

A novel method to decompose two potent greenhouse gases: Photoreduction of SF₆ and SF₅CF₃ in the presence of propene

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Abstract

SF₅CF₃ and SF₆ are the most effective greenhouse gases on a per molecule basis in the atmosphere. Original laboratory trial for photoreduction of them by use of propene as a reactant was performed to develop a novel technique to destroy them. The highly reductive radicals produced during the photolysis of propene at 184.9 nm, such as •CH₃, •C₂H₃, and •C₃H₅, could efficiently decompose SF₆ and SF₅CF₃ to CH₄, elemental sulfur and trace amounts of fluorinated organic compounds. It was further demonstrated that the destruction and removal efficiency (DRE) of SF₅X (X represented F or CF₃) was highly dependent on the initial propene-to-SF₅X ratio. The addition of certain amounts of oxygen and water vapor not only enhanced the DRE but avoided the generation of deposits. In both systems, employment nitrogen as dilution gas lessened the DRE slightly. Given the advantage of less toxic products, the technique might contribute to SF₅X remediation.
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1. Introduction

Our planet nowadays is 0.6–0.7 °C warmer than it was in 1880 and additional global warming of 0.57–0.6 °C will occur in the future even if atmospheric constituents and other climate forcings remain fixed at today's values [1,2]. Such an elevation of global temperature is predicted to raise sea level, increase ozone depletion [3], threaten water supplies, forests, agriculture and so on. The experts in the field of climate change have arrived at an agreement that the anthropogenic discharge of greenhouse gases is responsible for the observed global warming over the last 50 years [4].

Sulfur hexafluoride (SF₆) is a chemically inert gas possessing unique physical and chemical properties that make it ideal for plasma etching [5,6]. Being nontoxic, nonflammable, it is an ideal substance employed as dielectric gas in semiconductor and insulator in sealed electric power equipment, cover

gas in magnesium production and casting, as well as an atmospheric and subterranean tracer gas [7]. First detected in the atmosphere in 1999 [8], trifluoromethyl sulfur pentafluoride (SF₅CF₃) originates as a by-product of fluorochemical manufacture and a breakdown product in high-voltage equipment [9,10]. SF₆ and SF₅CF₃ are part of a class of super greenhouse gases that have GWP₁₀₀ (global warming potential with time horizon of 100 years) of up to 23,900 and 17,500–18,600 [11,12]. In spite of their low concentration, SF₆ and SF₅CF₃ can significantly contribute to global warming due to their extensive radiative forcing, 0.52 W m⁻² ppbv⁻¹ and 0.59 W m⁻² ppbv⁻¹ [8,13], respectively on a per molecule basis. Once released into the atmosphere, such molecules will only be removed in tens of centuries due to lightning and ion-molecule reactions in the atmosphere [14–17]. These features have brought such compounds into greenhouse gases that the Kyoto Protocol seeks to control. It is therefore the right time to devise methods of eliminating or reducing these gases.

Approaches to achieve the elimination of SF₆ include: combustion, chemical–thermal elimination, non-equilibrium plasma [18–22]. Owing to the high chemical stability of SF₆, a temperature over 1100 °C is a usual requirement for an ideal abatement efficiency in combustion. Even if the temperature is high enough,

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the combustion process is still incomplete with NO_x released. In addition, erosion-proof material for the equipment is somewhat expensive. SF_6 does undergo decomposition and oxidation in an electrical discharge. The by-products from plasma processing are discerned as SF_4 , SF_2 , S_2F_{10} , SO_2F_2 , SOF_2 , SOF_4 , and $\text{S}_2\text{O}_2\text{F}_{10}$, some of which are noxious to human health or harmful to the environment [18]. All these drawbacks inhibit the application of such technologies. As for SF_5CF_3 , the abatement technique has not been reported in literature hitherto.

Photoreduction technique for pollutants elimination still belongs to a new area. Nevertheless, it has exhibited its efficiency in specific pollutants abatement [23,24]. This paper focuses on photochemical approach to reduce the emission of SF_6 and SF_5CF_3 . The basic clue is to utilize the active species produced during the photolysis of propene to effectively dissociate SF_6 and SF_5CF_3 , so as to facilitate the development of a new process for the conversion of SF_6 and SF_5CF_3 . The end-products and photodegradation mechanism are discussed as well.

2. Experimental

2.1. Reagents

The reagents used, and their purities were as follows: SF_6 (99.9%) obtained from Shanghai Refrigerant Products Inc.; SF_5CF_3 (99.0%) and propene (99.5%) from Wuxi Xinnan Chemical Gas Inc.; argon ($\geq 99.99\%$), nitrogen ($\geq 99.999\%$) and oxygen ($\geq 99.2\%$) from Shanghai Pujiang Special Gas Corporation. Styrene at purity of 99.0% was purchased from Shanghai Chemical Reagent Inc. and was subjected to repeated freeze–pump–thaw cycling before use. Except for styrene, the reagents were not further purified before use.

2.2. Photodegradation devices and procedures

Photodegradation studies were conducted in a homemade stainless steel reaction cell (460 mm in length and 32 mm in diameter) (see Fig. 1). The low-pressure mercury lamp (15 W, Shanghai Huade Lighting Ltd.) emitting 184.9 nm and 253.7 nm radiation was placed inside the reaction cell. To begin with an experiment, specific reactant gases were introduced into the cell through a glass vacuum system that had been described in detail

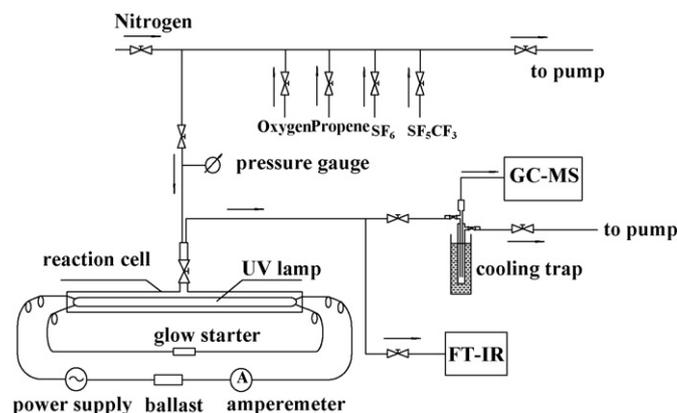


Fig. 1. Schematic diagram of the experimental system used in this work.

elsewhere [10]. Before being exposed to irradiation, the cell was stationed for long enough to ensure that the gases inside were fully mixed.

All the photochemical experiments were performed at 329 ± 1 K. For each experimental condition, three replicate experiments were carried out.

2.3. Analysis

2.3.1. Quantitative analysis

After irradiation, the concentration of SF_5X (X represented F or CF_3) remaining in the reaction cell was measured by FT-IR. The FT-IR spectrometer (Nexus-470IR, Nicolet) operated at a spectral resolution of 1 cm^{-1} over the range from 500 cm^{-1} to 4000 cm^{-1} . Gas sample from the reaction cell was directly expanded into an evacuated gas vessel (an infrared pathlength of 5.0 cm) equipped with a pair of KBr windows before FT-IR measurement. Each spectrum was averaged from 64 interferograms. Considering the absorbance of SF_6 and SF_5CF_3 , at $910\text{--}960 \text{ cm}^{-1}$ and $858\text{--}927 \text{ cm}^{-1}$, respectively, followed the Beer–Lambert law in the $0\text{--}2.14 \text{ mol m}^{-3}$ range, the destruction and removal efficiency of SF_6 or SF_5CF_3 (DRE, defined as the amount of SF_5X destructed/the amount of SF_5X before irradiation) was monitored by the absorbance at the corresponding band.

2.3.2. Qualitative analysis

GC–MS system was employed to identify the products in the gas phase. To achieve a better signal/noise ratio, the gaseous sample for product identification was collected from 16 duplicate experiments and condensed in a liquid nitrogen trap. After warmed to room temperature, the sample was analyzed by GC–MS. GC–MS system consisted of a gas chromatograph (Varian CP 3800) with a column (Gas-Pro, $30 \text{ m} \times 0.32 \text{ mm}$) swept by helium and a mass spectrometer (Varian Saturn 2000) with an electron impact ionization source of 70 eV energy operating at 200°C . The column temperature was initially held at 50°C for 2 min and then programmed up to 180°C at $10^\circ\text{C min}^{-1}$.

The chemical composition of the deposit generated during the photodegradation reaction was characterized by X-ray photoelectron spectroscopy (XPS). The photoelectron spectra were measured at room temperature under a vacuum of $1 \times 10^{-6} \text{ Pa}$ using ESCA system (PHI 5000C, PerkinElmer Co.). A monochromatic Al $\text{K}\alpha$ (1486.6 eV) with the working power of 250 W at the voltage of 14.0 kV was employed as the excitation source. Survey scans were performed with pass energy of 93.90 eV. For the Ag 3d $_{5/2}$ line, these conditions produced a full-width at half-maximum of 0.8 eV. The obtained spectra were calibrated from the charge effect using the C 1s featured at 284.50 eV.

3. Results and discussion

3.1. Photodegradation reaction

Propene and styrene are two potential reagents to dissociate SF_6 and SF_5CF_3 under UV irradiation on the assumption that

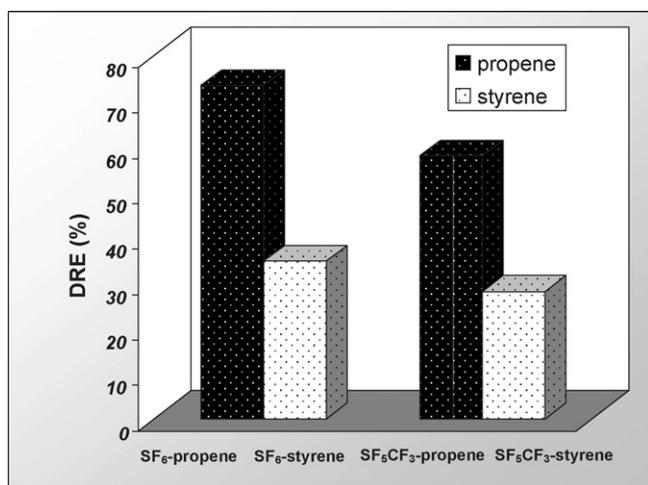


Fig. 2. DRE of SF₆ and SF₅CF₃ after 180 min of irradiation in the presence of propene as compared with in the presence of styrene. Reaction condition: $(C_{\text{SF}_6})_0 = (C_{\text{SF}_5\text{CF}_3})_0 = 0.107 \text{ mol m}^{-3}$, $(C_{\text{propene}})_0 = (C_{\text{styrene}})_0 = 0.214 \text{ mol m}^{-3}$.

these perfluorinated compounds were likely to be attacked by reductive fragments generated during the photolysis of propene and styrene at 184.9 nm. As illustrated in Fig. 2, efficient decomposition of SF₆ and SF₅CF₃ could be achieved by utilizing propene or styrene as photochemical reductant. As far as degradation rate was concerned, propene excelled styrene in both SF₆ and SF₅CF₃ abatement. Therefore, in the rest of this paper, only the photoreduction process of SF₅X in the presence of propene would be discussed in detail.

In the SF₆-propene system, the products identified by GC-MS analysis were: C₂F₆, C₃H₈, C₃H₇F, C₄H₁₀ (Fig. 3). Considering C₂F₆ was classified as one kind of potent greenhouse gas and had strong absorption in the atmospheric window [25], the same sample was analyzed by FT-IR for the purpose of C₂F₆ quantification. Whereas, there were no absorption peaks in the FT-IR spectrum at 1245 cm⁻¹, 1113 cm⁻¹ and 714 cm⁻¹ which were specific to C₂F₆. According to the GC-MS and FT-IR analysis, C₂F₆ was generated in the photodegradation reaction but only in trace amounts. The only products confirmed by FT-IR spectrum were CH₄ and SiF₄ (Fig. 4). Apparently, neither of the parent molecules con-

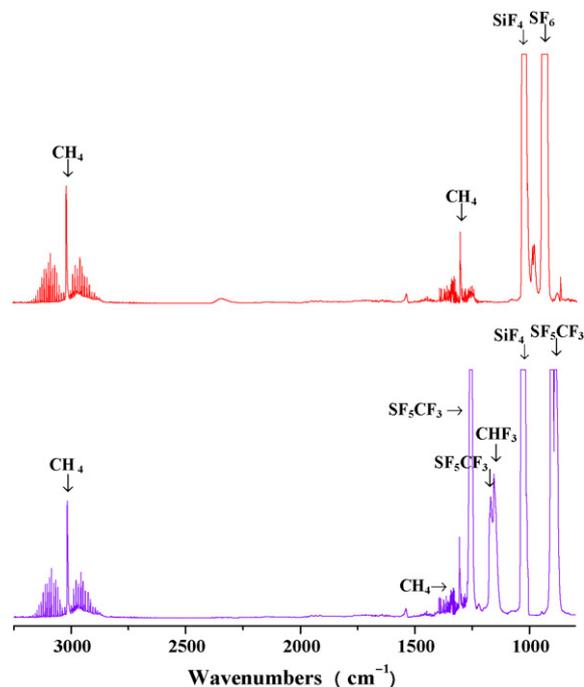


Fig. 4. Typical FT-IR spectra observed after SF₅X (0.107 mol m⁻³) and propene (0.214 mol m⁻³) were irradiated for 150 min.

tained silicon. The SiF₄ might originate from the collision of HF generated during the photochemical process with the wall of lamp. As for the SF₅CF₃-propene system, the products ascertained by means of GC-MS and FT-IR analysis included C₂F₆, CHF₃, CH₃CF₃, C₂H₅CF₂CF₂C₂H₅, CH₄, SiF₄ (Figs. 3 and 4). Similar to the SF₆-propene system, fluorinated organic compounds were also detected but in small quantities.

Under these reaction conditions, brown deposit continued to form over the whole time range. The XPS measurement was then carried out to investigate the chemical composition as well as the elemental state of the deposit. The survey spectrum (Fig. 5) indicated that the deposit was made up of S, C with low levels of F. Based on the fitting of the S_{2s} and S_{2p} peaks located at the binding energy of 229.2 and 164.8 eV, the sulfur existing in the deposit was mainly S⁰.

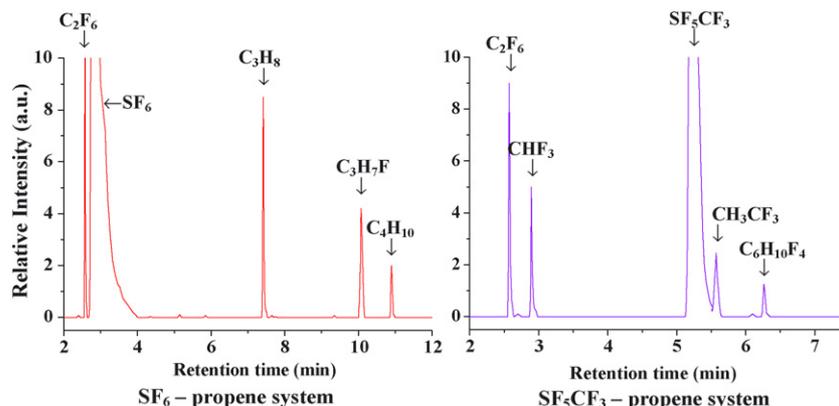


Fig. 3. GC-MS spectra of the gas mixture of SF₅X (0.107 mol m⁻³) and propene (0.214 mol m⁻³) after 150 min of irradiation.

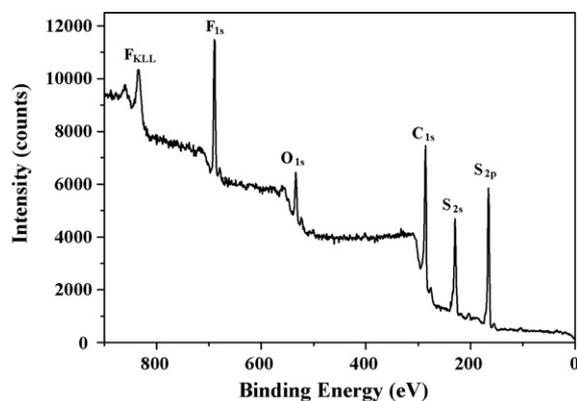


Fig. 5. Elemental analysis of deposit produced in the photoreduction of SF₆ in the presence of propene determined by XPS.

Almost all the initial sulfur in SF₆ and SF₅CF₃ was converted into elemental S via photoreduction in the presence of propene. The majority of initial fluorine resided in the gas phase in the form of SiF₄, which could be easily converted into CaF₂ using CaO/Ca(OH)₂ absorber [26]. Free from toxic by-products such as S₂F₁₀, degradation of SF₆ and SF₅CF₃ by use of propene as a photochemical reductant proved to be a safe method to abate these two greenhouse gases. In the subsequent section, the DRE of SF₅X was determined as a function of irradiation time, propene-to-SF₅X ratio, the amount of oxygen and water vapor, dilution gas, which would be reasonable for the potential application.

3.2. Factors affecting abatement efficiency

3.2.1. Effect of irradiation time

The time dependent destruction of SF₅X was tested by a set of experiments performed at initial SF₅X concentration ((C_{SF₅X})₀) of 0.107 mol m⁻³ and twofold molar excess of propene over SF₅X. As presented in Fig. 6, the DRE of SF₅X increased with irradiation time in both systems. SF₆ and SF₅CF₃ had no absorption above 160 nm [14,27], whereas propene had absorption below 195 nm [28] and therefore was the only substance that

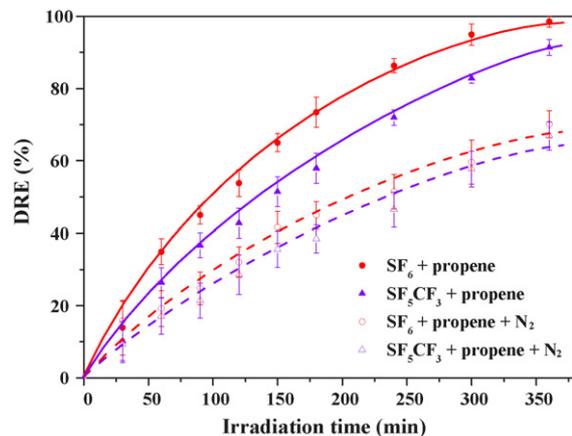


Fig. 6. The time dependent degradation of SF₅X in the presence (dash curve) and absence (solid curve) of dilution gas. Reaction condition: (C_{SF₅X})₀ = 0.107 mol m⁻³ (C_{propene})₀ = 0.214 mol m⁻³.

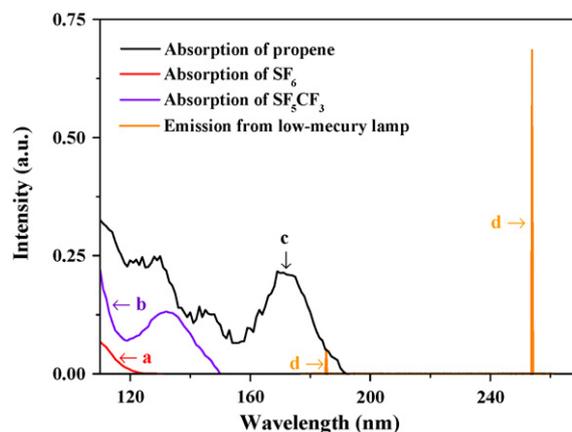
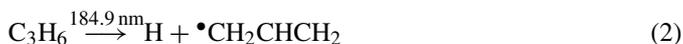


Fig. 7. Emission spectrum (d) from the 15 W low-pressure mercury lamp as compared with the absorption spectrum of (a) SF₆, (b) SF₅CF₃ and (c) propene.

could absorb the light from the mercury lamp (see Fig. 7). Since neither SF₆ nor SF₅CF₃ was able to react with propene in the dark, the photoreduction of SF₅X in the presence of propene must be initiated by the excitation of propene. When exposed to VUV irradiation, propene would be excited into its continuous $\pi \rightarrow \pi^*$ band, and followed by dissociation into fragments corresponding to the following equation [29]



When encountering an SF₆ molecule, the reductive radicals, i.e. methyl, vinyl, and allyl radical, generally acted as strong electron donors, attracted the highly electronegative fluorine atom in the SF₆ molecule to form HF or HFCs and resulted in the cleavage of S–F bond. Due to its low bond energy and absorption at UV band [30,31], $\bullet\text{SF}_5$ was unstable and split into SF₄ and F. And then, the generated SF₄ dissociated into $\bullet\text{SF}_3$, and subsequently $\bullet\text{SF}_2$, $\bullet\text{SF}$ and S analogously. These processes might be offered as an explanation for the final occurrence of elemental sulfur.

The geometry of SF₅CF₃ resembles that of SF₆, with the CF₃ group substituting one fluorine atom [32–34]. The photoreductive degradation mechanism of SF₅CF₃, therefore, was presumably consistent with that of the SF₆–propene system. SF₅CF₃ had to be first attacked by reductive radicals to form transient state and afterwards dissociated via elimination reaction.

Taking the following fact into account, SF₆ seemed to be more stable as compared with SF₅CF₃: (1) the structure of SF₆ and SF₅CF₃ are optimized in O_h symmetry and C_s symmetry, respectively; (2) owing to the electronegativity difference between F and CF₃, the average S–F distance in SF₅CF₃ is some longer than that in SF₆ while the axial bond length is indistinguishable from that in SF₆. To our surprise, the SF₆ decomposed slightly faster than SF₅CF₃ in the same reaction condition. In accordance with Lide [35], the bond energy of S–F bond in SF₆ (3.94 eV) is weaker than that of C–F bond in CF₄ (5.56 eV). The C–F and S–F bond strengths in SF₅CF₃ do not vary substantially from the strengths in the parent molecules [36,37]. Therefore, in contrast

with the S–F bond, the C–F bond in SF_5CF_3 was considerably stronger and accordingly harder to be broken down. Only when reductive radicals attacked the F in S–F bond could SF_5CF_3 dissociate efficiently. Actually, CF_3 group lessened the collision probability of the reductive radicals with F in S–F bond. This provided an explanation for the tiny difference in DRE between these two systems.

3.2.2. Effect of the initial ratio of propene-to- SF_5X

The influence of initial propene/ SF_6 ratio on DRE was determined with an irradiation time of 180 min and $(C_{\text{SF}_6})_0 = 0.107 \text{ mol m}^{-3}$ (Fig. 8). DRE increased with initial propene/ SF_6 ratio over the range from 0 to 2. However, further increase in the initial ratio of propene-to- SF_6 tended to bring about a slight decline instead of a further increase in DRE. The same trend of the influence of the initial propene/ SF_5CF_3 ratio on DRE was obtained using $(C_{\text{SF}_5\text{CF}_3})_0$ of 0.107 mol m^{-3} and an irradiation time of 180 min. The destruction rate of SF_5CF_3 reached its maximal value when the ratio of propene to SF_5CF_3 was 2 over the whole range studied.

The addition of excess propene to the reaction cell provided more molecules available to be photoexcited. However, what really determined the course of reaction was the exact number of photo-produced fragments encountered with SF_5X instead of the absolute number of excited propene. The increase in initial propene concentration prompted the collisions involving excited propene. Therefore, the collisional deactivation process was enhanced though more propene molecules brought about more excited propene. Moreover, alkenes were inclined to form dimer or polymer under UV exposure at high concentration [38–40]. With the increase of initial propene concentration, photo-polymerization process was accelerated simultaneously, leading to a decline in excited propene and a corresponding reduction in photo-produced fragments. The optimal concentration of added propene should be set by the balance between the increase of propene attainable to be excited and the decrease of fragments at the expense of collisional deactivation and polymerization.

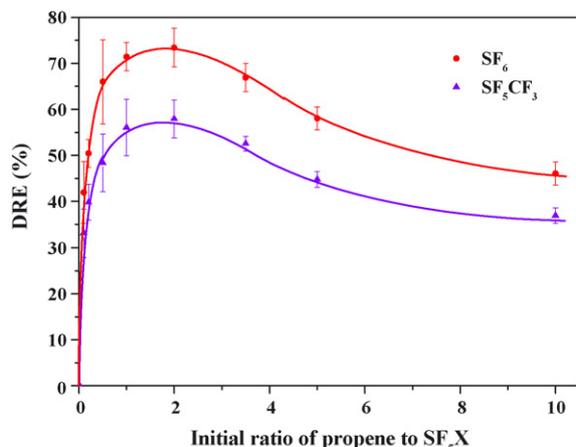


Fig. 8. The dependence of DRE on initial propene-to- SF_5X ratio. Reaction condition: $(C_{\text{SF}_5\text{X}})_0 = 0.107 \text{ mol m}^{-3}$, irradiation time = 180 min.

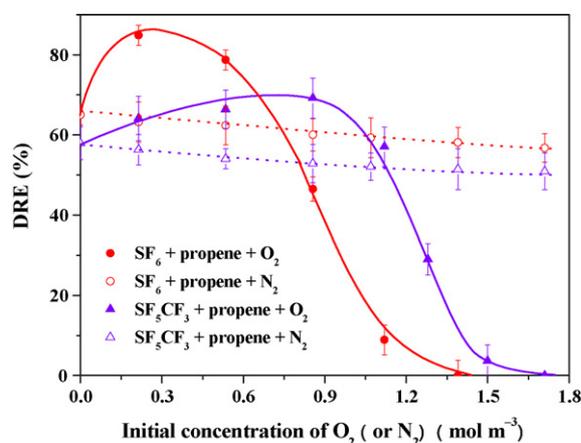
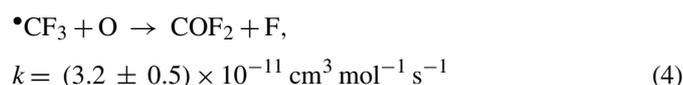
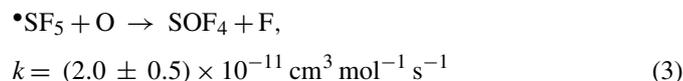


Fig. 9. The dependence of DRE on additive oxygen. Reaction condition: for SF_6 -propene system, $(C_{\text{SF}_6})_0 = 0.107 \text{ mol m}^{-3}$, $(C_{\text{propene}})_0 = 0.214 \text{ mol m}^{-3}$, irradiation time = 150 min; for SF_5CF_3 -propene system $(C_{\text{SF}_5\text{CF}_3})_0 = 0.107 \text{ mol m}^{-3}$, $(C_{\text{propene}})_0 = 0.214 \text{ mol m}^{-3}$, irradiation time = 180 min.

3.2.3. Effect of O_2

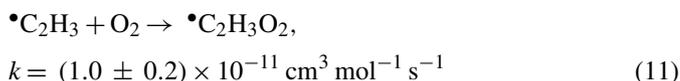
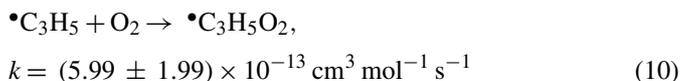
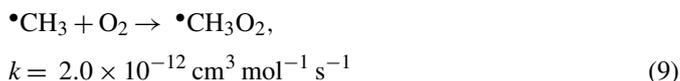
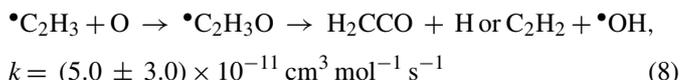
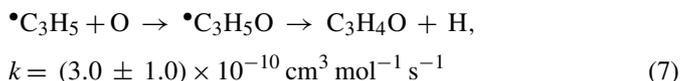
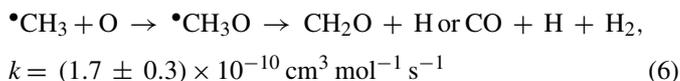
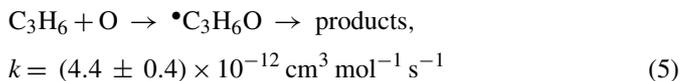
Fig. 9 summarize the DRE of SF_5X in the presence of oxygen. Obviously, the destruction of SF_5X molecules was highly dependent on the initial concentration of oxygen ($(C_{\text{O}_2})_0$). The DRE of SF_6 increased from 65.0% to 84.9% with $(C_{\text{O}_2})_0$ over the range from 0 mol m^{-3} to 0.214 mol m^{-3} and then decayed with increasing $(C_{\text{O}_2})_0$. No degradation could be detected by FT-IR analysis after $(C_{\text{O}_2})_0$ exceeded 1.39 mol m^{-3} . The effect of $(C_{\text{O}_2})_0$ on the SF_5CF_3 -propene system seemed not to be as great as that on the SF_6 -propene system. The DRE of SF_5CF_3 ascended gradually with $(C_{\text{O}_2})_0$ growing to 0.856 mol m^{-3} . There existed measurable dissociation even at $(C_{\text{O}_2})_0$ up to 1.65 mol m^{-3} .

Considering that the addition of nitrogen, one kind of stable diatomic molecule, led to a monotonous decrease in DRE, the role that oxygen played in the mixture could not be simply explained as an energy transfer. The fact that excessive oxygen was adverse to SF_5X removal efficiency might result from chemical competition. O atom will be produced during the photolysis of oxygen due to its absorption at 184.9 nm [41]. O atom and O_2 did affect DRE though they themselves didn't exhibit reactivity towards SF_6 and SF_5CF_3 [42,43]. Attributed to their oxidation, O atom and O_2 would not only baffle the recombination of SF_5X dissociation fragments but also remove them rapidly via the following reactions [44,45]:



As a result, a little elevation of DRE was shown at low $(C_{\text{O}_2})_0$. It was also noteworthy that the oxidation of propene and its fragments occurred synchronously. So that, other than SF_5X , O atom and O_2 had the possibility to react with propene and its

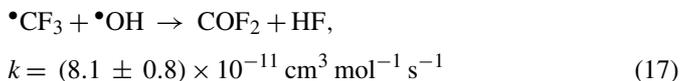
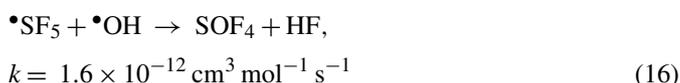
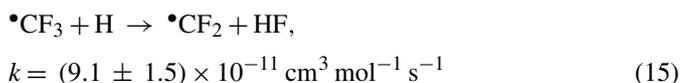
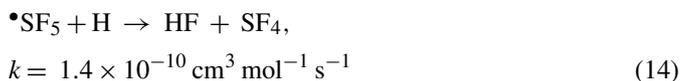
photofragments [46–51]:



The higher the concentration of O_2 was, the higher the fraction of propene and its fragments inclined to interact with O or O_2 . Elevating the concentration of O_2 lessened the percentage of propene photofragments reactive to SF_5X . When $(\text{C}_{\text{O}_2})_0$ was high enough, the elimination process of SF_6 and SF_5CF_3 was consequentially unobservable.

3.2.4. Effect of $\text{H}_2\text{O}(\text{g})$

In an attempt to investigate the influence of water vapor on DRE, a mixture of water, propene and SF_6 at 1:2:1 molar ratio ($\text{H}_2\text{O}(\text{g})$:propene: SF_6) was fed into the reaction cell. Averaged from three duplicate experiments, 6.4% increment of DRE was achieved when $\text{H}_2\text{O}(\text{g})$ was added. With respect to the SF_5CF_3 –propene system, we carried out a trial with initial molar ratio of $\text{H}_2\text{O}(\text{g})$ /propene/ SF_5CF_3 controlled at 1:2:1. The existence of $\text{H}_2\text{O}(\text{g})$ in the gas mixture turned out to enhance DRE by 6.3%. Both OH radical and H atom, generated from the direct photolysis of $\text{H}_2\text{O}(\text{g})$ [52], might account for the enhanced DRE [52–56]:



Of course, $\bullet\text{OH}$ could contribute to the complete oxidation of propene or its fragmentation products as well [57]. Considering that the concentration of hydroxyl radical was incomparable to that of reductive radicals in the SF_5X –propene– H_2O system, these processes could not occur to any significant extent.

3.2.5. Effect of dilution gas

SF_5X can be treated either at low-pressure or at atmospheric pressure. A favorable advantage of treatment process under atmospheric pressure is that the removal efficiency could be improved by adjustment of SF_5X concentration via adding dilution gas. Thus, the impact of dilution gas on DRE was also investigated in this research work. Fig. 6 compared the DRE in the presence of and absence of nitrogen as dilution gas. In both SF_6 –propene and SF_5CF_3 –propene systems, the employment of nitrogen as the dilution gas definitely caused a drop in DRE for the corresponding irradiation time. Nitrogen is a stable diatomic molecular with bond energy of 9.764 eV [58]. Although nitrogen would not undergo dissociation under 184.9 nm irradiation, it acted as a good quencher of the excited propene and photo-produced fragments by means of collision. The number of excited species that were able to react with SF_6 and SF_5CF_3 went down accordingly.

4. Conclusions

In brief, a simple photochemical technology might be utilized to efficiently decompose SF_6 and SF_5CF_3 , based on the reactivity of reductive radicals yielded in the direct photolysis of propene towards SF_6 and SF_5CF_3 . DRE of SF_5X exceeded 90% at irradiation time of 360 min and initial propene concentration of 0.214 mol m^{-3} . Despite the reaction mechanism proposed, the processes that took place were far more complicated. Only the primary process was elucidated in this paper. As a matter of fact, irradiation reactants provided an opportunity for secondary chemical reactions to occur.

As far as the obtained results were concerned, the SF_5X photodegradation products in the presence of propene were less harmful to not only human health but also the environment compared with the original SF_5X compounds. With addition of specific amounts of water vapor or oxygen, it was possible to enhance DRE and avoid the yield of deposits via the oxidation of fragments from dissociated SF_5X .

Although the method reported in this paper can contribute to the elimination of SF_6 and SF_5CF_3 , it must be pointed out that the whole system has not been totally optimized. Flow-state studies on the destruction and removal of these two greenhouse gases are in progress in our laboratory. In addition, the effects of reactor material and UV source, which will avail DRE modification, are being tested.

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