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A novel method to decompose two potent greenhouse gases: Photoreduction of SF_6 and SF_5CF_3 in the presence of propene

Li Huang, Yan Shen, Wenbo Dong*, Renxi Zhang, Jianliang Zhang, Huiqi Hou*

Center for Greenhouse Gas Research, Institute of Environmental Science, Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, PR China

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Abstract

SF_5CF_3 and SF_6 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 $^{\bullet}CH_3$, $^{\bullet}C_2H_3$, and $^{\bullet}C_3H_5$, could efficiently decompose SF_6 and SF_5CF_3 to CH_4, elemental sulfur and trace amounts of fluorinated organic compounds. It was further demonstrated that the destruction and removal efficiency (DRE) of SF_5X (X represented F or CF_3) was highly dependent on the initial propene-to-SF_5X 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 SF_5X remediation.

Keywords: Trifluoromethyl sulfur pentafluoride; Sulfur hexafluoride; Propene; Photodegradation; Reductive radicals

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 (SF_6) 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 (SF_5CF_3) originates as a by-product of fluorochemical manufacture and a breakdown product in high-voltage equipment [9,10]. SF_6 and SF_5CF_3 are part of a class of super greenhouse gases that have GWP_{100} (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, SF_6 and SF_5CF_3 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 SF_6 include: combustion, chemical–thermal elimination, non-equilibrium plasma [18–22]. Owing to the high chemical stability of SF_6, 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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* Corresponding authors. Tel.: +86 21 6564 2030/2293; fax: +86 21 6564 3849.

E-mail addresses: wbdong@fudan.edu.cn (W. Dong), lihuang1981@gmail.com (H. Hou).

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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 $S_2O_2F_{10}$, 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 exihibited 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 (≥99.99%), nitrogen (≥99.999%) and oxygen (≥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 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.

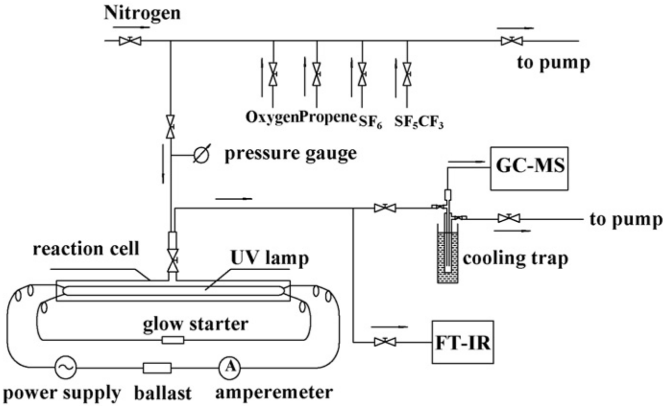

Fig. 1. Schematic diagram of the experimental system used in this work.

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 910–960 cm^{-1} and 858–927 cm^{-1}, respectively, followed the Beer–Lambert law in the 0–2.14 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 m × 0.32 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 °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 1×10^{-6} Pa using ESCA system (PHI 5000C, PerkinElmer Co.). A monochromatic Al Kα (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 3d5/2 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