

Production Rates for Oxyfluorides SOF_2 , SO_2F_2 , and SOF_4 in SF_6 Corona Discharges

R. J. Van Brunt

National Bureau of Standards, Gaithersburg, MD 20899

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The most abundant, long-lived stable gaseous species generated by corona discharges in SF_6 gas containing trace levels of O_2 and H_2O are the oxyfluorides SOF_2 , SO_2F_2 , and SOF_4 . Absolute energy and charge rates-of-production of these and the minor products SO_2 , OCS , and CO_2 have been measured at different total gas pressures from 100 kPa to 300 kPa and for discharges of different current, power, and polarity. Oxyfluoride yields for SF_6/O_2 mixtures containing up to 10% O_2 have also been measured. The results indicate that oxyfluoride production is not controlled by the concentrations of either O_2 or H_2O at levels below about 1%, and the rate controlling factor is the dissociation rate of SF_6 in the discharge. The discharge current and time dependence of the production rates are discussed in terms of gas-phase mechanisms that have been proposed to explain previous observations of electrical, thermal, and laser-induced decomposition of SF_6 and SF_6/O_2 mixtures. Upper limits on the total SF_6 decomposition rate in low-current discharges have been estimated. Details of the chemical analysis procedures are given, and application of the results to the design of chemical diagnostics for SF_6 -insulated, high-voltage apparatus is discussed.

Key words: corona discharges; decomposition rates; production rates; SF_6 ; SF_6/O_2 mixtures; SOF_2 ; SO_2F_2 ; SOF_4 ; sulfoxhexafluoride; sulfurylfluoride; thionylfluoride; thionyl tetrafluoride.

1. Introduction

The decomposition of gaseous SF_6 leading to formation of the oxyfluorides SOF_2 (thionylfluoride), SO_2F_2 (sulfurylfluoride), and SOF_4 (thionyl tetrafluoride) as major stable gaseous end products has previously been observed under a wide range of experimental conditions. These include: 1) oxidation of SF_6 in O_2 induced by exploding metals [1];¹ 2) decomposition

of SF_6 on metal surfaces by direct heating [2]; 3) high-power, laser-initiated dissociation of SF_6 and SF_6/O_2 mixtures [3-5]; 4) shock-tube pyrolysis of SF_6/O_2 mixtures [6]; 5) low-pressure rf and microwave discharges [7-10]; 6) high-pressure arcs [11-18]; 7) spark discharges [19-22]; and 8) corona and glow type discharges such as those considered here [14,18,23-26]. Precluding possible catalytic influences of metal vapors and surface reactions, it might be expected that, although the initial dissociation mechanisms and the degree of gas dissociation in these cases are quite different, the basic subsequent gas-phase chemical processes that yield oxyfluorides should be similar. The relative yields of SOF_2 , SO_2F_2 , and SOF_4 , however, can depend on the availability of oxygen and the degree to which the SF_6 molecules are dissociated, e.g., as determined by gas temperature or discharge power level. Generally as gas pressure, temperature, or discharge power increases, SOF_2 production is observed to become more dominant

About the Author, Paper: R. J. Van Brunt is a physicist in the Electrosystems Division of the NBS Center for Electronics and Electrical Engineering. The work he reports on was supported by the Electric Energy Systems Division of the U.S. Department of Energy.

¹Numbers in brackets indicate literature references.

[1,14,16,19]. At lower pressures, temperatures, or discharge power levels, SOF_4 often dominates [1,3,8–10], and when O_2 is added to the gas, it is noted that [3,15] both SO_2F_2 and SOF_4 increase relative to SOF_2 .

Most of the earlier experimental work on decomposition of SF_6 or SF_6/O_2 focused on the problem of identifying the final by-products or intermediate ion and neutral species (also see refs. [27–30]). There have been only a few attempts to determine absolute yields for the electric-discharge-generated by-products, and these were performed under conditions for which the discharge could not be easily controlled or quantitatively characterized, namely for arcs [15,18], sparks [20,22], and 60-Hz ac corona [18]. The motivation of the present work is to provide data on the absolute yield of the oxyfluorides from SF_6 in the presence of small quantities of O_2 and H_2O under steady, dc-corona discharge conditions which could be readily characterized and controlled. The measurements reported here have been made for different gas and discharge conditions selected to help elucidate the predominant mechanisms of oxyfluoride formation.

Quantitative data on oxyfluoride production are also needed to design chemical diagnostics for SF_6 -insulated high-voltage apparatus in which corona or partial discharges could occur [31–32]. The formation of the oxyfluorides is accompanied by production of highly reactive species such as free fluorine and HF. These species can cause serious damage to conductors and solid insulating materials present in practical systems [33–36]. Although most gas-insulated systems are designed to be free of internal discharges, low-level partial discharges similar to the corona phenomena considered here may be unavoidable, and in some applications, like high-energy electrostatic accelerators [26], continuous corona discharges are frequently maintained during normal operation. The highly reactive products of a discharge do not remain in the gas for long and are consequently difficult to detect. Their level of production, however, could be inferred indirectly from measurements of oxyfluoride content, provided that: 1) the production rates for the oxyfluorides are known, and 2) the connection between oxyfluoride and corrosive species production is understood. The results of the present study provide further insight into the latter item as well as data for the former.

Although the rate data presented here either include or are consistent with those that were previously reported from our laboratory [37–38], the measurements have been extended to a wider range of conditions. Moreover, the present results are expressed in a way deemed to be more useful in the design of chemical diagnostics for practical systems and are thus intended to supplant the earlier data.

2. Definitions of Production Rates

Production rates are usually specified in terms of change in the quantity of substance per unit of time, denoted here as dc/dt . This rate is determined by the rates of the reactions and concentrations of the reactants involved in formation of the particular species of interest. For electric discharge-generated products, it is more useful to express the rates in terms of either quantity generated per unit of energy dissipated (r_u) or per unit of charge transported in the discharge gap (r_q). These are related to the time rate-of-production by

$$dc/dt = p(t)r_u, \text{ and } dc/dt = i(t)r_q, \quad (1)$$

where $p(t)$ and $i(t)$ are respectively the instantaneous discharge power and current. The net quantity of a substance generated in a discharge of duration t' is then given either by

$$c(t') = \int_0^{t'} i(t)r_q[i(t)]dt \quad (2a)$$

or

$$c(t') = \int_0^{t'} p(t)r_u[p(t)]dt \quad (2b)$$

where it is assumed that in general r_q and r_u depend on $i(t)$ and $p(t)$, respectively. Stable gaseous products generated in a localized discharge will usually diffuse rapidly throughout the volume in which the gas is contained so that the concentration observed will be given by $c(t')/V_s$, where V_s is the volume of the system. If one knows the volume of the system, the production rates, and level of discharge activity specified by either $i(t)$ or $p(t)$, one can then use eq (2a) or (2b) to predict the concentrations of the by-products which can be observed after a given time.

The preference for either r_q or r_u is determined by the predominant dissociation mechanism and by variations of these with either current or power dissipation respectively. In the case of high-current, arc-type discharges in which heating of the gas is important and thermal dissociation dominates, the quantity r_u is preferred because it is found [15,18] to be relatively constant, i.e., $dc/dt \propto p(t)$. However, for cold, low-current discharges such as corona, in which the dissociation of the gas is primarily governed by electron collision processes, r_q is more useful for predicting by-product buildup in practical systems and for interpreting results of measurements as described here.

Examples of oxyfluoride energy or charge rates-of-production estimated from data that have previously been reported [15,18,39] for SF_6 are shown in table 1. In addition to these results, Castonguay [22] recently re-

Table 1. Estimated oxyfluoride production rates in electric discharges from earlier work.

Literature Reference	Discharge Type	Electrode Material	Production Rates			units
			SOF ₂	SOF ₄	SO ₂ F ₂	
Sauers et al. [39]	spark	S.S.*	1.8	0.22	0.021	(nmoles/J)
Boudene et al. [15]	arc	S.S.*	24	0.3	0.8	(nmoles/J)
Boudene et al. [15]	arc	Ag	0.4	0.4	0.3	(nmoles/J)
Boudene et al. [15]	arc	Cu	8.12	0.3	0.5	(nmoles/J)
Chu et al. [18]	corona	Al	(370–850)	–	(190–420)	(μmoles/C)

*Stainless steel

ported a total SF₆ decomposition rate in a 60 W arc employing stainless steel electrodes to be about 7 to 8 nmoles/J. In a much earlier work, Waddington and Heighes [24] estimated the total gaseous by-product production rate in SF₆ point-plane partial discharges to be about 2 μmoles/J. This estimate disagrees significantly with the results in table 1 and is not consistent with either the data or the theoretical upper limit on SF₆ decomposition to be discussed here.

3. Measurement Method

3.1 Discharge

The electric discharge used for this investigation was a highly localized, low-current, point-plane corona. Characteristics of this type of discharge have previously been described [40,41]. A schematic of the experimental arrangement is shown in figure 1. Polished stainless steel electrodes were used in a 3.7 liter cell with a point-to-plane gap of 1.5 cm and point radius-of-curvature at the tip of about 0.08 mm. The cell contained a static gas sample which was maintained at room temperature (~300 K).

The zone of ionization, assumed here to coincide with the chemically active region, is confined to the immediate vicinity of the point electrode tip due to the highly divergent nature of the electric field. It is estimated from consideration of the field [40] that the active region extends a distance from the point which is no more than 2% of the total point-to-plane gap spacing, i.e., no more than about 4 point-electrode tip radii. The extent of the active region and the ion drift volume were therefore small compared to the relatively inactive volume of gas contained in the discharge cell.

A continuous corona was generated with a high-voltage dc supply that could be operated at either polarity, and consistent with the usual convention [4], the designated sign of the discharge refers to the potential of the point electrode relative to the plane. The voltage across the cell was continuously monitored and adjusted to maintain a constant average discharge current (see fig. 2). During a typical experiment of 20 to 70 h duration it was usually necessary to initially decrease and then gradually increase the voltage in order to keep the current constant. The average currents could be kept constant for the positive and negative discharges to within ±1% and ±4% respectively. The adjustments in

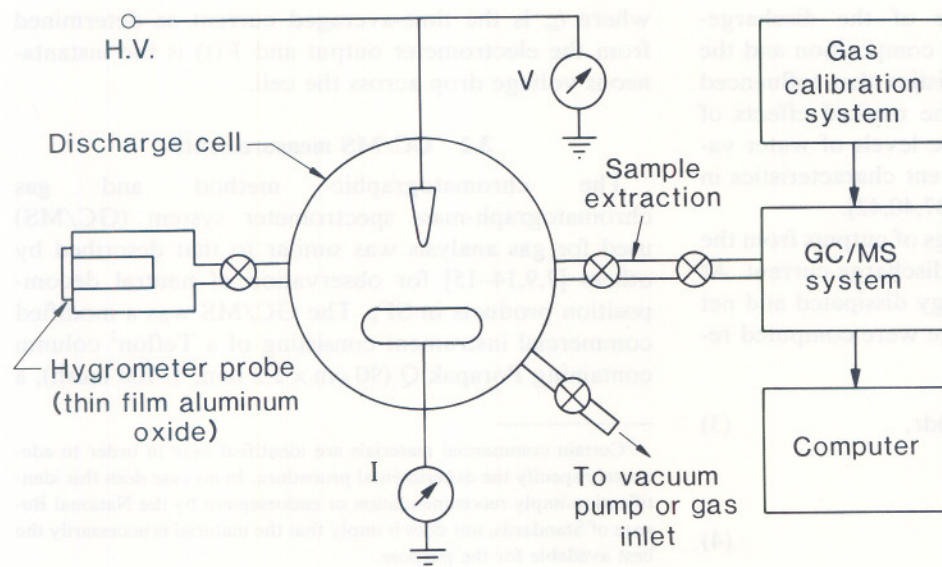


Figure 1—Experimental arrangement.

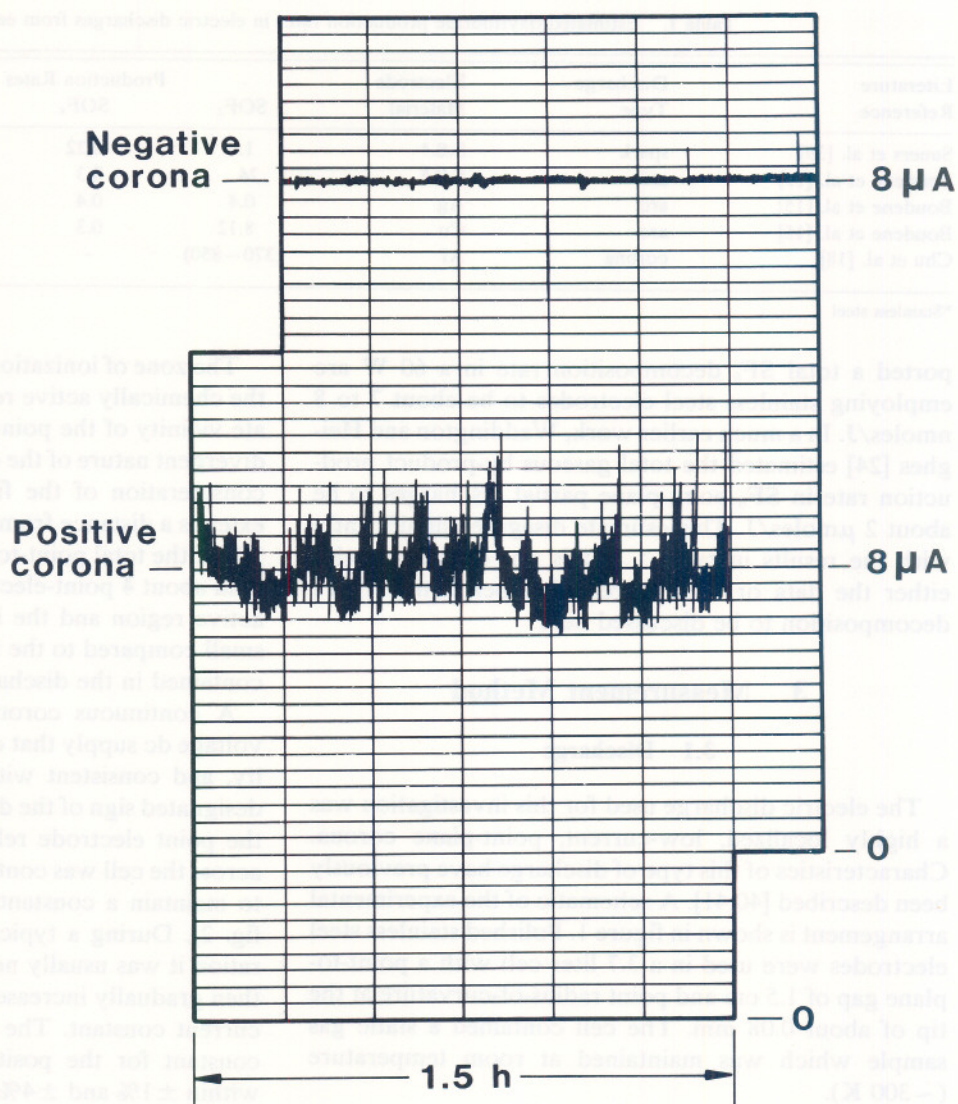


Figure 2—Examples of recordings showing the typical behavior of discharge current versus time for positive and negative corona discharges at comparable average current levels ($i_{av}=8.0 \mu A$) for a period of 1.5 h.

voltage were necessary because of the discharge-produced changes in both the gas composition and the point-electrode surface characteristics that influenced the ionization rate in the gas. The marked effects of “electrode conditioning” and trace levels of water vapor on the discharge voltage-current characteristics in SF_6 have previously been noted [37,40,42].

Figure 2 shows typical recordings of outputs from the electrometer used to measure the discharge current. At any time t' , the accumulated energy dissipated and net charge transported in the discharge were computed respectively using

$$u(t') = i_{av} \int_0^{t'} V(t) dt, \quad (3)$$

and

$$Q(t') = i_{av} t', \quad (4)$$

where i_{av} is the time-averaged current as determined from the electrometer output and $V(t)$ is the instantaneous voltage drop across the cell.

3.2 GC/MS measurements

The chromatographic method and gas chromatograph-mass spectrometer system (GC/MS) used for gas analysis was similar to that described by others [7,9,14–15] for observation of neutral decomposition products in SF_6 . The GC/MS was a modified commercial instrument consisting of a Teflon² column containing Porapak Q (90 cm \times 3.2 mm, 8/100 mesh), a

²Certain commercial materials are identified here in order to adequately specify the experimental procedure. In no case does this identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material is necessarily the best available for the purpose.

membrane separator, and a quadrupole mass analyzer. Gases which were separated in time by the column passed through the membrane and were ionized by a 70-eV electron beam. The mass spectrometer was programmed to sample repetitively a sequence of selected ions characteristic of the various molecular species observed. Examples of single-ion chromatograms obtained by this procedure are shown in figures 3 and 4.

Table 2 indicates the ions monitored (mass-to-charge

ratios, m/e), approximate column retention times, and corresponding boiling points at 100 kPa pressure for some of the species observed. The order of elution correlates with boiling points as expected and is like that previously reported for similar columns [9,14,15]. Retention time values varied somewhat depending on column temperature and carrier-gas flow rate. For most measurements the helium carrier-gas flow rate was 32 ml/min at a column temperature of 24 °C. Some mea-

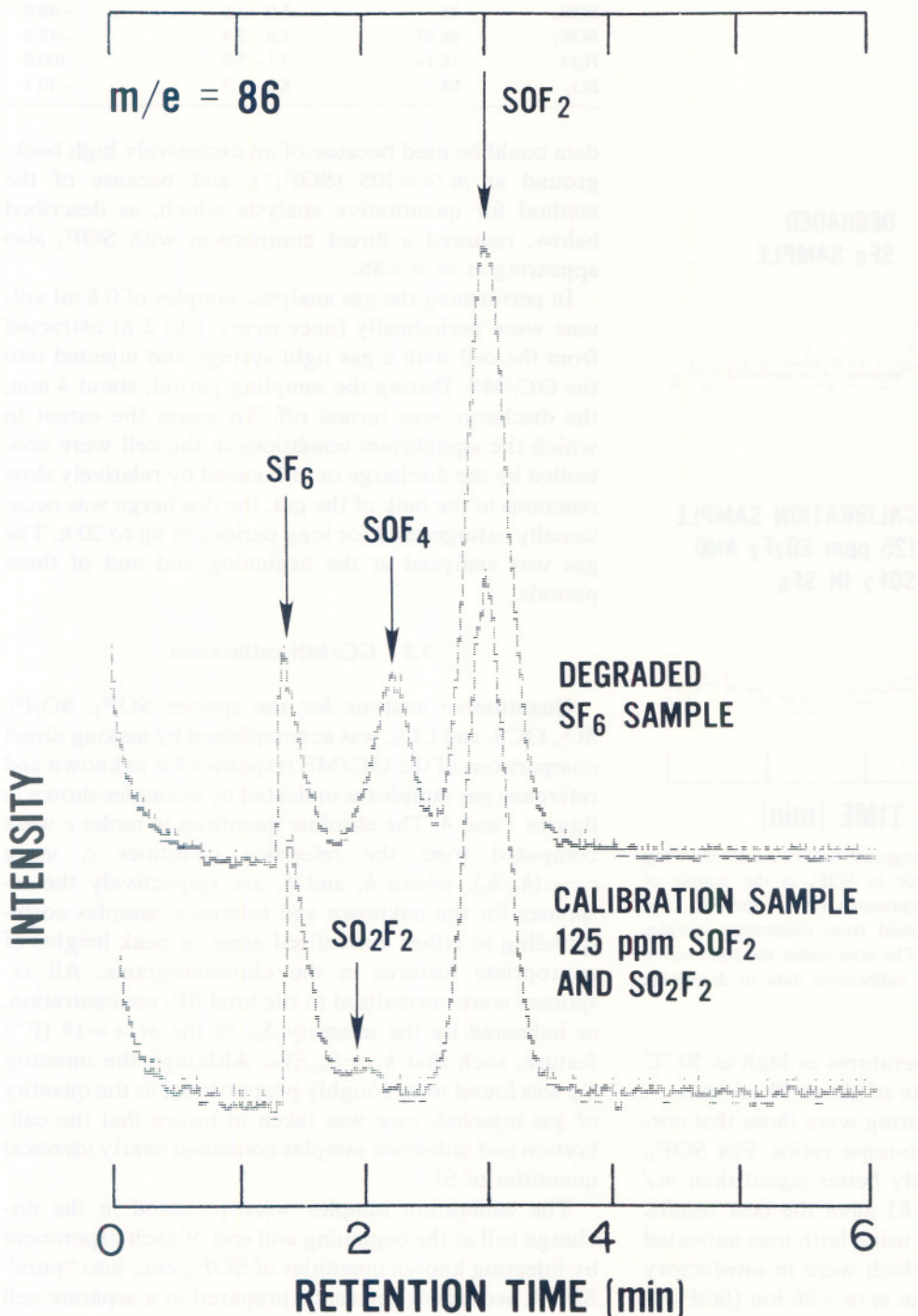


Figure 3—Typical single-ion chromatograms for $m/e = 86$ showing features associated with SF₆, SOF₂, SOF₄, and SO₂F₂ from decomposed SF₆ and from a calibration sample containing known amounts of SOF₂ and SO₂F₂ in SF₆. The gas sample injection was made at $t \approx 1$ min.

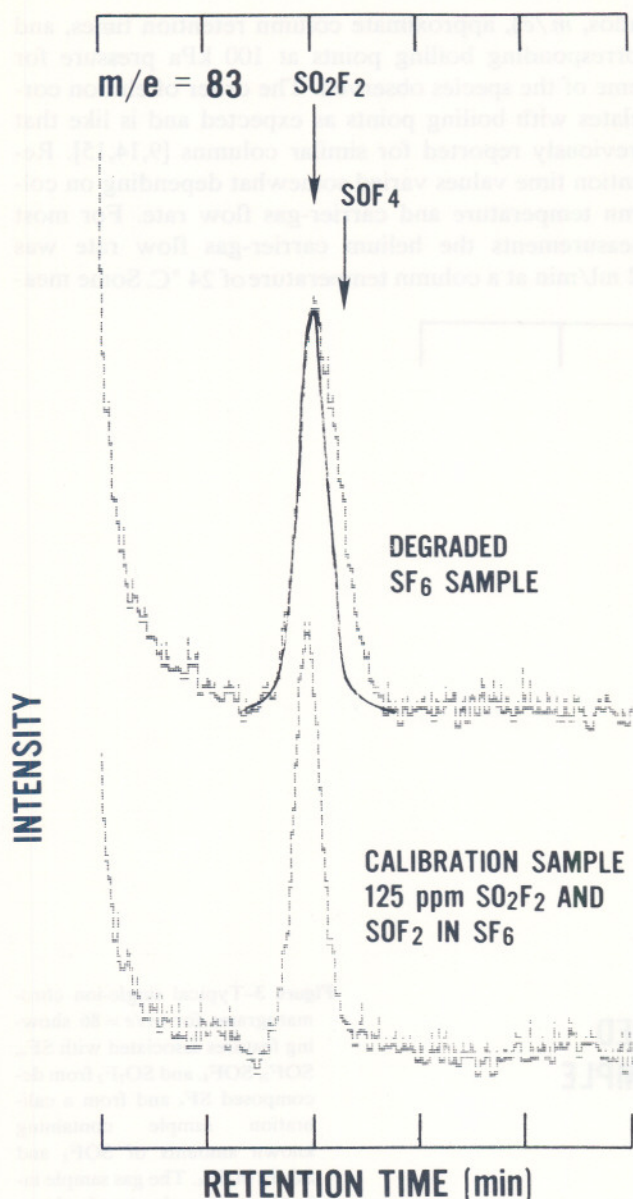


Figure 4—Typical single-ion chromatograms for $m/e=83$ showing broadening of the SO_2F_2 peak due to SOF_4 in the sample of decomposed SF_6 . The solid line represents a fit to the data of a curve which has a shape determined from calibration samples containing only SO_2F_2 and SOF_2 . The area under the solid curve is then compared with that from calibration data to determine SO_2F_2 concentration.

measurements were made at temperatures as high as 50°C with a corresponding flow rate of about 18 ml/min.

The ions selected for monitoring were those that corresponded to the best signal-to-noise ratios. For SOF_2 , the $m/e=86$ data gave slightly better signal than $m/e=67$, and for SO_2F_2 , $m/e=83$ gave the best results. However, analyses performed using both ions indicated for these gases gave results which were in satisfactory agreement. For SOF_4 , only the $m/e=86$ ion (SOF_2^+)

Table 2. Mass-to-charge ratios (m/e) of ions observed, approximate range of column retention times (at 24°C and 32 ml/min He flow rate), and boiling points (at 100 kPa pressure) for various gaseous species observed.

Gas	Observed m/e	Retention Time (min)	Boiling Points ($^\circ\text{C}$)
O_2	16	~ 0.2	-183.0
SF_3	19	$0.35-0.48$	-63.8
SO_2F_2	102,83	$0.8-1.3$	-55.4
SOF_4	86	$1.0-1.6$	-49.0
SOF_2	86,67	$1.6-2.4$	-43.8
H_2O	18,16	$3.1-5.0$	100.0
SO_2	64	$8.2-8.7$	-10.1

data could be used because of an excessively high background at $m/e=105$ (SOF_4^+), and because of the method for quantitative analysis which, as described below, required a direct comparison with SOF_2 also appearing at $m/e=86$.

In performing the gas analysis, samples of 0.8 ml volume were periodically (once every 1 to 2 h) extracted from the cell with a gas tight syringe and injected into the GC/MS. During the sampling period, about 4 min, the discharge was turned off. To assess the extent to which the equilibrium conditions in the cell were controlled by the discharge or influenced by relatively slow reactions in the bulk of the gas, the discharge was occasionally extinguished for long periods of up to 20 h. The gas was analyzed at the beginning and end of these periods.

3.3 GC/MS calibration

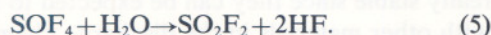
Quantitative analysis for the species SOF_2 , SO_2F_2 , SO_2 , OCS , and CO_2 , was accomplished by making direct comparisons of the GC/MS responses for unknown and reference gas samples as indicated by examples shown in figures 3 and 4. The absolute quantities in moles c were computed from the reference quantities c_r using $c = c_r(h_x/h_r)$, where h_x and h_r are respectively the responses for the unknown and reference samples corresponding to either normalized areas or peak heights of appropriate features in the chromatograms. All responses were normalized to the total SF_6 concentration, as indicated by the intensity S_{19} of the $m/e=19$ (F^+) feature, such that $h_{x,r} = S_{x,r}/S_{19}$. Although the intensity S_{19} was found to be roughly proportional to the quantity of gas injected, care was taken to insure that the calibration and unknown samples contained nearly identical quantities of SF_6 .

The calibration samples were prepared in the discharge cell at the beginning and end of each experiment by injecting known quantities of SOF_2 , etc., into "pure" SF_6 . A secondary reference prepared in a separate cell

was also sometimes used during discharge operation. Calibration samples prepared in the discharge cell usually agreed satisfactorily with the secondary reference. Nevertheless, averages of several calibrations made at the end of each experiment from references prepared in the discharge cell were used to calculate the absolute quantities reported here. This choice eliminated errors associated with determination of discharge-to-reference cell volume ratios, and ensured highest accuracy for the highest unknown sample concentrations which, as discussed below, were given the greatest weight in making fits to the data to determine limiting constant production rates. The calibrations performed at the beginning and during the experiments were used to estimate uncertainties.

In many cases calibrations were performed over a range of c_r values from 10 to 85 μ moles. Because the response of the instrument was linear over the range of interest (see fig. 5), it was usually sufficient to use a single, relatively high value of c_r for these measurements.

Care had to be taken in determining S_x or S_r to avoid errors due to peak interference, which was especially important in the case of SO_2F_2 as seen in figure 4. When SOF_4 was present, the SO_2F^+ peak at $m/e=83$ was broadened due to conversion of SOF_4 into SO_2F_2 within the column or membrane by hydrolysis [43],



An investigation of the influence of SOF_4 on the SO_2F_2 feature revealed that it affected only the area to

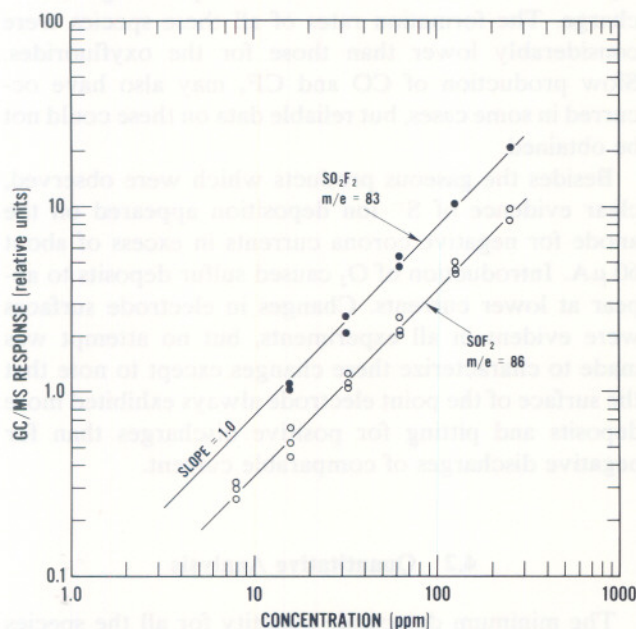


Figure 5—Calibration curves for SO_2F_2 and SOF_2 showing relative GC/MS response versus concentration.

the right of the peak. To correct for SOF_4 interference the SO_2F_2 data were analyzed by calculating, after background subtraction, the area under a curve fit to the peak and left side with a shape which was defined by a fit to SO_2F_2 data ($m/e=83$) from a reference sample not containing SOF_4 . This is indicated by the solid curve in figure 4. Generally, the conditions were uniform and stable enough that the peak shapes did not change appreciably during the course of a given experiment. Thus for the relatively broad oxyfluoride peaks, it was usually sufficient to consider only peak heights in the determination of either S_x or S_r .

The analysis of SOF_4 data was complicated by difficulties encountered in preparing and maintaining reliable reference sample for this gas. In earlier work, [37,38] quantitative data for SOF_4 were not reported. Recently SOF_4 was prepared by the method of DesMarteau [44] from direct reaction of SOF_2 with F_2 in a pressurized vessel. In a few cases, direct calibrations for SOF_4 were performed as described for the other oxyfluorides. However, for most of the results given here, the SOF_4 data were put on an absolute scale by making a direct comparison with measured SOF_2 concentrations using data at $m/e=86$.

From measurements made using many different reference samples containing different proportions of SOF_2 and SOF_4 , the relative response r of the instrument to these species at $m/e=86$ was determined, where

$$r = ([\text{SOF}_4]_r / [\text{SOF}_2]_r) (h_r(\text{SOF}_2) / h_r(\text{SOF}_4)). \quad (6)$$

The unknown concentrations $[\text{SOF}_4]_x$ were then computed from the SOF_2 concentrations using

$$[\text{SOF}_4]_x = r \frac{h_x(\text{SOF}_4)}{h_x(\text{SOF}_2)} [\text{SOF}_2]_x. \quad (7)$$

Examples of data from which SOF_4 concentrations were derived are shown in figure 6.

Either absolute or relative H_2O concentrations were measured in the gas for all cases. For the absolute measurements, the GC/MS calibration was performed using a previously calibrated, thin-film aluminum oxide hygrometer [45] inserted into the discharge cell containing SF_6 . The responses of the GC/MS to water vapor at $m/e=18$ and $m/e=16$ were compared to simultaneous readings from the hygrometer after sufficient time elapsed, usually more than 10 h, for the system to reach equilibrium. Because of the slow response time of the hygrometer and its susceptibility to damage from corrosive discharge by-products, it could not be used directly to monitor H_2O during discharge activity.

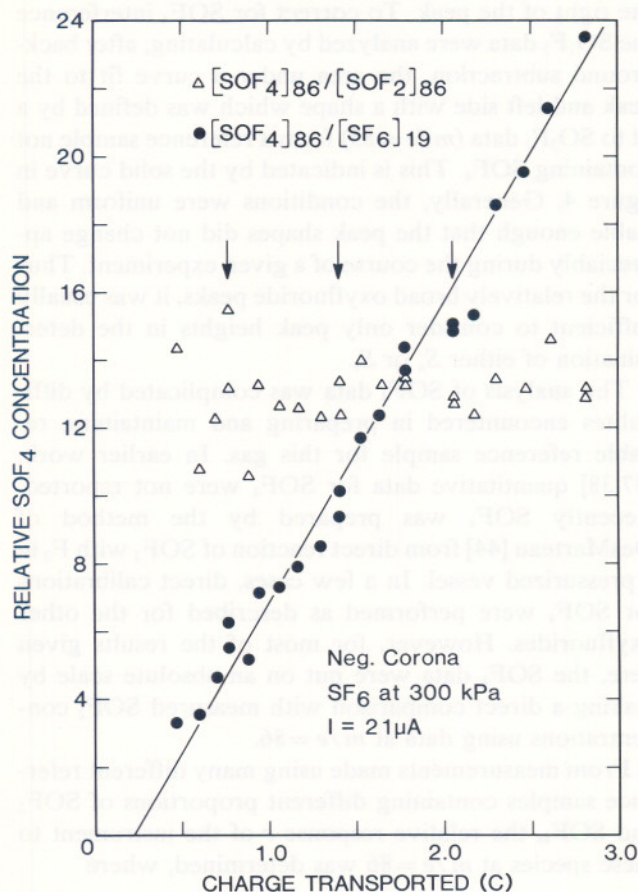


Figure 6—Relative normalized GC/MS response to SOF_4 and the ratios of SOF_4 to SOF_2 responses at $m/e=86$ versus net charge transported for 300 kPa SF_6 decomposed in negative corona at 21 μA . The arrows indicate times when the discharge was off for extended periods.

4. Results

4.1 Products Observed

The SF_6 gas was always analyzed after introduction into the cell and prior to turning on the discharge. The most common initial contaminants observed were varying trace amounts of CF_4 , H_2O , and air. Although the discharge chamber was evacuated to 1.3×10^{-5} Pa ($\sim 1 \times 10^{-7}$ Torr) before introducing the gas, it was not baked. Therefore, if left undisturbed, the water vapor concentration would build up slowly to an equilibrium level. In most cases it would rise from initial levels of less than 10 ppm by volume to an equilibrium level between about 150 and 300 ppm by volume determined by the ambient temperature, initial cleanliness of surfaces, etc. The initial H_2O concentration at the start of the discharge was thus determined by the time that the gas had been left undisturbed in the cell. Once the discharge was initiated, the concentration of H_2O was al-

ways observed to increase more rapidly than normal, presumably because of desorption from surfaces heated by the discharge [37]. However, the maximum H_2O concentration never significantly exceeded that associated with equilibrium under normal, undisturbed conditions. In later stages of discharge operation, a slow decrease in H_2O content was usually observed, which, as discussed later, was undoubtedly indicative of the role played by gas-phase H_2O in the discharge chemistry.

The O_2 concentration was observed to gradually increase during operation of the discharge. In "pure" SF_6 , its concentration was always too small to measure accurately by the present method. The increase in O_2 content during these experiments could be accounted for by release from electrode materials during the discharge and from introduction of low levels of air contamination during gas sampling. To assess its role in oxyfluoride production, a few measurements were made with controlled levels of O_2 between 1 and 10% content by volume.

Of the observable species generated in the discharge, the oxyfluorides SOF_2 , SO_2F_2 , and SOF_4 were produced in greatest abundance. Other highly reactive species such as HF and F_2 possibly formed in conjunction with the oxyfluorides at comparable rates could not be observed by the GC/MS method used. One could argue that on the time scales considered here these are not really stable since they can be expected to react rapidly with other materials in the discharge chamber.

Of the remaining species which could be observed in the gas only SO_2 , OCS , CO_2 , and previously mentioned O_2 , showed clear evidence of build-up during the discharge. The formation rates of all these species were considerably lower than those for the oxyfluorides. Slow production of CO and CF_4 may also have occurred in some cases, but reliable data on these could not be obtained.

Besides the gaseous products which were observed, clear evidence of S^- ion deposition appeared on the anode for negative corona currents in excess of about 60 μA . Introduction of O_2 caused sulfur deposits to appear at lower currents. Changes in electrode surfaces were evident in all experiments, but no attempt was made to characterize these changes except to note that the surface of the point electrode always exhibited more deposits and pitting for positive discharges than for negative discharges of comparable current.

4.2 Quantitative Analysis

The minimum detectable quantity for all the species observed was about 1.0 μmole . The experiments were typically terminated before the quantity of any oxy-

fluoride within the discharge chamber exceeded about 100 μ moles.

The major sources of uncertainty in the quantitative analysis were due to drifts in the GC/MS response and uncertainties in the reference samples. The dominant short-term drift associated with heating of the mass spectrometer ion source by the electron gun filament could be largely overcome by heating the source prior to gas sample injection. Of more significance in determining overall uncertainty were long-term drifts associated, for example, with slow changes in mass spectrometer tuning, ion detection efficiency, and GC-column conditions. To reduce accidental errors associated with reference sample preparations, several calibrations were always performed with different reference samples.

The estimated uncertainties in measured absolute SOF_2 and SO_2F_2 concentrations are less than $\pm 25\%$. The SOF_4 uncertainties are higher ($\pm 45\%$) because of the indirect method of determination and the required assumption that the relative GC/MS responses to SOF_2 and SOF_4 at $m/e = 86$ remained constant.

4.3 Production Rates

The production rates were derived from fits to the measured concentration data plotted versus either net energy dissipated or charge transported as shown in figures 7-13. The term "concentration" refers here to the absolute quantity of gas in moles which was produced in the discharge and which was assumed to be uniformly distributed within the cell volume. The production curves in most cases exhibit deviations from linearity which are most evident at the lowest values of u or Q . Best fits to the data over the entire ranges were found to be of the forms:

$$c(u) = c'_0 + A'u^{1+\epsilon}, \quad c(Q) = c_0 + A'Q^{1+\epsilon}, \quad (8)$$

where c_0 , c'_0 , A , A' , ϵ , and ϵ' are fitting parameters. The first pair allows for a small, usually undetectable initial concentrations, and the last pair represents a measure of deviations from linearity. Examples of values obtained for these parameters are tabulated and discussed in the Appendix.

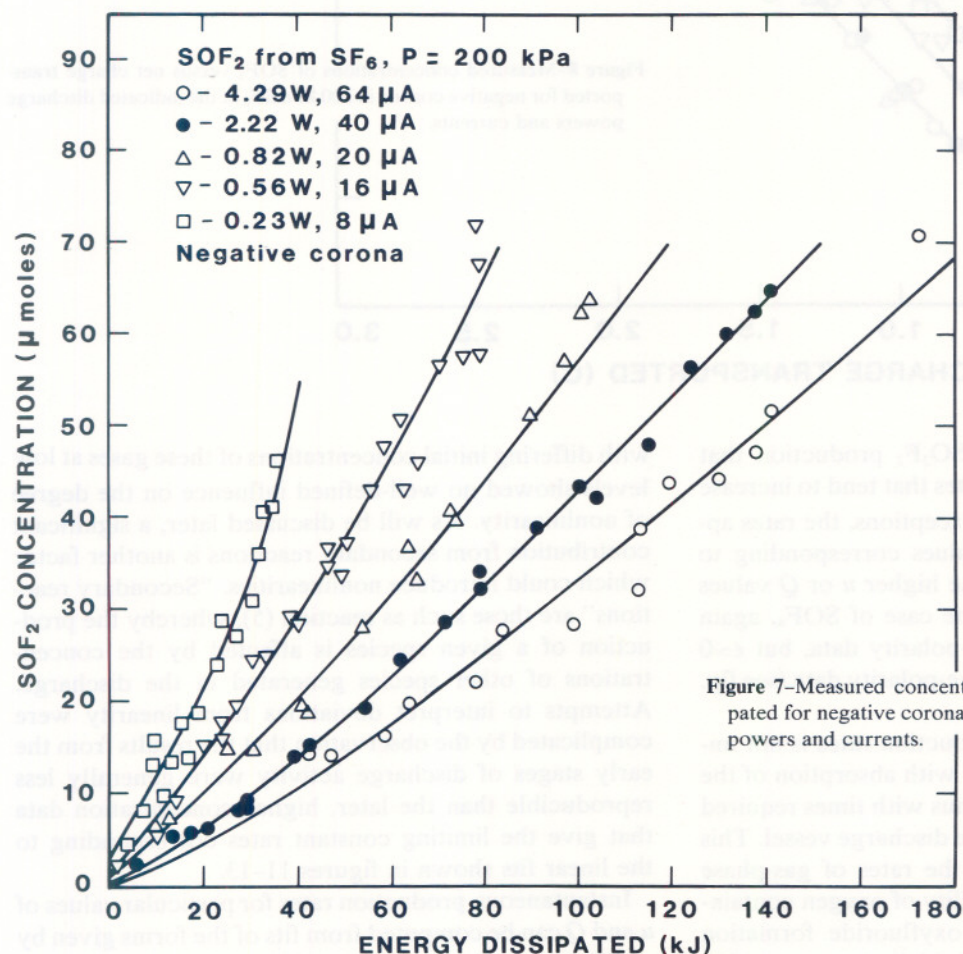


Figure 7—Measured concentrations of SOF_2 versus net energy dissipated for negative corona in 200 kPa SF_6 at the indicated discharge powers and currents.

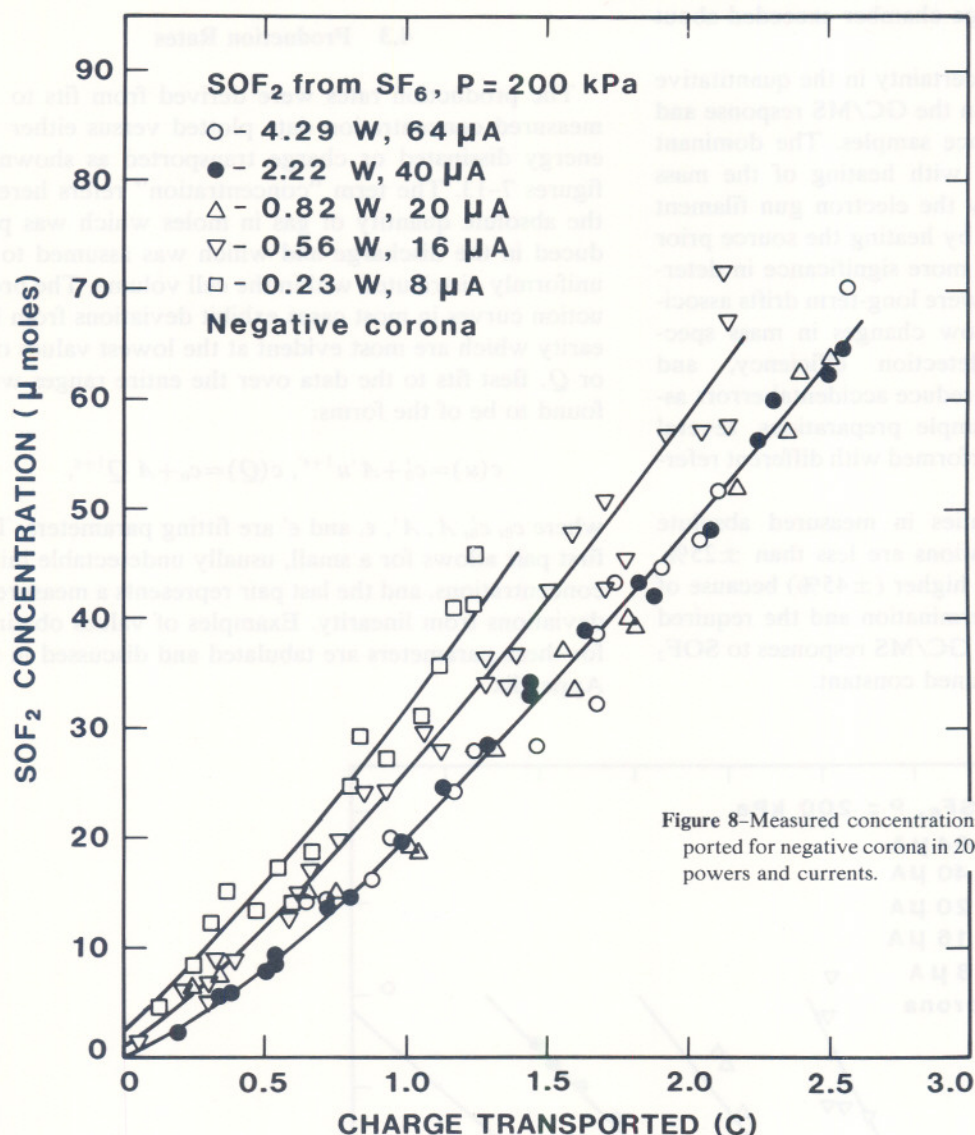


Figure 8—Measured concentrations of SOF₂ versus net charge transported for negative corona in 200 kPa SF₆ at the indicated discharge powers and currents.

It was found for SOF₂ and SO₂F₂ production that $1 > \epsilon > 0$ in all cases, indicating rates that tend to increase with time. However, with few exceptions, the rates appeared to approach constant values corresponding to straight line fits to the data at the higher u or Q values as shown in figures 11–13. In the case of SOF₄, again $1 > \epsilon > 0$ was found for positive-polarity data, but $\epsilon \approx 0$ gave the best fits for most negative-polarity data (see fig. 6).

The initial increase in the production rates is not understood but could be associated with absorption of the product gases on the walls and thus with times required to establish equilibrium within the discharge vessel. This effect might also be related to the rates of gas-phase reactions that depend on availability of oxygen containing contaminants required for oxyfluoride formation such as H₂O and O₂ which often initially increased after onset of the discharge. However, measurements made

with differing initial concentrations of these gases at low levels showed no well-defined influence on the degree of nonlinearity. As will be discussed later, a significant contribution from secondary reactions is another factor which could introduce nonlinearities. "Secondary reactions" are those such as reaction (5), whereby the production of a given species is affected by the concentrations of other species generated in the discharge. Attempts to interpret deviations from linearity were complicated by the observation that the results from the early stages of discharge activity were generally less reproducible than the later, higher concentration data that give the limiting constant rates corresponding to the linear fits shown in figures 11–13.

Instantaneous production rates for particular values of u and Q can be computed from fits of the forms given by eq (8) as previously reported [38] (see the Appendix). The limiting constant rates, however, appear to be more

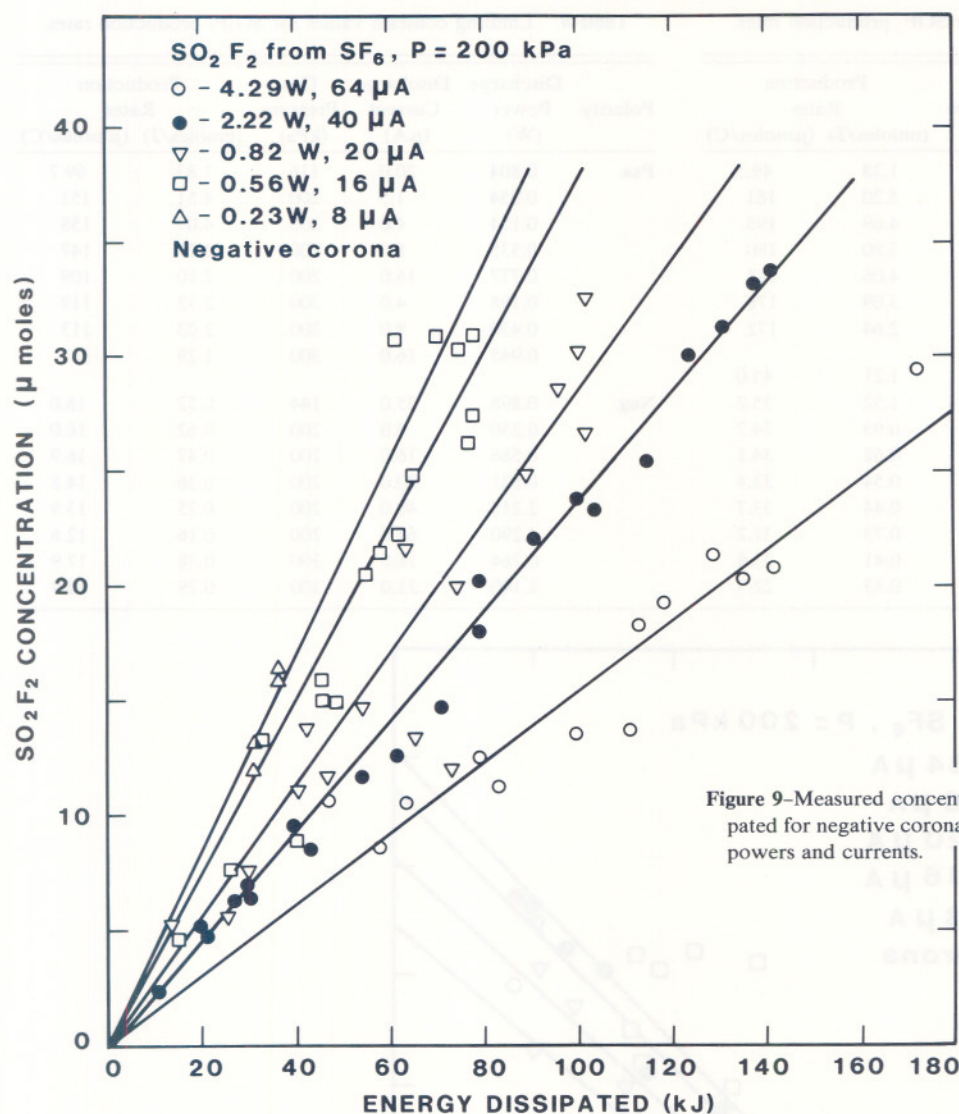


Figure 9—Measured concentrations of SO₂F₂ versus net energy dissipated for negative corona in 200 kPa SF₆ at the indicated discharge powers and currents.

useful in describing trends as functions of gas or discharge conditions. A precise definition of these rates and their relationship to the instantaneous rates from eq (8) are given in the Appendix.

Results for the limiting constant production rates of SOF₂, SO₂F₂, and SOF₄ are given in tables 3–5. Both r_u and r_q are listed as functions of discharge conditions (polarity, current, and power) and gas pressure. Gas pressures range from 114 kPa (~1.1 atm) to 300 kPa (~3 atm). Discharge currents from 1.5 μA to 64 μA with corresponding power dissipations from 0.054 W to 4.3 W are included.

Production rates were estimated in some cases for observable minor species, namely SO₂, OCS, and CO₂ as indicated in table 6. The rates for these are seen to be an order of magnitude or more smaller than those for the predominant oxyfluorides. Data for SO₂ are also shown in figure 13.

Although the results showed indications of gas-phase H₂O consumption, particularly in the later stages of discharge activity (see figs. 11–13), no attempt was made to determine the rates of consumption. The discharge appeared to suppress the equilibrium level of H₂O in the cell, and there was evidence that the degree of suppression increased with increasing current and therefore increasing oxyfluoride production (compare figs. 12 and 13). It was found in more recent studies [46] with corona in SF₆/O₂ mixtures that the CO₂ production is nonlinear and depends significantly on O₂ content and availability of carbon from the electrode surface. The same may apply to OCS, although this could not be ascertained from the data obtained.

Based on the previously noted dominant sources of error in quantitative analysis and the uncertainties in fitting the data, the limiting rate values given in tables 3 and 4 for SOF₂ and SO₂F₂ have been assigned a max-

Table 3. Limiting constant values for SO_2F_2 production rates.

Polarity	Discharge Power (W)	Discharge Current (μA)	Gas Pressure (kPa)	Production Rates (nmol/J) ($\mu\text{mol/C}$)
Pos.	0.804	20.0	116	1.28 49.5
	0.054	1.5	200	5.20 181
	0.335	8.0	200	4.69 195
	0.777	16.0	200	3.80 180
	0.198	4.0	300	4.06 187
	0.430	8.0	300	3.09 178
	0.945	16.0	300	2.64 172
Neg.	0.898	25.0	144	1.21 45.0
	0.230	8.0	200	1.52 35.2
	0.586	16.0	200	0.93 34.7
	0.821	20.0	200	0.68 34.1
	2.225	40.0	200	0.54 32.4
	4.290	64.0	200	0.44 33.7
	0.764	16.0	300	0.73 31.2
	1.140	21.0	300	0.41 23.9
	1.820	30.0	300	0.33 22.3

Table 4. Limiting constant values for SO_2F_2 production rates.

Polarity	Discharge Power (W)	Discharge Current (μA)	Gas Pressure (kPa)	Production Rates (nmol/J) ($\mu\text{mol/C}$)
Pos.	0.804	20.0	116	1.83 69.7
	0.054	1.5	200	4.51 151
	0.154	4.0	200	4.07 158
	0.335	8.0	200	3.27 147
	0.777	16.0	200	2.10 109
	0.198	4.0	300	2.32 119
	0.430	8.0	300	2.03 113
Neg.	0.945	16.0	300	1.29 111
	0.898	25.0	144	0.52 18.0
	0.230	8.0	200	0.62 16.0
	0.586	16.0	200	0.47 16.9
	0.821	20.0	200	0.36 14.8
	2.215	40.0	200	0.25 13.9
	4.290	64.0	200	0.16 12.6
	0.764	16.0	300	0.38 17.9
	1.140	21.0	300	0.29 16.9

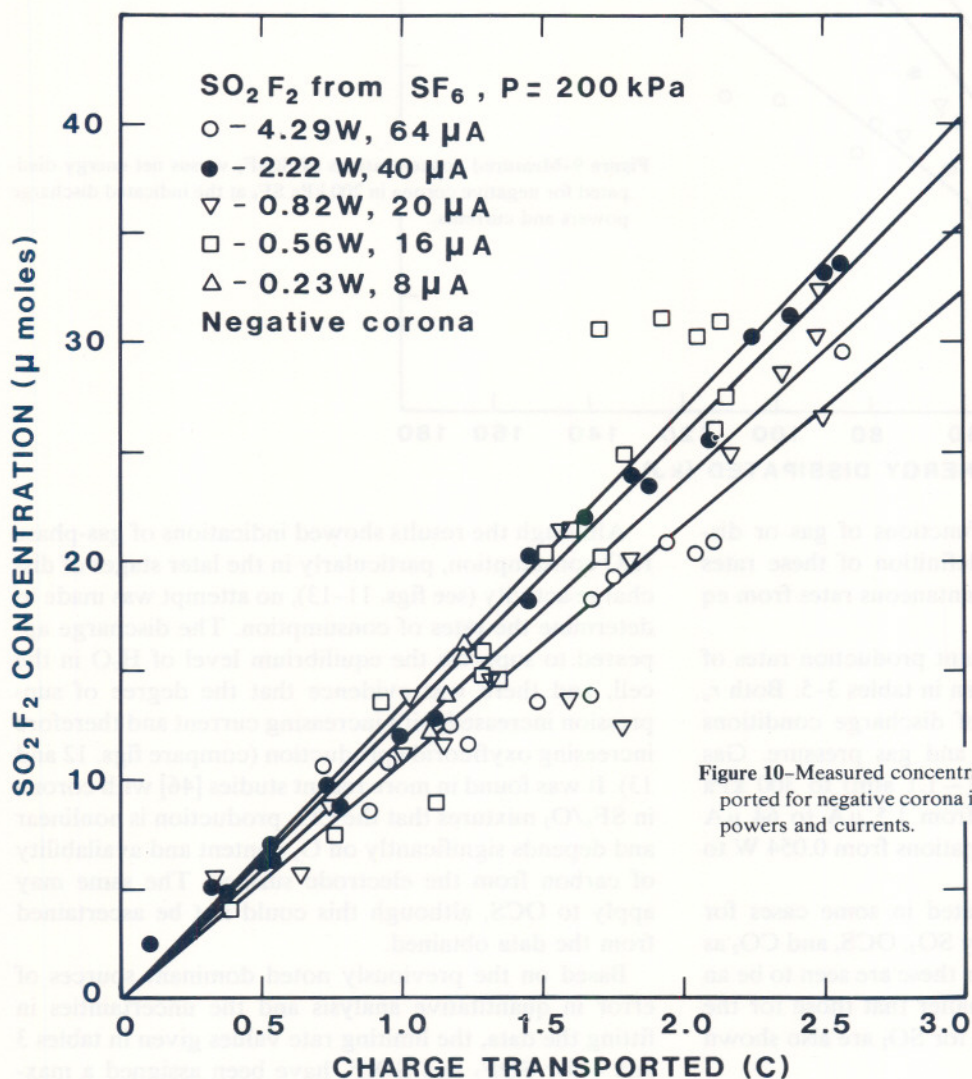


Figure 10—Measured concentrations of SO_2F_2 versus net charge transported for negative corona in 200 kPa SF_6 at the indicated discharge powers and currents.

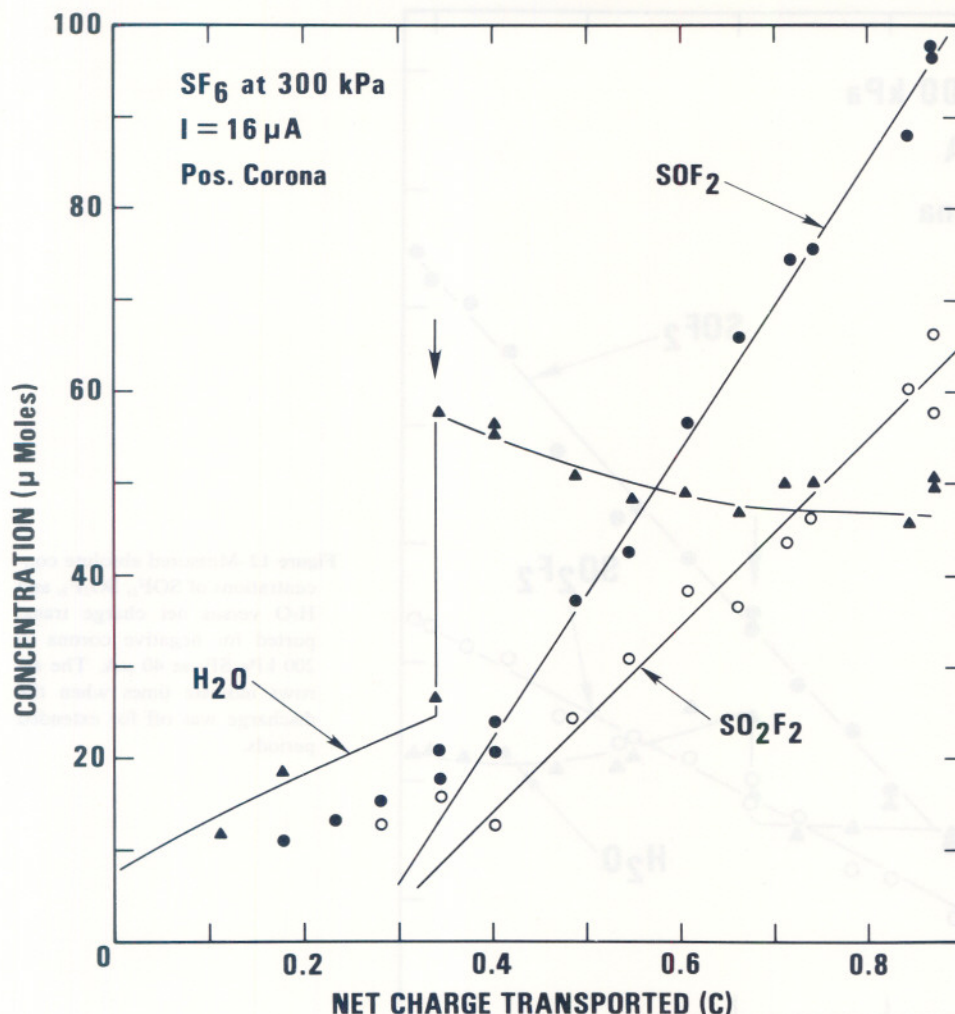


Figure 11—Measured absolute concentrations of SOF_2 and SO_2F_2 and relative concentrations of H_2O versus net charge transported for positive corona in 300 kPa SF_6 at 16 μA . The arrow indicates a time when the discharge was off for an extended period.

Table 5. Limiting constant values for SOF_4 production rates.

Polarity	Discharge Power (W)	Discharge Current (μA)	Gas Pressure (kPa)	Production Rates	
				(nmoles/J)	($\mu\text{moles/C}$)
Pos.	0.804	20.0	116	7.02	290
	0.054	1.5	200	7.04	260
	0.335	8.0	200	8.60	373
	0.777	16.0	200	8.45	418
	0.198	4.0	300	5.79	292
	0.430	8.0	300	5.92	343
	0.945	16.0	300	7.08	431
Neg.	0.898	25.0	144	0.85	30.1
	0.230	8.0	200	0.92	23.8
	0.586	16.0	200	0.97	34.6
	0.821	20.0	200	1.05	41.5
	2.215	40.0	200	0.90	49.7
	4.290	64.0	200	0.94	63.6
	0.764	16.0	300	0.44	20.6
	1.140	21.0	300	0.39	21.0

Table 6. Estimated production rates for minor species from negative corona in SF_6 .

Species	Discharge Current (μA)	Pressure (kPa)	Production Rates	
			(nmoles/J)	($\mu\text{moles/C}$)
SO_2	25	114	0.008	0.3
SO_2	40	200	0.002	0.1
OCS	40	200	1.3×10^{-5}	7.2×10^{-3}
CO_2	40	200	0.035	2.0

imum uncertainty of $\pm 35\%$. The rates for SOF_2 typically have less uncertainty than those for SO_2F_2 , and results from positive corona have higher uncertainty than those from negative corona. The latter trend is due to the greater fluctuations in the discharge current (see fig. 2). The uncertainties for SOF_4 are higher but are estimated to be always less than $\pm 57\%$. The rates given in table 6 for the minor products are only estimates since a reasonable error assessment was impossible.

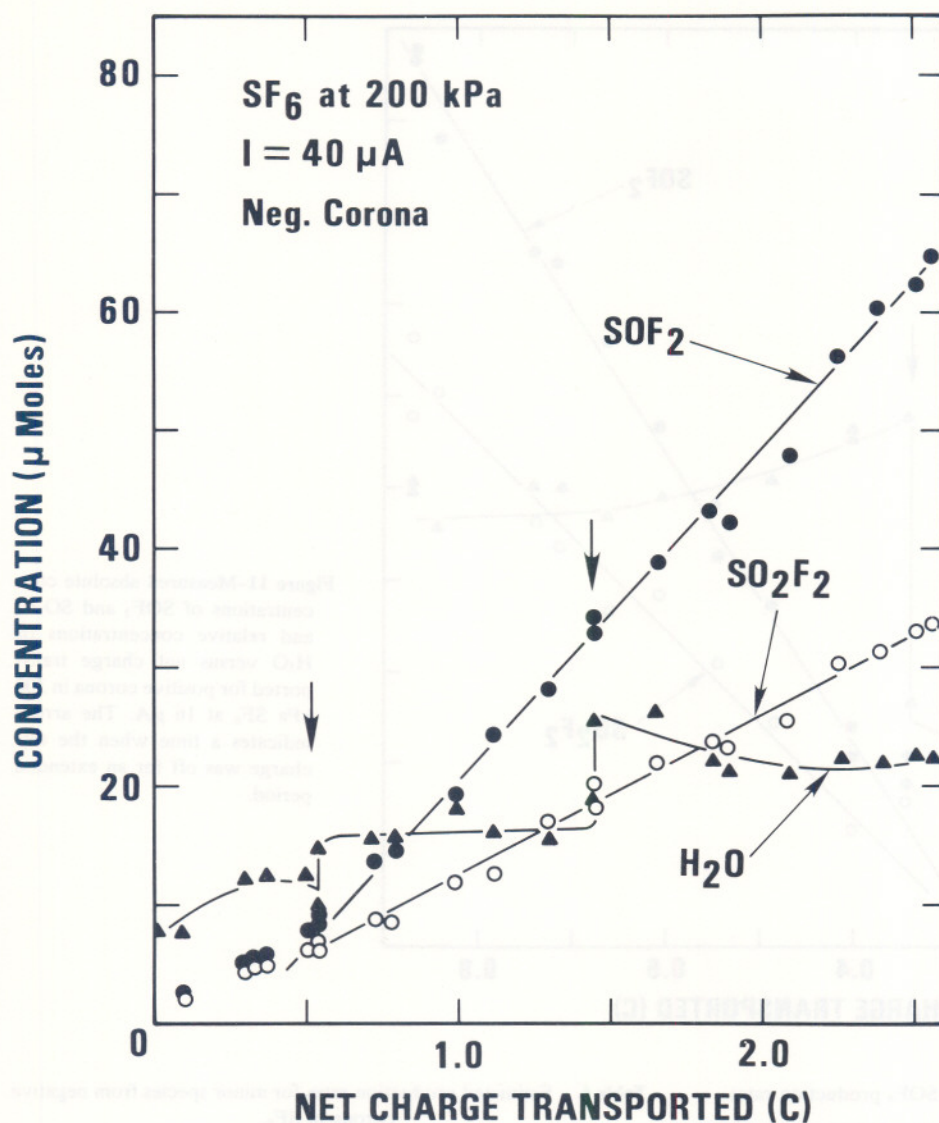


Figure 12—Measured absolute concentrations of SOF_2 , SO_2F_2 , and H_2O versus net charge transported for negative corona in 200 kPa SF_6 at 40 μA . The arrows indicate times when the discharge was off for extended periods.

Important observations from the data in tables 3–5 include:

- 1) The production rates for SOF_2 , SO_2F_2 , and SOF_4 are of comparable magnitude to within roughly a factor of 3. For most cases, particularly at the higher pressures and power levels, the order of production rates is $r_q(\text{SOF}_4) > r_q(\text{SOF}_2) > r_q(\text{SO}_2\text{F}_2)$.
- 2) Oxyfluoride production does not change dramatically with pressure. One exception is the large relative drop in the SOF_2 and SO_2F_2 rates compared to SOF_4 in going from 200 to 116 kPa for positive polarity.
- 3) Oxyfluoride production under most conditions increases by a factor of 5 or more in going from negative to positive polarities for discharges of comparable power levels.

- 4) The charge rates-of-production for SOF_2 and SO_2F_2 vary less with discharge level than the corresponding energy rates, whereas the opposite appears to be true for SOF_4 (see also figs. 14 and 15).

The trends noted for SOF_2 and SO_2F_2 from the fourth observation imply that the time rates-of-production for these are more nearly directly proportional to the current than the power, i.e., $dc/dt \propto i$. Because of the relatively large uncertainties, it can only be stated that the SOF_4 rates behave like $dc/dt \propto i^a$, with $1 < a < 2$. The results in figure 15 would in fact suggest that $dc/dt \propto p$ for this species.

The vertical arrows in figures 6 and 11–13 indicate times when the discharge was turned off for periods of 12 to 20 h. No significant changes in the oxyfluoride content occurred during these times, therefore indicating that reactions involving the oxyfluorides in the

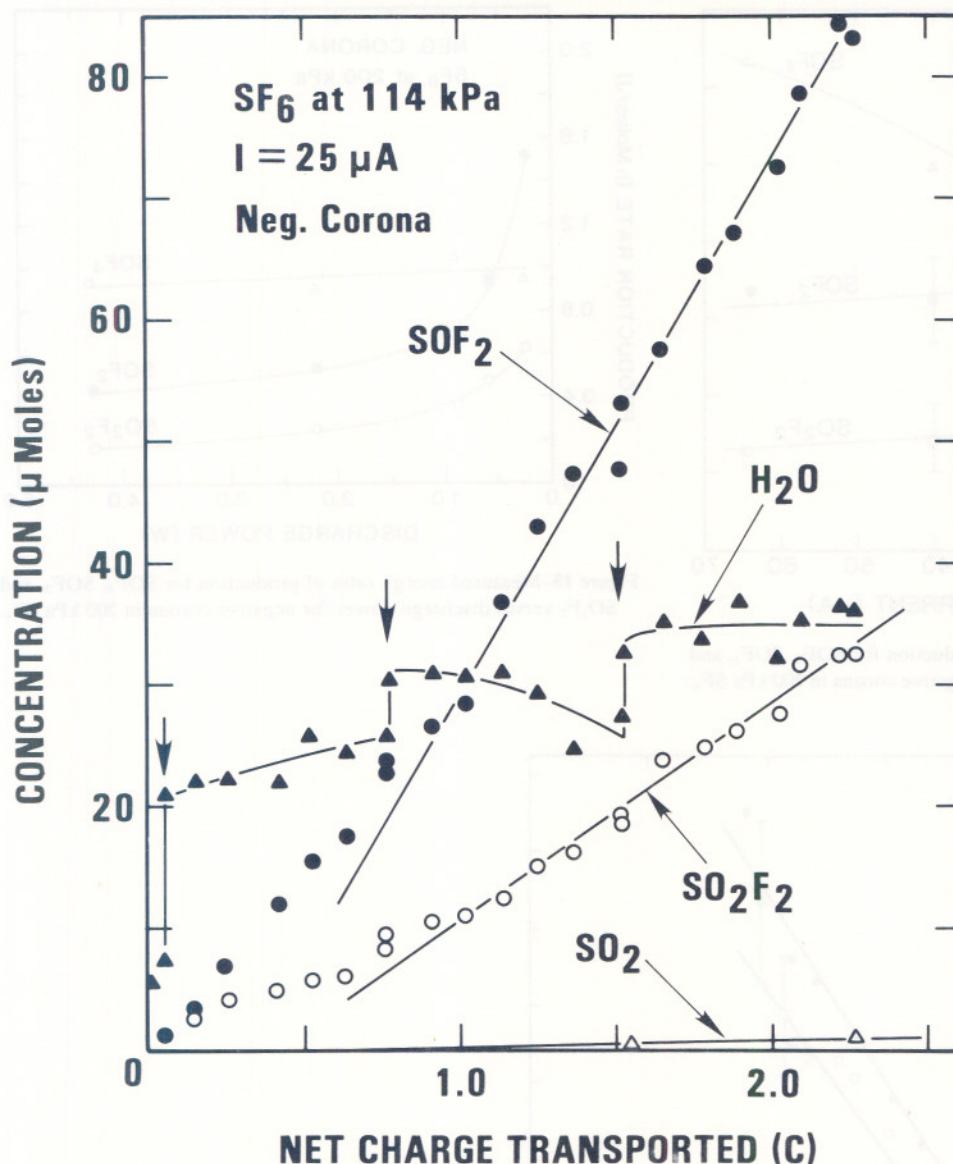


Figure 13—Measured absolute concentrations of SOF_2 , SO_2F_2 , SO_2 , and H_2O versus net charge transported for negative corona in 114 kPa SF_6 at 25 μA . The arrows indicate times when the discharge was off for extended periods.

bulk of the gas outside the discharge region were too slow to observe. The H_2O concentrations on the other hand exhibited increases during times when the discharge was off (see figures 11–13), consistent with the previously noted evidence that chemical processes associated with the discharge consume water vapor and suppress its equilibrium level in the gas.

4.4 SF_6/O_2 Mixtures

Extensive studies of discharge-induced gas chemistry in SF_6/O_2 and SF_6/N_2 mixtures are currently underway and will be reported later [46]. Because of the possible importance of gas-phase O_2 in oxyfluoride production, an assessment of its role could only be made by considering mixtures in which its content was increased signifi-

cantly above the normally occurring trace levels over which there was no control. Results are shown in figures 16–18 for SOF_2 , SO_2F_2 , and SOF_4 production in mixtures containing 1 to 10% O_2 in SF_6 compared with “pure” SF_6 containing the normal trace amounts of O_2 . The measurements for all these mixtures were performed at the same indicated total gas pressure and discharge current. The error bars correspond to estimated uncertainties in measured absolute concentrations.

These results show that to within the measurement uncertainties the addition of 1% O_2 has virtually no influence on the production of the oxyfluorides. However, at higher O_2 content, the total oxyfluoride yield actually drops, and the drop is most evident for SOF_2 (see fig. 16).

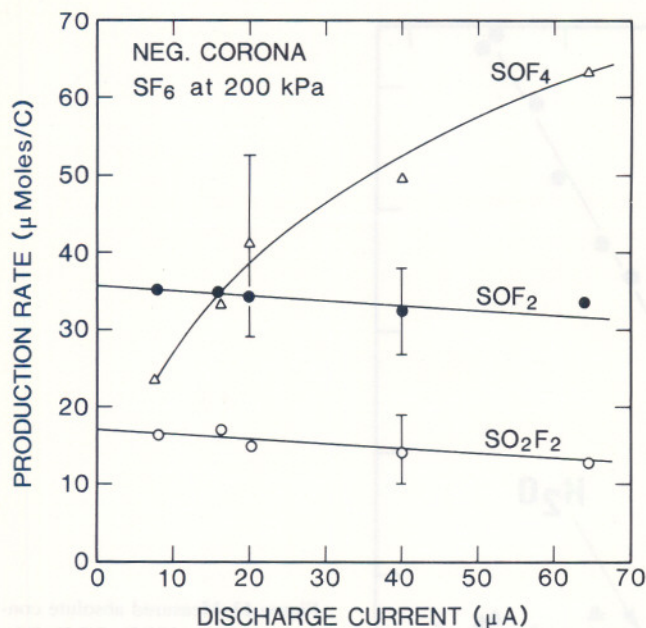


Figure 14—Measured charge rates of production for SOF_4 , SOF_2 , and SO_2F_2 versus discharge current for negative corona in 200 kPa SF_6 .

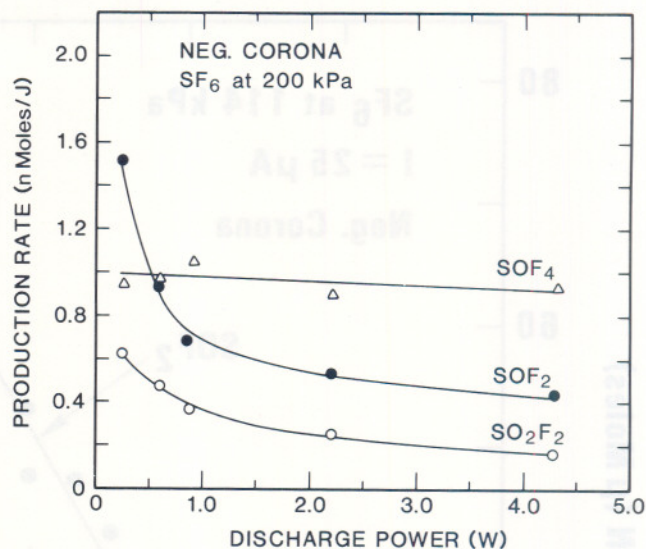


Figure 15—Measured energy rates of production for SOF_4 , SOF_2 , and SO_2F_2 versus discharge power for negative corona in 200 kPa SF_6 .

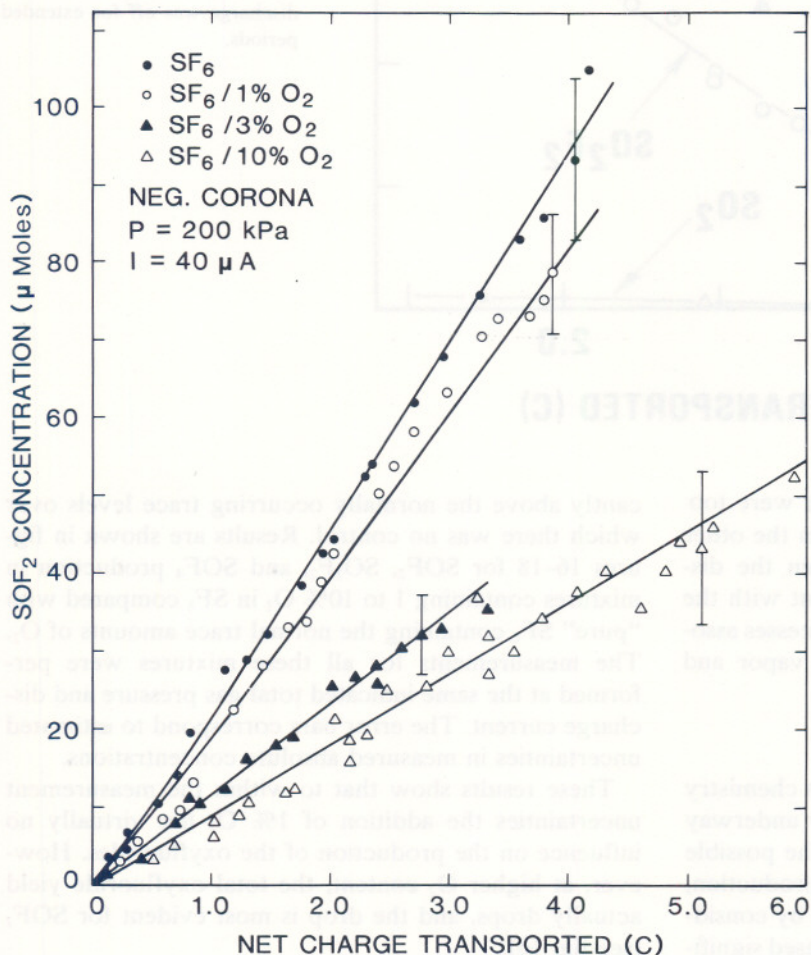


Figure 16—Measured absolute SOF_2 concentrations versus net charge transported for 40 μA negative corona in SF_6/O_2 mixtures containing the indicated percent-by-volume concentrations of O_2 . The "pure" SF_6 contained trace levels of O_2 which could not be accurately determined.

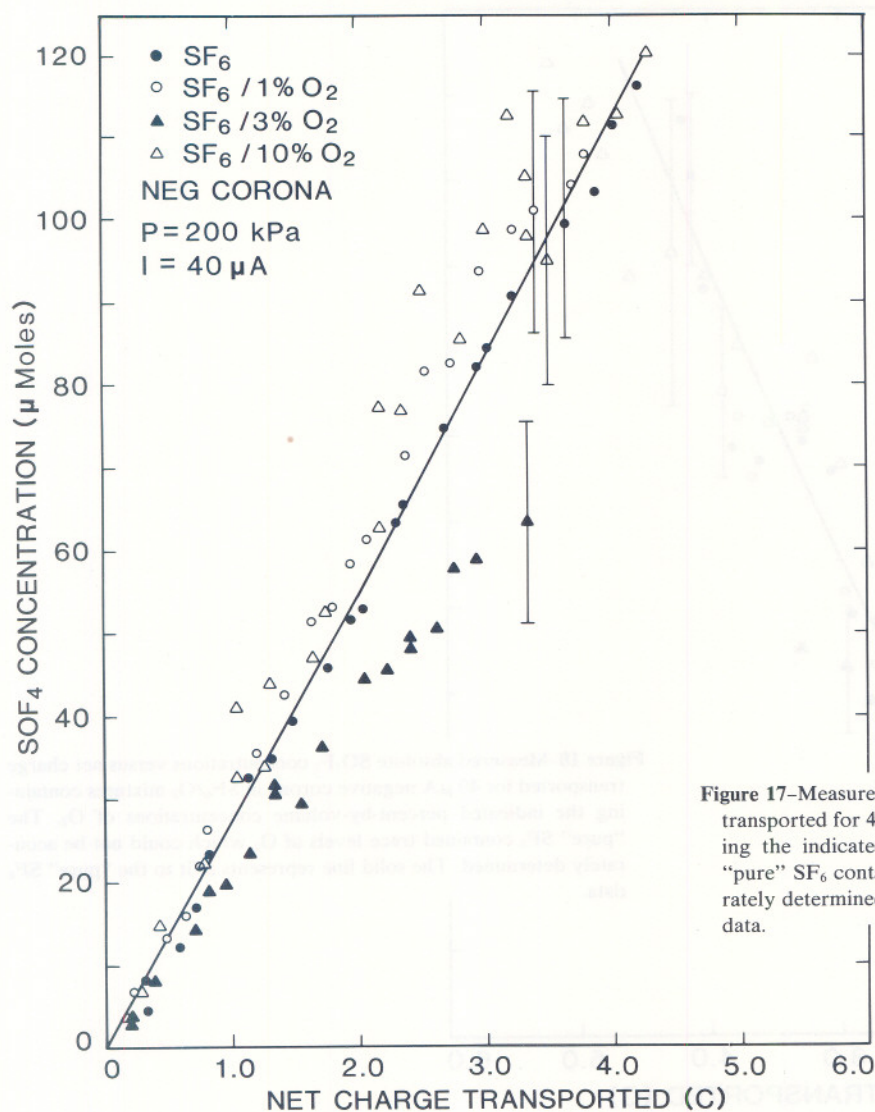


Figure 17—Measured absolute SOF_4 concentrations versus net charge transported for $40 \mu\text{A}$ negative corona in SF_6/O_2 mixtures containing the indicated percent-by-volume concentrations of O_2 . The “pure” SF_6 contained trace levels of O_2 which could not be accurately determined. The solid line represents a fit to the “pure” SF_6 data.

5. Discussion

5.1 Comparisons With Previous Observations

The oxyfluoride production rates found here are comparable in magnitude to many of those previously reported in other types of SF_6 electric discharges (see table 1). However, any comparisons with other results is of questionable significance since all previous measurements were performed under dissimilar conditions. The measurements by Chu et al. [18], which are most nearly like those of the present experiments, were performed with corona generated by 60-Hz ac voltage applied to aluminum electrodes in SF_6 at a pressure of about 155 kPa. The corona evidently occurred near the peaks of each half-cycle and was mainly characterized by pulses with an average magnitude of 10^3 pC and a repetition rate of 2 kHz. From the information provided, the total $\text{SOF}_2 + \text{SO}_2\text{F}_2$ production rate from this

measurement is estimated to lie between 620 and $1400 \mu\text{moles/C}$. The conditions most like this in the present work would correspond to the positive discharge at $1.5 \mu\text{A}$ which yielded a net rate for $\text{SOF}_2 + \text{SO}_2\text{F}_2 + \text{SOF}_4$ production of $592 \mu\text{moles/C}$.

Although the present result is close to that of Chu et al., it is disturbing that they do not observe SOF_4 . It is conceivable that this can be explained by a conversion of SOF_4 to SO_2F_2 via reaction (eq (5)) in the gas sampling process. Other cases [14,24] where there was failure to see SOF_4 from corona or “weak-current” discharges in SF_6 , even though SO_2F_2 was reported to be a predominant product, might also be accounted for by hydrolysis of SOF_4 . There are documented cases [8–10,23] where SOF_4 was observed in low-current discharges and even appeared as the dominant product.

Boudene et al. [15], Sauers et al. [20,39], and Castonguay [22] all report total oxyfluoride energy rates-of-

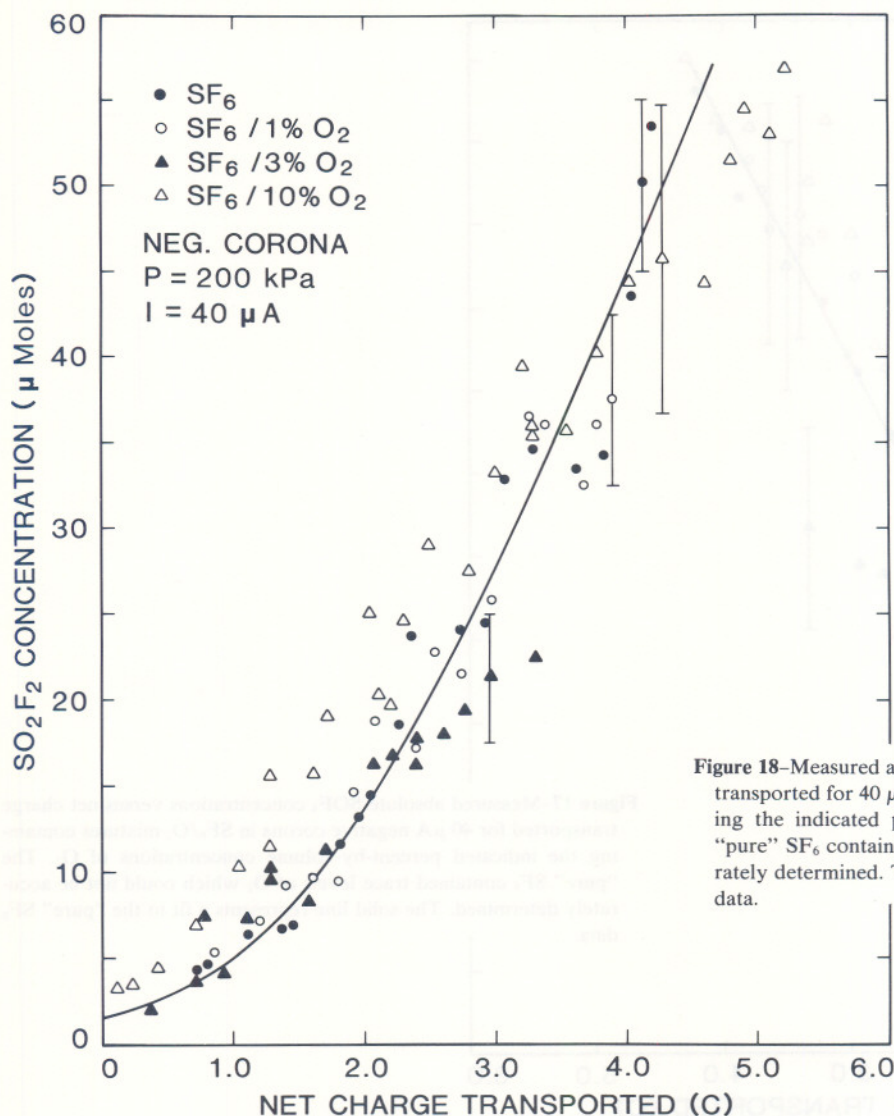


Figure 18—Measured absolute SO₂F₂ concentrations versus net charge transported for 40 μA negative corona in SF₆/O₂ mixtures containing the indicated percent-by-volume concentrations of O₂. The “pure” SF₆ contained trace levels of O₂ which could not be accurately determined. The solid line represents a fit to the “pure” SF₆ data.

production in SF₆ arcs and sparks with stainless steel electrodes that are comparable in magnitude to some of the rates found here (see table 1). However, in these types of discharges, which generate predominantly SOF₂, metal vapors and thermal dissociation may play an important role because of the high levels of power dissipation. The present results are consistent with previous observations and arguments [14,16,19,24] that SO₂F₂ and SOF₄ should become more prevalent as by-products when the discharge power level is reduced.

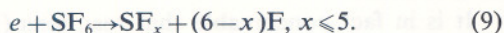
Net time rates-of-production that are directly proportional to discharge current rather than power are shown in recent relative measurements by Ophel et al. [26] of the total hydrolyzable fluoride production from stainless steel point-plane corona in flowing SF₆ at 440 kPa. This behavior would be consistent only with the results found here for SOF₂ and SO₂F₂. Were SOF₄ to become

a major component among the hydrolyzable species detected, then the present results indicate that for a single point electrode, proportionality to current need not be expected.

5.2 Possible Mechanisms for Oxyfluoride Formation

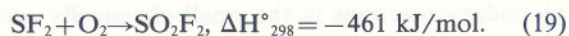
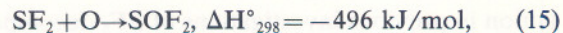
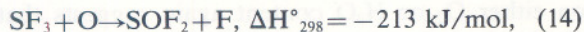
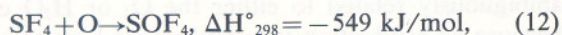
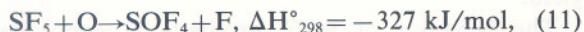
It is useful as a guide to the interpretation of the results to consider some of the plausible sequences of reactions which could account for production of SOF₂, SO₂F₂, and SOF₄ in a corona discharge. It should be cautioned, however, that the chemical processes that can occur in an electrical discharge are undoubtedly of a complicated, multistep nature, and no attempt will be made to present an exhaustive listing of the multitude of reactions possible. Instead the discussion here will be limited to previously suggested processes that appear relevant to the interpretation of the present results.

A corona is a relatively weak plasma in which the electron temperature greatly exceeds the gas temperature and in which nonequilibrium conditions prevail [47]. It is therefore expected that the initial stage of SF₆ decomposition predominantly results from dissociation of molecules by electron collisions. At electric field-to-gas density ratios, E/N , close to the critical value where a growth in the net ionization of the gas becomes possible, the mean electron energies in an SF₆ discharge are theoretically estimated [48–50] to be between 5 and 10 eV. Thus from a consideration of the known ionization, attachment, and bond dissociation energies [51–56] of SF₆, the initial step in the decomposition is presumed to involve the energetically favorable electron impact dissociation processes leading to various ion and neutral fragments, e.g.,



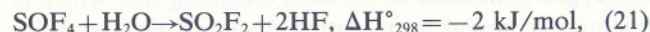
Multistep dissociation might also contribute, e.g., dissociation of the fragment such as $e + \text{SF}_4 \rightarrow \text{SF}_3 + \text{F} + e$. From energetic considerations, the greatest contribution will probably be from dissociation leading to the larger neutral fragments SF_{*x*}, $x = 3, 4, 5$. This presumption is supported by calculations by Masek et al. [57] of dissociative fragment production rates from electron swarms in SF₆ and SF₆/O₂ mixtures using numerical solutions of the Boltzmann equation. Moreover, the species SF₄ is reported to be the most stable and most abundant primary product from both thermal dissociation of SF₆ at moderate temperatures [60–61] and from relatively cool electric discharges [20,21,30].

It is known [8] that in the absence of reactive surfaces or gaseous contaminants, the products of SF₆ dissociation rapidly recombine through relatively fast processes such as proposed by Gonzalez and Schumacher [58] to explain the observed thermal conversion of SF₄ + F₂ into SF₆. The presence of oxygen, or oxygen containing species in the discharge region can interfere with the recombination process and give rise to the formation of oxyfluorides, free fluorine, and HF. Some of the energetically favorable bimolecular reactions that could lead directly to oxyfluoride formation include [62]:



Reactions (13), (14), and (18) have previously been invoked [1,6] to account for rapid SOF₂ and SO₂F₂ formation from pyrolysis of SF₆ in the presence of O₂. Reactions (11)–(14) have been mentioned by d'Agostino and Flamm [8] as mechanisms for oxyfluoride production from SF₆/O₂ mixtures in low-pressure, radio frequency discharges. Reaction (16) has been suggested by Leipunskii et al. [3]. From low-pressure SF₆/O₂ mixtures with relatively high O₂ content there is evidence [21,58,63] that ion and neutral species such as SOF₃⁺, SO₂F₃⁺, SO₂F₅⁺, S₃OF₇⁺, SF₅O₂, SF₅O, SF₅O₂SF₅, and SF₅O₃SF₅ are also formed which may act as intermediates in the production of the observed oxyfluorides. The large, relatively unstable species such as S₂F₁₀ and SF₅O₃SF₅ could not be observed by the present chromatographic method. It has been argued [58] that for conditions like those considered here, their formation is improbable.

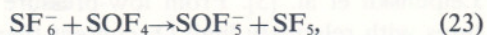
Within the bulk of the gas or on the walls, slower reactions may occur which could modify the gas composition. Processes previously mentioned in this category are:



The low rate of SO₂ production and failure to observe significant changes in oxyfluoride content after the gas was undisturbed for long periods suggest that reactions (21) and (22) occur only very slowly if at all in the gas phase at room temperature. Only reaction (20) is rapid enough to influence significantly the observed oxyfluoride production. Its rate has been estimated from measurements of Sauers et al. [20] to lie between 1.0 and 2.6×10^{-19} cm³/s at a temperature of 350 K. Assuming that this is a gas-phase reaction, and using typical water vapor concentrations found in the present experiments, it is estimated that SF₄ has a half-life in the cell of between 0.15 and 0.40 h. Since this is small compared to typical gas sampling intervals, it can be assumed that SF₄ is completely converted to SOF₂. Reaction (20) has frequently been invoked to account for SOF₂ prod-

uction in previous investigations of SF₆ decomposition; however, it has never been verified that it is actually a gas-phase reaction. If it does occur in the gas phase, then as Herron [65] has suggested it most likely proceeds through the intermediate SF₃OH in two steps.

Because the oxyfluoride concentrations were never permitted to exceed trace levels, it can be presumed that secondary reactions in the small chemically active region were unimportant. These are reactions in which the oxyfluorides are destroyed or undergo conversion from attack by free radicals and ions. It should be noted, however, that secondary ion-molecule reactions involving the expected predominant charge carrier SF₆⁻ might be significant since these can occur in the larger ion-drift region. One such reaction is the energetically favorable F⁻ exchange reaction



which could affect SOF₄ production. The observed uniformity of production with time suggests, nevertheless, that all secondary reactions are relatively unimportant.

5.3 Interpretation of Results

1. Influence of O₂ and H₂O. The sources from which oxygen is derived for formation of SOF₂, SO₂F₂, and SOF₄ have not been positively identified in these experiments, although, as alluded to in the previous section, some processes appear to be more likely than others. The following three sources deserve consideration: 1) gaseous O₂ contamination including that initially present plus that introduced during discharge operation; 2) oxygen contained on surfaces including that which is chemically bound in insulating materials such as SiO₂; and 3) H₂O present either in the gas or on surfaces. Interpretation of the present results in terms of the possible reactions discussed in the previous section suggests that the primary oxygen sources are not necessarily the same for all three species. Because of the high gas pressure and highly confined nature of the discharge which was located far from insulating surfaces, source (2) will be considered unimportant in the discussion that follows.

The data show that oxyfluoride production is not extremely sensitive to variations in the O₂ and H₂O concentrations at levels below 1%. In fact, when the O₂ is higher than 1%, the total oxyfluoride yield actually drops. This suggests that the oxyfluoride yields are controlled mainly by the electron-impact induced dissociation rate of SF₆, i.e., by the availability of SF_x fragments.

The significant drop in SOF₂ yield when O₂ is added can be attributed to at least two possible effects: 1) the

dissociation rate for SF₆ drops when O₂ is added, e.g., due to the influence of O₂ in reducing the mean electron energy within the discharge; and 2) an increasingly greater fraction of SF₄ is consumed by reactions leading to SOF₄ production rather than to SOF₂ production. The first of these is suggested by recent theoretical calculations of electron energy distributions in SF₆/O₂ mixtures by Masek et al. [58]. These calculations, however, pertain mainly to gas mixtures containing larger relative O₂ content than considered here, and there is reason to doubt that the predicted drop in the SF₆ dissociation rate is sufficient to entirely account for the effect reported here. Certainly the second effect can be expected since reaction (12) is energetically favored over reaction (13). However, failure of SOF₄ production to increase significantly when O₂ is added argues against dominance of this effect.

It is in fact conceivable that reactions (13)–(17) are relatively unimportant for SOF₂ formation compared to reaction (20). This is consistent with the observed discharge current dependence for SOF₂ production discussed below which suggests that its formation involves only one molecular dissociation fragment from the discharge. Thus the rate of SOF₂ production could be determined by the rate of SF₄ escape from the active region into the bulk of the gas where reaction (20) occurs. The observed consumption of water vapor might be accounted for by this reaction.

The insensitivity of SO₂F₂ production to variations in low-level O₂ content is more difficult to understand if the predominant mechanisms for its formation involve reactions (18) and (19). Processes such as those involving molecular oxygen are required to account for SO₂F₂ production by a single step mechanism, which, as discussed in the next section, is most consistent with the observed dependence on discharge current. Although other mechanisms for SO₂F₂ formation may be possible, the fact that its production does not drop as precipitously as that for SOF₂ with increasing O₂ content suggests that gas-phase molecular oxygen plays a more important role in its formation. The possible importance of O₂ in enhancing SO₂F₂ yield is suggested by earlier work [3,4,8,15] in which it is reported that in low-pressure discharges addition of O₂ increases SO₂F₂ production at the expense of SOF₄, and in high-pressure arcs O₂ has a much greater influence on SO₂F₂ yield than on SOF₂ yield.

The behavior of SOF₄ production cannot be unambiguously related to either the O₂ or H₂O content because its production is hypothesized here to involve oxygen containing free radicals independent of their source. Failure of SOF₄ to show significant dependence on either O₂ or H₂O content again suggests that the production of active SF_x fragments is the rate deter-

mining factor. Certainly some enhancement in the SOF_4 rate can be anticipated by addition of O_2 , and this is evidently consistent with the data in figure 17 if allowance is made for a possible reduction in the SF_6 dissociation rate. The overwhelming prevalence of SOF_4 in some diffuse, low-pressure discharges [8] can be understood in terms of the high free radical-to-neutral gas density ratios throughout the gas which would favor its formation according to the mechanisms suggested here.

It is proposed from the foregoing that the dominant oxygen sources for SOF_2 and SO_2F_2 production are derived respectively from H_2O and O_2 , whereas SOF_4 can receive oxygen from both of these. Verification of this assignment, however, must await further experiments.

2. Dependence on discharge current. The condition $dc/dt \propto i$, observed here for SOF_2 and SO_2F_2 , is expected if: 1) the formation process involves only one electron-impact-generated dissociation fragment; and 2) changes in i do not significantly modify the electron energy distribution in the discharge. The first condition is satisfied by the mechanisms suggested above that could predominate in SOF_2 and SO_2F_2 production. The second condition is open to question, but is evidently a reasonable assumption [41,47,65,66] for glow or corona-type discharges in which the electric field in the active region is strongly influenced by ion space charge. Increases in applied voltage required to increase the current will presumably expand the volume of space charge without significantly altering the mean E/N . Independent of i and corresponding space-charge development, dissociation is expected to occur predominantly in regions of comparable E/N .

Certainly if $dc/dt \propto i$ for SOF_2 and SO_2F_2 , then it is expected, on the basis of the proposed mechanisms, that $dc/dt \propto i^2$ for SOF_4 , since its formation involves two fragments from electron-impact dissociation. The production of SOF_4 increases with i as seen in figure 14, but probably somewhat more slowly than i^2 . The deviation from i^2 dependence, if significant, could be due to secondary reactions such as reactions (21) or (23) which could remove SOF_4 . As production of SOF_4 becomes more predominant, it could affect the production of the other oxyfluorides that compete in the consumption of reactive dissociation products like SF_4 and SF_5 . Rates for both SOF_2 and SO_2F_2 show a slow falloff with increasing i which may indicate competition with SOF_4 production. The extent to which SOF_4 production is competitive depends, however, on the extent to which it preferentially consumes free radicals used in SOF_2 or SO_2F_2 formation as opposed to those that would otherwise recombine.

3. Dependence on time. It has already been noted that a failure of the production curves to exhibit deviations from linearity would tend to indicate that secondary reactions in the active discharge region are relatively unimportant. The present results are consistent with production rates that are constant in time, provided that the initial portions of the production curves can be ignored. Certainly there is no evidence based on the present data to indicate that secondary reactions in the discharge play a dominant role in oxyfluoride production. This is expected because: 1) the concentrations of the gaseous by-products were always at trace levels; and 2) the chemically active volume was much smaller than the main gas volume. The results from gas analysis performed at times after the discharge was extinguished further indicate that secondary reactions in the bulk of the gas are also unimportant. It should be noted, however, that the diminution of secondary reactions may be peculiar to corona discharges, and would certainly not be expected in arcs or diffuse, low-pressure discharges in which a greater fraction of the gas is dissociated.

4. Polarity effect. The large effect of reversing polarity on the production rates of the oxyfluorides can be understood from consideration of corresponding pronounced changes in the discharge characteristics [40]. In evaluating this effect the following observations are noted: 1) the effect is greater for SO_2F_2 and SOF_4 than for SOF_2 ; 2) the power dissipation at a given current was always higher for positive polarity; 3) the discharge was more pulsating under positive polarity (see fig. 2); and 4) the point electrode surface suffered considerably more damage under positive polarity. In positive discharges the point electrode surface is evidently subjected to bombardment by more highly energetic ions or electrons from electron avalanches originating in the gas than is the case in negative discharges where a more uniform ion space charge is effective in shielding the electrode surface and moderating the energies of impacting ions. Higher mean electron energies and higher electrode surface temperatures would be consistent with a higher dissociation rate in the positive case. In addition to dissociation by electron impact, pyrolysis of SF_6 at the positive point surface could conceivably contribute to decomposition. The enhancement in oxyfluoride production in going from negative to positive polarity is consistent with the postulated increase in the gas dissociation rate.

Greater heating of the electrode in the positive case could also be accompanied by a higher rate of oxygen release into the discharge volume. This would influence oxyfluoride production and might at least partially account for the more pronounced effect for SO_2F_2 and

SOF₄, which are likely to be most affected by the presence of oxygen.

5. Magnitude of production rates. Information is not available at the present time on the rates for all of the various chemical processes which could account for oxyfluoride production. Thus accurate predictions of the production rates are not yet feasible. Nevertheless, sufficient information exists to at least allow upper limits to be placed on the magnitude of the total SF₆ decomposition rates for discharges such as considered here in which dissociation is controlled mainly by electron-collision processes.

Based on the evidence offered here that the rate determining factor is the initial SF₆ dissociation rate, then an upper limit on the total oxyfluoride production rate can be estimated using the following two assumptions: 1) all SF_x fragments convert to oxyfluorides; and 2) electronic excitation leads predominantly to dissociation so that the total electronic excitation rate k_{ex} coincides with the total dissociation rate. Contributions from ions might also be important, but could be included in the second assumption by making appropriate adjustments in k_{ex} .

For simplicity, a one dimensional approximation is made that electrons are released into the active ionization volume at a constant rate dn_e/dt , e.g., by field emission from the point cathode, and traverse the gap distance d along the point-to-plane axis. These assumptions enable one to compute the total oxyfluoride charge rate of production $r_{q,t}$ defined by

$$r_{q,t} = \sum_{j=1}^3 r_{q,j}, \quad (24)$$

where the $r_{q,j}$ are the rates for the individual oxyfluoride components. Allowing for the variations of electron production in the gap by ionization and attachment, one obtains the expression

$$r_{q,t} = i^{-1} (N/N_A) (dn_e/dt) \int_0^d \frac{k_{ex}(l)}{\bar{v}(l)} \exp\left[\int_0^l (\alpha(l') - \eta(l')) dl'\right] dl, \quad (25)$$

where α and η are respectively the usual ionization and attachment coefficients [41,47], \bar{v} is the electron drift velocity, and N_A is the Avogadro constant required to express the rate in units of moles-per-coulomb. In general, the quantities k_{ex} , \bar{v} , α , and η will depend on E/N and hence on position l' in the gap.

Precise variations of E/N within the gap are not easily predicted when the discharge is present due to the expected strong influence of ion space charge on the field. However, the active region near the point in

which significant ionization and excitation occur must satisfy the condition

$$\alpha(l') > \eta(l'). \quad (26)$$

When this condition no longer holds, electrons are quickly thermalized and removed from the gas by attachment to SF₆ molecules. Lacking knowledge of the exact dependence of E/N on l' , the active discharge volume will be modeled here as a region of extent l in which eq (26) holds, and E/N assumes a constant value close to the critical value $(E/N)_c$ where $\alpha = \eta$. This choice takes into consideration the expected moderating effect of the ion space charge which tends to reduce the field near the point.

Expressing N in terms of pressure P and temperature T using $N = P/kT$ (k is the Boltzmann constant), the approximation for $r_{q,t}$ becomes

$$r_{q,t} \approx \frac{k_{ex} P l}{e \bar{v} k T} \left(\frac{1}{N_0} \right), \quad (27)$$

where e is the electron charge, and k_{ex} and \bar{v} assume the values for the mean electronic-excitation-rate coefficient and drift velocity respectively at $E/N = (E/N)_c = 370 \times 10^{-21} \text{ Vm}^2$ corresponding to the known [67] critical value for SF₆. In deriving eq (27) it is assumed that the measured discharge current i corresponds to electron motion only. The parameter l is possibly pressure dependent since it is known [41,47] that the extent of the active discharge region contracts with increasing gas pressure for corona discharges. Thus the pressure dependence implied in eq (27) does not hold in general.

There appears to be some disagreement in the literature [48,49,68] about the correct total electronic-excitation cross sections needed to determine the rate coefficient k_{ex} for SF₆. It will be assumed here that $2 \times 10^{-15} \text{ m}^3/\text{s} \geq k_{ex} \geq 1 \times 10^{-15} \text{ m}^3/\text{s}$, where the lower value corresponds to that calculated by Masek et al. [57] at $E/N = 100 \times 10^{-21} \text{ Vm}^2$ and the upper value allows for the expected increase in k_{ex} for $E/N = (E/N)_c$. The values of k_{ex} considered here are comparable in magnitude to those reported in the literature for other molecules [69]. The observed [67,70] value for \bar{v} in SF₆ at $(E/N)_c$ is about $2 \times 10^5 \text{ m/s}$. The extent of the active region is expected [40] to lie between about 1 and 2% of the total gap spacing, i.e., for the present case, $0.24 \text{ mm} > l > 0.12 \text{ mm}$. Using eq (27), the predicted upper limit on the rate for a pressure of 200 kPa and temperature of 300 K lies in the range, $1800 \text{ } \mu\text{moles/C} > r_{q,t} > 450 \text{ } \mu\text{moles/C}$. This can be compared with the value obtained from tables 3–5 for a pressure of 200 kPa. For positive discharges at 8.0 μA and 16.0 μA

respectively it is found, for example, that $r_{q,t}=634$ $\mu\text{moles/C}$ and $r_{q,t}=717$ $\mu\text{moles/C}$, and for a negative discharge at 40 μA , $r_{q,t}=96$ $\mu\text{moles/C}$.

The results for positive discharges generally lie within the range of predicted upper limit values whereas results for negative discharges lie well below the range. The model used is perhaps more relevant to negative discharges where electrons originate from the point electrode surface and the space charge is expected to be uniformly distributed about the point. The space charge for positive discharges is probably less uniform, and as previously suggested, there may be contributions to dissociation from processes other than electron impact. Undoubtedly, the appropriate mean value of E/N in the active volume is greater than $(E/N)_c$ for the positive case. However, independent of polarity, the total rates $r_{q,t}$ should not lie significantly above the range of upper limits estimated here.

6. Conclusions

The oxyfluorides SOF_2 , SO_2F_2 , and SOF_4 have been identified as the major stable gaseous by-products from highly localized, low-current corona discharges in SF_6 containing trace levels of O_2 and H_2O for total gas pressures from 100 kPa to 300 kPa. The absolute charge and energy rates-of-production for these species were measured for different discharge conditions and found to be below the theoretically estimated upper limits and comparable in magnitude to rates previously determined for other types of electric discharges in SF_6 . From considerations of the dependences of the rates on varying O_2 and H_2O content, it has been possible to conclude that the controlling rate factor is the SF_6 dissociation rate in the discharge.

The charge rates-of-production for both SOF_2 and SO_2F_2 are found to be nearly independent of current, suggesting formation mechanisms for these species that involve only one fragment from molecular dissociation in the discharge. Interpretation of this observation in terms of possible reactions further suggests that SOF_2 and SO_2F_2 respectively derive their oxygen predominantly from gas-phase H_2O and O_2 . The charge rate-of-production for SOF_4 is observed to increase with current, thus suggesting a predominant mechanism for its formation involving more than one molecular dissociation fragment.

Gas analysis performed before and after the decomposed gas was left undisturbed for many hours showed that hydrolysis of SOF_4 leading to SO_2F_2 formation is too slow to observe in the gas phase and therefore cannot account for SO_2F_2 production as suggested by some earlier investigators. Hydrolysis of SOF_4 could nevertheless occur rapidly on surfaces, and this process may

account for a failure to observe this species in some previously reported experiments on corona discharges in SF_6 . The present results indicate that hydrolysis of SOF_2 in the gas phase is also not important. The observed uniformity of the production rates with time argues against significant influence from any secondary reactions involving the oxyfluorides.

The absolute production rates reported here are presently the most accurate available, and should prove useful in estimating detection sensitivities needed to design chemical diagnostics for practical SF_6 -insulated high-voltage systems. It should be cautioned, however, that there may be difficulties in applying the present results to ac corona because of the rather large polarity effect which has been observed. The data offered can at least permit upper and lower bounds to be placed on oxyfluoride production in ac discharges.

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APPENDIX

Examples of values for the parameters in eq (8) for $c(Q)$ which were obtained from fits to data for SOF_2 and SO_2F_2 are given in table 7. Also indicated in this table are the maximum values for net charge transported, Q_{\max} , to which these fits apply. Instantaneous production rates $r_q'(Q)$ at particular values of Q can be calculated using

$$r_q'(Q) = (1 + \epsilon)AQ^\epsilon, \quad (\text{A1})$$

which is derived from eq (8). Values for some rates computed in this way have previously been reported [38].

Fits to concentrations plotted versus energy dissipated yielded curves of essentially the same shape, i.e., $\epsilon' \simeq \epsilon$ and $c_0' \simeq c_0$. The values of A and A' depend, of course, on the different units in which the rates are expressed. The limiting, uniform rates r_q in tables 3 and 4 are generally slightly less than those calculated from eq (A1) at $Q = Q_{\max}$. The rates r_q are obtained from linear, least-squares fits ($\epsilon = 0$ in eq (8)) to the data for $Q_{\max} > Q > Q_{\min}$, where Q_{\min} is the lowest value of net accumulated charge at which the assumption of linearity holds. If $\epsilon \simeq 0$, as in the case of some SOF_4 data, then $r_q \simeq A$. It was found for all cases reported that $2r_q > 2A > r_q$.

Table 7. Values of parameters obtained from fits of the form given by eq (8) for $c(Q)$.

Species	Polarity	Pressure (kPa)	Current (μA)	c_0	Fitting Parameters		
					A	ϵ	$Q_{\max}(\text{C})$
SOF_2	Pos.	116	20.0	2.08×10^{-7}	2.32×10^{-5}	0.579	1.90
		200	1.5	9.28×10^{-7}	2.05×10^{-4}	0.449	0.40
		200	8.0	2.96×10^{-6}	2.45×10^{-4}	0.541	0.40
		200	16.0	3.04×10^{-11}	2.07×10^{-4}	0.634	0.48
		300	8.0	2.29×10^{-11}	1.92×10^{-4}	0.696	0.54
		300	16.0	1.06×10^{-6}	1.21×10^{-4}	0.684	0.93
	Neg.	114	25.0	6.77×10^{-7}	3.04×10^{-5}	0.250	2.42
		200	16.0	1.67×10^{-6}	2.46×10^{-5}	0.208	2.30
		200	40.0	2.37×10^{-7}	2.03×10^{-5}	0.227	2.74
		300	16.0	1.37×10^{-6}	1.96×10^{-5}	0.386	2.35
		300	21.0	8.32×10^{-7}	1.54×10^{-5}	0.166	3.01
		SO_2F_2	Pos.	116	20.0	4.59×10^{-8}	3.14×10^{-5}
200	1.5			1.41×10^{-6}	2.06×10^{-4}	0.583	0.40
200	8.0			2.61×10^{-6}	1.70×10^{-4}	0.490	0.40
200	16.0			2.67×10^{-12}	1.16×10^{-4}	0.477	0.48
300	8.0			6.46×10^{-11}	1.16×10^{-4}	0.393	0.54
300	16.0			$\sim 1 \times 10^{-14}$	0.75×10^{-4}	0.529	0.93
Neg.	114		25.0	2.47×10^{-6}	0.92×10^{-5}	0.486	2.42
	200		16.0	1.59×10^{-11}	1.20×10^{-5}	0.243	2.30
	200		40.0	2.03×10^{-6}	1.03×10^{-5}	0.204	2.74
	300		16.0	2.27×10^{-6}	0.92×10^{-5}	0.474	2.35
	300		21.0	3.72×10^{-12}	0.63×10^{-5}	0.586	3.01

