## 614. *Preparation and Some Reactions of Disulphur Decafluoride.*

By H. L. Roberts.

A simple preparation of disulphur decafluoride by photochemical reduction of sulphur chloride pentafluoride with hydrogen is described. Some reactions of disulphur decafluoride are compared with those of sulphur chloride pentafluoride with similar molecules.

Disulphur decafluoride was first isolated and characterised by Denbigh and Whytlaw-Gray[1] as a high-boiling residue in the preparation of sulphur hexafluoride by direct fluorination of sulphur. These authors gave b. p. 29° and f. p. $-92°$, but later workers[2] showed that the melting point was very sensitive to traces of impurities and gave m. p. $-55°$.[2]

This method of preparation is inconvenient to carry out as the yield of disulphur decafluoride is very low. A better method is the photochemical reduction with hydrogen of sulphur chloride pentafluoride:

$$2SF_5Cl + H_2 \longrightarrow S_2F_{10} + 2HCl$$

The reaction can conveniently be carried out continuously by cycling the reactants through the photochemical reactor and removing hydrogen chloride and disulphur decafluoride as they are formed. Provided that the reactants are dry no etching of the apparatus is observed which indicates that no reduction of S–F bonds occurs.

Analogy with sulphur chloride pentafluoride[3] suggests that disulphur decafluoride might react with olefins, two pentafluorosulphur groups being added across the double bond. In practice it has been found that, despite the fact that the S–S bond in disulphur decafluoride breaks readily at 150°[4] whereas the S–Cl bond in sulphur chloride pentafluoride is stable at 250°,[2] the reaction of disulphur decafluoride with olefins proceeds at best in very poor yield and in other cases not at all. Thus, sulphur chloride pentafluoride reacts readily with ethylene and propene to give stable addition products[3] in high yields. Disulphur decafluoride failed to add to ethylene under mild conditions and when treated more vigorously caused the ethylene to decompose. With propene a small quantity of a

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[1] Denbigh and Whytlaw-Gray, *J.*, 1934, 1346.
[2] Roberts, *Quart. Rev.*, 1961, **15**, 30.
[3] Case, Ray, and Roberts, *J.*, 1961, 2066.
[4] Trost and McIntosh, *Canad. J. Chem.*, 1951, **29**, 508.

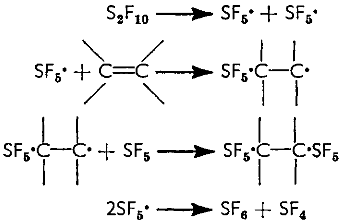
high-boiling liquid was formed but this was very unstable to heat and was not characterised. With vinyl chloride it proved possible to isolate a small quantity of adduct having the structure expected for 1 : 1 addition:

$$CH_2{:}CHCl + S_2F_{10} \longrightarrow SF_5{\cdot}CH_2{\cdot}CHCl{\cdot}SF$$

It is known that disulphur decafluoride is a powerful oxidising agent [2] and it is therefore likely that degradative oxidation is one cause for the poor yields obtained in these reactions. It was thought therefore that better yields might be obtained in addition to fluoro-olefins. With tetrafluoroethylene a solid product was obtained despite the fact that the disulphur decafluoride was present in excess of a 1 : 1 ratio. Infrared spectroscopic examination of the product revealed, in addition to the usual bands due to polytetrafluoroethylene, a strong absorption at 895 cm.$^{-1}$ which is characteristic of an $SF_5$ group bonded to $\cdot CF_2X$.[3] With hexafluoropropene, however, it proved possible to isolate a small yield of a 1 : 1 adduct along with some higher-boiling material, but the main reaction was the decomposition of disulphur decafluoride to sulphur tetrafluoride and sulphur hexafluoride in the usual manner: [4]

$$S_2F_{10} + CF_3{\cdot}CF{:}CF_2 \longrightarrow SF_5{\cdot}CF(CF_3){\cdot}CF_2{\cdot}SF_5$$

The cause for the very inefficient reaction of disulphur decafluoride with olefins, which is in such marked contrast to the very ready reaction of sulphur chloride pentafluoride in similar circumstances may lie in the inability of the former to act as a chain-transfer agent. Thus, if R• represents a radical in the reaction system, the step $R\cdot + S_2F_{10} \longrightarrow R{\cdot}SF_5 + SF_5\cdot$ is very inefficient by comparison with $R\cdot + SF_5Cl \longrightarrow RCl + SF_5$, and with disulphur decafluoride the reaction takes place only by radical–radical interaction.



$$S_2F_{10} \longrightarrow SF_5\cdot + SF_5\cdot$$
$$SF_5\cdot + \text{>C=C<} \longrightarrow SF_5{\cdot}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot$$
$$SF_5{\cdot}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot + SF_5 \longrightarrow SF_5{\cdot}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{\cdot}SF_5$$
$$2SF_5\cdot \longrightarrow SF_6 + SF_4$$

On the scale of work so far carried out it has not proved possible to isolate the higher-boiling products as individual components and this mechanism must remain speculative.

With benzene, sulphur chloride pentafluoride acts as a chlorinating agent:

$$SF_5Cl + C_6H_6 \longrightarrow C_6H_5Cl + SF_4 + HF$$

Disulphur decafluoride in similar circumstances gave some phenylsulphur pentafluoride,[5] but as with sulphur chloride pentafluoride much degradative oxidation took place.

$$S_2F_{10} + C_6H_6 \longrightarrow C_6H_5{\cdot}SF_5 + SF_4 + HF$$

It appears therefore that disulphur decafluoride gives as its principal reaction destructive oxidations due to the reactions:

$$S_2F_{10} \longrightarrow 2SF_5\cdot$$
$$SF_5\cdot \longrightarrow SF_4 + F\cdot$$

and that as a reagent for introducing the $SF_5$ group into organic molecules it is much less efficient than sulphur chloride pentafluoride with olefins and gives such low yields with benzene as to be of no practical value.

[5] Sheppard, *J. Amer. Chem. Soc.*, **1960**, **82**, 4751.

## EXPERIMENTAL

*Photochemical Reduction of Sulphur Chloride Pentafluoride with Hydrogen.*—A standard Hanovia 10-l. photochemical reaction vessel with a quartz centre tube was used. This tube acts as a container for a Hanovia 509/12 mercury-arc tube and provides a means of circulating cooling water between the lamp and the reactants. The reaction vessel was connected on the one side, through a drying tower packed with calcium sulphate, to a 20-l. reservoir to contain sulphur chloride pentafluoride and hydrogen, and on the other to a scrubbing tower by means of which gases can be washed counter-current-wise with water to remove hydrogen chloride. The effluent gas from the scrubber was led through a cold trap (−20°) to condense disulphur decafluoride and returned by a diaphragm circulating pump to the reservoir.

At the start of a run the reservoir was filled by displacement of water with a 2 : 1 molar ratio of sulphur chloride pentafluoride and hydrogen, and the reaction vessel was evacuated and filled with a similar mixture. The arc tube was energised and circulation commenced; a pressure of 1 atm. was maintained in the system by a constant-head device on the reservoir. The rate of circulation was adjusted to 20 l./hr.

In a typical series of experiments 69 l. of reaction mixture were used and the crude product collected in the cold trap was washed with water, refluxed with 5N-potassium hydroxide solution, dried ($CaSO_4$, followed by $P_2O_5$), and distilled to give disulphur decafluoride, b. p. 29°. This product became solid when kept in a trap at −60° and showed no impurity when examined by gas-chromatography or infrared spectroscopy. The weight of pure product obtained was 140 g., an overall yield of 41%.

*Reaction of Disulphur Decafluoride with Olefins.*—(a) *Propene.* Propene (5 g.) and disulphur decafluoride (30 g.) were condensed into a 55-c.c. "Hastelloy C" autoclave[3] and heated to 90° for 10 hr. There was obtained a dark liquid (22 g.) which on distillation gave disulphur decafluoride, b. p. 29° (15 g.), and a residue which could not be distilled without charring even at 0·1 mm. This product was not identified.

(b) *Vinyl chloride.* Vinyl chloride (6 g.) and disulphur decafluoride (25 g.) were heated together to 150° for 10 hr. There was obtained a liquid (12 g.) which on distillation gave two fractions and a residue: (1) b. p. 29°, disulphur decafluoride (6 g.); (2) b. p. 110—120°, 1-*chloro*-1,2-*bispentafluorothioethane* (2·5 g.). The latter was freed from traces of impurities by gas-chromatography before analysis (Found: Cl, 11·7; F, 60·1; S, 20·0. $C_2H_3ClF_{10}S_2$ requires Cl, 11·2; F, 60·1; S, 20·2%); it had $\nu_{max.}$ 850 cm.$^{-1}$. The residue was not examined.

(c) *Hexafluoropropene.* Hexafluoropropene (20 g.) and disulphur decafluoride (40 g.) were heated in a 55-c.c. autoclave to 200° for 15 hr. There was obtained a colourless liquid (4 g.) which apart from a short forerun boiled at 96° and was found to be *perfluoro*-1,2-*bispentafluorothiopropane* (Found: C, 9·0; F, 75·5; S, 16·0%; *M*, 407. $C_3F_{16}S_2$ requires C, 8·9; F, 75·2; S, 15·8%; *M*, 404], $\nu_{max.}$ 1210vs, 1150 triplet, 970, 930vs, 900vs, 880vs, 850, 810 cm.$^{-1}$.

(d) *Tetrafluoroethylene.* Tetrafluoroethylene (8 g.) and disulphur decafluoride (21 g.) were heated together to 200° for 10 hr. There was obtained a white solid (7 g.) whose infrared spectrum showed strong absorption at 895 cm.$^{-1}$. The solid softened at 260° and was wholly liquid at 310°. It contained 4% of sulphur.

*Reaction of Disulphur Decafluoride with Benzene.*—Disulphur decafluoride (25 g.), benzene (8 g.), and trichlorofluoromethane (30 c.c.) were heated to 180° for 10 hr. There were obtained 37 g. of liquid which on distillation after removal of unchanged reactants gave a fraction, b. p. 147°, $n_D^{24}$ 1·430 (0·6 g.), which was phenylsulphur pentafluoride.[5]

A similar reaction with toluene gave no identifiable product.

Imperial Chemical Industries Limited,
Alkali Division Research Laboratories,
Winnington, Northwich, Cheshire.

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