394. *Sulphur Chloride Pentafluoride: Reaction with Fluoro-olefins.*

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Sulphur chloride pentafluoride adds to tetrafluoroethylene, trifluoroethylene, chlorotrifluoroethylene, and hexafluoropropene, to give 2-chloropolyfluoroalkylsulphur pentafluorides. The orientation of the products formed has been determined, and a possible mechanism for the reactions is suggested.

THE reaction of sulphur chloride pentafluoride with hydrocarbon olefins was described in the preceding paper.[1] The reaction can take place either in the gas phase under the influence of ultraviolet light or in the liquid phase at an appropriate temperature, which

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[1] Case, Ray, and Roberts, preceding paper.

depends on the olefin used. With fluorocarbon olefins the reactions did not take place as readily; a free-radical initiator was desirable in the liquid-phase reactions to obtain reproducible results, and the gas-phase reactions gave other products in addition to chlorofluoroalkylsulphur pentafluorides.

With tetrafluoroethylene, sulphur chloride pentafluoride when in excess and in the presence of dibenzoyl peroxide as a catalyst at 100° reacts smoothly to give mainly 2-chlorotetrafluoroethylsulphur pentafluoride:

$$\mathrm{SF_3Cl + C_2F_4 \longrightarrow SF_5{\cdot}CF_2{\cdot}CF_2Cl}$$

If, however, the tetrafluoroethylene is in excess, telomers of the type $\mathrm{SF_5{\cdot}[CF_2{\cdot}CF_2]_{\mathit{n}}{\cdot}Cl}$ are obtained, the mean molecular weight, judged from the amount of high-boiling material present, depending on the molar ratio of sulphur chloride pentafluoride to tetrafluoroethylene.

Under similar conditions trifluoroethylene also reacts with sulphur chloride pentafluoride to give mainly 1 : 1 addition:

$$\mathrm{SF_5Cl + CHF{=}CF_2 \longrightarrow SF_5{\cdot}CHF{\cdot}CF_2Cl}$$

This compound, unlike all the other compounds prepared in which $\mathrm{SF_5}$ is attached to carbon, is unstable to aqueous alkali and decomposes, giving sulphite ions. The orientation of the addition reaction is proved by the reaction of the product with powdered potassium hydroxide in light petroleum, which gives perfluorovinylsulphur pentafluoride:

$$\mathrm{SF_5{\cdot}CHF{\cdot}CF_2Cl \xrightarrow{KOH} SF_5{\cdot}CF{=}CF_2 + HCl}$$

Chlorotrifluoroethylene also reacts with sulphur chloride pentafluoride under these conditions to give some 2,2-dichlorotrifluoroethylsulphur pentafluoride and much higher-boiling material, presumably telomers:

$$\mathrm{SF_5Cl + CF_2{=}CFCl \longrightarrow SF_5{\cdot}CF_2{\cdot}CFCl_2}$$

This compound has been shown by its infrared spectrum to be an isomer of the compound obtained by chlorination of vinylsulphur pentafluoride whose structure can only be $\mathrm{SF_5{\cdot}CFCl{\cdot}CF_2Cl}$.

In contrast to the three olefins so far discussed, hexafluoropropene does not react with sulphur chloride pentafluoride in the presence of benzoyl peroxide at 150°.

Under the influence of ultraviolet light tetrafluoroethylene, chlorotrifluoroethylene, and hexafluoropropene all react with sulphur chloride pentafluoride. In contrast to the behaviour of hydrocarbon olefins, which gave exclusively 1 : 1 addition under these conditions, a complex mixture was obtained. With tetrafluoroethylene, in addition to all the products observed in the free-radical catalysed reaction, 1,2-dichlorotetrafluoroethane $\mathrm{ClCF_2{\cdot}CF_2Cl}$ and disulphur decafluoride were obtained among the lower-boiling fractions, and it is probable that the higher-boiling fractions contained telomers of the type $\mathrm{Cl{\cdot}[C_2F_4]_{\mathit{n}}{\cdot}Cl}$. Hexafluoropropene gave a similar result, although the known reluctance of this olefin to polymerise meant that only compounds of low molecular weight were obtained. The result obtained with chlorotrifluoroethylene was of great interest, for in addition to the expected disulphur decafluoride and 1,2,2-trichlorotrifluoroethane, a compound was obtained in which one molecule of sulphur chloride pentafluoride had added to one molecule of olefin; this is the isomer of that obtained in the free-radical catalysed reaction:

$$\mathrm{SF_5Cl + CF_2{=}CFCl \longrightarrow SF_5{\cdot}CFCl{\cdot}CF_2Cl}$$

This compound has an infrared spectrum identical with that obtained from the reaction of chlorine with perfluorovinylsulphur pentafluoride. As with tetrafluoroethylene, in addition to the simple compounds mentioned, much higher-boiling material was obtained.

EXPERIMENTAL

Apparatus and Procedure.—Autoclave reactions were carried out in a stainless-steel autoclave of 100 c.c. capacity or a " Hastelloy C " autoclave of 55 c.c. capacity, both vessels being fitted with an electromagnetically operated reciprocating stirrer and having a maximum safe working pressure of 3000 atm. The experimental technique employed has been described in the preceding paper.

The columns used for gas-chromatographic analysis were packed with " Chromosorb " on which dinonyl phthalate, silicone grease, or a chlorofluorocarbon grease had been deposited. All these columns were tried before a given peak was assumed to contain only one substance.

Reaction of Sulphur Chloride Pentafluoride with Unsaturated Fluorocarbons.—*Tetrafluoroethylene.* Sulphur chloride pentafluoride (61 g.), tetrafluoroethylene (22 g.), and dibenzoyl peroxide (0·8 g.) were heated at 90° for 10 hr. The liquid product (49 g.) was washed with N-potassium hydroxide, water, and saturated brine and dried ($MgSO_4$). It gave the following fractions on distillation: (1) b. p. 44—54° (18·3 g.), (2) b. p. 90—102° (8·6 g.), and a residue of 4·2 g. Fraction (1) was carefully redistilled and gave *2-chlorotetrafluoroethylsulphur pentafluoride* (14 g.), m. p. −113°, b. p. 47° (Found: C, 9·6; Cl, 14·0; F, 65·8; S, 12·5%; *M*, 261. C_2ClF_9S requires C, 9·2; Cl, 13·5; F, 65·2; S, 12·2%; *M*, 262·5). The vapour pressure of this compound was measured and fits the equation $\log_{10} p = -1479/T + 7{\cdot}494$. The b. p. found by extrapolation was 47·5°, the latent heat of vaporisation calculated from the slope is 6770 cal. mole^{-1}, and the Trouton constant is 21·1. The infrared absorption spectrum showed intense bands at 1215, 1190, 1135, 1070, 1050, 950, 900vs, 840, 795vs cm.$^{-1}$.

Sulphur chloride pentafluoride (24 g.), tetrafluoroethylene (18 g.), and dibenzoyl peroxide (0·4 g.), dissolved in trichlorofluoromethane (30 g.), were heated at 100° for 10 hr. The liquid product (73 g.) was distilled. The first fraction, b. p. up to 30° (63·4 g.), was shown by gas chromatography to consist of three components whose retention times were equal to those of sulphur chloride pentafluoride, trichlorofluoromethane, and the preceding product respectively. There was then a sharp rise in b. p. to 90° at which a fraction (5 g.) of b. p. 90—110° was obtained. The residue (6 g.) solidified at room temperature. In a similar experiment sulphur chloride pentafluoride (21 g.) and tetrafluoroethylene (30 g.) gave products (18·3 g.) which were solid at room temperature, in addition to the usual liquid products.

The fractions boiling above 90° from several experiments were collected and fractionated, giving *4-chloro-octafluorobutylsulphur pentafluoride*, m. p. −90°, b. p. 99° (Found: C, 13·0; Cl, 10·2; F, 68·4; S, 9·0%; *M*, 357. $C_4ClF_{13}S$ requires C, 13·3; Cl, 9·8; F, 68·2; S, 8·8%; *M*, 362·5) and *6-chlorododecafluorohexylsulphur pentafluoride*, m. p. −5°, b. p. 142° (Found: C, 15·6; Cl, 8·5; F, 68·0; S, 7·5%; *M*, 467. $C_6ClF_{17}S$ requires C, 15·6; Cl, 7·7; F, 69·4; S, 6·9%; *M*, 462·5).

Higher telomers $SF_5{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}Cl$ were no doubt present in the higher-boiling fractions but were not isolated as pure compounds. Gas-chromatographic analysis of the products showed no trace of compounds boiling below 142° other than those mentioned. In the portion boiling above 142° one fraction obtained by gas chromatography was identified by its retention time and infrared spectrum as chlorobenzene.

Trifluoroethylene. Sulphur chloride pentafluoride (46 g.), trifluoroethylene (20 g.), and dibenzoyl peroxide (0·6 g.) in carbon tetrachloride (15 c.c.) were heated to 150° for 6 hr. This was done twice and the combined liquid product (182 g.) was distilled. The fraction, b. p. 59—61° (93 g.), was shown by gas chromatography to consist of two main fractions, the second of which had a retention time identical with that of carbon tetrachloride which constituted approximately 20% of the mixture. The first fraction was collected and shown to be *2-chloro-1,2,2-trifluoroethylsulphur pentafluoride* (Found: C, 9·6; F, 59·7. C_2HClF_8S requires C, 9·8; F, 62·1%), $\nu_{max.}$ 1225, 1150, 1075, 1000, 925, 880, 815, 780 cm.$^{-1}$.

Chlorotrifluoroethylene. Sulphur chloride pentafluoride (40 g.), chlorotrifluoroethylene (33 g.), and dibenzoyl peroxide (0·4 g.) in trichlorofluoromethane (30 c.c.) were heated to 100° for 10 hr. On removal of the solvent, the product separated as a wet solid which gave a clear liquid on warming. Distillation yielded a small fraction (2 g.), b. p. 80—83°, which was *2,2-dichlorotrifluoroethylsulphur pentafluoride* (Found: C, 8·3; Cl, 25·2; F, 53·8; S, 11·3%; *M*, 282. $C_2Cl_2F_8S$ requires C, 8·6; Cl, 25·4; F, 54·5; S, 11·5%; *M*, 279), $\nu_{max.}$ 1210s, 420s, 925vs, 900vs, and 765vs cm.$^{-1}$. The bulk of the products boiling above 82° were not further examined.

Hexafluoropropene. Several experiments, in which sulphur chloride pentafluoride and hexafluoropropene were heated to 150° in the presence of dibenzoyl peroxide, were carried out. In each case the starting materials, apart from a small handling loss, were recovered.

Dehydrochlorination of 2-*Chloro*-1,2,2-*trifluoroethylsulphur Pentafluoride.*—A round-bottom three-neck flask was fitted with a dropping-funnel, a stopper, and a reflux condenser the top of which was connected to a trap cooled to $-80°$. Light petroleum, b. p. 100—120° (100 c.c.), and the mixture of starting material with carbon tetrachloride (30 g.) were added and brought to a gentle reflux. Finely powdered potassium hydroxide (18 g.) was added through the stoppered opening during 3½ hr., the reaction then appearing to be complete. A colourless liquid (17·5 g.) had collected in the cold trap and was shown by gas chromatography to be pure *trifluorovinylsulphur pentafluoride* (Found: F, 72·4; S, 15·2%; *M*, 206. C_2F_8S requires F, 73·1; S, 15·4%; *M*, 208); the yield, based on 80% purity of the starting material, was 82%. The vapour pressure of this compound accorded with the equation $\log_{10} p = -1310/T + 6{\cdot}36$. The b. p. found by extrapolation was 19°, the latent heat of vaporisation calculated from the slope is 5990 cal. mole^{-1}, and the Trouton constant is 20·5. The infrared absorption spectrum of trifluorovinylsulphur pentafluoride showed intense bands at 1782 (C=C stretching), 1351, 1246, 898vs, 802vs, 614 cm.$^{-1}$. No other SF_5 compound was detected.

Photochemical Reactions.—*Sulphur chloride pentafluoride and tetrafluoroethylene.* The apparatus used was a standard Hanovia 10-l. photochemical reaction vessel with quartz centre tube. 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 vessel was evacuated, and filled with sulphur chloride pentafluoride (30 cm. Hg) and tetrafluoroethylene (45 cm. Hg). No reaction took place until the mercury arc was switched on, but then a reaction started which caused a decrease in pressure. The experiment was carried out three times and the liquid products (241 g.) were combined. The gaseous products were shown by gas chromatography to contain three major components whose retention and infrared spectra showed them to be unchanged tetrafluoroethylene,[2] sulphur chloride pentafluoride,[3] and 1,2-dichlorotetrafluoroethylene.[2] The liquid products were distilled and gave fractions (1), b. p. up to 100° (52·5 g.), (2) b. p. 100—150° (75·7 g.), (3) b. p. 150—200° (48·6 g.), and a residue (64·5 g.) which solidified at room temperature. The rise in b. p. was continuous throughout the distillation and each cut taken was shown by gas chromatography to contain several components. By comparing retention times, all the compounds formed in the autoclave reaction of sulphur chloride pentafluoride and tetrafluoroethylene were shown to be present. In addition, disulphur decafluoride [4] was identified by its retention time and infrared spectrum. The extra fractions present in the higher-boiling materials were not identified.

Sulphur chloride pentafluoride and chlorotrifluoroethylene. The 10-l. photochemical reaction vessel was evacuated, filled with sulphur chloride pentafluoride (30 cm. Hg) and chlorotrifluoroethylene (45 cm. Hg), and irradiated for 5 hr. during which more of the reagents in the same molar ratio were added, the total weight used being 190 g. There were obtained 148 g. of a liquid product which was washed with N-potassium hydroxide, water, and saturated brine and dried ($MgSO_4$). The bulk of the material (120 g.) boiled above 150° and was not investigated. The portion boiling below 150° was fractionated, giving: fraction (1) b. p. 26° disulphur decafluoride (2 g.); (2) b. p. 45—49°, 1,2,2-trichlorotrifluoroethane (4 g.); and (3) 1,2-*dichlorotrifluoroethylsulphur pentafluoride* (2 g.), b. p. 79·5—82° (Found: C, 8·3; Cl, 25·2; F, 53·8; S, 11·3%; *M*, 282. $C_2Cl_2F_8S$ requires C, 8·6; Cl, 25·4; F, 54·5; S, 11·5%; *M*, 279). The infrared spectrum of the last product differs from that of its 2,2-dichloro-isomer in having intense bands at 1180br,s, 1120s, 1045s, 935s, 895vs, 870s, 815s, 755vs cm.$^{-1}$, but is identical with that obtained (see below) from the reaction of chlorine with trifluorovinylsulphur pentafluoride.

Sulphur chloride pentafluoride and hexafluoropropene. The 10-l. photochemical reaction vessel was filled with an equimolar mixture of sulphur chloride pentafluoride and hexafluoropropene to a total pressure of 1 atm. The mixture was irradiated until there was no further decrease in pressure. There were obtained 54 g. of a colourless liquid which on distillation gave fractions (1), b. p. 25—30° (10 g.) (a mixture of disulphur decafluoride [4] and 1,2-dichlorohexafluoropropane,[2] identified by their infrared spectra), and (2), b. p. 71—73° (15 g.), shown by gas chromatography to contain two almost equal but poorly resolved components which were believed to be 2-chlorohexafluoro-propyl- and the isomeric -isopropyl-sulphur pentafluoride

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[2] Simons (ed.), " Fluorine Chemistry," Vol. II, 1954, Academic Press, New York, pp. 469 *et seq.*

[3] Cross, Roberts, Goggin, and Woodward, *Trans. Faraday Soc.*, 1960, **56**, 945.

[4] Dodd, Woodward, and Roberts, *Trans. Faraday Soc.*, 1957, **53**, 1545.

(Found: C, 11·8; Cl, 11·1; F, 67·5; S, 9·9%; *M*, 310. Calc. for $C_3ClF_{11}S$: C, 11·5; Cl, 11·4; F, 67·0; S, 10·2%; *M*, 312·5). The higher-boiling products gave no clear-cut fractions and were not further investigated.

Chlorination of Perfluorovinylsulphur Pentafluoride.—A 1-l. photochemical reaction vessel was filled with perfluorovinylsulphur pentafluoride (27 cm. Hg) and chlorine (41 cm. Hg). The mixture was irradiated for 30 min. during which the pressure fell by 17 cm. and a liquid product (3 c.c.) was obtained. The excess of chlorine was removed by evaporation. The liquid was found by gas chromatography to have only one major component which was shown by its retention time and infrared spectrum to be the 1,2-dichloro-product.

DISCUSSION

Addition of sulphur chloride pentafluoride to alkenes can proceed by either an ionic or a free-radical mechanism depending on the olefin used. With fluoro-olefins it is necessary to employ a free-radical catalyst to ensure reaction, indicating that, in the cases studied, the addition proceeds by a free-radical mechanism. When benzoyl peroxide is used as the catalyst it is possible to recover chlorobenzene from the products. This suggests that the reaction proceeds by the following stages:

$$(1)\ C_6H_5\cdot + SF_5Cl \longrightarrow C_6H_5Cl + SF_5\cdot$$

$$(2)\ SF_5\cdot + C_2H_4 \longrightarrow SF_5\cdot CF_2\cdot CF_2\cdot$$

$$(3)\ \text{either } (a)\ SF_5\cdot CF_2\cdot CF_2\cdot + C_2F_4 \longrightarrow SF_5\cdot [CF_2]_4\cdot \text{ (propagation)}$$

$$\text{or } (b)\ SF_5\cdot CF_2\cdot CF_2\cdot + SF_5Cl \longrightarrow SF_5\cdot CF_2\cdot CF_2Cl + SF_5\cdot \text{ (chain transfer)}$$

This mechanism accounts for the dependence of the molecular weight on the ratio of sulphur chloride pentafluoride to olefin and for the absence of $Cl\cdot CF_2\cdot CF_2Cl$ in the products which would certainly occur if there were any significant concentration of chlorine atoms present.

The orientation of the product formed in a reaction following this mechanism will depend on the point of attack of the $SF_5\cdot$ radical on the olefin. In this respect this radical appears to behave similarly to the $CF_3\cdot$ radical.[5] Thus with $CF_2{=}CFCl$ the primary attack is on the CF_2 group, leading to the formation of $SF_5\cdot CF_2\cdot CFCl_2$ and higher telomers. The reaction with $CF_2{=}CHF$ is interesting, as the analogy with other molecules suggests that where hydrogen is present radical attack occurs at the carbon atom carrying the most hydrogen, but in molecules derived from tetrafluoroethylene the attack is on the CF group. In this case the primary attack appears to be on the CHF group leading to $SF_5\cdot CHF\cdot CF_2Cl$. With hexafluoropropene there is no reaction under these conditions, which must mean that the $SF_5\cdot$ radical is insufficiently reactive to add to this olefin.

In the photochemical reaction the initial step is the homolysis of the SF_5Cl molecule to give an SF_5 radical and a Cl atom; from the results obtained it appears that the latter is very much more reactive than the former. Thus $CF_3\cdot CF{:}CF_2$ is found to react photochemically with SF_5Cl where both $SF_5\cdot$ radicals and $Cl\cdot$ atoms are present but fails to react in the presence of a peroxide where only $SF_5\cdot$ radicals are produced. In this case the primary process is probably the reaction

$$(4)\ Cl\cdot + CF_3\cdot CF{:}CF_2 \xrightarrow{a} CF_3\cdot CFCl\cdot CF_2\cdot$$

$$\xrightarrow{b} CF_3\cdot \dot{C}F\cdot CF_2Cl$$

followed by either further reaction with SF_5Cl to give $CF_3\cdot CFCl\cdot CF_2Cl$ in each case or reaction with $SF_5\cdot$ radicals to give a mixture of $SF_5\cdot CF_2\cdot CFCl\cdot CF_3$ and $SF_5\cdot CF(CF_3)\cdot CF_2Cl$. This production of a pair of isomers in an addition reaction is somewhat unusual and implies that in this case the $Cl\cdot$ is too reactive to discriminate between the two possible reaction sites. In the case of $CF_2{:}CF_2$ where the two reaction sites are identical this effect is not observed.

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[5] Haszeldine and Steele, *J.*, 1953, 1592.

With chlorotrifluoroethylene only a single addition product is obtained which must mean that in this case attack by Cl• takes place at one reaction site very much more readily:

$$(5)\ Cl\cdot + CF_2{:}CFCl \longrightarrow Cl{\cdot}CF_2{\cdot}CFCl\cdot$$

which can either lead to polymer formation with more $CF_2{:}CFCl$, abstract chlorine from SF_5Cl, or react with an SF_5 radical to give $CF_2Cl{\cdot}CFCl{\cdot}SF_5$. It is curious that the chlorine atoms should be selective here but not with $CF_3{\cdot}CF{:}CF_2$.

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