Radiolysis of CFC-113 Adsorbed on a Molecular Sieve

Yukio Yamamoto* and Seiichi Tagawa
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047

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Molecular sieve 13X adsorbing CFC-113 was irradiated with γ-rays and then was soaked in water. The concentrations of Cl^- and F^- of the supernatant solutions increased with irradiation time, indicating that both defluorination and dechlorination of CFC-113 occur. The dechlorination proceeds by a chain reaction when 2-propanol is adsorbed on the molecular sieve together with CFC-113. It is suggested that the dehalogenation of CFC-113 is promoted by the molecular sieve.

Researches on decomposition of chlorofluorocarbons (CFCs) and harmful organic chlorides such as polychlorinated biphenyls and a dioxin group are of current importance because of their increasing accumulation in the environment. Dehalogenation except for defluorination via electron attachment is known to be a major reaction of organic halides irradiated with ionizing radiation.[1] Adsorbents may be available for incorporation of volatile or dilute pollutants to be removed. We report here the results of γ-radiolysis of 1,1,2-trichloro-1,2,2-trifluoroethane, CFC-113, adsorbed on molecular sieve 13X.

Earlier studies on the radiolysis of liquid CFCs were mainly concerned with the relative proportions of the C-Cl, C-F, and C-C bond scissions.[2,3] It has been revealed that the C-F bond is stable because of the high bond energy. Reductive dechlorination by a chain reaction has been reported for alkaline 2-propanol solutions of CFC-113, where defluorination is very minor.[4] In the present study it was found that defluorination occurs as well as dechlorination in the molecular sieve adsorbing CFC-113. Effects of 2-propanol and water adsorbed on the molecular sieve together with CFC-113 were investigated.

The sample preparation was carried out by using a vacuum line ($<10^{-5}$ Torr, 1 Torr=133 Pa) with greaseless cocks. Molecular sieve 13X (Wako Chemicals, 5 g) was heated at 400°C for 6 h in a Pyrex ampule. CFC-113 (Tokyo Kasei) was degassed over calcium hydride and was transferred to a calibrated tube by trap-to-trap distillation. The CFC-113 (0.5 ml at 0°C) was adsorbed on the molecular sieve by introducing the vapor from the calibrated tube, cooled at 0°C, to the ampule at ambient temperature.[5] The ampule was sealed under cooling with liquid nitrogen and was irradiated with ^{60}Co γ-rays at a dose rate of 7.8 kGy h^{-1} and at ambient temperature. The irradiated molecular sieve was soaked in water (millipore-filtered) for more than one day with periodic stirring. In all runs the total volume of the aqueous solutions including the molecular sieve was held constant at 200 ml. The concentrations of Cl^- and F^- of the supernatant solutions were measured by using ion selective electrodes (Horiba, combination types). 2-Propanol (Wako Chemicals) and water (millipore-filtered) were degassed and adsorbed on the molecular sieve as well as CFC-113. The volume of the additives was the same as that of CFC-113, 0.5 ml at 0°C.

The concentrations of Cl^- and F^- and the pH of the supernatant solutions are plotted against irradiation time in Figures 1, 2, and 3, respectively. For the molecular sieve adsorbing CFC-113 alone, both of the Cl^- and F^- concentrations increase with irradiation time, accompanying a decrease in pH. When the molecular sieve only heated under vacuum was soaked in water, the Cl^- and F^- concentrations of the supernatant solution were 8.9×10^{-5} and 7.8×10^{-4} mol dm^{-3}, respectively, and the pH was 10.7. In the case of the molecular sieve not adsorbing CFC-113, neither the ion concentrations nor the pH changed by the γ-irradiation. These results demonstrate that defluorination occurs as well as dechlorination in the molecular sieve adsorbing CFC-113 alone.

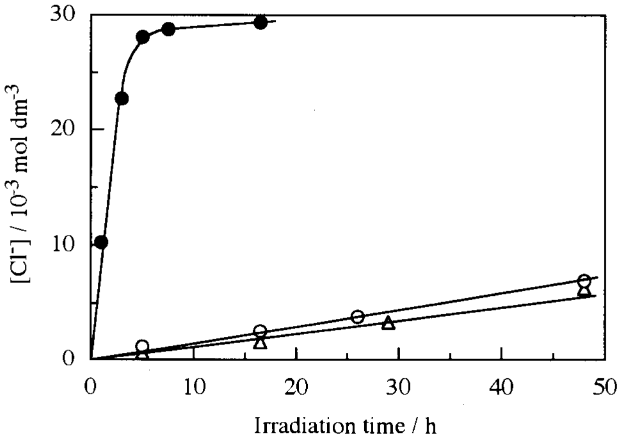

Figure 1 . Concentration of Cl^- *vs*. irradiation time: (○) CFC-113 alone, (△) with H_2O, and (●) with 2-propanol.

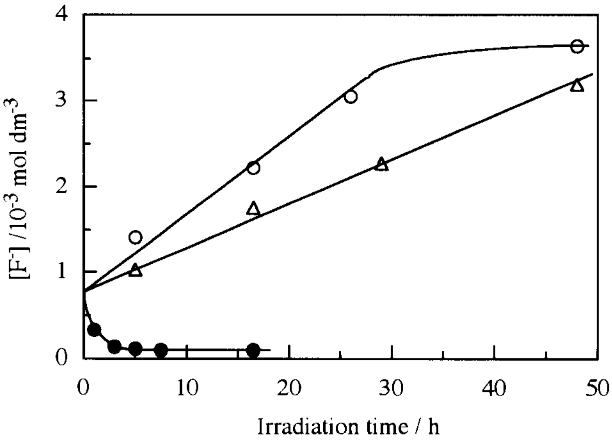

Figure 2 . Concentration of F^- *vs*. irradiation time; (○) CFC-113 alone, (△) with H_2O, and (●) with 2-propanol.

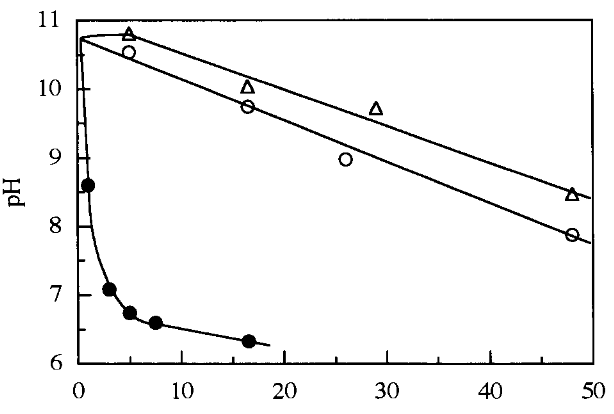

Figure 3 . pH *vs*. irradiation time; (○) CFC-113 alone, (△) with H_2O, and (●) with 2-propanol.

The radiation chemical yields of the dechlorination and the defluorination, $G(Cl^-)$ and $G(F^-)$, for the molecular sieve adsorbing CFC-113 alone were determined to be 9.3 and 5.3, respectively, from the increments of the ion concentrations in the early stage of the irradiation. The G values are the numbers of the ions per 100 eV energy absorbed by both CFC-113 and the molecular sieve. The $G(Cl^-)$ and $G(F^-)$ values based on the energy only absorbed by CFC-113 are 69 and 39, respectively. The G value of the C-Cl bond scission in the radiolysis of pure CFC-113 is 2.8, calculated from the G values of the radiolysis products reported in the literature.[2] The value of $G(Cl^-)$ for a neutral 2-propanol solution of CFC-113 (0.17 mol dm^{-3}) is 7.4.[4] The large $G(Cl^-)$ value of the present system compared with the literature values indicates that the dechlorination is promoted by the molecular sieve as well as the defluorination.

It can be seen in Figures 1 and 2 that the dehalogenation of CFC-113 is retarded by the adsorption of the same volume of water. But the retarding effect of water is not so significant, and the careful dehydration of the molecular sieve before the adsorption of CFC-113 may be unnecessary.

When the same volume of 2-propanol was adsorbed together with CFC-113, the concentration of Cl^- extremely increases, whereas that of F^- decreases by the irradiation (Figures 1 and 2). The decrease in the concentration of F^- eluted from the molecular sieve by the irradiation can be attributed to the presence of the high concentrations of Cl^-, because it was caused by adding KCl to water containing the original molecular sieve. The decrease in pH was enhanced in the presence of 2-propanol.

It is known that the dehalogenation (except for defluorination) of organic halides proceeds by a chain reaction in alkaline 2-propanol solutions but not in neutral ones.[1,4] The propagation steps are

$$\mathrm{R\cdot + (CH_3)_2CHOH \longrightarrow RH + (CH_3)_2\dot{C}OH} \qquad (1)$$

$$\mathrm{(CH_3)_2\dot{C}OH + B^- \longrightarrow (CH_3)_2\dot{C}O^- + BH} \qquad (2)$$

$$\mathrm{RX + (CH_3)_2\dot{C}O^- \longrightarrow R\cdot + X^- + (CH_3)_2CO} \qquad (3)$$

where RX and B^- denote an organic halide and a base, respectively. In the molecular sieve the negative framework may act as a base to propagate the chain reaction (Eq. 2). The dechlorination is extremely decelerated after the irradiation time of 5 h (Figure 1). At the irradiation time of 5 h, the conversion of chlorine of CFC-113 is 45%, which corresponds to 86% consumption of 2-propanol according to the above equations, and the pH decreases to be 6.7 (Figure 3). Thus, the deceleration of the dechlorination after the 5-h irradiation may be attributed to the loss of 2-propanol as well as to the neutralization of the molecular sieve framework. The $G(Cl^-)$ value based on the energy absorbed by CFC-113 and 2-propanol (not including the energy absorbed by the molecular sieve) is 2.1×10^3 in the early stage of the irradiation. This value is larger than the literature value of $G(Cl^-)$, 1.1×10^3, for an alkaline 2-propanol solution (KOH, 0.3 mol dm^{-3}) of CFC-113 (0.17 mol dm^{-3}). This seems to indicate that the energy transfer from the molecular sieve to CFC-113 occurs.

It is demonstrated that the decomposition of CFC-113 is promoted by molecular sieve 13X. The mechanism of the defluorination occurring in the molecular sieve will be a matter for further study. It is also important to study the potentials of this technique for removing harmful organic chlorides.

References and Notes

1 For example, see: S. Takamuku, in "Handbook of Radiation Chemistry," ed by Y. Tabata, Y. Ito, and S. Tagawa, CRC Press, Boca Raton (1991), Chap. XIII, p. 632.

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5 The maximum volume of CFC-113 adsorbed on the 5 g molecular sieve 13 X was 1.1 ml at 0°C, while it was less than 0.1 ml in the case of molecular sieve 5A.