

### 183. Pentafluorosulphuroxy-derivatives of Hexafluoropropene.

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Bis-pentafluorosulphur peroxide and pentafluorosulphur hypofluorite react with hexafluoropropene to give a series of compounds  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_n \cdot \text{O} \cdot \text{SF}_5$  where  $n = 2, 3, \text{ or } 4$ . The addition compounds are thermally decomposed at  $300^\circ$  with elimination of sulphur hexafluoride.

PENTAFLUOROSULPHUR HYPOFLUORITE reacts with ethylene or halogen-substituted ethylene to give simple addition compounds of the type  $\text{SF}_5 \cdot \text{O} \cdot \text{C}_2\text{H}_4\text{F}$ <sup>1,2</sup> but no addition compounds of bis-pentafluorosulphur peroxide with olefins have yet been reported.<sup>3</sup>

It has now been found that bis-pentafluorosulphur peroxide and hexafluoropropene react smoothly in an autoclave at  $150^\circ$  to give a series of compounds, identified as  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_n \cdot \text{O} \cdot \text{SF}_5$  where  $n = 2, 3, \text{ or } 4$  but no compound corresponding to  $n = 1$  was obtained.

A similar series of compounds was formed in a photochemical reaction between bis-pentafluorosulphur peroxide and hexafluoropropene at room temperature and atmospheric pressure.

When pentafluorosulphur hypofluorite and hexafluoropropene were refluxed in trichlorofluoromethane ("Arcton 11") solution a vigorous reaction occurred and a liquid of low volatility was produced. This was separated into two fractions which were identified as  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_2 \cdot \text{O} \cdot \text{SF}_5$  and  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_2 \cdot \text{F}$ .

These were the only products of the reaction and no compound corresponding to either  $\text{SF}_5 \cdot \text{O} \cdot \text{C}_3\text{F}_6 \cdot \text{O} \cdot \text{SF}_5$  or  $\text{SF}_5 \cdot \text{O} \cdot \text{C}_3\text{F}_7$  was obtained. Nor were any compounds of the type  $\text{F} \cdot [\text{C}_3\text{F}_6]_n \cdot \text{F}$ , which might have been expected to accompany the formation of  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_2 \cdot \text{O} \cdot \text{SF}_5$ , detected.

The reaction between pentafluorosulphur hypofluorite and hexafluoropropene in an autoclave resulted in explosive decomposition at about  $0^\circ$ , but when moderated by the addition of "Arcton 11" as solvent, the products were identical with those formed under reflux at atmospheric pressure and  $-25^\circ$ .

The compounds  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_n \cdot \text{O} \cdot \text{SF}_5$  were appreciably decomposed when heated to  $300^\circ$ . The compound  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_3 \cdot \text{O} \cdot \text{SF}_5$ , after being heated for 24 hours at  $300^\circ$ , gave  $\text{SF}_6$  as the sole gaseous product and only two liquid products which were  $\text{C}_9\text{F}_{16}\text{O}_2$  and  $\text{SF}_5 \cdot \text{O} \cdot \text{C}_9\text{F}_{17} \cdot \text{O}$ . The infrared spectrum of the second compound had bands in the region characteristic of the  $\text{SF}_5 \cdot \text{O} \cdot$  group at 870 and 807  $\text{cm}^{-1}$ . Both compounds showed bands characteristic of a carbonyl group, at 1897 and 1890  $\text{cm}^{-1}$ , but no distinction as between a ketone  $\cdot \text{CF}_2 \cdot \text{CO} \cdot \text{CF}_3$  and a carbonyl fluoride  $\cdot \text{CF}(\text{CF}_3) \cdot \text{COF}$  has been made.

The fact that compounds of the type  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_n \cdot \text{O} \cdot \text{SF}_5$  are formed both photochemically and thermally from bis-pentafluorosulphur peroxide and pentafluorosulphur hypofluorite indicates that a free-radical mechanism is involved, but the authors are unable to offer any convincing explanation for the anomalous absence in all the reactions of the 1 : 1 addition compound.

#### EXPERIMENTAL

Bis-pentafluorosulphur peroxide and pentafluorosulphur hypofluorite were prepared by known methods.<sup>4,5</sup>

Autoclave reactions were carried out using a 55-c.c. Hastelloy C vessel. Liquid reagents were added at room temperature while gaseous materials were condensed into the vessel cooled in liquid air. The autoclave could be heated to the desired temperature by a copper-block

<sup>1</sup> Williamson and Cady, *Inorg. Chem.*, 1962, **1**, 673.

<sup>2</sup> Williamson, *Inorg. Chem.*, 1963, **2**, 421.

<sup>3</sup> Merrill and Cady, *J. Amer. Chem. Soc.*, 1963, **85**, 909.

<sup>4</sup> Roberts, *J.*, 1960, 2774.

<sup>5</sup> Dudley, Cady, and Eggers, *J. Amer. Chem. Soc.*, 1956, **78**, 1553.

electric furnace. At the end of the reaction the vessel was cooled to room temperature and any pressure in the system released through two traps cooled in liquid air. The contents of the traps were allowed to expand to room temperature and the gases analysed by gas chromatography and infrared spectroscopy. Residual liquid in the traps was added to the contents of the autoclave and fractionated.

Molecular weights were measured by either a vaporimetric method or ebullioscopically in benzene. The first method was limited to compounds boiling below 210°/760 mm. while the ebullioscopic method was ineffective on occasions when considerable foaming of the solution occurred following the addition of the compound.

Fluorine was determined by fusing the sample with potassium metal for 10 hr. The residue was extracted cold with alcohol and water and then acidified with perchloric acid. The fluorine was steam-distilled from the solution as fluorosilicic acid and titrated against thorium nitrate with Chrome Azurol S as indicator. Some difficulty was experienced in breaking down the compounds completely on fusion with potassium and this probably accounts for the fluorine values being slightly lower than predicted.

The columns used for gas-chromatographic analysis were packed with "Chromosorb" (Johns Manville Ltd.) on which dinonyl phthalate had been adsorbed.

A Perkin-Elmer Infracord was used to record infrared spectra.

*Reaction of Bis-pentafluorosulphur Peroxide with Hexafluoropropene.*—Bis-pentafluorosulphur peroxide (20 g.) and hexafluoropropene (42 g.) were heated to 150° for 15 hr. in a 55-c.c. Hastelloy C vessel. A series of such reactions gave 33.5 g. of liquid product which when distilled gave a number of fractions:

Fraction 1, b. p. 49°, was bis-pentafluorosulphur peroxide (2.6 g.).

Fraction 2, b. p. 60°/18 mm., was  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_2 \cdot \text{O} \cdot \text{SF}_5$  (1.9 g.),  $d^{25}_4$  2.023,  $n_D^{20}$  1.2965; the infrared spectrum had major peaks at 1220, 1160, 980, 925, 880, 820, and 805—795  $\text{cm}^{-1}$  (Found: C, 12.6; F, 68.2; S, 11.2%;  $M$ , 574.  $\text{C}_6\text{F}_{22}\text{O}_2\text{S}_2$  requires C, 12.2; F, 71.5; S, 10.9%;  $M$ , 586).

Fraction 3, b. p. 70°/5 mm., was  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_3 \cdot \text{O} \cdot \text{SF}_5$  (10 g.),  $d^{25}_4$  2.042,  $n_D^{20}$  1.3055; the infrared spectrum had major peaks at 1240, 1180, 985, 920, 880, and 825—815  $\text{cm}^{-1}$  (Found: C, 15.0; F, 69.6; S, 8.9%;  $M$ , 719.  $\text{C}_9\text{H}_{28}\text{O}_2\text{S}_2$  requires C, 14.7; F, 72.2; S, 8.7%;  $M$ , 736).

Fraction 4, b. p. 92—94°/3 mm., was  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_4 \cdot \text{O} \cdot \text{SF}_5$  (5 g.),  $d^{25}_4$  2.054,  $n_D^{20}$  1.3125; the infrared spectrum had major peaks at 1240, 1175, 985, 920, 880, 820, and 805  $\text{cm}^{-1}$  (Found: C, 15.8; F, 70.3; S, 7.0%;  $M$ , 893.  $\text{C}_{12}\text{H}_{34}\text{O}_2\text{S}_2$  requires C, 16.2; F, 73.0; S, 7.2%;  $M$ , 886).

The higher-boiling residue was not examined any further.

The retention volumes of fractions 2, 3, and 4 on a dinonyl phthalate column at 110° were in the ratio 1 : 2 : 4 indicating that the compounds were consecutive members of an homologous series.<sup>6</sup>

*Reaction of Pentafluorosulphur Hypofluorite with Hexafluoropropene.*—Pentafluorosulphur hypofluorite (1.6 g.) and hexafluoropropene (2 g.) were condensed into a Pyrex-glass tube of 50 c.c. capacity, to which 35 c.c. of trichlorofluoromethane had been added. When the tube was warmed slowly a vigorous reaction commenced and the mixture refluxed steadily, with the reflux condenser cooled to -60°. After the vigorous reaction had ceased more pentafluorosulphur hypofluorite and hexafluoropropene was added to the solution and the reaction procedure repeated. In a series of consecutive reactions in the same solution, a total of 8 g. of pentafluorosulphur hypofluorite and 10 g. of hexafluoropropene was added.

The gases (10 g.) passing through the condenser were collected in a trap cooled to -80° and examined by gas chromatography and infrared spectroscopy and shown to be hexafluoropropene and trichlorofluoromethane.

The liquid product (4 g.) obtained after distilling off the trichlorofluoromethane gave two fractions. Fraction 1, b. p. 44°/20 mm., was 1-pentafluorothio-oxyperfluorohexane  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_2 \cdot \text{F}$  (Found: C, 15.9; F, 74.6; S, 7.4%;  $M$ , 463.  $\text{C}_6\text{F}_{18}\text{OS}$  requires C, 15.5; F, 74.0; S, 6.9%;  $M$ , 462).

Fraction 2 b. p. 65°/20 mm., was 1,6-bis-pentafluorothio-oxyperfluorohexane  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_2 \cdot \text{O} \cdot \text{SF}_5$ .

*Pyrolysis of  $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_3 \cdot \text{O} \cdot \text{SF}_5$ .*— $\text{SF}_5 \cdot \text{O} \cdot [\text{C}_3\text{F}_6]_3 \cdot \text{O} \cdot \text{SF}_5$  (20 g.) was added to the 55 c.c. Hastelloy C vessel and heated at 300° for 24 hr.

The gaseous product (5.2 g.) was identified as sulphur hexafluoride by its infrared spectrum.

<sup>6</sup> Keulemans, "Gas Chromatography," Reinhold, New York, 1959, 2nd edn., pp. 27—30.

The liquid product was separated into two fractions. Fraction 1, b. p. 33°/20 mm., was  $C_9F_{16}O_2$  (Found: C, 24.2; F, 66.0; S, 0.3%; *M*, 437.  $C_9F_{16}O_2$  requires C, 24.3; F, 68.4; S, 0%; *M*, 444).

The infrared spectrum had major peaks at 1897, 1890, 1300, 1245, 1145, and 985  $cm^{-1}$ . Fraction 2, b. p. 64°/20 mm., was  $SF_5O \cdot C_9F_{17}O$  (Found: C, 19.1; F, 69.1; S, 5.4.  $C_9F_{22}O_2S$  requires C, 18.3; F, 70.5; S, 5.4%). The infrared spectrum had major peaks at 1897, 1890, 1245, 1125, 1052, 1000, 920, 870, 807, 735, 715, and 695  $cm^{-1}$ .

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