$\begin{array}{c} Production \ of \ S_2F_{10}, \ S_2OF_{10}, \ and \ S_2O_2F_{10} \\ from \ Spark \ and \ Negative-Corona \ Discharges \ in \ SF_6 \\ and \ SF_6/O_2 \ Gas \ Mixtures \end{array}$

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Paper

Production of S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ from Spark and Negative-Corona Discharges in SF_6 and SF_6/O_2 Gas Mixtures

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The rates for production of the compounds S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ have been measured both in spark and continuous, constant-current negative glow corona discharges generated using point-to-plane electrode gaps in 'pure' SF₆ and SF₆/O₂ gas mixtures containing up to 10% oxygen by volume fraction. In the case of corona discharges in pure SF_6 , the S_2F_{10} concentrations were measured as a function of time during discharge operation using a gas chromatograph-mass spectrometer for gas pressures in the range of 100 kPa to 500 kPa and at discharge currents between 2 μ A and 80 μ A. The charge rate-of-production of S₂F₁₀ from negative corona is observed to drop with decreasing discharge current, and the yield curves exhibit nonlinearities in the early stages of the discharge associated with "conditioning" of the point electrode. The initial nonlinearities become more pronounced with increasing gas pressure. The absolute yields of S_2OF_{10} and $S_2O_2F_{10}$ were measured as a function of O_2 content in SF₆ for both negative glow corona (40 μ A and 200 kPa) and spark discharge (80 J/spark and 100 kPa). The gas analysis in the case of spark discharges was performed after each spark using a cryogenic enrichment chromatographic technique. When O_2 is added to the gas, there is a dramatic drop in the S_2F_{10} yield from both types of discharges with a corresponding increase in S_2OF_{10} yield from the spark and $S_2O_2F_{10}$ yield from the corona discharge. The results can be explained within the framework of a plasma-chemical model from considerations of the competition among the reactions of SF_5 radicals produced by dissociation of SF_6 in the discharge with SF_5 itself as well as with O_2 and O_2 , and the relative degree of O_2 dissociation in the two types of discharges.

Keywords: Decomposition, Negative Corona, Oxygen, Production Rates, SF₆, S₂F₁₀, S₂OF₁₀, S₂O₂F₁₀, Spark Discharge

1. Introduction

The production of disulfur decafluoride (S_2F_{10}) in SF₆ by electrical discharges is of concern because of its known high level of toxicity and because SF₆ is widely used as an insulating gas in electric-power systems where electrical discharges can occur.^(1,2)

The primary mechanism for its formation is believed to be the three-body reaction^(3,4)

$$M + \mathrm{SF}_5 + \mathrm{SF}_5 \to M + \mathrm{S}_2 \mathrm{F}_{10},\tag{1}$$

where SF_5 is produced by collisional dissociation of SF_6 in the discharge, and the above reaction involves stabilization via interaction with a third body denoted here by M. Since S_2F_{10} is thermally unstable above about 150 °C,⁽⁵⁾ 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 case of "hotter" spark and arc discharges, S_2F_{10} production is less efficient than in a corona, and it is expected to form primarily during the final cooling stages of these discharges.

The rate of S_2F_{10} formation in a gas should increase with pressure, and reach its high-pressure limit at the gas pressures (> 100 kPa) typically encountered in gas-insulated electric-power systems. The most important mechanisms for destruction of S_2F_{10} are: 1) surface catalyzed reaction with H_2O on the walls of the containment vessel to form SOF₂, HF, and other products,^(1,6,7) and 2) dissociation in the discharge by electron impact, e.g.,

$$e + S_2 F_{10} \to 2SF_5 + e. \tag{2}$$

For the discharge conditions considered here, the S_2F_{10} destruction rate is much lower than the production rate; therefore, its concentration should increase with time while the discharge is active. The production of S_2F_{10} in a discharge is affected by competing processes that produce or remove the radical SF₅. In pure SF₆ at high pressures, the predominant SF₅ radical removal process is that due to a reaction with F, namely⁽³⁾

$$M + F + SF_5 \to M + SF_6. \tag{3}$$

In the presence of water vapor, the following processes can be important in affecting the local SF_5 concentration:⁽⁴⁾

$$F + H_2O \rightarrow OH + HF$$
 (4)

$$OH + SF_5 \rightarrow SOF_4 + HF.$$
 (5)

It has been shown⁽³⁾ that the net effect of increasing gasphase H_2O is to enhance the S_2F_{10} production rate in a glow corona because reaction (4) decreases the F concentration and thereby decreases the rate of SF_5 removal by reaction (3). The effect of reaction (5) is probably more significant in corona discharges which tend to have a higher relative SOF₄ yield than a spark discharge.

There is evidence from recent investigations⁽⁸⁻¹¹⁾ that the compounds (pentafluorosulfur) oxide (S_2OF_{10}) and bis(pentafluorosulfur) peroxide $(S_2O_2F_{10})$ are also oxidation byproducts of SF₆ decomposition in electrical discharges. The latter compound is of particular concern because of its toxicological properties.⁽¹⁾ The influence of oxygen on the production of S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ from discharges at high pressures is of interest because air is a common contaminant in SF₆ insulation. It has been suggested that the production of these compounds as well as S_2F_{10} will be significantly affected by the presence of O_2 due to the occurrence of the fast reactions⁽³⁾

 $M + \mathrm{SF}_5 + \mathrm{O}_2 \to M + \mathrm{SF}_5\mathrm{O}_2 \tag{6}$

and

$$M + SF_5 + O \rightarrow M + SF_5O.$$
 (7)

Because of the differences between spark and corona discharges, it can be expected that the influence of O_2 on the relative yields of the compounds S₂F₁₀, S₂OF₁₀, and S₂O₂F₁₀ will be different in the two types of discharges. Negative point-plane glow corona is a nonthermal, highly localized, low-temperature discharge in which the electron temperature greatly exceeds the gas temperature. The continuous corona discharge current is relatively low and discharge activity is confined to the immediate vicinity of the point electrode. Dissociation of SF_6 and other molecules in a corona discharge occurs mainly by electron collisions. A point-plane spark discharge, on the other hand, is a transient electricalbreakdown phenomenon that bridges the entire electrode gap with a relatively high instantaneous current and energy deposition compared to a corona. In a spark channel, there is more opportunity for local heating of the gas and an expected higher degree of thermal dissociation giving rise to instantaneous concentrations of free radicals such as atomic oxygen and SF_6 dissociation fragments that are much higher than occur in a continuous corona. It might be expected therefore, that reactions involving molecular oxygen, e.g., process (6), will be relatively more important in a corona discharge, whereas reactions involving atomic oxygen, e.g., process (7), will be relatively more important in a spark discharge. In either case, the removal of SF₅ by the reactions (6) and (7) could contribute to a reduction in S_2F_{10} production when O_2 is added to SF_6 .

In the present work, the dependences of S_2F_{10} production from point-plane negative-glow corona discharges in SF₆ on pressure, current, and electrode surface conditions were experimentally investigated and the results are compared with measured⁽¹²⁻¹⁴⁾ and predicted⁽⁴⁾ rates for S_2F_{10} production from corona that have been reported previously. The production rates for S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ from both negative-glow corona and spark discharges were also measured for SF₆/O₂ mixtures containing up to 10 % by volume of O₂, and the results are compared with previous experimental results.^(10,11,15) Some of the data presented here have also been discussed in earlier conference reports.^(8,16,17)

2. Experimental Conditions and Measurement Methods

2.1 Corona Discharge

The experimental conditions and procedures are similar to those used in previous investigations of SF₆ decomposition and oxidation in point-plane corona discharges.⁽¹⁸⁾ For the investigation of electrode conditioning effects and the pressure and current dependences of S_2F_{10} production in pure SF₆, the discharges were generated in a 3.7 liter brass cell at room temperature (23 °C) 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. The investigations of S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ production from negativecorona discharges in SF₆/O₂ mixtures were carried out using the same electrode configuration installed in a 5.25 liter stainless-steel vessel. The experiments were performed using static gas samples.

The negative-glow corona was generated by applying a dc voltage to the point electrode that was negative relative to the grounded planar electrode and that was sufficiently high to maintain a self-sustained continuous discharge current, i.e., the discharge did not exhibit the pulsating behavior characteristic of negative corona in SF₆ at lower voltages.⁽¹⁹⁾ Most of the data reported here for pure SF_6 in the smaller cell were obtained with electrodes that were initially both polished and cleaned. For the experiments performed in the larger vessel, the point electrode was conditioned before each experiment by operating a 40 μ A discharge in pure SF₆ for about 1 hour or more prior to introducing the SF_6/O_2 gas mixture. As discussed later, this conditioning procedure eliminates the initial relatively rapid changes in the applied voltage required to maintain a constant current and also reduces the initial nonlinear behavior in the S_2F_{10} production that is presumably due to changes in the rate of catalytic destruction of this molecule on the point-electrode surface. The applied voltage was adjusted during all experiments to maintain a constant current. Once the electrode was conditioned, the changes in applied voltage required to maintain constant current were relatively small (less than \pm 3.0%) during the course of a typical experiment.

The investigations of S_2F_{10} production from pure SF_6 using the smaller cell were carried out for discharge currents in the range of 2 μ A to 80 μ A and for absolute gas pressures in the range of 100 kPa to 500 kPa. For the SF_6/O_2 mixtures, all of the results reported here were obtained with a dis-

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charge current of 40 $\mu \mathrm{A}$ and an absolute total gas pressure of 200 kPa.

During operation of the corona discharge, relatively small gas samples (1 mL \times 200 kPa) were extracted periodically from the vessel with a gas-tight syringe and subjected to quantitative chemical analysis using a gas chromatographmass spectrometer (GC/MS). The operation of the GC/MS is modified to achieve high sensitivity for detection of S_2F_{10} which is ordinarily susceptible to interference from SF₆. Details of the analytical method and procedure have been described previously.^(6,20,21) The most significant source of error was attributed to uncertainties in the S₂F₁₀, S₂O₂F₁₀ reference gas samples used for GC/MS calibration. The relative uncertainties in the measured production rates for S_2F_{10} and $S_2O_2F_{10}$ are estimated from the variability of results obtained from calibrations using different reference gas samples to always be less than $\pm 30\%$ and $\pm 18\%$ respectively. Although uncertainties in the quantitative analysis for S_2OF_{10} are much lower (due in part to its chemical stability and relative inertness), its production in corona was found to be too low to measure reliably.

2.2 Spark Discharge

The experimental procedure used to investigate S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ production in spark discharges is essentially the same as that described previously.⁽⁹⁾ The discharges were produced by applying a high voltage from a charged 0.4 μ F coupling capacitor to a 2.4 mm sphere-plane electrode gap within a 1.1 liter stainless-steel chamber that contained the SF_6/O_2 gas mixture at an absolute total pressure of 100 kPa. As for the corona discharge experiments, mixtures containing up to 10% by volume of O_2 were investigated. A reproducible spark discharge was triggered by illuminating the high-voltage, spherical electrode with ultra-violet radiation. The energy dissipated in each spark was determined by: 1) direct measurement of the instantaneous discharge voltage and current, and 2) calculation of the energy released by the coupling capacitor during the discharge. The two methods yielded discharge energies that agreed to within $\pm 5\%$. The results reported here were obtained under conditions where the mean energy dissipated per spark was (80 ± 4) J.

Small gas samples (2 mL^{*} × 100 kPa) were extracted from the chamber with a gas-tight syringe after each spark. The samples were analyzed quantitatively for S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ content using a cryogenic enrichment-gas chromatograph equipped with an electron-capture detector.^(9,20) By this method, the concentrations of the three compounds of interest are selectively enhanced in the sample relative to SF₆ and other major gaseous byproducts such as SOF₂, SO₂F₂, SOF₄, and SO₂. The enrichment process reduces the interference from SF₆ and enables a high sensitivity for detection of S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ which is comparable to that of the GC/MS method.⁽²⁰⁾ Again, the analysis procedure requires a calibration using reference gas samples of known concentration.

3. Results

3.1 Production of $\mathrm{S}_2\mathrm{F}_{10}$ from Negative Corona in Pure SF_6

Results are presented in this section on the dependences of S_2F_{10} production on discharge current, absolute gas pres-

sure, and electrode condition for negative-glow corona generated in pure SF₆. Shown in Figs. 1 (a) and (b) are examples of measured S₂F₁₀ yields versus net charge transported (Q) in coulombs for negative corona in SF₆ at a pressure of 200 kPa. 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.



Fig. 1. Measured yields of S_2F_{10} from negative point-plane corona in SF₆ at 200 kPa as a function of net charge transported for discharge currents of 40 μ A (open squares and closed circles) and 60 μ A (open circles). The data from the short-time experiment at 40 μ A (closed circles) delineated by the dashed lines in (a) are replotted in (b), which also indicates the corresponding elapsed discharge time and the S_2F_{10} concentration in the 3.7-liter cell in ppm (= parts in 10⁶ by volume ratio). The straight solid line in (a) is a linear fit to the data.

The data at $I = 40 \ \mu A$ and $I = 60 \ \mu A$ represented in Fig. 1(a) respectively by the open squares and open circles were obtained during experiments where the discharge was operated for relatively long times (~ 30 h). The closed circles in Fig. 1(a), which are replotted in Fig. 2(b), correspond to a separate experiment of shorter duration (~ 10 h) where the current was maintained at 40 μA .

The charge rate of S_2F_{10} production, $dC(S_2F_{10})/dQ$, is given by the slope of the $C(S_2F_{10})$ versus Q curve, where $C(S_2F_{10})$ is the quantity of S_2F_{10} in micromoles measured at any time, t, during operation of the discharge. The charge rate-ofproduction is related to the time rate-of-production by the formula⁽¹⁸⁾

$$\frac{dC(S_2F_{10})}{dQ} = I^{-1}\frac{dC(S_2F_{10})}{dt}.$$
(8)

The solid line in Fig. 1(a) is a linear fit to the data for $I = 40 \ \mu$ A. It is seen that this fit is quite good for Q > 0.3 C, thus indicating that at 40 μ A, $dC(S_2F_{10})/dQ$ tends after some time to reach a constant value of about 2.4 μ mol/C in this case. The fit is also seen to satisfactorily represent the data at 60 μ A. It can therefore be inferred from this observation that $dC(S_2F_{10})/dQ$ does not change significantly in the current range between 40 μ A and 60 μ A at 200 kPa, which also means that, according to Eq.(8), the time rate-of-production for S_2F_{10} is directly proportional to the current in this range.

From Fig. 1(b) it is seen that $dC(S_2F_{10})/dQ$ initially decreases with increasing Q up to about Q = 0.3 C. Similar nonlinear behavior in the initial production of S_2F_{10} starting with a cleaned and polished point electrode is evident from the data presented in Figs. 2 and 3 that show, respectively,



Fig. 2. Measured yields of S_2F_{10} versus net charge transported from 20 μ A negative corona discharges in SF₆ at the indicated discharge currents. The data designated (a) and (b) at 20 μ A and (c) and (d) at 40 μ A were obtained from separate experiments performed at different times.

examples of the discharge current and pressure dependences of the measured yields versus charge transported. The initial nonlinearity in the observed S2F10 yield curves is most pronounced at higher currents and pressure and is correlated with relatively rapid changes in the voltage required to maintain a constant current as illustrated by the data shown in Fig. 4 for a 20 μ A discharge at a gas pressure of 500 kPa. The initial changes in applied voltage generally cease within about 200 minutes of discharge operation. It was determined from microscopic examinations of the point electrode surface that during this early time of discharge operation, the initially polished stainless-steel point electrode develops a multitude of micro pits or depressions near the tip. The extent of the pitted region seems to increase slightly with the voltage required to sustain the discharge. Once this surface conditioning has occurred, the voltage required to sustain the discharge at constant current drops to a value below that needed to start the discharge, and only minor adjustments in the voltage are then required to maintain constant current during the remainder of the experiment (see Fig. 4).



Fig. 3. Measured yields of S_2F_{10} versus net charge transported from 20 μ 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.



Fig. 4. Time dependence of the applied voltage required to maintain a constant, 20 μ A, negative-corona discharge in pure SF₆ at an absolute pressure of 500 kPa. In this case, the point-electrode conditioning occurs during the first 125 minutes of discharge operation.

After the point electrode surface has been conditioned, the S_2F_{10} yield curves tend to remain linear, at least up to the maximum discharge times that were used for the present experiments. 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 corona discharges in SF_6 for times cor-

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responding to the initial rapid changes in voltage (typically up to 2 hours). After this conditioning, the SF₆ gas was pumped out of the cell and a fresh gas samples was introduced at the desired pressure before beginning the experiment. Generally, the cell was flushed with SF₆ several times to insure removal of byproducts formed during the conditioning. The fresh gas sample was subjected to analysis using the GC/MS before the discharge was initiated to check for residual contaminants.



Fig. 5. Measured yields of S_2F_{10} versus net charge transported from 40 μ 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.

Figure 5 shows a comparison between yield curves for a 40 μ A discharge in 400 kPa SF₆ 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 S₂F₁₀ production on pressure, such as shown in Fig. 4, and the initial degree of nonlinearity are significantly reduced by using preconditioned electrodes.

The results shown in Figs. 3 and 5 suggest that much of the observed pressure dependence of the S_2F_{10} production can be attributed to effects of electrode conditioning. It might be expected, as observed, that the initial conditioning effect would be greatest at the highest pressures for which the applied voltage and corresponding discharge power dissipation are the greatest. This interpretation is also consistent with the observed current dependence shown in Fig. 2 where the initial nonlinear behavior is seen to extend to higher values of Q as I increases. There appears, nevertheless, to be a significant drop in the S_2F_{10} production rate with discharge current below about 20 μ A that is not obviously related to electrode conditioning.

The results of making linear fits to the lower and upper parts of S_2F_{10} yield data such as shown in Figs. 2 and 3 are given in Table 1. The fits to the lower parts give the initial $(t, Q \rightarrow 0)$ values for $dC(S_2F_{10})/dt$ and the fits to upper parts give the limiting values to which $dC(S_2F_{10})/dt$ tends after the electrode becomes fully conditioned. The uncertainties given in this table are merely those associated with using different methods to analyze the chromatographic data. The data were usually analyzed by two methods, i.e., using either the ratios of known to unknown S_2F_{10} peaks in a sequence of single-ion chromatograms, or the ratios of the corresponding S₂F₁₀ peak areas.⁽²¹⁾ The peak-height comparison method is less susceptible to effects of possible interfering peaks from unknown compounds and the peak-area comparison is less susceptible to noise in the chromatogram. It was found that the two methods give results for $dC(S_2F_{10})/dQ$ that are in satisfactory agreement. Uncertainties due to drift in the response of the GC/MS were largely eliminated by using the procedure of bracketing an injection into the GC from an unknown gas sample with two or more injections from a known S_2F_{10} reference sample as previously described.^(20,21)

Table 1. The initial $(t \to 0)$ and limiting (after electrode conditioning) charge rates of S_2F_{10} production from negative-corona discharges in SF₆ at different indicated pressures and discharge currents.

Pressure	Current	Initial Rate	Limiting Rate
(kPa)	(μA)	$(\mu mol/C)$	$(\mu mol/C)$
100	20	2.68 ± 0.01	0.74 ± 0.03
200	2	2.29 ± 0.03	0.34 ± 0.01
200	5	2.46 ± 0.04	1.07 ± 0.01
200	20	2.65 ± 0.01	1.05 ± 0.01
200	20	2.56 ± 0.02	1.00 ± 0.05
200	40	3.64 ± 0.01	2.36 ± 0.05
200	40	5.01 ± 0.10	2.40 ± 0.07
200	60	4.43 ± 0.07	2.23 ± 0.03
200	80	4.26 ± 0.02	2.19 ± 0.06
400	20	11.04 ± 0.02	2.33 ± 0.09
400	40	7.24 ± 0.03	2.73 ± 0.07
400	40	4.09 ± 0.01	$2.77\pm0.16^*$
500	20	15.95 ± 0.40	2.80 ± 0.43
500	20	12.58 ± 0.09	2.45 ± 0.12

"Obtained with preconditioned point electrode.

It should be realized that, although the overall expected maximum uncertainty in the measured S_2F_{10} yields is $\pm 30\%$ due to uncertainties in the reference gas sample concentration, the relative reproducibility and comparisons of rates are much less uncertain than this provided the same reference gas is used for all measurements. The results shown in Figs. 2, 3, and 5 were all obtained using the same S_2F_{10} reference.

It should also be noted that although all of the results reported here were obtained using the ion of mass-to-charge ratio $m/z = 86 \text{ u},^{(6,20,21)}$ tests showed that, to within the limitations of noise, the measured S_2F_{10} yields using this ion agreed with those obtained using other ions, e.g., m/z = 48 u, that are characteristic of SOF₂ to which S_2F_{10} is converted in the GC/MS analysis process.⁽⁶⁾ The ion at m/z = 86 u was selected for the present analysis because it exhibited the lowest background level and the highest signal-to-noise ratio.

3.2 Production of $\rm S_2F_{10}$ and $\rm S_2O_2F_{10}$ from Negative Corona in $\rm SF_6/O_2$ Mixtures

The rates of S_2F_{10} and $S_2O_2F_{10}$ production from negativeglow corona were found to depend significantly on O_2 content. Although the compound S_2OF_{10} was also detected in corona discharges, its measured yield was found to be considerably below that of S_2F_{10} and $S_2O_2F_{10}$. The observed concentrations of S_2OF_{10} in SF_6 were not significantly increased during discharge operation above the trace levels (on the order of 0.5 parts in 10⁹ by volume ratio) initially present as a contaminant in SF_6 ; and therefore, a meaningful rate for its production could not be ascertained from the data.

It was found that in relatively pure SF_6 , the yield of $S_2O_2F_{10}$ is considerably below that of S_2F_{10} (often by more than an order of magnitude). Moreover, the measured $S_2O_2F_{10}$ production rates are not as reproducible as those for S_2F_{10} and are evidently sensitive to trace amounts of oxygen and/or water vapor initially present in the gas or generated during operation of the discharge. Given in Table 2 are examples of S2O2F10 charge rates-of-production that were estimated from the chromatographic data obtained during the same experiments used to determine the S_2F_{10} production for pure SF_6 given in Table 1. Unlike the data presented below on S₂O₂F₁₀ yields from SF₆/O₂ mixtures, the yields for this compound in pure SF₆ were not determined by immediate comparisons with $S_2O_2F_{10}$ reference samples, but rather by comparisons of the $S_2O_2F_{10}$ and S_2F_{10} responses in the m/z = 86 u single-ion chromatograms.⁽²¹⁾ Because tests using reference gas samples showed that the relative responses of the instrument to S_2F_{10} and $S_2O_2F_{10}$ can drift with time, the absolute production rates listed in Table 2 are likely to have a high relative uncertainty of $\sim \pm 45\%$. The uncertainties given for some values in the table represent extreme variations for cases where two or more measurements were made.

The rates given in Table 2 are based on linear fits to the measured $S_2O_2F_{10}$ yield versus Q data. In contrast to the yield curves for S_2F_{10} obtained for unconditioned electrodes, those for $S_2O_2F_{10}$ were found to either be linear (see Fig. 6(a)) or to exhibit a "concave" shape where $dC(S_2O_2F_{10})/dQ$ increases with increasing Q (see Fig. 6(b)). This latter behavior tended to be most evident for data obtained at the highest currents and is consistent with a corresponding increase in O_2 and H_2O content generated during the discharge. The occurrence of nonlinearities in the $S_2O_2F_{10}$ production adds to the uncertainties and ambiguities in determining and interpreting the rates for $S_2O_2F_{10}$ production from negative corona in pure SF_6 . It is nevertheless evident that the production of $S_2O_2F_{10}$ is not affected by electrode conditioning in the same way as the production of S_2F_{10} .

Table 2. Estimated charge rates-of-production for $S_2O_2F_{10}$ in initially pure SF_6 corresponding to the same conditions for which the S_2F_{10} results shown in Table 1 and Figs. 2, 3 and 5 were obtained.

Pressure (kPa)	Current (µA)	Production Rate (µmol/C)	
100	20	0.19	
200	2	0.15	
200	5	0.07	
200	20	0.26 ± 0.03	
200	40	0.31 ± 0.13	
200	60	0.17	
200	80	0.03	
400	20	0.12	
400	40	0.12 ± 0.02	
500	20	0.74 ± 0.19	



Fig. 6. Examples of measured $S_2O_2F_{10}$ yields from negative point-plane corona in "pure" SF_6 for an absolute pressure of 200 kPa and for discharge currents of (a) 40 μ A, and (b) 60 μ A.

The absolute yields of S_2F_{10} versus Q are shown in Fig. 7 for five different experiments performed with different indicated oxygen content. The lines correspond to linear fits to the data used to estimate the charge rates of production listed in Table 3. As noted previously, all of the data in Fig. 7 and Table 3 were obtained for a 40 μ A discharge at a total absolute gas pressure of 200 kPa using preconditioned electrodes. The S₂F₁₀ yield curves do not exhibit the significant initial nonlinearities characteristic of those obtained without preconditioning of the electrode. In the case of pure SF₆, two different sets of data are shown in Fig. 7 that correspond to experiments performed using different S2F10 reference samples. The results for the SF_6/O_2 mixtures were obtained using the reference sample that produced the data for pure SF_6 plotted with open symbols. The corresponding production rate from these data is $(3.51 \pm 0.40) \ \mu \text{mol/C};$ and for the data represented by closed symbols, the rate is $(2.75 \pm 0.25) \,\mu \text{mol/C}$, which is in better agreement with the data in Table 1. The former value is the one given in Table 3 for pure SF_6 . The uncertainties in this case are those that arise from making linear fits using different subsets of the data points, i.e., they indicate the degree of reliability of the assumed linearity for the yield curves.

It is seen from Fig. 7 and Table 3 that the S_2F_{10} production rate in a 40 μ A discharge drops dramatically when O_2 is added to the gas at a concentration of 3% by volume. For a mixture containing 10% O_2 , the S_2F_{10} production rate is more than an order of magnitude below that in pure SF₆.

Shown in Fig. 8 are examples of measured absolute yields of $S_2O_2F_{10}$ versus Q from 40 μ A negative-glow corona in 200 kPa SF_6/O_2 mixtures containing between 3% and 10% O_2 by volume. Again, the straight lines in this figure are linear fits to the data used to determine the production rates



Fig. 7. Measured absolute yields of S_2F_{10} versus net charge transported in the discharge for a 40 μ A negative point-plane corona in the indicated SF_6/O_2 gas mixtures for an absolute total pressure of 200 kPa and 5.25 liter chamber volume. The data for 100% SF_6 indicated by the closed circles and open triangles were obtained from separate experiments using different S_2F_{10} reference samples for calibration of the GC/MS. The reference sample used to obtain the open triangle data were also used to obtain the S_2F_{10} yields for the indicated SF_6/O_2 mixtures.

Table 3. Measured production rates for SF_6 oxidation byproducts in negative-glow corona (μ mol/C) for conditions corresponding to those given in Figs. 7 and 8.

$%O_2$	S_2F_{10}	$S_2O_2F_{10}$	SOF_2	SO_2F_2
0.0	3.51	< 0.3	21.3	13.6
3.0	0.79	0.87	14.4	14.8
5.0	0.58	0.80	18.5	27.3
10.0	0.35	0.40	11.0	24.4

listed in Table 3. The production rate for $S_2O_2F_{10}$ is seen to increase significantly to 0.87 μ mol/C when the oxygen content is increased from 0% to 3% and then decrease at higher oxygen content to about 0.40 μ mol/C at 10% O₂.

Also given in Table 3 for purposes of comparison are production rates for the oxyfluorides SOF_2 and SO_2F_2 that were estimated from a quantitative analysis for these compounds that was performed at the end of each experiment assuming that the yield curves should be linear. Despite the fact that the linearity assumption cannot always be justified,⁽¹⁸⁾ the production rates for these compounds are found to be in agreement with previously published results.^(18,22,23) The relative insensitivity of the SOF₂ and SO₂F₂ production rates to O₂ content in SF₆ is also consistent with earlier observations^(18,22,23) and model predictions.⁽³⁾ The compounds SOF₂ and SO₂F₂, together with SOF₄, are known to be the most abundant stable SF₆ oxidation byproducts from corona discharges.⁽¹⁸⁾



Fig. 8. Measured absolute yields of $S_2O_2F_{10}$ versus net charge transported in the discharge for a 40 μ A negative point-plane corona in the indicated SF_6/O_2 gas mixtures for an absolute total pressure of 200 kPa and 5.25 liter chamber volume.

3.3 Production of S_2F_{10} and S_2OF_{10} from Spark Discharges in SF_6/O_2 Mixtures

In contrast to the results from corona discharges, the data for spark discharges show significant oxygen-dependent S₂OF₁₀ production and a lack of measurable S₂O₂F₁₀ formation. However, as in the case of corona, the S_2F_{10} production rate exhibits a pronounced drop with the addition of small quantities of O_2 to SF_6 . Examples of measured spark yields for S_2F_{10} and S_2OF_{10} are shown, respectively, in Figs. 9 and 10 for O_2 content in the range of 0 to 10%. The quantities produced in nanomoles are plotted versus the number of sparks. These data were obtained at a total absolute pressure of 100 kPa for a discharge energy per spark of (80 ± 4) J. The maximum number of sparks used for any experiment is five. The O2 dependencies of absolute yields (energy-ratesof-production) in moles per joule for S₂F₁₀ and S₂OF₁₀ are given, respectively, in Figs. 11 and 12. These results are derived from the yield curves shown in Figs. 9 and 10. The error bars correspond to uncertainties in making linear fits to the data in Figs. 9 and 10.

The S_2F_{10} yield drops precipitously as the O_2 concentration is increased, becoming more than an order of magnitude lower than that for pure SF_6 at the 10% O_2 level. The S_2OF_{10} yield initially increases with increasing O_2 content and then reaches a maximum at 3% O_2 concentration.

As in the case of the corona discharge experiments, the predominant uncertainties in the measured absolute yields of S_2F_{10} and S_2OF_{10} are due to uncertainties in the reference gas samples used for calibration of the GC responses for these compounds. Because the same reference samples were used to obtain the data presented here, differences in the relative rates for S_2F_{10} and S_2OF_{10} production in sparks for different O_2 content are much more significant and reliable than would be implied by the uncertainties associated with the reference samples.



Fig. 9. Production of S_2F_{10} in sparked mixtures of O_2 in SF_6 at a total pressure of 100 kPa and energy per spark of (80 ± 4) J delivered in a 1.1 liter stainless-steel chamber.



Fig. 10. Production of S_2F_{10} in sparked mixture of O_2 in SF_6 at a total pressure of 100 kPa and energy per spark of (80 ± 4) J delivered in a 1.1 liter stainless-steel chamber.

4. Discussion

The rates for S_2F_{10} production from negative-glow corona discharges in pure SF_6 are found to depend on discharge current, gas pressure, and initial condition of the pointelectrode surface. The charge rates-of-production for this compound are comparable in magnitude to the rate of 2.3 μ mol/C reported by Casanovas and coworkers⁽¹²⁾ for a 25 μ A negative corona in 100 kPa SF₆, and a rate of 3.5 μ mol/C inferred from the data of Belarbi and coworkers⁽¹⁴⁾ for a current of 23 μ A and pressure of 300 kPa. Both of these previously reported rates were obtained using stainless-steel electrodes under "dry" conditions. The S₂F₁₀ production rate of 9.3 μ mol/C recently reported by Piemontesi and coworkers⁽¹⁵⁾ from negative corona in relatively dry SF₆ with low O₂ content for $I = 50 \ \mu$ A and a pressure of 100 kPa is considerably higher than the rates reported here. The rate of 2.8 μ mol/C given by these investigators for H₂O content greater than 0.2% by volume is more consistent with the results presented here.



Fig. 11. Spark yields (energy rates-of-production) of S_2F_{10} in units of 10^{-11} mol/J versus percent O_2 concentration in SF₆ at a total pressure of 100 kPa and for a discharge dissipation energy of (80 ± 4) J/spark.

No attempt was made in the present experiments to either measure or control the water-vapor content during operation of the discharge. It is known,⁽¹⁸⁾ however, that regardless of the initial dryness of the SF_6 , the H_2O content in the discharge cell will depend on gas pressure, temperature, and surface conditions. Moreover, it is also found that the equilibrium level of H₂O in the gas can be measurably reduced during operation of the discharge.^(15,18) From previous investigations⁽²⁴⁾ into the influence of water vapor on SF_6 discharges in the same brass cell used for the experiments on "pure" SF₆, it appears doubtful that the H₂O concentration ever exceeded 0.03% by volume in the present experiments. The H₂O level was probably significantly lower than this in the stainless-steel cell. The initial H₂O content in SF₆ immediately after introduction into the cell is estimated from GC/MS measurements to be below 12 parts in 10⁶ by volume ratio. During operation of the discharge, it rises to an equilibrium value that is considerably higher than this.

The decrease in the S_2F_{10} production rate from negative corona in SF₆ for increasing H₂O content reported by



Fig. 12. Spark yields (energy rates-of-production) of S_2OF_{10} in units of 10^{-11} mol/J versus percent O_2 concentration in SF₆ at a total pressure of 100 kPa and for a discharge dissipation energy of (80 ± 4) J/spark.

Piemontesi and coworkers⁽¹⁵⁾ is also consistent with results obtained by Belarbi and coworkers^(13,14) and Sauers and coworkers.⁽¹⁶⁾ A decrease in S_2F_{10} yields with increasing H_2O content was also observed for spark discharges.⁽²⁵⁾ The initial decrease in the S_2F_{10} product rate that was seen in the present experiments using unconditioned electrodes could be partly due to an increase in H₂O content that occurs during the early stages of discharge operation. However, the fact that this decrease is largely eliminated by preconditioning of the electrodes in a discharge, suggests that the initial decrease in the S₂F₁₀ production rate is predominantly related to the condition of the point electrode surface. Earlier investigations⁽¹⁶⁾ have shown that the rate for S_2F_{10} production decreases in negative corona when a tungsten point electrode is conditioned by previous exposure to a discharge. There is also evidence that the S_2F_{10} production rate depends on the material used for the plane electrode, and is generally higher for an aluminum electrode than for a stainless-steel electrode.⁽¹²⁾ It has been speculated⁽³⁾ that the roughening of the stainless-steel point-electrode surface during conditioning serves to enhance the rate for catalytic destruction of S_2F_{10} on this surface. Reactions of S_2F_{10} on the point-electrode surface could be important because the reaction (1) by which it is formed occurs most efficiently in the active glow region of the discharge that is in the immediate vicinity of this electrode.

In general, the influence of H_2O on S_2F_{10} production is not easy to assess or explain. The concentration of H_2O in the gas cannot be readily measured or controlled during the discharge. Model calculations⁽³⁾ show that the presence of gas-phase H_2O tends to enhance the production of S_2F_{10} , whereas laboratory tests^(6,7) indicate that the S_2F_{10} destruction rate on surfaces is significantly increased (especially at higher temperatures above ambient) if H_2O is present. The role that water plays in the catalytic destruction of S_2F_{10} on electrodes in the present experiments is probably important but remains unclear.

The measured charge rate-of-production for S_2F_{10} was found to be nearly independent of discharge current above about 20 μ A. Below this value, the production rate was found to drop abruptly. This behavior, which agrees with similar observations of Belarbi and coworkers,⁽¹⁴⁾ is not explained by the modél of Van Brunt and Herron.⁽³⁾ It was suggested⁽³⁾ that the decrease of $dC(S_2F_{10})/dt$ with I is most likely due to the increasing role played by destruction processes in the main gas volume as I decreases, i.e., when the time rateof-destruction, which may be nearly constant, begins to become a significant fraction of the time rate-of-production. Assuming that the time rate-of-production is proportional to I, this condition can be expressed mathematically as

$$\frac{dC(S_2F_{10})}{dt} = KI - r_d,\tag{9}$$

where K is a proportionality constant and r_d is a constant destruction rate. Using Eq(8) gives

$$\frac{dC(\mathbf{S}_2\mathbf{F}_{10})}{dQ} = K - \frac{r_d}{I}.$$
(10)

From this expression it is seen that $dC(S_2F_{10})/dQ$ decreases rapidly as $I \rightarrow r_d/K$.

Although $dC(S_2F_{10})/dQ$ was also found to depend on the SF₆ gas pressure, the results shown in Fig. 5 indicate that most of the changes with pressure occur during the initial electrode conditioning phase of the discharge, and that the pressure dependence is significantly diminished by using preconditioned electrodes.

The results reported here show that the addition of small quantities of O_2 to SF_6 (up to 10% by volume) dramatically reduces the rates for S_2F_{10} production in both negative corona and spark discharges. The introduction of oxy-gen also enhances markedly the production of $S_2O_2F_{10}$ in negative corona and the production of S_2OF_{10} in spark discharges. These observations are in agreement with results for corona and spark discharges in SF_6 and SF_6/O_2 mixtures recently reported by Piemontesi and coworkers.^(10,11) No significant S_2OF_{10} production was observed from corona and no significant $S_2O_2F_{10}$ production was observed from sparks.

In corona, the compound $\rm S_2O_2F_{10}$ is probably formed by the reaction $\rm scheme^{(26,27)}$

$$M + \mathrm{SF}_5 + \mathrm{O}_2 \to M + \mathrm{SF}_5\mathrm{O}_2 \tag{11}$$

$$M + \mathrm{SF}_5 + \mathrm{SF}_5\mathrm{O}_2 \to M + \mathrm{S}_2\mathrm{O}_2\mathrm{F}_{10} \tag{12}$$

and in a spark discharge, $\mathrm{S}_2\mathrm{OF}_{10}$ is probably formed by the reaction scheme

$$M + \mathrm{SF}_5 + \mathrm{O} \to M + \mathrm{SF}_5\mathrm{O} \tag{13}$$

$$M + \mathrm{SF}_5 + \mathrm{SF}_5\mathrm{O} \to M + \mathrm{S}_2\mathrm{OF}_{10}.$$
 (14)

The failure to see significant S_2OF_{10} formation in negative corona suggests that the density of SF_5O radicals must be sufficiently low to rule out $S_2O_2F_{10}$ formation by the process

$$M + 2SF_5O \rightarrow M + S_2O_2F_{10}.$$
 (15)

The removal of SF_5 by processes (11–14) undoubtedly contributes to the decline of S_2F_{10} yield with increasing O_2 concentration in both types of discharges.

It is speculated that the difference in the observed SF_6 oxidation chemistry that occurs in corona and spark discharges is attributable to differences in the degree of O_2 dissociation and the relative roles played by O_2 and O in the two discharges. It might be expected that, because a spark is the "hotter" discharge, it will produce a more complete dissociation of oxygen and its chemistry will be influenced more by the presence of O than O_2 .

In both types of discharges, the production rates for the oxygen-containing compounds S_2OF_{10} and $S_2O_2F_{10}$ were found to decrease significantly when the O_2 content increases above the 5% level. The decreases in the production rates for these compounds are more rapid than implied by the simple effect of diluting the SF_6 . In order to fully explain the dependence of the production rates on oxygen concentration, it would be necessary to employ a chemical kinetics model that includes all competing oxidation processes and is more complete than previously developed models.⁽³⁾

5. Conclusions

The main conclusions of this work can be summarized as follows:

- 1. The compound S_2F_{10} is produced during negativeglow type corona discharges from point-plane electrode gaps in SF₆. The rate of production of this compound depends on discharge current, gas pressure, and electrode surface conditions.
- 2. The measured rates for S_2F_{10} production from negative corona are consistent with previous experimental results and with a chemical kinetics model of the discharge that allows for S_2F_{10} destruction on surfaces.
- 3. The addition of low levels of O_2 to SF_6 dramatically reduces the S_2F_{10} yield from both negative corona and spark discharges, and this reduction can be attributed to the occurrence of oxidation reactions that deplete the concentration of SF_5 radicals.
- 4. The addition of O₂ to SF₆ causes a significant increase in the yields of S₂O₂F₁₀ and S₂OF₁₀ respectively from negative corona and spark discharges; whereas there is no significant production of S₂OF₁₀ in corona or S₂O₂F₁₀ in sparks.
- 5. The differences in the SF_6 oxidation that occur in corona and sparks can be attributed to the big differences in temperature of these discharges and the corresponding differences in the relative degrees of O_2 dissociation.

It has previously been suggested^(8,9) that negative corona and spark discharges can be used to prepare reference gas samples that contain known concentrations of S_2F_{10} . Although reproducible results can be obtained using these discharges, it is clear from the information uncovered about S_2F_{10} production in this work that care must be taken to define the conditions of the electrodes and to control the presence of common trace contaminants such as O_2 in any attempt to define reliable reference discharges for generating S_2F_{10} . The results from the present work also prove that the concentrations of S_2F_{10} and the related compounds S_2OF_{10} and $S_2O_2F_{10}$ can build up in the high-voltage systems insulated with SF_6 if internal faults occur that are associated with continuous corona, spark, or partial-discharge activity.

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