Reactions of Isomeric Transition-Activated ^{80}Br in the H^{80m}Br-CH$_4$ System

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The reaction of isomeric transition-activated ^{80}Br was studied in the gaseous H^{80m}Br–CH$_4$(HBr/CH$_4$=0.1±0.01) system. CH$_3{}^{80}$Br, CH$_2{}^{80}$BrBr and CH^{80}BrBr$_2$ were identified as the products, and their absolute yields were 1.60, 2.65, and 0.05%, respectively. The effects of Kr and Xe additives show that these products were produced only through kinetic-energy independent (thermal ionic) processes. The results are compared with those obtained in the ^{80m}BrBr (or ^{82m}BrBr)–CH$_4$ system, in which the C–*Br formation proceeds mainly *via* kinetic-energy dependent processes, and the difference between them is explained on the basis of the cross sections for charge neutralization and capture collision complex formation of bromine ions as a function of the kinetic energies initially acquired by the ^{80}Br and ^{82}Br atoms. The persistent complex ion, CH$_4{}^{80}$Br$^+$, is considered to be a precursor of the product formations, and the formation of individual products is discussed on the basis of ion-molecule reactions of CH$_4{}^{80}$Br$^+$ with surrounding molecules. Furthermore, the effect of HCl and CH$_2$=CH$_2$ additives on the yield distribution were examined to elucidate the reaction mechanisms of the product formations.

The chemical effects associated with the nuclear transformations of bromine atoms in gaseous systems have been studied extensively,[1–10] and one of the most interesting subjects is to determine the relative importance of kinetic energy and charge in the recombination reactions involving recoiling bromine atoms.

So far the reactions of (n,γ)[1,2,4] and/or fission[11] activated bromine in gaseous CH$_4$ have been found to proceed principally through kinetic processes. Similary, it has been reported that the recoiling halogen atoms produced by the ^{19}F(γ,n)^{18}F[12] and ^{40}Ar(γ,p)^{39}Cl[13] reactions enter into organic combinations only through kinetic-energy dependent (hot) reactions as neutral atoms in a gaseous CH$_4$ system. It is conceivable that these recoiling atoms initially have positive charges. However, these experimental results indicate that the charge neutralization of positively-charged recoiling atoms proceeds fast and is nearly completed before the recoiling atom reaches the energy region causing hot reactions.

On the other hand, in the case of isomeric transitions (IT) of ^{80m}Br and ^{82m}Br, the initial high positive charge on the bromine atom, as a consequence of the Auger process following the isomeric transition, is partially neutralized by intra-molecular electron transfer, resulting in Coulombic repulsion. Therefore, the bromine atom can acquire appreciable kinetic energy. When ^{80m}BrBr is used as a source molecule, the kinetic energy of the ^{80}Br is calculated to be 40.3 eV[14] on the average, assuming that the original charge of the ^{80}Br is 8 and is equally divided between the bromine atoms. This value is fairly small compared with those for the other nuclear transformations stated above. It has been reported that, not only the kinetic energy, but also the positive charge plays a very important role in the reactions of ^{80}Br and/or ^{82}Br activated by isomeric transitions for the Br$_2$–CH$_4$ system.[3,7,15–17] These results indicate that some of the positively-charged bromine atoms lose their kinetic energies and have the opportunity to undergo ion-molecule reactions leading to C–*Br formation before charge neutralization occurs. The cross sections for charge neutralization and ion-molecule reactions depend largely on the kinetic energy of the ions. Thus, it is very interesting to estimate the organic yields due to the thermal ionic process on the basis of the kinetic energy of the charged bromine atom.

This is the record of an experiment of I.T.-activated ^{80}Br reactions with CH$_4$ using HBr as the source molecule. In this case, the kinetic energy of the ^{80}Br atoms is 0.75 eV on the average,[5] and therefore, this experiment is considered to be highly suited to evaluating the role of the charge and kinetic energy of the ^{80}Br atom on recombination reactions in the near-thermal energy region. The results were compared with those obtained from (n,γ) and IT experiments using Br$_2$,[1,2,10] and can be explained in terms of competition between charge-transfer and ion-molecule reactions involving bromine ions.

Furthermore, the formation mechanisms of individual products were examined by adding HCl and CH$_2$=CH$_2$ to the system. These are discussed on the basis of ion-molecule reactions involving the ^{80}Br$^+$ ion.

Experimental

Materials. All gaseous reagents were used directly as supplied by Takachiho Chemical Co. without further purification. The nominal purities are 99.95% for Kr and CH$_4$, 99.9% for Xe, 99.8% for CH$_2$=CH$_2$, and 99.5% for HCl. The purities of all other reagents purchased from the Junsei Chemical Co., Ltd., were extremely high.

Preparation of H^{80m}Br. First, the ^{80m}Br$_2$ molecules were obtained by the thermal decomposition of palladium bromide irradiated by bremsstrahlung, which was produced by the impact of 40—60 MeV electrons from the linear electron accerelator of Tohoku University on a Pt plate (2 mm thick). The bombardment was carried out for about 2 h at an average electron-beam intensity of 150 μA. The ^{80m}BrBr molecules thus obtained were introduced into a vessel containing red phosphorus and a small amount of distilled water. Then, the vessel was closed with a stopcock and the temperature of the vessel was increased to about room temperature. After completion of the Br$_2$ reaction, the H^{80m}Br thus obtained was further purified by distillation through a P$_2$O$_5$ column and a Dry Ice trap for the sake of complete removal of trace amounts of unreacted species.

Sample Preparation. The amount of CH$_4$, HBr, and other additives required was measured with a mercury manometer, all reaction mixtures were sealed into cylindrical pyrex glass ampoules with capacities of 50, 100, and 200 ml and fitted to the long neck of a capillary tube.

All these procedures were carried out using a vacuum line incorporating greaseless stopcocks and joints. The ratio of HBr to CH_4 and total pressure were maintained constant at 0.1±0.01 and 660±30 mmHg, respectively, throughout the series of addition experiments.

Extraction Procedures, Activity Measurements, and Yield Determinations. The reaction mixture was allowed to stand for more than 2 h in the dark at 40 °C to permit a ^{80m}Br–^{80}Br parent-daughter equilibrium to be established. Then, the tip of the ampoule was broken, and 4 ml of 0.5 N Na_2SO_3, 1 ml of 0.5 N KBr and 5 ml of CCl_4 were added to the ampoule which was cooled to liquid-nitrogen temperature. Care was taken so that these solutions did not come into direct contact with reactants deposited on the walls during the cooling of the ampoule. Then the temperature was increased to approximately −100 °C to exclude air liquefied in the ampoule. Then, radioactive bromine was extracted into the organic and inorganic layers by vigorous shaking. The organic layer was washed twice with distilled water. After the addition of carriers, such as CH_3Br, CH_2Br_2, CH_2BrCl, *etc.*, a portion of the organic fraction was submitted to gas chromatography and product analysis was carried out using a column (75 cm long, 3 mm in diameter) filled with 60—80 mesh celite 545, which was coated with silicone oil (20% in weight).

A fraction of each product was collected in a glass tube cooled in a Dry Ice-ethanol bath at the outlet of the column. The radioactive emissions from each product were measured with a NaI(Tl) scintillation counter, and the relative yields of the individual products were determined. Also the organic and inorganic fractions in a given quantity were pipetted into test tubes. The inorganic fraction was allowed to stand for more than 1.5 h to establish ^{80m}Br–^{80}Br equilibrium, and only the 0.618 MeV photopeak from ^{80}Br was counted for a period of about eight half-lifes of ^{80m}Br (4.38 h). No other radioactive contamination was observed in the organic fraction. The radioactivity measurements of the organic fractions were usually started about 7 min after extraction. The radioactivity measurements of these fractions was performed with a high-resolution Ge(Li) semiconductor detector (36 ml in volume) connected to a 4096-channel pulse-height analyzer.

The activities of both the inorganic and organic fractions were corrected for the separation time. The organic yields were determined as the percent ratio of the radioactivity of the organic fraction to the total radioactivity, and the individual product yields were obtained by simply multiplying the relative yield of each product by the organic yield. For several runs, the product yields were determined by the radio gas chromatographic technique adopted by Tachikawa and Kahara for the $^{80m}BrBr$–CH_4 system.[3] However, there was no difference in the yields for both methods.

The experimental error resulting from statistical fluctuations in the counting were approximately 7—15%. The experimental error due to inefficiencies in the extraction and collection of the products at the outlet of the gas chromatograph column were almost negligible.

Results

The bromine exchange reactions were first examined in the $H^{82}Br$–CH_3Br and/or CH_2Br_2 (HBr/CH_3Br (or CH_2Br_2)=0.1±0.01) systems at a constant pressure of 150 mmHg prior to the actual experiment. After storage in the dark for 2 h at 40 °C, the radioactivity of the organic fraction after extraction was less than 0.1% of the total activity. Furthermore, no dependence of the yields on the storage period of the reaction vessels was found for storage periods between 2 and 10 h.

From the radio gas chromatograms of the organic fractions, $CH_3{}^{80}Br$, $CH_2{}^{80}BrBr$, and $CHBr_2{}^{80}Br$ were identified as the products in the $H^{80m}Br$–CH_4 system. However, the $CHBr_3$ yields were very small and in most cases less than 0.1%. On the other hand, $CH_2{}^{80}BrCl$ and $CH_3CH^{80}BrCl$ for the system with the HCl additive and $CH_3CH_2{}^{80}Br$ for that with the CH_2=CH_2 additive were observed, in addition to $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$, respectively.

No pressure dependence of the organic and product yields was observed in the range from 100 to 1400 mmHg at a constant HBr/CH_4 ratio of 0.1±0.01.

In order to differentiate the kinetic-energy dependent from the kinetic-energy independent (thermal ionic) yield for the $H^{80m}Br$–CH_4 system, Kr and Xe were added as moderators for ^{80}Br while the HBr/CH_4 ratio was maintained constant at 0.1±0.01. The results are given in Table 1 and depicted graphically in Fig. 1. The $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ yileds were 1.60 and 2.65% for 0 mf of additives, respectively. The $CH_2{}^{80}BrBr$ yield was much greater than that for $CH_3{}^{80}Br$ over the entire additive concentration range, contrary to the results obtained from the IT-experiments of the $^{80m}Br_2$[1,10] and/or $^{82m}Br_2$[3,15]–CH_4 systems. No change in the yield distribution was observed for additive concentrations less than about 0.6 mf, while the $CH_2{}^{80}BrBr$ yiled showed a tendency to increase gradually at concentrations greater than 0.6 mf, as was observed for

Table 1. Percent ^{80}Br stabilized in organic combinations in a gaseous mixture of an additive and CH_4
(HBr/CH_4=0.1±0.01, Total pressure=660±30 mmHg)

Molar fraction additive (mf) Kr	Xe	CH_3Br (%)	CH_2Br_2 (%)	Organic yield (%)
0	0	1.6±0.2	2.7±0.2	4.3±0.3
0	0	1.6±0.1	2.6±0.3	4.2±0.3
0	0	—	—	4.2±0.3
—	0.10	1.6±0.3	2.6±0.3	4.2±0.5
—	0.10	—	—	4.4±0.3
0.20	—	1.6±0.2	2.6±0.3	4.2±0.3
0.21	—	—	—	4.0±0.2
0.29	—	1.4±0.1	2.5±0.2	3.9±0.4
—	0.30	1.6±0.2	2.4±0.3	4.0±0.3
0.40	—	1.7±0.3	2.5±0.3	4.2±0.3
0.50	—	—	—	4.2±0.5
0.60	—	1.6±0.2	2.5±0.3	4.1±0.4
—	0.61	1.3±0.2	2.8±0.2	4.1±0.4
0.60	—	—	—	4.2±0.5
0.70	—	0.81±0.1	3.2±0.4	4.2±0.3
—	0.70	1.2±0.1	3.2±0.4	4.4±0.4
0.70	—	—	—	4.3±0.4
—	0.75	0.9±0.09	3.4±0.3	4.3±0.5
0.80	—	0.81±0.08	3.8±0.4	4.6±0.4
—	0.80	1.0±0.09	3.7±0.3	4.7±0.4
0.85	—	0.85±0.08	3.7±0.3	4.6±0.5
—	0.85	0.94±0.09	4.0±0.4	4.9±0.4

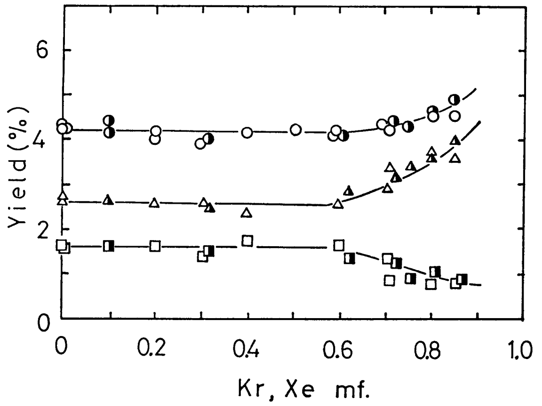


Fig. 1. Effect of Kr and Xe additives on the product yield distribution (H^{80m}Br/CH$_4$=0.1±0.01).

Kr additive	Xe additive	
-○-	-◑-:	total organic yield
-△-	-▲-:	CH$_2$^{80}BrBr
-□-	-◧-:	CH$_3$^{80}Br

the H^{82m}Br–CH$_4$[18] and ^{80m}BrBr–CH$_4$[19] systems. However, the CH$_3$^{80}Br yield decreased slightly at high additive concentrations.

The effect of the HCl additive on the yield distributions is shown in Fig. 2. The organic yield is almost constant for 0—0.6 mf of HCl, and the decrease in the CH$_3$^{80}Br and CH$_2$^{80}BrBr yileds nearly offset the increase in the CH$_2$^{80}BrCl and CH$_3$CH^{80}BrCl yields.

In addition, the effect of the CH$_2$=CH$_2$ additive on the yield distribution is shown in Fig. 3. From preliminary experiments using ^{77}Br-labeled HBr($t_{1/2}$=57 h for ^{77}Br) under the same experimental conditions, no addition reaction of HBr with CH$_2$=CH$_2$ was observed and therefore, this indicates that the yields are derived from reactions associated with the isomeric transition of ^{80m}Br. A sharp increase in the CH$_3$CH$_2$^{80}Br yield was observed upon the addition of a small amount of CH$_2$=CH$_2$, and for concentrations above about 0.05 mf, the yield gradually increased. However, the addition of a small quantity of CH$_2$=CH$_2$ resulted in a sharp decrease in the CH$_2$Br^{80}Br yield, and the CH$_3$^{80}Br yields decreased relatively slowly with increasing CH$_2$=CH$_2$ concentration.

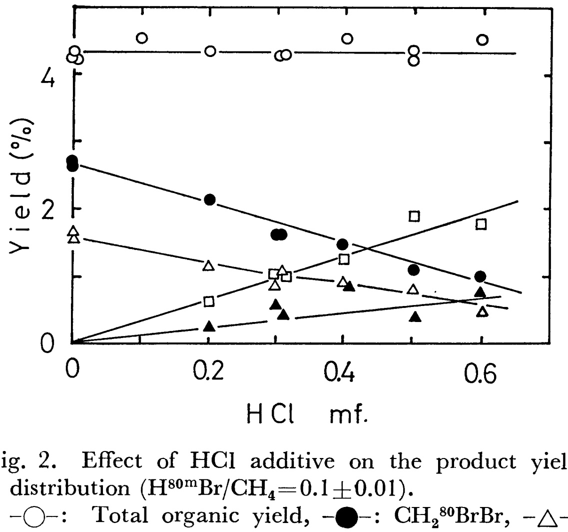


Fig. 2. Effect of HCl additive on the product yield distribution (H^{80m}Br/CH$_4$=0.1±0.01).
-○-: Total organic yield, -●-: CH$_2$^{80}BrBr, -△-: CH$_3$^{80}Br, -□-: CH$_2$^{80}BrCl, -▲-: CH$_3$CH^{80}BrCl.

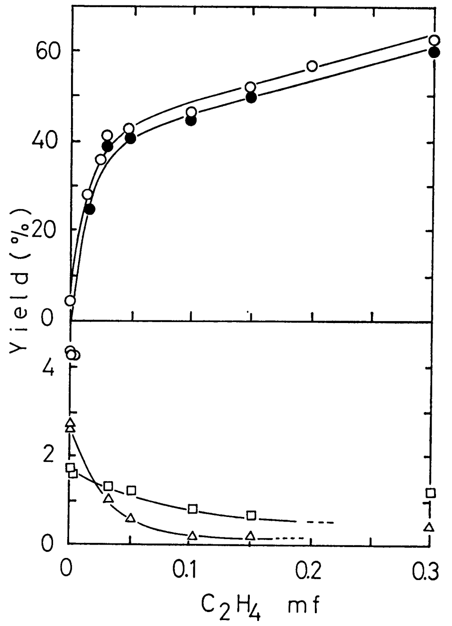


Fig. 3. Effect of CH$_2$=CH$_2$ additive on the product yield distribution (H^{80m}Br/CH$_4$=0.1±0.01).
-○-: Total organic yield, -△-: CH$_2$^{80}BrBr,
-●-: CH$_3$CH$_2$^{80}Br, -□-: CH$_3$^{80}Br.

Discussion

Evaluation of the Yields via *Kinetic and Thermal Process.* Up to the present time, many investigations have been carried out on the reactions of bromine produced by a variety of nuclear transformations in gaseous systems, especially in order to evaluate the role of the charge and kinetic energy of the bromine atom in the recombination reactions. The most convenient way to differentiate an energetic reaction from a kinetic energy independent (thermal ionic) reaction is by the addition of an inert gas which can serve as an energy sink for the energetic Br atoms. Kr is the most effective moderator since the mass of Kr is almost equal to that of Br, and Kr is also found to have small cross sections for quenching excited species and for undergoing charge transfer with Br$^+$ ions due to its high ionization potential of 13.99 eV.[15] Therefore, if the yield decreases upon the addition of Kr, it must be due to the removal of the ^{80}Br kinetic energy, and the remainder, which is insensitive to the Kr additive, can be derived from thermal ionic reactions. The high electron affinity of Br^{+n} ($n\geq 2$) suggests that the thermal ionic reaction concerns mostly the reaction involing the ^{80}Br$^+$ ion.

As Fig. 1 shows, no change in the CH$_3$^{80}Br and CH$_2$^{80}BrBr yields was observed in the range from 0 to 0.6 mf of Kr and Xe. This indicates that both products are formed *via* thermal ionic reactions. These findings are very different from those obtained for the ^{80m}BrBr-(^{82m}Br$_2$)–CH$_4$[3,15,20] and (n,γ)-activated ^{80}Br–CH$_4$ systems,[4] for which the organic yields resulted mainly from kinetic-energy dependent reactions. This difference can be explained on the basis of the kinetic energy acquired initially by the Br atom.

In the case of the isomeric transition of ^{80m}Br, the kinetic energy of ^{80}Br ranges from 0 eV to maxima of 1.3 and 158 eV when HBr and Br_2, respectively, are used as source molecules, with the most probable energies being 0.75 and 37 eV, respectively.[5)]

On the other hand, it is known from neutron binding-energy data[21)] that the ^{80}Br and $^{82m}Br+^{82}Br$ produced by (n,γ) activation have kinetic energy spectra ranging from 0 to 417 eV, and from 0 to 378 eV, respectively. Wexler has also determined that approximately 18 and 25% of the neutron activation processes resulted in positively-charged ^{80}Br and ^{82}Br, respectively.[8)] The present data are compared with those obtained from the IT and (n,γ) experiments in Table 2. Thermal ionic yields increase with decreasing kinetic (recoil) energy, E_{max}, but on the contrary, the kinetic-energy dependent yields tend to increase with increasing E_{max}. It is considered that the thermal ionic yield largely depends on the probability of the bromine ions reaching the thermal energy region upon escaping from the charge neutralization. Therefore, it is very interesting to estimate the cross sections for charge neutralization and ion-molecule reactions as a function of the $^{80}Br^+$ kinetic energy.

Rapp and Francis[22a)] have calculated the cross section for resonant charge transfer at intermediate impact velocities (10^5—10^8 cm/s) using the semiclassical impact-parameter method. The values obtained are in good agreement with experimental values in many cases. The cross sections for the resonant charge-transfer reaction of Br^+ with Br, which is the highest of the charge-transfer reactions involving the Br^+ ion, can be obtained by interpolating the resonant charge-transfer cross sections calculated by Rapp and Francis.[22a)] Whereas the velocity, v_{max}, for which the asymmetric charge-transfer cross section is maximum, was calculated from

$$v_{max} = \frac{|\Delta E|a}{h}, \tag{1}$$

assuming that the asymmetric charge-transfer cross section is close to that for resonant charge transfer at velocities above v_{max}.[22a)] The threshold energy (E_{th})[23)] for *endo*-energetic charge-transfer reactions was calculated using the relation

$$E_{th} = \frac{M_{Br^+} + M_{target}}{M_{target}}, \tag{2}$$

where ΔE, h, a, and M are the energy defect, Planck's constant, the adiabatic parameter (7×10^{-8} cm),[24)] and the mass, respectively. The values of v_{max} and E_{th} are tabulated in Table 3.

TABLE 2. THE PERCENTAGE YIELDS OF ORGANIC PRODUCTS DUE TO KINETIC AND THERMAL IONIC PROCESSES IN IT AND (n,γ) EXPERIMENTS ($HBr(or\ Br_2)/CH_4=0.1\pm0.01$)

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

a) Present work. b) Ref. 35. c) Ref. 4. * Br_2/CH_4= 0.02—0.03.

On the other hand, the cross sections for capture collisions between Br^+ and CH_4 were calculated using[22b)]

$$\sigma(v) = (2\pi e/v)(\alpha/\mu)^{1/2}, \tag{3}$$

where μ, α, v and e are the reduced mass of the collision pair, the polarizability of CH_4 (2.60×10^{-24} cm^3/mol),[25)] the relative velocity of the ion and the charge on the ion, respectively. Pottie *et al.*,[26)] Boelrük and Hamill,[27)] and Kubose and Hamill[28)] have indicated that Eq. 3 is applicable to ions with energies below about 1 eV. The cross sections thus obtained are shown in Fig. 4 as a function of the Br^+ velocity (lower abscissa). The velocity dependence for reactions C and D in Fig. 4 are hypothetical and are drawn on the basis of values of v_{max} and E_{th}. E_{max} for the $^{79}Br(n,\gamma)^{80}Br$ reaction and the isomeric transition of ^{80m}Br in Br_2 and HBr are shown by arrows pointing downward on the upper abscissa of this figure.

This figure indicates that the charge-neutralization reaction is predominant in the high-energy region above about 1 eV, and the formation of a capture collision complex is favorable at energies below 1 eV. Therefore, most Br^+ ions produced by the (n,γ) reaction and IT in Br_2 lose their charges before reaching the energy region in which the collision-complex formation reactions preferentially occur. In the present case, the kinetic energy initially acquired by the ^{80}Br atom is 0.75 eV on the average.[5)] Therefore, the formation of the capture collision complex competes with the charge transfer reaction, as is seen in Fig. 4 and occurs with higher probability in the energy region below 1 eV.

TABLE 3. v_{max} AND E_{th} FOR ASYMMETRIC CHARGE-TRANSFER REACTIONS OF Br^+ WITH CH_4, Kr, AND Xe

Electronically excited state of Br^+	Excitation energy (eV)	Energy defect ΔE (eV)			E_{th} (eV)			v_{max} (cm/s)		
		CH_4	Kr	Xe	CH_4	Kr	Xe	CH_4	Kr	Xe
$^3P_2$	0	1.11	2.11	0.29	6.65	4.12	0.47	1.88×10^7	3.57×10^7	4.91×10^6
$^3P_1$	0.39	0.72	1.72	0.10	4.31	3.36	—	1.22×10^7	2.91×10^7	1.69×10^6
$^3P_0$	0.48	0.63	1.63	0.19	3.78	3.18	—	1.07×10^7	2.76×10^7	3.22×10^6
$^1D_2$	1.41	0.30	0.70	1.12	—	1.36	—	5.07×10^6	1.19×10^7	1.89×10^7

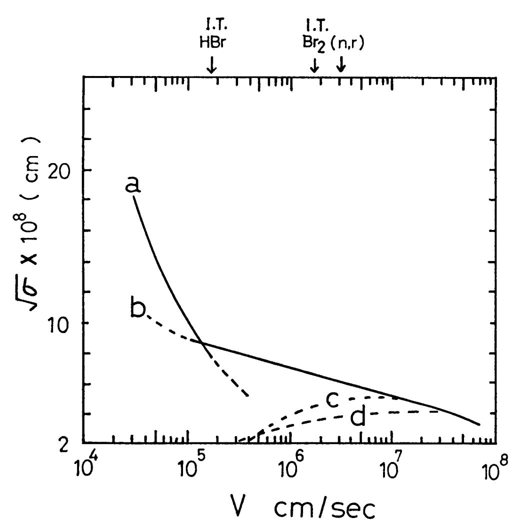


Fig. 4. Relationship between the velocity of Br^+ and cross sections for ion-molecule and charge neutralization reactions.
(a): Capture collision $Br^+ + CH^4 \rightarrow CH_4Br^+$,
(b): resonant charge transfer $Br^+ + Br \rightarrow Br^0 + Br^+$,
(c): $Br^+(^3P_2) + CH_4 \rightarrow Br + CH_4^+$,
(d): $Br^+(^3P_2) + Kr \rightarrow Br + Kr^+$.

Here, the charge transfer reaction of Br^+ with HBr is exothermic by 0.2 eV and is expected to occur efficiently from a consideration of the vibrationally-excited states of HBr. Even if neutralization occurs, the ^{80}Br cannot undergo any kinetic-energy dependent reaction leading to C–^{80}Br bond formation because its kinetic energy is not sufficient for H and/or Br substitution reactions to proceed. Thus, the present data can be explained in terms of competition between the charge neutralization and ion-molecule reactions.

On the other hand, Kazanjian and Libby[14)] have studied the reaction of IT-activated ^{80}Br using HBr as the source molecule in a solution of *n*-PrBr with 1% HBr, and found that the type of products and the organic yields are almost the same as those obtained in the (n,γ) experiment for a pure *n*-PrBr system. They explained these results assuming that the IT-activated ^{80}Br can acquire appreciable kinetic energy due to Coulomb repulsion during partial inter-molecular neutralization and then reacts in a manner identical to the hot bromine produced by the (n,γ) reaction.

However, the present experimental results indicate that even if the ^{80}Br atoms acquire kinetic energy to some extent by a similar process, this kinetic energy is not sufficient for hot reactions to occur.

Formation of $CH_2{}^{80}BrBr$ and $CH_3{}^{80}Br$ via *Thermal Ionic Processes.* It was indicated in the previous section that the $CH_2{}^{80}BrBr$ and $CH_3{}^{80}Br$ molecules are formed through thermal ionic reactions involving the $^{80}Br^+$ ion. From the energetics of the reactions, the capture collision complexes, such as $CH_4{}^{80}Br^+$ and $HBr^{80}Br^+$ will be formed first by the reactions

$$^{80}Br^+ + CH_4 \longrightarrow CH_4{}^{80}Br^+ \qquad (4)$$

and

$$^{80}Br^+ + HBr \longrightarrow HBr^{80}Br^+, \qquad (5)$$

since generally no activation energy is required for these reactions.

Although there is no direct evidence for the presence of these complexes in the present case, the presence of sticky collision complexes of a similar type has been confirmed in various alkyl halide and hydrocarbon systems by mass-spectroscopic studies.[29–31)] Henglein and Muccini have pointed out that the complex ion, CH_4I^+, had a lifetime longer than about 10^{-6} s.[32)] From a calculation of the lifetime of the $CH_4{}^{80}Br^+$ ion, using the equation proposed by Magee and Burton,[33)] it is expected that the $CH_4{}^{80}Br^+$ ion has a relatively long lifetime ($\approx 10^{-2}$ s).[34)]

As a possible explanation for the formation of $CH_2{}^{80}BrBr$ *via* thermal ionic processes in IT experiment involving the $^{80m}BrBr$–CH_4 system, Tachikawa[35)] has previously suggested that the $CH_4{}^{80}Br^+$ formed by Reaction 4 undergoes charge neutralization following decomposition to fragments, such as $CH_3{}^{80}Br$ and $CH_2{}^{80}Br$, and the $CH_2{}^{80}Br$ radical thus formed can easily be scavenged by Br_2 to form $CH_2{}^{80}BrBr$. If this is the case, the reaction

$$CH_2{}^{80}Br + HBr \longrightarrow CH_3{}^{80}Br + Br, \qquad (6)$$

which leads to $CH_3{}^{80}Br$ formation will be more energetically favorable than the reaction

$$CH_2{}^{80}Br + HBr \longrightarrow CH_2{}^{80}BrBr + H, \qquad (7)$$

which gives the $CH_2{}^{80}BrBr$ of this experiment using HBr as the source molecule, since Reaction 6 is exothermic by 6.8 kcal/mol, while Reaction 7 is endothermic by 24.9 kcal/mol.[36)] However Fig. 1 showed that the $CH_2{}^{80}BrBr$ yield was greater than that of $CH_3{}^{80}Br$ over a whole range of additive concentrations.

Similarly, it is thought that the $CH_2{}^{80}Br$ radical in the HCl-additive system reacts with HCl to form $CH_3{}^{80}Br$ in preference to the formation of $CH_2{}^{80}BrCl$, since the reaction

$$CH_2{}^{80}Br + HCl \longrightarrow CH_3{}^{80}Br + Cl \qquad (8)$$

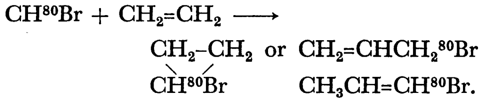
is less endothermic than the reaction

$$CH_2{}^{80}Br + HCl \longrightarrow CH_2{}^{80}BrCl + H. \qquad (9)$$

However, both $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ yields decreased almost linearly with increasing HCl concentration, as is seen in Fig. 2, and the $CH_2{}^{80}BrCl$ yield was greater than that of $CH_3{}^{80}Br$ at HCl concentrations above 0.35 mf. Therefore, the assumption that the $CH_2{}^{80}Br$ radical is present in this system as a precursor for $CH_2{}^{80}BrBr$ formation is unacceptable.

On the other hand, if $CH^{80}Br$ (bromocarbene) is present as a precursor, which can be produced through decomposition following the charge neutralization of $CH_4{}^{80}Br^+$ or through some other pathway, it is believed that the $CH^{80}Br$ present reacts readily with HBr and/or HCl to form $CH_2{}^{80}BrBr$ and $CH_2{}^{80}BrCl$, respectively, since these reactions are energetically very efficient.

In order to determine this point, an experiment using a CH_2=CH_2 additive was conducted. CH_2=CH_2 reacts instantaneously with $CH^{80}Br$ to form arylbromide or cyclo-bromopropane.[37)]



$$CH^{80}Br + CH_2{=}CH_2 \longrightarrow \underset{\displaystyle CH^{80}Br}{CH_2{-}CH_2} \text{ or } CH_2{=}CHCH_2{}^{80}Br \qquad (10)$$
$$CH_3CH{=}CH^{80}Br.$$

However, the radio gas chromatogram showed no radioactive peaks at retention times corresponding to these compounds and, therefore, the above assumption also unacceptable.

In the study of ion-molecule reactions using mass spectrometers, it has been observed that collision complex ions are formed effectively at high pressures and have ample opportunity to react with surrounding molecules during subsequent collisions.[38] Under the present experimental conditions, the possibility exsits that the $CH_4{}^{80}Br^+$ reacts with surrounding molecules giving the individual products.

Although no precise information is available concerning the ion-molecule reactions leading to $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ because of lack of knowledge concerning the chemical behaviour of complex ions at high pressure, the possibility of formation of $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ by ion-molecule reactions of $CH_4{}^{80}Br^+$ with CH_4 and/or HBr were evaluted from a thermodynamic viewpoint.

Loberg *et al.*[39] have studied reactions of thermal $^{123}I^+$ ions, formed by the $^{123}Xe \xrightarrow{EC,\beta^+} {}^{123}I$ process, in gaseous CH_4, and the formation of $CH_3{}^{123}I$ was explained in terms of the H^+-transfer reaction from the complex ion, $CH_4{}^{123}I^+$, to CH_4. Assuming that the intermediate $CH_4{}^{80}Br^+$ is a persistent collision complex rather than a molecular ion, we can estimate the ΔH°_{298} for Reaction 4. The potential energy (V) between $^{80}Br^+$ and CH_4, which is stored in the $CH_4{}^{80}Br^+$ ion as binding energy, is calculated to be 5.5 kcal/mol, using the relation,[40]

$$V = -\frac{1}{2}\cdot\frac{\alpha e^2}{r^4}, \tag{11}$$

where α is the polarizability of CH_4 (2.69×10^{-24} cm/mol),[25] r is the distance between ^{80}Br and CH_4 (3 Å),[41] and e is the charge. From this calculation, the heat of reaction for the reactions

$$CH_4{}^{80}Br^+ + CH_4 \longrightarrow CH_3{}^{80}Br + CH_5{}^+, \tag{12a}$$

and

$$CH_4{}^{80}Br^+ + HBr \longrightarrow CH_3{}^{80}Br + H_2Br^+, \tag{12b}$$

can be calculated roughly to be exothermic by 47 and 63 kcal/mol for ground-state Br^+, respectively. Therefore, it is conceivable that the H^+-transfer reactions from $CH_4{}^{80}Br^+$ to CH_4 and/or HBr are the principal reactions for the formation of $CH_3{}^{80}Br$.

On the other hand, it appears reasonable to assume that $CH_3{}^{80}Br$, $CH_2{}^{80}BrBr$, $CH_2{}^{80}BrCl$, and $CH_3CH{}^{80}BrCl$ are formed *via* the same precursor on the basis of the fact that both the $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ yields decrease linearly with increasing HCl concentration, and the decrement in their yields is almost equal to the increment of the $CH_2{}^{80}BrCl$ and $CH_3CH{}^{80}BrCl$ yields, as is shown in Fig. 2. As far as was observed, no ion-molecule reactions of $CH_4{}^{80}Br^+$ and $HBr{}^{80}Br^+$ with additives leading directly to the formation of these products are favored because of their high endothermicities. Of the various types of ion-molecule reactions concerning the intermediate ions, the following reactions are all exothermic, and probably one-step, reaction routes leading to the final products:

$$CH_4{}^{80}Br^+ + HBr \longrightarrow CH{}^{80}BrBr^+ + 2H_2 \quad (\Delta H^\circ = -45\ \text{kcal/mol}), \tag{13}$$

$$CH_4{}^{80}Br^+ + HCl \longrightarrow CH{}^{80}BrCl^+ + 2H_2 \quad (\Delta H^\circ = -28\ \text{kcal/mol}), \tag{14}$$

$$CH_4{}^{80}Br^+ + CH_2{=}CH_2 \longrightarrow CH_4 + CH_2CH_2{}^{80}Br^+ \quad (\Delta H^\circ = -88\ \text{kcal/mol}), \tag{15}$$

and

$$CH_4{}^{80}Br^+ + CH_2{=}CH_2 \longrightarrow CH_3{}^{80}Br^+ + CH_3CH_2 \quad (\Delta H^\circ = -29\ \text{kcal/mol}). \tag{16}$$

However, along which pathways the product ions thus formed lose their charges, and result in the end products appears to be rather complicated. If these ions lose their charge through free-electron capture, the high exothermicity resulting from these processes is dissipated in the form of internal energy of the molecule and probably results in the rupture of the C–^{80}Br bond. Therefore, these processes could not lead to the formation of $CH_3{}^{80}Br$, $CH_2{}^{80}BrBr$, and $CH_2{}^{80}BrCl$. Further, charge-transfer reactions of these ions with additives cannot occur because these reactions are also highly endothermic.

However, if these product ions lose their charges through charge-transfer reactions with the impurities present in the system or with the walls of the reaction vessel, and the energy defects (ΔE) for charge transfer are not so large as to lead to C–^{80}Br bond rupture, there is the possibility that the radicals and molecules in somewhat excited states thus formed are stabilized by collisions with their surroundings and undergo H-abstraction to give corresponding products.

Thus, ion-molecule reactions (13—16) may finally lead to the formation of $CH_2{}^{80}BrBr$, $CH_2{}^{80}BrCl$, $CH_3CH_2{}^{80}Br$, and $CH_3{}^{80}Br$, respectively, and the effect of additives on the yield distributions in Figs. 2 and 3 can be explained on the basis of these competitive reactions involving the precursor, $CH_4{}^{80}Br^+$.

Generally, it is known that thermal ions at high pressure form ion clusters containing several molecules held together by the electrostatic force between the ion and the molecules.[42–44] If this is the case, the energy ΔE deposited on the radical or molecule during the neutralization process can be effectively dissipitated to the cluster molecules. Even if the lifetimes of these excited radicals are relatively short, the radicals can be stabilized easily by collisions under liquid-like conditions,[33] and undergo H-abstraction reactions with surrounding molecules to form corresponding products, since the H-abstraction reactions are energetically most favorable. The above discussion is somewhat qualitative, but details of it will be elucidated upon the further accumulation of knowledge concerning ion-molecule reactions involving Br^+ in gases at atmospheric pressure.

The most prominent feature in Fig. 3 is the sharp increase in the $CH_3CH_2{}^{80}Br$ yield for a small amount of $CH_2{=}CH_2$. This can be explained on the basis of the thermal ^{80}Br reaction with $CH_2{=}CH_2$ (Reaction 17), in which ^{80}Br is produced through charge neutralization of $^{80}Br^+$ with HBr, CH_4 and/or $CH_2{=}CH_2$, thus

$$^{80}Br + CH_2{=}CH_2 \longrightarrow CH_2CH_2{}^{80}Br, \tag{17a}$$

$$CH_2CH_2{}^{80}Br + HBr \longrightarrow CH_3CH_2{}^{80}Br + Br. \tag{17b}$$

However, the gradual increase in the $CH_3CH_2{}^{80}Br$ yield at concentrations above 0.03 mf is attributable to reactions of ^{80}Br and $^{80}Br^+$ with $CH_2{=}CH_2$ and/or Reaction 15.

As Fig. 1 shows, the marked change in the yield curves is due to the additional formation of $CH_2{}^{80}BrBr$ for Kr and Xe concentrations greater than 0.6 mf. A similar increase in the CH_2BrBr yield was observed for a highly-moderated system in IT-experiments of the ^{80m}BrBr[19] and H^{82m}Br–CH$_4$ systems.[18] The collision frequency of ^{80}Br$^+$ ions with Kr and Xe atoms increases abruptly for concentrations over 0.6 mf. This additional formation of CH$_2$^{80}BrBr may thereby be explained in terms of (i) the increase in the number of ^{80}Br$^+$ ions with lower kinetic energies and of electronically-excited states, since the kinetic energy spectra of ^{80}Br$^+$ shifts to lower energies at high concentrations of Kr and Xe, and (ii) ion-molecule reactions involving complex ions containing inert gas molecules. If assumption (i) is valid, a similar increase in the CH$_3$^{80}Br yield will be observed, because CH$_3$^{80}Br formation greatly depends on the number of ^{80}Br$^+$ ions. However, no increase in the CH$_3$^{80}Br yield was observed, as can be seen in Fig. 1. Although no information on ion-molecule reactions of Br$^+$ with inert gases is available, there may be some reaction pathways for the additional formation of CH$_2$^{80}BrBr involving, presumably, the reactions of the Kr^{80}Br$^+$ (or Xe^{80}Br$^+$) ion with the surrounding molecules. However, the details of the reaction pathways leading to the additional formation of CH$_2$^{80}BrBr must await further experiments.

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34) The lifetime of collision complexes can be expressed by the equation[33]

$$\tau = \nu^{-1}\left(1-\frac{E_\beta}{E}\right)^{1-\alpha}$$

where E is the actual relative energy of the system, E_B is the binding energy of the two entities which form the complex, α is the number of vibrational degrees of freedom of the complex, and ν is a constant having dimensions of frequency and of the order of magnitude of a molecular vibrational frequency. From a rough approximation, $\tau_{CH_4Br^+}$ is calculated to be 2.0×10^{-2} s for $\nu=10^{13}$, $\alpha=12$, $E_B=0.24$ eV, and $E=E_B+kT$. (k is Boltzmann's constant and T is the absolute temperature (298 K)).

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