Photoreductive degradation of sulfur hexafluoride in the presence of styrene

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Abstract

Sulfur hexafluoride (SF6) is known as one of the most powerful greenhouse gases in the atmosphere. Reductive photodegradation of SF6 by styrene has been studied with the purpose of developing a novel remediation for sulfur hexafluoride pollution. Effects of reaction conditions on the destruction and removal efficiency (DRE) of SF6 are examined in this study. Both initial styrene-to-SF6 ratio and initial oxygen concentration exert a significant influence on DRE. SF6 removal efficiency reaches a maximum value at the initial styrene-to-SF6 ratio of 0.2. It is found that DRE increases with oxygen concentration over the range of 0 to 0.09 mol/m3 and then decreases with increasing oxygen concentration. When water vapor is fed into the gas mixture, DRE is slightly enhanced over the whole studied time scale. The X-ray Photoelectron Spectroscopy (XPS) analysis, together with gas chromatography-mass spectrometry (GC-MS) and Fourier Transform Infrared spectroscopy (FT-IR) analysis, prove that nearly all the initial fluorine residing in the gas phase is in the form of SiF4, whereas, the initial sulfur is deposited in the form of elemental sulfur, after photodegradation. Free from toxic byproducts, photodegradation in the presence of styrene may serve as a promising technique for SF6 abatement.

Key words: SF6; 184.9 nm irradiation; styrene; reductive radicals; photodegradation

Introduction

Attributed to its special properties, such as, chemical inertness, nontoxicity, and nonflammability, sulfur hexafluoride is currently the most widely used gas insulator in high-voltage equipments (Maiss and Brenninkmeijer, 1998; Chistophorou et al., 1997). However, extensive attention has been paid to sulfur hexafluoride (SF6) for its GWPs up to 23900 (Houghton et al., 1996). In recent years, SF6 has been globally recognized as the strongest greenhouse gas. Moreover, as one type of fully fluorinated compound, sulfur hexafluoride exhibits a very low reactivity toward the oxidative species, such as, O(1D) and OH, and is therefore classified as a long-lived atmospheric constituent (Ravishankara et al., 1993; Zhang et al., 2005). Input of SF6 into the atmosphere will lead to its accumulation, and even if its input were to be curtailed, it will take a rather long time, possibly tens of centuries, for the atmosphere to recover to its initial state. Hence, SF6 is among the six prominent greenhouse gases that the Kyoto Protocol seeks to control. The concentration of SF6 in the atmosphere must be absolutely limited.

The great global warming potential and extraordinary long lifetime of SF6 have triggered a significant effort to reduce its emissions. Technologies available for abating SF6 emissions include combustion (Dervos and Vassiliou, 2000), chemical-thermal reduction (Lee and Choi, 2004), and plasma processing (Shih et al., 2002, 2003; Lee et al., 2004). Combustion is the most developed technology. To achieve a reasonable destruction efficiency, a temperature higher than 1100°C is required. Other abatement technologies are based on the electron impact reactions of SF6. Because of its strong electroaffinity, SF6 will probably undergo dissociative attachment and direct dissociation processes in electrical discharge. Despite the relatively high destruction and removal efficiency (>90% in general), toxic byproducts, including S2F10, SO2F2, SOF2, SOF3, and SF3, can be produced simultaneously during these treatments (Lee et al., 2004). Such drawbacks inhibit the application of these technologies. Photochemical technology is capable of abating a lot of recalcitrant contaminants. Direct photolysis and photo-oxidation processes are reported to be inefficient in terms of SF6 abatement. However, strong reductants can completely decompose many perfluorinated compounds (Perry, 1986). Therefore, the authors have developed one photoreduction technology to abate SF6 at ambient temperature in this research study. As a common industrial waste gas, styrene has been selected as a photoreductant. Reductive photofragments from styrene have been used to dissociate SF6 for the first trial. Results have been presented and the photodegradation mechanism has been discussed as well.
1 Experimental

1.1 Reagents

SF$_6$ (purity 99.9\%) was obtained from Shanghai Refrigerant Products Inc., China; N$_2$ (purity 99.999\%) and O$_2$ (purity 99.2\%) from Shanghai Pujiang Specific Gas Corporation, China. Styrene (purity 99.0\%) was purchased from Shanghai Chemical Reagent Inc. and was purified by repeated freeze-pump-thaw cycling. All the other reagents were not further purified before use.

1.2 Photodegradation devices and procedures

The cylindrical reaction cell (460 mm in length and 32 mm in diameter) was made up of stainless steel to avoid erosion by fluorinated products. A 15-W low-pressure mercury lamp (Shanghai Huade, China), which emitted 184.9 nm irradiation, was equipped in the reaction cell, to initiate photochemical reactions. To begin the experiment, reactant gases were admitted into the reaction cell through a set of glass vacuum systems, with a standard manometer (Huang et al., 2005).

On the basis of the previous studies (Krete et al., 2001; Lee et al., 2004), FT-IR was an ideal method for fluorine-containing compounds detection because of the strong absorption cross-section. After irradiation, the gas was subjected to FT-IR spectrometry (Nexus-470IR, resolution: 1 cm$^{-1}$, Nicolet, USA), to quantify the destruction and removal efficiency of SF$_6$ (DRE, defined as the amount of SF$_6$ destructed/the amount of SF$_6$ before irradiation). In addition, FT-IR spectra were used to identify other fluorine-containing gaseous species. Apparently, other than fluorine-containing compounds, the sulfur-containing and carbon-containing ones might present in the gas phase after irradiation. Hence, the gaseous byproducts formed were also analyzed by GC-MS using Varian CP 3800 gas chromatography with Varian Saturn 2000 mass spectrometry (E.L. 70 eV) for a better understanding of all the products. A Gas-pro capillary column with 30 m length and 0.32 mm i.d. was used. The initial temperature of 50°C was maintained for 2 min, and then the temperature was programmed to 180°C at a rate of 10°C/min. The chemical composition and state of the deposit generated during the photodegradation reaction was characterized by X-ray photoelectron spectroscopy (XPS) using the ESCA system (PHI 5000C, Perkin Elmer Co., USA).

All the experiments were carried out at 329.0 ± 1.0 K. The data points reported were results derived from at least triplicate experiments.

2 Results and discussion

2.1 Photodegradation of SF$_6$ in the presence of styrene

Figure 1 shows that the efficient decomposition of SF$_6$ could be achieved by utilizing styrene as photochemical reductant.

The photoreduction of SF$_6$ in the presence of styrene must involve the excitation of styrene, because (1) SF$_6$ cannot be photolyzed by 184.9 nm irradiation (Kendall and Mason, 2001) and (2) styrene cannot react with SF$_6$ in the dark.

To have a clear picture of the photoreduction mechanism, one should first understand the photochemical behavior of styrene at 184.9 nm. The previous studies (Yu et al., 1985; Lee et al., 2003) demonstrated that the photolysis process seemed to be rather complicated. Styrene had to proceed with a structural rearrangement to an intermediate, bicyclo[4.2.0]octa-2,4,7-triene (BOT), before photodissociation. The dissociation course could be characterized as:

\[
\text{C}_6\text{H}_5\text{CH} \rightarrow \text{C}_6\text{H}_6 + \text{H}_2 \quad (1) \\
\text{C}_6\text{H}_5\text{CH} \rightarrow \text{C}_6\text{H}_6 + \text{C}_2\text{H}_2 \\
\rightarrow \text{C}_6\text{H}_3 + \text{H} + \text{C}_2\text{H}_2 \quad (2)
\]

Apparently, abundant reductive photofragments were produced. The structure of SF$_6$ was optimized in O$_h$ symmetry, that is, the six fluorine atoms were at the corners of a regular octahedron with the sulfur atom at the center. Reductive species, principally acting as strong electron donors, were inclined to interact with the highly electronegative fluorine atom in the SF$_6$ molecule and resulted in the fission of S–F bond. Therefore, it was fairly comprehensible that satisfactory DRE could be achieved when SF$_6$ was subjected to 184.9 nm irradiation together with styrene.

2.2 Influence of gas characteristics on the photodegradation of SF$_6$

Photoinduced destruction of SF$_6$ in the presence of styrene was later tested over a variety of initial reactant ratios, initial SF$_6$ concentrations, O$_2$ and H$_2$O$_{(g)}$ concentrations, and dilution gas.

2.2.1 Effect of initial reactant ratio

The influence of the initial reactant ratio on DRE was determined with an irradiation time of 180 min and SF$_6$ initial concentration of 0.107 mol/m$^3$ (Fig. 2). The removal efficiency reached a peak value at a specific initial reactant ratio. DRE continued ascending with the initial styrene-to-SF$_6$ ratio until it reached (72.1±4.0)% at an initial styrene-
to-SF$_6$ ratio of 0.2. Further increase in initial styrene-to-SF$_6$ ratio resulted in a little decline in DRE.

As mentioned in Section 2.1, styrene is the sole substance that absorbs the light from the mercury lamp. At low styrene concentration, scarce photofragments can interact with SF$_6$ and the DRE is rather small. More styrene brought about more molecules attainable to be photoexcited. It must also be noted that collisional deactivation and photo-polymerization processes are prompted simultaneously with an increase in the initial reactant ratio. Therefore, the amount of styrene in excited state was reduced, followed by a corresponding decrease in the reductive fragments. This might provide an explanation for a bit of decline in the DRE at a high styrene concentration.

2.2.2 Effect of initial SF$_6$ concentration

The destruction of SF$_6$ was then tested by a set of experiments performed at SF$_6$, initial concentration varied from 0.107 to 1.61 mol/m$^3$. As presented in Fig.3, for a given irradiation time, the extent of SF$_6$ decomposition descended along with its increasing initial concentration. Increasing SF$_6$ concentration resulted in a sharp decrease of DRE, especially in the range of 0 to 0.535 mol/m$^3$.

The increase of reactant concentration encouraged the collision process in the reaction cell. In other words, the collisions occurred between photoproduced fragments, and those between the fragments and SF$_6$, increased with the initial reactant concentration. Indeed, the chemical reaction between molecules relied on collisions (Moore, 1978). Nevertheless, only the collisional partners that brought sufficient kinetic energy to overcome the activation energy were effective (Espenson, 1981). On account of collisional deactivation, the amount of high-energy fragments did not increase in proportion with the concentration of SF$_6$. This might be responsible for the DRE reduction.

2.2.3 Effect of dilution gas

Figure 4 plots the variation of DRE at atmospheric pressure with nitrogen as dilution gas. In the presence of nitrogen, the DRE of SF$_6$ went down slightly for the corresponding irradiation time. Analysis of these phenomena called for certain remarks correlative with the molecular structure of N$_2$. On account of the bond energy of nitrogen up to 9.764 eV (Gaydon, 1950), nitrogen could barely dissociate under 184.9 nm irradiation. Yet, it was capable of quenching the excited molecules and photoproduced fragments via collision. The number of high-energy fragments which were available to react with SF$_6$ declined accordingly.

2.2.4 Effect of O$_2$ and H$_2$O(g) content

To avoid the recombination of SF$_6$ photofragments, using additive species that can rapidly react with SF$_6$ fragments is a reasonable approach. O$_2$ and H$_2$O(g) have been identified as good candidates for these reactions.

As indicated in Fig.5, the influence of O$_2$ content on SF$_6$ destruction efficiency was significant. Approximately 88% of the initial SF$_6$ was decomposed after 180 min of irradiation when only 0.09 mol/m$^3$ oxygen was added into the gas mixture. Oxygen was known as a good quencher of excited molecules. Considering that the addition of nitrogen resulted in a decrease in DRE, the role that oxygen played in the mixture could not be simply explained as a quench effect. A little amount of O$_2$ was beneficial to DRE, as described in Reactions (3)–(7). The unit of the reaction
constant is cm$^3$/mol-s.

\[
\begin{align*}
\text{O}_2 & \xrightarrow{184.9 \text{ nm}} \text{O}^\cdot(3\Sigma) + \text{O}^\cdot(1\Delta) \\
\text{H}_2 + \text{O}^\cdot(1\Delta) & \rightarrow \text{HO} + \text{H} \quad \text{(Atkinson et al., 1997)} \\
k & = 1.1 \times 10^{-10} \\
\text{SF}_5 + \text{O} & \rightarrow \text{SOF}_4 + \text{F} \quad \text{(Plumb and Ryan, 1986)} \\
k & = (2.0 \pm 0.5) \times 10^{-11} \\
\text{SF}_5 + \text{OH} & \rightarrow \text{SOF}_4 + \text{HF} \quad \text{(Pradayol et al., 1997)} \\
k & = 1.6 \pm 10^{-12} \\
\text{SF}_5 + \text{H} & \rightarrow \text{SF}_4 + \text{HF} \quad \text{(Malins and Setser, 1980)} \\
k & = 1.26 \pm 10^{-10}
\end{align*}
\]

However, too much O$_2$ in the gas mixture would actually reduce DRE. As shown in Fig. 5, the destruction efficiency fell off gradually with initial oxygen concentration when it exceeded 0.23 mol/m$^3$. No detectable degradation of SF$_6$ could be observed at initial oxygen concentrations of 0.96 mol/m$^3$. Although O could scavenge SF$_6$ dissociation fragments, the rapid oxidation of styrene and its photofragments by O or O$_2$ could not be neglected at high initial oxygen concentrations (Sloane and Brudzynski, 1979; Yu and Lin, 1994; Eichholtz et al., 1994; DeMore et al., 1997). With an increase in the initial concentration of oxygen, the proportion of reductive fragments consumed in the interaction with O or O$_2$ was elevated. Hence, the number of reductive fragments attainable to attack SF$_6$ lessened, which led to the low destruction efficiency of SF$_6$.

Figure 6 compares the photoreduction of SF$_6$ in the presence and absence of H$_2$O$_{(g)}$. Over the whole time range studied, DRE increased slightly as 0.021 mol/m$^3$ H$_2$O$_{(g)}$ was fed into the gas mixture. The results were quite comprehensible because both the hydroxyl radical and hydrogen atom produced from the photolysis of H$_2$O$_{(g)}$ (Welge and Stuhl, 1967) could contribute to DRE enhancement. The generated hydrogen atom, as one kind of reductive radical, would no doubt help the acceleration of SF$_6$ decomposition. Although the OH radical itself did not exhibit reactivity toward SF$_6$ (Ravishankara et al., 1993), it helped to elevate DRE according to Reaction (6). Indeed, the OH radical helped to oxidize styrene and its photofragments (Sloane and Brudzynski, 1979). H$_2$O$_{(g)}$ might also scavenge the excited styrene. These processes would not exert any detectable impact, considering the fact that the addition of H$_2$O$_{(g)}$ led to a monotonous increase in DRE.

### 2.3 Product distribution

After 0.107 mol/m$^3$ SF$_6$ and 0.021 mol/m$^3$ styrene were irradiated for 150 min, the gas sample was analyzed by FT-IR. As shown in Fig. 7, the main fluorinated product discerned by the IR spectrum was SiF$_4$. The silicon (Si) contained in the products originated from the wall of the UV lamp. The presence of SiF$_4$ in the products confirmed the reaction pathway proposed in Section 2.1. Reductive radicals attacked the fluorine atom in the SF$_6$ molecule, leading to the cleavage of the S–F bond, by eliminating HF. On account of the reaction between HF and the cell wall, SiF$_4$, instead of HF, was detected. GC-MS analysis was also performed to improve the authors’ knowledge of the byproducts. Identifiable fluorine containing species included CH$_3$F, C$_6$H$_5$F, and CHF$_3$. All these fluorine containing species were found in trace amounts, although the gas sample had been accumulated from 16 duplicate experiments to reach an appropriate signal-to-noise ratio.
Surprisingly, no sulfur containing products were detected in the gaseous sample. A careful check of the reaction cell showed that a thin film had formed on the wall of the reactor as the reaction proceeded. XPS analysis was then employed to investigate the chemical composition of the deposit. The survey spectra (Fig.8) indicated that it was composed of sulfur, carbon, and fluorine. Based on the fitting of the S\textsubscript{2p} and S\textsubscript{2s} peaks located at the binding energy of 164.8 and 229.2 eV, the sulfur existing in the deposit was mainly S\textsuperscript{0}. That is, nearly all the initial sulfur was deposited in the form of elemental sulfur after photodegradation.

3 Conclusions

A simple approach to abate SF\textsubscript{6} that had not been previously exploited was addressed in this article. A common industrial waste gas, styrene, was used as a reducing agent to effectively decompose SF\textsubscript{6}. More than 90% of the initial SF\textsubscript{6} was decomposed after 0.107 mol/m\textsuperscript{3} SF\textsubscript{6} and 0.020 mol/m\textsuperscript{3} styrene were irradiated for 360 min (Fig.1). In addition, the potential of photochemical technology for the destruction of SF\textsubscript{6} had been carefully discussed. Reaction conditions, such as, initial reagent ratio, O\textsubscript{2} and H\textsubscript{2}O\textsubscript{(g)} content, and dilution gas were found to have an impact on DRE. It was established that the addition of certain amounts of oxygen and water vapor were beneficial to SF\textsubscript{6} destruction.

It is noteworthy that the whole system has not been totally optimized. It takes time and effort for the application of this technique in spite of the present study having been performed. Reductive radical precursors other than styrene will be employed to photodecompose SF\textsubscript{6}. In addition, the authors will further extend this research study with more studies focused on the influence of reactor structure and UV source.

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References


Malins R J, Setser D W, 1980. Rate constants and vibrational energy disposal for reaction of H atoms with Br\textsubscript{2}, SF\textsubscript{3}Br, PBr\textsubscript{3}, SF\textsubscript{3}, and SF\textsubscript{4}. J Chem Phys, 73: 5666–5680.


