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Radiolytic and Thermal Dehalogenation of CFC-113 Adsorbed on Molecular Sieve 13X

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The reductive dehalogenation of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) has been radiolytically and thermally initiated on molecular sieve 13X. The molecular sieve adsorbing CFC-113 was irradiated with γ-rays or heated, and was then soaked in water. The Cl^- and F^- concentrations and the pH of the supernatant solutions were measured to follow the dehalogenation reaction. These values for samples irradiated at a dose rate of 7.8 $\mathrm{kGy\,h^{-1}}$ and heated at 150 °C were almost the same when the irradiation time was twenty-times longer than the heating time. The F^- concentration once increased and then decreased with the reaction time, whereas the Cl^- concentration increased continuously. The F^-, once produced, may be consumed with the denatured molecular sieve. When the molecular sieve adsorbing 2-propanol together with CFC-113 was irradiated, the dechlorination proceeded by a chain reaction, but the defluorination was inhibited. On the other hand, when heated in the presence of 2-propanol, both the dechlorination and the defluorination were largely suppressed. The pH of the supernatant solutions decreased from an alkaline value to a neutral or acidic one along with dehalogenation. Radiolysis of CFC-113 on activated charcoal was also examined, but the dehalogenation rates were much slower than those on the molecular sieve.

Decomposition of chlorofluorocarbons (CFCs) and harmful organic chlorides, such as trichloroethylene, polychlorinated biphenyls (PCBs), and a dioxin group, is an important research subject because of their increasing accumulation in the environment. In the preceding communication,[1] we have reported on the radiolysis of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) adsorbed on molecular sieve 13X. Dehalogenation via electron attachment is known to be a major reaction of organic halides irradiated with ionizing radiation.[2] The radiolytic dehalogenation yields of CFC-113 adsorbed on the molecular sieve were larger than the usual radiation chemical yields of electrons, and the molecular sieve is considered to promote dehalogenation.[1] In the present paper the results of the thermal dehalogenation of CFC-113 adsorbed on the molecular sieve are included as well as those of the extended radiolysis investigation. A comparison is made of the radiolytic and thermal dehalogenation. The effects of 2-propanol, adsorbed on the molecular sieve together with CFC-113, on the radiolytic and thermal dehalogenation are described.

Since an adverse effect of CFCs on the stratospheric ozone layer was recognized,[3] a number of studies have been reported on the decomposition of CFCs. Most of them are concerned with thermal decomposition on catalysts by using flow reaction systems.[4—14] The decomposition of CFCs has also been studied by using photocatalyst,[15] ionizing radiation,[16] arc plasma,[17,18] ultrasonic wave,[19,20] sodium naphthalenide,[21,22] sodium vapor,[23] supercritical water,[24] and pyrolysis,[25,26] combustion,[27] and electrochemical[28—30] methods.

Zeolites have been used as oxidative catalyst giving carbon dioxide and carbon monoxide as major decomposition products.[4,8,11,12] The decomposition on molecular sieve 13X, which is an alumino-silicate similar to zeolite Y, has been investigated for CFCs, such as CFC-113, dichlorodifluoromethane, trichlorofluoromethane, dichlorofluoromethane, and chlorodifluoromethane, by passing nitrogen gas containing the CFCs through a tubular reactor heated at 150 and 320 °C.[4] It has been reported that among these CFCs, only CFC-113 does not decompose at the lower temperature, 150 °C; in the early stage of gas flowing, CFC-113 is adsorbed on the molecular sieve and then passes through the reactor without decomposition after the molecular sieve is saturated with CFC-113.[4] In the present study, the molecular sieve adsorbing CFC-113 was sealed in a Pyrex tube and heated at 150 °C. It was found that the dehalogenation of the adsorbed CFC-113 occurs at 150 °C.

Adsorbents are available for the incorporation of volatile or dilute pollutants to be removed. Zeolites have been recognized as a separation medium for CFCs and halocarbons as well as activated charcoal, and their adsorption behaviors have been investigated from an environmental point of view.[31—36] Dehalogenation of the adsorbates may be necessary to make them less harmful before desorption, especially when regeneration of the adsorbents is required. Irradiation with ionizing radiation is expected to be effective for the decomposition of the adsorbates as well as thermal heating. The present technique is also applicable to the decomposition of harmful organic chlorides. The radiolysis of CFC-113 on activated charcoal was examined for the sake of a comparison.

Experimental

Sample preparation was carried out by using a vacuum line ($< 10^{-5}$ Torr, 1 Torr = 133 Pa) with greaseless cocks. The sampling system is illustrated in Fig. 1. Molecular sieve 13X 1/16 (Wako Chemicals, 5 g) adsorbing CFC-113 (Tokyo Kasei, 0.5 ml at 0 °C) was sealed in a Pyrex ampule in the following manner. The molecular sieve was heated at 400 °C for 6 h in the Pyrex ampule. CFC-113 was degassed over calcium hydride in the vessel and then transferred to a calibrated tube by cooling the calibrated tube with ice-cold water. For an accurate sampling, more than 0.5 ml of CFC-113 was once transferred to the calibrated tube, and any excess was returned by cooling the vessel with liquid nitrogen. CFC-113 vapor was introduced from the calibrated tube, cooled with ice-cold water, to the ampule left at room temperature. Within ten minutes the 0.5 ml CFC-113 passed into the ampule through adsorption on the molecular sieve. After the adsorption was completed, the ampule was sealed under cooling with liquid nitrogen. The maximum volume of CFC-113 adsorbed on the 5 g molecular sieve 13 X was 1.1 ml at 0 °C. 2-Propanol (Wako Chemicals) was degassed and adsorbed on the molecular sieve as well as CFC-113. The volume of the adsorbed 2-propanol was the same as that of CFC-113, 0.5 ml at 0 °C. The maximum volume of 2-propanol adsorbed on the 5 g molecular sieve was 1.2 ml at 0 °C.

The sample was irradiated with ^{60}Co γ-rays at a dose rate of 7.8 kGy h^{-1} at room temperature or heated in an electric heater. The molecular sieve was then 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 using ion selective electrodes (Horiba, combination types).

When the molecular sieve (5 g) not adsorbing CFC-113 was soaked in water for a total volume of 200 ml after being evacuated at 400 °C for 6 h, the Cl^- and F^- concentrations of the supernatant were 8.9×10^{-5} and 7.8×10^{-4} mol dm^{-3}, respectively, and the pH was 10.7. The background concentrations of the halide ions, $[Cl^-]_0$ and $[F^-]_0$, were subtracted to calculate the dehalogenation yields; $[Cl^-]_0$ and $[F^-]_0$ corresponded to 0.71 and 6.2% of the total amounts of Cl and F of the adsorbed CFC-113, respectively.

Activated charcoal (Wako Chemicals, 2 g) was evacuated for 2 h at room temperature, and then CFC-113 (0.5 ml at 0 °C) was adsorbed in the same manner as in the case of the molecular sieve. The maximum volume of CFC-113 adsorbed on 5 g activated charcoal was 2.22 ml at 0 °C. It was larger than the maximum adsorption volume on the molecular sieve, and therefore 2 g activated charcoal was used for 0.5 ml CFC-113.

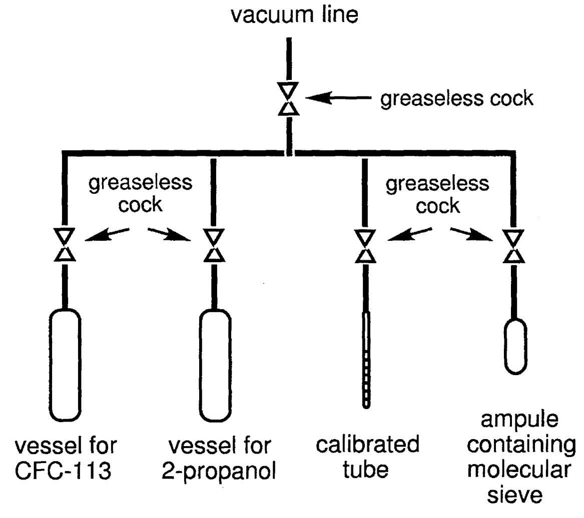

Fig. 1. Schematic illustration of the sample preparation system.

Results and Discussion

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.[37,38] It has been revealed that the C–F bond is stable because of the high bond energy. In the preceding communication,[1] we have reported that both dechlorination and defluorination occur in the radiolysis of CFC-113 adsorbed on molecular sieve 13X. The Cl^- and F^- yields for the molecular sieve adsorbing CFC-113 alone increased with the irradiation time up to 48 h. The irradiation time was prolonged in the present study. In Fig. 2, the halide ion yields are plotted against the irradiation time, prolonged to 118 h. The yield of F^- is apparently decreased by the prolonged irradiation, whereas that of Cl^- continues to increase up to the longest irradiation time examined. The pH of the supernatant solutions varied from the original alkaline value to a neutral value, 7.1, at the longest irradiation time. The radiation chemical yields of the dechlorination, $G(Cl^-)$, and the defluorination, $G(F^-)$, 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 produced halide ions per 100 eV energy absorbed by the whole mediums including both CFC-113 and the molecular sieve. The total G value of the dehalogenation, 14.6, is apparently larger than the usual radiation chemical yields of electrons. For example, the G value of the water cluster trapped electrons in fully hydrated zeolite NaY has been reported to be 5.8.[39] Therefore, the reductive dehalogenation of CFC-113 is not explicable by only electron attachment.

Similar time-conversion curves were obtained when the

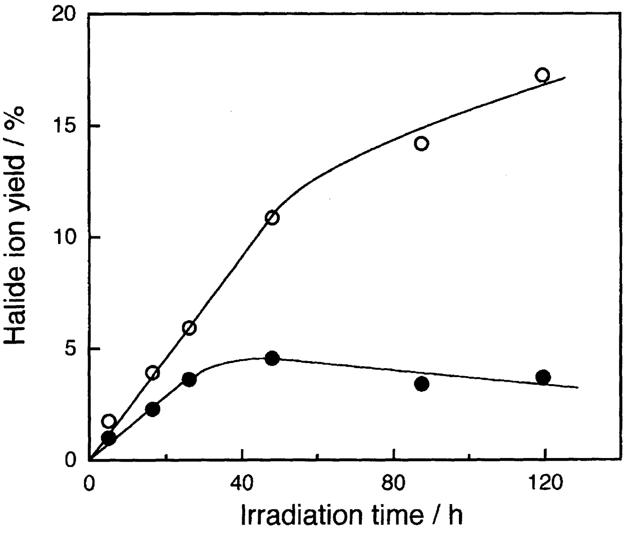

Fig. 2. The (○) Cl^- and (●) F^- yields for the irradiated molecular sieve adsorbing CFC-113 alone plotted as a function of the irradiation time.

samples were heated at 150 °C, as shown in Fig. 3. The dehalogenation yields for the heated samples are almost the same as those for the irradiated samples, when the irradiation time is twenty-times longer than the heating time. Figure 4 shows the change in pH for the irradiated and heated samples plotted against the irradiation and heating times, respectively. It is shown that the pH change caused by heating at 150 °C is also similar to that caused by twenty-times longer irradiation at room temperature. The reactions initiated in the irradiated and heated samples adsorbing CFC-113 alone may be similar.

As described above, the F$^-$ yield decreased with the reaction time after taking a maximum value, whereas the Cl$^-$ yield increased continuously (Figs. 2 and 3). The influence of the coexistence of Cl$^-$, F$^-$, and the molecular sieve on the ion concentration measurement was examined by using solutions of known amounts of NaCl and/or NaF containing the molecular sieve, 5 g for 200 ml of the total volume of the solutions. The solutions were kept for more than one day with periodic stirring before the measurement. As shown in Fig. 5, the measured Cl$^-$ concentration subtracted by the background one, $[\mathrm{Cl}^-]-[\mathrm{Cl}^-]_0$, agrees fairly well with the added NaCl concentration in both the presence and absence of NaF. A similar calibration plot for F$^-$ is shown in Fig. 6. The $[\mathrm{F}^-]-[\mathrm{F}^-]_0$ value is somewhat smaller than the added NaF concentration in the low-concentration region, espe-

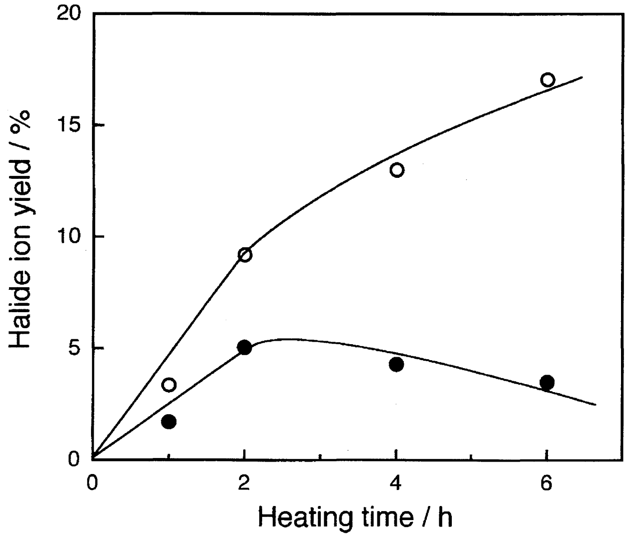

Fig. 3. The (○) Cl$^-$ and (●) F$^-$ yields at 150 °C for the heated molecular sieve adsorbing CFC-113 alone plotted as a function of the heating time.

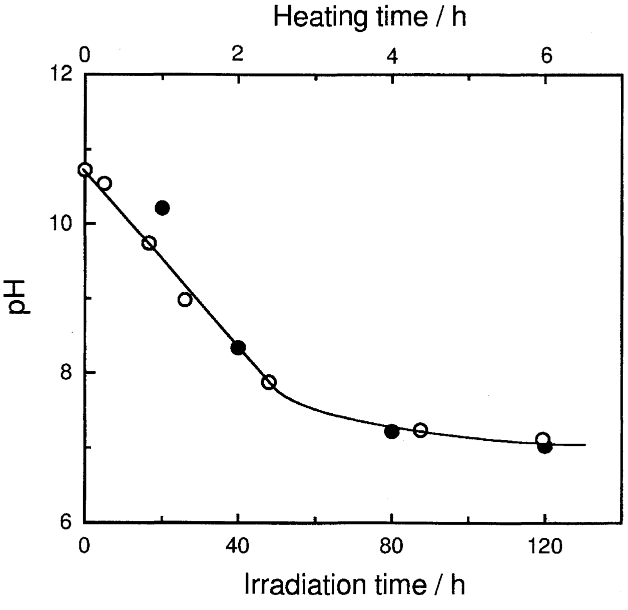

Fig. 4. The pH for the (○) irradiated and (●) heated molecular sieve adsorbing CFC-113 alone plotted as a function of the irradiation and heating times, respectively.

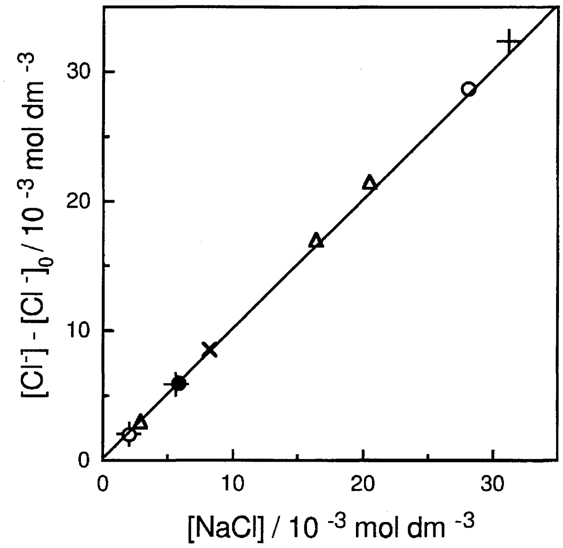

Fig. 5. Calibration for the mesurement of the Cl$^-$ concentration: the concentrations of added NaF are (○) 0, (△) 1.6×10^{-3}, (●) 3.1×10^{-3}, (×) 8.2×10^{-3}, and (+) 1.1×10^{-2} mol dm^{-3}.

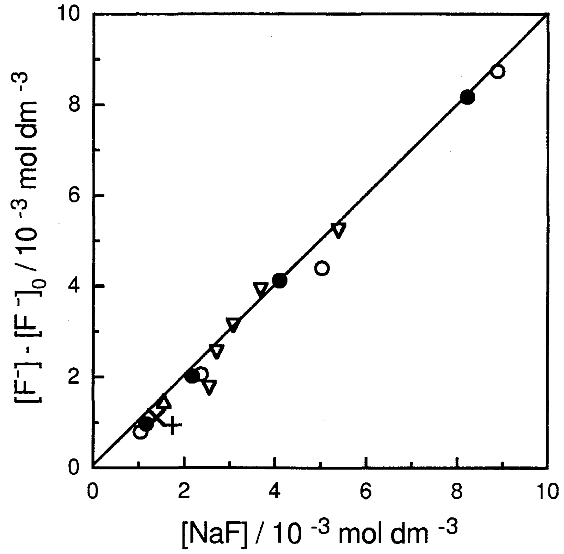

Fig. 6. Calibration for the mesurement of the F$^-$ concentration: the concentrations of added NaCl are (○) 0, (△) 2.9×10^{-3}, (▽) 5.7×10^{-3}, (●) 8.2×10^{-3}, (×) 1.6×10^{-2}, and (+) 2.1×10^{-2} mol dm^{-3}.

cially in the presence of NaCl. However, the relationship between the deviation and the added NaCl concentration is not clear. The error in the measurements is noticeable only in the $[F^-]-[F^-]_0$ range below 2×10^{-3} mol dm^{-3}, which corresponds to 3.2% of the F^- yield. Since the decrease in the F^- yield begins at a higher yield, ca. 5% (Figs. 2 and 3), it can be attributed neither to the error in the measurements nor to the coexistence of the produced Cl^-. A possible explanation for the observation is a consumption of F^- with the reaction products such as the denatured molecular sieve.

The results of thermal dehalogenation at 100, 150, and 200 °C at a heating time of 3 h are presented in Table 1. The dehalogenation yields and the change in pH are negligible at 100 °C. The F^- yield is smaller at 200 °C than at 150 °C, whereas the Cl^- yield is much larger at 200 °C than at 150 °C. This also suggests the consumption of F^- at the high conversions of the dehalogenation.

It is known that the dechlorination of organic chlorides proceeds by a chain reaction upon irradiation in alkaline 2-propanol solutions, but not in neutral ones.[2,40] The propagation steps are:

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

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

$$(CH_3)_2\dot{C}O^- + RCl \longrightarrow (CH_3)_2CO + R\cdot + Cl^- \quad (3)$$

where RCl and B^- denote an organic chloride and a base, respectively. An efficient dechlorination in alkaline 2-propanol solutions has been reported for CFC-113[16] and chlorinated pollutants, such as PCBs[41,42] and 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT).[43] In the present study, the effect of 2-propanol adsorbed on the molecular sieve together with CFC-113 was examined for radiolytic and thermal dehalogenation. The dehalogenation yields and the pH change in the presence of 2-propanol are shown in Figs. 7 and 8, respectively, as a function of the irradiation and heating times. As reported in the preceding communication,[1] when irradiated with γ rays, the dechlorination proceeds by a chain reaction, but the defluorination is inhibited in the presence of 2-propanol. The decrease in pH in the radiolysis is also enhanced in the presence of 2-propanol. These results are similar to the case of the radiolysis of CFC-113 in alkaline 2-propanol solution.[16] The negatively charged alumino-silicate framework of the molecular sieve may act as a base to propagate the chain reaction. The $G(Cl^-)$ value based on the total energy absorbed by the molecular sieve and the adsorbates is 400, determined from the Cl^- yield in the early stage of the irradiation. On the other hand, when heated at 150 °C, both the dechlorination and the defluorination were very limited in the presence of 2-propanol as well as the change in pH.

As reported in the preceding communication,[1] the F^- concentration for the irradiated samples containing 2-propanol decreased below $[F^-]_0$ with the irradiation time. The result has been interpreted in terms of the coexistence of the increasing concentration of Cl^-. However, on the basis of the

Table 1. Dehalogenation Yields and pH at a Heating Time of 3 h

Temp/ °C	Cl^-/%	F^-/%	pH
100	ca. 0.07[a)]	ca. 0[b)]	11.0
150	9.01	4.28	8.29
200	47.9	1.63	6.39

a) The Cl^- concentration of the supernatant solution is 1.3×10^{-4} mol dm^{-3} and is close to the background Cl^- concentration, 8.9×10^{-5} mol dm^{-3}. b) The F^- concentration of the supernatant solution, 7.5×10^{-4} mol dm^{-3}, is almost the same as the background F^- concentration, 7.8×10^{-4} mol dm^{-3}.

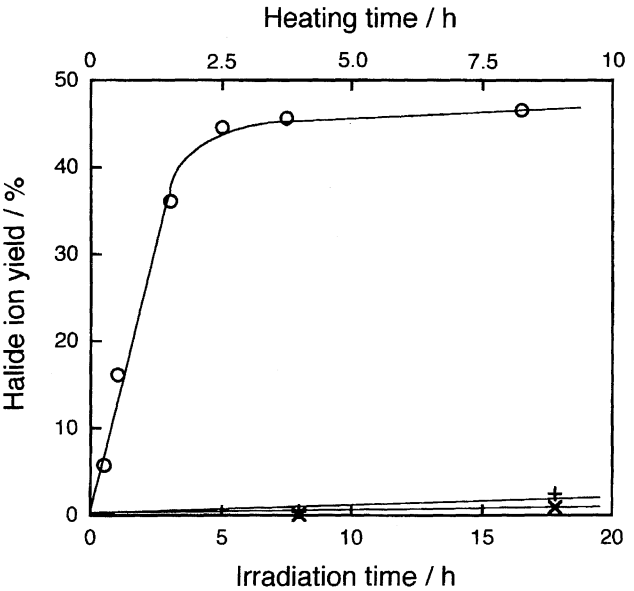

Fig. 7. The Cl^- yields for the (○) irradiated and (+) heated samples and (×) the F^- yields for the heated samples in the presence of 2-propanol plotted as a function of the irradiation and heating times, respectively.

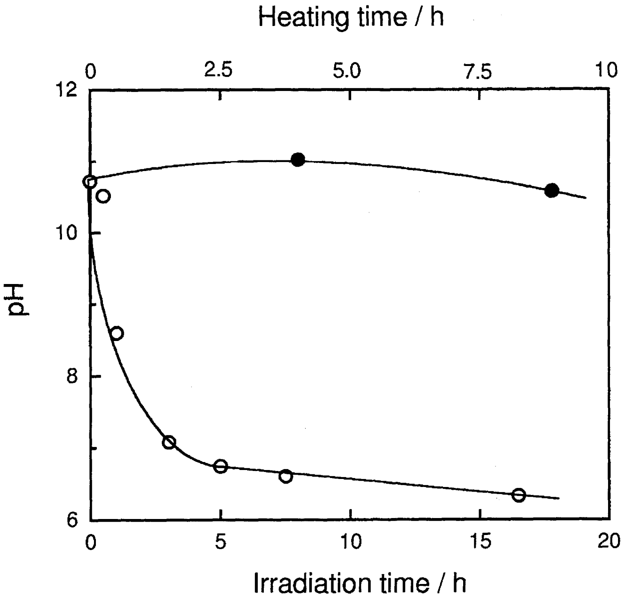

Fig. 8. The pH for the (○) irradiated and (●) heated samples in the presence of 2-propanol as a function of the irradiation and heating times, respectively.

calibration for the measurement of the F^- concentration in the presence of NaCl (Fig. 6), it should be attributed to the consumption of F^- with the denatured molecular sieve.

The radiolytic dechlorination in the presence of 2-propanol is extremely decelerated after the irradiation time of 5 h (Fig. 7). At an irradiation time of 5 h, the conversion of chlorine of CFC-113 was 45%, which corresponds to 86% consumption of 2-propanol according to the above equations, and the pH decreased to 6.7 (Fig. 8). 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 negatively charged alumino-silicate framework of the molecular sieve.

The change in pH is correlated to the dechlorination yield. Figure 9 shows plots of the dechlorination yields against pH for the irradiated and heated samples in the presence and absence of 2-propanol. The plots for the irradiated and heated samples in the absence of 2-propanol are on the same curve. They are apart from the plots for the irradiated samples containing 2-propanol. The plots for the heated samples containing 2-propanol are close to those obtained in the absence of 2-propanol, although both the dechlorination yield and the change in pH are very small.

As shown above, the ratios of the Cl^- and F^- yields were similar for the irradiated and heated samples adsorbing CFC-113 alone (Figs. 2 and 3), suggesting that similar reactions occur in these systems. The thermal dehalogenation was inhibited in the presence of 2-propanol. On the other hand, the radiolytic dechlorination in the presence of 2-propanol proceeded by the chain reaction through the one-electron reduction of CFC-113 (Eq. 3). These results seem to suggest that the one-electron reduction is not important for irradiated samples adsorbing CFC-113 alone. This is supported by the fact that the G value of the dehalogenation is larger than the usual G values of electrons. It is reasonable to consider that the radiolytically generated electrons are stabilized through trapping by charge-balancing sodium cation clusters in the molecular sieve.[44]

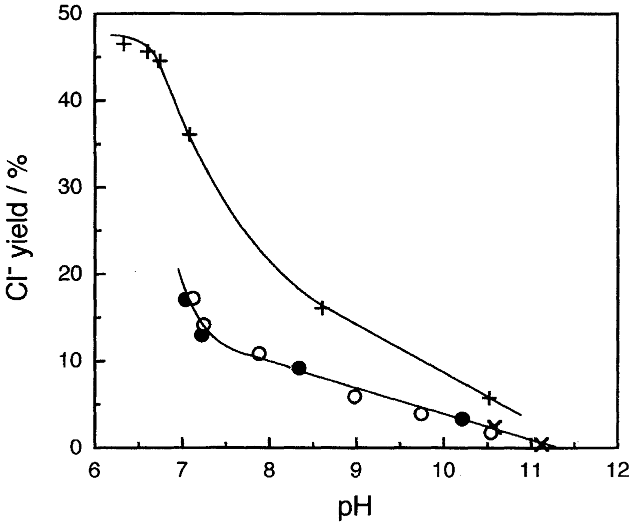

Fig. 9. Correlation between the Cl^- yields and the change in pH for the samples (○) irradiated in the absence of 2-propanol, (●) heated in the absence of 2-propanol, (+) irradiated in the presence of 2-propanol, and (×) heated in the presence of 2-propanol.

The radiolytic and thermal dehalogenation in the presence and absence of 2-propanol may be explained if we consider as follow. The dehalogenation reactions in the absence of 2-propanol are catalytic processes on the molecular sieve to give the same ratio of the Cl^- and F^- yields for the irradiated and heated systems. They do not involve the formation of radical species. Otherwise, when heated in the presence of 2-propanol, the chain dechlorination reaction should be initiated through H-abstraction from 2-propanol (Eq. 1). The catalytic reactions are inhibited when 2-propanol is adsorbed on the molecular sieve. When irradiated in the presence of 2-propanol, the chain dechlorination reaction is initiated through the radiation-induced reactions of 2-propanol, such as the ion-molecule reaction of the radical cations, giving the initiating radical:

$$(CH_3)_2CHOH^{+\bullet} + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH_2^{+} + (CH_3)_2\dot{C}OH \qquad (4)$$

The radical cation formation of organic adsorbates has been reported for irradiated zeolites.[44,45]

When activated charcoal (2.0 g) adsorbing CFC-113 (0.5 ml at 0 °C) was irradiated, the $G(Cl^-)$ values in the absence and presence of 2-propanol (0.5 ml at 0 °C) were 0.09 and 0.71, respectively; defluorination could not be detected. The $G(Cl^-)$ values are much smaller than those in the case of the molecular sieve, demonstrating the promotion of dehalogenation by the molecular sieve.

Conclusion

The dehalogenation yields of CFC-113 adsorbed on molecular sieve 13X could be determined from the Cl^- and F^- concentrations of the supernatant solutions obtained by soaking irradiated or heated samples in water. γ-Irradiation is considered to initiate the same reactions as heating, resulting in both dechlorination and defluorination. In the presence of 2-propanol, the dechlorination proceeds by a chain reaction including the one-electron reduction of CFC-113 in the propagation step. The molecular-sieve framework acts as a base to propagate the chain reaction. Radiolytic defluorination does not occur in the presence of 2-propanol. Thermal dehalogenation is inhibited in the presence of 2-propanol. The radiolytic dehalogenation yields of CFC-113 are much smaller on the activated charcoal than on the molecular sieve.

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