EFFECT OF WATER VAPOR ON THE PRODUCTION OF S_2F_{10} AND S_2OF_{10} BY SPARK DISCHARGES IN SF_6

Isidor Sauers*

* Health Sciences Research Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA 37831-6123

ABSTRACT

Production rates of the compounds disulfur decafluoride (S_2F_{10}) and bis(pentafuorosulfur) oxide (S_2OF_{10}) have been measured following spark discharges in SF_6 as a function of water content for water concentrations in the range 600-3400 ppm (parts-per-million). Sparks were produced by capacitive discharge (80 J per spark) into SF_6 at a pressure of 100 kPa. Absolute yields were determined from the spark energy from direct measurement of the voltage and current waveforms. In dry SF_6 the spark yield of S_2F_{10} is 2.2 x 10^{-11} mol J^{-1}. Adding water to SF_6 results in a decrease in the yield of S_2F_{10} and an increase in the S_2OF_{10} yield. Production of both S_2F_{10} and S_2OF_{10} are believed to be formed via the precursor SF_5. Mechanism for production of these two disulfur compounds will be discussed.

INTRODUCTION

The decomposition byproduct, disulfur decafluoride (S_2F_{10}), of sulfur hexafluoride (SF_6), has been found to be produced by a wide range of electrical discharges including corona, spark and power arc [1-5]. Because of its toxicity [6-9], S_2F_{10} is of concern to users of SF_6-filled electrical equipment. While no significantly high concentrations of S_2F_{10} has been found in high voltage power equipment, thus far, it is important to understand the mechanism of and the influence of SF_6 impurities on the formation of S_2F_{10} in order to assess the potential buildup of this byproduct in high voltage equipment under a wide range of discharge conditions. In another paper in this conference [10], the effect of oxygen on production of S_2F_{10} is assessed, both for negative point-plane corona and for capacitively coupled spark discharges. The effect of gas phase water, in SF_6, on the spark yield of S_2F_{10} will be examined in this paper.

It is assumed that the reaction mechanism for S_2F_{10} formation is given by (1) where two SF_5 radicals combine to form S_2F_{10}.

$$SF_5 + SF_5 + M \rightarrow S_2F_{10} + M \tag{1}$$

If only SF_6 and its fragments are involved then reaction (1) competes primarily with (2) in which SF_5 reacts with F to form SF_6.

$$SF_5 + F + M \rightarrow SF_6 + M \tag{2}$$

The spark yield of S_2F_{10} in relatively pure SF_6 has been found to be 1-2 x 10^{-11} mol J^{-1}, over the energy range 7-80 J per spark. When other species are present in the spark channel immediately following a spark then other reactions with SF_5 radicals are possible leading to the formation of other byproducts and to a reduction in the yield of S_2F_{10}. This is observed in the case of oxygen addition where the rates of formation of S_2F_{10} is found to decrease with added oxygen in either negative point to plane corona or in spark discharges. It can be argued however that the presence of new species to the SF_6 spark channel can lead to reactions with fluorine atoms, F, reducing the F concentration, which would have the effect of slowing the rate of (2), thereby enhancing the production of other byproducts such as S_2F_{10}. For water addition the production of OH via reaction (3) in a discharge could lead to a fast reaction of OH with SF_5 in reaction (4).

$$F + H_2O \rightarrow OH + HF \tag{3}$$

$$OH + SF_5 \rightarrow SOF_4 + HF \tag{4}$$

When either oxygen or water is present in SF_6, the production of oxygen containing species has been observed and their rates of formation measured in both corona and spark discharges. These include SOF_2, SOF_4, SO_2F_2, and SO_2. In addition to these mono-sulfur compounds, there has been recent evidence for the production of the oxygen containing disulfur compounds, bis(pentafluorosulfur) oxide (S_2OF_{10}) and bi(pentafluorosulfur) peroxide ($S_2O_2F_{10}$) [3]. Although there is a lack of toxicological data for these disulfur compounds there is evidence to suggest that $S_2O_2F_{10}$ is nearly as toxic as S_2F_{10}, while S_2OF_{10} is relatively non-toxic (compared to S_2F_{10}). It was found in the work on oxygen-SF_6 mixtures that $S_2O_2F_{10}$ is produced preferentially to S_2OF_{10} in negative point-to-plane corona while in spark discharges the opposite is true. This difference between spark and corona discharge is attributed to the degree of dissociation of oxygen in the two discharges and the subsequent reactions of O or O_2 with SF_5 given in reactions (5) and (6), where S_2OF_{10} is formed (in spark discharges) via the intermediate SF_5O, and $S_2O_2F_{10}$ is formed (in negative point-plane corona) via the intermediate SF_5O_2.

$$O + SF_5 + M \rightarrow SF_5O + M \tag{5}$$

$$O_2 + SF_5 + M \rightarrow SF_5O_2 + M \tag{6}$$

EXPERIMENT

Spark Discharge

Spark discharges in SF_6 were produced by discharging a 0.4 µF capacitor into a 1.1-ℓ stainless steel chamber shown schematically in Fig. 1 [2]. The electrode geometry was sphere-plane where the position of the grounded plane electrode was adjustable via a linear motion feedthrough. Both electrodes were also made of stainless steel and the gap was set to 2.4 mm. Reproducible breakdowns were obtained by illuminating the electrodes, through a sapphire window on the spark chamber, with continuous ultraviolet light from a deuterium-filled lamp. For the water-SF_6 measurements reported here the energy dissipated in one spark was 80 J. Measurements of the spark energy were made in two ways: (1) from the time integrated product of the voltage and current (determined from the voltage across a 4 ohm shunt resistor on the ground side of the circuit, as shown in Fig. 1, captured by digital storage oscilloscope; and (2) from the net energy released from the capacitor, determined from the voltage measured before and after breakdown. The two measurements provided agreement in spark energy to within ± 5%.

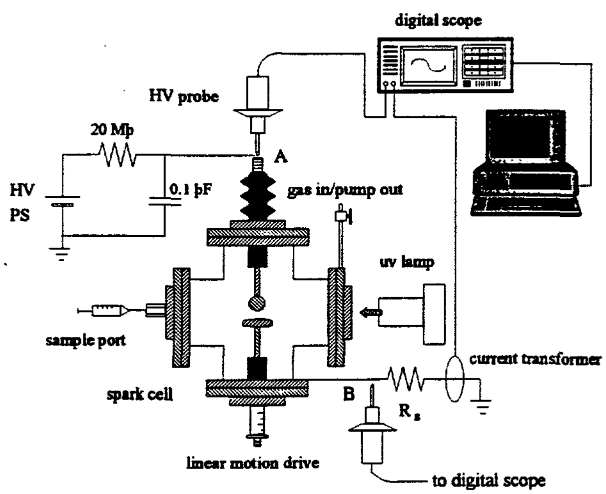

Figure 1 Schematic of spark cell and energy measurement system.

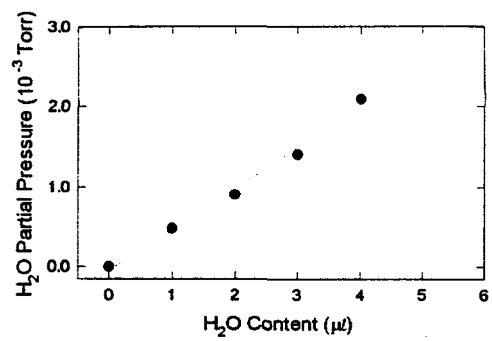

Figure 2 Partial pressure (in 10^{-3} Torr) of water vapor after introducing liquid water into 1.1-ℓ spark cell.

Preparation of SF_6/H_2O Mixtures

After initially evacuating the spark chamber to 10^{-1} Pa, water was introduced by injecting 1-5 µℓ liquid water samples in a 10-µℓ syringe. Water vapor pressure was monitored with a capacitance manometer pressure transducer as the water sample equilibrated with the walls of the chamber. When the water vapor pressure reached a constant value (after about 30 minutes) the pressure was recorded and SF_6 was added to a total pressure of 100 kPa. The water concentration was determined from the ratio of the water vapor partial pressure to the total gas pressure in the cell. The water vapor pressure is plotted as a function of the volume of liquid water introduced into the spark cell in Fig. 2. The concentration of water was assumed to be constant during the course of the experiment lasting up to about 6 hours after preparation of the mixture. Linear increases in byproduct production with successive sparks indicate that the concentration was not changing during an experimental run at a given concentration.

Byproduct Analysis

Gas samples, taken by syringe, of 2-ml x 100 kPa (8.1 x 10^{-8} mol) were taken after each spark from the spark cell via a septum located on one of the stainless steel flange port as shown in Fig. 1. After each spark, a sample was taken and immediately (within about 30 s) injected into a cryogenic-enrichment gas chromatograph with electron capture detection for analysis. Details of the analytical technique are described in [11].

The elution order of all three disulfur compounds studied was S_2OF_{10}, S_2F_{10}, and $S_2O_2F_{10}$. The same elution order was found using a packed chromasorb WAW column. The elution order of these species is consistent with other gas chromatographic data [11-13].

Reference samples of S_2F_{10} and S_2OF_{10} were synthesized at Clemson University and received in stainless steel cylinders as liquid, each under its own vapor pressure. S_2F_{10} was found to be relatively stable as a liquid but decays in the gas phase by reactions associated with the cylinder walls. S_2OF_{10} was found to be stable both in the liquid and gas phase showing no indication of decay.

RESULTS AND DISCUSSION

Production of S_2F_{10} and S_2OF_{10} as a function of the number of sparks in SF_6/H_2O mixtures is shown in Figs. 3 and 4. Byproduct concentrations are given in parts-per-billion (ppb) or parts per 10^9. The yields in 10^{-11} mol J^{-1} of S_2F_{10} and S_2OF_{10} were determined from the slopes of the plots in Figs. 5 and 6. As water is added to SF_6, the yield of S_2F_{10} decreases while the yield of S_2OF_{10} increases. This behavior is qualitatively similiar to that observed for SF_6/O_2 mixtures. The yields are also summarized in Table 1. The solid line in Figs. 4 and 5 are curve fits to the data. From a plot of the S_2F_{10} yield as a function of concentration of either water or O_2 additive, shown in Fig. 7, water is found to be more effective than oxygen in reducing the S_2F_{10} yield. However, the production of S_2OF_{10} is not a great when water is added than when O_2 is added to SF_6. This could possibly be attributed to reaction (4) in which SF_5 is converted to SOF_4 (or some other product) in reactions with OH. S_2OF_{10} is expected to be formed by reaction (7).

$$SF_5O + SF_5 + M \rightarrow S_2OF_{10} + M \quad (7)$$

However since reaction (4) would not lead to SF_5O formation, S_2OF_{10} would not be expected to be efficiently produced.

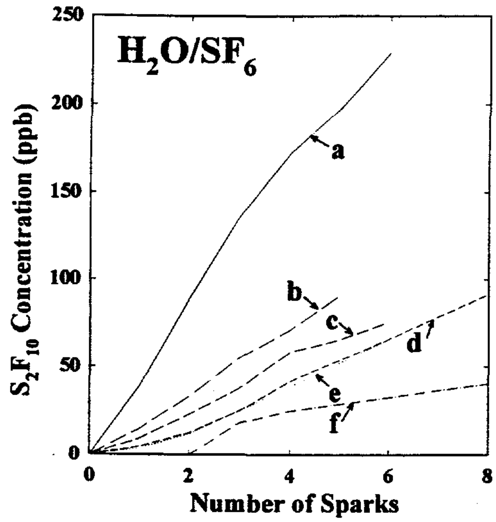

Figure 3 Concentration (in ppb) of S_2F_{10} as a function of number of sparks in SF_6/H_2O mixtures for different water concentrations (in ppm): (a) 0; (b) 630; (c) 1190; (d) 1840; (e) 2750; (f) 3355.

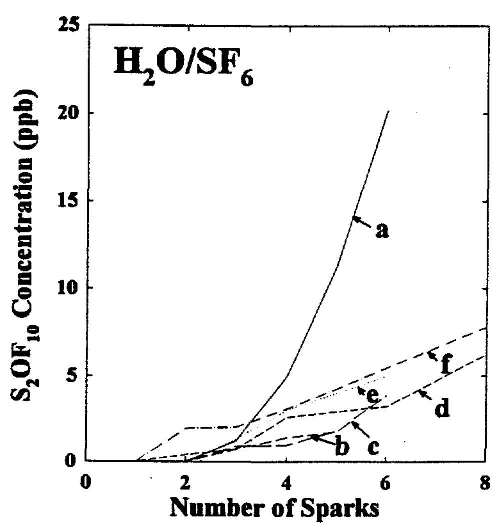

Figure 4 Concentration (in ppb) of S_2OF_{10} as a function of number of sparks in SF_6/H_2O mixtures for different water concentrations (in ppm): (a) 0; (b) 630; (c) 1190; (d) 1840; (e) 2750; (f) 3355.

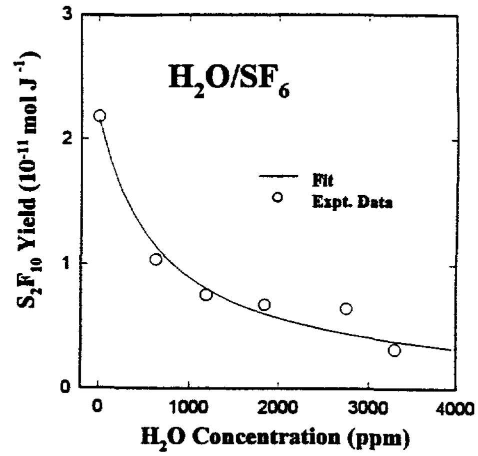

Figure 5 S_2F_{10} yield (in 10^{-11} mol J^{-1}) in sparked SF_6 (80 J per spark) as a function of water concentration (in ppm). Solid line is a curve fit to the data.

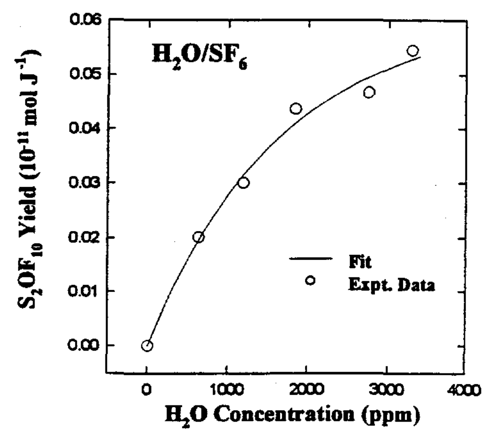

Figure 6 S_2OF_{10} yield (in 10^{-11} mol J^{-1}) in sparked SF_6 (80 J per spark) as a function of water concentration (in ppm). Solid line is a curve fit to the data.

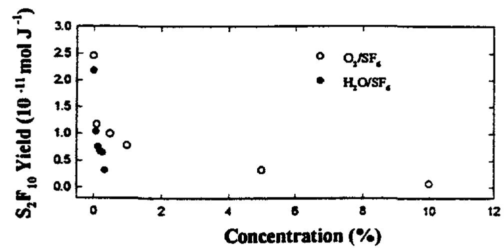

Figure 7 Comparison of the effects of water and oxygen on the yield of S_2F_{10}.

Table 2. Spark yield (in 10^{-11} mol J^{-1}) of S_2F_{10} and S_2OF_{10} in H_2O/SF_6 mixtures

Byproduct	H_2O Content (μl)				
	1	2	3	4	5
S_2F_{10}	1.03	0.75	0.67	0.64	0.32
S_2OF_{10}	0.02	0.03	0.043	0.047	0.054

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REFERENCES

[1] Van Brunt, R. J., Olthoff, J. K., and Shah, M., *"Rate of S_2F_{10} Production from Negative Corona in Compressed SF_6,"* Conf. Record - 1992 IEEE Int. Symp. Elect. Insul., IEEE No. 92CH3150, 328-331 (1992).

[2] Sauers, I. and Mahajan, S. M., *"Detection of S_2F_{10} Produced by a Single-Spark Discharge in SF_6,"* J. Appl. Phys. 74, 2103-2105 (1993).

[3] Sauers, I., Mahajan, S. M., and Cacheiro, R. A., *"Production of S_2F_{10}, S_2OF_{10}, and $S_2O_2F_{10}$ by Spark Discharges in SF_6,"* Gaseous Dielectrics VII, (James, D. R. and Christophorou, L. G., Eds), Plenum Press, 423-431 (1994).

[4] Morrison, H. D., Chu, F. Y., Eygenraam, M., Sauers, I., and Van Brunt, R. J., *"Decomposition of SF_6 and Production of S_2F_{10} in Power Arcs,"* Gaseous Dielectrics VII, (James, D. R. and Christophorou, L. G., Eds), Plenum Press, 475-480 (1994).

[5] Morrison, H. D., Cronin, V. P., Chu, F. Y., Egenraam, M., Sauers, I., and Dallavalli, M. J., *"Production and Decay of S_2F_{10} in a Disconnect Switch,"* Gaseous Dielectrics VII, (James, D. R. and Christophorou, L. G., Eds), Plenum Press, 433-439 (1994).

[6] Greenberg, L. A. and Lester, D., *"The Toxicity of Sulfur Pentafluoride,"* Arch. Indust. Hygiene and Occupat. Med. 2, 350-353 (1950).

[7] James, D. R., Sauers, I., Griffin, G. D., Van Brunt, R. J., Othoff, J. K., Stricklett, K. L., Chu, F. Y., Robins, J. R., and Morrison, H. D., *"Investigation of S_2F_{10} Production and Mitigation in Compressed SF_6-Insulated Power Systems,"* IEEE Elec. Insul. Mag., 9, 29-40 (1993).

[8] Griffin, G. D., Nolan, M. G., Kurka, K., Sauers, I., and James, D. R., *"Disulfur Decafluoride (S_2F_{10}): A Review of the Biological Properties and Our Experimental Studies of this Breakdown Product of SF_6,"* Gaseous Dielectrics VI (Christophorou, L. G. and Sauers, I., eds.), Plenum Press, 545-52 (1991).

[9] Griffin, G. D., Nolan, M. G., Sauers, I., Kurka, K., Morris, M. D., and Votaw, P. C., *"Cytotoxic Activity of Disulfur Decafluoride (S_2F_{10}), a Decomposition Product of Electrically-Stressed SF_6,"* In Vitro, 25(8), 673-675 (1989).

[10] Van Brunt, R. J., Olthoff, J. K., Firebaugh, S. L., and Sauers, I., *"Measurement of S_2F_{10}, S_2OF_{10}, and $S_2O_2F_{10}$ Production Rates from Spark and Negative Glow Corona Discharge in SF_6/O_2 Gas Mixtures,"* The Eleventh International Conference on Gas Discharges and Their Applications, Tokyo, Japan, (1995).

[11] Sauers, I. and Cacheiro, R. A., *"A Cryogenic Enrichment Technique for Gas Chromatographic Detection of S_2F_{10} in SF_6 Discharges,"* Conference Record of the 1992 IEEE International Symposium on Electrical Insulation, 340-44 (1992).

[12] Sauers, I., Harman, G., Olthoff, J. K., and Van Brunt, R. J., *"S_2F_{10} Formation by Electrical Discharges in SF_6: Comparison of Spark and Corona,"* Gaseous Dielectrics VI, (Christophorou, L. G. and Sauers, I., eds.) Plenum, New York, 553-562 (1991).

[13] Gutbier, J. and Luy, J., *"Nachweis und Bestimmung von Spuren höhersiedender Verunreinigungen in Schwefelhexafluorid,"* Anal. Chemie, 231, 329-339 (1967).

[14] Hanrahan, J. M. and Paterson, A. R., *"Adsorption-desorption Gas Chromatographic Infrared Determination of Trace Disulfur Decafluoride in Sulfur Hexafluoride,"* J. Chromatog. 193, 265-270 (1980).