Journal of Environmental Sciences Vol. 9, No. 1, pp. 11—19, 1997 ISSN 1001-0742

Decomposition of gaseous CF_2ClBr by cold plasma method

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Abstract——The paper presented the results regarding the decomposition of gaseous CF_2ClBr by cold plasma method. After two minutes discharge, the maximum decomposition rate of 2660 Pa CF_2ClBr pure and 2660 Pa CF_2ClBr plus 7980 Pa O_2 reached 60% and 80%, respectively. The paper also studied the cold plasma gas phase chemistry reaction mechanism of CF_2ClBr at low pressure, and the pressure effects of CF_2ClBr and added gas (He, N_2, O_2 and dry air) on the CF_2ClBr decomposition respectively by cold plasma method. These studies will be helpful to application of cold plasma method in the treatment of hazardous gaseous wastes.

Keywords: decomposition; gaseous CF_2ClBr; cold plasma method.

1 Introduction

Cold plasma is also called nonthermal equilibrium plasma in which the electrons have a much higher energy or temperature than the heavier particles like ions, the neutral gas particles etc. This means that the whole system can be kept at a low temperature, even at room temperature, while the electrons have enough energy to give rise to the excitation, ionization and dissociation of the gaseous molecules, which result in the production of many chemically active species such as atoms, molecules, radicals, ions, electrons and so on. The interaction of these species can lead to the destruction of a chemical substance, and the production of a new one. So plasma chemistry method can be used for aimed destruction or removal of certain undesired substances.

The application of the cold plasma method in the treatment of the environmental pollutants has been paid more and more attentions in recent years. The cold plasma method is known as an effective, easily obtained, low costing, and low energy consuming method in treating some environmental pollutants. We used this method to decompose gaseous CF_2ClBr, which (also called Halon 1211 or Freon 12B1 or BCF) is a typical example of Halons substances. After delivered to the stratosphere, Halons will release Br radical under

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UV irradiation. The chain reaction of Br and O_3 plays one of the most important roles for O_3 depletion in the stratosphere and therefore the studies on the decomposition of CF_2ClBr by cold plasma method has practical significance.

2 Experimental

The purity of CF_2ClBr is 99.95%. It is not further purified before uses. He, N_2, O_2 and air are commercial gases. The purities of He, N_2 and O_2 are all 99.99%.

The cold plasma apparatus is shown in Fig. 1. A cylindrical sample tube, the middle of which is a hollow, is made of glass. The tube is 19.5 cm long. Its outside diameter is 2 cm and inside diameter is 1.2 cm. A layer of aluminum foil is kept close to the inside wall of the sample tube and is well grounded. The coils of the high frequency generator, whose frequency is lower than 20 MHz and whose voltage is about 1.5—3 kV, are evenly winded on the outside wall of the sample tube. An induced electric field is occurred in the tube when the high frequency generator works, that is, when discharge works. The electrons will certainly impact with gas molecules to make the molecules ionize during the process of their being accelerated by the induced field. A cold plasma is thus formed in the volume of the sample tube.

The main analysis methods in our study are Fourier transform IR spectrophotometer and gas chromatography. The parameters of gas chromatography are shown as follows. Detector: thermal conductivity cell; Carrier gas: N_2; Chromatography column: 2-meter long stainless steel column containing G.D.X-105 80—100 mesh; Column temperature: 170℃; Vaporization temperature: 190℃; Flowing velocity of N_2: 18 ml/min; Current of thermal conductivity cell: 120 mA.

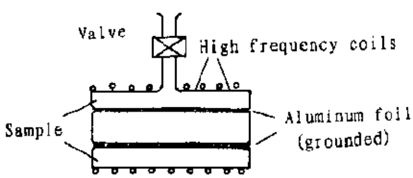

Fig. 1 The cold plasma apparatus

3 Results and discussions

3.1 The cold plasma volume gas phase reaction of CF_2ClBr at low pressure

The GC and IR spectrum of 2660 Pa CF_2ClBr after 5 minutes discharge are shown in Fig. 2 and Fig. 3 respectively. In Fig. 2, there are 5 new peaks and these new peaks are respectively labeled as 1, 2, 3, 4 and 5 according to their order of peaks' presenting. Fig. 3 shows that the new products are CF_4, CF_3Br, CF_2Cl_2, CF_2Br_2, $CFCl_3$ and $CFCl_2Br$. Through the careful analysis, it is attributed peak 1, 2, 3, 4 and 5 of Fig. 2 correspond respectively to CF_4, CF_3Br, CF_2Cl_2, CF_2Br_2 (compared with these materials's GC spectrum) and the mixture of $CFCl_3$ and $CFCl_2Br$. The changes of CF_2ClBr and the products with the discharge time are shown in Fig. 4 and Fig. 5 respectively. In Fig. 4, the decomposition rate of CF_2ClBr increases with the discharge time first. The decomposition rate is 44% when the discharge time being 2 minutes. And then it reaches a constant, 80% with 10 minutes or longer discharge

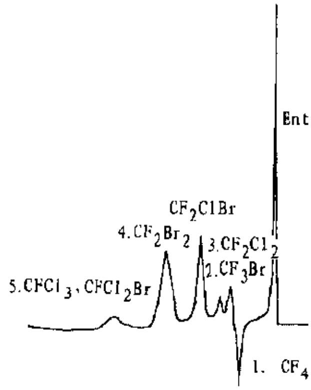

Fig. 2 The gas chromatogram of 2660 Pa CF_2ClBr after 5-minute discharge

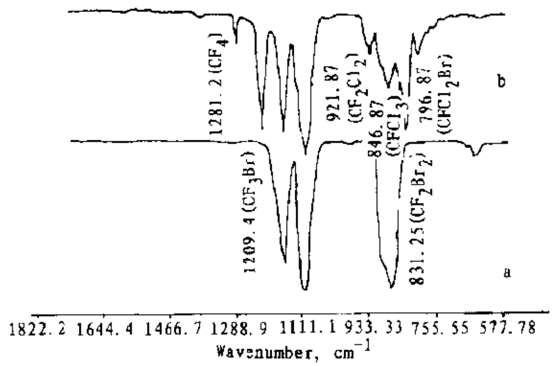

Fig. 3 a: The IR spectrum of 2660 Pa CF_2ClBr before discharge

b: The IR spectrum of 2660 Pa CF_2ClBr after 5-minute discharge

time. In Fig. 5, the changes of CF_3Br, CF_2Br_2 and the mixture of $CFCl_3$ and $CFCl_2Br$ are like that of CF_2ClBr in Fig. 4. But the changes of CF_4 and CF_2Cl_2 are competing, with one increasing while the other decreasing.

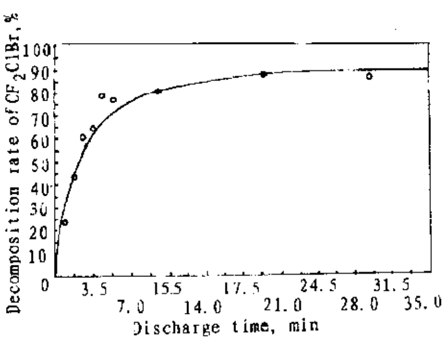

Fig. 4 The change of CF_2ClBr with the discharge time

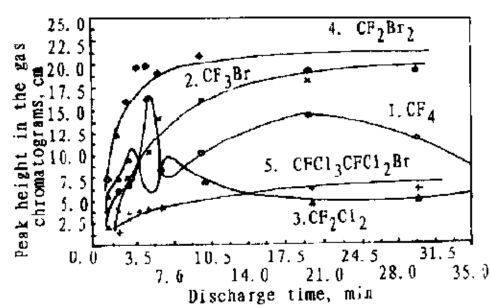

Fig. 5 The change of the products with the discharge time

In order to explain the changes of CF_2ClBr and the products with discharge time, the plasma chemistry reaction mechanism is presented as follows.

Only the gas-phase reactions occurring in the volume part of the plasma is discussed here, not including the surface reaction. Plasma chemistry results from the complex impacts between the chemically active species such as electrons, ions, atoms, radicals and molecules in the plasma form. We suppose that the main chemically active species taking part in the reactions in the CF_2ClBr cold plasma are the radicals Br, Cl, F, CF, CF_2, CF_2Cl and the ions Br^-, Cl^-, F^-, CF^+, $CF_2{}^+$, CF_2Cl^+. The concentration relation of these species is Br>Cl>F, $CF_2Cl>CF_2>CF$, $B^->Cl^->F^-$, $CF_2Cl^+>CF_2{}^+>CF^+$ because the bond energy of C-F in CF_2ClBr is stronger than that of C-Br and the bond energy of C-Cl is stronger than that of C-Br (Driscoll, 1992). These species are produced by the ways as follows:

$CF_2ClBr + e \longrightarrow CF_2Cl + Br + e$; $CF_2ClBr + e \longrightarrow CF_2Cl + Br^-$;

$CF_2ClBr + e \longrightarrow CF_2Cl^+ + Br + 2e$; $Br + e \longrightarrow Br^-$;

$CF_2Cl^+ + e \longrightarrow CF_2Cl$; $CF_2Cl + e \longrightarrow CF_2 + Cl + e$;

$CF_2 + e \longrightarrow CF_2 + Cl^-$; $CF_2Cl + e \longrightarrow CF_2^+ + Cl + 2e$;

$Cl + e \longrightarrow Cl^-$; $CF_2^+ + e \longrightarrow CF_2$;

$CF_2 + e \longrightarrow CF + F + e$; $CF_2 + e \longrightarrow CF + F^-$;

$CF_2 + e \longrightarrow CF^+ - F + 2e$; $F + e \longrightarrow F^-$.

Because Br, Cl and F are elements having great affinity and so the step, $Br(Cl,F) + e \longrightarrow Br^+(Cl^+,F^+) + 2e$, is negligible. It is believed the concentration of Br^+, Cl^+, F^+ are very low and these particles may be negligible compared with Br, Cl, F on discussing the mechanism. The main reactions worthy to be considered are as follows:

$CF_2Cl + Br \longrightarrow CF_2ClBr$, $CF_2Cl^+ + Br^- \longrightarrow CF_2ClBr$ (1)

$CF_2Cl + Cl \longrightarrow CF_2Cl_2$, $CF_2Cl^+ + Cl^- \longrightarrow CF_2Cl_2$ (2)

$CF_2Cl + F \longrightarrow CF_3 + Cl$, $CF_2Cl^+ + F^- \longrightarrow CF_3 + Cl$ (3)

$CF_2 + Br \longrightarrow CF_2Br$, $CF_2^+ + Br^- \longrightarrow CF_2Br$ (4)

$CF_2 + Cl \longrightarrow CF_2Cl$, $CF_2^+ - Cl^- \longrightarrow CF_2Cl$ (5)

$CF_2 + F \longrightarrow CF_3$, $CF_2^+ - F^- \longrightarrow CF_3$. (6)

The reason that CF_3Cl is not to be produced in step (3) are: (a) CF_3Cl is not found in the product analysis through IR spectrum; (b) the loss of the kinetic energy of $F(F^-)$ is small during the impact between $F(F^-)$ and other species in the electrical field because F is a light element. So $F(F^-)$ can easily amass its energy when being accelerated by the induced electric field and pass its energy to CF_2Cl (CF_2Cl^+) to make Cl dissociated from CF_2Cl (CF_2Cl^+); (c) in view of the bond energy relation, C-F > C-Br, step (3) is exothermic, permitted to occur by thermal dynamics. In addition, the mechanism is also analyzed from the products.

The source of CF_3Br is:

$CF_2Cl + F \longrightarrow CF_3 + Cl$

$CF_2Cl^+ + F^- \longrightarrow CF_3 + Cl$

$CF_2 + F \longrightarrow CF_3$

$CF_2^+ + F \longrightarrow CF_3$

$CF_3 + Br \longrightarrow CF_3Br$

The source of CF_2Br_2 is:

$CF_2 + Br \longrightarrow CF_2Br$

$CF_2^+ + Br^- \longrightarrow CF_2Br$

$CF_2Br + Br \longrightarrow CF_2Br_2$

CF_2Cl, CF_2, F, Br and CF_2Cl^+, CF_2^+, F^-, Br^- in the CF_2ClBr plasma will increase with the increase of discharge time first and then keep unchanged after a period of discharge time. So the changes of products CF_3Br, CF_2Br_2 produced from the impacts between these species with the time (Fig. 5) take on the same as those of these species.

The competing mechanism of CF_4 and CF_2Cl_2 is:

$CF_2 + F \longrightarrow CF_3$, $CF_2^+ + F^- \longrightarrow CF_3$

$CF_2Cl + F \longrightarrow CF_3 + Cl$, $CF_2Cl^+ + F^- \longrightarrow CF_3 + Cl$

$CF_2Cl + Cl \longrightarrow CF_2Cl_2$, $CF_2Cl^+ + Cl^- \longrightarrow CF_2Cl_2$

$CF_3 + F \longrightarrow CF_4$

When discharge begins, in addition to its reacting with Br(Br^-) to return to CF_2ClBr, the main reaction of CF_2Cl(CF_2Cl^+) is that it reacts with Cl(Cl^-) to produce CF_2Cl_2 because the concentration of Cl(Cl^-) is greater than that of F(F^-) in the sample tube. Because the concentration of Br(Br^-) is far greater than those of Cl(Cl^-) and F(F^-). Cl(Cl^-) and F(F^-) will not compete with Br(Br^-), and the reaction between CF_3 and Br will restrain the reaction between CF_3 and F to produce CF_4. So at the beginning of the discharge, CF_2Cl_2 increases while CF_4 decreases as shown in Fig. 5. With the continuing of discharge, Cl(Cl^-) is soon depleted because of the rapid reaction between CF_2Cl(CF_2Cl^+) and Cl(Cl^-). Then CF_2Cl(CF_2Cl^+) reacts with F(F^-) to produce CF_3 and Cl. CF_3 increases because of the reaction. Besides the reaction between CF_3 and Br, CF_3 will react with F to produce CF_4. So CF_4 increases but CF_2Cl_2 decreases. Then Cl(Cl^-) begins to increase and F(F^-) is depleted with the discharge time. When the concentration of Cl(Cl^-) is greater than that of F(F^-) again, the reaction between CF_2Cl(CF_2Cl^+) and Cl(Cl^-) plays a leading role. So the competing reaction takes place circularly as above discussed.

The production of $CFCl_3$ and $CFCl_2Br$ connects with CF(CF^+) whose concentration is low in the CF_2ClBr plasma. So the concentration of $CFCl_3$ and $CFCl_2Br$ is also low and their change is slow. The reaction mechanism is not discussed in detail in our paper.

3.2 The pressure effects of CF_2ClBr and added gases (He, N_2, O_2 and air) on the CF_2ClBr decomposition respectively by the cold plasma method

Fig. 6 shows the pressure effect of CF_2ClBr on the CF_2ClBr decomposition. Fig. 7 shows the pressure effects of added gases (He, N_2, O_2 and air) on the CF_2ClBr decomposition.

Fig. 6 and Fig. 7 show the decomposition rate of CF_2ClBr decreases with the increase of the gas pressure. The change of the CF_2ClBr decomposition rate is mainly decided by the two kinds of reactions as follows:

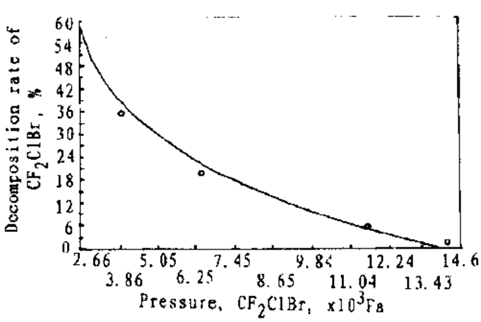

Fig. 6 The pressure effect of CF_2ClBr on the CF_2ClBr decomposition with the discharge time being 2 minutes

$$\begin{aligned} CF_2ClBr + e &\longrightarrow CF_2Cl + Br + e \\ CF_2ClBr + e &\longrightarrow CF_2Cl + Br^- \\ CF_2ClBr + e &\longrightarrow CF_2Cl^+ + Br + 2e \end{aligned} \qquad (7)$$

$$\begin{aligned} CF_2Cl + Br + M &\longrightarrow CF_2ClBr + M + \text{energy} \\ CF_2Cl^- + Br^- + M &\longrightarrow CF_2ClBr + M + \text{energy} \end{aligned} \qquad (8)$$

In step (7), the energy of the electrons is an important factor. CF_2ClBr will be dissociated only when its energy is greater than the bond energy of CF_2ClBr. In the plasma, the energy of the electrons is dependent on the intensity of the induced electrical field and the impacts with the gas molecules (Eliasson, 1991). In step (8), M, the gas, is also an important factor. The pressure effects of gases on the decomposition of CF_2ClBr are discussed in detail as follows.

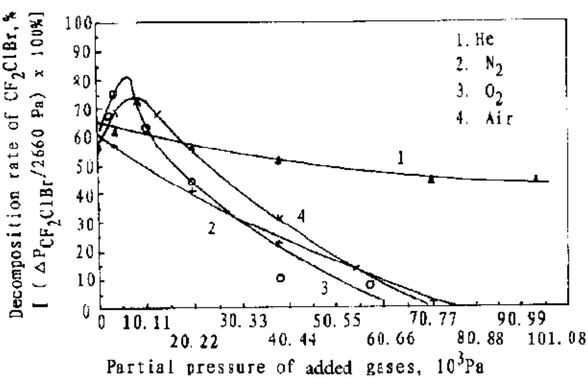

Fig. 7 The pressure effects of added gases on the CF_2ClBr decomposition with CF_2ClBr being 2660 Pa and the discharge time being 2 minutes

3.2.1 CF_2ClBr

In Fig. 6, the CF_2ClBr decomposition rate decreases rapidly with the increase of the CF_2ClBr pressure. The decomposition rate decreases from 60%, when CF_2ClBr pressure being 2660 Pa, to about 0%, when CF_2ClBr pressure is 14630 Pa. Comparing of Fig. 6 with Fig. 7, it is concluded the CF_2ClBr pressure effect on the CF_2ClBr decomposition is the greatest as compared to that of He, N_2, O_2 and air.

With the increase of the CF_2ClBr pressure, the electrons will impact with more CF_2ClBr molecules during their acceleration by the induced electric field. Because CF_2ClBr is a polyatomic molecule and its distribution of energy level is very complex, the electrons will easily take nonelastic impact with the CF_2ClBr molecules and pass most of their energy to the CF_2ClBr molecules to excite them. The CF_2ClBr molecules at excited state will transfer their energy to the neighboring molecules through the collision with the other moleculcs. The high energy contained by the electrons is rapidly averaged by the CF_2ClBr molecules at high pressure and the cold plasma can not be formed. So the electrons amass their energy with more difficulty and the quantity of the electrons having enough energy to make CF_2ClBr dissociate decreases and therefore step (7) is restrained. This is the reason that the CF_2ClBr decomposition rate decreases with the increase of the CF_2ClBr pressure.

3.2.2 He

In Fig. 7, the CF_2ClBr decomposition rate decreases slowly with the increase of the Helium pressure. The decomposition rate of 2660 Pa pure CF_2ClBr is about 65% and it also keeps to 45% when the partial pressure of He reaches 94430 Pa. So the pressure effect of Helium on the CF_2ClBr decomposition is the least.

Helium is an inert gas with large ionization energy, 24.587 eV (Yang, 1983), and light mass. And it also is a single-atom molecule with relatively simple energy level distribution. It could be explained that electronic energy is not enough to make Helium ionize in our experiment conditions and the impact between the electrons and the Helium molecules is mainly elastic. So Helium does not absorb the energy of the electrons, that is to say, Helium does not influence the electrons' amassing their energy in the induced field. The pressure effect of Helium on the CF_2ClBr decomposition lies in the fact that the high pressure of Helium increases the impact frequency between CF_2Cl(CF_2Cl^+) and Br(Br^-) and facilitates step (8), and this effect is small.

3.2.3 N_2

In Fig. 7, the decomposition rate of CF_2ClBr decreases rapidly with the increase of N_2

pressure. When the partial pressure of N_2 reaches 71820 Pa, the CF_2ClBr decomposition rate decreases from 57%, the decomposition rate of 2660 Pa pure CF_2ClBr, to 0%. The pressure effect of N_2 on the CF_2ClBr decomposition is between that of CF_2ClBr and that of Helium.

N_2 will change as follows after impacting with the electrons.

$N_2 + e \longrightarrow N_2^*$; $N_2^* + e \longrightarrow N + N + e$;

$N_2^* + e \longrightarrow N^- + N^+ + e$.

With the increase of N_2 pressure, the energy of more and more electrons is absorbed by N_2 and more and more electrons lack enough energy to make CF_2ClBr dissociate, restraining step (7). So the CF_2ClBr decomposition rate decrease rapidly with the increase of the N_2 pressure shown in Fig. 7.

3.2.4 O_2

In Fig. 7, the plot describing the pressure effect of O_2 on the CF_2ClBr decomposition is very special, having a peak. The CF_2ClBr decomposition increases with the increase of the O_2 pressure first and it reaches the maximum, 80%, when O_2 partial pressure is 7980 Pa. Then the CF_2ClBr decomposition rate decreases rapidly with the continuous increase of the O_2 partial pressure and it is only 10% when O_2 partial pressure is 39900 Pa.

The systems, CF_2ClBr-He and CF_2ClBr-N_2, have the same products as the pure CF_2ClBr after discharge. But CF_2ClBr-O_2 has different products. Through IR spectrum analysis, it is known the main products of CF_2ClBr-O_2 are CF_2O, CF_2Cl_2 and CF_3Br when the partial pressure of O_2 is low and the main product is only CF_2O when the partial pressure of O_2 is high.

O_2 is very active and may be dissociated to O when impacting with the electrons. The main reactions in CF_2ClBr-O_2 system are discussed as follows.

$$CF_2Cl + O_2 \longrightarrow \ldots \longrightarrow CF_2O + Cl \tag{9}$$

$$CF_2Cl + O \longrightarrow CF_2O + Cl \tag{10}$$

$$CF_2Cl + Br + M \longrightarrow CF_2ClBr \tag{8}$$

$$CF_2Cl + Cl \longrightarrow CF_2Cl_2$$

$$CF_2Cl + F \longrightarrow CF_3 + Cl$$

$$CF_2 + O \longrightarrow CF_2O \tag{11}$$

$$CF_2 + Br \longrightarrow CF_2Br$$

$$CF_2 + Cl \longrightarrow CF_2Cl$$

$$CF_2 + F \longrightarrow CF_3$$

$$CF_3 + Br \longrightarrow CF_3Br$$

When the quantity of O_2 is small, the above reactions all can occur and the products include CF_2O, CF_2Cl_2 and CF_3Br. With the increase of the O_2 pressure, step (9), (10), (11) play leading roles with step (8) restrained. So the decomposition rate of CF_2ClBr increases. With the continuing increase of the O_2 pressure, the product is simpler and is CF_2O only. At the same time, the energy of more and more electrons is passed to O_2, restraining step (7) with the increase of the O_2 pressure. So the decomposition rate of CF_2ClBr decreases rapidly. In a word, the plot is the synthesis of two effects, O_2 itself or O dissociated from O_2 taking part in the plasma chemistry reactions, which restrain step (8) and O_2 absorbing the energy of the electrons at the same time restrains step (7).

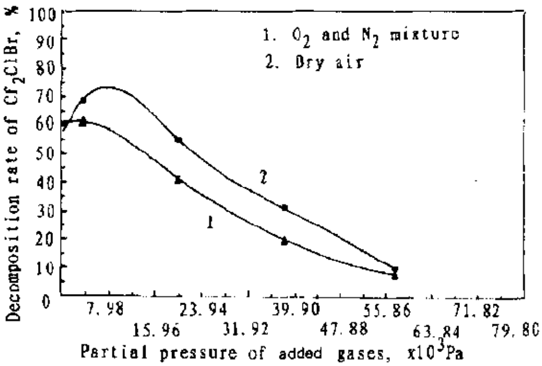

Fig. 8 a: The pressure effect of air on the CF_2ClBr decomposition
b: The synthetic of the pressure effects of N_2 and O_2 on the CF_2ClBr decomposition

3.2.5 Air

In Fig. 7, the plot describing the pressure effect of air on the CF_2ClBr decomposition is like that describing O_2. The main component parts of air and N_2 and O_2 whose velumes occupy 79% and 21% of the total volume respectively. There are the two plots describing the pressure effect of N_2 and O_2 on the CF_2ClBr decomposition multiple 0.79 and 0.21 respectively in the paper and then plus the two modified plots to one plot shown in Fig. 8b. The plot is very alike to that describing the pressure effect of air on the CF_2ClBr decomposition shown in Fig. 8a. So the influence of air is may be understood the synthesis of the effects of N_2 and O_2.

4 Conclusions

In this paper, gaseous CF_2ClBr using the cold plasma method, is decomposed at low pressure. The maximum decomposition rate of 2660 Pa pure CF_2ClBr is 60% after 2-minute discharge; and is 80% after 10-minute discharge. And the decomposition rate of CF_2ClBr in 2660 Pa CF_2ClBr 7980 Pa O_2 system is 80% after 2-minute discharge. The main products of pure CF_2ClBr after discharge are CF_4, CF_3Br, CF_2Cl_2, CF_2Br_2, $CFCl_3$ and $CFCl_2Br$ which also are Freons or Halons having O_3 depleting potential. But in CF_2ClBr-O_2, the main product is only CF_2O which can be easily removed by water steam. So CF_2ClBr-O_2 is the ideal system in which CF_2ClBr is decomposed by the cold plasma method.

We also studies the cold plasma bulk gas phase reaction mechanism of CF_2ClBr at low pressure and analyzes in detail the forming paths and the changing tendency with discharge time of the products. It can be known how to facilitate the advantageous reactions and restrain the disadvantageous reactions only after learning clearly the reaction mechanism. In addition, it studies the pressure effects of CF_2ClBr and alien gases (He, N_2, O_2 and air) on the CF_2ClBr decomposition respectively by the cold plasma method. It is concluded the main reason that the high pressure is disadvantageous to the CF_2ClBr decomposition is that the frequent impact between the electrons and the gas molecules at high pressure influences greatly the amassing of the electrons' energy and does not benefit the forming of the cold plasma. The impact between the electrons and the gas molecules connects tightly with the gas character such as energy level distribution, the ionization energy, etc. These studies will be helpful to the application of cold plasma method in the treatment of hazardous gaseous wastes at about atmospheric pressure and the acceptance of the cold plasma method by industry.

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(Received June 19, 1995)