CATALYTIC DECOMPOSITION OF $S_2F_{10}$ AND ITS IMPLICATIONS ON SAMPLING AND DETECTION FROM $SF_6$-INSULATED EQUIPMENT

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ABSTRACT

Recent findings indicate that $S_2F_{10}$ 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 $S_2F_{10}$ 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 $S_2F_{10}$ samples are discussed. Additionally, the use of this surface decomposition mechanism to enhance the detection sensitivity of small concentrations of $S_2F_{10}$ in $SF_6$ using a gas chromatograph/mass spectrometer (GC/MS) is investigated. Detection sensitivities of 1 ppm by volume (ppmv) of $S_2F_{10}$ in $SF_6$ are routinely achievable using this new technique.

INTRODUCTION

Recent studies [1,2] have shown the important role that $S_2F_{10}$ plays in accounting for the toxicity of decomposed $SF_6$ in gas-insulated equipment. Because of these studies, there has been increased interest in quantifying the rate of $S_2F_{10}$ production in electrical discharges. Other work has indicated that $S_2F_{10}$ is unstable and decomposes into SOF$_2$, SF$_6$, and other by-products [3] when stored in stainless steel gas-sampling cylinders at room temperature. This instability brings into question the reliability of gas sampling procedures used for $S_2F_{10}$ analysis. It also raises questions about maintenance of reliable reference samples containing known amounts of $S_2F_{10}$ that are necessary for calibration of analytical equipment.

Since the half-life for gas-phase unimolecular decay of $S_2F_{10}$ at room temperature is extremely long (≈10$^6$ years) [4], it is speculated that the observed decomposition of $S_2F_{10}$ inside sample cylinders must be due to unknown catalytic processes occurring on surfaces. We report the first results of a study performed jointly at the National Institute of Standards and Technology (NIST) and Oak Ridge National Laboratory (ORNL) to investigate these surface reactions. Possible reaction mechanisms for surface decomposition of $S_2F_{10}$ are proposed and approximate rates of decay have been determined. Additionally, conditions which affect the decay rates have also been studied. The findings of these experiments provide a basis for preliminary recommendations on $S_2F_{10}$ sampling, storage, and testing procedures.

We also discuss the use of these catalytic decomposition reactions to improve the detection sensitivity of $S_2F_{10}$ in $SF_6$ using gas chromatography/mass spectrometry. By detecting the products SOF$_2$ and H$_2$ from the $S_2F_{10}$ surface reactions occurring on a membrane separator in a GC/MS system, this species can be routinely detected in the presence of $SF_6$ down to concentrations of less than 1 ppmv.

EXPERIMENTAL METHOD

The experimental method for the study of $S_2F_{10}$ 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 $S_2F_{10}$ [5] and argon. Argon was used as a buffer gas because of its chemical inertness and because its presence did not interfere with either the detection of $S_2F_{10}$ or its decomposition products. In other buffer gases, such as N$_2$ and SF$_6$, $S_2F_{10}$ exhibited similar decomposition properties. The concentrations of $S_2F_{10}$ and the primary decomposition products, such as SOF$_2$ and SF$_6$, 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 $S_2F_{10}$ detection was a 24' x 1/8" Teflon® tube containing 30% SP-2100 (Supelco) on 80/100 chromosorb W AW [6]. The conditions employed in the two GC analyzers were similar: Carrier gas, He; Oven temperature, 25-50°C; and He flow rate, 20-30 ml/min. The absolute quantities of $S_2F_{10}$ 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 $S_2F_{10}$, SF$_6$, SOF$_2$, and Ar.

RESULTS AND DISCUSSION

Figure 1 shows the decomposition curves for $S_2F_{10}$ and the related production curves for the two main observable gas-phase products, SOF$_2$ and SF$_6$, in two experiments with different experimental conditions (see figure caption). Note that the $S_2F_{10}$ 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 $S_2F_{10}$ 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 $S_2F_{10}$ which ultimately formed SF$_6$ 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.
Figure 1. Decomposition of SF$_{10}$ and corresponding production of SOF$_2$ and SF$_6$ with time for two experiments with the following conditions: (a) 78 ml stainless steel cylinder; 2.1 cm$^{-1}$ 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$^{-1}$ surface-to-volume ratio; Argon buffer gas; Pressure = 1 atm; 1500 ppm, starting concentration; Temperature = 25°C; 1 µl water added.

The approximate rate coefficients corresponding to the SF$_{10}$ decay curves in Figures 1a and 1b may be calculated as approximately $7 \times 10^{-7}$ s$^{-1}$ and $2 \times 10^{-5}$ s$^{-1}$, respectively. While both coefficients are fairly small and differ by more than an order of magnitude from each other, both values are significantly larger than the estimated gas-phase unimolecular decay rate coefficient of SF$_{10}$ at room temperature ($2.9 \times 10^{-15}$ s$^{-1}$) [4], and anticipated gas-phase hydrolysis rates of SF$_{10}$ [7]. This implies that the decomposition of SF$_{10}$ must occur preferentially on the surface of the stainless steel cylinders. The facts that the decomposition rate goes up with H$_2$O contamination and that SOF$_2$ and SF$_6$ are initially the primary products suggests that water plays a major role in the decomposition, and that at least a portion of the SF$_{10}$ decomposes via a reaction such as

$$\text{SF}_{10} + \text{H}_2\text{O} \rightarrow \text{SOF}_2 + \text{SF}_6 + 2\text{HF}. \quad (1)$$

Although HF is detected in the sample cylinder as the SF$_{10}$ 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 SF$_{10}$ on the surface, or perhaps a disproportionation reaction into SF$_6$ + SF$_4$ followed by hydrolysis of the SF$_4$ product.

Surface hydrolysis of other sulfur fluoride compounds has been previously [8] observed but is not fully understood. Note that SOF$_2$ also decomposes in stainless steel cylinders as is evident by the eventual decrease in the SOF$_2$ concentration shown in Figure 1 and by the decomposition data shown in Figure 2 from SOF$_2$ stored in a stainless steel cylinder under conditions similar to those in Figure 1. This decomposition cannot be due to gas-

Figure 2. Decomposition of SOF$_2$ with time under the following experimental conditions: 32 ml stainless steel cylinder; 2.6 cm$^{-1}$ surface-to-volume ratio, Argon buffer gas; Pressure = 1 atm; 6000 ppm, starting concentration; Temperature = 25°C; and no water added.

phase hydrolysis because the rate [9] for the gas-phase reaction

$$\text{SOF}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_3 + 2\text{HF} \quad (2)$$

is much too slow to account for the observed loss of SOF$_2$ and because SO$_3$ was detected as only a minor product in the experiments shown in Figures 1 and 2. Therefore the SOF$_2$ decomposition is probably due to surface catalyzed reactions.

Were reaction (1) the sole mechanism for SF$_{10}$ decomposition, then the amount of decomposed SF$_{10}$ should equal the amount of SOF$_2$ and SF$_6$ produced. However it is obvious from the sum of the absolute concentrations of the identified gas-phase sulfur-containing compounds (SF$_{10}$, SF$_6$, SOF$_2$) in the cylinder, that all of the sulfur initially present in the cylinder as SF$_{10}$ cannot be accounted for by the observed gaseous products (see Figure 3).

While the decomposition of SOF$_2$ 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 SF$_{10}$ decomposition and the hydrolysis of SOF$_2$ were the only source of the loss of sulfur, then at long times (i.e. after all the SF$_{10}$ has decomposed) the concentration of SF$_6$ should equal the initial concentration of SF$_{10}$ since, as expected, SF$_6$ does not exhibit any decomposition. However, it is obvious from Figures 1 and 3 that the final concentrations of

Figure 3. Total normalized sulfur content in identifiable gas-phase molecules as a function of time for the two decomposition experiments described in (a) Figure 1a and (c) Figure 1b.
SF$_6$ are only about 20–30% of the initial S$_2$F$_{10}$ concentrations and account for only 10–15% of the available sulfur. Thus it appears that some of the end products of S$_2$F$_{10}$ decomposition adhere to the surfaces or are gaseous species that have yet to be identified.

An electron impact mass spectrum of a decomposed S$_2$F$_{10}$ 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 S$_2$F$_{10}$ or ions from sulfur-containing decomposition products. The other peaks represent unidentified gaseous products from the decomposition of S$_2$F$_{10}$ 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 CH$_3$ 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 SOF$_2$ is initially present. Interestingly, S$_2$F$_{10}$ samples in N$_2$ buffer gas produce products with mass spectra that differ considerably from Figure 4a. Evidence exists of unidentified products containing nitrogen, thus indicating that N$_2$ 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, S$_2$F$_{10}$ samples decompose significantly within a matter of hours (Figure 1b). This could affect the accuracy and sensitivity of tests used to determine concentrations of S$_2$F$_{10}$ in gas-insulated equipment if appropriate sampling guidelines are not determined and followed. Even if the decomposition rate of a particular S$_2$F$_{10}$ sample is not as great as that shown in Figure 1b, the long-term decomposition of S$_2$F$_{10}$ reference samples makes careful quantification of S$_2$F$_{10}$ 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 S$_2$F$_{10}$ samples is essential in the ongoing research to investigate S$_2$F$_{10}$ production in SF$_6$-insulated equipment.

As indicated by the above discussion, water appears to be an essential component in the decomposition of S$_2$F$_{10}$. The possible influence of water was examined further by preparing two identical S$_2$F$_{10}$ samples (1400 ppm, S$_2$F$_{10}$ 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 S$_2$F$_{10}$ 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 S$_2$F$_{10}$ decomposition in stainless steel cylinders. Figure 6 shows the results of an experiment where three S$_2$F$_{10}$ 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 S$_2$F$_{10}$ observed in Figure 6. Thus the temperature of the sample (and/or the surface) clearly affects the rates of the reactions occurring on
the surface of the sample cylinders.

While storing samples of $\text{SF}_6$ 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 ($\sim$ 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 $\text{SF}_6$ decomposition depends could be affected by the gas pressure.

From chemical kinetics theory [10], it is expected that the reaction rate for decomposition of $\text{SF}_6$ on a surface will be proportional to surface area. This behavior is supported by a large body of evidence from our work indicating that $\text{SF}_6$ samples decompose more rapidly as sample cylinder surface-to-volume ratio increases. However, a direct proportionality of $\text{SF}_6$ decay rate to cylinder surface-to-volume ratio has not yet been verified.

The data shown in Figures 1-5 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 $\text{SF}_6$ 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 $\text{SF}_6$ in the Monel cylinder decayed at a rate four times greater than the $\text{SF}_6$ in the other cylinders. The stainless steel, Teflon and glass cylinders all exhibited decay rates that were within 12% of each other.

**$\text{SF}_6$ DETECTION USING SURFACE-CATALYZED DECOMPOSITION**

An interesting aspect of the surface-catalyzed decomposition of $\text{SF}_6$ is that this same process apparently occurs on the membrane separator of the GC/MS instrument used for $\text{SF}_6$ detection in some of the previously discussed experiments. During analysis of $\text{SF}_6$ samples, this decomposition causes features to appear in the GC/MS chromatograms at retention times corresponding to $\text{SF}_6$ 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 $\text{SF}_6$ sample in argon.

The $\text{SO}^+$ and $\text{SO}_2^+$ ions are the result of electron-impact ionization of $\text{SO}_2$ 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 $\text{SF}_6$ surface decomposition. The presence of these ions is further proof that at least a portion of the $\text{SF}_6$ molecules experience a decomposition process represented by reaction (1), and the fact that the signal occurs at retention times corresponding to $\text{SF}_6$ indicates that the conversion takes place after the $\text{SF}_6$ elutes from the GC column. The mass 127 ions can be due to ionization of either $\text{SF}_6$ or $\text{SF}_7$ but not $\text{SF}_6$. The standard electron-impact energy of 70 eV used for the mass spectrometer ionizer.

In order to determine the presence of $\text{SF}_6$ in gas-insulated equipment, very low concentrations of $\text{SF}_6$ must be detected in $\text{SF}_6$. Because $\text{SF}_6$ and $\text{SF}_6$ have nearly identical mass spectra [13], the GC/MS detection technique is normally not very sensitive when $[\text{SF}_6] >> [\text{SF}_6]$. Even though $\text{SF}_6$ and $\text{SF}_6$ have significantly different retention times (typically more than 1 minute), the tail of the extremely large $\text{SF}_6$ signal completely obscures the much smaller $\text{SF}_6$ signal at concentrations much below 50 ppm. The conversion of $\text{SF}_6$ into $\text{SO}_2$ on the membrane separator provides a means of improving the detection sensitivity of $\text{SF}_6$ in $\text{SF}_6$ because the mass spectrum of $\text{SO}_2$ contains several ion masses (i.e. 86 and 48) which do not appear in the $\text{SF}_6$ mass spectrum. Thus for masses 86 and 48 there is no signal due to the ionization of $\text{SF}_6$ and thus no interference with the $\text{SF}_6$ peak.

Figure 8 shows the differences in $\text{SF}_6$ detection sensitivities for mass 19, 48, and 86 ions in the presence of $\text{SF}_6$. The mass 19 signal has no observable $\text{SF}_6$ feature due to the large sloping background signal from $\text{SF}_6$. However the mass 48 and 86 signals exhibit no background from $\text{SF}_6$ and have clearly defined $\text{SF}_6$ features. The detection limit of $\text{SF}_6$ in $\text{SF}_6$ by this technique is
CONCLUSION

The results of this study indicate that the decomposition of SF$_{10}$ in standard sample cylinders is a problem in any attempt to determine the presence of SF$_{10}$ in SF$_6$-insulated equipment. Obviously SF$_6$ gas samples that contain low-levels of SF$_{10}$ 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 SF$_{10}$ decay greater than observed in the experiments discussed here. Thus care must be taken to eliminate or compensate for the loss of SF$_{10}$ in samples obtained for quantitative analysis.

While additional investigation of the mechanisms of SF$_{10}$ decomposition need to be performed, preliminary guidelines for SF$_{10}$ sample storage are suggested from the results of this study. To minimize the rate of decomposition, gas samples containing SF$_{10}$ 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 standards-reference SF$_{10}$ samples and for assessing sample stability.

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