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Isomeric Transition-activated ^{80}Br and ^{82}Br Reactions in the Gaseous CH_3Br–HBr System

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The isomeric transition(IT)-activated ^{80}Br and ^{82}Br reactions in the gaseous $H^{80m}Br$–CH_3Br and $H^{82m}Br$–CH_3Br systems have been compared and the roles of the charge and kinetic energy imparted to ^{80}Br and ^{82}Br in recombina tion reactions studied using a Kr moderator. The products CH_3Br, CH_2Br_2, $CHBr_3$, and CH_3CH_2Br in both reactions are only formed *via* thermal ionic processes. This differs from the ^{82m}BrBr–CH_3Br system, in which the reaction products are only formed through excess kinetic energy processes. The difference between the two reactions has been explained on the basis of the cross sections for charge neutralization and ion molecule reactions of Br^+ ions as a function of the kinetic energy initially imparted to the ^{80}Br or ^{82}Br atoms. An isotope effect has been observed between the IT-activated ^{80}Br and ^{82}Br reactions with CH_3Br, and attributed to the difference in the decay modes of ^{80m}Br and ^{82m}Br. Furthermore, the analysis of product yields due to the successive internal conversion process in ^{80m}Br suggested that the second Auger process from the excited ^{80}Br occurs in a liquid-like condition such as ion-clusters.

Generally, the radioactive bromine atoms produced by a variety of nuclear transformations have an appreciable recoil kinetic energy and charges. Many investigations have been made in order to evaluate and interpret the kinetic energy and charges in the recombination reactions of radioactive bromine atoms in the gas phase.[1–11] It has been demonstrated that the formation of the C–*Br bond by the reactions of (n,γ)[11–13] and/or fission[14] activated energetic bromine with CH_4 proceeds principally through kinetic energy processes, and that not only kinetic energy but also the charges of IT-activated ^{80}Br and ^{82}Br in the $^{80m}Br_2$ and/or $^{82m}Br_2$–CH_4 system play important roles in determining the chemical reactions of these atoms.[5–9] Furthermore the authors have recently reported that IT-activated ^{80}Br and ^{82}Br in the $H^{80m}Br$–CH_4 and $H^{82m}Br$–CH_4 systems undergo only thermal ionic reactions (kinetic energy independent).[1–4] Since the kinetic energy imparted to the ^{80}Br and ^{82}Br by molecular explosion processes following the internal conversion in HBr molecule is 0.75 eV on average,[15] being very small compared with that (40.3 eV)[16] for the IT in $^{80m}Br_2$ and/or $^{82m}Br_2$, this indicates that the organic yields by thermal ionic processes are largely dependent on the kinetic energy of the positively charged $*Br^+$ ion.

This paper will report the contribution of the charge and kinetic energy of IT-activated ^{80}Br and ^{82}Br to the organic product yields in the $H^{80m}Br$–CH_3Br and $H^{82m}Br$–CH_3Br systems, by comparing the results previously reported for the reactions of CH_3Br with *Br activated by (n,γ)[11] and IT[11,17,18] in Br_2. An isotope effect between thermal ionic ^{80}Br and ^{82}Br reactions has been found in the $H^{80m}Br$–CH_4 and $H^{82m}Br$–CH_4 systems,[1] and a similar isotope effect between the IT-activated ^{80}Br and ^{82}Br reactions with CH_3Br using HBr as a source molecule will be reported.

Experimental

Materials. The listed purities of gaseous reagents, supplied by Takachiho Chemical Co., were 99.95% for Kr and 99.5% for CH_3Br. Krypton gas was used without further purification and CH_3Br was purified by a vacuum distillation technique so that the impurity was reduced below less than 0.1% for gas chromatographic analysis. The ^{80m}Br and ^{82m}Br labeled HBr were prepared by procedures described previously.[1,2,4]

Sample Preparation. The gaseous samples were prepared in the same manner as reported elsewhere.[1,2,4] The reaction mixtures were sealed in cylindrical Pyrex glass ampoules or breakable glass tubes using a vaccum line. The ratio of HBr to CH_3Br and the total pressure were maintained constant at 0.1 ± 0.01 and 660 ± 30 mmHg,[†] respectively, throughout the series of gas phase experiments. In the solid phase experiments, the reaction gases of HBr (^{80m}Br-labeled) (200 mmHg) and CH_3Br (700 mmHg) were mixed thoroughly by the freeze-thaw method and solidified at liquid nitrogen temperature.

Product Analysis and Yield Determination. The details concerning product analysis and yield determination have been reported elsewhere.[1,2,4]

The experimental errors due to the standard deviation for counting statistics and chemical procedures were estimated as 5—9% for the organic yields in the ^{80m}Br-experiments and less than 10% for those in the ^{82m}Br-experiments.

Results and Discussion

Role of Charge and Kinetic Energy of IT-Activated ^{80}Br and ^{82}Br in Product Formation. The conventional method for discriminating between the charge contribution and the kinetic energy of bromine in the reactions of product formation is the addition of an inert gas to the system. The yield of products formed through kinetic energy processes is expected to decrease by the addition of an inert gas due to the removal of Br kinetic energy by the moderation effect. Hence, a yield which is insensitive to the addition of an inert gas is considered to be due to thermal ionic processes.

Krypton was used as the moderator which has an ionization potential of 13.99 eV, (Br (11.84 eV)), and a mass almost equal to that of Br. Kr therefore appears to be the most effective moderator for energetic Br atoms and appropriate for distinguishing between the yields

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[†] 1 mmHg≈133.3 Pa.

from kinetic processes and thermal ionic processes.

Table 1. Percentage of ^{80}Br stabilized in organic combinations in a gaseous mixture of HBr, CH_3Br, and Kr[a)]

X_{Kr}[b)]	Product yield % CH_3Br	Product yield % CH_2Br_2	Product yield % Other	Org. yield %
0	2.6±0.2	1.3±0.1	0.8±0.1	4.8±0.2
0	2.4±0.1	1.5±0.1	0.6±0.1	4.5±0.2
0	—	—	—	4.5±0.2
0	2.5±0.1	1.3±0.1	0.5±0.1	4.3±0.4
0.1	2.1±0.2	1.4±0.1	0.6±0.1	4.1±0.2
0.1	2.4±0.2	1.4±0.1	0.8±0.1	4.6±0.2
0.1	2.4±0.2	1.3±0.1	0.7±0.1	4.4±0.3
0.2	2.3±0.1	1.3±0.1	0.8±0.1	4.4±0.4
0.3	2.5±0.2	1.3±0.1	0.5±0.1	4.2±0.4
0.3	—	—	—	4.1±0.4
0.4	2.4±0.2	1.3±0.1	0.8±0.1	4.5±0.3
0.5	2.5±0.2	1.5±0.1	0.6±0.1	4.6±0.3
0.5	—	—	—	4.4±0.3
0.6	2.2±0.1	1.7±0.1	0.4±0.1	4.3±0.2
0.7	1.7±0.1	2.1±0.2	0.3±0.1	4.2±0.3
0.7	—	—	—	4.3±0.3
0.8	1.9±0.1	2.2±0.2	0.5±0.1	4.6±0.3

a) $H^{80m}Br/CH_3Br=0.1\pm0.01$. b) Mole fraction of krypton.

Table 2. Percentage of ^{82}Br stabilized in organic combinations in a gaseous mixture of HBr, CH_3Br, and Kr[a)]

X_{Kr}[b)]	Product yield % CH_3Br	Product yield % CH_2Br_2	Product yield % Other	Org. yield %
0	3.9±0.2	1.1±0.1	0.3±0.1	5.3±0.2
0	3.9±0.3	1.3±0.1	0.2±0.1	5.4±0.2
0	—	—	—	5.4±0.3
0	3.5±0.2	1.4±0.1	0.1±0.1	4.9±0.2
0.1	3.8±0.2	1.1±0.1	0.2±0.1	5.1±0.2
0.2	—	—	—	5.0±0.4
0.2	3.4±0.3	1.4±0.1	0.2±0.1	5.1±0.3
0.3	3.8±0.3	1.4±0.1	0.2±0.1	5.4±0.3
0.3	3.6±0.3	1.3±0.1	0.4±0.1	5.3±0.2
0.3	—	—	—	5.5±0.5
0.4	3.7±0.2	1.2±0.1	0.3±0.1	5.2±0.2
0.5	3.8±0.3	0.9±0.1	0.1±0.1	4.8±0.2
0.5	3.5±0.3	1.5±0.1	0.3±0.1	5.3±0.2
0.6	—	—	—	5.0±0.4
0.6	3.7±0.3	1.2±0.1	0.2±0.1	5.1±0.3
0.7	—	—	—	5.4±0.5
0.7	3.4±0.3	1.3±0.1	0.3±0.1	5.0±0.2

a) $H^{82m}Br/CH_3Br=0.1\pm0.01$. b) Mole fraction of krypton.

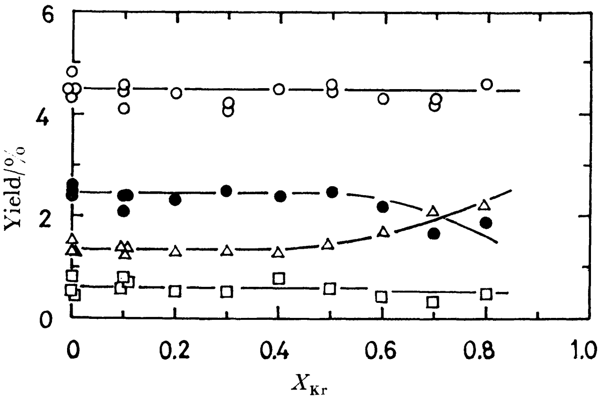

Fig. 1. Effect of Kr additive on the yield distribution in the $H^{80m}Br-CH_3Br$ system.
$HBr/CH_3Br=0.1\pm0.01$, ○: organic yield, ●: $CH_3{}^{80}Br$, △: $CH_2{}^{80}BrBr$, □: other.

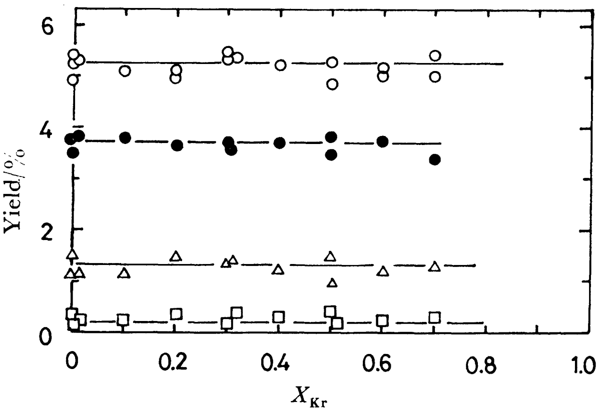

Fig. 2. Effect of Kr additive on the yield distributions in the $H^{82m}Br-CH_3Br$ system.
$HBr/CH_3Br=0.1\pm0.01$, ○: organic yield, ●: $CH_3{}^{82}Br$, △: $CH_2{}^{82}BrBr$, □: other.

The effect of Kr as an additive on the product yield distributions in the $H^{80m}Br-CH_3Br$ and $H^{82m}Br-CH_3Br$ systems is summarized in Tables 1 and 2, and also illustrated in Figs. 1 and 2. The ^{80}Br and ^{82}Br labeled CH_3Br, CH_2Br_2, C_2H_5Br, and $CHBr_3$ were identified as the reaction products in both systems. The products were similar to those found previously for (n,γ)-[11)] and IT-[17,18)] activated ^{80}Br and ^{82}Br reactions in the Br_2-CH_3Br system. The C_2H_5Br and $CHBr_3$ yields are listed as the other product yield (the 4th column) in the Tables. The $C_2H_5{}^{82}Br$ yields were less than 0.1% in most cases, while the $CHBr_2{}^{80}Br$ yields were approximately 60 to 80% of the other yield. As is shown in Figs. 1 and 2, the product yield distributions was not altered by the addition of Kr in the range 0—0.5 mole fraction indicating that the reaction products in both systems are formed only through thermal ionic processes, similar to the results observed in the $H^{80m}Br-CH_4$[1)] and $H^{82m}Br-CH_4$[2)] systems. The thermal ionic yields of CH_3Br and CH_2Br_2 at 0 mole fraction of Kr were 3.8% and 1.3% for the ^{82m}Br system, and 2.4% and 1.5% for the ^{80m}Br system, respectively.

Oate *et al.*,[17)] and Okamoto and Tachikawa[18)] have reported that the IT-activated ^{82}Br in the $^{82m}BrBr-CH_3Br$ system undergoes only kinetic energy dependent reactions. Similarly, Spicer and Gordus[11)] have pointed out that the (n,γ)-activated ^{80}Br in the same system reacts to give the products through kinetic energy processes. The present results are however largely different from the above earlier findings. The present

Table 3. Percentage yields of organic products due to kinetic and thermal ionic processes in the IT and (n,γ) experiments[a)]

		$H^{82m}Br$–CH_3Br[b)]	$H^{80m}Br$–CH_3Br	$^{82m}BrBr$–CH_3Br		(n,γ)-Activated[e)] ^{80}Br–CH_3Br
E_{max}/eV		1.3	1.3	158		417
Org. yield/%		5.3	4.5	2.3[c)]	5.9[d)]	4.0
Kinetic process	CH_3Br/%	0	0	1.5[c)]	4.6[d)]	3.0
	CH_2Br_2/%	0	0	0.8[c)]	1.3[d)]	1.0
Thermal ionic process	CH_3Br/%	3.8	2.4	0	0	0
	CH_2Br_2/%	1.3	1.4	0	0	0

a) HBr or $Br_2/CH_3Br = 0.1 \pm 0.01$. b) Present work. c) Ref. 17. d) Ref. 18.
e) Ref. 11, $Br_2 = 0.0254$ mole fraction.

authors have pointed out that the product yields due to both kinetic and thermal ionic processes largely depend on the Br kinetic energy acquired initially as results of a nuclear event.[1,2)] The maximum kinetic energies (E_{max})[15)] of Br for (n,γ) and IT in HBr and Br_2 are shown in Table 3. In contrast to the present results, there is no contribution of thermal ionic reaction to the product formation in both (n,γ)[11)] and IT[17,18)] in Br_2 because of the large values of E_{max}. This difference suggests that there is a close relationship between the kinetic energy of Br and the yields due to both thermal ionic and kinetic energy processes. The yields due to thermal ionic reactions are largely dependent on the number of Br^+ ions reaching the thermal energy region by escaping from the charge neutralization.[1–4)] Therefore it is of paramount importance to estimate the cross sections for charge neutralization and ion-molecule (capture collision) reactions as a function of the kinetic energy of Br^+ in the present systems. These relationships are shown in Fig. 3. The cross sections (σ) for capture collision between Br^+ and CH_3Br were calculated from the following equation,[20)] which is applicable for ions with a kinetic energy <1 eV.

$$\sigma = (2\pi e/v)(\alpha/\beta) + (2\pi e/v^2)(\mu/m)$$

where v is the relative velocity of Br^+, e the charge on the ion, α the polarizability of CH_3Br (2.8×10^{-24} cm^3/mol),[21)] m the mass of Br^+, β the reduced mass of collision pair, and μ the dipole moment of CH_3Br (1.45×10^{-18} esu. cm).[22)] The cross sections for resonant charge transfer reaction between Br^+ and Br, which are the highest of several types of charge neutralization concerning Br^+, were obtained by interpolating the resonant charge transfer cross sections at intermediate impact velocity (10^5—10^8 cm/s) as calculated by Rapp and Francis using the semi-classical impact-parameter method.[23)] Furthermore, V_{max}, giving the maximum cross sections for asymmetric charge transfer reactions of ground state Br^+ with CH_3Br, Kr, and HBr, were calculated from the "adiabatic rule."[24)] V_{max} for CH_3Br is 2.2×10^7 cm/s, 3.5×10^6 for HBr, and 3.6×10^7 for Kr. The threshold velocity (V_{th})[25)] of Br^+ for endo-energetic charge transfer reaction with Kr was obtained as 2.3×10^5 cm/s. The dotted line in Fig. 3, showing the velocity dependence of cross sections for the charge transfer reactions of Br^+ with Kr, is drawn on the basis of values of V_{max} and V_{th}, assuming that the asymmetric charge transfer cross section is close to that for the resonance charge transfer at velocities above V_{max}.[23)] The charge transfer reactions of the ground state Br^+ with HBr and CH_3Br are exothermic, 0.2 and 1.3 eV respectively. In consideration of the vibrationally excited states of those molecules, it is expected that the charge neutralization of Br^+ takes place effectively, and its cross section is close to that of the resonant charge transfer between Br^+ and Br. The thus formed neutral Br cannot however enter into chemical combination *via* kinetic energy processes because the kinetic energy is not sufficient to substitute for H and/or Br in the CH_3Br molecule. The values of E_{max} for (n,γ) and IT in HBr and Br_2 are shown by arrows in the upper abscissa of the Fig. 3.

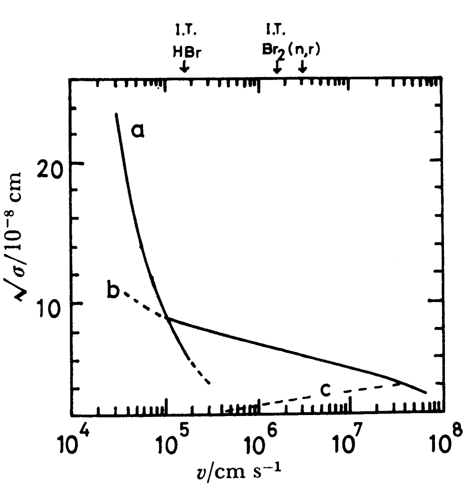

Fig. 3. Relationship between the velocity of $^*Br^+$ and cross sections for capture collision and charge neutralization.
a: Capture collision; $^*Br^+ + CH_3Br \rightarrow CH_3Br^*Br^+$, b: resonant charge transfer; $^*Br^+ + Br \rightarrow {}^*Br + Br^+$, c: $Br^+(^3P_2) + Kr \rightarrow Br + Kr^+$.

Figure 3 indicates that the charge transfer reactions occur predominantly in the energy range >1 eV, while the formation of the capture collision complex is favoured at energies <1 eV. It is readily seen therefore that the Br atoms produced by (n,γ) and IT in Br_2 undergo charge neutralization before reaching the reaction range because of the large values of E_{max}. The average kinetic energy of Br in the case of IT in HBr is only 0.75 eV,[15)] which is very small compared with that for (n,γ) and IT in Br_2. It is presumed therefore that the formation of the capture collision complex competes with the charge neutralization under the present experimental systems using HBr as a source molecule, and a part of *Br$^+$ which escapes charge neutralization reacts with CH$_3$Br to form the capture collision complex, CH$_3$Br*Br$^+$. This complex ion is thought to be a precursor for product formation *via* a thermal ionic process as will be described in the following section.

Isotope Effect in the Reactions of IT-Activated ^{80}Br and ^{82}Br with CH$_3$Br. As Figs. 1 and 2 illustrate, the organic yields were a little larger in the H^{82m}Br–CH$_3$Br system than in the H^{80m}Br–CH$_3$Br system. An outstanding difference between the results in both systems was found in the yield distribution of individual products. The yield ratios of CH$_3$Br to CH$_2$Br$_2$ were 3.0±0.5 for ^{82m}Br and 1.8±0.2 for ^{80m}Br at 0 mole fraction of Kr. Evidently there is an isotope effect between the thermal ionic reactions of IT-activated ^{80}Br and ^{82}Br in the gaseous HBr–CH$_3$Br system. The mass difference between ^{80}Br and ^{82}Br cannot be considered to be responsible for the above isotope effect and therefore the isotope effect may be attributed to the differences in the decay modes of ^{80m}Br and ^{82m}Br.[19)]

The de-excitation of ^{82m}Br to the ground state occurs in a single step and is fully converted. The ^{80m}Br however is de-excited in two successive steps through an intermediate state with a half-life of 7.4 ns; the first step is fully converted and the second, partially converted (61%). Since the first de-excitation step of ^{80m}Br is essentially the same as that of ^{82m}Br, the charge and kinetic energy distribution on the excited ^{80}Br should be identical with those on the ^{82}Br. Furthermore, the excited ^{80}Br undergoes successive de-excitation to the ground state; 61% of the excited ^{80}Br is de-excited through the second internal conversion process, while the remaining 39% is directly de-excited to the ground state by means of a 37 keV gamma-ray emission. The chemical effect due to this gamma-emission is however considered to be negligible since the kinetic energy achieved on the ^{80}Br is of the order of 10^{-2} eV. On the basis of the foregoing the reaction processes of IT-activated ^{80}Br may be classified into two types:[1,3)]

Process (A); 39%, internal conversion (IC)
+ 37 keV gamma-ray emmission

Process (B); 61%, IC + IC

The chemical effects due to process (A) are essentially identical with those of the ^{82m}Br, and therefore the yields due to process (A) are equal to 39% of those obtained in the ^{82m}Br. Hence the normalized yields due to process (B) may be calculated by the following equation.

$$\text{Yield/\% due to process (B)} = 100/61\,(^{80m}\text{Br-yield} - 39\% \text{ of } ^{82m}\text{Br-yield})$$

and are depicted in Fig. 4. The isotope effect in both systems may be elucidated by comparing the yields due to process (B) with those due to the ^{82m}Br.

As Fig. 4 shows, the CH$_3{}^{80}$Br and CH$_2{}^{80}$BrBr yields were constant in the range 0—0.6 mole fraction of Kr, indicating that the products due to process (B) are also formed through kinetic energy independent processes. The yield ratio of CH$_3$Br to CH$_2$Br$_2$ was between 0.9 and 1.3 for 0.6 mole fraction of Kr, being largely different from that due to the ^{82m}Br (3.0). The other product yields due to process (B) were much higher compared to those due to the ^{82m}Br.

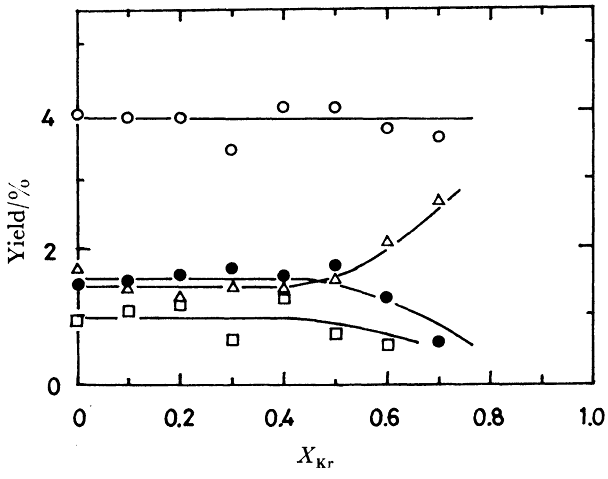

Fig. 4. Effect of Kr additive on the product yield distributions due to process (B).
○: Organic yield, ●: CH$_3{}^{80}$Br, △: CH$_2{}^{80}$BrBr, □: other.

Assuming the excited ^{80}Br does not react within its life time (1.1×10^{-8} s), and/or assuming that the excited ^{80}Br forms chemical combinations, such as H*Br, H$_2{}^*$Br, H*Br$^+$, *etc.*, the chemical effect due to the successive IC (process B) should also be identical to that due to the ^{82m}Br because the following IC leads to an additional build-up of the charge on the free atom, and/or the kinetic energy of ^{80}Br resulting from the molecular explosion in such a species is very small. In this case, an isotope effect will be absent.

Assuming the excited ^{80}Br reacts with the surroundings to form a C–*Br and/or Br–*Br combination prior to the second IC, the resulting ^{80}Br by successive IC acquires an appreciable kinetic energy and undergoes kinetic energy dependent reactions. As Fig. 4 illustrates, the experimental results show that there is no contribution to the yield by excess kinetic energy processes, *i.e.*, these chemical species will not be present in process (B). The existence of an isotope effect suggests that the life-time of the excited ^{80}Br$^+$ (1.1×10^{-8} s) is sufficiently long to form some chemical species containing the excited ^{80}Br$^+$. The environment surrounding the excited ^{80}Br is thought to be different from those for the ions present as single species. Accordingly, it has been concluded that the ^{82}Br$^+$ and excited ^{80}Br$^+$ undergo capture collision complex formation (Reactions 1a and 2). Typically this type of ion-molecule reaction does not require any activation energies.[1,2)]

$$^*\text{Br}^+ + \text{CH}_3\text{Br} \longrightarrow \text{CH}_3\text{Br}^*\text{Br}^+ \qquad (1a)$$

$$^*\text{Br}^+ + \text{HBr} \longrightarrow \text{HBr}^*\text{Br}^+ \qquad (2)$$

Furthermore, the thermal complex ions have an ample opportunity to interact with the surroundings within the life-time of the excited ^{80}Br[26)] since the life-time is relatively long compared to the collision time under the present experimental conditions.[27)]

It is generally known that at high pressure thermal ions preferentially form ion-clusters by electro-static forces.[28-30] The authors have demonstrated that the isotope effect observed in the $H^{80m}Br$–CH_4 and $H^{82m}Br$–CH_4 systems may be explained by introducing the above cluster model.[1,3] The complex ions formed by the above reactions undergo successive attachment reactions with surrounding molecules to form ion-clusters, and the second IT in process (B) proceeds in a liquid-like condition such as ion-clusters. Thus the chemical effect due to process (B) is expected to be very similar to that in the condensed phase. Table 4 shows the results obtained in the solidified $H^{80m}Br$–CH_3Br system. The yield ratio of CH_3Br to CH_2Br_2 was 0.8, which compare favourably with the values of 0.9—1.3 for process (B). This indicates that the chemical effect due to process (B) is very similar to that in the solid phase, which qualitatively supports the above cluster model. The large amount of energy evolved from the second molecular explosion in process (B) is dissipated to the rigid sphere of the cluster and used in the formation of ions, radicals and excited species, which contribute directly or indirectly to individual product formation.

Table 4. The yield ratio of individual products relative to CH_3Br in the solidified $H^{80m}Br$–CH_3Br system

Product	CH_3Br	C_2H_5Br	CH_2Br_2	$C_2H_4Br_2$	$CHBr_3$
Relative yield ratio	1	<0.1	1.3	0.2	0.4

There is little precise information on the ion-molecule reactions leading to the $CH_3{}^*Br$ and $CH_2Br{}^*Br$ in process (A) because of a lack of knowledge concerning the chemical behaviour of the complex ion ($CH_3Br{}^*Br^+$) under high pressure. The following reactions are considered to be possible reaction routes for the formation of the above products from thermodynamics.

$$CH_3Br{}^*Br^+ \longrightarrow CH_3{}^*Br^+ + Br \qquad (1b)$$

$$CH_3Br{}^*Br^+ + HBr \longrightarrow CH_2Br{}^*Br + H_2Br^+ \qquad (3)$$

$$CH_3Br{}^*Br^+ + CH_3Br \longrightarrow CH_2Br{}^*Br + CH_4Br^+ \qquad (4)$$

The heat of reaction for the above reactions has been calculated approximately as 29, 65, and 87 $\text{kcal}_{\text{th}}^{\dagger\dagger}$/mol (exothermic) for Reactions 1a, 1b, 3, and 4, respectively.[32]

The second IC in process (B) proceeds *via* an ion-cluster, so that the molecular explosion following the second IC is responsible for the chemical effect due to process (B). Although no information on the IT-activated ^{80}Br reactions under such specific conditions is available, both ion-molecule reactions and the reactions concerning radicals and excited species produced in the clusters appear to be responsible for product formation in analogy with the results previously obtained in the $H^{80m}Br$–CH_4 system.[1,3] The details of such reactions must however await further analysis.

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