

A-2 オゾン層保護対策技術の開発と評価に関する研究  
(7) フロン等の光分解に関する研究

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[要旨] 1、1-ジフロロエタンの二酸化チタン表面での254 nm光による光触媒分解を行った。光触媒分解の速度は185 nm光による光分解速度とほぼ同じであった。両分解反応ともに反応速度の一次式に従った。分解反応生成物をFT-IRとGCMSで分析した。この生成物の同定に基づいて反応過程を推定した。

## **A-2 Development of protection technique of ozone layer and its evaluation**

### **7. Photodegradation of 1,1-difluoroethane**

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#### **Abstract**

The photocatalytic degradation of 1,1-difluoroethane on the surface of  $\text{TiO}_2$  has been studied at  $\lambda = 254$  nm. The degradation rate is found to be about the same as direct photolysis at  $\lambda = 185$  nm. Furthermore, the degradation rate decreases when the  $\text{TiO}_2 / \text{SiO}_2$  is used as the catalyst. The reactions, photolysis and photocatalysis, follow the first order kinetic. The degradation products have been analyzed by FT-IR and GC/MS. The reaction path ways are proposed on the basis of degradation products found in this work.

**Keywords:** Photolysis, Photocatalyst,  $\text{TiO}_2$ , Intermediate

#### **1. Introduction**

Chlorofluorocarbons (CFCs) were developed in the 1930s as safe alternatives to ammonia and sulfur dioxide refrigerants. Since then the uses of CFCs have been expanded to include air conditioning, cleaning of critical electronic and mechanical components, and expansion of plastics for energy and foams. The CFCs are extremely chemically stable and are transported into the stratosphere where photolysis releases active chlorine atoms<sup>1</sup>. The active chlorine atoms effect the ozone depletion in the stratosphere. This led to the limiting of CFCs production as restricted by the Montreal Protocol and to develop substitutes for CFCs<sup>2</sup>. Hydrochlorofluorocarbons (HCFCs) and Hydrofluorocarbon (HFCs) have been studied world wide for CFCs replacement.

The HFCs and HCFCs are water insoluble and are unreactive with oxidizer such as

ozone. The removal process in the troposphere are the reactions with hydroxyl radicals<sup>3, 4</sup>. The HFCs have a zero ozone depletion potential, but they can cause greenhouse effects<sup>5</sup>.

Very few studies of the photocatalysis of HCFCs and HFCs have been reported in the literature. K. Tanaka and T. Hisanaga<sup>6</sup> studied the photodegradation of HCFCs and HFCs on the surface of metal oxides. The photocatalytic degradation proceeded via the reaction with OH radicals. The reactions of OH radicals with the HCFCs and HFCs have been extensively studied<sup>4, 7</sup>.

This paper presents results of the study of photodegradation of  $\text{CH}_3\text{CHF}_2$  (HFC-152a) on the surface of  $\text{TiO}_2$  at 185 and 254 nm. The reaction path ways are proposed on the basis of the degradation products found in this work.

## 2. Experimental

### 2.1 Materials.

The HFC-152a( $\text{CH}_3\text{CF}_2\text{H}$ ) and  $\text{CO}_2$  (99.9%) from GL Sciences Inc. were used without further purification.  $\text{TiO}_2$  (TP-2, Fuji Titan Co.), Sodium Silicate solution (52-57%, Wako) were used as supplied. The 185 nm and 254 nm radiations were provided by Sen(6W) low pressure mercury lamps.

### 2.2 Preparation of Catalysts.

Two types of catalyst were used in this experiment,  $\text{TiO}_2$  and  $\text{TiO}_2/\text{SiO}_2$

#### 2.2.1 $\text{TiO}_2$

$\text{TiO}_2$  ( $\sim 2.7\text{g}$ ) was mixed with deionized water( $\sim 2.0\text{ ml}$ ). A dry-clean Pyrex glass tube (15 cm. long, 3.6 cm. in diameter and 0.2 mm. thickness) was weighed before it was coated with  $\text{TiO}_2$ . The coated glass tube was dried in the oven at  $70^\circ\text{C}$  for 1 hr. then weighed again after it was cool to room temperature.

### 2.3 Method

The experiments were carried out at room temperature and atmospheric pressure in the Pyrex glass line (as shown in Figure 1.) equipped with IR cell, bottle shaped cell, lamp housing, gas circulating controller and vacuum pump. The IR cell was fitted with KRS-5 windows. The line was evacuated before introducing  $\text{CH}_3\text{CF}_2\text{H}$  into it by syringe. The  $\text{CH}_3\text{CF}_2\text{H}$  was circulated in the line by gas circulating controller. The system was allowed to equilibrate for 20 minutes before determining the initial concentration. Illumination was started after the achievement of initial concentration.

After illumination, the concentration of  $\text{CH}_3\text{CF}_2\text{H}$ ,  $\text{CO}_2$ , the presence of  $\text{F}^-$ , and intermediate products were analyzed.

## 2.4 Analysis

The  $\text{CH}_3\text{CF}_2\text{H}$  was analyzed by FID gas-chromatography ( Shimadzu, model GC-17A) using capillary column ( Fused Silica, DB-624 of dimensions 60 m.  $\times$  0.324mm. i.d. with a film thickness of 1.80  $\mu\text{m}$  ) and Helium as a carrier gas. The injector, column, and detector temperature were 120, 250, and 250  $^\circ\text{C}$  , respectively.

The evolution of  $\text{CO}_2$  was monitored with Shimadzu GC-6 AM equipped with an active carbon 80/100 mesh column and a FID detector after catalytic conversion to methane.

For the presence of  $\text{F}^-$  , the deionized water was introducing into the bottle-shaped glass cell and  $\text{F}^-$  was measured by ion-chromatography using JASCO 880-PU HPLC chromatography equipped with a Shodex IC 1-524A ion exchange column and a conductivity detector. The eluent was a solution of 2.5 mM Phthalic acid, pH4.0 .

The other products were identified by IR Spectroscopy (Horiba FT-IR model FT200) and coupled gas chromatography-mass spectrometry (Shimadzu, model QP-5000).

## 3. Results

The photolysis of  $\text{CH}_3\text{CF}_2\text{H}$  has been studied at 185 nm. The disappearance of  $\text{CH}_3\text{CF}_2\text{H}$  obeys the pseudo-first order reaction. At 254 nm, the  $\text{CH}_3\text{CF}_2\text{H}$  has not been degraded. However  $\text{CH}_3\text{CF}_2\text{H}$  disappeared in the presence of  $\text{TiO}_2$  and  $\text{TiO}_2/\text{SiO}_2$  at 185 and 254nm. Illumination at 185 nm in the presence of  $\text{TiO}_2$  is the combination of photolysis and photocatalysis.

To obtain the information about photocatalysis, it is necessary to carry out such the experiments that direct photolysis is excluded. Resulting from above, the 254 nm is chosen for studying photocatalytic degradation of  $\text{CH}_3\text{CF}_2\text{H}$  on the surface of  $\text{TiO}_2$  . The initial rate,  $r_0$  ,of  $\text{CH}_3\text{CF}_2\text{H}$  photocatalytic degradation is a function of the initial concentration,  $C_0$  . The plot of  $r_0^{-1}$  as a function of  $C_0^{-1}$  yields a straight line, therefore this reaction obeys the Langmuir-Hinshelwood eq.,

$$r = kKC_0 / (1 + KC_0)$$

where  $k$  is the rate constant and  $K$  is the adsorption constant. The value of  $k = 1.887 \mu\text{mol}\cdot\text{hr}^{-1}$  and  $K = 0.837 \text{ml} \cdot \mu\text{mol}^{-1}$  are obtained.

The kinetics of evolution of  $\text{CO}_2$  during  $\text{CH}_3\text{CF}_2\text{H}$  degradation has been measured by GC. The rate of producing  $\text{CO}_2$  in the photocatalysis is about twice of the photolysis process. To determine the presence of  $\text{F}^-$  during the  $\text{CH}_3\text{CF}_2\text{H}$  degradation, the gas mixture is dissolved in water before introduces to the ion-chromatograph. The  $\text{F}^-$  has

been found in both cases, photolysis and photocatalysis reactions.

FT-IR spectra have been recorded during the photodegradation in the absence of  $\text{TiO}_2$  at 185 nm. After illumination the spectra show that new absorption bands are produced and their intensities are increased during the degradation. The major absorptions are observed at 669.2, 1027.9, 2360.4  $\text{cm}^{-1}$  and a weak band between 1900-1700  $\text{cm}^{-1}$ . The 669.2 and 2360.4  $\text{cm}^{-1}$  bands correspond to  $\text{CO}_2$  while the intense 1027.9  $\text{cm}^{-1}$  band is assigned to  $\text{SiF}_4$ . The absorption band between 1900 and 1700  $\text{cm}^{-1}$  indicates the presence of the carbonyl compound. The major new absorption bands are observed at 669.2, 1027.9, and 2360.4  $\text{cm}^{-1}$ . The 1027.9  $\text{cm}^{-1}$  band is also identified as Si-F vibration. It is interesting to note that during the photocatalysis, no significant change has been observed.

By GCMS analysis the degradation products,  $\text{HCOH}$ ,  $\text{HCOOCH}_3$ ,  $\text{HCOF}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{H}_2\text{O}$  and  $\text{SiF}_4$  have been found for photolysis while  $\text{CH}_3\text{COF}$ ,  $\text{H}_2\text{O}$ ,  $\text{SiF}_4$  and traces of  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_2\text{CFH}$  and  $\text{HCOF}$  are detected during photocatalysis degradation.

#### 4. Discussion

The degradation rates at 185 nm in the absence of  $\text{TiO}_2$  and at 254 nm in the presence of  $\text{TiO}_2$  are about the same. In both cases, 88% disappearance of  $\text{CH}_3\text{CF}_2\text{H}$  are obtained after 6 hours under our conditions. Since the photolysis takes place at 185 nm, in the presence of  $\text{TiO}_2$  the photodegradation is the combination of photolysis and photocatalysis which enhance the degradation rate. Identification of compounds resulting from the photolysis and photocatalysis of  $\text{CH}_3\text{CF}_2\text{H}$  is difficult because of lacking in the authentic samples.

The  $\text{CO}_2$  is found as the major product of photolysis and photocatalysis but the evolution rate in both reactions are different. For photolysis, the rate of  $\text{CO}_2$  is about the same as the rate of  $\text{CH}_3\text{CF}_2\text{H}$  degradation while it is twice for photocatalysis. This suggests that the intermediates which are formed during photocatalytic degradation will decompose faster than the photolytic degradation intermediates. Furthermore, the overall reactions will be different. As seen from the IR spectra, no significant change during photocatalysis except the presence of  $\text{CO}_2$  and  $\text{SiF}_4$ .

Since  $\text{SiF}_4$  has been found during photolytic and photocatalytic degradation, the 1027.9  $\text{cm}^{-1}$  absorption band is clearly identified as Si-F vibration. The  $\text{SiF}_4$  is produced in the Pyrex glass reactor. The presence of  $\text{SiF}_4$  was also observed in the IR spectrum of  $\text{COF}_2$  after a few hours of storage in the Pyrex glass cell<sup>8</sup>. One might suspect that the 1027.9  $\text{cm}^{-1}$  absorption band assigned here in this work as Si-F vibration, dues to OF or  $\text{O}_3$ . The IR

spectrum of  $O_3$  is also recorded and the weak band at  $1027.9\text{ cm}^{-1}$  has been observed. The significance of the OF radical as a chemical intermediate has been discussed by Arkell, Reinhard and Larson<sup>9</sup>. However, OF has been predicted to be unstable by Linnett<sup>10</sup> using the double quartet bonding scheme. After two hours of complete degradation, the  $1027.9\text{ cm}^{-1}$  is still observed. Undoubtedly, this absorption band is belong to  $SiF_4$ .

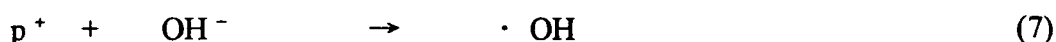
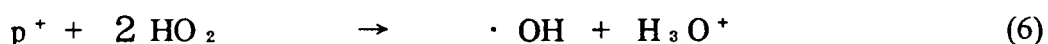
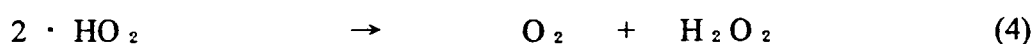
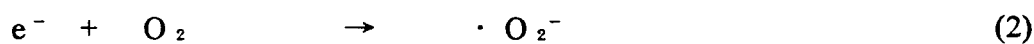
Significant changes are observed in the GC/MS chromatogram during the photolysis of  $CH_3CF_2H$ . The carbonyl compounds are found to be the major intermediate products, as expected from the IR data. Difficulty in identifying the intermediate products during photocatalytic degradation has been found since it is the fast reaction. Perhaps, the *in situ* technique should be performed for such a kind of this reaction.

The products which have been found during  $CH_3CF_2H$  photolytic degradation are  $HCOOH$ ,  $HCOF$ ,  $HCOOCH_3$ ,  $CH_2F_2$ ,  $H_2O$ ,  $CO_2$  and  $F^-$ . The formation of  $HCOOH$  and  $HCOOCH_3$  are directly related to the presence of atomic fluorine in the system. The IR data also support the formation of  $HCOOH$  and  $HCOOCH_3$ . Since trace of  $CH_2F_2$  has been found, this observation suggests that the photolytic degradation is mainly proceeded via the formation of atomic fluorine.

It has been known that irradiation of  $TiO_2$  with light of energy higher than the band gap results in the creation of electron and positive holes.



Both electron and positive hole form OH radical according to the following process:



The reactions of the  $\cdot OH$  radical with several HCFC and HFC have been reported in the literature<sup>4,7</sup>. The products, which have been found during photocatalytic degradation, are  $CH_3COF$ ,  $CO_2$ ,  $H_2O$ ,  $F^-$  and trace of  $CH_2F_2$  and  $CH_2CFH$ . The formation of these compounds suggest that the photocatalytic degradation of  $CH_3CF_2H$  proceeds via the reaction with OH radical.

As notice from the rate of  $CH_3CF_2H$  degradation and  $CO_2$  formation, the rapid degradation of intermediate products are found to be supported by the GC/MS data. However, the formation of  $SiF_4$  during photodegradation indicates that the atomic fluorine is