

DECOMPOSITION OF SF₆ AND PRODUCTION OF S₂F₁₀ IN POWER ARCS

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INTRODUCTION

Decomposition of SF₆ in electrical discharges produces many toxic solids and gases. S₂F₁₀ is the most toxic of the gaseous byproducts and has been found in arcs, sparks and corona [1]. Of these, S₂F₁₀ production in arcs is the least understood, in part because S₂F₁₀ is known to decay rapidly at temperatures above 250°C [1]. As temperatures in an arc are considerably higher, it is believed that S₂F₁₀ cannot be formed directly by an arc. The first experiments where S₂F₁₀ was detected in SF₆ decomposed by a power arc employed a burn-through configuration into another chamber containing SF₆ at a lower pressure [2,3]. In those experiments the S₂F₁₀ may have been formed during the volume expansion and cooling of the SF₆ decomposition products into the second chamber. We have conducted a series of tests of a power arc discharge contained completely within a bus duct configuration. Among the many other gaseous byproducts, we have detected S₂F₁₀ at or below the part per million (ppm) by volume level, proving that S₂F₁₀ can be formed directly by a power arc within SF₆-insulated equipment. The relative production rate of S₂F₁₀ with respect to that of SOF₂ and SF₄, however, implies that S₂F₁₀ is not a significant contributor to the hazard of exposure to decomposed SF₆.

EXPERIMENT

The power arc tests were performed in an arc cell designed to simulate a section of bus duct. The arc cell consisted of two coaxial aluminum pipes with plastic end plates to support the inner pipe as the inner conductor, as indicated in Figure 1. The inner diameter

of the outer conductor was 154 mm, and the outer diameter of the inner conductor was 72.5 mm. The end plates were separated by 1.83 m, enclosing a volume of 26.5 L. Connections on the end plates provided for gas filling and sampling, and for pressure relief. The arc cell was designed to be re-usable. The original cell was used for the first two tests, both pipes were replaced for the the third test, and finally a new inner pipe was used for the last test. Any re-used components were thoroughly cleaned before being used in another test.

At least 24 hours before each test, the arc cell was evacuated and then filled with commercial grade, virgin SF₆ to a pressure of about 200 kPa. Just before each test, the equilibrium humidity of the gas in the cell was measured by flowing some of the gas through a chilled-mirror hygrometer. Then, the final pressure in the cell was read from the portable rack and the valve at the cell was closed.

The tests were performed in an outdoor, explosion-proof room attached to the high current laboratory at Ontario Hydro. The current source was connected to the inner

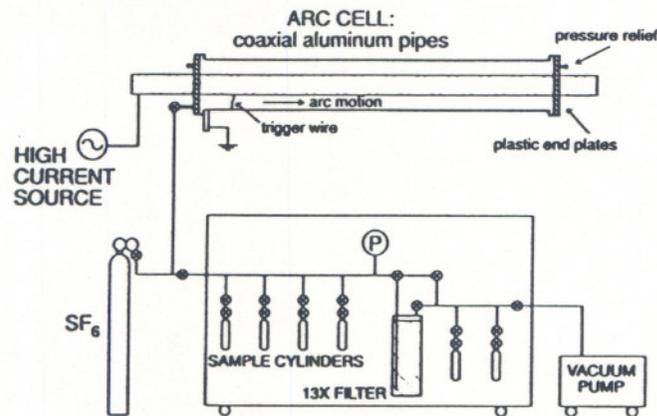


Figure 1. Schematic diagram of the arc cell and portable sampling rack used in the power arc experiments. The internal volume of the arc cell is 26.5 litres.

conductor at one end only, and the outer conductor was grounded at the same end. A fuse wire between the two conductors, inside the cell and near one end, served to initiate the arc discharge when the current was applied.

The top part of Table 1 lists the experimental conditions for each of four tests: SF₆ pressure and quantity, water vapour concentration, arc current (rms) sustained, and energy dissipated in the cell. The energy dissipated is expressed as energy per unit volume of SF₆ at atmospheric pressure (101.3 kPa). For each test, the duration of the arc current was fixed between 50 and 150 ms set to provide a range of energy discharged into the cell without burning through the conductors or the end plates. For a single-ended current, the arc is not stationary; we measured current-normalized arc velocities of about 1 m/(s.kA) [4].

After each test, the solid byproducts, mostly AlF₃, were allowed to settle for at least 15 minutes before withdrawing any gas samples. Several gas samples were taken from each test in stainless-steel cylinders, either 150 or 1000 ml in volume. At least one sample from

Table 1. The test conditions of four power arcs, labelled A, B, C, and D, and the production rates of the SF₆ decomposition byproducts of interest.

		A	B	C	D
SF ₆ : Pressure	(kPa)	158	210	208	195
Quantity	(moles)	1.74	2.47	2.26	2.25
Water	(ppm)	>800	100	860	340
Current	(kA)	9.5	7.8	7.5	7.2
Energy Dissipated	(kJ/L)	1.59	0.97	2.53	2.47
SOF ₂ & SF ₄	(mol/J)	1.74x10 ⁻⁶	5.31x10 ⁻⁷	7.31x10 ⁻⁷	8.43x10 ⁻⁷
SO ₂ F ₂	(mol/J)	5.3x10 ⁻¹⁰	9x10 ⁻¹¹	5.3x10 ⁻¹⁰	8.7x10 ⁻¹⁰
S ₂ F ₁₀	(mol/J)	4x10 ⁻¹¹ (a)	<2x10 ⁻¹⁰ (b)	7.5x10 ⁻¹² (a)	1.38x10 ⁻¹¹ (a)

(a) Measured by cryo-GC at ORNL.

(b) Measured by GC-MS at NIST.

each test was analyzed by infrared absorption spectroscopy in a Fourier Transform infrared (FTIR) spectrometer at Ontario Hydro [1]. A typical infrared absorption spectrum of the gas in the arc cell, before and after the arc, is shown in Fig. 2. Another sample from each test was analyzed either by gas chromatography-mass spectrometry (GC-MS) at the National Institute for Standards and Technology (NIST) [5] or by cryogenic enrichment gas chromatography (cryo-GC) at Oak Ridge National Labs (ORNL) [6].

RESULTS AND DISCUSSION

The example spectra in Fig. 2 show absorption bands due to SF₆ and other absorption bands, appearing in various windows of the SF₆ spectrum, due to a variety of decomposition byproducts. The main byproducts of interest here are SF₄ and SOF₂. As Fig. 2 indicates, analysis of these two compounds individually by FTIR can be straightforward. However, as SF₄ reacts rapidly with water to produce SOF₂ and HF, most GC analysis techniques cannot readily distinguish SF₄ from SOF₂. Thus, many reports of SF₆ decomposition in arcs relying on GC analysis have lumped SF₄ in with SOF₂ production rates. To facilitate comparison with previously published results, we report SF₄ production and SOF₂ production, measured separately by FTIR, together in the bottom part of Table 1. Table 1 also lists the production rates of SO₂F₂ and S₂F₁₀. The analysis of SO₂F₂ was performed by GC-MS at all three sites. The S₂F₁₀ measurements were split between the GC-MS at NIST and the cryo-GC at ORNL, as indicated in Table 1.

The combined production rates of SF₄ and SOF₂ observed in the last three arc tests are each comparable to the average production rate for SOF₂ in arcs of 6.0x10⁻⁷ mol/J reported in Ref. 7. The much higher than average production rate of SF₄/SOF₂ in arc test A has not been adequately explained. Pettinga [3], however, noted a correlation between lower vacuum attained in preparation of an arc cell and lower production of SF₄/SOF₂. In our case, the cell for test A was pumped a shorter time than the cells for the subsequent tests.

In contrast to the SOF₂ production, the very low production rates of SO₂F₂ are typical of power arcs. SO₂F₂ production is enhanced in cooler discharges, such as sparks and corona. Thus, the ratio of SOF₂ to SO₂F₂ in decomposed SF₆ is a simple measure of the type of discharge. For equal concentrations, the absorption peaks of SOF₂ and SO₂F₂ are

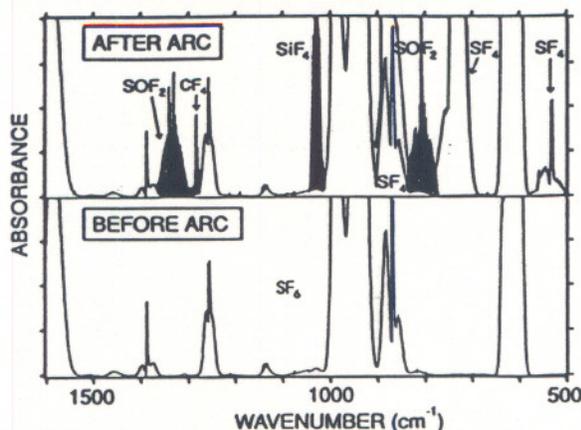


Figure 2. The two panels show the infrared absorption spectrum of gas samples from the arc cell before and after a power arc. In the lower panel, the spectrum is entirely due to SF_6 . In the upper panel, absorptions due to major byproducts of the arc are indicated: SF_4 , SOF_2 , SiF_4 , and CF_4 . The region near 550 cm^{-1} is of greatest interest for detecting S_2F_{10} .

about the same height in FTIR spectra such as Fig. 2. Absorption peaks due to SO_2F_2 are not apparent in Fig. 2 because the concentration is about 0.1% of that of SOF_2 .

In the absence of SOF_2 and SF_4 , our detection limit for S_2F_{10} is about 0.10 ppm by FTIR and is less than 0.010 ppm by GC-MS. The concentration of S_2F_{10} in the virgin SF_6 used to fill the arc cell was less than 0.010 ppm as measured by GC-MS. The high concentrations of SOF_2 and SF_4 found in the arc samples created problems for detecting S_2F_{10} either by FTIR or GC-MS. The S_2F_{10} production rates listed in Table 1 for arc B represents a lower limit of 5 ppm for detection by GC-MS. Fortunately, the cryo-GC method at ORNL for detecting S_2F_{10} is not affected by high concentrations of either SOF_2 or SF_4 . The detection limit for S_2F_{10} with the cryo-GC was about 0.1 ppm for arc A and less than 0.010 ppm for the analysis of arcs C and D. Thus, analysis of the samples C and D revealed S_2F_{10} concentrations of 0.43 and 0.76 ppm, respectively, which correspond to the production rates shown in Table 1.

A problem frequently encountered in the sampling of S_2F_{10} , at concentrations on the order of 1 ppm or less, is its decay with time in sample cylinders [5]. In general, higher pressures, larger volumes and dryer surfaces result in slower decay. Thus, 1000-ml cylinders are usually superior to 150-ml cylinders for retaining S_2F_{10} . The samples from arc A were taken in 150-ml cylinders, before we realized fully the problem of sample decay. The samples for arcs B, C and D were taken in 1000-ml stainless-steel cylinders. The measurement of sample C, however, was delayed about two months beyond the time of the arc test. In that time, the S_2F_{10} within the sample may have decayed.

Sample D was measured within 24 hours of sampling, and then re-measured several times over a period of several months. These measurements showed that S_2F_{10} was stable

over a 50 day period, and decreased to about 50% after 200 days. We believe that the stability of the S_2F_{10} in the cylinder may be attributed to the dryness caused by the large amount of SF_4 present. As arcs C and D were very similar, the measurement of arc C, delayed as it was, probably represents more than 50% of the initial, unknown value.

The guidelines for exposure to many compounds are defined by the Threshold Limit Values (TLV) set out by the American Conference of Governmental Industrial Hygienists (ACGIH) [8]. The TLV for SF_6 is 1000 ppm, for SOF_2 is 1.6 ppm, for SF_4 is 0.10 ppm, and for S_2F_{10} is 0.010 ppm (see Ref. 1 for discussion). In all four arc tests, the combined production rate of SOF_2 and SF_4 was about 10,000 times greater than the production rate of S_2F_{10} . Thus, the limit for exposure to SF_6 decomposed by a power arc is governed by the presence of SF_4 and SOF_2 , and not by the presence of S_2F_{10} .

CONCLUSIONS

We have performed four arc tests enclosed in a bus duct configuration with aluminum electrodes and have confirmed the presence of S_2F_{10} as a decomposition byproduct of SF_6 . In two of the tests, we measured S_2F_{10} concentrations of 0.43 and 0.76 ppm, with a detection limit of 0.01 ppm, by a cryogenic-enrichment-GC technique. Of the three techniques investigated for measuring S_2F_{10} , the cryo-GC was the only one unaffected by the large concentrations of SOF_2 and SF_4 in the samples. The detection limits for S_2F_{10} by an FTIR technique and by a GC-MS technique were degraded to the range of 5-10 ppm. The concentrations of SOF_2 and SF_4 were measured separately by the FTIR technique. In every test, the combined production rate for SOF_2 and SF_4 exceeded the production rate for S_2F_{10} by a factor of about 10,000. The limits for exposure to SOF_2 and SF_4 are only about 160 times and 10 times more, respectively, than for S_2F_{10} , as specified by the Threshold Limit Values set out by the ACGIH. Therefore, the hazard of exposure to SF_6 decomposed by a power arc is determined by the SOF_2 and SF_4 and not by the presence of S_2F_{10} .

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DISCUSSION

J. CASTONGUAY: Your test A shows a much larger production rate of SO_2 , that is, twice the usual "maximum" yield ever measured by any other experimenter. Any comment?

H. MORRISON: Yes. I mention this point in the paper. The higher yield may be related to the fact that the cell for test A was not pumped down as long as was done for the other tests.

J. CASTONGUAY: Do you think that the level of moisture has some effect in your power arc tests?

H. MORRISON: I believe that the humidity level in the gas must have some effect on the by-products, but the effect is not very strong. Water adsorbed on the surfaces of the chamber where the arc passes may be just as important as the water vapor in the gas.