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Effect of Inorganic Additives on the Reactions of Isomeric Transition-Activated ^{80}Br and ^{82}Br in the Gaseous HBr–CH_4 System

Kenjiro KONDO* and Masuo YAGI

Laboratory of Nuclear Science, Tohoku University, Tomizawa, Sendai 982

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Synopsis. The effects of various inorganic additives with and without dipole moments on the product yield distributions have been examined in the CH_4–H^{80m}Br and CH_4–H^{82m}Br systems. Indications were that the ion-clusters formed in the reactions of IT-activated ^{80}Br and ^{82}Br play an important role in determining individual product yield distributions.

It has been reported that isomeric transition (IT)-activated ^{80}Br and ^{82}Br undergo only thermal ionic reactions in the H^{80m}Br–CH_4 and H^{82m}Br–CH_4 systems, and that the large isotope effect observed can be explained in terms of the difference in decay schemes between ^{80m}Br and ^{82m}Br.[1,2] The γ-transition of ^{82m}Br to the ground state is attained in a single transition and fully converted. The ^{80m}Br has two successive transitions through the intermediate with a half-life of 7.4 ns, and the first stage is fully converted and the second is partially converted (61%). The organic yield of ^{80m}Br therefore can be classified into the following two types;[2] Processes A (39%): internal conversion (IC)+37 keV γ-ray emission; Process B (61%): IC+IC. The chemical effect due to Process A is essentially identical to that of ^{82m}Br. The above isotope effect has been explained by assuming that complex ions CH_4Br^+ or $HBrBr^+$ produced *via* the thermal ionic process interact with the surroundings to form an ion-cluster, and that the second IC in Process B occurs in such a cluster.[2] This has been qualitatively supported from the experimental results obtained in the condensed phase.[2] The aim of this paper is to confirm the presence of ion-clusters in the reactions of IT-activated ^{80}Br and ^{82}Br in the CH_4–H^{80m}Br and CH_4–H^{82m}Br systems by the addition of polar and/or nonpolar molecules, since the polarizability of molecules is one of the most important controlling factors in ion-cluster formation. The ratio of HBr to CH_4 and total pressure in all samples were kept constant at 0.1±0.01 and 660±30 mmHg respectively. Details of experimental procedures may be found elsewhere.[1-3]

Results and Discussion

The effects of inorganic additives (0.3 mf) on the yield distribution in both systems are shown in Table 1. Here, X and Y in the Table are CH_2BrCl and $CH_3CHBrCl$ respectively in the HCl additive experiment. In the case of the H_2S additive, X is thought to be CH_2BrSH. The minor products in low yields ($\approx$0.1%) in other additive experiments have not been identified. CH_3Br yields were larger with ^{80m}Br than ^{82m}Br, while CH_2Br_2 yields with ^{82m}Br were much greater than with ^{80m}Br. Table 2 shows the normalized yields Y due to Process B, which have been calculated by the following equation:[2]

$$Y(\%) = \frac{100}{61}(^{80m}\text{Br-yield} - 0.39 \text{ of } ^{82m}\text{Br-yield}).$$

As previously reported, the isotope effect in both systems can be elucidated by comparing the yields due to Process B with ^{82m}Br yields.[2] The yield ratios of CH_3Br to CH_2Br_2 were 0.2—0.7 for ^{82m}Br and more than unity for Process B. CH_3Br yields in both systems were not affected by the addition of non-polar molecules without dipole moments, while a slight decrease in CH_3Br yields was observed in the system of polar ad-

TABLE 1. EFFECT OF INORGANIC ADDITIVES ON THE YIELD DISTRIBUTION OF ORGANIC PRODUCTS FORMED BY THE IT-ACTIVATED ^{80}Br AND ^{82}Br REACTIONS WITH CH_4
(H^{80m}Br or H^{82m}Br/CH_4=0.1±0.01, total pressure: 660±30 mmHg)

Additive (0.3 mf)	Org. yield (%)		CH_3Br (%)		X (%)		CH_2Br_2 (%)		Y (%)	
	^{80m}Br	^{82m}Br	^{80m}Br	^{82m}Br	^{80m}Br	^{82m}Br	^{80m}Br	^{82m}Br	^{80m}Br	^{82m}Br
none	4.2	4.5	1.6	0.8	0	0	2.6	3.7	0	0
Kr	3.9	4.4	1.4	0.7	0	0	2.6	3.7	0	0
Xe	4.0	4.2	1.6	0.9	0	0	2.4	3.3	0	0
CO_2	4.0	4.1	1.5	0.7	0.1	0.1	2.4	3.3	0	0
O_2	4.1	4.1	1.5	0.9	0.1	0.1	2.3	3.0	0.2	0.1
N_2	4.0	4.3	1.6	0.9	0	0	2.4	3.4	0	0
CO	2.9	2.6	1.3	0.9	0.1	0	1.4	1.7	0.1	0
HBr	3.1	3.1	1.3	0.5	0	0	1.8	2.6	0	0
H_2S	2.9	4.2	1.1	0.5	1.3	2.6	0.4	1.1	0.1	0
HCl	4.2	4.0	1.2	0.7	1.0	1.5	1.5	1.8	0.5	0
SO_2	2.1	2.2	1.5	0.8	0.1	0.1	0.5	1.2	0	0.1

The experimental errors were 7—15% for ^{80m}Br and less than 10% for ^{82m}Br.

Table 2. Effect of additives on the yield distribution of organic products formed *via* process (B) in the $H^{80m}Br$-CH_4 system

($H^{80m}Br/CH_4=0.1\pm0.01$, total pressure: 660 ± 30 mmHg)

Additive (0.3 mf)	Ionization potential (eV)	Dipole moment (Debye)	Org. yield (%)	CH_3Br (%)	X (%)	CH_2Br_2 (%)	Y (%)
none	—	—	4.0	2.1	0	1.9	0
Kr	13.9	0	3.7	1.8	0	1.9	0
Xe	12.1	0	3.8	2.0	0	1.8	0
CO_2	14.1	0	3.9	2.0	0.1	1.8	0
O_2	12.5	0	4.1	1.9	0.1	1.9	0.2
N_2	15.5	0	3.8	2.0	0	1.8	0
CO	14.1	0.112	3.0	1.6	0.1	1.2	0.1
HBr	11.6	0.82	3.1	1.8	0	1.3	0
H_2S	10.4	0.97	2.1	1.5	0.5	0	0.1
HCl	13.8	1.08	4.4	1.6	0.7	1.3	0.8
SO_2	13.1	1.47	2.0	1.9	0.1	0	0
Br	11.8	0					
CH_4	12.9	0					

ditives with dipole moments. CH_2Br_2 yields in both systems showed a sharp decrease by the addition of polar molecules, contrary to the results for non-polar additives.

The $^{80}Br^+$ and $^{82}Br^+$ ions formed by IT processes react with CH_4 and/or HBr to form collision complex ions, CH_4Br^+ and/or $HBrBr^+$ at first, as has been reported previously.[1,2] Further, these thermal ions are thought to have ample opportunity to form ion-clusters. Loeb has proposed the following equation indicating that an ion-cluster is formed when the potential energy between the ion and molecule is greater than the relative kinetic energy of the ion,[4)]

$$\frac{(D-1)\beta}{8\pi N r^4}/KE \geq 1,$$

where D is the dielectric constant of additive molecules, N, the number of molecules per cm^3, r, the distance between the ion and molecule, β, the statistical weight factor and KE, the relative kinetic energy of the ion. The ratio was found to be 3.4 for CH_4 at 660 mmHg ($D=1.00094$, $r=3\times10^{-8}$ cm[1)] and 0.5 assumed for β) and therefore it is reasonable to presume the formation of ion-clusters in the ^{82}Br and ^{80}Br reactions. Since the potential energies between the ion and nonpolar additives are smaller than for CH_4, and moreover the concentration of CH_4 is larger than those of the additives, the ion-cluster thus formed in the case of nonpolar additives contains mainly CH_4 and/or HBr molecules. In addition polar additives play an important role in cluster formation since the potential energies between the ion and additives are much greater than those for nonpolar additives. Consequently, the ion-cluster thus formed contains an appreciable number of additives as constituents.

The formation of $CH_3{}^{82}Br$ in the CH_4-$H^{82m}Br$ system has been explained energetically by the H^+ transfer reaction from $CH_4{}^{82}Br^+$ to CH_4 and/or HBr as previously reported.[2)]

Similarly, the fact that $CH_3{}^{82}Br$ yields were almost constant in the present experiment can be explained on the basis of the exothermicity of the H^+ transfer reaction from $CH_4{}^{82}Br^+$ to CH_4 and/or additives. On the other hand, the $CH^{82}BrBr^+$ ion formed by the ion-molecule reaction of $CH_4{}^{82}Br^+$ with HBr is considered to be a precursor for $CH_2{}^{82}BrBr$. $CH^{82}BrBr$ formed by charge neutralization of $CH^{82}BrBr^+$ undergoes H-abstraction to give $CH_2Br^{82}Br$.[1,2)] In the presence of polar additives, $CH_4{}^{82}Br^+$ is effectively surrounded by these molecules in the process of ion-cluster formation, therefore the concentration of HBr in the vicinity of $CH_4{}^{82}Br^+$ decreases, and eventually the above reaction leads to the $CH_2{}^{82}BrBr$ formation being hindered by the addition of polar molecules. Thus the remarkable decrease in $CH_2{}^{82}BrBr$ yields in polar additives can be explained qualitatively.

The second IC in Process B proceeds in an ion-cluster like a condensed phase. Therefore, the molecular explosion following the second IC is responsible for the chemical effect due to Process B. Although no precise information on the IT activated ^{80}Br reactions under such condition is available, both the ion-molecule reactions and primary radical recombinations in the clusters appear to be responsible for product formation. Previously it has been pointed out that radical reactions are not concerned with the formation of CH_3Br and CH_2Br_2.[1,2)] This does not always mean however that the primary recombination involving ^{80}Br-radicals does not occur. In Process B that $CH_3Br > CH_2Br_2$ may be qualitatively interpreted by the above assumption since similar results were obtained in the solid CH_4-$H^{80m}Br$ system.[2)] Furthermore, it is assumed that ion-molecule reactions also contribute to product formation, judging from the similarity of reaction products in both ^{82m}Br and Process B. The effect of additives on the CH_3Br and CH_2Br_2 yields in Process B may be explained in terms of the difference in concentration of polar and nonpolar molecules contained in the clusters in the same manner as ^{82m}Br. However the details of the reaction mechanisms must await until further experiments are conducted.

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