147. *The Photochemical Reactions of Some Pentafluorosulphur Derivatives with Sulphur Dioxide.*

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Photochemical reactions (2537 Å) of pentafluorosulphur chloride, bis-(pentafluorosulphur) peroxide, and disulphur decafluoride with sulphur dioxide gave, in varying yields, the compound pentafluorosulphur fluorosulphate, $F_5S{\cdot}O{\cdot}SO_2F$. The photochemical decomposition of disulphur decafluoride was investigated and possible paths for its reaction with sulphur dioxide are discussed. Some physical properties, including the ^{19}F nuclear magnetic resonance and infrared spectra, of pentafluorosulphur fluorosulphate are described.

Interest in sulphur–fluorine chemistry has recently been revived by the preparation of numerous compounds containing the pentafluorosulphur group [1] and the extensive

[1] Roberts and Ray, *J.*, 1960, 665; B.P. Appl. 31,320/1958, 2534/1959; Roberts, *J.*, 1960, 2774; *Quart. Rev.*, 1961, **15**, 30; Case, Ray, and Roberts, *J.*, 1961, 2066; *J.*, 1961, 2070; Cady and Merrill, *J. Amer. Chem. Soc.*, 1961, **83**, 298; Cady, " Fluorine-containing Compounds of Sulphur " (" Advances in Inorganic and Radiochemistry ") (ed. Emeléus and Sharpe), Academic Press, New York, 1960, Vol. II, p. 105.

investigation of the preparation and chemistry of sulphur tetrafluoride.[2] Also, disulphur decafluoride, originally prepared in very small yields ($\ll$1%) by the action of fluorine on sulphur,[3] can now be made in relatively large quantities by the photochemical reduction of pentafluorosulphur chloride with hydrogen.[4]

In attempts to prepare compounds containing the pentafluorosulphur group we have investigated the photochemical reaction of pentafluorosulphur chloride, bis(pentafluorosulphur) peroxide, and disulphur decafluoride with sulphur dioxide in light of wavelength 2537 Å. The reaction of pentafluorosulphur chloride with sulphur dioxide was incomplete after 48 hours' irradiation. The major products were shown by infrared spectroscopy and gas–liquid partition chromatography to be thionyl fluoride, sulphuryl fluoride, silicon tetrafluoride (from attack of the glass vessel), and sulphuryl chloride. Also obtained were pentafluorosulphur fluorosulphate, $F_5S{\cdot}O{\cdot}SO_2F$, in <1% yield based on the pentafluorosulphur chloride taken, and a trace of disulphur decafluoride. A slight solid deposit was observed. When the reaction of pentafluorosulphur chloride with sulphur dioxide was carried out by letting the gases flow past an ultraviolet lamp, trapping the products involatile at −40°, and recycling the remaining gases, the relative yield of disulphur decafluoride increased and only a trace of pentafluorosulphur fluorosulphate was formed. This indicated that the latter was formed by the reaction of the former with sulphur dioxide.

Photochemical reaction of disulphur decafluoride with sulphur dioxide was almost complete after 48 hours. The products were pentafluorosulphur fluorosulphate in yields of up to 20% (based on the disulphur decafluoride taken), thionyl fluoride, sulphuryl fluoride, sulphur hexafluoride, silicon tetrafluoride, and some solid deposit which fumed in air and part of which dissolved in water forming sulphate ions (it was probably a mixture of sulphur trioxide and sulphur).

Photochemical reaction of bis(pentafluorosulphur) peroxide with sulphur dioxide was complete after 48 hours. The products were pentafluorosulphur fluorosulphate, in yields of up to 45% (based on the peroxide taken), sulphur oxide tetrafluoride (F_4SO), thionyl fluoride, sulphuryl fluoride, sulphur hexafluoride, silicon tetrafluoride, a little sulphur trioxide, and sulphur.

Vibrational assignments can be made for all the strong bands in the infrared spectrum of pentafluorosulphur fluorosulphate by analogy with the spectra of sulphuryl fluoride [5] and other compounds containing the pentafluorosulphur group.[6] The ^{19}F nuclear magnetic resonance spectrum of pentafluorosulphur fluorosulphate is consistent with the presence of a pentafluorosulphur group coupling with a single fluorine nucleus. The molecule is an example of an AB_4X system of magnetic nuclei.[7]

From the optical densities of sulphur dioxide and disulphur decafluoride, determined from their ultraviolet spectra recorded under identical conditions on a Cary recording spectrophotometer, it is deduced that of the total light absorbed by a 2 : 1 mixture of sulphur dioxide and disulphur decafluoride the sulphur dioxide absorbs over 99% at 2537 Å (the ratio of the optical densities is 50 : 1). Sulphur dioxide is reported to undergo a photochemical decomposition, $3SO_2 \xrightarrow{h\nu} 2SO_3 + S$, brought about by light of 2537 or 3130 Å wavelength.[8] The reaction at 3130 Å is reported to reach a photostationary state [8b] with equilibrium at about 3·3% decomposition of the sulphur dioxide. However, it is difficult to visualise a photostationary state, *i.e.*, an equilibrium, in a gaseous system when one of the products is solid sulphur. It is more likely that, owing to the deposition

[2] Smith and his co-workers, *J. Amer. Chem. Soc.*, 1960, **82**, 539, 543, 551, 3835, 3838, 6176; *ibid.*, 1961, **83**, 3422.
[3] Denbigh and Whytlaw-Gray, *Nature*, 1933, **131**, 763.
[4] Roberts, B.P. Appl. 30,908/1960.
[5] Hunt and Wilson, *Spectrochim. Acta*, 1960, **16**, 570.
[6] Cross, Cushing, and Roberts, *Spectrochim. Acta*, 1961, **17**, 344.
[7] Harris and Packer, *J.*, 1961, 4736.
[8] (*a*) Coehn, *Z. Elektrochem.*, 1907, **21**, 545; (*b*) Hill, *Trans. Faraday Soc.*, 1924—25, **20**, 107.

of sulphur on the walls of the vessel, which was irradiated from outside, the ultraviolet light was prevented from reaching the sulphur dioxide, thus stopping the decomposition. Sulphur trioxide is also said to be decomposed by ultraviolet light to give sulphur dioxide and oxygen.[9] This is also claimed to give a photostationary state. Where the equilibrium lies, if any exists in this complex system, is not clear but the most important fact is that sulphur trioxide is produced from sulphur dioxide by the action of ultraviolet light.

Investigation of the rate of decomposition of disulphur decafluoride by light of wavelength 2537 Å showed that, although the optical density of this fluoride is small at 2537 Å compared with that of sulphur dioxide, its rate of decomposition is quite rapid. *E.g.*, it is >50% decomposed under the experimental conditions of pressure and light intensity in 100 minutes. This decomposition probably occurs by the initial splitting of the sulphur–sulphur bond to give two pentafluorosulphur radicals as is postulated in its thermal decomposition.[10] Thus the most probable path for the photochemical reaction of disulphur decafluoride with sulphur dioxide to give pentafluorosulphur fluorosulphate involves reaction of pentafluorosulphur radicals with sulphur trioxide formed by photochemical decomposition of sulphur dioxide. Another possibility is that the sulphur trioxide produced decomposes in part to sulphur dioxide and oxygen, and that disulphur decafluoride reacts with the oxygen under the influence of ultraviolet light to give some bis(pentafluorosulphur) peroxide or oxide which then react with the sulphur dioxide. However, the absence of sulphur oxide tetrafluoride from the products of this reaction seems to make this unlikely. So also would the yield of pentafluorosulphur fluorosulphate.

The paths of the other two reactions postulated are probably:

$$2SF_5Cl + SO_2 \xrightarrow{h\nu} S_2F_{10} + SO_2Cl_2$$

Then, as for the disulphur decafluoride–sulphur dioxide reaction,

$$SF_5{\cdot}O{\cdot}O{\cdot}SF_5 \xrightarrow{h\nu} 2SF_5{\cdot}O{\cdot}$$

$$SF_5{\cdot}O{\cdot} + SO_2 \longrightarrow SF_5{\cdot}O{\cdot}SO_2{\cdot}$$

$$SF_5{\cdot}O{\cdot}SO_2{\cdot} + SF_5{\cdot}O{\cdot} \longrightarrow SF_5{\cdot}O{\cdot}SO_2{\cdot}F + SOF_4$$

Experimental

Static, gas-phase, photochemical reactions were carried out in a vessel of ~1 l. capacity, consisting of a cylindrical Pyrex vessel ~50 mm. in diameter and ~60 cm. in length, down the centre of which was a quartz finger of 17 mm. bore housing a 7-watt, 12″, low-pressure mercury discharge lamp (Hanovia, Bactericidal Series). This type of lamp gives rise to nearly monochromatic radiation of wavelength 2537 Å.

Circulatory irradiation reactions were carried out in a similar vessel except that it had an inlet and an outlet. The gases were pumped round the system at about 10 l./hr. by an all-Polythene circulating pump made by the Vanton Pump Corporation, New York.

Reaction of Pentafluorosulphur Chloride with Sulphur Dioxide.—Pentafluorosulphur chloride and sulphur dioxide in equimolar proportion were admitted to the evacuated 1-l. vessel to a total pressure of 60 cm. and were irradiated for 48 hr. The volatile products were divided into two fractions by distilling them, *in vacuo*, through a trap cooled to −95°. The involatile fraction was shaken with 10% aqueous alkali to remove sulphur dioxide and was then subjected to gas–liquid chromatography that showed it to be a mixture of two components, one greatly in excess. The infrared spectra both of the mixture and of pure disulphur decafluoride over the range 4000—400 cm.$^{-1}$, together with the gas–liquid chromatogram of disulphur decafluoride, showed that the latter was the minor constituent. The infrared spectrum of the mixture indicated that the major constituent contained a sulphone grouping attached to two electronegative groups,[5] and also a pentafluorosulphur group.[6] The products volatile at −95° were shown by infrared spectroscopy and gas–liquid chromatography to be thionyl fluoride, sulphuryl fluoride, silicon tetrafluoride, and unchanged pentafluorosulphur chloride and sulphur dioxide.

[9] Glasstone, " A Textbook of Physical Chemistry," Macmillan, London, 2nd edn., p. 1184.
[10] Trost and McIntosh, *Canad. J. Chem.*, 1951, **29**, 508.

Since the yields of the involatile mixture were less than 1%, based on the pentafluorosulphur chloride taken, the reaction was carried out in the circulatory system in an attempt to increase the yield.

Pentafluorosulphur chloride and sulphur dioxide in equimolar proportion were admitted to the evacuated system to a total pressure of 70 cm. The cold trap was cooled to −40°, the circulating pump switched on, and the mixture irradiated for 48 hr. The products held in the cold trap were washed with 10% aqueous alkali in a 250-ml. bulb and the remaining volatile products were shown, by infrared spectroscopy and gas–liquid chromatography, to be a mixture of the same two compounds as above, the disulphur decafluoride being the major constituent in this case.

Reaction of Disulphur Decafluoride with Sulphur Dioxide.—Disulphur decafluoride and sulphur dioxide in a 1 : 2 molar ratio were admitted to the evacuated 1-l. irradiation vessel to a total pressure of 60 cm. and irradiated for 48 hr. The volatile products were treated as described above, the fraction involatile at −95° showing, after being washed with 10% aqueous alkali, two components on gas–liquid chromatography. The major product was that formed in the static irradiation of pentafluorosulphur chloride and sulphur dioxide, shown by the fact that the infrared spectra of the two were identical after gas–liquid chromatography on either a polar or a non-polar column. The minor constituent of the mixture was present in very small amount (probably $\ll$1%) and was probably a small amount of unchanged disulphur decafluoride. It had the same retention time on the gas–liquid chromatography column as authentic disulphur decafluoride. The product was finally purified by gas–liquid chromatography in a modified Perkin–Elmer model 154 Vapour Fractometer with a 4-m. column packed with di-isodecyl phthalate on Celite. This gave pure *pentafluorosulphur fluorosulphate* (Found: S, 28·2; F, 50·0%; *M*, 225. $F_6O_3S_2$ requires S, 28·4; F, 50·4%; *M*, 226). Yields were ~20% based on the disulphur decafluoride taken.

Reaction of Bis(pentafluorosulphur) Peroxide with Sulphur Dioxide.—Photochemical reaction of bis(pentafluorosulphur) peroxide with sulphur dioxide under the same conditions as for disulphur decafluoride gave yields of up to 45% of pentafluorosulphur fluorosulphate identical with the previous products (molecular weight; infra-red spectrum; gas–liquid chromatography; vapour pressures at −45° to 20°. The other product in this reaction did not appear in the other two reactions; it was sulphur oxide tetrafluoride, F_4SO.

Pentafluorosulphur fluorosulphate is a colourless, mobile liquid, melting at −107° ± 0·5°; between −45° and 20° its vapour pressure is related to the temperature by the expression $\log_{10} p$ (mm.) = $-(1629/T) + 8{\cdot}144$, and the latent heat of evaporation is 7450 ± 50 cal. mole^{-1}.

The infrared spectrum of pentafluorosulphur fluorosulphate was recorded over the range 4000—400 cm.$^{-1}$ by a Perkin–Elmer model 21, double-beam, recording spectrophotometer, with sodium chloride and potassium bromide prisms. The main observed frequencies are shown in Table 1, with vibrational assignments.

TABLE 1.

ν (cm.$^{-1}$)	Assignment	Analogy	ν (cm.$^{-1}$)	Assignment	Analogy
1495s	 as. stretch	1502 in SO_2F_2	603ms	SF_5 deform.	Cf. ref. 6
1256s	,, sym. ,,	1269 ,,	573vs	 bend	553 in SO_2F_2

S–F stretching (cf. ref. 6) at 945vs, 905sh, 884vs, 842sh, 826vs, 795sh, 724ms.

The ^{19}F nuclear magnetic resonance spectrum was recorded at 40 Mc./sec. by means of a Varian Associates V4300B spectrometer with 12″ electromagnet with flux stabilisation and sample spinning, and trichlorofluoromethane as solvent and internal standard. The values for the chemical shifts and coupling constants between the three types of fluorine nucleus in the molecule are shown in Table 2. The fluorine nuclei of the pentafluorosulphur group are designated AB_4 and the single fluorine nucleus of the $-SO_2F$ group as X.

Rate of Decomposition of Disulphur Decafluoride by Light of Wavelength 2527 Å.—The apparatus was similar to that used for the static gas-phase irradiations described above, except

TABLE 2.

				Chemical shift from CCl_3F †		
J_{AB} *	J_{BX} *	J_{AX} *	δ_{AB} *	A	B	X
156 ± 1·5	7·2	0·9	655 ± 2	−55·6	−72·0	−45·1

* In c./sec. † In p.p.m.

that the diameter of the vessel was smaller, the volume being ~150 c.c. Qualitative investigation of the decomposition showed that the products were sulphur hexafluoride, thionyl fluoride, silicon tetrafluoride, and sulphuryl fluoride. Quantitative investigation was carried out as follows. Disulphur decafluoride was admitted to the evacuated irradiation vessel to a pressure of 200 mm. It was then irradiated for *t* minutes after which the mixture was washed with 10% aqueous alkali in a 250-ml. bulb. This removed thionyl fluoride and silicon tetrafluoride. The remaining gases were then transferred to a vacuum-line where they were passed twice through traps cooled to −45° to remove water vapour. They were finally distilled through a trap cooled to −132° into a trap cooled with liquid nitrogen. When distillation was complete the traps were opened to the pump until no more material distilled from the trap at −132° into the trap at −196°. This ensured that sulphur hexafluoride, which has a vapour pressure of about 2 mm. at −132° but is solid at this temperature, was completely transferred into the liquid-nitrogen trap. The material remaining in the trap at −132° was shown to be pure disulphur decafluoride. It was weighed as such ina small bulb. Thus, the amount of disulphur decafluoride taken being known from calibration of the irradiation vessel, the percentage decomposition was calculated for different values of *t* (see Table 3).

TABLE 3.

t (min.)	15	32	60	90	120	150	180
Decomp. (%)	11·1	22·5	35·4	43·4	58·5	66·0	70·3

We are grateful to Dr. N. Sheppard for discussions concerning spectra, to Imperial Chemical Industries Limited, Alkali Division, for gifts of pentafluorosulphur chloride, disulphur decafluoride, and bis(pentafluorosulphur) peroxide, and to the Department of Scientific and Industrial Research for a maintenance grant (to K. J. P.).

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[*Received, October 20th,* 1961.]