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INORGANIC VOLATILE FLUORIDES OBTAINED FROM ELECTRICAL
DECOMPOSITION OF SULFUR HEXAFLUORIDE IN A QUARTZ TUBE

GIOVANNI BRUNO, PIO CAPEZZUTO AND FRANCESCO CRAMAROSSA

Centro di Studio per la Chimica dei Plasmi del C.N.R.
Istituto di Chimica Generale ed Inorganica dell'Università
Via Amendola 173, 70126 - BARI. ITALY

ABSTRACT

Recent investigations on sulfur hexafluoride decomposition have shown the need of a rapid and efficient method for the qualitative and quantitative analysis of the reaction products. An analytical method for characterizing the gas mixture obtained from the decomposition of sulfur hexafluoride in a quartz reactor submitted to an r.f. discharge, is presented. A combination of gas-chromatographic, mass spectrometric and infrared spectrophotometric techniques has shown the presence of SF₆, SO₂F₂, SOF₄, SOF₂, SiF₄ and F₂ in the gas mixtures examined. For quantitative purposes a gas-chromatographic method has been found to be most suitable.

INTRODUCTION

The growing interest devoted to the study of sulfur hexafluoride decomposition is not only due to its peculiar dielectric properties [1], for which a wide utilization as electric insulating gas is made, but also to its potential use as a good

source of atomic fluoride for the etching of semiconductors in the integrated circuits industry [2] and for the production, in electrical discharge, of vibrationally excited hydrogen fluoride chemical lasers.

More recently laser induced decomposition of SF_6 has been made in connection with the isotope separation of uranium compounds [3]. Neither for the thermal [4, 5], low pressure electrical discharges, nor for laser induced decomposition [3], has sufficient information been reported on the reaction products and their qualitative and quantitative analysis.

Some information has been found in the work of Emel us and Tittle [6], which was carried out in a microwave discharge, where the discharge conditions, the product distribution and the analytical techniques utilized, were different from those reported in the present paper.

In the present investigation we report an accurate method for the qualitative and quantitative analysis of the products of decomposition of SF_6 which has been subjected to an RF electrical discharge, in a quartz tube flow reactor, at a pressure of 20 torr.

Under our experimental conditions, the qualitative analysis of the discharged gases, carried out by means of IR and gas-mass spectrometry, has shown the presence of sulfur hexafluoride (SF_6), sulfuryl fluoride (SO_2F_2), thionyl fluoride (SOF_2), sulfur oxytetrafluoride (SOF_4), silicon tetrafluoride (SiF_4) and fluorine (F_2). The presence of the oxygenated compounds and of SiF_4 in the gas mixture derives from the reaction of fluorine atoms or SF_x radicals with the quartz reactor walls. The principal difficulty encountered for the analysis of this

type of gas mixture arises from the high reactivity and the corrosive action of the components.

Gas mixtures of inorganic volatile fluorides have been separated by gas-chromatography on 33% Kel-F on Chromosorb W [7] and on 50% halocarbon oil on Kel-F powder [8]. The mixtures analyzed, however, do not contain all the fluorides which appear in our reaction products.

A gas mixture very similar to the one obtained under our conditions has been analyzed by Engelbrecht et al. [9] using a stainless steel column containing halocarbon oil on silica-gel. The result cannot, however, be considered satisfactory both for the pronounced tail of the SiF_4 peak and for the poor resolution of SO_2F_2 , SOF_2 and SF_4 .

Padma and Vasudeva [10] have analyzed the thermal decomposition products of SF_6 in a quartz reactor (SF_6 , SF_4 , SOF_2 , SiF_4 , OF_2) by means of titrimetric determinations. The authors, however, admit that this method is unsatisfactory for a complete quantitative estimate of the SiF_4 and OF_2 content.

The quantitative analysis of fluorine has been effected by C.W. Weber and O.H. Howard [11] by a photometric method, after converting fluorine to chlorine in a NaCl reactor while P.C. Nordine and D.E. Rosner [12] have utilized the reaction of fluorine with mercury.

EXPERIMENTAL

Qualitative analysis

The discharge products, sampled from the quartz reactor by means of an independent pumping system and collected in calibrated Pyrex bulbs equipped with Teflon stopcocks, were essen-

tially SF_6 , SO_2F_2 , SOF_2 , SOF_4 , SiF_4 and F_2 . These products, with the exception of fluorine, have been identified by IR spectroscopy, utilizing a Perkin-Elmer model 577 spectrometer and a 8 cm cell equipped with NaCl windows. In Table I we report the characteristic frequencies of the bands which have been utilized for the identification of compounds and in Fig. 1 the complete spectrum of the mixture is shown in full lines, for two different values of pressure. The dotted line of Fig. 1 shows the spectrum of the gas mixture after admission of water vapor into the cell. The SiF_4 band at 1030 cm^{-1} disappears, that of SOF_4 at 1380 cm^{-1} decreases, while the intensities of the bands due to SO_2F_2 (1270 ; 1503 cm^{-1}) remarkably increase. This is the result of hydrolytic processes and the formation of SO_2F_2 from SOF_4 , according to the



The presence of fluorine was detected by pouring mercury into the sampling bulb and by observing the formation of the fluoride.

The separation of the components of the gas mixture has been attempted using three different gas-chromatographic columns as shown below:

No	Solid support	Liquid phase	Loading	Stainless Steel Column	
				Dimension	Temp. ($^{\circ}\text{C}$)
1	Silica gel	Ke1-FN.10	30	4m x 6mm	30
2	Porapak-Q	Ke1-FN.10	1	2m x 3mm	40
3	Porapak-QS	----	--	2m x 3mm	60

TABLE I

I.R. characteristic frequencies (in cm^{-1}) of fluorine compounds

SF ₆		SO ₂ F ₂		SOF ₄		SOF ₂		SiF ₄	
Lit. 1	Obs	Lit. 2	Obs.	Lit. 3	Obs.	Lit. 4	Obs.	Lit. 5	Obs.
615(s)		848(m)	850(m)	637(s)	630(s)	748(s)	750(s)	1031(s)	1030(s)
940(s)		885(s)	888(s)	752(m)	760(m)	808(s)	810(s)		
		1269(s)	1270(s)	821(vs)	821(vs)	1353(s)	1330(s)		
		1502(s)	1503(s)	928(s)	930(s)				
						1383(s)	1380(s)		

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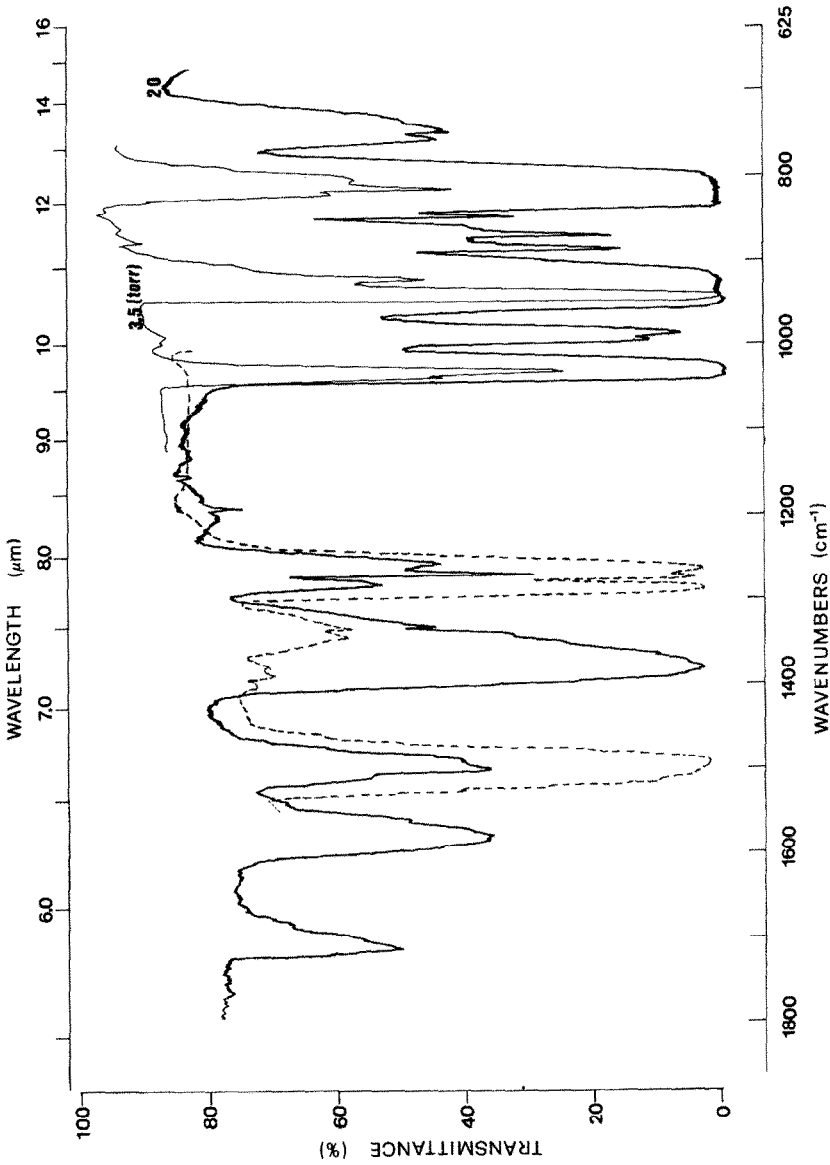


Fig. 1 - Infrared spectra of the gas mixture at two different pressures 3.5 and 20 torr (solid line); after admission of water vapor (dotted line).

All the analyses were carried out on a Hewlett-Packard gas chromatograph model 5700A, with thermoconductivity detector. The carrier gas was helium and the gases were injected with a gas sampling valve, after the admission of mercury into the glass bulbs.

The first column was found to give an insufficient separation between SiF_4 and SF_6 and between SOF_4 , SO_2F_2 and SOF_2 . The second column gave a good separation between SiF_4 , SF_6 and SOF_2 , but low resolution between SOF_4 and SO_2F_2 . The best results were obtained utilizing the third type of column and a typical gas-chromatogram is reported in Fig. 2. The identification of

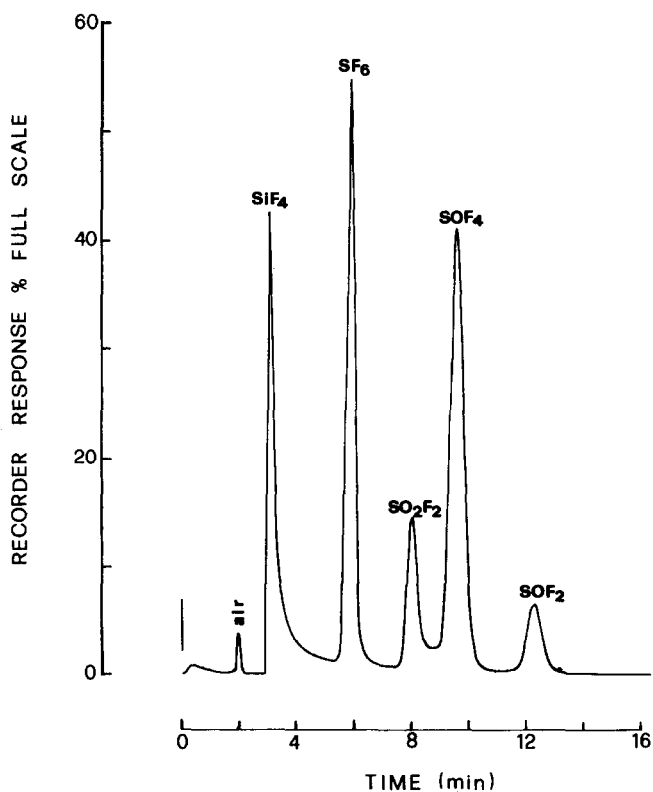


Fig. 2 - Typical gas-chromatogram of some fluorine compounds.

the peaks was made utilizing pure samples of SF_6 , SiF_4 and SO_2F_2 . The last peak was identified by trapping the eluted component directly in an evacuated infrared gas cell, which showed the characteristic spectrum of SO_2F_2 . The assignment of the peak of SOF_4 was made by exclusion on the basis of the IR analysis.

In most of the previously quoted investigations on SF_6 decomposition, the presence of SF_4 has been reported and in many cases the gas-chromatographic separation of SF_4 from SOF_2 was difficult. In order to ascertain the presence of SF_4 in our gas mixtures, we have carried out a gas-mass spectrometric analysis (HP model 5990/A), which has confirmed the identification of all the G.C. peaks but excluded definitely the presence of SF_4 . Table II shows the retention times, the relative abundances of the parent molecule ions and the most plentiful ionic species derived therefrom. When ionic species were sufficiently plentiful, it was also possible to detect the presence of ^{33}S and ^{34}S isotopes (1 and 5% respectively).

Quantitative analysis

After the admission of mercury into the glass bulbs to convert fluorine in fluoride, the sample was introduced into the gas-chromatograph for quantitative analysis. The system of sample introduction is illustrated in Fig. 3. It consists of a conventional gas sampling valve and of a vacuum line fitted with a pressure gauge (accuracy 1%). The discharge gases, sampled at about 15 torr, were admitted from the bulbs to the previously evacuated sample loop,

TABLE II
 Mass Spectrum of the discharge products, obtained at 70 eV.

SUBSTANCE (Time retention) sec.	TYPE OF PEAK									
	Mass/Charge ratio - Relative intensities									
SiF ₄ (178)	SiF	SiF ₃	SiF ₄	²⁹ SiF ₃						
	47-1.7	85-100	104-2.1	86-5.3						
SF ₆ (349)	SF	SF _{4,d}	SF ₂	SF ₃	SF ₄	SF ₅				
	51-5.3	54-1.3	70-5.4	89-32.5	108-16.0	127-100				
SO ₂ F ₂ (482)	SO	SF	SO ₂	SOF	SF ₂	SO ₂ F	SOF ₂	SO ₂ F ₂		
	48-6	51-2.4	64-6.3	67-22.3	70-2.2	83-100	86-2.3	102-86.9		
SOF ₄ (571)	SO	SF	SOF	SF ₂	SOF ₂	SF ₃	SOF ₃			
	48-2.6	51-1.9	67-8.9	70-2.5	86-14.7	89-7.2	105-100			
SOF ₂ (738)	SO	SF	SOF	SF ₂	SOF ₂	SOF ₂	SOF ₂			
	48-13.5	51-4.5	67-100	70-3.8	86-54.5					

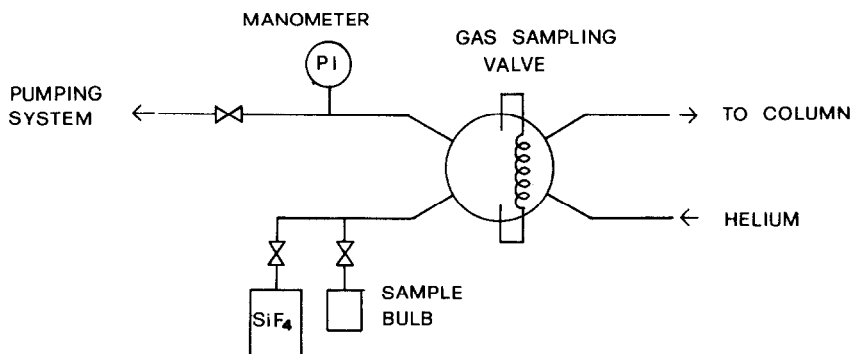


Fig. 3 - Scheme of gas-chromatographic injection system.

and after recording the gas pressure injected into the column. Typical analytical conditions adopted are given in Table III.

The carrier gas was dried in a condenser containing molecular sieves cooled with liquid nitrogen, in order to prevent the fast hydrolysis of the reactive components.

TABLE III.
Operating Conditions.

Instrument	Hewlett-Packard gas-chromatograph Model 5700A and Hewlett-Packard integrator, Model 3370A
Column	6.5 ft x 1/8 in, stainless steel column, Porapak-QS
Oven temperature	60 °C
Detector	Thermal conductivity detector
Current	270 mA
Detector block temperature	100 °C
Helium flow rate	20 cc/min.
Sample volume	3 ml
Time for single analysis	13 min.

Calibration curves of SF_6 , SO_2F_2 and SiF_4 have been obtained by utilizing the corresponding pure gases (Matheson). It was observed that successive injections of equal amounts of SiF_4 produced a gradual increase in the heights of the relative peaks up to a constant maximum value. This was clearly due to the absorption of small amounts of the gas into the column. An injection of about 200 torr of pure SiF_4 before each set of analyses was sufficient to prevent this effect for at least an hour.

The calibration curve of SOF_2 was obtained indirectly, after the gas-chromatographic analysis. The gas sample was subjected to base hydrolysis and the resulting sulphites titrated iodometrically.

The quantitative measurement of SOF_4 was obtained by a difference between the total pressure of the sampled gas and the sum of the partial pressures of the other components. The values thus obtained were in good agreement with those resulting from the internal oxygen balance of SiO_2

$$P_{\text{SiF}_4} = P_{\text{SO}_2\text{F}_2} + \frac{1}{2}(P_{\text{SOF}_4} + P_{\text{SOF}_2}) \quad (1)$$

The right side of equn. (1) does not contain the partial pressure of free oxygen because it completely reacts to give the other mentioned compounds.

Calibration plots, obtained as described above, are shown in Fig. 4, for pressures up to 1.5 torr using a 3 ml sampling volume. With the exception of SiF_4 , which shows a pronounced curvature, the plots are linear. The uncertainty in the detector calibration has been found for all gases to be $\pm 1\%$ (relative error) over 0.05-10 torr pressure range and this

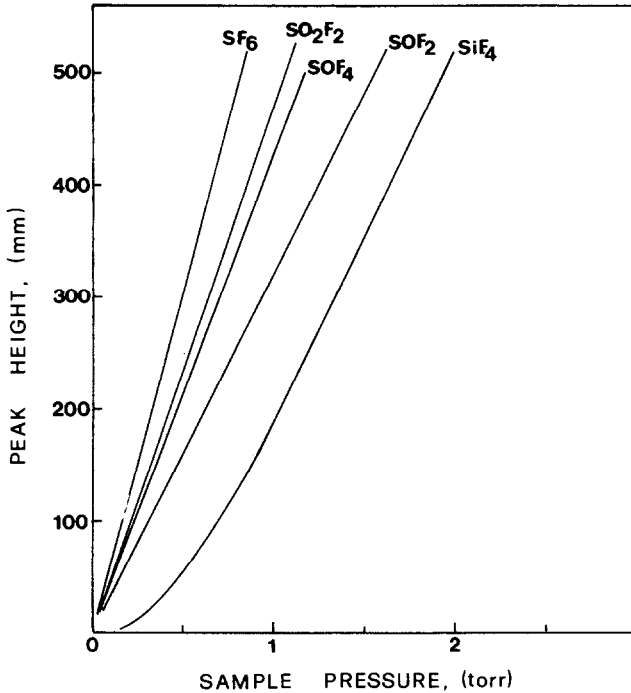


Fig. 4 - Calibration plots.

error is mainly due to the accuracy of the pressure gauge of the sampling system.

The lowest detection limit reached for all the components of the mixture was 0.05 torr, with the exception of SiF₄, the detection limit of which was 0.2 torr. These data are given in torr for the component in the mixture, at ambient temperature, for a total pressure of 10 torr, using a 3 ml sample loop volume.

After the gas-chromatographic analysis, the glass bulb containing the gas mixture, the mercury fluoride and the unreacted mercury, was evacuated from the remaining gases. The mercury fluoride was then dissolved in distilled water

and the fluoride ion determined volumetrically by means of thorium nitrate solution, using as indicator sodium alizarin sulfonate. Nitric acid has been used for acidifying the solution, instead of HCl as reported by J.M. Salsbury et al. [13], in order to prevent the formation of calomel.

CONCLUSIONS

With the analytical technique outlined above we have been able to study the decomposition of SF₆ under R.F. discharge at 20 torr, as a function of the power density and gas flow rate [14]. For particular conditions of power density and flow rate a 100% conversion is almost reached. A typical distribution of the products, in terms of molar fraction, is: 0.06 SF₆; 0.33 SiF₄; 0.27 SOF₄; 0.16 SO₂F₂; 0.10 F₂; 0.07 SOF₂. The presence of SiF₄ as a major reaction product is a clear indication of the high concentration of atomic fluorine and/or SF_x radicals which rapidly react with the reactor walls. The system can therefore be profitably utilized for the dry etching of the semiconductor surfaces.

The formation of SiF₄ is an indication of the possibility of gasification of silica particles to give silicon tetrafluoride, whose reduction with H₂ under plasma conditions can lead to solar grade silicon for the production of photovoltaic cells.

Another possible utilization of the fluorine atoms produced under discharge conditions could be, as already mentioned in the introduction, the production of excited hydrogen fluoride for laser emission. The etching of reactor walls must at all times be avoided. Preliminary results obtained in our labora-

tory using an alumina tube reactor fed with mixtures of SF₆ and O₂, have shown the clear absence of SiF₄ and the presence of relevant amounts of fluorine, together with the same oxygenated compounds reported above.

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