## 393. *Sulphur Chloride Pentafluoride: Reaction with Unsaturated Hydrocarbons.*

By J. R. Case, N. H. Ray, and H. L. Roberts.

Sulphur chloride pentafluoride adds to certain olefins and chloro-olefins to give 2-chloroalkylsulphur pentafluorides; acetylene and propyne give 2-chlorovinyl- and 2-chloropropenyl-sulphur pentafluoride, respectively. These products eliminate hydrogen chloride on treatment with potassium hydroxide, to give pentafluorosulphur-substituted olefins and acetylenes.

Sulphur chloride pentafluoride [1] does not react with paraffin hydrocarbons, but when heated under moderate pressures with certain olefins and chloro-olefins it adds to the double bond, giving 2-chloroalkylsulphur pentafluorides:

$$SF_5Cl + R{\cdot}CH{:}CH_2 \longrightarrow R{\cdot}CHCl{\cdot}CH_2{\cdot}SF_5$$

This reaction has been carried out with ethylene, propene, cyclohexene, butadiene, and vinyl chloride; it failed with isobutene and styrene because these olefins polymerised very rapidly in the presence of sulphur chloride pentafluoride. Ethylene and vinyl chloride also showed a tendency to polymerise, for the simple addition compounds were accompanied by smaller amounts of higher-boiling fractions from which compounds were isolated which were evidently telomers containing two molecules of the olefin. The 2-chloroalkylsulphur pentafluorides eliminated hydrogen chloride on treatment with potassium hydroxide, to give the corresponding unsaturated pentafluorosulphur compounds; however, it was not possible to remove more than one molecule of hydrogen chloride from 2,2-dichloroethylsulphur pentafluoride, and attempts to prepare the substituted acetylene from this compound only resulted in complete decomposition.

Addition of sulphur chloride pentafluoride to propene gave a high yield of 2-chloropropylsulphur pentafluoride, the structure of which was established by showing that two isomeric pentafluorosulphur-substituted propenes were formed by elimination of hydrogen chloride whereas 2-chloro-1-methylethylsulphur pentafluoride could only give one compound:

$$CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}SF_5 \longrightarrow CH_2{:}CH{\cdot}CH_2{\cdot}SF_5 + CH_3{\cdot}CH{:}CH{\cdot}SF_5$$

$$CH_3{\cdot}CH(SF_5){\cdot}CH_2Cl \longrightarrow CH_3{\cdot}C(SF_5){:}CH_2$$

The isomers were separated by gas chromatography and differentiated by their infrared absorption spectra; a more detailed account of the spectra of compounds containing the pentafluorosulphur group is to be published elsewhere.

Even with an excess of sulphur chloride pentafluoride only one molecular proportion reacted with butadiene, and some polymer was also produced. The main product is believed to be 2-chlorobut-3-enylsulphur pentafluoride rather than the isomeric 4-chlorobut-2-enyl derivative because its infrared absorption spectrum showed bands which are attributed to a vinyl group.

With cyclohexene, in addition to the expected 2-chlorocyclohexylsulphur pentafluoride, a chlorofluorocyclohexane was formed as a by-product. This is assumed to be 1-chloro-2-fluorocyclohexane, and a possible mechanism for its formation is discussed below.

Vinyl chloride with sulphur chloride pentafluoride gave 2,2-dichloroethylsulphur pentafluoride and not the 1,2-dichloro-analogue, for the latter isomer was obtained by chlorination of vinylsulphur pentafluoride and was shown to be a different compound:

$$CH_2{:}CHCl + SF_5Cl \longrightarrow SF_5{\cdot}CH_2{\cdot}CHCl_2$$

$$CH_2{:}CH{\cdot}SF_5 + Cl_2 \longrightarrow CH_2Cl{\cdot}CHCl{\cdot}SF_5$$

[1] Roberts and Ray, *J.*, 1960, 665.

Sulphur chloride pentafluoride also adds to the triple bond in acetylene and propyne; the product from propyne was shown to be 2-chloropropenylsulphur pentafluoride by reaction with potassium hydroxide which gave prop-1-ynylsulphur pentafluoride; the isomeric 2-chloro-1-methylethyl compound could not give this reaction:

$$CH_3{\cdot}C{\vdots}CH + SF_5Cl \longrightarrow CH_3{\cdot}CCl{:}CH{\cdot}SF_5 \longrightarrow CH_3{\cdot}C{\vdots}C{\cdot}SF_5$$

Some of the reactions described above were also carried out at atmospheric pressure with ultraviolet irradiation; the products thus obtained from propene and from propyne were identical with the corresponding products from autoclave reactions. For safety reasons the addition of sulphur chloride pentafluoride to acetylene was attempted only at atmospheric pressure, under the influence of ultraviolet light.

The products obtained in these reactions are generally those to be expected if sulphur chloride pentafluoride adds to olefins by a free-radical mechanism; and the isolation of telomers from the reactions with ethylene and vinyl chloride supports this view. The initial attack of a radical on sulphur chloride pentafluoride is more likely to be at the chlorine than at the sulphur atom, owing to the screening effect of the fluorine atoms; the orientation of the products obtained from propene, vinyl chloride, and propyne can be explained on this basis:

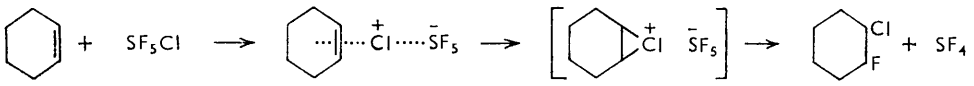
$$R{\cdot} + SF_5Cl \longrightarrow RCl + SF_5$$

$$SF_5{\cdot} + CH_3{\cdot}CH{:}CH_2 \longrightarrow CH_3{\cdot}\dot{C}H{\cdot}CH_2{\cdot}SF_5$$

$$CH_3{\cdot}\dot{C}H{\cdot}CH_2{\cdot}SF_5 + SF_5Cl \longrightarrow CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}SF_5 + SF_5{\cdot}$$

Further examples of radical reactions involving sulphur chloride pentafluoride will be described in a subsequent publication.

The rapid polymerisation of isobutene and styrene by sulphur chloride pentafluoride suggests that it can sometimes react ionically, and the formation of chlorofluorocyclohexane from cyclohexene is probably the result of attack by a sulphur chloride pentafluoride molecule on the olefin, followed by heterolysis of the S–Cl bond; the labile species $SF_5^-$ would quickly decompose into a fluoride ion and the stable molecule $SF_4$:




## Experimental

*Apparatus and Procedure.*—Autoclave reactions were normally carried out in a stainless-steel autoclave of 250 c.c. capacity and 2500 atm. maximum working pressure, fitted with a bursting disc (usually 1000 atm.) close to the head of the vessel, and provided with a magnetically operated reciprocating stirrer. For some experiments a similar autoclave of 100 c.c. capacity and 3000 atm. maximum working pressure was used. The autoclave was heated by a copper-block electric furnace and the temperatures measured were the temperatures of the outer wall of the vessel, adjacent to the furnace.

The autoclave was charged with sulphur chloride pentafluoride by evacuating it, cooling it with liquid air, and distilling in the required amount of reagent from a weighed cylinder. Other gaseous reagents were added in a similar way; liquid reagents were put into the autoclave before it was evacuated. After the reaction the autoclave was cooled to room temperature and any gas pressure remaining was released through a system of traps cooled in liquid air. The traps were allowed to warm slowly to room temperature and their residual contents were combined with the contents of the autoclave.

*Reaction of Sulphur Chloride Pentafluoride with Unsaturated Hydrocarbons.—Ethylene.* Sulphur chloride pentafluoride (approx. 1 mole) and ethylene (approx. 1 mole) were heated together at 90° for 10 hr. The pressure was initially 250 atm., falling to 30 atm. at the end of the reaction. The products from four experiments, involving a total of 686 g. (4·22 moles) of sulphur chloride pentafluoride, were combined for working up. The liquid (515 g.) was washed

with sodium hydrogen carbonate solution, dried ($CaCl_2$), and distilled, giving *2-chloroethylsulphur pentafluoride* (377 g., 47%), b. p. 92°, $n_D^{20}$ 1·3590, $d_4^{20}$ 1·64 (Found: C, 12·7; H, 2·3; Cl, 19·1; F, 52·0; S, 16·1%; *M*, 190. $C_2H_4ClF_5S$ requires C, 12·6; H, 2·1; Cl, 18·6; F, 49·9; S, 16·8%; *M*, 190·5). Its infrared absorption spectrum showed an intense band centred on 870 cm.$^{-1}$ which is characteristic of the $SF_5$ group.

The higher-boiling residue yielded a fraction (78 g.), b. p. 171—172°, which is believed to be *4-chlorobutylsulphur pentafluoride* (Found: C, 23·0; H, 3·3; Cl, 16·2; F, 43·5; S, 15·3%; *M*, 212. $C_4H_8ClF_5S$ requires C, 22·0; H, 3·6; Cl, 16·2; F, 43·5; S, 14·6%; *M*, 218·5). Its infrared absorption spectrum showed an intense band at 870 cm.$^{-1}$.

*Propene.* Sulphur chloride pentafluoride (165 g., 1·01 mole) and propene (42 g., 1·0 mole) were heated for 3 hr. at 100°. The pressure was initially 40 atm. and fell to about 2 atm. at the end of the reaction. The product (184 g.) was washed with sodium hydrogen carbonate solution, dried ($CaCl_2$), and distilled, giving *2-chloropropylsulphur pentafluoride* (161 g., 78%), b. p. 109° (Found: C, 17·8; H, 3·2; Cl, 16·6; F, 41·3; S, 15·8%; *M*, 199. $C_3H_6ClF_5S$ requires C, 17·6; H, 3·0; Cl, 17·4; F, 46·5; S, 15·7%; *M*, 204·5). Its infrared absorption spectrum showed an intense band at 870 cm.$^{-1}$.

*Butadiene.* Sulphur chloride pentafluoride (158 g., 0·97 mole) and butadiene (20 g., 0·37 mole) were heated at 100° for 2 hr. The product (66 g.) was washed with sodium hydrogen carbonate solution and distilled with steam; the residue appeared to be a polymer of butadiene. The lower layer of the distillate was dried ($CaCl_2$) and distilled, giving a fraction (29·5 g.), b. p. 78—80°/26 mm., believed to be *2-chlorobut-3-enylsulphur pentafluoride* (Found: C, 22·2; H, 3·3; Cl, 20·2; F, 44·0; S, 14·3. $C_4H_6ClF_5S$ requires C, 22·0; H, 3·2; Cl, 16·2; F, 43·5; S, 14·6%). Its infrared absorption spectrum showed an intense band at 870 cm.$^{-1}$ ($SF_5$) and strong bands at 970 and 890 cm.$^{-1}$ (vinyl).

*Isobutene.* Sulphur chloride pentafluoride (160 g.) and isobutene (50 g.) were heated at 100° for 3 hr. There was no pressure change, and the product was found to be a mixture of carbon and polyisobutene; most of the sulphur chloride pentafluoride was recovered unchanged, accompanied by a minor amount of sulphur tetrafluoride.

*Cyclohexene.* Sulphur chloride pentafluoride (160 g.) and cyclohexene (77 g.) were stirred at 20° for 18 hr. The product (200 g.) was washed with aqueous sodium hydrogen carbonate and distilled with steam. The lower layer of the distillate was dried ($CaCl_2$) and fractionally distilled, giving cyclohexene (15 g.), b. p. 83°, and two main fractions: (i) b. p. 150—152° (25 g.), (ii) b. p. 188—190° (37 g.). The residue could not be distilled without decomposition.

Fraction (i) was a chlorofluorocyclohexane, presumably *1-chloro-2-fluorocyclohexane* (Found: C, 52·5; H, 7·3; Cl, 25·9; F, 13·9%; *M*, 141. $C_6H_{10}ClF$ requires C, 52·6; H, 7·3; Cl, 26·0; F, 15·6%; *M*, 137). Its infrared absorption spectrum showed strong bands at 740, 800, 955, 1460, and 2900 cm.$^{-1}$, with a triplet at 1044 cm.$^{-1}$.

Fraction (ii) was *2-chlorocyclohexylsulphur pentafluoride*, $n_D^{20}$ 1·4320, $d_D^{20}$ 1·4783 (Found: C, 29·8; H, 4·3; Cl, 14·6; F, 36·9; S, 12·6%; *M*, 245. $C_6H_{10}ClF_5S$ requires C, 29·4; H, 4·1; Cl, 14·5; F, 38·8; S, 13·1%; *M*, 244·5), having $\nu_{max.}$ 870 cm.$^{-1}$.

*Styrene.* Styrene (10 ml.) was stirred at atmospheric temperature and pressure in a flask from which the air had been displaced by sulphur chloride pentafluoride. After about 30 min., there was a violent exothermic reaction and the product was mainly polystyrene. Its infrared absorption spectrum showed no bands that were not also present in the spectrum of normal polystyrene.

*Propyne.* Sulphur chloride pentafluoride (90 g.) and propyne (20 g.) were heated at 90° for 4 hr. in a 100 c.c. autoclave. The product (47 g.) was washed with dilute potassium carbonate solution and dried ($MgSO_4$). Distillation gave as a main fraction *2-chloropropenylsulphur pentafluoride* (25 g.), b. p. 92° (Found: C, 17·2; H, 2·6; Cl, 18·4; F, 44·6; S, 16·6. $C_3H_4ClF_5S$ requires C, 17·7; H, 2·0; Cl, 17·6; F, 46·8; S, 15·8%), and an unidentified higher-boiling fraction (8 g.). The infrared absorption spectrum of the main fraction showed an intense band at 870 cm.$^{-1}$ ($SF_5$) and strong bands at 990, 1100, and 1650 cm.$^{-1}$, indicating unsaturation.

*Vinyl chloride.* Sulphur chloride pentafluoride (149 g.) and vinyl chloride (38 g.) were heated at 150° for 6 hr. in an autoclave. The product (116 g.) was washed with dilute potassium carbonate solution, dried, and distilled, giving (i) *2,2-dichloroethylsulphur pentafluoride* (50 g.), b. p. 108° (Found: C, 11·0; H, 1·4; Cl, 32·7; F, 40·6; S, 13·9%; *M*, 221. $C_2H_3Cl_2F_5S$ requires C, 10·7; H, 1·4; Cl, 31·6; F, 42·0; S, 14·2%; *M*, 225), and (ii) a fraction (22 g.), b. p. 72°/9 mm., believed to be *2,4,4-trichlorobutylsulphur pentafluoride* (Found: C, 16·6; H, 2·7; Cl, 38·1;

F, 30·9; S, 11·5%; *M*, 267. $C_4H_6Cl_3F_5S$ requires C, 16·7; H, 2·1; Cl, 37·1; F, 33·0; S, 11·1%; *M*, 288).

*Preparation of Unsaturated Sulphur Pentafluoride Compounds.—Vinylsulphur pentafluoride.* Potassium hydroxide (19 g.) was dissolved in water (20 c.c.), and ethanol (60 c.c.) added. This solution was boiled under a reflux condenser, the outlet of which was connected to a trap cooled with solid carbon dioxide and methanol. 2-Chloroethylsulphur pentafluoride (33 g.) was added to the solution from a tap-funnel during 15 min. Boiling was continued for 1 hr. after all the reagent had been added. The reflux condenser was then heated by passing water at 50° ± 5° through it, and the reaction flask was kept at 70° until no more liquid collected in the cold trap. The product was redistilled, giving *vinylsulphur pentafluoride* (22·5 g., 85%), b. p. 41° (Found: C, 15·9; H, 2·0; F, 61·3; S, 21·0%; *M*, 153. $C_2H_3F_5S$ requires C, 15·6; H, 2·0; F, 61·6; S, 20·9%; *M*, 154). The vapour pressure of this compound was measured and the results fitted the equation [v. p. (mm.) at $T$°K]: $\log_{10} p = -3420/T + 13{\cdot}68$. The latent heat of vaporisation is 6800 cal. per mole, and the Trouton constant is 21·6. The infrared absorption spectrum of the liquid showed an intense band at 870 cm.$^{-1}$ ($SF_5$) and strong bands at 965, 1040, and 1390 cm.$^{-1}$.

*Allylsulphur pentafluoride and propenylsulphur pentafluoride.* A mixture of potassium hydroxide (75 g.), methanol (300 c.c.), and 2-chloropropylsulphur pentafluoride (145 g.) was heated under reflux for 2½ hr., then allowed to cool and stored at room temperature for 12 hr. The mixture was added to 1 l. of water, and the lower layer was separated, washed with water, and dried ($MgSO_4$). A Beilstein test showed that chlorine was absent. The liquid was fractionally distilled, giving a main fraction (43 g.), b. p. 80—82°, and a higher-boiling residue which was not examined. The main fraction was separated by gas chromatography into two components: that of shorter retention time (4·4 g.) was *allylsulphur pentafluoride* (Found: C, 21·7; H, 3·0; F, 54·3; S, 19·0%; *M*, 168. $C_3H_5F_5S$ requires C, 21·4; H, 3·0; F, 56·5; S, 19·0%; *M*, 168). The second and larger fraction (38·5 g.) was *propenylsulphur pentafluoride* (Found: C, 22·0; H, 2·7; F, 54·3; S, 19·1%; *M*, 170). The infrared absorption spectra of both of these compounds showed bands at 602, 606, 613, and 885 cm.$^{-1}$; propenylsulphur pentafluoride also showed methyl bands at 1449, 2865, and 2967 cm.$^{-1}$, and allylsulphur pentafluoride showed vinyl bands at 995 and 3090 cm.$^{-1}$.

*Cyclohexenylsulphur pentafluoride.* A mixture of 1-chlorocyclohexylsulphur pentafluoride (12·2 g.), potassium hydroxide (5·6 g.), water (5 c.c.), and ethanol (75 c.c.) in a 250 c.c. flask with a reflux condenser was cautiously warmed to about 75°; as soon as the reaction started, the heat was removed. After the initial exothermic reaction had subsided the mixture was boiled for 15 min., then cooled and poured into water (350 c.c.). The lower layer was separated, dried ($MgSO_4$), and distilled. *Cyclohexenylsulphur pentafluoride* (8 g., 79%) was collected at 112—115°/100 mm.; it had b. p. 161°/760 mm., $n_D^{20}$ 1·4282 (Found: C, 34·9; H, 4·7; F, 44·2; S, 15·3%; *M*, 190. $C_6H_9F_5S$ requires C, 34·6; H, 4·3; F, 45·6; S, 15·4%; *M*, 208), $\nu_{max.}$ 870 ($SF_5$) and 940 cm.$^{-1}$ (unsaturation).

*Prop-1-ynylsulphur pentafluoride.* Powdered potassium hydroxide (10 g.) was suspended in ligroin (25 c.c.; b. p. 100—120°) and heated to 60° under a condenser. 2-Chloropropenylsulphur pentafluoride (10 g.) was added to the suspension and the mixture was kept at 75° for 20 min.; after cooling, it was filtered, and the filtrate distilled. The fraction of b. p. 65—70° (2 g.) was collected and divided by gas chromatography into two fractions: the retention time of the second was identical with that of the starting material; the sub-fraction of shorter retention time (*ca.* 0·2 g.) was *prop-1-ynylsulphur pentafluoride* (Found: F, 57·3; S, 18·7%; *M*, 166·5. $C_3H_3F_5S$ requires F, 57·5; S, 19·3%; *M*, 166). Its infrared absorption spectrum showed a band at 2261 cm.$^{-1}$ characteristic of C≡C, but no absorption at 3300 cm.$^{-1}$, indicating the absence of C–H. The S–F stretching frequencies were at 893 (vs), 855—852 (vs), 706—704—697 cm.$^{-1}$ and the S–F deformation was at 622—618—612 cm.$^{-1}$. The P–R separation is that expected for a symmetric top molecule whose moments of inertia correspond to $SF_5{\cdot}C{\equiv}C{\cdot}CH_3$.

*2-Chlorovinylsulphur pentafluoride.* 2,2-Dichloroethylsulphur pentafluoride (23 g.) was dissolved in methanol (25 c.c.) and cooled to −20°. A solution of potassium hydroxide (9 g.) in methanol (30 c.c.) was added dropwise, the temperature being kept between −20° and −10°. The mixture was filtered, and water (50 c.c.) added to the filtrate. The lower layer was separated, washed with saturated aqueous sodium chloride, dried ($MgSO_4$), and distilled, giving *2-chlorovinylsulphur pentafluoride* (12 g., 63%), b. p. 66° (Found: C, 11·9; H, 1·2;

Cl, 19·5; F, 49·8; S, 17·5%; *M*, 185. $C_2H_2ClF_5S$ requires C, 12·7; H, 1·1; Cl, 18·8; F, 50·4; S, 17·0%; *M*, 189), $\nu_{max.}$ 870 ($SF_5$) and 920 and 1580 cm.$^{-1}$ (unsaturation).

*Photochemical Reactions of Sulphur Chloride Pentafluoride.—Apparatus and procedure.* A Pyrex tube of 600 c.c. capacity was provided with an inner tube made of fused quartz containing a Hanovia 509/12 mercury discharge tube. The tube was vertical and liquid products were collected in a small well at the bottom. Gaseous reagents were introduced from a vacuum-line connected at the top of the reaction tube, and a mercury manometer was used to measure the pressure in the apparatus. In each experiment, equal volumes of the hydrocarbon and sulphur chloride pentafluoride were admitted to the previously evacuated reaction vessel, so that the pressure was approximately 1 atm. The discharge tube was energised, and irradiation of the mixture was continued until no further pressure change was observed. The liquid product was collected, and purified by gas chromatography.

*Reaction with propene.* The liquid product (3 c.c.) was chromatographically homogeneous and identical in chromatographic retention time and infrared absorption spectrum with the 2-chloropropylsulphur pentafluoride obtained in an autoclave.

*Reaction with acetylene.* The liquid product (2·5 c.c.) was almost pure 2-chlorovinylsulphur pentafluoride, identical in chromatographic retention time and infrared absorption spectrum with the product obtained by reaction of 2,2-dichloroethylsulphur pentafluoride with alkali.

*Reaction with propyne.* The product (3 c.c.) was identical with the sample of 2-chloropropenylsulphur pentafluoride obtained in an autoclave.

*Chlorination of Vinyl Sulphur Pentafluoride.*—A 10-l. photochemical reaction vessel was charged with chlorine to 0·5 atm. and the ultraviolet lamp was switched on. Vinylsulphur pentafluoride (39 g., 1·0 mol.) was added gradually from a tap-funnel; the pressure fell during 15 min. to about 10 cm. The product was a liquid containing some dissolved hydrogen chloride, but free from chlorine. It was washed with dilute potassium carbonate solution and water, dried ($MgSO_4$), and distilled, giving (i) recovered vinylsulphur pentafluoride (6·8 g.), b. p. 41—42°, (ii) 1,2-dichloroethylsulphur pentafluoride (18·5 g.), b. p. 111°, and (iii) a higher-boiling residue which was not examined. The infrared absorption spectra of fraction (ii) from this experiment and of 2,2-dichloroethylsulphur pentafluoride prepared from vinyl chloride and sulphur chloride pentafluoride (see above) were compared, and the following observations were made: both compounds showed very strong absorption bands in the region of 860 cm.$^{-1}$ ($SF_5$) and moderately strong bands in the region from 1300 to 1450 cm.$^{-1}$ due to C–H bonds; there were marked differences in the region from 700 to 800 cm.$^{-1}$, where 2,2-dichloroethylsulphur pentafluoride showed a single strong absorption at 772 cm.$^{-1}$, and 1,2-dichloroethylsulphur pentafluoride [fraction (ii) from this experiment] showed a pair of strong bands at 781 and 732 cm.$^{-1}$. Their retention times on a gas-chromatography column were in the ratio of 1 to 1·12.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
ALKALI DIVISION RESEARCH DEPARTMENT,
WINNINGTON, NORTHWICH, CHESHIRE.

[*Received, September 28th*, 1960.]