ABSTRACT

Recent findings indicate that $\text{SF}_\text{g}$ is unstable with respect to decomposition on a surface. This paper reports the first results of a study investigating the mechanisms and rates of surface decomposition of $\text{SF}_\text{g}$ under various conditions. Initial results indicate that surface decomposition rates on stainless steel increase with increased water content, temperature, and surface-to-volume ratio, and with decreased gas pressure. The implications of these results for the preparation and storage of $\text{SF}_\text{g}$ samples are discussed. Additionally, the use of this surface decomposition mechanism to enhance the detection sensitivity of small concentrations of $\text{SF}_\text{g}$ in $\text{SF}_\text{g}$ using a gas chromatograph/mass spectrometer (GC/MS) is investigated. Detection sensitivities of 1 ppm by volume of $\text{SF}_\text{g}$ in $\text{SF}_\text{g}$ are routinely achievable using this new technique.

INTRODUCTION

Recent studies [1,2] have shown the important role that $\text{SF}_\text{g}$ plays in accounting for the toxicity of decomposed $\text{SF}_\text{g}$ in gas-insulated equipment. Because of these studies, there has been increased interest in quantifying the rate of $\text{SF}_\text{g}$ production in electrical discharges. This work has indicated that $\text{SF}_\text{g}$ is unstable and decomposes into $\text{SOF}_\text{g}$, $\text{SF}_\text{g}$, and other by-products [3] when stored in stainless steel gas-sampling cylinders at room temperature. This instability brings into question the reliability of analytical equipment.

EXPERIMENTAL METHOD

The experimental method for the study of $\text{SF}_\text{g}$ decomposition on surfaces was straightforward. Gas sampling cylinders of various sizes and materials (primarily stainless steel) were conditioned so that for each test all cylinders began with surface conditions that were as similar as possible. Each cylinder was then filled with a known mixture of pure $\text{SF}_\text{g}$ and argon. Argon was used as a buffer gas because of its chemical inertness and because its presence did not interfere with the detection of $\text{SF}_\text{g}$ or its decomposition products. In other buffer gases, such as $\text{N}_\text{g}$ and $\text{SF}_\text{g}$, $\text{SF}_\text{g}$ exhibited similar decomposition properties. The concentrations of $\text{SF}_\text{g}$ and the primary decomposition products, such as $\text{SOF}_\text{g}$ and $\text{SF}_\text{g}$, were then monitored as a function of time to determine the rate of decomposition.

Two different analytical techniques were used to monitor the gas compositions inside the sample cylinders. A GC/MS was used at NIST and a gas chromatograph/thermal conductivity analyzer (GC/TCD) was used at ORNL. In both systems, the GC column employed for $\text{SF}_\text{g}$ detection was a 24' x 1/8' Teflon tube containing 30% SP-2100 (Supelco) on 80/100 chromosorb AW-DMCS [6]. The conditions employed in the two GC analyzers were similar: Carrier gas, He; Oven temperature, 50°C; and He flow rate, 20-30 ml/min. The absolute quantities of $\text{SF}_\text{g}$ and its decomposition products were determined by making direct comparisons of the observed GC/MS and GC/TCD responses with those from reference gas samples containing known quantities of $\text{SF}_\text{g}$, $\text{SF}_\text{g}$, $\text{SOF}_\text{g}$, $\text{SF}_\text{g}$, and Ar.

RESULTS AND DISCUSSION

Figure 1 shows the decomposition curves for $\text{SF}_\text{g}$ and the related production curves for the two main observable gas-phase products, $\text{SF}_\text{g}$ and $\text{SOF}_\text{g}$, in two experiments with different experimental conditions (see figure caption). Note that the $\text{SF}_\text{g}$ sample in the experiment shown in Figure 1a took approximately 75 days to decompose, while the sample from Figure 1b took only 75 hours to disappear. This large variation in decay times indicates the importance of understanding the mechanisms of the $\text{SF}_\text{g}$ decomposition in order to minimize the effects on experiments and sample storage. Interestingly, despite the differences in decay times and experimental conditions, the curves in Figures 1a and 1b are very similar in shape and magnitude and the fraction of $\text{SF}_\text{g}$ which ultimately formed $\text{SF}_\text{g}$ is about the same in both cases. The most significant difference between these two experiments is in the amount of water contamination that was present (see the caption for Figure 1).

*The identification of commercial materials and their sources is made to describe the experiment adequately. In no case does this identification imply recommendation by the National Institute of Standards and Technology, nor does it imply that the instrument is the best available.

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the S2F10 decomposes via a reaction such as

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\text{S}_2\text{F}_{10} + \text{H}_2\text{O} \rightarrow \text{SOF}_2 + \text{SF}_6 + 2\text{HF}.
\]  

Figure 1. Decomposition of S2F10 and corresponding production of SOF2 and SF6 with time for two experiments with the following conditions: (a) 78 ml stainless steel cylinder; 2.1 cm⁻³ surface-to-volume ratio; Argon buffer gas; Pressure = 1 atm; 4500 ppm, starting concentration; Temperature = 25°C; no water added; (b) 24 ml stainless steel cylinder; 2.5 cm⁻³ surface-to-volume ratio; Argon buffer gas; Pressure = 1 atm; 1500 ppm, starting concentration; Temperature = 25°C; 1 µl water added.

Although HF is detected in the sample cylinder as the S2F10 decomposes, the amounts are difficult to quantify and therefore not shown in Figure 1. The exact nature of reaction (1) has not been determined. It may correspond to direct hydrolysis of S2F10 on the surface, or perhaps a disproportionation reaction into SF6 + SF4 followed by hydrolysis of the SF4 product. Surface hydrolysis of other sulfur fluoride compounds has been previously observed but is not fully understood. Note that SOF2 also decomposes in stainless steel cylinders as is evident by the eventual decrease in the SOF2 concentration shown in Figure 1 and by the decomposition data shown in Figure 2 from SOF2 stored in a stainless steel cylinder under conditions similar to those in Figure 1. This decomposition cannot be due to gas-

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\text{SOF}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_2 + 2\text{HF}
\]  

Figure 2. Decomposition of SOF2 with time under the following experimental conditions: 32 ml stainless steel cylinder; 2.6 cm⁻³ surface-to-volume ratio, Argon buffer gas; Pressure = 1 atm; 5000 ppm, starting concentration; Temperature = 25°C; and no water added.

phase hydrolysis because the rate [9] for the gas-phase reaction is much too slow to account for the observed loss of SOF2 and because SO2 was detected as only a minor product in the experiments shown in Figures 1 and 2. Therefore the SOF2 decomposition is probably due to surface catalyzed reactions.

Were reaction (1) the sole mechanism for S2F10 decomposition, then the amount of decomposed S2F10 should equal the amount of SOF2 and SF6 produced. However it is obvious from the sum of the absolute concentrations of the identified gas-phase sulfur-containing compounds (S2F10, SF6, SOF2) in the cylinder, that all of the sulfur initially present in the cylinder as S2F10 cannot be accounted for by the observed gaseous products (see Figure 3).

While the decomposition of SOF2 is obviously a contributing factor to the overall loss of sulfur atoms, it cannot account for the entire effect since even at very short times the amount of detectable sulfur in gas-phase molecules is less than that present when the sample was prepared. Additionally, if reaction (1) were the only mechanism for S2F10 decomposition and the hydrolysis of SOF2 were the only source of the loss of sulfur, then at long times (i.e. after all the S2F10 has decomposed) the concentration of SF6 should equal the initial concentration of S2F10 since, as expected, SF6 does not exhibit any decomposition. However, it is obvious from Figures 1 and 3 that the final concentrations of
Thus, in a very practical way, a more complete understanding production rates more difficult and significantly more uncertain. In Figure 1b, the long-term decomposition of SzFlo reference accuracy and sensitivity of tests used to determine concentrations of SzFlo samples makes careful quantification of SzFlo concentrations and account for only 10-15% of the available sulfur. Thus it appears that some of the end products of SzFlo decomposition adhere to the surfaces or are gaseous species that have yet to be identified. An electron-impact mass spectrum of a decomposed SzFlo sample in argon from a stainless steel container (Figure 4a) provides evidence to support the latter speculation. Only the labeled peaks in Figure 4a are identifiable as ions from SzFlo or ions from sulfur-containing decomposition products. The other peaks represent unidentified gaseous products from the decomposition of SzFlo in stainless steel cylinders. GC/MS analysis indicates that the mass 47, 81, and 96 peaks correspond to ions that are most likely from the same compound. Although a positive identification of the species with a mass spectrum containing these ions has not been made, the 15 amu difference between mass 96 and 81 (possibly due to a CHJ fragment) suggests that the compound contains carbon, thus indicating reactions with the container wall. It is significant that this species does not appear in glass or Teflon containers and appears in stainless steel even when only SOF₂ is initially present. Interestingly, SzFlo samples in N₂ buffer gas produce products with mass spectra that differ considerably from Figure 4a. Evidence exists of unidentified products containing nitrogen, thus indicating that N₂ can play an active role in the catalytic process. While the observed decomposition processes discussed in the preceding paragraphs are not fully understood, many of the implications of the decomposition processes are clear. Under the most extreme conditions, SzFlo samples decompose significantly within a matter of hours (Figure 1b). This could affect the accuracy and sensitivity of tests used to determine concentrations of SzFlo in gas-insulated equipment if appropriate sampling guidelines are not determined and followed. Even if the decomposition rate of a particular SzFlo sample is not as great as that shown in Figure 1b, the long-term decomposition of SzFlo reference samples makes careful quantification of SzFlo concentrations and production rates more difficult and significantly more uncertain. Thus, in a very practical way, a more complete understanding of the parameters which affect the decomposition rate of SzFlo samples is essential in the ongoing research to investigate SzFlo production in SF₆-insulated equipment.

As indicated by the above discussion, water appears to be an essential component in the decomposition of SzFlo. The possible influence of water was examined further by preparing two identical SzFlo samples (1400 ppm, SzFlo in 1 atm Ar in 150 ml stainless steel cylinders) with 1 μl of water added to one of the samples. No attempt was made to remove all of the initial moisture on the walls of the cylinders beyond initially evacuating the cylinder to ~3 Pa (20 mtorr) before preparing the samples. The SzFlo concentrations were then monitored as a function of time and the results are shown in Figure 5. Consistent with the results in Figure 1, the sample with added water decomposed significantly faster than the sample exposed to only residual moisture in the cylinder, again confirming that water plays a significant role.

Temperature has also been identified as a factor in the rate of SzFlo decomposition in stainless steel cylinders. Figure 6 shows the results of an experiment where three SzFlo samples (500 ppm, in 1 atm Ar in 150 ml stainless steel cylinders) were allowed to decompose at different temperatures. The rate of decomposition increased dramatically as the sample temperature increased. Calculations show that the gas-phase unimolecular decay rate increases from 25°C to 50°C, but is still many orders of magnitude lower than required to account for the decomposition of SzFlo observed in Figure 6. Thus the temperature of the sample (and/or the surface) clearly affects the rates of the reactions occurring on samples.

Figure 4. (A) Electron impact mass spectra of an SzFlo sample stored in a 75 ml stainless steel cylinder for 35 days. Only 100 ppmS of an original 5000 ppm, of SzFlo remains. (B) Mass spectrum of an undeveloped 3000 ppm, SzFlo sample in Ar.

Figure 5. Decomposition of SzFlo as a function of time for two 1400 ppm, SzFlo samples in 1 atm Ar in 150 ml stainless steel cylinders. For one sample (•), 1 μl of liquid water was injected into the cylinder prior to filling with gas.

Figure 6. Decomposition of SzFlo as a function of time at different temperatures. Samples were 500 ppm, SzFlo in 1 atm Ar in 150 ml stainless steel cylinders.
the surface of the sample cylinders. While storing samples of $S_2F_{10}$ in our laboratories for long periods of time, it became evident that samples at lower pressure often decayed more rapidly than those at higher pressures. More careful studies of this pressure dependence indicate that at pressures below approximately 100 kPa (~ 1 atm), lower pressure samples decompose faster than higher pressure samples. However, above 100 kPa little or no difference was observed in decomposition rates for samples at different pressures. Since this type of pressure dependence is not expected from simple gas-kinetic considerations [10], it is speculated that the surface conditions upon which $S_2F_{10}$ decomposition depends could be affected by the gas pressure.

From chemical kinetics theory [10], it is expected that the reaction rate for decomposition of $S_2F_{10}$ on a surface will be proportional to surface area. This behavior is supported by a large body of evidence from our work indicating that $S_2F_{10}$ samples decompose more rapidly as sample cylinder surface-to-volume ratio increases. However, a direct proportionality of $S_2F_{10}$ decay rate to cylinder surface-to-volume ratio has not yet been verified.

The data shown in Figures 1-6 apply only to 304 stainless steel sample cylinders. It is important to determine if the use of cylinders made of other materials would significantly affect the observed $S_2F_{10}$ decomposition rates. Preliminary comparative experiments using stainless steel, Monel, Teflon, and glass cylinders have indicated that under reasonably dry conditions [11] all decay rates were within approximately 20% of each other. When the same cylinders were prepared under “wetter” conditions [12] the $S_2F_{10}$ in the Monel cylinder decayed at a rate four times greater than the $S_2F_{10}$ in the other cylinders. The stainless steel, Teflon and glass cylinders all exhibited decay rates that were within 12% of each other.

$S_2F_{10}$ DETECTION USING SURFACE-CATALYZED DECOMPOSITION

An interesting aspect of the surface-catalyzed decomposition of $S_2F_{10}$ is that this same process apparently occurs on the membrane separator of the GC/MS instrument used for $S_2F_{10}$ detection in some of the previously discussed experiments. During analysis of $S_2F_{10}$ samples, this decomposition causes features to appear in the GC/MS chromatograms at retention times corresponding to $S_2F_{10}$ molecules but at ion masses corresponding to the molecular decomposition products shown on the right side of reaction (1). Figure 7 shows these features at several different ion masses for a 400 ppm, $S_2F_{10}$ sample in argon.

The $SO^+$ and $SOF_2^+$ ions are the result of electron-impact ionization of $SOF_2$ in the mass spectrometer, and the mass 20 signal must be due to the ionization of HF. Both of these species are products of the $S_2F_{10}$ surface decomposition. The presence of these ions is further proof that at least a portion of the $S_2F_{10}$ molecules experience a decomposition process represented by reaction (1), and the fact that the signal occurs at retention times corresponding to $S_2F_{10}$ indicates that the conversion takes place after the $S_2F_{10}$ elutes from the GC column. The mass 127 ions can be due to ionization of either $S_2F_{10}$ or $SF_6$ while the $F^+$ ions may be formed by the ionization of any of the molecules represented in reaction (1). The fact that ions 19 and 127 may be produced from either $S_2F_{10}$ or the conversion products, makes it difficult to estimate the conversion efficiency at this time. It has been shown in recent experiments [13] that it is extremely difficult to distinguish the $S_2F_{10}$ and $SF_6$ mass spectra at the standard electron-impact energy of 70 eV used for the mass spectrometer ionizer.

In order to determine the presence of $S_2F_{10}$ in gas insulated equipment, very low concentrations of $S_2F_{10}$ must be detected in $SF_6$. Because $S_2F_{10}$ and $SF_6$ have nearly identical mass spectra [13], the GC/MS detection technique is normally not very sensitive when $[SF_6] >> [S_2F_{10}]$. Even though $SF_6$ and $S_2F_{10}$ have significantly different retention times (typically more than 1 minute), the tail of the extremely large $SF_6$ signal completely obscures the much smaller $S_2F_{10}$ signal at concentrations much below 50 ppm. The conversion of $S_2F_{10}$ into $SOF_2$ on the membrane separator provides a means of improving the detection sensitivity of $S_2F_{10}$ in $SF_6$ because the mass spectrum of $SOF_2$ contains several ion masses (i.e. 86 and 48) which do not appear in the $SF_6$ mass spectrum. Thus for masses 86 and 48 there is no signal due to the ionization of $SF_6$ and thus no interference with the $S_2F_{10}$ peak.

Figure 8 shows the differences in $S_2F_{10}$ detection sensitivities for mass 19, 48, and 86 ions in the presence of $SF_6$. The mass 19 signal has no observable $S_2F_{10}$ feature due to the large sloping background signal from $SF_6$. However the mass 48 and 86 signals exhibit no background from $SF_6$ and have clearly defined $S_2F_{10}$ features. The detection limit of $S_2F_{10}$ in $SF_6$ by this technique is on the order of 1 ppm, using a standard, un-modified GC/MS instrument. Greater sensitivities may be achievable by modifying the membrane separator assembly. This technique possesses the lowest detection limits for $S_2F_{10}$ in $SF_6$ of any known direct analysis technique currently available which does not require elaborate $S_2F_{10}$ sample enrichment procedures [14].
CONCLUSION

The results of this study indicate that the decomposition of S2F10 in standard sample cylinders is a problem in any attempt to determine the presence of S2F10 in SF6-insulated equipment. Obviously SF6 gas samples that contain low-levels of S2F10 can decompose significantly before they reach the analytical laboratory if stored under conditions similar to those considered here. Moreover, it is conceivable that improper gas extraction procedures in practical situations could result in rates of S2F10 decay greater than observed in the experiments discussed here. Thus care must be taken to eliminate or compensate for the loss of S2F10 in samples obtained for quantitative analysis.

While additional investigation of the mechanisms of S2F10 decomposition need to be performed, preliminary guidelines for S2F10 sample storage are suggested from the results of this study. To minimize the rate of decomposition, gas samples containing S2F10 should be prepared under conditions that are as dry as possible in cylinders that are as large as possible and stored at low temperatures. However, it must be noted that in this study, even the samples which were stored under the most favorable conditions exhibited significant decomposition over sufficiently long periods of time. Thus continued research needs to be pursued in order to develop better methods for maintaining standard-reference S2F10 samples and for assessing sample stability.

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REFERENCES

[5] Pure S2F10 was synthesized in a high-temperature reactor containing sulfur and fluorine by Dr. Darryl Desmarteau, Clemson Univ., Clemson, S.C. The identity of the sample was determined by IR absorption spectroscopy.
[11] Each cylinder was flushed with SF6 and evacuated before the preparation of the samples to remove as much surface moisture as possible.
[12] Each cylinder was exposed to humid atmosphere for 14 hours before being evacuated and filled with an S2F10 sample.