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Decomposition of CF_3Cl by corona discharge*

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Abstract——In this paper pulsed corona discharge is shown to be effective for the decomposition of CF_3Cl(Freon-13). The pressure of CF_3Cl was 2.67×10^3 Pa, after discharged for 2 min, 39.5% of CF_3Cl was decomposed. The products were mainly CF_4, Cl_2 and CF_2Cl_2. The yield increased by adding O_2 or air. Under the same conditions, more than 94% decomposition yield was obtained if 5.32×10^3Pa O_2 or air was added. The composition of products became CF_2O, Cl_2 and CF_4. While the partial pressure of O_2 or air reached 1 atm, the decomposition yield decreased to 54.5% and 48.5% respectively.

Keywords: decomposition; Freon-13; plasma.

1 Introduction

Since the 1970's many authors have realized that the CFCs emitted by human may cause ozone depletion. It is reported that the abundance of chlorine compounds in the stratosphere is about 3 ppb and they are mainly halocarbons or their photochemical by-products (Prather, 1990). Most CFCs's lifetime in atmosphere is as long as 100 years (Prather, 1990; Hammitt, 1987), so they are readily transported into the stratosphere where they are excited by the ultraviolet light and then released chlorine radicals, which cause ozone depletion. The appearance of Antarctic ozone "hole" makes people paying more concern for emitting CFCs.

Plasma has been applied in chemical field since 1960. Because of its efficiency and practicability, it was widely used in waste treatment, especially in treating air pollutants. In the gaseous phase, pulsed streamer corona discharge was found to be much more effective for promoting the reactions leading to desulfurization and denitrification than other methods. This is attributed to the more efficient production of hydroxyl radicals using pulsed streamer

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corona discharge (Clements, 1986). In aqueous solutions, Sharma also used this method for degradation of phenol. They found it was to be effective in breaking down phenol in aqueous solutions by adding flowing O_2 (Sharma, 1993).

In this study, a pulsed high-frequency power was used to generate spark discharge or streamer corona discharge for CF_3Cl decomposition. Spark discharge turned to streamer corona discharge when the reactor's total pressure was above 5.4×10^4 Pa.

2 Experimental

Pulsed high-frequency voltage was generated by a capacitor bank and spark gap, with a peak voltage of ± 6.5 kV, high-frequency of 1 MHz, and a repetition frequency of 330 Hz. The reactor used in these experiments was a cylindrical glass tube (inner diameter = 1.9 cm, length = 13.5 cm), the electrodes coiled by Fe-W alloy were located in the central axis of the reactor.

A series of pumps were used for keeping high vacuum. The reactor was evacuated before filling 2.67×10^3Pa CF_3Cl (purity of 99.5%) with or without a certain amount of O_2 (purity of 99.5%) or air and then discharged for a definite time. Samples were analyzed by using a HP 8542 UV-Visible spectrometer and a Nicolet 5Dx FT-IR spectrophotometer. The GC peaks were obtained by a 102G gas chromatography with a thermal conductivity detector. All gases were used as supply without further purification.

3 Results and discussion

3.1 Decomposition of CF_3Cl

In Fig. 1, the dotted curve is the GC spectrum of 2.67×10^3Pa CF_3Cl before discharge and the solid line is the GC spectrum after discharge for 2 min. The spectrum shows three new peaks after discharge. UV-Vis spectrum (Fig. 2) shows that there is Cl_2 (Mishalanie, 1986; Ying, 1988) among products. FT-IR spectrum (In this paper all FT-IR spectra are omitted) indicates the discharge products are CF_4 (FT-IR 1281.2 cm^{-1}, GC peak 1; Plyer, 1951; Shimanouchi, 1977), CF_2Cl_2 (FT-IR 925 cm^{-1}, 890 cm^{-1}, GC peak 3; Plyer, 1951; Shimanouchi, 1977), and a small amount of by-product SiF_4 (1028.1 cm^{-1}) produced by F reacting with SiO_2. CF_4, CF_2Cl_2 and Cl_2 are identified by GC standard samples. And the decomposition yield of CF_3Cl is about 39.5%. The dependence of the decomposition yield on the discharge time is shown in Fig. 3. The decomposition yield of CF_3Cl increases rapidly from 30s to 90s, then becomes slowly. When the discharge time is 30s the decomposition yield is 20.0%, as the discharge time increases to 90s the decomposition yield is going up to

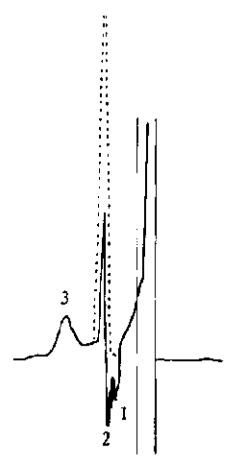

Fig. 1 GC spectrum of 2.67×10^3Pa CF_3Cl discharged 2 min The dotted curve is before discharge 1 CF_4 2 Cl_2 3 CF_2Cl_2

37.0%. After this time, the decomposition yield only increases 6.5% from 90s to 240s.

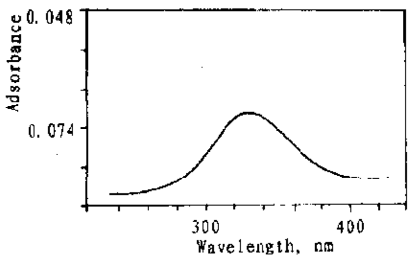

Fig. 2 UV-Vis spectrum of 1.33×10^4 Pa CF_3Cl discharged 3 min

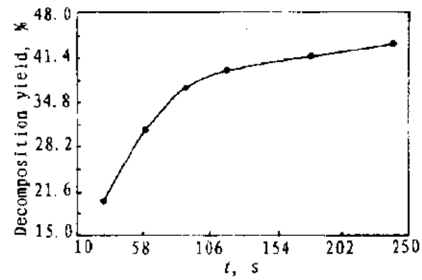

Fig. 3 Decomposition yield of 2.67×10^3Pa CF_3Cl versus discharge time

One question must be answered: why the decomposition yield is so low. CF_3Cl molecule when bombarded with electrons is dissociated as follows:

$CF_3Cl + e \longrightarrow CF_3 + Cl$, $\quad CF_3Cl + e \longrightarrow CF_2Cl + F$,

$CF_3 + e \longrightarrow CF_2 + F$, $\quad CF_2Cl + e \longrightarrow CF_2 + Cl$.

During corona discharge, the kinetic energy of electrons varies from 1 eV to 10 eV. It is much higher than the bond energy of CF_3Cl. So the reactions mentioned above can take place. Other dissociation reactions can be neglected. Then the radicals collide with each other and lead to the formation of the following products:

$CF_3 + F \longrightarrow CF_4$, $\quad CF_2Cl + Cl \longrightarrow CF_2Cl_2$, $\quad Cl + Cl \longrightarrow Cl_2$

$CF_3 + Cl \longrightarrow CF_3Cl$, $\quad CF_2Cl + F \longrightarrow CF_3Cl$.

From the possible reactions it reflects that the reverse reactions play an important role in all reactions. They compete with other reactions. This makes the decomposition process reaching an equilibrium state within a short time and thus causes a low decomposition yield.

3.2 Decomposition of CF_3Cl in the presence of O_2 and air

The decomposition yield of CF_3Cl dramatically increases by adding O_2 or air. Fig. 4 is the decomposition yield of CF_3Cl with an initial pressure of 2.67×10^3Pa versus O_2 and air pressure. When 5.32×10^3 Pa O_2 or air is added to the reactor. Approximately 94% yield is obtained. However, the decomposition yield decreases if too much O_2 or air is added. And the partial pressure of O_2 or air reach 1 atm the decomposition yield decreases to 54.5% and 48.5% respectively. The composition of products become CF_2O (FT-IR 1941 cm^{-1}, 1249 cm^{-1}, 956 cm^{-1}, 775 cm^{-1}; Nielsen, 1952), Cl_2 and CF_4. Fig. 4 also shows the same case of O_2 and air affecting decomposition of CF_3Cl. It is clear that O_2 is the only factor affecting decomposition of CF_3Cl.

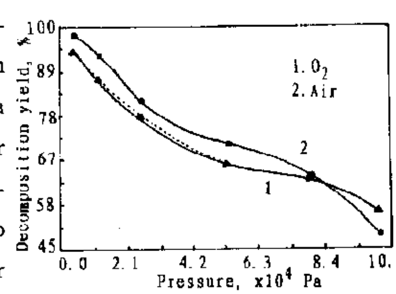

Fig. 4 Decomposition yield of 2.67×10^3Pa CF_3Cl versus O_2 and air pressure

Oxygen is excited or dissociated by electron impact. The excited O_2 or active O reacts with CF_3 or CF_2, leading to the CF_2O molecules. This may enhance the decomposition yield of CF_3Cl as to increases the reaction paths than decomposing pure CF_3Cl. Such as the reactions lead to yield HOCl and CF_2O. So the reverse reactions play a relatively insignificant role in all reactions, which lead to a higher decomposition yield. However, the pressure of oxygen or air is too high, the free path of the electron is greatly diminished and the energy acquired from the electric field also dwindles, thus leads to a low decomposition yield.

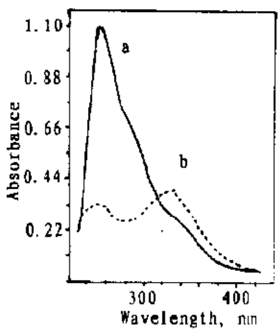

Fig. 5 UV-Vis spectrum of CF_3Cl discharged 3 min 1.33×10^4 Pa CF_3Cl + 1.33×10^4 Pa O_2

Fig. 5a is the UV-Vis spectrum of 1.33×10^4 Pa CF_3Cl + 1.33×10^4 Pa O_2 after discharged 3 min. It is quite different from Fig. 2, in which Cl_2 is identified and is in good agreement with its previous studies. But in Fig. 5, the products are more complicated. They are identified as CF_2O (Judge, 1983), Cl_2(Mishalanie, 1986; Ying, 1988) and HOCl (Mishalanie, 1986). CF_2O and Cl_2 are the main products of decomposition. But the quantity of Cl_2 is much more than decomposing pure CF_3Cl. HOCl is the new component appearing in the UV spectrum. Fig. 5a is in agreement with the UV spectrum of HOCl proposed by Mishanlaie, beside the UV absorption of Cl_2 overlapping from 280 nm to 380 nm and CF_2O overlapping at 254 nm. HOCl generation connects with the small amount of H_2O existing in the system. Fig. 5b is the UV spectrum of Fig. 5a after an hour. It is clear that the absorption peak of Cl_2 is separated from Fig. 5a. And the absorbance of Cl_2 also increases from 0.251 to 0.454. This can be explained by the instability of HOCl. Photolysis initiates the following reactions: $HOCl + h\gamma \longrightarrow OH + Cl$, $Cl + Cl \longrightarrow Cl_2$.

4 Conclusion

Corona discharge is an effective method for the treatment of CF_3Cl. Though it is not efficient for treating pure CF_3Cl even at a low pressure. But in the presence of oxygen or air the decomposition rate is greatly enhanced. When 5.32×10^3 Pa O_2 or air is added the decomposition yield is more than 94%, while at a partial pressure of O_2 or air at 1 atm the decomposition yield decreases to 54.5% and 48.5% respectively, with an initial CF_3Cl pressure of 2.67×10^3 Pa. Oxygen affects the decomposition by increasing the number of reaction paths which make the reverse reactions playing a relatively insignificant role in all reactions. When the pressure of the reactor is too high, the free path of the electron and the energy acquiring from the electric field are dwindled, thus leads to a lower decomposition yield.

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