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PRODUCTION OF S_2F_{10} BY SF_6 SPARK DISCHARGES

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Introduction

Sulfur hexafluoride (SF_6) is known to fragment in an electrical discharge, leading to the formation of various sulfur-fluorides (Frees and others, 1981; Sauers and others, 1986; Van Brunt, 1985). Of particular interest is the compound S_2F_{10} (sulfur decafluoride) which has been reported in spark discharges (Becher and Massonne, 1970; Bartakova, 1978), in corona (Bartakova, 1978), and in arc discharges (Pettinga, 1985). The potential presence of this by-product in electrical systems is significant due to its extremely high toxicity and its relatively low thermal stability. The TLV-TWA (threshold limit value-time weighted average) for human exposure to S_2F_{10} recommended by the American Conference of Governmental Industrial Hygienists is 25 parts per billion. At room temperature S_2F_{10} is extremely stable, having a calculated half-life of 10^5 years based on the unimolecular decomposition rate constant k (Trost and McIntosh, 1952; Benson and Bott, 1969; Herron, 1987) given by

$$k = 5.6\times10^{18} \exp(-45{,}700/RT) \qquad (1)$$

where k is in s^{-1} and RT is in calories. However at elevated temperatures, S_2F_{10} will decompose as indicated by the gas chromatograms shown in Fig. 1 (Sauers and others, 1988). Above ~200°C S_2F_{10} is considered to be thermally unstable. This decomposition temperature is relatively low compared to other sulfur-fluorides, and its formation in discharges where high temperatures exist has been controversial. In this paper, we report on the influence of moisture on S_2F_{10} formation and the product yield under our experimental conditions.

Experiment

Sparked SF_6 was prepared by repeatedly discharging a 0.1 μF capacitor into a stainless-steel (SS) chamber housing SS electrodes with concentric cylindrical geometry. The energy discharged in one spark was typically 15 J, and the total energy discharged into the gas fell in the range 4-32 kJ. The gas was analyzed primarily for S_2F_{10} using a Perkin-Elmer Sigma 3 gas chromatograph (GC) with a thermal conductivity detector. The column used for separating S_2F_{10} from SF_6 was 30% SP-2100 on chromosorb WAW packed in 24' x 1/8" teflon tubing obtained from Supelco. Table 1 lists the retention times for various compounds expected to be found in sparked SF_6.

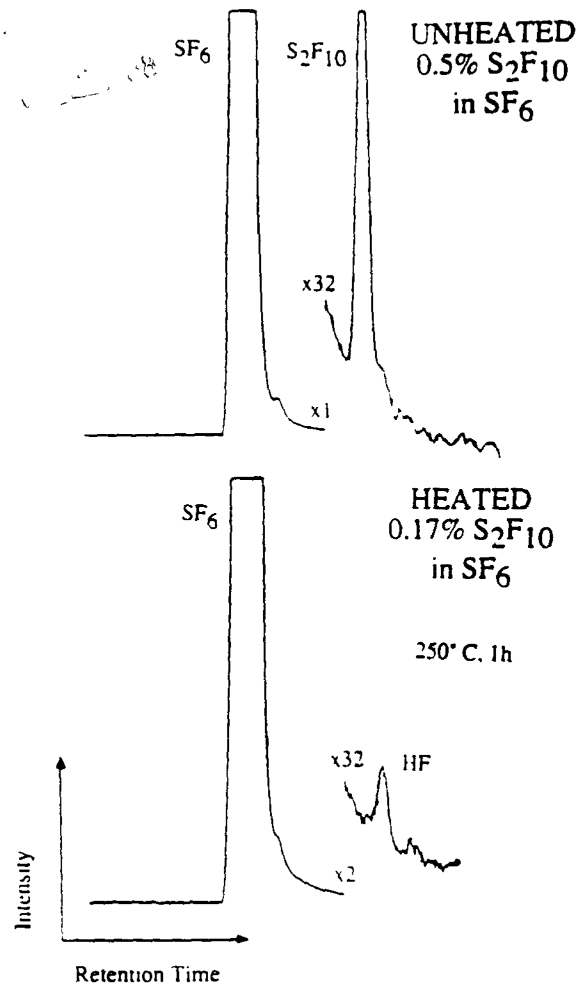

Fig. 1. Gas chromatograms of unheated (upper trace) and heated (lower trace) S_2F_{10}/SF_6 mixtures. The heating parameters were 250°C for 1 h, corresponding to over 2000 half-lives for S_2F_{10} decomposition. Note the relative sensitivities as indicated by the multiplication factors given in this figure and in Fig. 2.

Results and Discussion

Effect of moisture. Generally S_2F_{10} was observed under dry conditions. Moisture was removed from the spark cell by treating the inside surfaces with SF_4 (sulfur tetrafluoride). SF_4 is known to react with water, having a gas phase rate constant for hydrolysis of $k = 1.5 \pm 1\times10^{-19}$ cm^3 s^{-1} (Sauers and others, 1985) for the reaction

$$SF_4 + H_2O \rightarrow SOF_2 + 2HF \qquad (2)$$

The spark cell was filled with SF_4 to P = 0.5 atm for 0.5 h. The gas was pumped out, and the process was repeated, followed by overnight pumping. The cell was then filled with SF_6 to P = 133 kPa and sparked. The GC analysis is illustrated in the upper trace of Fig. 2. After calibrating the analyzer with pure S_2F_{10}, the peak area was found to correspond to 160 ppm S_2F_{10} in SF_6.

DISCLAIMER

TABLE 1 Retention times (relative to N_2) of various compounds injected in a 24' x 1/8" teflon column containing 30% SP-2100 on chromosorb WAW. The oven temperature and He flow were 50°C and 30 ml/min, respectively.

Compound	Retention Time (min)
SF_6	0.194
SO_2F_2	0.481
SOF_4	0.503
SOF_2; SF_4	0.735
SO_2	1.8-2.5†
S_2F_{10}	2.154
HF	2.487
SiF_4	2.7-4.7†

†The retention time for this compound was found to be concentration dependent. At low concentrations (i.e., where peak heights were comparable to that of S_2F_{10}) the range for SO_2 was 2.2 to 2.5 min. The SO_2 peak was clearly distinguishable from S_2F_{10} by its retention time and peak shape.

Moisture was then added to "pure" SF_6 in the amount of ~600 ppm, and the sparking experiment was repeated. The striking absence of S_2F_{10} is illustrated in the lower trace of Fig. 2. Although the moisture level in the dried cell is not known, the effect of drying and, hence, the effect of moisture on S_2F_{10} production is very apparent. On the other hand, S_2F_{10}, once formed, does not react with water at room temperature (Bailar, 1973). We have found that S_2F_{10} may be stored in an ordinary SS cylinder with no loss of S_2F_{10} over several weeks.

In a recent computational model study of S_2F_{10} formation in decomposed SF_6, Herron (1987) and Herron and Tsang (1987) address specifically the influence of water on S_2F_{10} formation. Two cases were considered: in the first case, it was assumed that SF_6 decomposes at a slow rate to SF_4 + 2F; while in the second case, it was assumed that SF_6 fragments to SF_5 + F. In either case Herron (1987) argues that water reacts with fluorine by the process

$$F + H_2O \rightarrow HF + OH \quad (3)$$

to form OH radicals which, subsequently, react with SF_5 in the reaction

$$SF_5 + OH \rightarrow SOF_4 + HF \quad (4)$$

This reaction competes with the recombination process

$$SF_5 + SF_5 \rightarrow S_2F_{10} \quad (5)$$

which occurs more efficiently in the absence of water. Because our spark discharges are expected to fragment H_2O as well as SF_6, OH radicals may be formed even without reaction (3), but the effect of OH on S_2F_{10} suppression might well be the same. Our present results on the effect of moisture qualitatively support this model.

The effect of moisture on S_2F_{10} formation raises important implications on the controlling factors for S_2F_{10} production. The view that is widely held is that S_2F_{10} is not expected to be formed in "hot" discharges such as arc discharges as opposed to "cold" discharges such as corona due to the thermal insta-

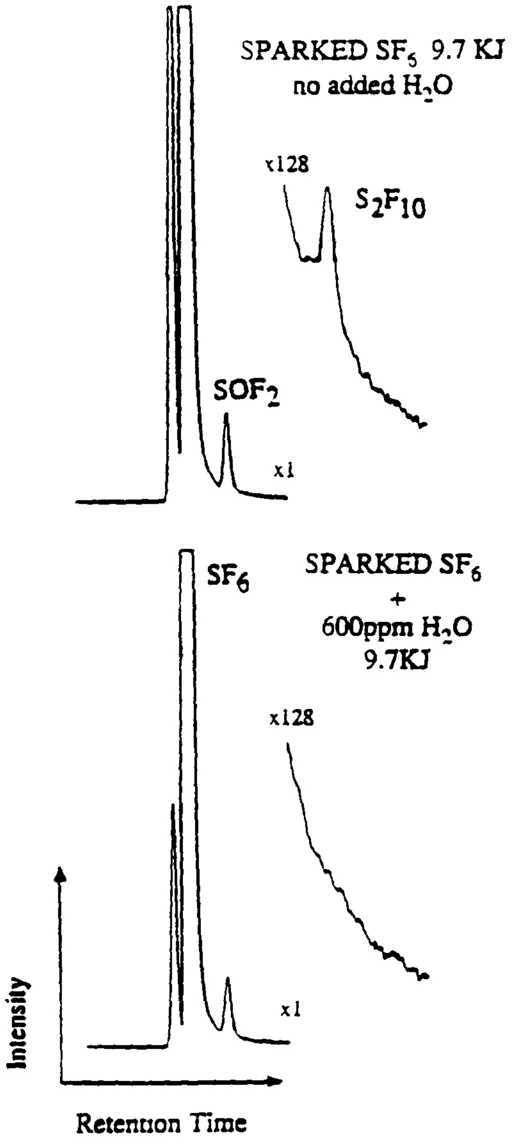

Fig. 2. Gas chromatograms of sparked SF_6 at 9.7 k showing the effects of added moisture. S alone (upper trace), SF_6 + 600 ppm H (lower trace).

bility of S_2F_{10} above 200°C. Spark discharges mig be considered an intermediate case. However, in a types of localized discharges, there are regions the outer edges that could be cool enough to fo stable S_2F_{10}. The moisture level, however, may be more important factor in S_2F_{10} suppression than t arc temperature itself.

S_2F_{10} Yield. The S_2F_{10} peak in Fig. 2 corresponds a spark yield of 6.8×10^{-11} mol/J. This value may compared to the spark yield of S_2F_{10} reported Becher and Massonne (1970). Their results showed th after 30 min of sparking, corresponding to 54-90 total energy dissipation, the concentration of S_2F (plus $S_2F_{10}O$) in the range of 40-140 ppm were pr duced. It is not entirely clear which of the two te cells, described in their paper, was used for t S_2F_{10} measurements; however, if we assume that the 2 cell was employed, then the S_2F_{10} + $S_2F_{10}O$ yields fa in the range $0.05-0.17 \times 10^{-9}$ mol/J. Our results a consistent with those values, indicating that t Becher and Massonne experiments were conducted und similarly dry conditions.

Conclusions

The highly toxic compound S_2F_{10} is formed in SF_6 following spark discharges. When the spark cell is dried, the S_2F_{10} yield was 6.8×10^{-11} mol/J at an SF_6 pressure P = 133 kPa. Moisture appears to suppress the S_2F_{10} yield, although once formed, the S_2F_{10} is quite stable with respect to moisture. This could explain the variation in observation from experiment to experiment in the literature. These results also raise important questions as to the influence of drying agents that are used in high-voltage systems on the S_2F_{10} yield.

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