RATE OF S_2F_{10} PRODUCTION FROM NEGATIVE CORONA IN COMPRESSED SF_6

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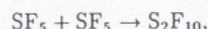Gaithersburg, MD   20899

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ABSTRACT

Using a mass spectrometer-gas chromatograph capable of detecting S_2F_{10} concentrations in SF_6 down to the part in 10^9 level, the rates of S_2F_{10} production from dc glow-type negative point-plane corona discharges in pressurized SF_6 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_2F_{10} 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_2F_{10} in SF_6.

INTRODUCTION

Disulfur decafluoride (S_2F_{10}) is now known to be formed when electrical discharges occur in compressed sulfur hexafluoride (SF_6) commonly used as a gaseous dielectric in high-voltage apparatus [1,2]. The possible presence of this compound in SF_6 is of concern because it is known to be highly toxic [3]. The primary mechanism for its formation is believed to be the reaction

$$SF_5 + SF_5 \rightarrow S_2F_{10},$$

where SF_5 is formed by collisional dissociation of SF_6 in the discharge and the above reaction involves stabilization via interaction with a third body. Since S_2F_{10} 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_6-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_2F_{10} production under these conditions in order to determine gas toxicity levels and assess possible hazards associated with exposure to decomposed SF_6.

The dc point-plane negative glow corona in SF_6 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_2F_{10} in SF_6 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_2F_{10} for two reasons: 1) it eliminates the necessity of dealing with pure S_2F_{10} which requires

special procedures because of its high toxicity, and 2) it avoids the problems associated with long-term decomposition of S_2F_{10} 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_2F_{10} reference samples, more must be known about the factors that affect S_2F_{10} yield in such discharges. Information is needed about how S_2F_{10} production rates are influenced by changes in such parameters as discharge current, gas pressure, and the initial purity of the SF_6. 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_2F_{10} in SF_6, e.g., SOF_4, S_2OF_{10}, and $S_2O_2F_{10}$.

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_2F_{10} in SF_6. The dependencies of measured S_2F_{10} 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_6 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_6 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_2F_{10} content in SF_6. 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_2F_{10} is converted to SOF_2 by reaction with water adsorbed on the surface of a jet separator heated to a temperature of about 180°C. The SOF_2 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_2^+. This method achieves a high sensitivity ($\sim$2 ppb) for detection of S_2F_{10} in SF_6 because it eliminates the background interference from ions associated with SF_6 [8].

Figure 2 shows an example of a GC/MS single-ion chromatogram for m/e = 86 used to determine the quantity of S_2F_{10} generated
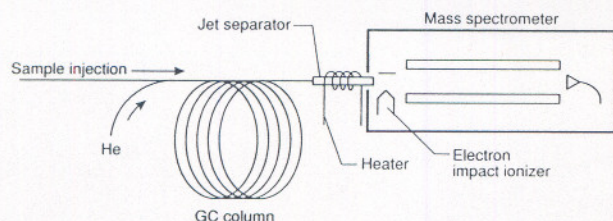
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Figure 1. Gas chromatograph mass spectrometer system used to detect S_2F_{10} in SF_6 [8]. S_2F_{10} is converted to SOF_2 in the heated jet separator.
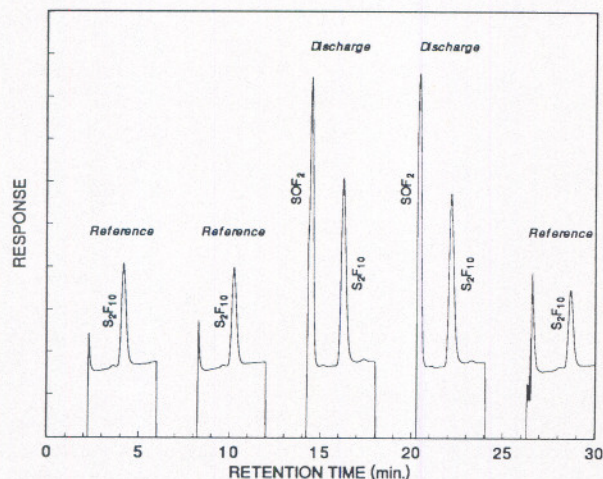

Figure 2. Single-ion chromatogram at $m/e = 86$ for a typical injection sequence showing three injections from a reference cell and two from a corona discharge cell. Peaks associated with SOF_2 and S_2F_{10} are indicated.

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.
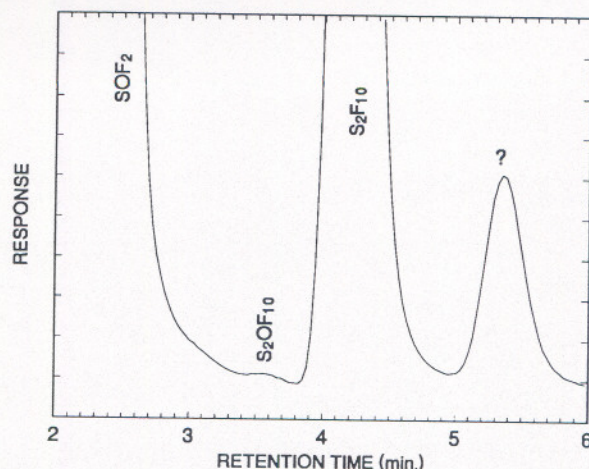

Figure 3. Blow-up of a single-ion chromatogram at $m/e = 86$ indicating features associated with SOF_2, S_2OF_{10}, and S_2F_{10}. The peak designated with a question mark is presently unknown, but is suspected to be $S_2O_2F_{10}$.

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 ($\simeq 2$ 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 $I < 40$ μA. This means that the measured time rate-of-production, $d[S_2F_{10}]/dt$, is not directly proportional to the current. However, above 40 μA 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 $I \geq 40$ μA, consistent with preliminary results previously reported [2].
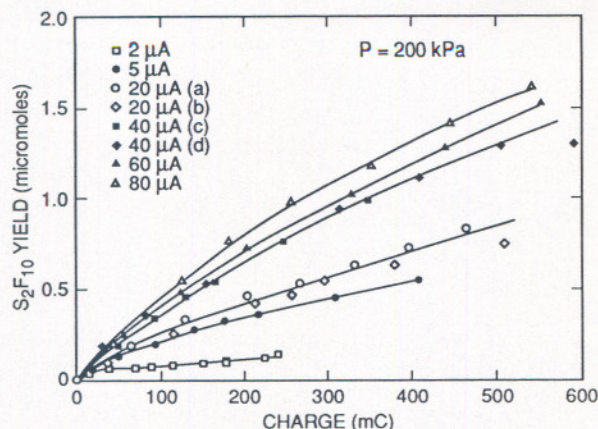
Figure 4. Measured yields of S_2F_{10} versus net charge transported from negative corona discharges in 200 kPa SF_6 at the indicated discharge currents. The data designated (a) and (b) at 20 μA and (c) and (d) at 40 μA were obtained from separate experiments performed at different times.

The data obtained from two different experiments performed at widely separated times for both 20 and 40 μA 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 SOF_4 production from negative corona in SF_6 [9,11].

The data for $I = 20$ μA 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
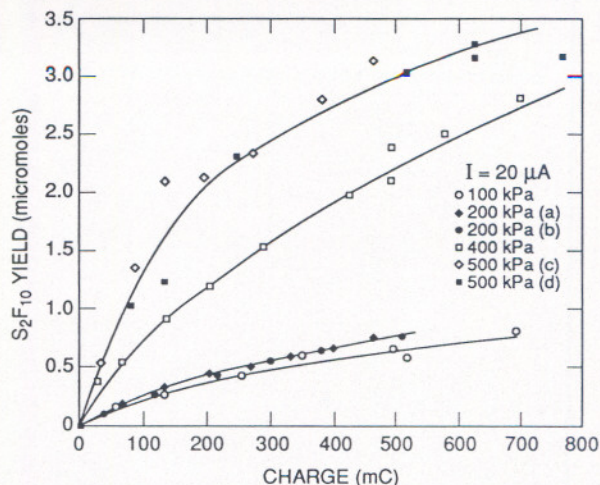

Figure 5. Measured yields of S_2F_{10} versus net charge transported from 20 μA negative corona discharges in SF_6 at the indicated absolute gas pressures. The data designated (a) and (b) at 200 kPa and (c) and (d) at 500 kPa were obtained from separate experiments performed at different times.

increases in gap voltage.

Figure 6 shows a comparison between yield curves for a 40 μA 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.
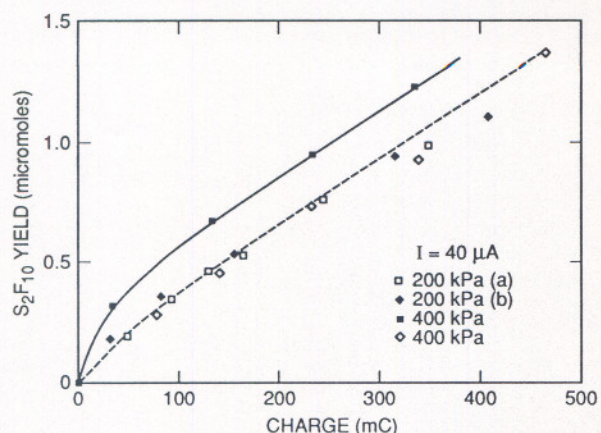
DISCUSSION AND CONCLUSIONS

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 μA 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.

ACKNOWLEDGEMENTS

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