Decomposition of Chlorofluorocarbon CFC-113 in Water by Ultrasonic Irradiation

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Chlorofluorocarbon CFC-113 was readily decomposed by ultrasonic irradiation in water with high efficiency to inorganics, such as CO, CO_2, HCl, and HF.

Chlorofluorocarbons (CFC's) have been used in large quantity in everyday life and in various manufactural fields for their excellent physical and chemical properties. However, when they are released into atmospheric circumstance, they diffuse to stratosphere and eventually cause the depletion of ozone layer.[1] Therefore in the near future the production and the use of CFC's will be prohibited.[2] However the problem on the disposal of used CFC's has not yet been solved although several methods for decomposition of CFC's such as combustion or pyrolysis,[3] plasma decomposition,[4,5] and catalytic decomposition[6-8] have been investigated. On the other hand, recent studies on aqueous sonochemistry[9] have revealed that gaseous hydrocarbons were susceptible to rapid pyrolysis or combustion in cavitation bubbles[10] and that the greater the hydrophobicity of a dissolved substance, the more readily it can enter and be accumulated in the bubbles.[11,12] CFC's are hydrophobic and have appreciably high vapor pressure. Accordingly, they can be concentrated in the bubbles and are expected to undergo decomposition by combustion or pyrolysis which are the most efficient reactions in aqueous sonochemical process. Recently preliminary results of CFC-11 and CFC-113 in dilute aqueous solution have been reported[13] but decomposition products have not been elucidated.

We report here the results of sonolyses of CFC-113 of wide range of concentration and discuss the mechanism of sonolytic degradation of CFC's which resist to degradation by OH radicals.

An aqueous solution of 25-1000 ppm of $F_2ClC\text{-}CClF_2$ (CFC-113) was subjected to high intensity ultrasonic irradiation (6 W/cm^2, 200 kHz) under air or argon atmosphere. A cylindrical glass vessels (50 mmϕ) of 105.0, 75.0 and 70.4 ml were used for ultrasonic irradiation. Each vessel has a side arm with a silicon rubber septum for gas bubbling, CFC-113 injection or sample withdrawing, and a separatory funnel at the top with a greaseless valve in-between. The bottom of the vessel was planar and 1 mm in thickness. After irradiation CFC-113 was extracted with isoamyl acetate under closed system, and then the amounts of CFC-113 were determined by a gas chromatograph. The yields of gaseous (CO, CO_2) and ionic (Cl^-, F^-) products were determined by the gas chromatograph and an ion chromatograph, respectively.

CFC-113 has low solubility in water (e.g. 170 ppm at saturated vapor pressure at 22°C) and has high volatility, so that in the case of 60 ml of solution prepared to be 25 ppm in total volume of 105 ml of closed reaction vessel (liquid phase volume/gas phase volume (l/g)=60/45), over 95 % of CFC-113 was vaporized into gas phase at 22°C (i.e. concentration of CFC-113 in water was lower than 1.25 ppm but hereafter we define the concentration of CFC-113 in this solution as 25 ppm). The amount of CFC-113 in the liquid phase increased with increasing l/g ratios, therefore l/g ratio is an important factor affecting the rate of decomposition of CFC-113 because the sonochemical reactions occur only in liquid phase.

Figure 1 shows the decomposition of 100 ppm solutions of CFC-113 under various l/g ratios. The decomposition rates of CFC-113 increased with increasing l/g ratios, that is, with increasing concentrations in water. The rate was faster under argon atmosphere than under air atmosphere. This may be because the cavitation effect is larger under argon than under air owing to the higher γ value (Cp/Cv) of argon.[9]

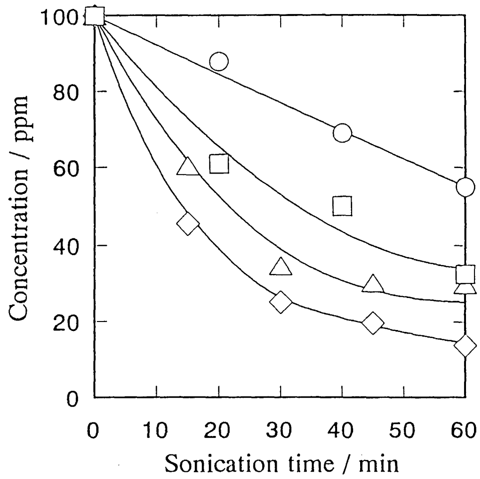

Figure 1. Decomposition of CFC-113 (100ppm) by ultrasonic irradiation at various volume ratios of liquid/gas part under argon or air atmosphere. ○: 60ml/45ml under air, □: 60/45 under Ar, △: 60/15 under Ar, ◇: 60/10.4 under Ar.

The initial rates of the decomposition at ambient temperature increased with increasing initial concentrations of CFC-113: 3.5 μM/min at 25 ppm, 40.1 μM/min at 100 ppm and 66.8 μM/min at 1000 ppm in reaction vessel of l/g=60/10.4 under argon atmosphere. The rates were slower than those of chloroform and other chlorinated hydrocarbons,[14,15] but at high concentrations, far exceeded the rate of formation of OH radicals (20 μM/min) by sonolysis of pure water. The rate was little affected by the addition of t-butyl alcohol which is known to be an effective OH radical scavenger. These results suggest that the degradation proceeds not via reaction with OH radicals nor combustion with O_2 under air but via gas phase pyrolysis in water vapor.

The decomposition efficiencies became lower with irradiation time particularly after 30 min. We assume that the decrease in concentration of CFC-113 in water by a rise in temperature during the irradiation causes the slow-down of the decomposition rate. The temperature of the solution rose by 8.8°C by the irradiation of 30 mim under the present experimental conditions though the reaction vessel was cooled by running water. The rate was increased to 168 μM/min when 1000 ppm of the solution was sonicated at 5°C under argon.

Figure 2 shows the decomposition profiles of CFC-113 under periodical sonication-substrate addition cycles. It is revealed that a lowering of efficiency upon continuous irradiation is caused by a rise in temperature, and not by the interference of decomposition products from CFC-113.

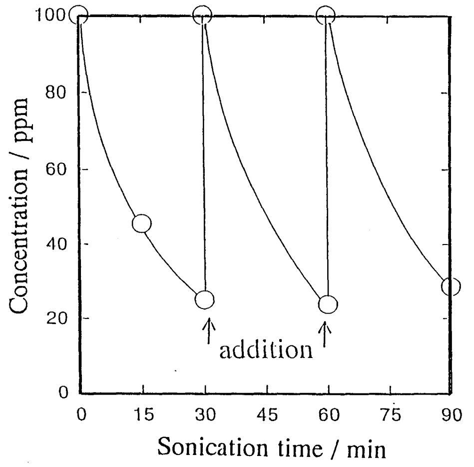

Figure 2. Decomposition profile of CFC-113 at sonication-addition cycles. After 30min of the sonication CFC-113 was added up to its initial concentration of 100ppm then the sample was allowed to stand for about 1 h till the solution reverted to ambient temperature, then the irradiation was re-opened.

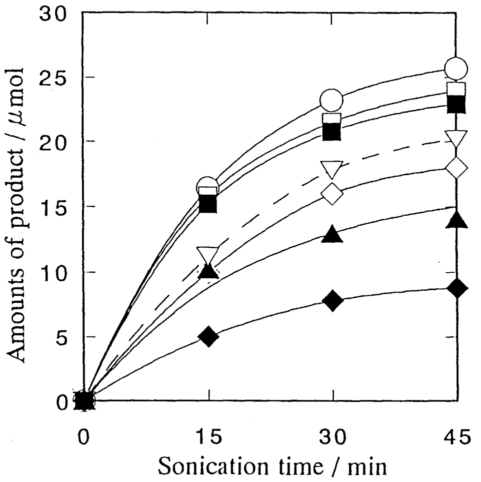

Figure 3. Formation of CO, CO_2, Cl^-, and F^- relative to the consumption of CFC-113 (100ppm) under argon. ◆: CO/2, ▲: $CO_2/2$, ■: $(CO+CO_2)/2$, □: $Cl^-/3$, ◇: $F^-/3$, ▽: corrected $F^-/3$, ○: CFC-113.

Figure 3 shows the yields of inorganics: CO, CO_2, Cl^- and F^- by sonolysis of CFC-113 under argon atmosphere.

Almost all of the carbon atoms and chlorine atoms in CFC-113 molecules changed to CO or CO_2 and Cl^-, respectively, but the conversion of fluorine atoms to F^- was not quantitative. The concentration of F^- in aqueous solution of HF decreased by ultrasonic irradiation probably due to capture of the F^- at the glass surface of the irradiation vessel during sonication. In fact, the decrease of 10 % of F^- concentration was observed at 30 min irradiation of 10 ppm of HF solution. The corrected conversion of fluorine atoms to F^- was 80 % of the decomposed CFC-113. The overall reaction under argon approximately satisfied the following reaction stoichiometry:

$$C_2F_3Cl_3\ (\text{CFC-113}) + 3H_2O \rightarrow 1.2CO_2 + 0.8CO + 3HCl + 3HF$$

All of the inorganics were formed with constant proportions to the degraded CFC-113 at all irradiation time, suggesting that the degradation proceeds in a single cavitation event.

Three different regions have been postulated to exist in aqueous sonochemistry. 1. The interior of collapsing gas bubbles with high temperature and high pressure where pyrolysis or combustion of volatile solute molecules take place. Water vapour is pyrolyzed to OH radicals and H atoms. 2. The interface between the hot bubble and the bulk solution with large gradients of temperature and pressure where thermal reactions and reactions with OH radicals and H atoms, which are reported to be concentrated in this region, occur. 3. The bulk solution at ambient temperature and pressure. In this region there occur reactions of solute molecules with OH or H radicals which have migrated from the cavitation bubbles.

The results obtained in the present experiments suggest that main pathway of sonochemical decomposition of CFC-113 is a high temperature pyrolysis in cavitation bubbles where the most exhaustive and rapid degradation in sonochemical processes would occur, and therefore, ultrasonic irradiation appears a promising method for the decomposition of CFC's.

References and Notes

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