

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 (ppm_v) 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 ($\sim 10^7$ 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 HF 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 ppm_v.

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' \times 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, SF_6 and SOF_2 , 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.

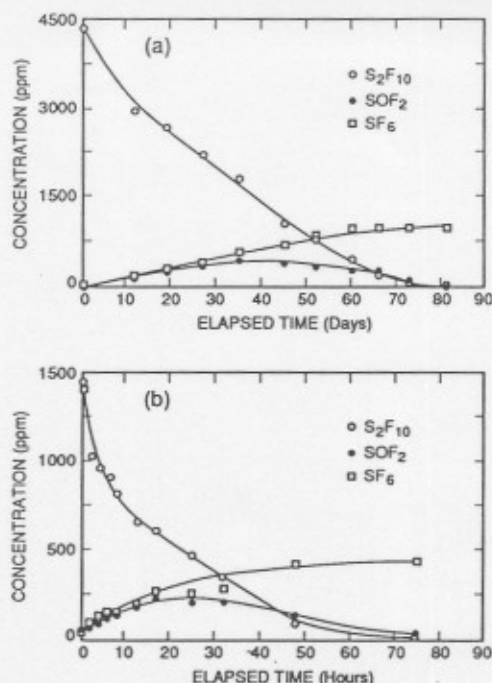
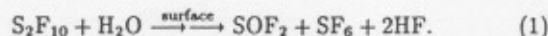


Figure 1. Decomposition of S_2F_{10} and corresponding production of SOF_2 and SF_6 with time for two experiments with the following conditions: (a) 78 ml stainless steel cylinder; 2.1 cm^{-1} surface-to-volume ratio; Argon buffer gas; Pressure = 1 atm; 4500 ppm_v starting concentration; Temperature = 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_v starting concentration; Temperature = 25°C; 1 μl water added.

The approximate rate coefficients corresponding to the S_2F_{10} decay curves in Figures 1a and 1b may be calculated as approximately $7 \times 10^{-7}\text{ s}^{-1}$ and $2 \times 10^{-5}\text{ s}^{-1}$, 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 S_2F_{10} at room temperature ($2.9 \times 10^{-15}\text{ s}^{-1}$) [4], and anticipated gas-phase hydrolysis rates of S_2F_{10} [7]. This implies that the decomposition of S_2F_{10} must occur preferentially on the surface of the stainless steel cylinders. The facts that the decomposition rate goes up with H_2O 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 S_2F_{10} decomposes via a reaction such as



Although HF is detected in the sample cylinder as the S_2F_{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 S_2F_{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-

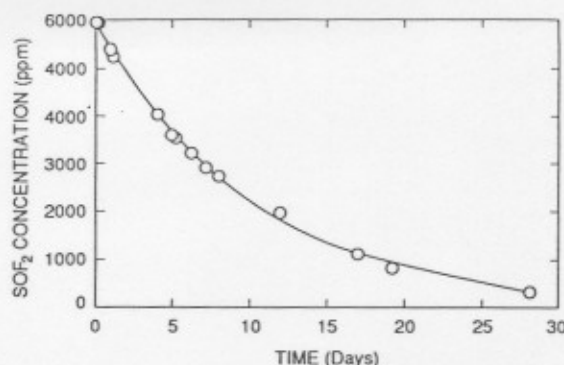


Figure 2. Decomposition of SOF_2 with time under the following experimental conditions: 32 ml stainless steel cylinder; 2.6 cm^{-1} surface-to-volume ratio, Argon buffer gas; Pressure = 1 atm; 6000 ppm_v starting concentration; Temperature = 25°C; and no water added.

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



is much too slow to account for the observed loss of SOF_2 and because SO_2 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 S_2F_{10} decomposition, then the amount of decomposed S_2F_{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 (S_2F_{10} , SF_6 , SOF_2) in the cylinder, that all of the sulfur initially present in the cylinder as S_2F_{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 S_2F_{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 S_2F_{10} has decomposed) the concentration of SF_6 should equal the initial concentration of S_2F_{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

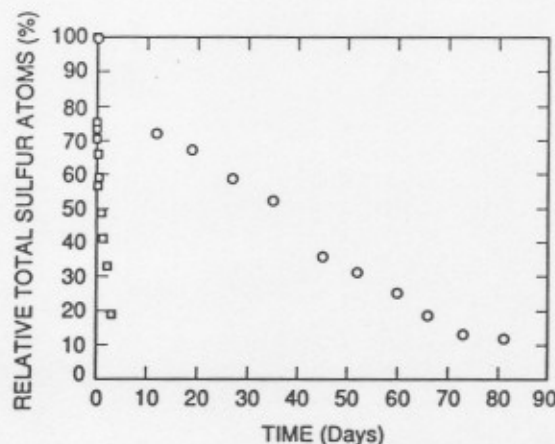


Figure 3. Total normalized sulfur content in identifiable gas-phase molecules as a function of time for the two decomposition experiments described in (○) Figure 1a and (□) Figure 1b.

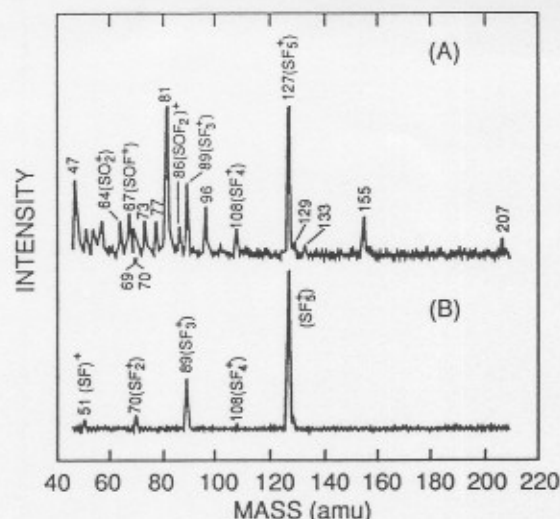


Figure 4. (A) Electron impact mass spectra of an S_2F_{10} in Ar sample stored in a 75 ml stainless steel cylinder for 35 days. Only 100 ppm_v of an original 5000 ppm_v of S_2F_{10} remains. (B) Mass spectrum of an undecomposed 3000 ppm_v S_2F_{10} sample in Ar.

SF_6 are only about 20–30% of the initial S_2F_{10} concentrations and account for only 10–15% of the available sulfur. Thus it appears that some of the end products of S_2F_{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_2F_{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_2F_{10} or ions from sulfur-containing decomposition products. The other peaks represent unidentified gaseous products from the decomposition of S_2F_{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 walls. 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_2F_{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_2F_{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_2F_{10} in gas-insulated equipment if appropriate sampling guidelines are not determined and followed. Even if the decomposition rate of a particular S_2F_{10} sample is not as great as that shown in Figure 1b, the long-term decomposition of S_2F_{10} reference samples makes careful quantification of S_2F_{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_2F_{10}

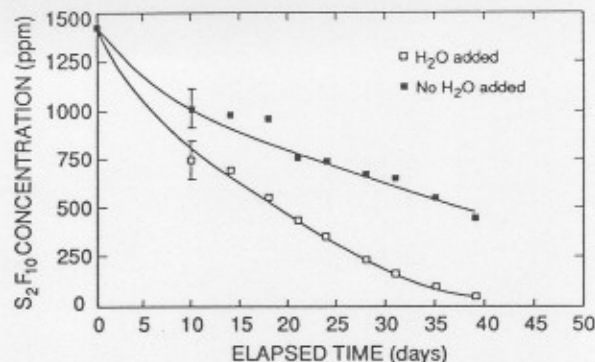


Figure 5. Decomposition of S_2F_{10} as a function of time for two 1400 ppm_v S_2F_{10} samples in 1 atm Ar in 150 ml stainless steel cylinders. For one sample (\square), 1 μ l of liquid water was injected into the cylinder prior to filling with gas.

samples is essential in the ongoing research to investigate S_2F_{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_2F_{10} . The possible influence of water was examined further by preparing two identical S_2F_{10} samples (1400 ppm_v S_2F_{10} in 1 atm Ar in 150 ml stainless steel cylinders) with 1 μ l 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_2F_{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_2F_{10} decomposition in stainless steel cylinders. Figure 6 shows the results of an experiment where three S_2F_{10} samples (500 ppm_v 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_2F_{10} observed in Figure 6. Thus the temperature of the sample (and/or the surface) clearly affects the rates of the reactions occurring on

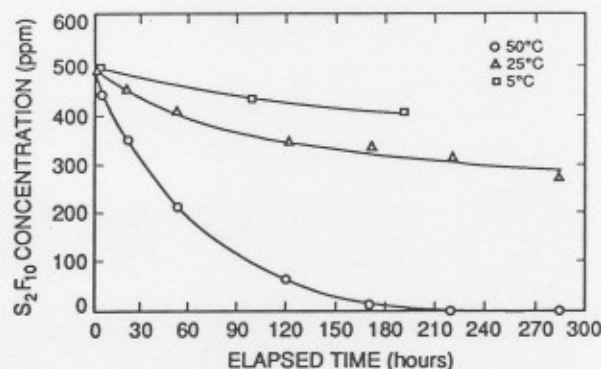


Figure 6. Decomposition of S_2F_{10} as a function of time at different temperatures. Samples were 500 ppm_v S_2F_{10} in 1 atm Ar in 150 ml stainless steel cylinders.

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^+ 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^+ ion

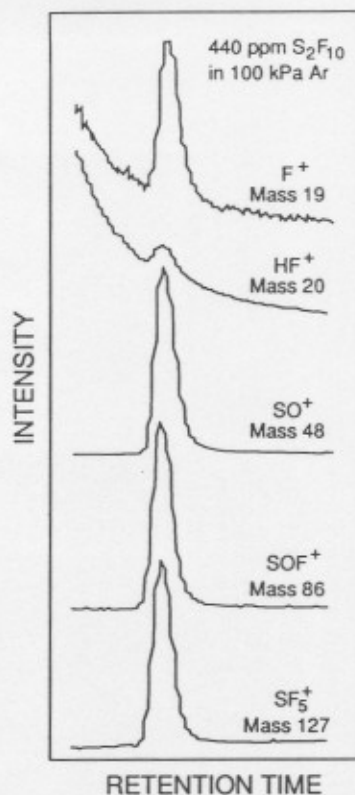


Figure 7. S_2F_{10} features observed using a GC/MS with a silicon-rubber membrane separator. For masses 19 and 20 there is a large sloping background from doubly charged argon ions.

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 $[SF_6] \gg [S_2F_{10}]$. 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

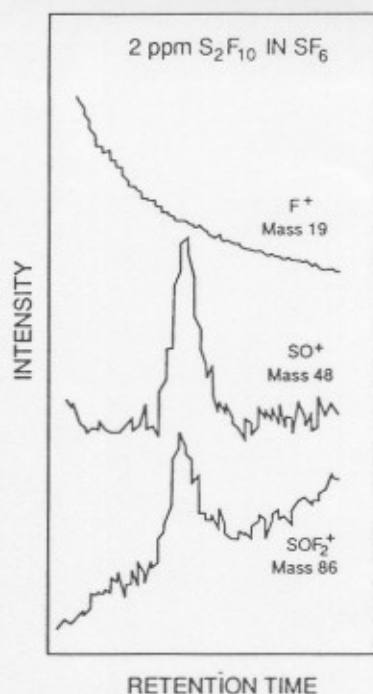


Figure 8. S_2F_{10} features observed using a GC/MS with a silicon-rubber membrane separator to analyze a very dilute (2 ppm) mixture of S_2F_{10} in SF_6 .

CONCLUSION

The results of this study indicate that the decomposition of S_2F_{10} in standard sample cylinders is a problem in any attempt to determine the presence of S_2F_{10} in SF_6 -insulated equipment. Obviously SF_6 gas samples that contain low-levels of S_2F_{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 S_2F_{10} decay greater than observed in the experiments discussed here. Thus care must be taken to eliminate or compensate for the loss of S_2F_{10} in samples obtained for quantitative analysis.

While additional investigation of the mechanisms of S_2F_{10} decomposition need to be performed, preliminary guidelines for S_2F_{10} sample storage are suggested from the results of this study. To minimize the rate of decomposition, gas samples containing S_2F_{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 standard-reference S_2F_{10} samples and for assessing sample stability.

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