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Short Communication

Thermal decomposition of sulphur hexafluoride

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Sulphur hexafluoride is unaffected by most reagents under room-temperature conditions, but is known to react with most metals at high temperatures [1] and with alkali metals at about 200 °C. Solutions of sodium in diphenyl ethylene glycol dimethyl ether [2] react with sulphur hexafluoride at temperatures as low as —78 °C. Ceramic oxides (Al_2O_3, MgO, ThO_2, ZrO and BeO) react [3] in the temperature range 700 - 900 °C. However, no definite information exists concerning the products of the reaction. In the present investigation, attempts have been made to identify the products of the reaction of sulphur hexafluoride with quartz, stainless steel and copper tubes at temperatures between 700 °C and 900 °C. In the case of quartz tubes, the reaction products are silicon tetrafluoride, sulphur tetrafluoride, thionyl fluoride and oxygen difluoride. In the case of metal tubes, the first decomposition product is sulphur tetrafluoride, with the formation of the metal fluoride. At this temperature, the final reaction products are the metal sulphide and the metal fluoride.

The experimental arrangement used consisted of two traps (all glass) with appropriate ground glass joints and stopcocks connected on either side of a reaction tube (quartz/stainless steel/copper). The centrally mounted tube could be heated electrically up to 1000 °C by means of a tubular furnace. The whole assembly was evacuated and a known volume (250 cm^3 at N.T.P.) of sulphur hexafluoride condensed into one of the traps. When the temperature of the tube was about 800 °C, the condensed gas was allowed to thaw and flow through the hot tube, an equilibrium being finally established in both traps. After an interval of 20 - 30 min the gas was condensed in the second trap, then allowed to thaw and recycled through the hot tube into the first trap. This alternate thawing and condensing of the gases in the two traps was repeated *ca.* 10 times over a period of 3 h. At the end of this period the heating was discontinued and the gaseous mixture condensed out into one of the traps. The products of the decomposition were identified *via* the infrared spectrum of the gaseous mixture, the results obtained being presented in Table 1. From this table, it is seen that silicon tetrafluoride, sulphur

TABLE 1

Infrared absorption spectra (frequencies in cm^{-1}) of fluorine compounds formed during thermal decomposition of sulphur hexafluoride

SF_6		SF_4		SOF_2		SiF_4		OF_2	
Lit. [4]	Obs.	Lit. [5]	Obs.	Lit. [6]	Obs.	Lit. [7]	Obs.	Lit. [8]	Obs.
613 (s)	613 (s)	532 (m)	530 (m)	530 (m)	530 (m)	391 (s)	—	461 (d)	461 (d)
932 (s)	930 (s)	557 (m)	558 (m)	748 (s)	750 (s)	1031 (s)	1031 (s)	826 (s)	830 (s)
		728 (s)	730 (s)	808 (s)	810 (s)			929 (s)	930 (s)
		867 (s)	860 (s)	1353 (s)	1330 (s)			1700 (m)	1720 (m)
		889 (s)	890 (s)					1764 (m)	
		1281 (m)	1280 (m)						
		1744 (m)	1740 (m)						

TABLE 2

Thermal decomposition of sulphur hexafluoride in quartz and metal tubes

Tube material	Expt No.	SF_6^* (mol × 10^{-3})	$SF_4 + SOF_2^*$ (mol "S" × 10^{-3})		SF_4^* (mol "S" × 10^{-3})		SiF_4^* (mol "F" × 10^{-3})		OF_2^* (mol "F" × 10^{-3})	
			Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.
Quartz	1	1.29	1.29	1.23	0.65	0.63	2.58	1.66	1.29	
	2	8.84	8.84	9.13	4.42		17.68	13.36	8.84	6.68
Copper	1	2.03	—	—	2.03	1.63	—	—	—	—
Stainless steel	1	5.17	—	—	5.17	3.45	—	—	—	—

*All concentrations expressed in mol $\left\{\begin{array}{l}\text{"S" = sulphur} \\ \text{"F" = fluorine}\end{array}\right\} \times 10^{-3}$

tetrafluoride, thionyl fluoride and oxygen difluoride are the products of the thermal decomposition of sulphur hexafluoride in a quartz tube.

Attempts have been made to obtain a quantitative analysis of each of these products by the methods developed in this laboratory. Thus, sulphur tetrafluoride and thionyl fluoride were passed through aqueous sodium hydroxide (4 *N*) and the sulphite formed estimated iodometrically. The sulphur tetrafluoride content was determined by the reaction of this product with anhydrous hydrogen iodide [9, 10]. The sulphur content of sulphur tetrafluoride was reduced to hydrogen sulphide while that of thionyl fluoride yielded elemental sulphur. Estimation of the hydrogen sulphide formed gave the sulphur tetrafluoride content of the gaseous mixture. Oxygen difluoride was estimated by utilising its oxidation reaction with potassium iodide [11] after isolating the product by low-temperature fractionation, any silicon tetrafluoride being separated from the gaseous mixture as an adduct with pyridine [12]. This solid adduct was then analysed for its fluorine content after hydrolysis in alkali. At room temperature (27 °C) sulphur tetrafluoride does not form an adduct with pyridine [13]. The analytical results of a few typical experiments are given in Table 2 in terms of sulphur and fluorine concentrations. The results are quite reproducible.

From the analytical results and IR absorption frequencies, the reaction between quartz and sulphur hexafluoride can be visualised in terms of the equation:

$$2SF_6 + SiO_2 \rightarrow SiF_4 + SF_4 + SOF_2 + OF_2$$

However, a complete quantitative estimate of the silicon tetrafluoride and oxygen difluoride content could not be obtained because of secondary reactions.

In stainless steel and copper reaction tubes, sulphur hexafluoride decomposes to sulphur tetrafluoride and the metal fluoride. As pointed out previously, it is necessary to separate sulphur tetrafluoride from any undecomposed sulphur hexafluoride by fractional condensation, otherwise the sulphur tetrafluoride will react with the metal at high temperatures to yield the metal sulphide and metal fluoride, as indicated by the complete drop of pressure when the reaction is completed.

From thermodynamic calculations, Wilkins [14] has shown that at temperatures up to 1500 °C sulphur hexafluoride dissociates principally to sulphur tetrafluoride. The experimental results reported in this paper lend further support to these theoretical calculations.

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