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Isotope Effect in Thermal Ionic Reactions of Isomeric Transition-Activated ^{80}Br and ^{82}Br in the HBr–CH_4 System

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The reactions of isomeric-transition activated ^{82}Br were studied in the gaseous H^{82m}Br–CH_4(HBr/CH_4=0.1±0.01) system. $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ were identified as the reaction products; their absolute yields were 0.8% for $CH_3{}^{82}Br$ and 3.7% for $CH_2{}^{82}BrBr$ respectively. The results were compared with those obtained in the H^{80m}Br–CH_4 and $^{80m}Br_2$ (or $^{82m}Br_2$)–CH_4 systems. The effect of Kr and Xe additives showed that these products were formed only through kinetic energy-independent (thermal-ionic) reactions, as opposed to the results obtained in the $^{80m}Br_2$ (or $^{82m}Br_2$)–CH_4 system. This difference was explained on the basis of the kinetic energies initially acquired by the bromine atoms in the molecular-explosion process. In addition, an outstanding isotope effect resulting from the difference in the decay schemes of ^{80m}Br and ^{82m}Br was observed between the I. T.-activated ^{80}Br and ^{82}Br reactions in the H^{80m}Br–CH_4 and H^{82m}Br–CH_4 systems, and it was pointed out from the analysis of the ^{80m}Br-data that the two successive internal conversions in the ^{80m}Br decay were responsible for this isotope effect. It was considered that the second internal conversion started in a liquid-like condition such as ion-clusters containing the ^{80}Br in the intermediate state; this idea is supported by the experimental results obtained in the condensed phase.

There is a definite difference between the decay schemes of ^{80m}Br and ^{82m}Br.[1)] ^{80m}Br($t_{1/2}$=4.38 h) is de-excited to the ground state of ^{80}Br through the intermediate state with a half-life of 7.4 ns, whereas ^{82m}Br ($t_{1/2}$=6.1 min) is de-excited by a one-stage transition. The first transition of ^{80m}Br and the single transition of ^{82m}Br are fully converted (≈100%), while the second transition of ^{80m}Br is partly converted (≈61%). These internal conversions are followed by the Auger-electron emission, and the resulting atom is left with a high positive charge.[2–4)] Furthermore, the intramolecular electron transfer between the highly positively charged bromine and the remainder in a source molecule results a molecular explosion; consequently, the bromine atom acquires an appreciable kinetic energy.

So far it has been reported that both the kinetic energy and the positive charge of the I. T.-activated ^{80}Br and ^{82}Br play very important roles in determining the chemical reactions of these atoms in the $^{80m}Br_2$ and/or $^{82m}Br_2$–CH_4 systems.[5–9)] However, the present authors have previously pointed out that the ^{80m}Br undergoes only kinetic energy-independent (thermal-ionic) reactions in the H^{80m}Br–CH_4 system,[10)] in which the kinetic energy imparted to the ^{80}Br is 0.75 eV[11)] on an average, being greatly different from the kinetic energy (40.3 eV)[12)] for the $^{80m}Br_2$. In order to elucidate further the roles of the kinetic energy and the charge in the recombination reactions, the I. T.-activated ^{82}Br reactions were studied in this work by using H^{82m}Br as a source molecule in gaseous CH_4.

On the other hand, several experimental evidences have been accumulated for the isotope effect in the reactions of ^{80}Br and ^{82}Br activated by the isomeric transition in the CH_4[13)] and CH_3Br[14b)] systems. Previously Tachikawa has reported that the isotope effect resulting from the difference of the above decay modes appears in the energetic process to form CH_3Br, but not in the thermal process in the gaseous CH_4 system, using Br_2 as a source molecule.[13)] Similarly, it is very interesting to examine an isotope effect by using H^{80m}Br and H^{82m}Br as source molecules in gaseous CH_4. The chief purpose of this paper is to search for a possible isotope effect, especially between thermal ionic reactions in the two systems. Furthermore, the mechanisms of the formation of individual products were examined by the addition of HCl and CH_2=CH_2 to the system instead of inert gases, and discussed on the basis of ion-molecule reactions involving $^{82}Br^+$.

Experimental

Materials. All the gaseous reagents used, supplied by the Takachiho Chemical Co., were used directly without additional purification. The listed purities were 99.95% for CH_4, Kr, and HCl, 99.8% for CH_2=CH_2, and 99.9% for Xe respectively. All the other reagents were of an extremely pure grade, purchased from the Junsei Chemical Co., Ltd.

Preparation of H^{80m}Br and H^{82m}Br. H^{80m}Br was synthesized from the $^{80m}Br_2$, obtained by the thermal decomposition of palladium bromide irradiated by the bremsstrahlung which was produced by the impact of a 40—60 MeV electron on a Pt converter in the linear-electron accelerator of Tohoku University. The details of preparation have been shown in previous papers.[10,14a)] On the other hand, H^{82m}Br was prepared by the thermal neutron irradiation of liquid HBr, sealed in a thin quartz ampoule. Thermal neutron irradiations were performed for 1—2 min by using the pneumatic tube No. 3 of the Kyoto University Reactor at a neutron flux of 3×10^{13} n cm^{-2} s^{-1}, with a concomitant gamm-ray dose rate of about 10^6 R h^{-1}. A trace amount of bromine, produced by the radiation-induced decomposition of HBr, was observed. In order to remove the Br_2 thus formed, the irradiated ampoule was broken by a mechanical shock in the vacuum line, and then the H^{82m}Br purified was distilled into a storage bulb through a Dry Ice trap. The H^{80m}Br produced at the same time by thermal-neutron irradiations was used in several runs to find out if there is a difference between the yields in the two experiments using HBr prepared by the above two different methods.

Sample Preparation. The quantities of CH_4, HBr (^{80m}Br or ^{82m}Br labeled), and other additive gases required were measured with a mercury manometer. These gases were introduced into cylindrical Pyrex glass ampoules (50, 100, and 200 ml in capacity) with a long neck of capillary tubing cooled at the temperature of liquid nitrogen, and then sealed off. All these procedures were carried out by using a vacuum line composed of greaseless stop-cocks and joints. A quick sample preparation was requested to provide as many ^{82m}Br as possible for the isomeric transition experiments because of the short-life of ^{82m}Br($t_{1/2}$=6.1 min). The volatilization of the reaction mixtures by immersing the ampoule into hot water was done just 6 minutes after the end of irradiation; about 60% of the ^{82m}Br remained, provided for the I.T-induced reaction. The ratio of HBr to CH_4 and the total pressure were kept constant at 0.1±0.01 and 660±30 mmHg, respectively, throughout the series of gas-phase experiments. On the other hand, in the solid-phase experiment using $H^{80m}Br$ as a source molecule, reaction mixtures of HBr(65 cmHg), CH_4(130 cmHg), and/or HCl (130 cmHg) were solidified at the temperature of liquid nitrogen. The CH_4 deposited on the wall of the reaction vessel was thawed and mixed well with HBr and/or HCl by shaking, and then the mixture was solidified again at the bottom of the vessel.

Extraction, Activity Measurement, and Yield Determination. The radioactive bromine was separated into organic and inorganic layers by solvent extraction after the reaction mixture has been allowed to stand for more than 2 h in a dark place at 40 °C. The solvent extraction procedure was the same as that in the earlier experiments.[10,14a] A portion of the organic fraction was submitted to a gas chromatograph, while the product analysis was carried out by the use of a column (75 cm in length, 3 mm in diameter) filled with 60—80 mesh Celite 545, and coated with silicon oil (20% in weight). The fraction of each product was collected in glass tubes cooled in a Dry Ice ethanol bath at the outlet of the column. The radioactivity of each fraction was counted with a NaI(Tl) scintillation counter and/or a Ge(Li) semiconductor detector. Thus, the relative yields of the individual products were determined.

On the other hand, given volumes of organic and inorganic fractions were pipetted to test tubes. The photopeaks of 0.618 MeV from the ^{80}Br and/or 0.554 MeV from the ^{82}Br in both fractions were counted with a high resolution Ge(Li) semiconductor detector connected to a multichannel pulse-height analyser. In the ^{82m}Br-experiments, the solvent extraction and the activity measurement were performed after the ^{80m}Br had completely decayed out. The activities of both the inorganic and organic fractions were corrected for the separation time.

The organic yields were determined as the ratio (in percentage) of the activity of the organic fraction to the total activity, while the individual product yield was obtained by simply multiplying the relative yield of each product by the organic yield. For the several runs in the $H^{82m}Br$-CH_4 system, the individual product yields were determined directly by the radio-gas chromatograph technique adopted by Tachikawa *et al.* in the ^{80m}BrBr-CH_4 system.[5] However, there was no difference between the yields in the two methods, as well as the result previously obtained in the $H^{80m}Br$ experiments.[10]

The experimental errors arising from the standard deviation due to statistical fluctuations in the counting and chemical procedures were 7—15% for the ^{80m}Br-experiments and less than 10% for the ^{82m}Br.

Results

From the product analysis using a radio-gas chromatograph, we identified the $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ in the $H^{82m}Br$–CH_4 system, as well as the early observations obtained in the $H^{80m}Br$–CH_4 system.[10] The effect of Kr and Xe additives on the yield distribution is shown in Table 1 and depicted graphically in Fig. 1, together with the results in the $H^{80m}Br$–CH_4 system.[10,14a] The $H^{80m}Br$ prepared by thermal-neutron irradiations was used in several runs to find out if the results are different from those previously obtained by using the $H^{80m}Br$ prepared by the (γ, n) reaction.[10,14] However, no difference in the yields was observed between them. The $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ yields were 0.8% and

Table 1. Percentage of ^{82}Br stabilized in organic combiantions in a gaseous mixture of an additive and CH_4
(HBr/CH_4=0.1±0.1; total pressure: 660±30 mmHg)

Mole fraction additive (mf)		CH_3Br (%)	CH_2Br_2 (%)	Organic yield (%)
Kr	Xe			
0	0	0.8±0.1	3.7±0.2	4.5±0.2
0	0	0.8±0.1	3.8±0.2	4.6±0.2
0	0	0.7±0.1	3.8±0.3	4.5±0.2
0.10	0	0.7±0.1	3.7±0.3	4.4±0.3
0	0.20	0.9±0.1	3.9±0.4	4.8±0.4
0.25	0	0.8±0.1	3.7±0.2	4.5±0.2
0	0.30	0.9±0.1	3.3±0.2	4.2±0.2
0.40	0	0.6±0.1	3.6±0.3	4.2±0.3
0.45	0	0.7±0.1	3.8±0.3	4.5±0.3
0	0.50	0.7±0.1	3.6±0.3	4.3±0.3
0.60	0	0.7±0.1	3.4±0.3	4.1±0.3
0.70	0	0.6±0.1	3.8±0.3	4.4±0.3
0.80	0	0.5±0.1	4.5±0.4	5.0±0.3
0.85	0	0.7±0.1	4.8±0.5	5.5±0.4
0.90	0	0.8±0.1	5.3±0.4	6.1±0.4

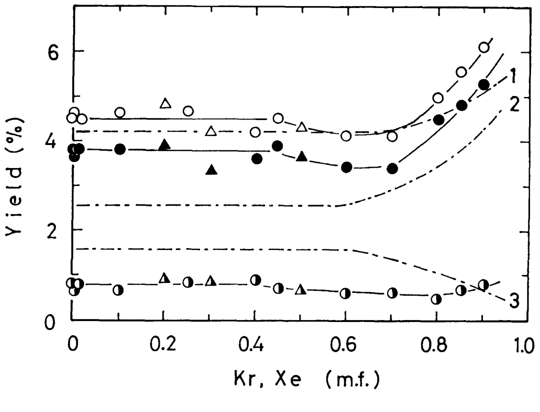

Fig. 1. Effect of Kr and Xe additives on the yield distributions.
($H^{82m}Br$(or $H^{80m}Br$)/CH_4=0.1±0.01)
Kr additive Xe additive
-○- -△-: organic yield
-●- -▲-: $CH_2{}^{82}BrBr$
-◑- -▲-: $CH_3{}^{82}Br$
The dashed lines were those previously obtained in the $H^{80m}Br$-CH_4 system.[10]
Line 1: organic yield, line 2: $CH_2{}^{80}BrBr$, line 3: $CH_3{}^{80}Br$.

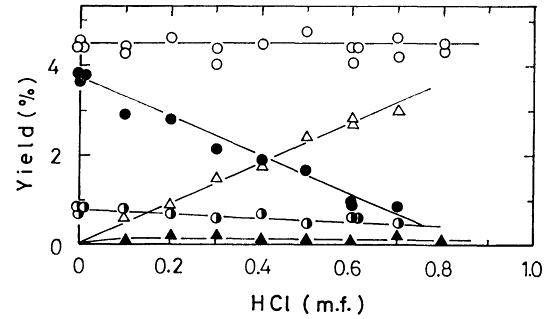

Fig. 2. Effect of HCl additive on the yield distributions.
($H^{82m}Br/CH_4=0.1\pm0.01$).
-○-: Organic yield, -△-: $CH_2{}^{82}BrCl$, -●-: $CH_2{}^{82}BrBr$, -▲-: $CH_3CH^{82}BrCl$, -◐-: $CH_3{}^{82}Br$.

3.7%, respectively, at 0 mf of additives. The $CH_2{}^{82}BrBr$ yield was much greater than the $CH_3{}^{82}Br$ yield over the whole range of additive concentrations, contrary to the results in the I.T.-experiments of the $^{80m}Br_2$ and/or the $^{82m}Br_2$–CH_4 system.[13]

The organic yields were slightly greater in the $H^{82m}Br$–CH_4 than in the $H^{80m}Br$–CH_4 system, and no change in the yield distributions upon the addition of Kr and Xe was observed in the range of 0—0.5 mf. The additional formation of $CH_2{}^{82}BrBr$ was observed in additive concentrations over about 0.6 mf, as well as in the early findings reported by the present authors and Tachikawa *et al.* in the $H^{80m}Br$–CH_4[10] and $^{80m}Br_2$–CH_4[16,17] systems respectively.

The outstanding difference between the results in the $H^{82m}Br$–CH_4 and $H^{80m}Br$–CH_4 systems was found in the distribution of individual products, as can be seen in Fig. 1. The yield ratio of $CH_3{}^{82}Br$ to $CH_2{}^{82}BrBr$ was 0.22, very different from the value of 0.59 obtained in the $H^{80m}Br$–CH_4 system. Obviously there is an isotope effect between the reactions of I.T.-activated ^{80}Br and ^{82}Br in the $H^{80m}Br$ and/or $H^{82m}Br$–CH_4 systems. The effect of the HCl additive instead of inert gases was also examined in the $H^{82m}Br$–CH_4 system; the results are shown in Fig. 2. The $CH_2{}^{82}BrCl$ and $CH_3CH^{82}BrCl$ were observed to be other than the $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ from its radio-gas chromatogram. The organic yield was almost constant in 0—0.7 mf of HCl, and the decrease in $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ yields almost offset the increase in $CH_2{}^{82}BrCl$ and $CH_3CH{}^{82}BrCl$ yields. The results suggested that these products were formed through the reactions of the same precursor.

In addition, the $CH_3CH_2{}^{82}Br$ was observed in the experiment using $CH_2{=}CH_2$ additive other than the $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$, much as in the findings obtained in the $H^{80m}Br$–CH_4–$CH_2{=}CH_2$ system.[10]

The relative yield ratio of each product to the $CH_2{}^{80}BrBr$ obtained in the solid phase are shown in Table 3. The yield ratios of $CH_3{}^{80}Br$ to $CH_2{}^{80}BrBr$ were about 1.2 for the $H^{80m}Br$–CH_4 and 1.6 for the $H^{80m}Br$–CH_4–HCl system, different from the value of 0.22 for the gas-phase experiment in the $H^{82m}Br$–CH_4 system.

Discussion

Contribution of Charge and the Kinetic Energy to the I.T.-Induced ^{80}Br and ^{82}Br Reactions. The most convenient method of differentiating the energetic reaction from thermal ionic reactions is through the addition of inert gas as an energy sink of the energetic bromine atom. Especially, Kr moderates most effectively the kinetic energy of the bromine atom, since the mass of Kr is almost equal to that of bromine. In addition, Kr, and Xe, used in the present experiment, are chemically inert; also, the charge transfer from the Br^+ ion to the inert gas molecules seems not to be important, judging from the ionization potentials of the Br atom (11.8 eV) and the inert gases (Kr: 13.9 eV, Xe: 12.1 eV). Therefore, if the organic yields decrease upon the addition of Kr and Xe, it must be due to the removal of ^{82}Br kinetic energy; the rest, insensitive to these inert-gas additives, must be derived from thermal ionic reactions.

As Fig. 1 shows, the addition of Kr and Xe did not cause any changes in either the organic or the individual product yields in the concentration of 0—0.5

Table 2. Percentage yields of organic products due to kinetic and thermal-ionic processes in the I. T. and (n,γ)-experiments (HBr (or Br_2)/CH_4=0.1±0.01)

System		$H^{82m}Br$-CH_4 a)	$H^{80m}Br$-CH_4 b)	$Br^{82m}Br$-CH_4 c)	$Br^{80m}Br$-CH_4 c)	(n,γ)-activated d)* $^{82m}Br_2$-CH_4
E_{max} (eV)		1.3	1.3	158	158	417
Org. yield (%)		4.5	4.25	6.1	4.7	13.8
Kinetic process	CH_3Br (%)	0	0	4.5	3.0	11.4
	CH_2Br_2 (%)	0	0	0	0	1.0
Thermal-ionic process	CH_3Br (%)	0.8	1.60	0.5	0.5	0.9
	CH_2Br_2 (%)	3.7	2.65	1.1	1.1	0.5

a) Present work. b) Ref. 10. c) Ref. 13. d) Ref. 15. *) Br_2/CH_4=0.2—0.03.

Table 3. The yield ratios of products to CH_2Br_2 in the solid $H^{80m}Br$-CH_4 and $H^{80m}Br$-CH_4-HCl systems

System	CH_3Br	CH_2BrCl	CH_2Br_2	$CH_3CHBrCl$	CH_3CHBr_2	CH_2BrCH_2Br	$CHBr_3$
$H^{80m}Br$-CH_4	1.2	—	1	—	0.90	0.18	0.34
$H^{80m}Br$-CH_4-HCl	1.6	0.96	1	0.51	0.79	—	<0.1

These are all average values of three runs.

mf. This fact is indicative that the I.T.-activated ^{82}Br enters the organic chemical combination only through a thermal ionic process in the $H^{82m}Br$–CH_4 system, much as in the early findings obtained in the $H^{80m}Br$–CH_4 system.10) The thermal ionic yields were 0.8% for CH_3Br and 3.7% for CH_2Br_2. The present results are summarized in Table 2, together with those previously obatined in the I.T.-10,13) and (n,γ)-experiments15) in gaseous CH_4. As is shown in Table 2, the recombination reactions of I.T.-activated ^{80}Br and ^{82}Br in both $H^{80m}Br$–CH_4 and $H^{82m}Br$–CH_4 systems are greatly different from those in other systems, in which the reaction proceeds mainly through kinetic energy dependent reactions. This difference can be explained on the basis of the kinetic energies initially acquired by the Br atom, which depend on the nature of the source molecule. In the case of the isomeric transition of ^{80m}Br and ^{82m}Br, the kinetic energy of the bromine atom ranges from 0 eV to maximum (E_{max}) of 1.3 and 158 eV respectively for the HBr and Br_2 used as source molecules, the most probable energies being 0.75 and 37 eV.11) On the other hand, the ^{80}Br born from the (n,γ) activation has kinetic energy spectrum ranging from 0 to 417 eV.11) The thermal ionic yields increase with a decrease in E_{max}, while, on the contrary, the kinetic energy-dependent yields tend to increase with an increase in E_{max}.

Previously it has been pointed out that the thermal ionic yield depends largely on the probability of the bromine ion reaching the thermal energy region by escaping from the charge neutralization.10) From a comparison of the cross-sections for the charge-transfer reaction of bromine ions and for the formation of a capture-collision complex as a function of the velocity of the Br^+ ion, it was indicated that the charge neutralization takes place predominantly in the high-energy region over than about 1 eV, while the capture-collision complex is formed favourably at the energies below 1 eV.10,17) Therefore, it is considered that most of the $^{80}Br^+$ and $^{82}Br^+$ produced by the (n,γ) reaction and the I.T. in Br_2 lose their charges before they reach the energy region in which the collision complex formation occurs preferentially. Thus, in these systems, the reactions are thought to be mainly due to a kinetic (hot) process involving neutral bromine atoms. On the other hand, it is considered that the formation of complex ions, such as ^{80}Br and/or ^{82}Br labeled CH_4Br^+ and $HBrBr^+$, proceeds at first in the I.T.-induced reaction in HBr; even if the charge neutralization takes place, the Br atom thus formed cannot undergo kinetic energy-dependent reactions because its kinetic energy is not sufficient for the Br to replace directly the H atom of CH_4. As has been mentioned in the following section, the CH_4Br^+ is considered to be a precursor of the formation of individual products.

Isotope-Effects in the Reactions of I.T.-Activated ^{80}Br and ^{82}Br. There have been several studies relating to the isotope effects (differences in organic yields) of (n,γ)- and I.T.-activated bromine reactions in the condensed and gas phases. Tachikawa13) and Helton *et al.*18) observed the kinetic-energy isotope effects of I.T.-and (n,γ)-activated bromine reactions in gaseous $^{80m}Br_2$ (or $^{82m}Br_2$)–CH_4 and Br_2–CH_3F systems respectively; these results were explained on the basis of the average number of possible collisions of the energetic bromine atom in the E_1—E_2 reactive region,19) in which the energetic (hot) reactions take place. However, thus far no thermal ionic isotope effect has been reported in the bromine reactions induced by unclear transformations. As Fig. 1 shows, obviously there is the isotope effect between thermal ionic reactions in the $H^{80m}Br$–CH_4 and $H^{82m}Br$–CH_4 systems; also the yield distributions in the system of the HCl additive shown in Fig. 2 were greatly different from those previously obtained in the $H^{80m}Br$–CH_4–HCl system.10)

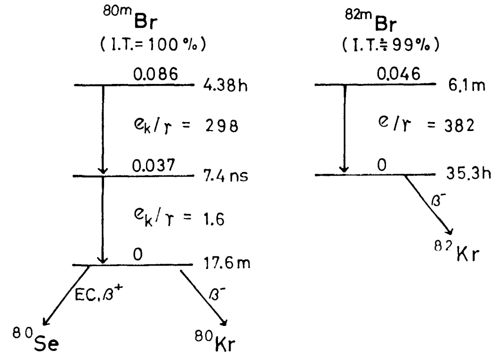

Fig. 3. Decay schemes of ^{80m}Br and ^{82m}Br.

Since the mass difference between ^{80}Br and ^{82}Br can not be considered to be responsible for the above isotope effect, this isotope effect may be brought about by the difference in the decay schemes of ^{80m}Br and ^{82m}Br,1) shown in Fig. 3. The ^{80m}Br is de-excited in two stages through the intermediate state with a half-life of 7.4 ns; the first stage is a M3 transition of 49 keV, and the second, an E1 transition of 37 keV. From the internal conversion coefficients, the first transition is internally almost 100% converted, while the second is only 61% converted. On the other hand, the isomer of ^{82}Br is de-excited in a single stage by means of a M3 transition with an internal conversion coefficient of 382 (fully converted, $\approx$100%). Since the M3 transitions in ^{80m}Br and ^{82m}Br are essentially the same, the charge and kinetic-energy distribution on the excited ^{80}Br should be identical with those on the ^{82}Br. However, the excited ^{80}Br has a successive transition to the ground state. 61% of the excited ^{80}Br is de-excited through the second internal conversion process, while the remaining 39% undergoes de-excitation to the ground state by means of 37 keV γ-ray emission. However, even if the ^{80}Br is in a chemical combination, the chemical consequence resulting from this γ-emission is considered to be negligible since the kinetic energy achieved on the ^{80}Br is of an order of 10^{-2} eV, which is not sufficient to break any bond in the molecule, only enough to produce a little excitation of it. From these considerations, the reaction processes of isomeric transition-activated ^{80}Br can be classified into the following two types:

Process (A): 39%
internal conversion + 37 keV γ-ray emission
(no chemical effect)

Process (B): 61%
internal conversion+internal conversion

Since the chemical effect resulting from Process (A) is essentially identical to those in the $H^{82m}Br$–CH_4 system, the yields due to Process (A) is equal to 39% of that obtained in the $H^{82m}Br$–CH_4 system. Therefore, the yield due to Process (B) is provided by subtracting that due to Process (A) from the organic yield in the $H^{80m}Br$–CH_4 system. The organic yields due to Process (B) were calculated by means of the following equation (I); they are depicted in Figs. 4 and 5, where the yields have been normalized by multiplying them by the factor of 100/61=1.64:

Yield (%) due to Process (B)

$$= \frac{100}{61}(^{80m}\text{Br-Yield} - 39\% \text{ of } ^{82m}\text{Br-Yield}) \qquad \text{(I)}$$

As Fig. 4 shows both the $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ yields were constant in 0—0.6 mf of Kr; this indicates that these products due to Process (B) are also formed through reactions independent of the kinetic energy of the ^{80}Br. The yield ratio of CH_3Br to CH_2Br_2 in Process (B) was 1.14, very different from the value of 0.22 for Process (A). This fact indicates that the $CH_3{}^{80}Br$ is formed more preferentially in Process (B) than in Process (A). Similarly, the $CH_3CH^{80}BrCl$ was found to be formed mainly in Process (B) in the $H^{80m}Br$–CH_4–HCl system, and the yield ratio of CH_3Br to CH_2Br_2 was close to unity over a wide range of HCl concentration, as can be seen in Fig. 5. Thus, there is a striking difference between the yield distributions of individual products for Process (A) and Process (B), and it is evident that Process (B) is responsible for the above isotope effect.

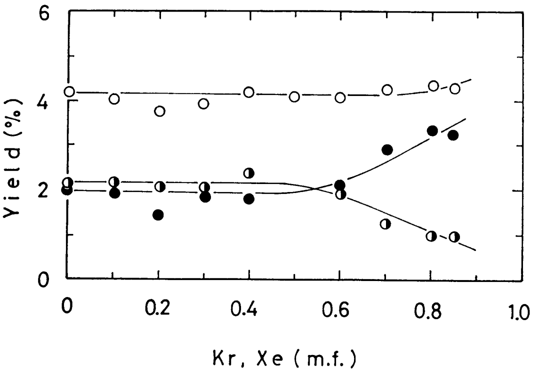

Fig. 4. Normalized yields due to the process (B) in the system of Kr and Xe additives.
-○-: Organic yield, -◐-: $CH_3{}^{80}Br$, -●-: $CH_2{}^{80}BrBr$.

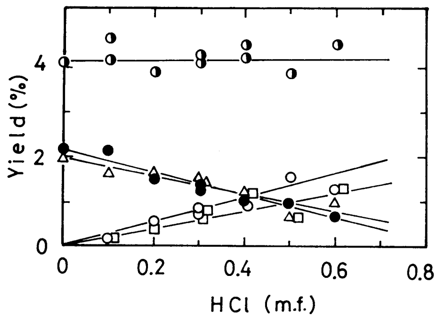

Fig. 5. Normalized yields due to the process (B) in the system of HCl additive.
-◑-: Organic yield, -●-: $CH_3{}^{80}Br$, -△-: $CH_2{}^{80}BrBr$, -○-: $CH_2{}^{80}BrCl$, -□-: $CH_3CH^{80}BrCl$.

If the life-time of the intermediate of $^{80m}Br(1.1\times10^{-8}$ s) is too short for the excited bromine atom to undergo chemical reactions prior to the transition to the ground state, the successive transition will result in only an additional build-up of the charge on the free atom, and this process will not give any kinetic energy to the ^{80}Br. In this case, no isotope effect will appear. The existence of an isotope effect, therefore, supports the idea that its life-time is long enough for the bromine atom to undergo chemical reactions prior to the second transition. However, this does not necessarily mean that all of the excited ^{80}Br react with surroundings to enter into certain chemical combinations within its life-time.

As has been stated in the previous section, the kinetic energy of ^{80}Br freed *via* the molecular explosion following the second internal conversion is very much dependent on the remainder of the molecule containing the excited ^{80}Br. However, both the $CH_3{}^{80}Br$ and the $CH_2{}^{80}BrBr$ due to Process (B) are formed only through kinetic energy-independent reactions. This fact may be suggestive that the second molecular explosion occurs from such chemical species as $H^{80}Br$, $H^{80}Br^+$, and $H_2{}^{80}Br^+$,[20] but if so, its chemical consequence will also be identical to the one due to Process (A) and no isotope effect will appear between them. From these considerations, it seems to be more likely that, even if the excited ^{80}Br is in certain chemical combinations, the environment surrounding the ^{80}Br is different from that in Process (A).

From an energy standpoint, it is considered that the $^{82}Br^+$ and $^{80}Br^+$ ions undergo at first ion-molecule reactions to form the capture collision complexes, $CH_4{}^*Br^+$ and HBr^*Br^+, since generally no activation energy is required for these reactions (Eqs. 1 and 2);

$$^*Br^+ + CH_4 \rightarrow CH_4{}^*Br^+, \qquad (1)$$

$$^*Br^+ + HBr \rightarrow HBr^*Br^+. \qquad (2)$$

(Here, the Br^+ with a star sign shows the $^{82}Br^+$ and/or excited $^{80}Br^+$.)

So far the presence of sticky collision complexes of such a type has been confirmed by using a mass-spectrometer in the various alkyl halide and hydrocarbon systems.[21–23] Further, it is expected, from a rough calculation by using the equation proposed by Magee *et al.*,[24] that the life-times of complex ions are at least longer than that of the ^{80}Br intermediate state (1.1×10^{-8} s).[10] Therefore, these complex ions have an ample opportunity to collide with surroundings prior to the successive transition in Process (B), since the collision time is about 10^{-9} s under the present experimental conditions. In the study of the radiation chemistry in the gas phase, Lind has suggested that thermal ions have a big chance to form an ion-cluster containing several molecules before they give the final products.[25] The attractive force considered here is that arising between the ion and the ion-induced dipole or dipole moment on the molecule; also, it is generally known that thermal ions at high pressures form, more preferentially, ion-clusters.[26–28] In the present experiment, it is thought that the $CH_4{}^{80}Br^+$ and $HBr^{80}Br^+$ complex ions interact with surrounding molecules to form the ion-cluster before the second isomeric transition occurs. Therefore, the chemical effect due to Process (B) is considered to be very similar to that in the condensed phase. This idea was confirmed by the fact that the yield distributions of CH_3Br and CH_2Br_2 in the solid phase were very similar to those due to Process (B). That is, the yield ratios of CH_3Br to CH_2Br_2 obtained in the solid phase experiments were 1.2 for the $H^{80m}Br$–CH_4 and 1.6 for the $H^{80m}Br$–CH_4–HCl system, as is shown in Table 3; these values are very close to those obtained in Process (B). Thus, this ion-cluster model is qualitatively supported by the fact that the $CH_3{}^{80}Br$ is formed more preferentially than the $CH_2{}^{80}BrBr$ in the condensed phase. The large amount of energy evolved from the second molecular explosion is considered to be dissipated readily to the rigid sphere of the cluster and spent in the formation of ions, radicals, and excited species, which contribute directly or indirectly to the individual product formation.

Thus, the isotope effect found in the thermal ionic reactions of I.T.-activated ^{80}Br and ^{82}Br can be qualitatively explained by introducing the idea that the ion-cluster containing the ^{80}Br in Process (B) is formed in the intermediate state. However, the details of the reactions in such a field must await until further experiments.

The Formation of $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ via *Thermal Ionic Reactions.* As a possible explanation for the formation of $CH_2{}^{80}BrBr$ *via* the thermal ionic process in the I.T.-experiment on the $^{80m}BrBr$–CH_4 system, Tachikawa has previously suggested that the $CH_4{}^{80}Br^+$ complex ion undergoes charge neutralization following its decomposition to such fragments as $CH_3{}^{80}Br$, and $CH_2{}^{80}Br$, and that the $CH_2{}^{80}Br$ radical thus formed can be easily scavenged by Br_2 to form the $CH_2{}^{80}BrBr$.[13] However, the present authors previously pointed out that the $CH_2{}^{80}Br$ and $CH^{80}Br$ radicals would not be present in the $H^{80m}Br$–CH_4 as precursors for the formation of $CH_2{}^{80}BrBr$.[10,14]

Similarly, it was confirmed experimentally in this work that the precursors responsible for the formation of $CH_2{}^{82}BrBr$ were not the $CH_2{}^{82}Br$ and $CH^{82}Br$ radicals. That is, if the $CH_2{}^{82}Br$ is present in the system, the radical reacts with HBr to form $CH_3{}^{82}Br$ more preferentially than to form $CH_2{}^{82}BrBr$, since the reaction leading to the $CH_3{}^{82}Br$ is more exothermic by about 18 kcal/mol than that giving the $CH_2{}^{82}BrBr$. Similarly, the $CH_2{}^{82}Br$ radical reacts with HCl to form the $CH_3{}^{82}Br$ more preferentially than to form the $CH_2{}^{82}BrCl$ in the system of the HCl additive. However, as Figs. 1 and 2 show, the $CH_2{}^{82}BrBr$ yields were greater than those of $CH_3{}^{82}Br$ over the entire range of additive concentrations; further, the $CH_2{}^{82}BrCl$ yields increased with an increase in the HCl concentration in the system of the HCl additive. Furthermore, if the $CH^{82}Br$ is present in the system, it is considered that the radical reacts readily with $CH_2{=}CH_2$ to give ^{82}Br labeled-bromocyclopropane and/or aryl bromide in the system of the $CH_2{=}CH_2$ additive,[24] but no radioactive peak corresponding to these products was observed on the radio-gas chromatograms, as is shown in Table 4. Thus, the radicals such as $CH_2{}^{82}Br$ and $CH^{82}Br$ are not considered to be the precursors leading to the formation of $CH_2{}^{82}BrBr$ *via* a thermal-ionic process.

TABLE 4. EFFECT OF $CH_2{=}CH_2$ ADDITIVE ON THE YIELD DISTRIBUTIONS ($H^{82m}Br/CH_4 = 0.1 \pm 0.01$)

$CH_2{=}CH_2$ mf	Organic yield (%)	CH_3Br (%)	CH_3CH_2Br (%)	CH_2Br_2 (%)
0.1	40.3	0.8	39.3	0.2
0.3	49.3	0.4	48.9	<0.1

Although there are no precise information on the ion-molecule reactions leading to the $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$ in Process (A) because of lack of knowledge concerning the chemical behaviour of complex ions under high pressures, the possibility of the formation of these products by the ion-molecule reactions involving $CH_4{}^{82}Br^+$ was evaluated from a thermodynamical point of view. Most ion-molecule reactions of $^{82}Br^+$, $CH_4{}^{82}Br^+$, and $HBr^{82}Br^+$ with additives, leading directly to the formation of $CH_3{}^{82}Br$ and $CH_2{}^{82}BrBr$, are not favoured because of their high endothermicities. However, the H^+-transfer reaction from $CH_4{}^{82}Br^+$ to CH_4 and/or HBr are considered to be the principal reactions for the formation of $CH_3{}^{80}Br$, since Reactions 3 and 4 are roughly exothermic by 47 and 63 kcal/mol respectively for the $^{82}Br^+$ ground state:[10]

$$CH_4{}^{82}Br^+ + CH_4 \rightarrow CH_3{}^{82}Br + CH_5{}^+ \tag{3}$$

$$CH_4{}^{82}Br^+ + HBr \rightarrow CH_3{}^{82}Br + H_2Br^+ \tag{4}$$

On the other hand, among the various types of ion-molecule reactions involving the $^{82}Br^+$, $CH_4{}^{82}Br^+$, and $HBr^{82}Br^+$, only the following reactions, 5 and 6, are conceivable as steps in the reaction routes leading to the formation of $CH_2{}^{82}BrBr$ and $CH_2{}^{82}BrCl$, since these reactions are exothermic by about 45 and 28 kcal/mol respectively:[10]

$$CH_4{}^{82}Br^+ + HBr \rightarrow CH^{82}BrBr^+ + 2H_2 \tag{5}$$

$$CH_4{}^{82}Br^+ + HCl \rightarrow CH^{82}BrCl^+ + 2H_2 \tag{6}$$

As was pointed out in a previous paper,[10] it is considered that these ions lose their charges through charge-transfer reactions with impurities present in the system or with the wall of the reaction vessel, and that the radicals thus formed undergo H-abstraction from surrounding molecules to give $CH_2{}^{82}BrBr$ and $CH_2{}^{82}BrCl$ respectively. The details of these reactions will be revealed by accumulating data concerning ion-molecule reactions of these ions under high pressures.

The additional formation of $CH_2{}^{82}BrBr$ in concentrations of Kr and Xe over than 0.5 mf might be explained by ion-molecule reactions involving such ions as $Kr^{82}Br^+$ (or $Xe^{82}Br^+$), as well as by the explanation previously proposed in the $H^{80m}Br$–CH_4 system.[10] However, the answer to this problem must await more information concerning the ion-molecule reactions of Br^+ with inert gases and the reactivities of these complex ions containing an inert molecule.

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