# $S_2F_{10}$ FORMATION BY ELECTRICAL DISCHARGES IN $SF_6$: COMPARISON OF SPARK AND CORONA

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## ABSTRACT

Among the $SF_6$ by-products of electrical discharges that have been investigated $S_2F_{10}$ is probably the least understood (physical, chemical, and biological properties) and the most toxic. Its production in electrical discharges has been controversial because the presence of this chemical has been reported by only a few groups. We report on the yields of $S_2F_{10}$ in two types of discharges: spark and corona. The $S_2F_{10}$ yields for corona and spark were 2-4 $\mu$mol/C and 0.04-0.37 nmol/J respectively for experiments where the water content was low. For both types of discharges we have found that $S_2F_{10}$ formation is dependent on the presence of moisture. For corona discharges model calculations based on known sulfur-fluorine chemistry are shown to yield reasonable agreement with experimental data. We show $S_2F_{10}$ is formed in electrical discharges that occur in compressed-gas insulated equipment and address questions concerning effects of moisture and surface conditions.

## INTRODUCTION

In addition to the desirable electrical properties of sulfur hexafluoride ($SF_6$), $SF_6$ is nontoxic and chemically inert (below $\sim 500\,°C$). However, decomposition of $SF_6$ will occur when $SF_6$ is exposed to breakdown conditions including corona, spark, and arc. The major decomposition products ($SOF_2$, $SF_4$, $SOF_4$, $SO_2F_2$) have been examined in previous studies [1-3] and in some cases the production mechanisms are understandable in terms of interactions with impurities such as water or oxygen.

Probably the least understood $SF_6$ by-product is $S_2F_{10}$ which can be formed by the reaction of $SF_5$ radicals

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

where $SF_5$ is formed by electron-impact induced fragmentation of $SF_6$. Prior to 1985 this compound had only been observed by a few investigators [4,5]. Failure to detect $S_2F_{10}$ in electrical discharges might be due to several factors including the use of inappropriate detection techniques such as mass spectrometry alone, or gas chromatography in which the column is not suitable for either separating or transmitting $S_2F_{10}$, and/or there is a lack of detection sensitivity. In addition, problems associated with low thermal and chemical stability, failure to use proper reference standards, and inappropriate sampling techniques can lead to

significant errors in detection and identification of $S_2F_{10}$ in $SF_6$. It is known that $S_2F_{10}$ undergoes rapid unimolecular decomposition above about 200° C. At lower temperatures, $S_2F_{10}$ has been found to undergo catalytic decomposition on surfaces[6]. As a result of its relatively low thermal stability, formation of $S_2F_{10}$ in high-pressure $SF_6$ discharges has, been largely dismissed in the past. However, recent work has indicated that $S_2F_{10}$ is formed in all major types of electrical discharges that can occur in practice, i.e., corona,[7] spark,[8] and arc.[9].

The importance of establishing the existence of $S_2F_{10}$ in $SF_6$ discharges stems from its high degree of toxicity as indicated by the low ceiling TLV (threshold limit value) of 10 ppb (parts per billion) as set by the American Conference of Governmental and Industrial Hygienists. Occupational Safety and Health Administration (OSHA) has adopted this limit but has stayed enforcement until suitable detection techniques down to the TLV have been developed. Thus even at $S_2F_{10}$ concentrations significantly lower than that of other $SF_6$ by-products, $S_2F_{10}$ may be important in controlling biological and health effects. This was evidenced by the earlier cytotoxicity studies,[10] in which the major by-products of spark discharges excluding $S_2F_{10}$ could not account for the total cytotoxicity in "in vitro" cell culture assays.

In this paper we present the results of a collaborative quantitative study of the corona and spark induced yields of $S_2F_{10}$ formation in $SF_6$ and examine some of the factors that influence formation and destruction of $S_2F_{10}$.

## EXPERIMENT

### Corona discharge experiment

Sulfur hexafluoride was subjected to corona discharges in a negative point-to-grounded plane geometry. Corona experiments were performed both at National Institute of Standards and Technology (NIST) and Oak Ridge National Laboratory (ORNL) using three different discharge cells: 3.7 liter at NIST and 1.1 and 0.2 liter at ORNL. Discharges were run at constant current, $i_c$, and data were obtained on the $S_2F_{10}$ production rate measured in moles per total charge collected $q = i_c \cdot t$, where t is the total discharge time. A detailed description of the NIST discharge cell and method of corona-discharge data analysis is given in Van Brunt[1]. Except where noted the electrodes were stainless steel.

### Spark discharge experiment
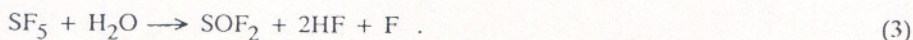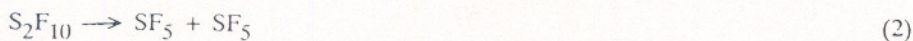
Spark discharges were produced by repetitively discharging a 0.1 $\mu$F capacitor into a small 70-ml stainless-steel cell with concentric cylindrical electrode geometry. The spark energy was determined by $E_s = 1/2\ nCV^2$ where n is the number of sparks, C is the capacitance of the charging capacitor and V is the voltage prior to breakdown. Since $E_s$ is an upper limit to the injected energy, the energy-normalized yield is a lower limit. In the past, diagnostics have indicated that most of the energy is injected into the cell. However recent data of Derdouri et al[11] suggest that not all of the stored energy went into the spark in their spark experiment. Because of the strong dependence of $S_2F_{10}$ production on conditions such as moisture and surface contamination, possible errors in spark energy cited above are not significant.

### Method of gas analysis

All gas analyses were made using samples taken from the discharge cell by syringe and injected into a gas chromatograph (GC). Analyses were performed on two different GC systems: GC-MS (mass spectrometer) at NIST and GC-TCD (thermal conductivity detector)

at ORNL. The GC parameters were similar in both systems as previously specified [6,7,12]. Calibration was made with reference samples containing $S_2F_{10}$ in either $SF_6$, $N_2$, or Ar. The $S_2F_{10}$ was synthesized at Clemson University and provided to us in liquid form with greater than 99% purity determined by infrared absorption spectroscopy and GC-MS. The reference samples were prepared at ORNL in a gas mixing vacuum manifold. Maintaining reliable reference samples was not trivial since $S_2F_{10}$ was found to deteriorate on surfaces in the presence of moisture. A study of $S_2F_{10}$ decomposition on surfaces has been reported recently [6]. Due to the slow decay of $S_2F_{10}$ in reference mixtures, new reference samples were prepared periodically for use in quantitative analysis of $S_2F_{10}$ in $SF_6$. Because of errors due to unstable reference mixtures, preliminary corona yields reported by Sauers et al [7] were overestimated in the NIST 60 $\mu$A data (presented in Fig. 4 of ref. 7). By taking proper account of $S_2F_{10}$ decay in the reference sample, the apparent current dependence originally observed was eliminated as discussed in the following section.

The GC-MS technique employed for $S_2F_{10}$ detection has been described in detail [12] and only the most salient points of the method will be given here. As a general rule, a gas sample of $SF_6$ containing a mixture of trace components is passed through a GC where the components are separated both spatially and temporally. Each component passing into the mass spectrometer is ionized by a 70 eV electron beam and one or more positive ions characteristic of that species may be used to monitor the relative concentration of that species. Because of the similarity of the $S_2F_{10}$ and $SF_6$ electron-impact positive-ion mass spectra [13], the monitoring of ions characteristic of $S_2F_{10}$ is severely hindered by background contributions from $SF_6$ ions, thereby reducing $S_2F_{10}$ sensitivity to about 50 ppm. However, it has been found that when the $S_2F_{10}$ containing effluent from the GC flows through a heated metal tube (T> 150° C) incomplete decomposition of the $S_2F_{10}$ occurs to form $SOF_2$ possibly by surface processes such as:

$$S_2F_{10} \longrightarrow SF_5 + SF_5 \tag{2}$$

$$SF_5 + H_2O \longrightarrow SOF_2 + 2HF + F \ . \tag{3}$$

Thus the $S_2F_{10}$ content can be monitored by observing the ion signals from $SOF_2$ (e.g. $SOF_2^+$, m/z=86 or $SOF^+$, m/z=67). Because the ion background signals are significantly lower at these m/z ratios than at m/z corresponding to $SF_6$ ion fragments, the $S_2F_{10}$ detection sensitivity is improved by several orders of magnitude to below 10 ppb. This method of analysis was employed for the corona experiments made using the NIST 3.7-$l$ cell. The GC-TCD used for the analyses of spark and corona in the ORNL experiments was applied in the conventional manner with sensitivity of ~25 ppm.

## RESULTS OF CORONA EXPERIMENTS

### "Clean" Cell, no water added

In Figs. 1 and 2 are shown the data obtained from the 3.7-$l$ corona discharge cell (p=2 atm, T=23°C, stainless-steel electrodes, 1 cm gap spacing). The data points in Fig. 1 are a composite of three experiments, corresponding to one experiment at 60 $\mu$A and two at 40 $\mu$A. The 60 $\mu$A data supercedes the data reported earlier [7]. There is no indication of a dependence on $i_c$ of the charge rate-of-production, $r_q$, of $S_2F_{10}$. This set of data gives a production rate of $r_q$=2.4 $\mu$mol/C. However there are factors including surface contamination and humidity that can either increase or decrease the net $S_2F_{10}$ charge rate-of-production from this value. Interestingly the least squares fit of the data in Fig. 1 does not pass through the origin, indicating a non-linear production rate at short times. This is shown more clearly by the data bounded by the dashed lines and replotted in Fig. 2. These data were obtained from a 40 $\mu$A experiment at short elapsed times and analyzed by GC-MS, after modification for increased sensitivity. This data set indicates a steeper initial rise corresponding to a somewhat higher initial production rate ($\sim$4 $\mu$mol/C).
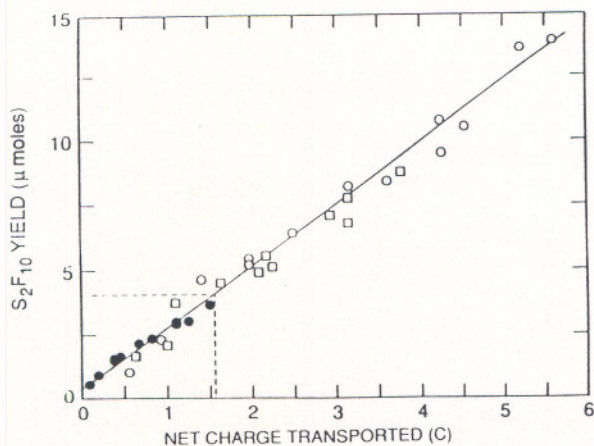
Fig. 1. Production of $S_2F_{10}$ in corona discharge of $SF_6$ at 200 kPa (3.7-$l$ cell) as a function of the net charge transported: $i_c=40$ $\mu A$, open squares and closed circles; $i_c=60$ $\mu A$, open circles. Data in the region delineated by the dashed lines are replotted in Fig. (2).
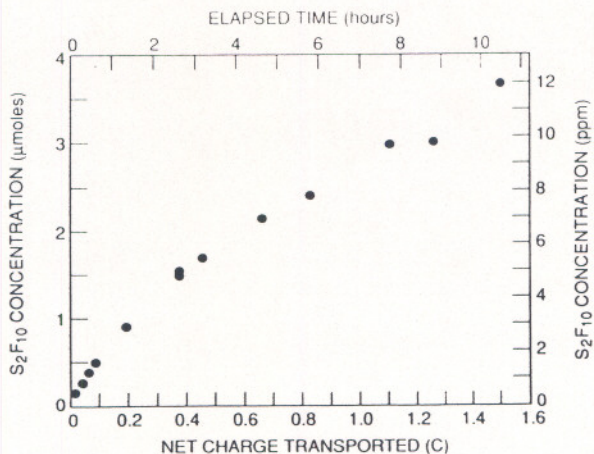


Fig. 2. Production of $S_2F_{10}$ in corona discharge of $SF_6$ at 200 kPa (3.7-$l$ cell) at short times, corresponding to $S_2F_{10}$ concentrations in the low- and sub-ppm range. The actual elapsed time during which the discharge was active is shown on the top scale.

Effects of contaminated surface

When the electrodes were not cleaned between experimental runs, that is, the $SF_6$ gas plus gaseous by-products were pumped out and the cell refilled with $SF_6$, the $S_2F_{10}$ yield increased as shown in Fig. 3. Thus $r_q > 10$ $\mu mol/C$ were obtained. The initial run (Run 1) yielded a charge rate of production within a factor of two of that shown in Fig. 1, but made
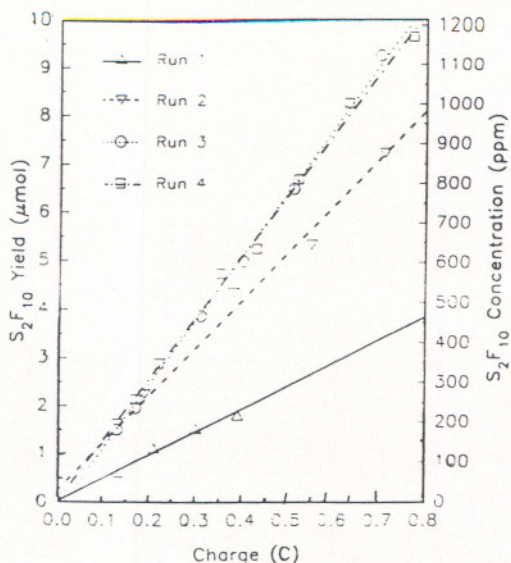
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Fig. 3. Production of $S_2F_{10}$ in corona discharge of $SF_6$ at 100 kPa (0.2-$l$ cell) as a function of total charge for consecutive runs (Run 1-4) showing effects due to electrode contamination.

with a 0.2-$l$ cell and tungsten (W) "point" electrode for $i_c=24$ $\mu A$. It is not known at this time what causes this increase in $S_2F_{10}$ production, but it could be an effect associated with the buildup of solid contaminants on the electrode surface. It should be noted that the differences in $S_2F_{10}$ concentrations shown in Figs. 1 and 3 are due to the differences in cell volumes used for the two experiments.

## Influence of moisture: $SF_6/H_2O$ mixtures

It was previously shown that adsorbed moisture will increase the consumption of $S_2F_{10}$ on surfaces [7]. Gas-phase water can also influence the net yield of $S_2F_{10}$ in $SF_6$ corona. Figure 4 shows a comparison of data taken with the 1.1-$l$ corona chamber (P=2 atm, T=23°C, stainless-steel electrodes, 1 mm gap spacing) under relatively dry conditions with data obtained after introduction of water vapor prior to the run, for $i_c=20$ $\mu A$. The water concentration was determined from the partial pressure of water after introducing water into the corona cell by syringe and allowing sufficient time ($\sim 1$ h) for the water vapor to reach equilibrium with the walls of the chamber. Yields obtained after accumulation of q=2 C total charge were substantially lower for water concentrations of 600 and 1200 ppm as shown in the figure. The three data sets represented by the open symbols were for experiments where the cell was "dry" meaning only that the cell was pumped down to 0.1 Pa prior to the run. The non-linear behavior for q>1 C could be due to electrode contamination as indicated by the data in Fig. 3, while the initial charge rate-of-production at q=1 C is similar to that exhibited in Fig. 1 and curve "Run 1" in Fig. 3. Because of the lower net $S_2F_{10}$ yield ($r_q<1$ $\mu mol/C$) and the low sensitivity for the GC-TCD (25 ppm) used for these experiments, no data are shown below q=1C for the $SF_6/H_2O$ experiments.

The above result appears contrary to previous data which showed a correlation between increased charge rate of production of $S_2F_{10}$ with increased water as measured by GC-TCD using a Porapak T (Supelco) column [7]. The results of reference 7 were obtained in a 0.2-$l$ corona discharge cell and W "point" electrode. It was pointed out in that work that the GC peak areas for $H_2O$ content were not always consistent with the amounts of water added. However, as will be shown in the next section, decomposition of $S_2F_{10}$ on the walls can account for lower yields. The results shown here and in reference 7 suggest that it may be necessary to consider the combined counteracting effects associated with electrode
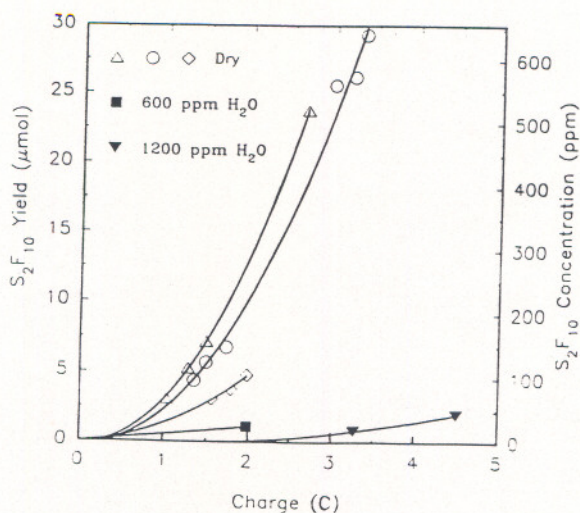
Fig. 4. Production of $S_2F_{10}$ in corona discharge of $SF_6$ at 200 kPa (1.1-$l$ cell) and $i_c = 10$ $\mu$A as a function of total charge, showing the effect of water addition: open symbols correspond to the "dry" case (no water addition); closed square, 600 ppm water; closed triangle, 1200 ppm water. Differences in the three "dry" curves are probably due to small but different amounts of adsorbed water.

contamination which increases $S_2F_{10}$ production and adsorbed water which decreases $S_2F_{10}$ production.

## RESULTS OF SPARK EXPERIMENTS

The energy rates-of-production for spark discharges (see Table 1) exhibited considerably more scatter than the rates obtained for corona, falling in the range 0.04-0.37 nmol/J. The experimental conditions covered the range 9.7-30 kJ total energy. In a 10 kJ experiment, when 600 ppm water was added to $SF_6$, the $S_2F_{10}$ yield dropped from 160 ppm to below detection limits (in this case 25 ppm using GC-TCD). As in the case of corona discharges, the $S_2F_{10}$ yields probably depend on both surface conditions and on adsorbed trace moisture.

## DISCUSSION

### Model calculation of $SF_6$ corona

Previous model calculations using a chemical kinetics code[14] have achieved reasonable success in accounting for the charge rates-of-production of $SOF_2$, $SOF_4$, and $SO_2F_2$. In assessing the $S_2F_{10}$ reaction scheme, reactions (4)-(8) were considered to be most important to $S_2F_{10}$ formation:

$$SF_6 \xrightarrow{\text{corona}} SF_5 + F \tag{4}$$

$$SF_5 + SF_5 \longrightarrow S_2F_{10} \tag{5}$$

$$SF_5 + SF_5 \longrightarrow SF_4 + SF_6 \tag{6}$$

$$F + H_2O \longrightarrow HF + OH \tag{7}$$

$$SF_5 + F \longrightarrow SF_6 \tag{8}$$

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**Table 1.** Comparisons of sulfur-oxyfluoride and $S_2F_{10}$ by-product production rates from $SF_6$ discharges

Discharge Type

| Species | Corona[a] | | Spark[e] | Arc[g] |
|---|---|---|---|---|
| | $(\mu mol/C)$ | $(nmol/J)$ | $(nmol/J)$ | $(nmol/J)$ |
| $SOF_4$ | 50 | 0.90 | 0.2 | 0.2-100 |
| $SOF_2$ | 32 | 0.54 | 1-3 | 100-600 |
| $SO_2F_2$ | 14 | 0.25 | 0.02 | |
| $S_2F_{10}$ | 2-4[b],(3.5±1.4)[c],(1-12)[d] | 0.05 [b] | 0.04-0.37 [f] | 5.5-11x10^{-5} [h] |

(a) NIST data: P=200 kPa, $i_c$=40 $\mu$A (see Ref 1)
(b) Present data (see Fig 1), P=200 kPa, 3.7-$l$ cell
(c) Present data (see Fig 4), P=200 kPa, $i_c$=20 $\mu$A, 1.1-$l$ cell
(d) Model calculation: $[H_2O]$=50-400 ppm (see Fig. 5)
(e) Data from Ref. 3
(f) Present data; range probably due to adsorbed water and varying electrode contamination
(g) Various sources and conditions (taken from Ref. 2)
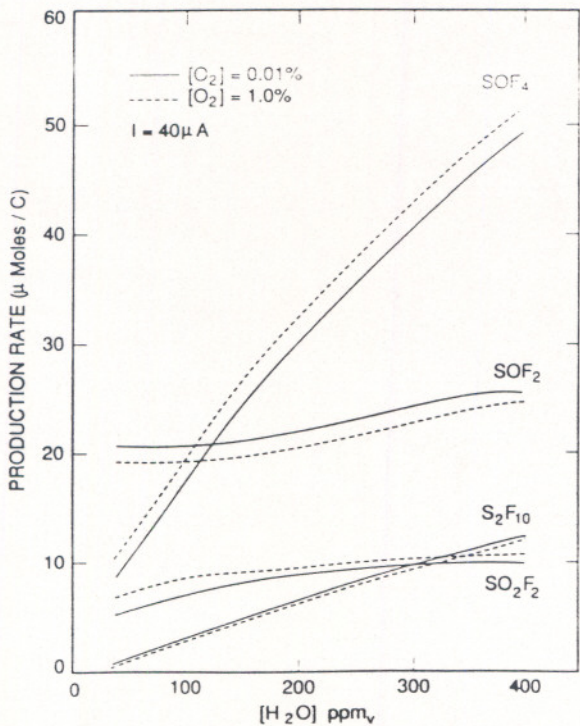(h) Yield determined from Refs. 9,15 (see text).



Fig. 5. Calculated charge rates-of-production of the oxyfluorides and $S_2F_{10}$ as a function of $H_2O$ content in 200 kPa $SF_6$ for a 40 $\mu$A discharge and the different indicated $O_2$ concentrations.

In this scheme, the presence of $H_2O$ enhances the production of $S_2F_{10}$ by reaction with F (reaction (7)) which suppresses reformation of $SF_6$ (reaction (8)) allowing $SF_5$ radicals to

combine (reaction (5)) to form $S_2F_{10}$. According to this argument an increase in the gas-phase water concentration $[H_2O]$, would lead to an increase in the charge rate-of-production of $S_2F_{10}$. In Fig. 5 we show the results of model calculations for $S_2F_{10}$, $SOF_2$, $SOF_4$, and $SO_2F_2$ production rates as a function of gas-phase water concentration. In this model, only gas-phase reactions are considered, i.e., the model does not include loss of $S_2F_{10}$ due to reactions occurring on surfaces, the rate of which depends on water as well.

The rate of $S_2F_{10}$ production can be expressed by

$$\frac{d[S_2F_{10}]}{dt} = r_t - k_d[S_2F_{10}] \qquad (9)$$

where $[S_2F_{10}]$ is the $S_2F_{10}$ concentration, $r_t = r_q i_c$ is the initial rate of $S_2F_{10}$ formation as determined for example by reactions (4)-(8), and $k_d$ is a rate constant for $S_2F_{10}$ decay which can depend on time and in some unknown way on the conditions of the surface on which $S_2F_{10}$ decomposition occurs. Assuming a constant $k_d$, $[S_2F_{10}]$ will approach an equilibrium value, $[S_2F_{10}]_{eq} = r_t/k_d$. If we use $r_q = 3 \ \mu mol/C$ (typical of the data reported here) and $i_c = 20$ $\mu A$ then $k_d > 2.8 \times 10^{-5}$ would account for the low net yield shown in Fig 4. In previous work [6,7] $S_2F_{10}$ was found to decay exponentially with rate constants falling in the range $0.001\text{-}2 \times 10^{-5} \ s^{-1}$ depending on the size of the chamber, amount of adsorbed water, and on the temperature. Since the previously measured [6,7] decay rates are slower than this, a possible explanation for the faster decay during discharges is that the $S_2F_{10}$ decay rate via surface reactions is higher at lower $S_2F_{10}$ concentration ($<<$ 25 ppm).

<u>Comparison of Corona and Spark yields</u>

In Table 1 we summarize the results of $S_2F_{10}$ production measurements from $SF_6$ in corona and spark discharges. In either case $S_2F_{10}$ production rates are lower than for the other sulfur oxyfluorides listed. However the corona-induced $S_2F_{10}$ charge rate-of-production is only an order of magnitude below that of the sulfur oxyfluorides for "clean" conditions where the water and oxygen contents are low. In the case of spark discharges, the yield of $S_2F_{10}$ is lower relative to the most abundant by-product $SOF_2$. Included in the table for comparison are the production rates for the same sulfur oxyfluorides produced by arc discharges. The arc rate for $S_2F_{10}$ production was determined from the $S_2F_{10}$ concentration reported by Pettinga [9] in a power arc burn-through experiment and arc energy was taken from the related work of Janssen [15]. In either the spark or corona cases $S_2F_{10}$ formation is significant enough to merit consideration in any evaluation of the potential health effects of decomposed $SF_6$.


## CONCLUSIONS

Results of measuring $S_2F_{10}$ production from both corona and spark discharges in $SF_6$ are reported here. Although the $S_2F_{10}$ yield falls below the yields for $SOF_2$, $SOF_4$, and $SO_2F_2$, it is significant in light of the relatively high toxicity of $S_2F_{10}$. The results presented here demonstrate that during a continous low-level corona discharge, it is possible for the concentration of $S_2F_{10}$ in an enclosed chamber containing $SF_6$ to build up to levels far in excess of the TLV within a matter of minutes. The charge rate-of-production of $S_2F_{10}$, $r_q = 2.4 \ \mu mol/C$, found for clean electrodes and relatively dry conditions can increase substantially under contaminated conditions. Under wet conditions, the net yield depends significantly not only on the formation rate of $S_2F_{10}$ in the discharge, but also on the rate of decay as a result of contact with chamber walls. The larger the cell the smaller is the effect of degradation of $S_2F_{10}$ after it is formed. An understanding of the influence of water on the $S_2F_{10}$ formation rate requires additional experimental investigation. Results from model calculations of $SF_6$ by-product formation which show reasonable agreement with

experimental data on sulfur oxyfluorides, also indicate an increase in $S_2F_{10}$ yield with increasing gas-phase water concentration. It is not clear from the present data whether a model which neglects surface reactions involving $S_2F_{10}$ is sufficient to adequately account for the low $S_2F_{10}$ yield reported here when water is added to the discharge cell.

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