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A PRELIMINARY STUDY ON THE RADIOLYSIS OF CHLOROFLUOROCARBONS

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The radiolysis products from liquid CF_2Cl_2, $CFCl_3$, CF_2ClCF_2Cl and their mixtures with bromine were analyzed by gas chromatography. The C-Cl and C-C bonds appear to be broken far more readily than the C-F bond in the γ radiolysis of these chlorofluorocarbons.

While chlorofluorocarbons appear to be very interesting systems for radiation chemistry, there is only one previous report on the radiolysis of liquid 1,1,2-trichlorotrifluoroethane.[1] In connection with our work on the reactions of energetic recoil bromine atoms with chlorofluoromethanes,[2] we have initiated a systematic study of the γ radiolysis of chlorofluorocarbons and their mixtures with bromine. The object of our study is (1) to elucidate the mechanisms of both recoil and radiolysis reactions in chlorofluorocarbons by comparing the reactivities of different kinds of bonds such as C-C, C-Cl and C-F, and (2) to investigate properties and chemical behaviors of various carbon mixed halides (bromochlorofluorocarbons, etc., which cannot be prepared easily by ordinary methods of synthesis) prepared by recoil labeling or radiation synthesis.

In the present article are reported preliminary data on the γ radiolysis of some liquid chlorofluorocarbons (CF_2Cl_2, $CFCl_3$ and CF_2ClCF_2Cl) and their mixtures with bromine.

Dichlorodifluoromethane, CF_2Cl_2, trichlorofluoromethane, $CFCl_3$, and 1,2-dichloro-1,1,2,2-tetrafluoroethane, CF_2ClCF_2Cl, were obtained from Tokyo Chemical Industry Co., as of guaranteed reagent grade. To prepare the samples for irradiation, one of the chlorofluorocarbons, or its mixture with bromine (10～20% Br_2 by molar ratio) was sealed in vacuo into Pyrex glass tubes. These liquid samples were irradiated with Co-60 γ-rays at an ambient temperature and at a dose rate of about 1.3×10^{18} eV/g.min, up to a total dose of 7×10^{21} eV/g.[3] Conversion of the irradiated samples was usually a few percent. Irradiated samples were directly introduced into a gas chromatograph and analyzed with a 5-m Silicone DC 550 column. If the sample contained bromine, it was removed by a column packed with dehydrated potassium ferrocyanide powder and placed before the main column.

In Figs. 1 and 2 are shown typical gas chromatograms of the radiolysis products from CF_2Cl_2, CF_2ClCF_2Cl and their mixtures with bromine. The unknown

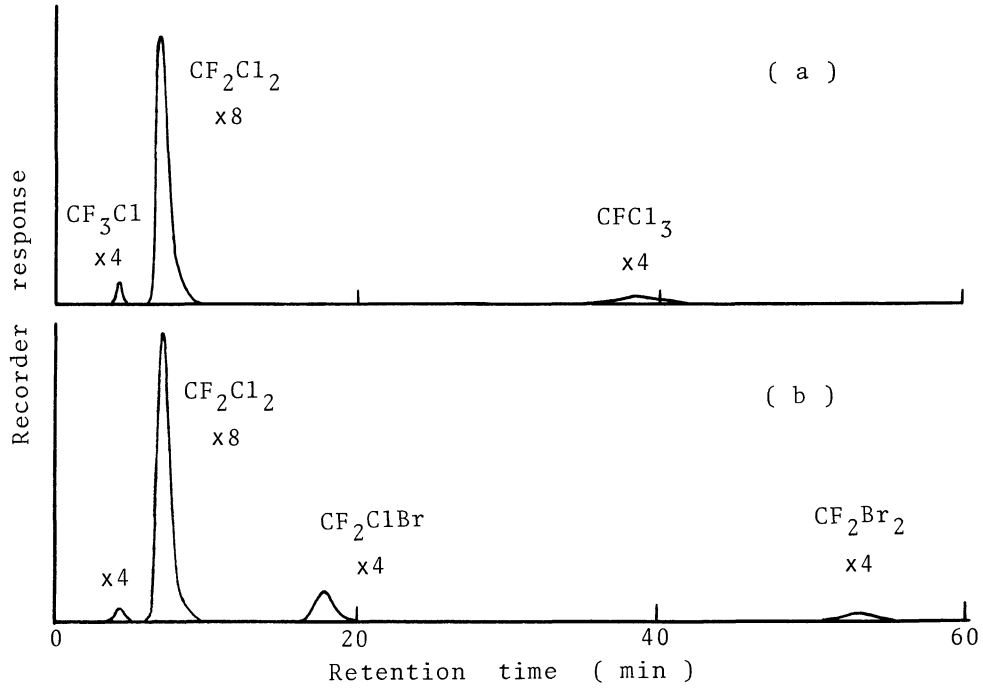

Fig.1. Gas chromatograms of the radiolysis products from (a) CF_2Cl_2, and (b) CF_2Cl_2—Br_2 systems [column: Silicone DC 550 / Chromosorb W (20 wt%), 3 mm i.d. x 5 m, 0°C; carrier gas: He 15 ml/min].

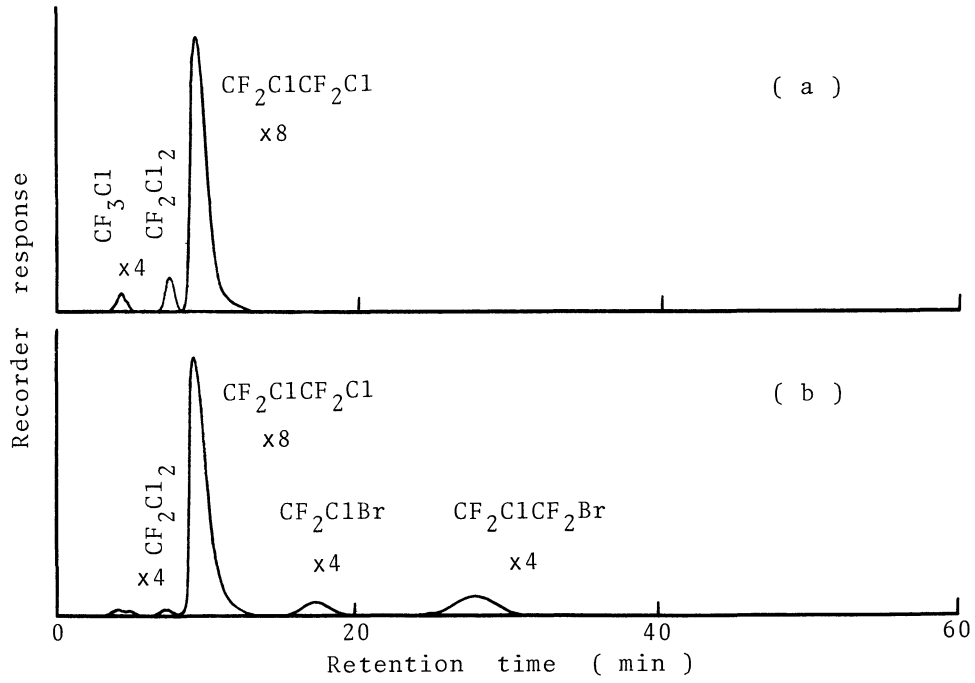

Fig.2. Gas chromatograms of the radiolysis products from (a) CF_2ClCF_2Cl, and (b) CF_2ClCF_2Cl—Br_2 systems [analytical conditions are the same as in Fig.1].

peaks were identified by one, or combination, of the following procedures: (1) comparison of their retention times with those of known compounds, (2) comparison of their retention times with those of the ^{82}Br-labeled products obtained by thermal neutron activation of similar systems, such as CF_2Cl_2—Br_2,[2] $CFCl_3$—Br_2,[2] and CF_2ClCF_2Cl—Br_2,[4] and (3) application of the known correlation between the logarithm of the retention time and the composition of halogen atoms in carbon mixed halides such as $CF_1Cl_mBr_n$ $(1 + m + n = 4)$.[5] Since detailed quantitative analyses of the radiolysis products under various irradiation and scavenging conditions are still in progress, we present only the qualitative results in this report.

CF_2Cl_2 and CF_2Cl_2—Br_2 systems. Main products obtained from the γ radiolysis of CF_2Cl_2 were CF_3Cl and $CFCl_3$ (Fig.1a).[6] In the CF_2Cl_2—Br_2 system,[7] the major radiolysis products included CF_2ClBr and CF_2Br_2 (Fig.1b). After irradiations up to a heavier dose (1.8×10^{22}eV/g), a trace peak of $CFCl_2Br$ was also observed on the chromatogram. These results indicate that the C-Cl bond is broken far more readily than the C-F bond. It is worthwhile to mention that the yields of the ^{82}Br-labeled products from the recoil bromine reactions with CF_2Cl_2 decreased in the order, $CF_2Cl^{82}Br > CF_2Br^{82}Br > CFCl_2{}^{82}Br$, indicating that the C-Cl bond is more reactive towards hot bromine than the C-F bond.[2]

$CFCl_3$ and $CFCl_3$—Br_2 systems. CF_2Cl_2 and $CFCl_2CFCl_2$ were mainly obtained as the γ radiolysis products from $CFCl_3$. In the presence of bromine, the major products were identified as $CFCl_2Br$ and $CFClBr_2$. Hence, predominant C-Cl bond scission was again observed in this compound. For the sake of comparison, the yields of the ^{82}Br-labeled products from the recoil bromine reactions with $CFCl_3$ were in the order, $CFCl_2{}^{82}Br > CFClBr^{82}Br$, showing that the ^{82}Br-for-Cl substitution took place predominantly.[2]

CF_2ClCF_2Cl and CF_2ClCF_2Cl—Br_2 systems. As shown in Fig.2a, CF_2Cl_2 and CF_3Cl were the major γ radiolysis products from CF_2ClCF_2Cl. A very small quantity of $CF_2ClCFCl_2$ was also observed after irradiations up to a heavier dose (3.2×10^{22}eV/g). In the irradiated CF_2ClCF_2Cl—Br_2 system, CF_2ClCF_2Br, CF_2ClBr and CF_2Cl_2 were mainly produced (Fig.2b). Small amounts of CF_2Br_2, $CFCl_2Br$, and CF_2BrCF_2Br were also found after irradiations up to a heavier dose. The yields of the ^{82}Br-labeled products from the recoil bromine reactions in the CF_2ClCF_2Cl—Br_2 system were found to decrease in the order, $CF_2ClCF_2{}^{82}Br > CF_2Cl^{82}Br \sim CF_2Br^{82}Br$, implying that the C-Cl and C-C bonds were reactive.[4]

It may be concluded that the C-Cl and C-C bonds are broken more readily than the C-F bond in the γ radiolysis of chlorofluorocarbons. Bromine can scavenge the radicals produced in the radiolysis of such systems, and bromochlorofluorocarbons, or bromofluorocarbons, are usually formed as the result of scavenging reactions. For the purpose of synthesis, γ irradiations up to heavier doses ($\sim 10^{23}$ eV/g, for example) of chlorofluorocarbons and their mixtures with bromine appear to be useful, since a variety of carbon mixed halides can be obtained in reasonable yields if an adequate system is chosen as the parent. We have already used mixtures of the γ radiolysis products from CF_2Cl_2—Br_2,

$CFCl_3$—Br_2, or CF_2ClCF_2Cl—Br_2 system as carriers in order to identify the ^{82}Br recoil products obtained from thermal neutron activation of such systems. Studies of gas chromatographic behavior of various carbon mixed halides are now in progress, using the products prepared by γ radiation synthesis from related systems.

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1) A.R. Kazanian and D.R. Horrell, J. Phys. Chem., 75, 2217 (1971).
2) T. Tominaga, Y. Makide, S. Okada, Y. Kunimasa and K. Wada, Radioisotopes, 20, 541 (1971).
3) Gamma irradiations up to heavier doses ($1.8 \sim 3.2 \times 10^{22}$ eV/g) were also performed for the purpose of comparison. In those occasions, however, conversion of the samples was as high as 20～30 % and the spectrum of the radiolysis products was more complicated by secondary conversion of the primary products.
4) T. Tominaga, R. Iwata and Y. Makide, unpublished data.
5) Y. Makide and N. Saito, Presented at the 24th Annual Meeting of the Chemical Society of Japan (April, 1971, Osaka).
6) CF_2ClCF_2Cl could have been formed in the radiolysis of this compound. However, it was not verified in the present work since its peak is expected to follow closely the parent peak (CF_2Cl_2) and may be obscured by the large overlapping peak of the parent compound.
7) Bromine was added as a radical scavenger.

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