

# RATE OF S<sub>2</sub>F<sub>10</sub> PRODUCTION FROM NEGATIVE CORONA IN COMPRESSED SF<sub>6</sub>

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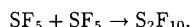
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## ABSTRACT

Using a mass spectrometer-gas chromatograph capable of detecting S<sub>2</sub>F<sub>10</sub> concentrations in SF<sub>6</sub> down to the part in 10<sup>9</sup> level, the rates of S<sub>2</sub>F<sub>10</sub> production from dc glow-type negative point-plane corona discharges in pressurized SF<sub>6</sub> have been measured at different absolute gas pressures in the range of 100 to 500 kPa (1 to 5 atm) and at different constant discharge currents in the range 2 to 80 μA. The charge rate-of-production for S<sub>2</sub>F<sub>10</sub> is observed to drop with decreasing discharge current and the yield curves exhibit nonlinearities in the early stages of the discharge that appear to be associated with "conditioning" of the point electrode. The nonlinearities become more pronounced with increasing gas pressure. The results are found to be quite reproducible and suggest the possibility of using this type of corona discharge as a reliable method for preparing reference gas samples that contain predictable trace quantities of S<sub>2</sub>F<sub>10</sub> in SF<sub>6</sub>.

## INTRODUCTION

Disulfur decafluoride (S<sub>2</sub>F<sub>10</sub>) is now known to be formed when electrical discharges occur in compressed sulfur hexafluoride (SF<sub>6</sub>) commonly used as a gaseous dielectric in high-voltage apparatus [1,2]. The possible presence of this compound in SF<sub>6</sub> is of concern because it is known to be highly toxic [3]. The primary mechanism for its formation is believed to be the reaction



where SF<sub>5</sub> is formed by collisional dissociation of SF<sub>6</sub> in the discharge and the above reaction involves stabilization via interaction with a third body. Since S<sub>2</sub>F<sub>10</sub> is thermally unstable above about 150°C [4], it tends to form only in the "cold" regions of the discharge. Favorable conditions for its production thus exist in low-level negative glow-type corona discharges in which there is no significant heating of the gas.

In the normal operation of SF<sub>6</sub>-insulated power equipment, it can be expected that internal corona or partial discharges will occur that cause decomposition of the gas. It is therefore desirable to know the rates for S<sub>2</sub>F<sub>10</sub> production under these conditions in order to determine gas toxicity levels and assess possible hazards associated with exposure to decomposed SF<sub>6</sub>.

The dc point-plane negative glow corona in SF<sub>6</sub> is a constant-current discharge that is easily controlled and amenable to theoretical chemical kinetics modelling [5,6]. It shows promise as a type of reference discharge capable of generating gas samples containing known trace quantities of S<sub>2</sub>F<sub>10</sub> in SF<sub>6</sub> suitable for calibration of analytical detection methods. The ability to quickly produce reliable reference gas samples in the laboratory is especially desirable in the case of S<sub>2</sub>F<sub>10</sub> for two reasons: 1) it eliminates the necessity of dealing with pure S<sub>2</sub>F<sub>10</sub> which requires

special procedures because of its high toxicity, and 2) it avoids the problems associated with long-term decomposition of S<sub>2</sub>F<sub>10</sub> in gas sample cylinders noted in previous work [7,8].

Before serious consideration can be given to the use of a negative corona for preparing S<sub>2</sub>F<sub>10</sub> reference samples, more must be known about the factors that affect S<sub>2</sub>F<sub>10</sub> yield in such discharges. Information is needed about how S<sub>2</sub>F<sub>10</sub> production rates are influenced by changes in such parameters as discharge current, gas pressure, and the initial purity of the SF<sub>6</sub>. Effects of electrode geometry, material, and surface conditions must also be evaluated. Attention should be given to the formation of gaseous by-products that can interfere with the detection of S<sub>2</sub>F<sub>10</sub> in SF<sub>6</sub>, e.g., SOF<sub>4</sub>, S<sub>2</sub>OF<sub>10</sub>, and S<sub>2</sub>O<sub>2</sub>F<sub>10</sub>.

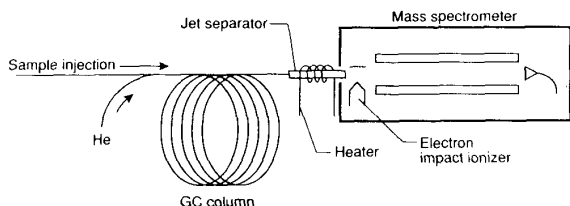
The present work represents a step toward acquisition of the information required to determine the reliability of using a negative point-plane corona to generate known trace quantities of S<sub>2</sub>F<sub>10</sub> in SF<sub>6</sub>. The dependencies of measured S<sub>2</sub>F<sub>10</sub> yields on discharge current, gas pressure, and preconditioning of electrodes are reported here.

## MEASUREMENT METHOD

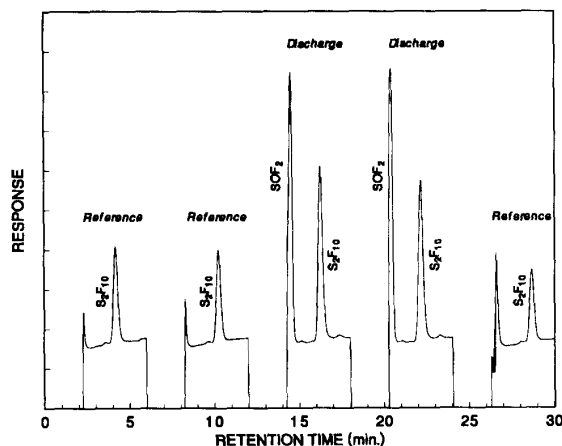
The measurement procedures used to obtain the data reported here are similar to those described previously to investigate the decomposition of SF<sub>6</sub> in corona discharges [2,9]. The discharges were generated in a 3.7 liter cell at room temperature using stainless-steel electrodes with a point-to-plane gap spacing of 1.0 cm and a point tip radius-of-curvature of about 0.08 mm. Most of the data reported here were obtained with electrodes that were initially both polished and cleaned. For some measurements, as noted below, point electrodes were preconditioned by using them to generate a negative corona in SF<sub>6</sub> for several hours. These electrodes were then cleaned, but not polished, prior to use in an experiment.

A previously described analytical technique [8] employing a gas chromatograph-mass spectrometer (GC/MS) was used to measure the S<sub>2</sub>F<sub>10</sub> content in SF<sub>6</sub>. The GC/MS configuration is shown in Figure 1. Gas samples extracted from the discharge region of the corona test cell with a gas-tight syringe are injected into the GC-column. After passing through the column, the S<sub>2</sub>F<sub>10</sub> is converted to SOF<sub>2</sub> by reaction with water adsorbed on the surface of a jet separator heated to a temperature of about 180°C. The SOF<sub>2</sub> formed by this process is ionized by electron impact and detected with a quadrupole mass spectrometer tuned to select ions with a mass-to-charge ratio (m/e) of 86 corresponding to SOF<sub>2</sub><sup>+</sup>. This method achieves a high sensitivity (~2 ppb) for detection of S<sub>2</sub>F<sub>10</sub> in SF<sub>6</sub> because it eliminates the background interference from ions associated with SF<sub>6</sub> [8].

Figure 2 shows an example of a GC/MS single-ion chromatogram for m/e = 86 used to determine the quantity of S<sub>2</sub>F<sub>10</sub> generated



**Figure 1.** Gas chromatograph mass spectrometer system used to detect  $S_2F_{10}$  in  $SF_6$  [8].  $S_2F_{10}$  is converted to  $SOF_2$  in the heated jet separator.

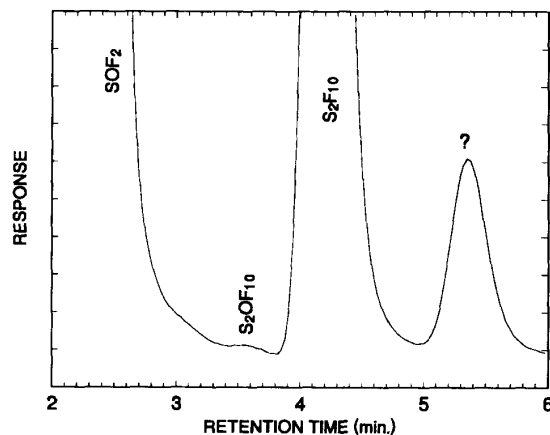


**Figure 2.** Single-ion chromatogram at  $m/e = 86$  for a typical injection sequence showing three injections from a reference cell and two from a corona discharge cell. Peaks associated with  $SOF_2$  and  $S_2F_{10}$  are indicated.

by a corona discharge in  $SF_6$ . Indicated in this chromatogram are the responses from a typical 30 minute sequence of five individual injections. Two injections from the discharge cell are bracketed by three injections from a reference cell containing a known quantity of  $S_2F_{10}$  in  $SF_6$  at the same absolute pressure as the  $SF_6$  in the discharge cell. The samples from the discharge cell exhibit peaks associated with  $SOF_2$  that was produced in the discharge. These peaks are not present in the reference samples. The  $SOF_2$  peak in the discharge sample is well separated in time from the  $S_2F_{10}$  peak and causes no interference at these concentrations.

The  $S_2F_{10}$  concentrations were determined by comparing the areas under the peaks for the discharge samples with those for the reference samples. At present, the largest source of error in the measurement of  $S_2F_{10}$  concentrations is associated with uncertainties in the reference sample concentrations. Other errors result from systematic changes in the GC/MS response to  $S_2F_{10}$  following each successive injection; presumably due to conditioning effects from depletion of adsorbed  $H_2O$  in the jet separator. The method indicated in Figure 2 of bracketing injections allows assessment of this source of error.

It should finally be noted that the injection sequence, as shown in Figure 2, is programmed to turn off the mass spectrometer during those times when  $SF_6$  elutes from the column, e.g., between 0 and 2.2 minutes. This is necessary to reduce the background and avoid overstressing the ion detector.



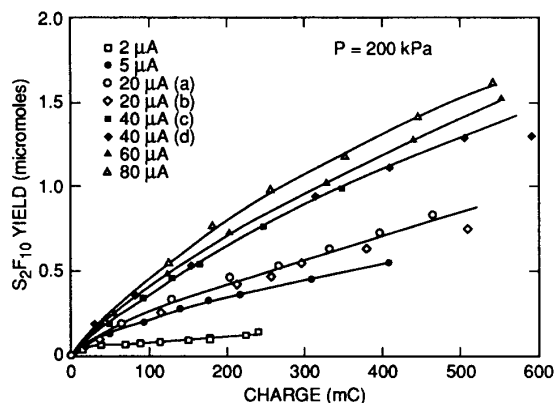
**Figure 3.** Blow-up of a single-ion chromatogram at  $m/e = 86$  indicating features associated with  $SOF_2$ ,  $S_2OF_{10}$ , and  $S_2F_{10}$ . The peak designated with a question mark is presently unknown, but is suspected to be  $S_2O_2F_{10}$ .

## RESULTS

Figure 3 shows a blow-up of a chromatogram at  $m/e = 86$  corresponding to a single injection from the discharge cell. This chromatogram shows features associated with  $SOF_2$ ,  $S_2OF_{10}$ ,  $S_2F_{10}$  and an unknown species, indicated by the question mark, which is tentatively identified as  $S_2O_2F_{10}$ . The presence of  $S_2OF_{10}$  and  $S_2O_2F_{10}$  is of particular concern because these species are reported to have column retention times close to that of  $S_2F_{10}$  [10] and because they can produce  $SOF_2^+$  by collision with electrons in the ionizer of the mass spectrometer. These species thus appear in the  $m/e = 86$  chromatogram and may interfere with the detection of  $S_2F_{10}$  by the method used here. The data in Figure 3 indicate that the features associated with the different species that appear at  $m/e = 86$  are sufficiently well separated under the operating conditions used to avoid significant interference effects. It should be noted that the peaks identified here with  $S_2OF_{10}$  and  $S_2O_2F_{10}$  always appeared in the decomposed  $SF_6$  for all of the discharge conditions considered in this work.

The measured  $S_2F_{10}$  yields in micromoles versus net charge,  $Q$ , transported in millicoulombs are shown in Figure 4 for different discharge currents and for a gas pressure of 200 kPa ( $\approx 2$  atm). The transported charge is given by  $Q = It$ , where  $I$  is the discharge current and  $t$  is the time during which the discharge has been operated. The uncertainties in the measured  $S_2F_{10}$  yields are estimated to be no more than  $\pm 30\%$  in all cases. However, since this uncertainty is due primarily to uncertainties in the reference gas and since the same reference was used for all measurements, relative reproducibility can be determined with an uncertainty that is much less than implied by uncertainties in absolute yields. The differences between the measured yields obtained for different discharge currents are believed to be significant for the same reason.

The data shown in Figure 4 indicate that the charge rate-of-production,  $d[S_2F_{10}]/dQ$ , decreases with decreasing current, especially for  $I < 40 \mu A$ . This means that the measured time rate-of-production,  $d[S_2F_{10}]/dt$ , is not directly proportional to the current. However, above  $40 \mu A$  the slopes of the  $[S_2F_{10}]$  versus  $Q$  curves are nearly parallel, thus indicating that  $d[S_2F_{10}]/dt$  is approximately proportional to  $I$  for  $I \geq 40 \mu A$ , consistent with preliminary results previously reported [2].



**Figure 4.** Measured yields of  $S_2F_{10}$  versus net charge transported from negative corona discharges in 200 kPa  $SF_6$  at the indicated discharge currents. The data designated (a) and (b) at 20  $\mu A$  and (c) and (d) at 40  $\mu A$  were obtained from separate experiments performed at different times.

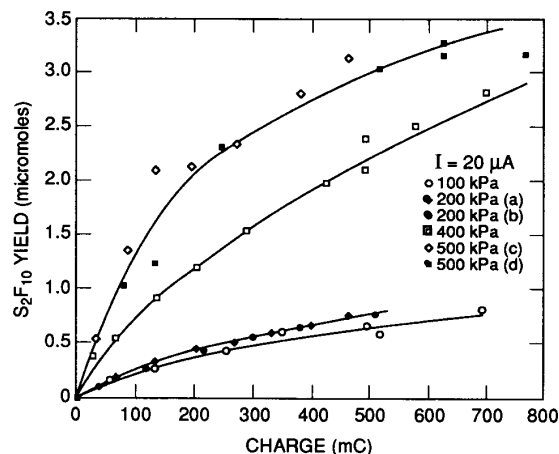
The data obtained from two different experiments performed at widely separated times for both 20 and 40  $\mu A$  are seen to be in good agreement thus demonstrating that the results are reproducible and the difference between the  $S_2F_{10}$  production rates at these two currents is significant.

The yield curves in Figure 4 are seen to exhibit significant nonlinearities in the early stages of the discharge, i.e. for  $Q < 100$  mC. The rate,  $d[S_2F_{10}]/dQ$ , is seen to drop significantly from its initial value with increasing  $Q$  (or equivalently with increasing time) and eventually approaches a limiting constant value. The initial nonlinear behavior of the  $S_2F_{10}$  production is similar to that previously reported for  $SO_2F_2$  production from negative corona in  $SF_6$  [9,11].

The data for  $I = 20$   $\mu A$  shown in Figure 5 indicate that the nonlinearities in the  $S_2F_{10}$  yield curves become more accentuated as the absolute gas pressure is increased from 100 kPa (1 atm) to 500 kPa (5 atm). There also appears to be a tendency for the limiting  $S_2F_{10}$  production rate to increase with increasing pressure. In obtaining the data shown in Figure 5, it was noticed that the initial rapid increase in  $d[S_2F_{10}]/dQ$  was correlated with times during which it was necessary to make significant changes in the discharge gap voltage in order to maintain a constant current. It was then suspected that the observed changes in  $S_2F_{10}$  production rate were due at least in part to changes in the discharge behavior or discharge-induced changes in electrode surface conditions.

In an attempt to assess the influence of electrode conditioning on  $S_2F_{10}$  production, experiments were performed with electrodes that were preconditioned by using them to generate a corona discharge. The stainless steel point electrodes used to obtain the data in Figures 4 and 5 were polished before being used in the discharge cell.

It was determined from microscopic observations that a polished point electrode develops a multitude of micro pits or depressions near the tip after being exposed to the discharge. The extent of the pitted region seems to increase slightly with the voltage required to sustain the discharge. The fact that the initial nonlinearities in  $S_2F_{10}$  yield become more pronounced with increasing current and gas pressure may be related to corresponding



**Figure 5.** Measured yields of  $S_2F_{10}$  versus net charge transported from 20  $\mu A$  negative corona discharges in  $SF_6$  at the indicated absolute gas pressures. The data designated (a) and (b) at 200 kPa and (c) and (d) at 500 kPa were obtained from separate experiments performed at different times.

increases in gap voltage.

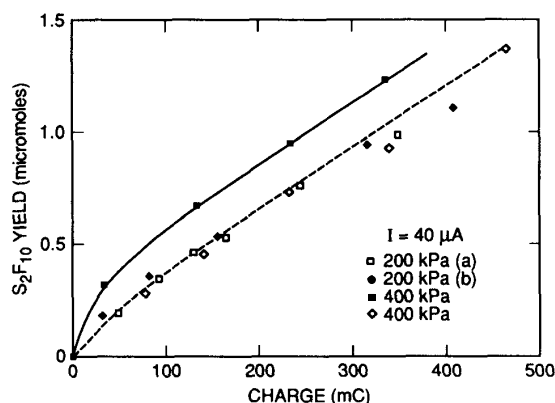
Figure 6 shows a comparison between yield curves for a 40  $\mu A$  discharge in 400 kPa (4 atm)  $SF_6$  that were obtained with and without preconditioning of the point electrode surface. A fit to the 400 kPa data obtained using the preconditioned electrode, as indicated by the dashed line, is seen to agree reasonably well with data from two separate experiments performed at 200 kPa with polished electrodes. It is thus evident from these data that the dependence of  $S_2F_{10}$  production on pressure, such as shown in Figure 5, and the initial degree of nonlinearity are significantly reduced by using preconditioned electrodes.

## DISCUSSION AND CONCLUSIONS

It has been demonstrated from the results presented here that it may be possible to use a negative point-plane glow discharge as a relatively quick method for preparing reliable reference gas samples containing predictable trace levels of  $S_2F_{10}$  in pressurized  $SF_6$ . Measured  $S_2F_{10}$  yields from corona in  $SF_6$  were found to be quite reproducible. The rates for  $S_2F_{10}$  production are found to depend on discharge current, gas pressure, and initial condition of the point-electrode surface.

The  $S_2F_{10}$  production rate from discharges generated by point electrodes that were initially polished show a tendency to decrease with time and eventually approach a constant value. This nonlinearity may be partly a consequence of changes in the discharge characteristics with time, e.g., changes in the volume of the glow region. The changes in  $S_2F_{10}$  production would tend to decrease as the discharge stabilizes. Discharge-induced changes in the point-electrode surface may also affect  $S_2F_{10}$  production. Local heating and increased surface roughness at the tip of the electrode may enhance surface catalyzed breakup of  $S_2F_{10}$  molecules that diffuse to this surface from the nearby discharge volume.

In general, the results reported here yield  $S_2F_{10}$  production rates that are lower, by at least a factor of two, than those predicted using a previously proposed chemical kinetics model of the discharge [5,6]. The model also fails to predict the nonlinearities and pressure and current dependencies reported here. The tendency



**Figure 6.** Measured yields of  $S_2F_{10}$  versus net charge transported from 40  $\mu A$  negative corona discharges in  $SF_6$  at the indicated absolute gas pressures. The data at 400 kPa fitted by a solid line were obtained using a point electrode that was initially polished and the data at 400 kPa fitted by a dashed line were obtained using a preconditioned point electrode. The data designated (a) and (b) at 200 kPa were obtained from separate experiments performed at different times using polished electrodes.

for the model to over-estimate the  $S_2F_{10}$  production rates probably results in part from a failure to include  $S_2F_{10}$  destruction mechanisms and processes that compete with  $S_2F_{10}$  formation such as could result in production of  $S_2OF_{10}$  or  $S_2O_2F_{10}$ . The initial conditioning of electrode surfaces may be accompanied by an increase in the  $S_2F_{10}$  destruction rate on these surfaces. This process could account for the types of nonlinear behavior observed under some conditions with polished electrodes. Moreover, the model includes simplifying assumptions about the discharge characteristics, e.g., the volume of the discharge, that simply may not apply at the lowest discharge currents and highest pressures considered here.

Although  $S_2OF_{10}$ , and possibly also  $S_2O_2F_{10}$ , are always observed together with  $S_2F_{10}$ , the mechanisms for formation of these species is not understood. Preliminary measurements made using the present analytical technique showed that the  $S_2OF_{10}$  detection sensitivity is relatively low compared with  $S_2F_{10}$  and therefore the  $S_2OF_{10}$  concentration in  $SF_6$  decomposed by corona may be considerably greater than suggested by the response seen in Figure 3.

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