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MEASUREMENT OF S_2F_{10} , S_2OF_{10} , AND $S_2O_2F_{10}$ PRODUCTION RATES FROM SPARK AND NEGATIVE GLOW CORONA DISCHARGE IN SF_6/O_2 GAS MIXTURES

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ABSTRACT

The rates for production of the compounds S₂F₁₀, S₂OF₁₀, and S2O2F10 have been measured both in spark and continuous, constant-current (40 µA) negative glow corona discharges generated using point-to-plane electrode gaps in 'pure' SF6 and SF₆/O₂ gas mixtures containing different relative amounts of oxygen, up to 10 percent. The measurements were performed for total gas pressures in the range of 100 to 200 kPa, and the SF6 discharge byproduct concentrations were measured using a gas chromatograph-mass spectrometric technique and a crvogenic enrichment chromatogtraphic technique, respectively, for the corona and spark experiments. When O2 is added to the gas, there is a dramatic drop in the S₂F₁₀ yield from both types of discharges with a corresponding increase in S_2OF_{10} yield from the spark and S2O2F10 yield from the corona discharge. The results can be explained within the framework of a plasmachemical model from considerations of the competition among the reactions of SF5 radicals produced by dissociation of SF6 in the discharge with SF₅ itself as well as with O₂ and O, and the relative degree of O2 dissociation in the two types of discharges.

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]. There is evidence from earlier work [2,3] 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. The influence of oxygen on the production of S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ from disharges at high pressures is of interest because air is a common contaminant in SF₆ insulation.

The experimental results on S_2F_{10} production in a negative glow-type corona discharge are consistent with a plasmachemical model [4] for this discharge in which S_2F_{10} is primarily formed from SF₅ radicals produced from dissociation of SF₆ via the process:

(1)
$$M + SF_5 + SF_5 \longrightarrow M + S_2F_{10}$$
,

where M is a third body required for stabilization, i.e., the process has a pressure dependence, and should be efficient at the relatively high pressures (> 100 kPa) encountered in gasinsulated 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 [1,5], and 2) dissociation in the discharge by electron impact, e.g.,

(2) $e + S_2F_{10} \longrightarrow 2SF_5 + e$.

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 removal process is that due to a reaction with F, namely [4]

 $(3) \qquad M + F + SF_5 \longrightarrow M + SF_6 .$

In the presence of water vapor, the following processes can be important in affecting the local SF₅ concentration:

- (4) $F + H_2O \longrightarrow OH + HF$
- (5) $OH + SF_5 \longrightarrow SOF_4 + HF.$

It has been shown [4] that the net effect of increasing gas-phase 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 SOF_4 yield than a spark discharge.

The influence of gas-phase H_2O on the relative yields of S_2OF_{10} and $S_2O_2F_{10}$ in SF₆ discharges is unknown, but is expected, at least for corona, to be relatively minor [4]. It has been suggested [4], however, that the production of these compounds as well as S_2F_{10} could be significantly affected by the presence of O_2 due to the occurrence of the fast reactions

$$(6) \qquad M + SF_5 + O_2 \longrightarrow M + SF_5O_2$$

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

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 S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ 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 electrical-breakdown 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 SF₆ dissociation fragments that are much higher than occur in a continuous corona.

EXPERIMENTS

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 [2,6]. Mixtures of SF6 and O_2 with O_2 concentrations in the range of 0 to 10% by volume were subjected to a continuous, constant-current, glowtype dc negative point-plane corona discharge generated using stainless-steel electrodes with a point-to-plane gap spacing of 1.0 cm in a 5.25 liter stainless-steel vessel. The polarity refers to the voltage applied to the point electrode which had a radius of curvature at the tip of 0.08 mm. The point electrode was conditioned before each experiment by operating a 40 µA discharge in pure SF6 for about 1 hour prior to introducing the SF₆/O₂ gas mixture. This conditioning procedure reduces the initial time variation in the S₂F₁₀ production rate due to changes in the rate of destruction on the point electrode surface as previously discussed [2]. All of the results reported here were obtained with a discharge current of 40 μ 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 chromatograph-mass spectrometer (GC/MS). The operation of the GC/MS is modified to achieve high sensitivity for detection of S₂F₁₀ which is ordinarily susceptible to interference from SF₆. Details of the analytical method and procedure have been described previously [5,7,8]. The most significant source of error was attributed to uncertainties in the S₂F₁₀, S₂OF₁₀, and S₂O₂F₁₀ reference gas samples used for GC/MS calibration [8] which are estimated to be always less than ±20%. At the end of each experiment, the SOF₂ and SO₂F₂ concentrations in the discharge vessel were also measured.

Spark Discharge

The experimental procedure used to investigate S2F10, S2OF10, and $S_2O_2F_{10}$ production in spark discharges is essentially the same as that described previously [3]. 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% O2 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 J.

Small gas samples (2 ml \times 100 kPa) were extracted from the chamber with a gas-tight syringe after each spark. The samples were analyzed quantitatively for S₂F₁₀, S₂OF₁₀, and $S_2O_2F_{10}$ content using a cryogenic enrichment-gas chromatograph equipped with an electron-capture detector [3,7]. By this method, the concentrations of the three compounds of interest are selectively enhanced in the sample relative to SF_6 and other major gaseous byproducts such as SOF_2 , SO_2F_2 , SOF_4 , and SO_2 . The enrichment process reduces the interference from SF_6 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 [7]. Again, the analysis procedure requires a calibration using reference gas samples of known concentration.

RESULTS

Corona Discharge

In the case of negative-glow corona, both S_2F_{10} and $S_2O_2F_{10}$ are produced with rates that depend significantly on O2 content. Although the compound S2OF10 was also detected, its measured yield from corona falls considerably below that of the other compounds and was too low to allow a meaningful determination of its production rate from the data obtained in the present experiments. The absolute yields of S2F10 versus net charge (current x time) are shown in Fig. 1 for four 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 given in Table 1. It is seen from this figure and Table 1 that the S_2F_{10} production rate in a 40 μ A discharge drops dramatically when O₂ 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.



Figure 1. Measured absolute yields of S_2F_{10} versus net charge transported in the discharge (discharge current \times time) 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.

In relatively pure SF₆, the production rate for $S_2O_2F_{10}$ was barely measurable and not reproducible, suggesting that its formation is highly sensitive to trace oxygen content. The production rate for this compound increases significantly to 0.87 μ mol/C when 3% O₂ is added and then gradually decreases with increasing O₂ content as seen in Fig. 2 and Table 1. The $S_2O_2F_{10}$ yields exceed those for S_2F_{10} when the O₂ concentration is greater than 3%. The production rates for the oxyfluorides SOF₂ and SO₂F₂ estimated from gas analysis performed at the end of each test are consistent with previous results [6,9] and are not extremely sensitive to the O₂ concentration (see Table 1).

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Table 1. Measured production rates for SF_6 oxidation byproducts in negative-glow corona (μ mol/C).



Figure 2. Measured absolute yields of $S_2O_2F_{10}$ versus net charge transported in the discharge (discharge current \times time) for a 40 μ A negative point-plane corona in the indicated SF₆/O₂ gas mixtures for an absolute total pressure of 200 kPa and 5.25 liter chamber volume.

Spark Discharge

In contrast to the results from corona discharges, the data for spark discharges show significant, oxygen-dependent S_2OF_{10} production and a lack of measurable $S_2O_2F_{10}$ 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. 3 and 4 for O_2 content in the range of 0 to 10%. The O_2 dependences of absolute yields (energy rates of production) in moles per joule for S_2F_{10} and S_2OF_{10} are given respectively in Figs. 5 and 6. These results are derived from the yield curves shown in Figs. 3 and 4.

The S_2F_{10} yield drops precipitously as O_2 concentration is increased, becoming more than an order of magnitude below 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.

DISCUSSION AND CONCLUSIONS

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. In the case of corona, the addition of O_2 up to the 3% level results in a significant enhancement of the $S_2O_2F_{10}$ yield. This compound is probably formed by the reaction

(8) $M + SF_5 + SF_5O_2 \longrightarrow M + S_2O_2F_{10}$.

The failure to see significant S_2OF_{10} formation in negative corona suggests that the density of SF_5O radicals must be suf-



Figure 3. 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 J delivered in a 1.1 liter stainless-steel chamber. Curves (a)-(f) correspond to the following percent oxygen concentrations: (a) 0%, (b) 0.1%, (c) 0.5%, (d) 1.0%, (e) 5.0%, and (f) 10.0%. The S_2F_{10} concentration is indicated in parts in 10⁹ by volume (ppb = parts per billion).



Figure 4. Production of S_2OF_{10} in sparked mixture of O_2 in SF₆ at a total pressure of 100 kPa and energy per spark of 80 J delivered in a 1.1 liter stainless-steel chamber. Curves (a)-(f) correspond to the following percent oxygen concentrations: (a) 0%, (b) 0.1%, (c) 0.5%, (d) 1.0%, (e) 5.0%, and (f) 10.0%. The S_2OF_{10} concentration is indicated in parts in 10⁹ by volume (ppb = parts per billion).





Figure 5. Spark yield (energy rate of production) of S_2F_{10} in units of 10^{-11} mol/J as a function of percent O_2 concentration in SF₆ at a total pressure of 100 kPa and for a discharge dissipation energy of 80 J/spark. The open points are experimental data and the solid curve is a fit to these data.



Figure 6. Spark yield (energy rate of production) of S_2OF_{10} in units of 10^{-11} mol/J as a function of percent O_2 concentration in SF₆ at a total pressure of 100 kPa and for a discharge dissipation energy of 80 J/spark. The open points are experimental data and the solid curve is a fit to these data.

ficiently low to rule out $S_2O_2F_{10}$ formation by the process:

(9) $M + 2SF_5O \longrightarrow M + S_2O_2F_{10}$.

The removal of SF_5 by processes (6) and (8) undoubtedly contribute to the decline of S_2F_{10} yield with increasing O_2 concentration.

In the case of spark discharges, S_2OF_{10} is seen instead of $S_2O_2F_{10}$ as an oxidation byproduct. The S_2OF_{10} is presum-

ably formed by the process:

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

where SF_5O is generated by reaction (7). It would thus appear that processes (7) and (10) are effective in removing SF_5 and competing with S_2F_{10} production in a spark.

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 O than O_2 .

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