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Recoil ^{82}Br Reactions with Liquid Chlorofluorocarbons

Takeshi Tominaga, Ren Iwata, and Yoshihiro Makide*

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

**The Institute of Physical and Chemical Research, Wako-shi, Saitama 351*

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The study of recoil halogen reactions with chlorofluorocarbons appears to be interesting since one can make an intramolecular comparison of the reactivities of different types of bonds, such as C–C, C–Cl, and C–F. While recoil iodine and chlorine reactions with chlorofluoromethanes have been investigated,[1,2] the study of recoil bromine reactions with similar systems had not been reported before our preliminary work.[3] In the present article we wish to report our recent data on the recoil ^{82}Br reactions with chlorofluorocarbons, such as CF_2Cl_2, $CFCl_3$, and CF_2ClCF_2Cl.

Experimental

The samples for neutron irradiation were prepared by sealing one of the chlorofluorocarbons (CF_2Cl_2, $CFCl_3$, or CF_2ClCF_2Cl) *in vacuo* in quartz capillaries, along with varying amounts of bromine. These liquid samples were irradiated with thermal neutrons (flux: 5×10^{11} n/cm^2·s) for 5 min at room temperature in the rotary specimen rack of the TRIGA Mark II reactor at Rikkyo University. The accompanying γ dose was approximately 7×10^4 R.

The irradiated samples were analyzed after the decaying out of the shorter-lived bromine activities other than ^{82}Br. Hence, the observed radiochemical yields of recoil products were predominantly the results of the isomeric transition of ^{82m}Br.[4] The samples were directly introduced into a gas chromatograph and analyzed by means of a 5 m Silicone DC 550 column. The inorganic bromine was removed by means of a short column packed with dehydrated potassium ferrocyanide powder and placed before the main column. Procedures for the radioactivity measurement and determination of the ^{82}Br radiochemical yields of these products were the same as those in the previous work.[3]

Results and Discussion

Since radiogas chromatograms of irradiated CF_2Cl_2–Br_2 and $CFCl_3$–Br_2 systems were reported previously,[3] a typical radiogas chromatogram of ^{82}Br-labeled products from the irradiated CF_2ClCF_2Cl–Br_2 system is illustrated in Fig. 1. In the thermal conductivity measurements, only the mass peak of the parent compound could be observed (the position of the parent mass peak is indicated by an arrow in Fig. 1). The unknown radioactivity peaks were identified either by comparing their retention times with those of known

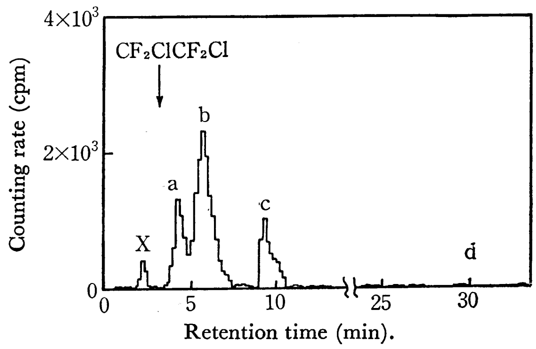

Fig. 1. Radiogas chromatogram of ^{82}Br-labeled products from the neutron-irradiated CF_2ClCF_2Cl—Br_2 system.
a: $CF_2Cl^{82}Br$; b: $CF_2ClCF_2{}^{82}Br$; c: $CF_2Br^{82}Br$; d: $CF_2ClCFCl^{82}Br$ (expected position, but not observed); X: presumably $CF_3{}^{82}Br$.

compounds added as carriers, or by applying the known correlation between the logarithm of the retention time and the composition of halogen atoms in bromochlorofluorocarbons.[5] If the carrier compounds are neither commercially available nor readily prepared by ordinary chemical syntheses, γ-irradiations up to a heavy dose of similar systems (*i.e.*, the mixtures of chlorofluorocarbons with bromine) appear to be useful

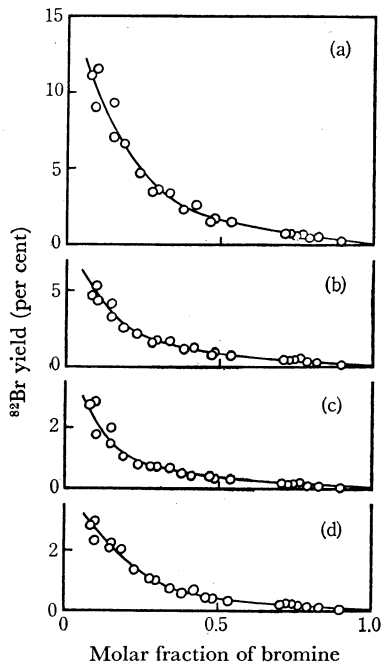

Fig. 2. Yields of major ^{82}Br-labeled products from CF_2ClCF_2Cl—Br_2 system *vs.* molar fraction of bromine.
(a) Total organic yield; (b) $CF_2ClCF_2{}^{82}Br$; (c) $CF_2Cl^{82}Br$; and (d) $CF_2Br^{82}Br$.

1) N. J. Parks and E. P. Rack, *Radiochim. Acta*, **10**, 26 (1968).
2) S. C. Lee and C. O. Hower, *J. Phys. Chem.*, **75**, 2685 (1971).
3) T. Tominaga, Y. Makide, S. Okada, Y. Kunimasa, and K. Wada, *Radioisotopes*, **20**, 541 (1971).
4) Since the reactivities of recoil ^{82}Br produced by either isomeric transition of ^{82m}Br(91%) or $^{81}Br(n,\gamma)^{82}Br$ reaction (9%) are qualitatively similar, the contribution from $^{81}Br(n,\gamma)^{82}Br$ reaction may be less than one-tenth of the overall observed results.
5) Y. Makide and N. Saito, presented at the 24th National Meeting of the Chemical Society of Japan (April 1971, Osaka).

for the preparation of the desired compounds in reasonable yields.[6] Hence, we have used mixtures of radiolysis products from the CF_2Cl_2–Br_2, $CFCl_3$–Br_2, and CF_2ClCF_2Cl–Br_2 systems preirradiated with γ-rays up to a total dose of about 10^{22} eV/g, as special samples for neutron irradiation in order only to identify the peaks of the ^{82}Br-labeled products from such systems.[7]

Figure 2 represents the radiochemical yields of the major ^{82}Br-labeled products from the CF_2ClCF_2Cl–Br_2 system as a function of the molar fraction of bromine. Very similar curves were observed for the radiochemical yields of the major ^{82}Br-labeled products from the CF_2Cl_2–Br_2 and $CFCl_3$–Br_2 systems. Bromine in these systems can scavenge carbon mixed halide radicals[6] as well as thermal ^{82}Br atoms or ions. A simple analysis of these curves, *i.e.*, an extrapolation of the almost linear portion of the curves to the yields at zero molar fraction of bromine, may reveal approximately the ^{82}Br yields from hot processes. Table 1 summarizes the ^{82}Br yields (estimated by extrapolation) of the major recoil products from the neutron-irradiated CF_2Cl_2–Br_2, $CFCl_3$–Br_2, and CF_2ClCF_2Cl–Br_2 systems. The following conclusions may be drawn from the results:

Table 1. Yields of major ^{82}Br-labeled recoil products from liquid CF_2Cl_2–Br_2, $CFCl_3$–Br_2 and CF_2ClCF_2Cl–Br_2 systems

Product	^{82}Br yield (%)[a]
(1) Liquid CF_2Cl_2–Br_2 system.	
$CF_2Cl^{82}Br$	2
$CF_2Br^{82}Br$	0.8
$CFCl_2{}^{82}Br$	0.4
$CFClBr^{82}Br$	0.2
(2) Liquid $CFCl_3$–Br_2 system.	
$CFCl_2{}^{82}Br$	6
$CFClBr^{82}Br$	2
$CCl_3{}^{82}Br$, $CCl_2Br^{82}Br$	not observed
(3) Liquid CF_2ClCF_2Cl–Br_2 system.	
$CF_2ClCF_2{}^{82}Br$	1.6
$CF_2Cl^{82}Br$	0.6
$CF_2Br^{82}Br$	0.7
$CF_2ClCFCl^{82}Br$, $CFClBr^{82}Br$	not observed
X ($CF_3{}^{82}Br$)[8]	<0.2

a) Estimated ^{82}Br yield from hot processes.

CF_2Cl_2–Br_2 System. At least four ^{82}Br-labeled species, *i.e.*, $CF_2Cl^{82}Br$, $CF_2Br^{82}Br$, $CFCl_2{}^{82}Br$, and $CFClBr^{82}Br$, were obtained from the recoil ^{82}Br reactions with CF_2Cl_2; of those the yield of $CF_2Cl^{82}Br$ (derived from ^{82}Br-for-Cl substitution) was larger than that of $CFCl_2{}^{82}Br$ (dreived from ^{82}Br-for-F substitution). Although the mechanisms for the formation of CF_2Br-^{82}Br and $CFClBr^{82}Br$ are not yet clear, it is likely that they are produced *via* radicals arising from the decomposition of the excited $CF_2Cl^{82}Br$ and $CFCl_2{}^{82}Br$ molecules.

$CFCl_3$–Br_2 System. The main ^{82}Br recoil products from the $CFCl_3$–Br_2 system were $CFCl_2{}^{82}Br$ and CF-$ClBr^{82}Br$, both originating from ^{82}Br-for-Cl substitution, whereas no ^{82}Br-for-F substitution product, such as $CCl_3{}^{82}Br$, was observed.

CF_2ClCF_2Cl–Br_2 System. $CF_2ClCF_2{}^{82}Br$, CF_2Cl-^{82}Br, and $CF_2Br^{82}Br$ were the major products from the CF_2ClCF_2Cl–Br_2 system,[8] indicating that ^{82}Br-for-Cl or ^{82}Br-for-CF_2Cl substituion took place predominantly. The ^{82}Br-for-F substituion product, $CF_2ClCFCl^{82}Br$, was not obtained.

In conclusion, the C–Cl and C–C bonds appear to be more reactive than the C–F bond in the recoil ^{82}Br reactions with these chlorofluorocarbons. It is worth mentioning that the C–Cl and C–C bonds are broken more readily than the C–F bond in the γ-radiolysis of these systems.[6] However, there is one point still to be clarified: whether or not such an apparent similarity between the isomeric-transition-induced ^{82}Br reactions and the γ-radiolysis reactions reflects the essential similarity of their reaction mechanisms.

Further work is in progress on the general application of the recoil technique to the selective preparation of labeled bromochlorofluorocarbons.

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6) T. Tominaga, R. Iwata, and Y. Makide, *Chem. Lett.*, **1972**, 871.

7) A variety of carbon mixed halides were produced by γ-irradiation up to a heavy dose, whereas no radiolysis products could be observed after 5 minutes' neutron irradiation in the reactor.

8) Another small unidentified peak (X) in Fig. 1 may presumably be $CF_3{}^{82}Br$, yet its origin is not fully understood.