.1\ \text{kcal.} \\ +\ 2(105.4) & +\ 3(68.4) & =\ 46.1 \end{array}$$

$$-x = -\ 59.91\ \text{kcal. or}$$

$$Si + 2S \longrightarrow SiS_2 + 59.9 \pm 0.5\ \text{kcal.}$$

For $SiSe_2$:

$$\begin{array}{llll} SiSe_2 & +\ 6NaOH\ (aq.) & \longrightarrow & Na_2SiO_3\ (aq.) \\ -x & -\ 6(112.04) & & +\ 362.25 \end{array}$$

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(2) H. Moissan, "Traite de chemie minérale," Masson et Cie., Paris, 1904, Metalloides II, pp. 450 ff.

(3) P. Sabatier, *Compt. rend.*, **113**, 132 (1903).

(4) P. Sabatier, *Ann. chim.*, [v] **22**, 86 (1881).

(5) N. A. Lange, ed., "Handbook of Chemistry," 5th Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1944.

(6) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans Green and Co., London, 1931, Vol. VI, p. 859.

(7) "International Critical Tables," Vol. V. McGraw-Hill Book Co., New York, N. Y., 1929.

(8) Observation of this effect was first made by Dr. Tostado and Mr. Harlow, while attempting this synthesis at the Chemistry Laboratories of Stanford University. Patent applied for.

$$+\ 2Na_2Se\,(aq.) + 3H_2O + 72.78\ \text{kcal.}$$
$$+\ 2(88.12) + 3(68.4) = 72.78$$
$$-x = 1.33\ \text{kcal. or}$$
$$Si + 2Se \longrightarrow SiSe_2 - 1.33 \pm 0.5\ \text{kcal.}$$

Thomsen[9] investigated the reaction between aqueous sodium hydroxide and aqueous silicic acid; he found the heat of reaction for aqueous sodium metasilicate to be +5.23 kcal., at the exact equivalence point. Excess reagents produced different results so that the figure is of uncertain reliability. However, it is the only figure available and the calculation of the heat of formation of $Na_2SiO_3(aq)$ when compared to that of $Na_2SiO_3(s)$ is a reasonable one, giving a negative heat of solution of about 6 kcal. per mole.

$$2NaOH\,(aq.) + SiO_2 \longrightarrow Na_2SiO_3\,(aq.) + H_2O + 5.23\ \text{kcal.}$$
$$-2(112.04) - 201.34 + x + 68.4 = 5.23$$
$$x = 362.25$$

To account for the differences between the figures obtained by this calculation and those of Sabatier, the latter's equation must be considered.

$$SiS_2 + 2H_2O \longrightarrow SiO_2(\text{diss}) + 2H_2S(g) + 38\ \text{kcal.}$$
$$-x - 2(68) + 201 + 10 = 38$$

in round figures using recent values $-x = -37$ kcal. Sabatier considered the heat of solution of silica a negligible quantity and failed to consider the formation of a saturated solution of hydrogen sulfide. It is also possible that the dissolved silica was a mixture of silicic acids. The use of 6 *M* sodium hydroxide in this study resulted in the formation of dissolved salts of predictable composition, especially since a large excess of sodium hydroxide was always present.

Properties of Silicon Diselenide.—The freshly sublimed silicon diselenide was a white, crystalline solid, which was deposited in a hard compact mass on the wall of the tube.

Silicon diselenide reacts with the oxygen of the air at room temperature in a simple replacement reaction.

$$SiSe_2 + O_2 \longrightarrow SiO_2 + 2Se\ (\text{red}).$$

It reacts vigorously with water, forming hydrogen selenide and silica. With strong bases, the corresponding selenides and silicates are formed. Evidence of the reaction in the crude material was obtained by the formation of zinc selenide and the odor of hydrogen selenide immediately evident when the material was in contact with moist air. Due to its instability and the nature of its decomposition products, extreme caution should be exercised in its preparation and handling.

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(9) J. Thomsen, "Thermochemische Untersuchingen," Vol. II, Johan Ambrosius Barth, Leipzig, 1882, p. 413.

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Preparation of Radioactive Sodium Metal by Exchange of Na^{23} and $Na^{22}Cl$

BY NORMAN H. NACHTRIEB, JOHN A. WEIL AND EDWARD CATALANO

In the course of investigating diffusion phenomena among the alkali metals, we have found it convenient to prepare metallic radioactive sodium by means of the reaction

$$Na^{23}(l) + Na^{22}Cl(s) \longrightarrow Na^{22}(l) + Na^{23}Cl(s)$$

The distribution of Na^{22} between the metal and salt should stand in the approximate ratio of the weights of sodium in the two phases. Under the conditions of our experiments, when the ratio of sodium to sodium chloride was about 10^4, essentially quantitative conversion was obtained. No effort was made to determine the distribution coefficient. On the face of it, it looks as if the reaction occurs between solid sodium chloride and liquid sodium metal, but the detailed nature is not known. The high conversion rate rules out the possibility that the reaction involves only the contact surfaces. Conceivably, the sodium chloride may dissolve in the metal; alternatively, reaction may take place by diffusion of sodium through sodium chloride.

Experimental

The exchange reaction and the subsequent distillation of the metal took place in a specially designed Pyrex tube. An iron thimble made from a 6″ length of $^7/_8$″ dia. seamless tubing, with a bottom plug pressed into place, was sealed into one end of the tube. Adjacent to the thimble was a U shaped section with a seal-off tube connected at the bottom. The other end of the tube led to a vacuum line. 1.00 ml. of a tracer solution,[1] having an activity of 1.13×10^7 disintegrations min.$^{-1}$ and containing a total of 2.39 mg. of carrier sodium chloride, was transferred to the thimble. The water was removed by evacuation of the tube with an oil diffusion pump through an intervening liquid nitrogen trap. A quantity of freshly cut sodium, estimated to weigh about 10 g., was then placed in the thimble and the system was again evacuated. A cylindrical electric furnace was slipped over the end of the tube and the contents of the thimble maintained at 250° overnight.

A thin iridescent metal mirror appeared on the walls of the tube beyond the thimble. Since its thickness did not increase with time, it was assumed to be a trace of potassium and was flamed out of the tube. When the temperature was raised to 525°, all of the sodium distilled from the thimble and condensed in the U section. Careful flaming transferred almost all of the metal into the seal-off tube. The 7.60 g. of sodium thus recovered was found to have a specific activity of 1500 disintegrations min.$^{-1}$ mg.$^{-1}$. The possibility that $Na^{22}Cl$ was carried over mechanically was ruled out by the fact that redistillation did not diminish the activity of the metal. Some discoloration of the U section appears to be unavoidable, but can be minimized by care in flaming. Five preparations have been carried out in this manner.

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(1) Supplied by Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee.

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Thallous Salts as Derivatives of Sulfonic Acids. II

BY HENRY GILMAN AND H. SMITH BROADBENT

The present report is an extension of previous preliminary studies[1] on the use of thallous salts for the characterization of some sulfonic and other acids or their soluble salts. Several advantages of these salts as derivatives of sulfonic acids were mentioned in the earlier reports.[1] Among the salts now reported is found additional support

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(1) (a) Gilman and Abbott, THIS JOURNAL, **65**, 123 (1943); (b) Gilman and Abbott, *ibid.*, **71**, 659 (1949).