

# Photooxidation of hydrochlorofluorocarbons and hydrofluorocarbons initiated by OH radicals\*

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**Abstract**— Under simulated atmospheric condition, photooxidation for HCFC-22 + H<sub>2</sub>O<sub>2</sub>, HCFC-22 + H<sub>2</sub>O<sub>2</sub>+O<sub>2</sub>, HFC-134A + H<sub>2</sub>O<sub>2</sub> and HFC-134A + H<sub>2</sub>O<sub>2</sub>+ O<sub>2</sub> systems were studied. H<sub>2</sub>O<sub>2</sub> was irradiated by low pressure mercury lamp and produced OH radicals. The OH radicals can initiate photooxidation of HCFC-22 and 134A. The products of photooxidation were determined by a Fourier Transform Infrared Spectroscopy with a 20ml long path cell. The products were COF<sub>2</sub>, CO<sub>2</sub>, HCl, H<sub>2</sub>O and HF for HCFC-22 + H<sub>2</sub>O<sub>2</sub> system, HO, CO<sub>2</sub>, HCl and HF for HCFC-22 + H<sub>2</sub>O<sub>2</sub>+O<sub>2</sub> system, HCOF, CF<sub>3</sub>OOFCF<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>O and HF for HFC-134A +H<sub>2</sub>O<sub>2</sub> system, HCOF, CO<sub>2</sub>, H<sub>2</sub>O, and HF for HFC-134A + H<sub>2</sub>O<sub>2</sub>+ O<sub>2</sub> system. Based on those results, the mechanisms of photooxidation were suggested.

**Keywords:** hydrochlorofluorocarbons; hydrofluorocarbons; photooxidation; OH radicals; FTIR.

## 1 Introduction

Chlorofluorocarbons (CFCs) such as CFC1<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, and CF<sub>2</sub>ClCFCl<sub>2</sub> are currently in widespread use as refrigeration fluids, cleaning agents and foam blowing agents. The CFCs are chemically inert in the troposphere, and are transported into the stratosphere where their photolysis leads to the production of Cl atoms and the depletion of stratospheric ozone (Rowland, 1990). To protect the stratospheric ozone layer and to reduce ozone depletion in the polar regions spring-time, a phase out of the CFC, and at least partial replacement by hydrofluorocarbons (HFC,) and/or hydrochlorofluorocarbons (HCFC,) is being implemented.

These replacement compounds such as HCFC-22 and/ or HFC-134A differ from CFC, by the presence of reactive atoms and will react to a large degree in the troposphere by reaction with hydroxyl radicals (OH), thus limiting their atmosphere lifetimes to a few years and

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minimizing transport into the stratosphere. The HFC-134A and HCFC-22 under consideration will then be largely removed by chemical reaction in the troposphere, and the reaction mechanisms and products formed subsequent to those OH radical reactions in the troposphere need to be understood prior to the widespread use of these compounds. However, this removal process alone does not eliminate the possibility of the compounds contributing to stratospheric O<sub>3</sub> depletion, global warming, or other effects but rather shifts such questions to the role of oxidation products, especially those that may have relatively long atmospheric lifetimes. Recent review which explored the tropospheric degradation mechanisms of the HCFC<sub>n</sub> and HFC<sub>n</sub>, and the products formed (Atkinson 1990; COX, 1990; Niki, 1990; Zellner, 1990) were largely based on the available data base for the tropospheric reactions of C<sub>1</sub> haloalkyl and C<sub>1</sub>-C<sub>4</sub> alkyl radicals, because of the general lack of experimental data for the HCFC<sub>n</sub> and HFC<sub>n</sub>, themselves. Experimental data on the tropospheric degradation schemes for some to the HFC<sub>n</sub> and HCFC<sub>n</sub>, of interest are now appearing in the literature (Edney, 1991; Wallington, 1992; Edney, 1992; Tuazon, 1993) but those works are for chlorine initiated photooxidation studies of HCFC<sub>n</sub> and HFC<sub>n</sub>.

This work describes the products formed and mechanisms for OH radicals photooxidation of HFC<sub>n</sub> and HCFC<sub>n</sub>. The H<sub>2</sub>O<sub>2</sub> was irradiated by low pressure mercury lamp and produced OH radicals. The OH radicals initiated photooxidation of HFC<sub>n</sub> and HCFC<sub>n</sub>. The products formed were determined by a Fourier Transform Infrared Spectroscopy with 20m long path cell. Based on these products, the mechanisms of photolysis were suggested.

## 2 Experimental section

### 2.1 Materials

HCFC-22 (99.5%, purity) was obtained from Dupont Company, USA.

HFC-134A (99.5%, purity) was obtained from the Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai.

H<sub>2</sub>O<sub>2</sub> 30% concentration was obtained from Tianjin East Chemical Factory.

All agents were used without further purification.

### 2.2 Gaseous sample preparation

The scheme of gaseous sample preparation used in this study is shown in Fig. 1. The system was pumped to 13 Pa, and liquid nitrogen was added to cooled trap 7 for keeping the pressure of the system lower than 1.3 Pa. The HCFC-22 or HFC-134A container was connected and liquid nitrogen was added to cooled container 11, for HCFC-22 or HFC-134A into container 11, then photolysis cell 22 was connected.

50μl H<sub>2</sub>O<sub>2</sub> was added into the photolysis cell, then the cell was connected to the vacuum system. The valve 8 was closed when the pressure was lower than 400Pa. Then the valve 12 was opened for inletting HCFC-22 or HFC-134A to the photolysis cell until the pressure of the system reaches 3400Pa.

### 2.3 Irradiation experiments

The irradiation source used in this work was a low pressure mercury lamp. The power

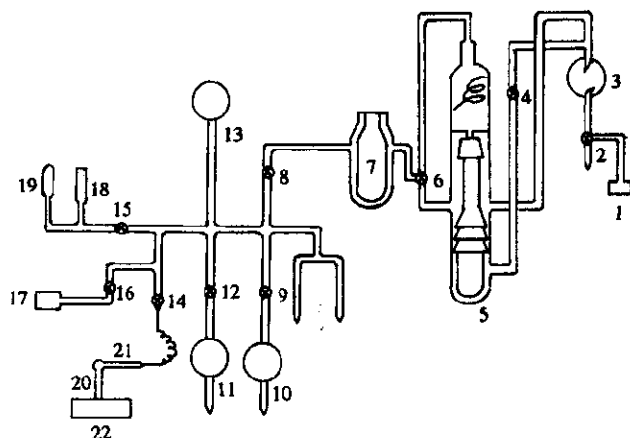


Fig. 1 Schematic drawing of installation for gaseous sampler

1. vacuum pump; 2, 4. vacuum valves; 3. buffer bottle; 5 diffuse pump; 6. three-way vacuum valves; 7. coiled trap; 8, 9, 12, 14, 15, 16, 20. oil-free vacuum valves; 10. oxygen bottle; 11. HCFC-22 or HFC-134A container; 13. vacuum gauge; 17. millibar barometer; 18, 19. vacuum tube; 21. silicon gel spacer; 22. photolysis cell

of the lamp used during the irradiation experiments was about 125W. The irradiation wavelength was 253.7nm, and the radical intensity was  $5.4 \text{ mV/cm}^2$ . The photolysis cell was 20 cm path length and its ends were made of quartz so that the ultraviolet or action radiation could pass. The irradiation system was placed in dark box.

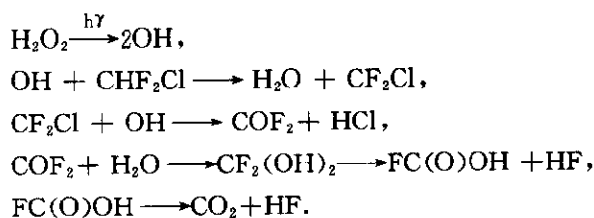
#### 2.4 Detection of the photochemical products by FTIR

After irradiation of the samples for a given time, the photochemical products were transferred into a 20 m long path cell. Then, the products were detected by a Nicolet 60 saß FTIR. The detector is type MCT-B and wave number region is  $6000-400 \text{ cm}^{-1}$ . Infrared spectra are collected by co-adding 64 scans at  $2 \text{ cm}^{-1}$  resolution.

### 3 Results and discussion

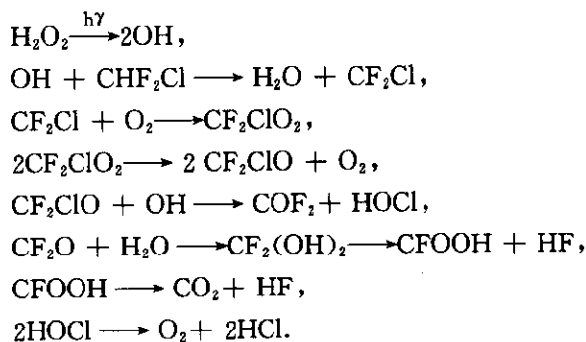
#### 3.1 HCFC-22 + H<sub>2</sub>O<sub>2</sub> system

The infrared spectrum of 3000 Pa HCFC-22 and  $50 \mu\text{l H}_2\text{O}_2$  after 5 hours irradiation obtained by subtracting the spectrum of 3000Pa HCFC-22 and  $50 \mu\text{l H}_2\text{O}_2$  before irradiation. The results indicated that weaker transmittance bands at  $1100-1250 \text{ cm}^{-1}$ , and transmittance bands in  $1750-1850 \text{ cm}^{-1}$  region are in agreement with  $\text{COF}_2$  absorption, transmittance bands in the range  $2300-2390 \text{ cm}^{-1}$  and  $667 \text{ cm}^{-1}$  are in agreement with  $\text{CO}_2$ , transmittance bands in the range  $2900-3000 \text{ cm}^{-1}$  are in agreement with HCl. The weaker transmittance bands at  $3600-3800 \text{ cm}^{-1}$  and  $1600 \text{ cm}^{-1}$  are in the agreement with  $\text{H}_2\text{O}$ . So that after irradiation HCFC-22 +  $\text{H}_2\text{O}_2$  system, the products are  $\text{COF}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and HCl. The OH initiated reaction with HCFC-22 to form  $\text{COF}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and HCl might be consistent with the following mechanism:



### 3.2 HCFC-22 + H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> system

The infrared spectrum of 3000Pa HCFC-22 + 50 $\mu$ l H<sub>2</sub>O<sub>2</sub> + 1000Pa O<sub>2</sub> after 3.5 hours irradiation and product infrared spectrum obtained by subtracting the spectrum of 3000 Pa HCFC-22 + 50 $\mu$ l H<sub>2</sub>O<sub>2</sub> + 1000Pa O<sub>2</sub> before irradiation. The results indicated that transmittance bands in the range 1400–1800 cm<sup>-1</sup> and 3600–3800 cm<sup>-1</sup> are in agreement with H<sub>2</sub>O, transmittance bands in range 2300–2390 cm<sup>-1</sup> and 667cm<sup>-1</sup> are in agreement with CO<sub>2</sub>. Weaker transmittance bands in the range 2900-3000cm<sup>-1</sup> are in agreement with HCl. So that after irradiation of HCFC-22 + H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> system, the products are H<sub>2</sub>O, CO<sub>2</sub>, and HCl. The following mechanism might be compatible with those products.



From these reactions analyzed, the first reaction is H<sub>2</sub>O<sub>2</sub> photolysis by UV, forming OH radicals (Volman, 1963). The OH radicals initiated oxidation of HCFC-22, forming CF<sub>2</sub>Cl and H<sub>2</sub>O (Orkin, 1993). Then the CF<sub>2</sub>Cl reacts with OH or O<sub>2</sub>, producing COF<sub>2</sub>, HCl or HOCl (Edney, 1992). If the system did not contain any H<sub>2</sub>O, the COF<sub>2</sub> and HCl would be the finishing products. Because H<sub>2</sub>O is a reactant, and H<sub>2</sub>O<sub>2</sub> contains a large quantity of H<sub>2</sub>O, the formed COF<sub>2</sub> can further react with H<sub>2</sub>O. Based on Francisco's (Francisco, 1993) molecular orbital calculations, the reaction of CF<sub>2</sub>O with H<sub>2</sub>O involves several steps. The first reaction pathway in the hydrolysis of CF<sub>2</sub>O, is the addition of H<sub>2</sub>O to CF<sub>2</sub>O to produce chemically active CF<sub>2</sub>(OH)<sub>2</sub>, which could be collisionally stabilized or revert to reactants, or react further to yield FC(O)OH and HF. The FC(O)OH can be chemically stabilized or react to form CO<sub>2</sub> and HF. In order to produce the final products (CO<sub>2</sub> + HF) from the reaction of CF<sub>2</sub>O + H<sub>2</sub>O three intermediate steps are needed. Two of these steps are thermodynamically favorable because they are likely exothermic reactions. In the first reaction step in which CF<sub>2</sub>O + H<sub>2</sub>O yields CF<sub>2</sub>(OH)<sub>2</sub>, the exothermicity is 25.1 kJ/mol. The second intermediate step, which involves the unimolecular dissociation of CF<sub>2</sub>(OH)<sub>2</sub> into CF(O)OH + HF, is 8.79 kJ/mol exothermic. The final step which involves the unimolecular dissociation of FC(O)OH to CO<sub>2</sub> + HF is a slightly endothermic by 47.7 kJ/mol. Nevertheless, the kinetics as

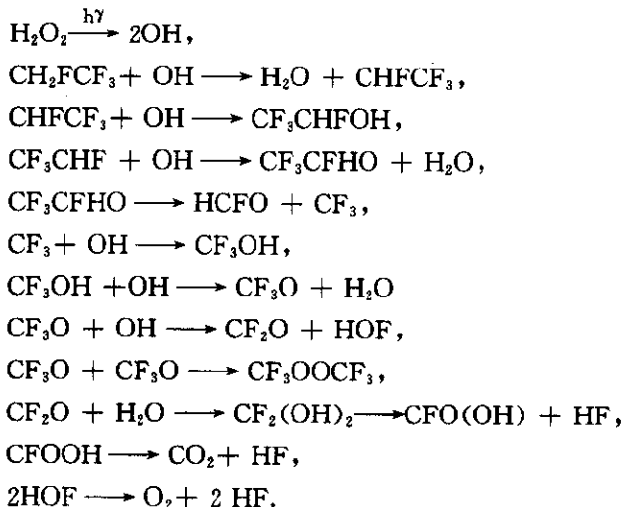
governed in part by the activation energy determines the relative importance and rate ordering of the pathways in the conversion of  $\text{CF}_2\text{O} + \text{H}_2\text{O}$  into  $\text{CO}_2 + 2\text{HF}$ . The calculated barrier for reaction I is 152.3 kJ/mol. The calculated activation for reaction II is 143.9 kJ/mol, while that for reaction III is 116.7 kJ/mol. In fact, the rate limiting step in the conversion process is step I. If the barrier for step I is surmounted, it is possible that the  $\text{CF}_2\text{O} + \text{H}_2\text{O}$  reaction could proceed rapidly to the products  $\text{CO}_2 + 2\text{HF}$ .

It is obvious that the photolysis products are  $\text{COF}_2$ ,  $\text{CO}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  for  $\text{HCFC-22} + \text{H}_2\text{O}_2$  system, and  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{HCl}$  and  $\text{HF}$ , for  $\text{HCFC-22} + \text{H}_2\text{O}_2 + \text{O}_2$  system. In  $\text{HCFC-22} + \text{H}_2\text{O}_2 + \text{O}_2$  system,  $50\mu\text{l}$   $\text{H}_2\text{O}_2$  was added to the system, and the system was pumped only for 2 min. So the system contained a large quantity of  $\text{H}_2\text{O}$ . On the other hand, the excess  $\text{H}_2\text{O}$  can react completely with  $\text{COF}_2$ , so transmittance bands of  $\text{COF}_2$  is not observed. It is suggested that 3.5 hours irradiation in the presence of oxygen,  $\text{CO}_2$  yield was 26.9%, 5 hour irradiation in the absence of oxygen,  $\text{CO}_2$  yield was 13.9%. Therefore oxygen plays as a catalytic agent and promotes the oxidizing ability of  $\text{H}_2\text{O}_2$ .

### 3.3 HFC-134A + H<sub>2</sub>O<sub>2</sub>

The infrared spectrum obtained after irradiating a mixture of 3000 Pa HFC-134A +  $50\mu\text{l}$   $\text{H}_2\text{O}_2$  for 5 hours and the product infrared spectrum by subtracting the spectrum of 3000 Pa HFC-134A +  $50\mu\text{l}$   $\text{H}_2\text{O}_2$  before irradiation. The results indicated that transmittance bands located at  $\nu = 950$ , 1150 and  $1750-1850\text{ cm}^{-1}$  are consistent with the formation of  $\text{HCOF}$ , transmittance bands in range  $2300-2390\text{ cm}^{-1}$  and  $667\text{ cm}^{-1}$  are in agreement with  $\text{CO}_2$ . The transmittance bands at  $3600-3800\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  are in agreement with  $\text{H}_2\text{O}$ .

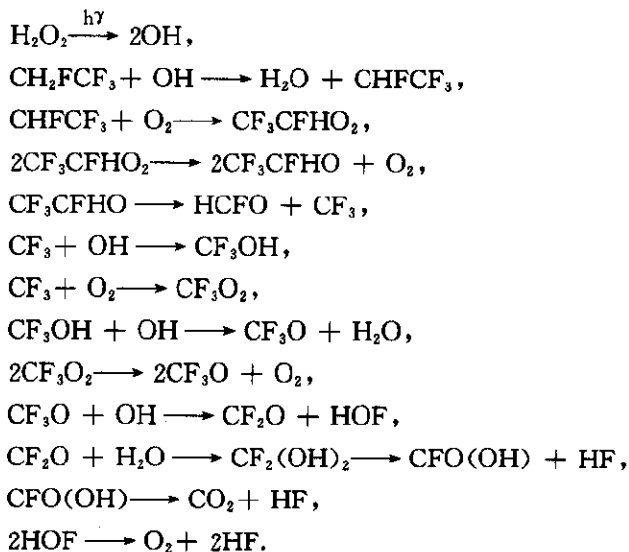
The infrared spectrum of 3000 Pa HFC-134A +  $10\mu\text{l}$   $\text{H}_2\text{O}_2$  after irradiation for 5 hours and the product infrared spectrum obtained by subtracting before irradiation of 3000 Pa HFC-134A +  $10\mu\text{l}$   $\text{H}_2\text{O}_2$ . The results indicated that products of reaction are  $\text{HCOF}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , but the transmittance bands of  $\text{CO}_2$  are weaker. There are three additional transmittance bands at 1167, 1265 and  $1285\text{ cm}^{-1}$  respectively. According to Arria and Aymonino (Arria, 1962), the transmittance bands are consistent with the formation of  $\text{CF}_3\text{OOCF}_3$ . The formation of products  $\text{HCOF}$ ,  $\text{CF}_3\text{OOCF}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  for HFC-134A +  $\text{H}_2\text{O}_2$  system might be consistent with the following mechanism.



According to this mechanism, after through OH radicals initiated oxidation of HFC-134A, the intermediated  $\text{CF}_3\text{CFHO}$  alkoxy radical was formed via three successive oxidation reactions. The intermediate  $\text{CF}_3\text{CFHO}$  alkoxy radicals is then expected to decompose to form HCOF and  $\text{CF}_3$  radical (Edey, 1992). The  $\text{CF}_3$  radical can react with OH to form  $\text{CF}_3\text{OH}$ . The  $\text{CF}_3\text{OH}$  reacts further with OH to produce  $\text{CF}_3\text{O} + \text{H}_2\text{O}$ . Other  $\text{CF}_3\text{OH}$  can photolyze or homogeneously decompose to  $\text{COF}_2$  and HF (Wallington, 1994). Then  $\text{CF}_3\text{O}$  can react with OH to form  $\text{CF}_2\text{O} + \text{HOF}$ . The  $\text{CF}_2\text{O}$  can finally react with  $\text{H}_2\text{O}$  to form  $\text{CO}_2 + \text{HF}$ . Two molecules of HOF are decomposed to  $\text{O}_2 + 2\text{HF}$  by UV. So that the photolysis products for HFC-134A +  $\text{H}_2\text{O}_2$  system, if an excess of  $\text{H}_2\text{O}_2$  is contained in the systems, the products are HCOF,  $\text{CO}_2$  and HF. The yields of  $\text{CO}_2$  and HCOF were 29% and 21%, respectively. If a substochimetric quantity of  $\text{H}_2\text{O}_2$  is added in the systems, the products are HCOF,  $\text{CF}_3\text{OOCF}_3$ ,  $\text{CO}_2$  and HF. The yields of  $\text{CO}_2$ , HCOF and  $\text{CF}_3\text{OOCF}_3$  were 13.5%, 34% and 9.4%, respectively.

### 3.4 HFC-134A + $\text{H}_2\text{O}_2$ + $\text{O}_2$

The results of infrared spectrum after irradiating a mixture of 3000 Pa HFC-134A + 50  $\mu\text{l}$   $\text{H}_2\text{O}_2$  + 1000 Pa  $\text{O}_2$  for 5 h indicated that the transmittance bands at 950, 1150 and 1750–1850  $\text{cm}^{-1}$  are in agreement with HCOF, transmittance bands at 2300–2390  $\text{cm}^{-1}$  and 667  $\text{cm}^{-1}$  are consistent with the formation of  $\text{CO}_2$ . The transmittance bands at 3600–3800  $\text{cm}^{-1}$  and 1600  $\text{cm}^{-1}$  are in agreement with  $\text{H}_2\text{O}$ . In conclusion, the irradiation of HFC-134A +  $\text{H}_2\text{O}_2$  +  $\text{O}_2$  produce HCFO,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . The products are consistent with the following mechanism:



According to the mechanism, the  $\text{CF}_3$  radicals can react with OH to form  $\text{CF}_3\text{OH}$ . Besides, the  $\text{CF}_3$  radicals can also react with  $\text{O}_2$  to form  $\text{CF}_3\text{O}_2$ . Then, the  $\text{CF}_3\text{O}_2$  can split into  $\text{CF}_3\text{O}$  and  $\text{O}_2$ . The  $\text{CF}_3\text{O}$  radical can react further with OH to form  $\text{CF}_2\text{O}$  and HOF. The  $\text{CF}_2\text{O}$  reacts with  $\text{H}_2\text{O}$  to form  $\text{CO}_2$  and HF. So the photolysis products of HFC-134A +  $\text{H}_2\text{O}_2$  +  $\text{O}_2$  are HCOF,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and HF. The  $\text{CO}_2$  and HCOF yields were 37% and 30%,

respectively.

The reaction mechanism of the four systems shown that HF is a reaction product, but transmittance bands at  $\nu=4141\text{ cm}^{-1}$  for HF is not observed. The absence of HF absorption bands is reasonable. Because the photolysis cell is made of glass and silica, that HF can react with them.

As compared with Cl initiated photooxidation of HCFC-22 or HFC-134A, the OH radicals reaction with HCFC-22 or HFC-134A is slower, owing to the higher concentrations of OH radicals in the atmosphere, the OH radical reactions with HFCs and HCFCs are important.

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