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Comparison of the Recoil Reactions in the ^{80m}Br-CH_4 and ^{82m}Br-CH_4 Systems

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The reactions of ^{80}Br and ^{82}Br excited by the isomeric transition processes with CH_4 have been compared with each other. Similar reaction processes; energetic and thermal ionic, are involved in both cases. However, the isotope effect appears in the energetic process to form CH_3Br, but not in the thermal ionic process to form CH_3Br and CH_2Br_2. The difference in the γ-transitions of ^{80m}Br and ^{82m}Br to the ground states is responsible for the above results. It is concluded that at least a part of the recoil Br atoms enter chemical combinations with surrounding molecules within 10^{-8}sec, the life-time of the excited ^{80}Br atom. Furthermore, the yield of $CH_3{}^{80}Br$, lower than that of $CH_3{}^{82}Br$, is discussed on the basis of the different kinetic energies achieved on the Br atoms.

The atom or ion formed as result of nuclear transformation loses its energy or its charge, or both, in collisions with other molecules of the medium until most of the charges have been lost and its energy reduced to tens or *ev.* or even below, at which time it may enter a permanent stable combination if an appropriate reaction path is available.[1]

The investigations of such processes in the gas phase have now been extended by many workers to studied of the nature of the reactive species in the reaction of Br formed by the (I. T.) process with methane. Using additives, it has been concluded that CH_3 ^{82}Br in gaseous methane must, principally, result from an atom with excess kinetic energy, and CH_2 ^{82}BrBr, from the thermal ionic Br atom.[2,3]

Other experiments[4] strongly indicate that the reaction of the ^{80}Br from the ^{79}Br$(n,\gamma)^{80}$Br process with CH_4 is probably not dependent upon the charge. This remarkable difference in reactive species must result from the characteristics of the Br atoms activated by the different nuclear reactions; the (n, γ) process is strictly a high-energy recoil phenomenon, while on the other hand, the (I.T.) process involves little recoil and a high positive charge, ranging from $+1$ to $+14$.[5,6]

It was though interesting to see if differences in the product distribution could also be found between the ^{80}Br and the ^{82}Br formed by (I. T.) processes in the reactions with CH_4, since the γ-transitions involved are somewhat different in the two species. The γ-transition of ^{82m}Br to the ground state is performed in a single transition, whereas that of ^{80m}Br is attained in two steps.[7]

Nicholas and Rack[8] dealt with a comparison of the total organic yields from ^{80m}Br-CH_4 and ^{82m}Br-CH_4. The difference found between them does not exceed the experimental uncertainties. However, this does not provide any comparisons of the individual reaction processes, the energetic and thermal ionic processes.

In the present paper, we will deal in more detailed investigations of the reactions in these systems; particular, we look for a possible isotope effect between them in order to obtain some information on the time scale of the reactons of the recoil Br atom.

1) J. E. Willard, "Chemical Effects of Nuclear Transformation," Vol. I, IAEA, Vienna (1961), p. 215.
2) J. Okamoto and E. Tachikawa, This Bulletin, **42**, 1504 (1969).
3) E. Tachikawa, *ibid.*, **42**, 2404 (1969).
4) E. P. Rack and A. A. Gordus, *J. Phys. Chem.*, **65**, 944 (1961).
5) A. R. Kazanjian and W. F. Libby, *ibid.*, **42**, 2779 (1965).
6) S. Wexler and G. Anderson, *ibid.*, **33**, 850 (1960).
7) C. M. Lederer, J. M. Hollander and I. Perlman, "Table of Isotopes," John Willey & Sons. Inc., New York (1968), pp. 215, 217.

Experimental

The general experimental techniques are quite similar to those used in earlier bromine experiments.[2] The ^{80m}BrBr was formed by irradiating gaseous Br_2, sealed in a thin-wall quartz capillary, with thermal neutrons for one minute; it was used in the I.T. experiments 2—3 hr after irradiation. As a neutron source, the JRR-4 reactor in the JAERI was used.

Under these conditions, the percentage of ^{82}Br activity for which correction had to made was less than one per cent. The ^{80m}BrBr reaction mixture was allowed to stand more than 2 hr to permit a ^{80m}Br-^{80}Br parent-daughter equilibrium to be established. The sample were then analyzed by a radio-gas-chromatograph equipped with a G-M counter. The total activity was also measured by a G-M counter and corrected for ^{82}Br activity. The results obtained were expressed in per cent yields by applying decay corrections. In the experiments on the ^{82m}Br-CH_4 system, the neutron-irradiated bromine was mixed with CH_4 before the decaying-out of ^{82m}Br. The products were analyzed 48 hr later. The radioactive assays in a radio-gas-chromatograph and the total activity measurements were performed by a scintillation counter (2″×2″ well-type NaI(Tl) scintillator). A correction for ^{80}Br was not required in these procedures.

The experiments were carried out a total pressure of 51±2 cmHg. The ratio of Br_2 as a scavenger to CH_4 was kept constant. In some experiments, however, a constant amount of Br_2 was used.

Materials. The methane was obtained from the Takachiho Chemical Co., had a listed purity of 99.5%. The bromine used was the highest grade available. Xenon and argon, supplied by the Takachiho Chemical Co. and the Nihon Sanso Co., were used without additional purification (the listed purities are 99.995% and 99.994% respectively).

Result

CH_3Br and CH_2Br_2 are the only products from the reactions of ^{80}Br or ^{82}Br with gaseous methane; this is consistent with the finding in the early observations.[3]

The moderator effects on these products have been studied under a constant pressure of 5 cmHg Br_2 in both systems, ^{80m}Br-CH_4 and ^{82m}Br-CH_4. The results obtained using Xe are summarized in Table 1. A significant difference between the two systems is seen in the yields of CH_3Br; $CH_3{}^{82}Br$ is higher than $CH_3{}^{80}Br$ over the entire range of mole fractions of Xe. However, both could be extrapolated to 0.0±0.3% at 1.0 m.f. of Xe. Contrarily, both $CH_2{}^{80}BrBr$ and $CH_2{}^{82}BrBr$ decrease from 1.1±0.2% to 0.5±0.3% upon the addition of Xe.

As was the case in Table 1, the presence of a constant amount of Br_2 alters the reaction conditions so that the amount of Br_2 relative to CH_4 varies with the mole fraction of the moderator. Accordingly, the probability of the reactive collision of the energetic or thermal ionic Br atom with Br_2, relative to that with CH_4, rapidly increases with the amount of the moderator. In a highly-moderated system, thus, the Br-flux available to the reaction with CH_4 is very much reduced.

The most suitable conditions for studying the moderator effect specifically on these products is, thus, to keep the value of Br_2/CH_4 constant over the entire range of mole fractions of the moderator. Table 2 shows the results obtained with the addition of Br_2/CH_4=0.11±0.01, using Ar as a moderator.

Table 1. Moderator effects on CH_3Br and CH_2Br_2 from the ^{80m}Br-CH_4 and ^{82m}Br-CH_4 systems (Br_2 is 5.0 cmHg)

Gas pressure added Xe (cmHg)	CH_4 (cmHg)	m.f. of Xe	CH_3Br (%)	CH_2Br_2 (%)
^{80m}Br-CH_4 system				
0.0	46.4	0.0	3.5±0.3	1.3±0.1
5.6	40.4	0.111	2.3±0.2	0.9±0.1
21.5	25.2	0.416	1.2±0.1	0.6±0.1
28.3	18.3	0.548	0.8±0.1	0.7±0.1
42.1	4.3	0.819	0.2±0.1	0.6±0.1
^{82m}Br-CH_4				
0.0	45.9	0.0	5.0±0.5	1.1±0.1
3.4	43.8	0.064	3.6±0.3	0.8±0.1
5.5	41.8	0.104	4.0±0.4	1.1±0.1
11.1	35.8	0.214	3.1±0.3	0.8±0.1
14.4	32.6	0.276	3.0±0.3	1.0±0.1
16.3	30.9	0.311	2.3±0.2	0.7±0.1
17.8	28.9	0.344	1.9±0.2	0.9±0.1
20.7	25.8	0.402	1.6±0.1	0.9±0.1
33.6	12.5	0.658	0.7±0.1	0.9±0.1
38.8	8.9	0.736	0.5±0.1	0.6±0.1

Table 2. Moderator effect on CH_3Br and CH_2Br_2 from the ^{80m}Br-CH_4 and ^{82m}Br-CH_4 systems (Br_2/CH_4=0.11±0.01)

Gas pressure added Br_2 (cmHg)	Ar (cmHg)	CH_4 (cmHg)	m.f. of Ar	CH_3Br (%)	CH_2Br_2 (%)
^{80m}Br-CH_4					
5.0	0.0	46.2	0.0	3.5±0.3	1.2±0.1
4.0	10.7	36.7	0.209	2.3±0.2	1.1±0.1
3.0	20.5	27.4	0.404	1.6±0.2	1.0±0.1
2.5	25.9	22.8	0.506	1.4±0.1	1.1±0.1
2.0	31.0	18.4	0.608	1.0±0.1	1.1±0.1
1.5	36.1	14.5	0.697	0.8±0.1	1.1±0.1
1.0	40.0	9.4	0.798	0.6±0.1	1.2±0.1
0.5	45.8	5.3	0.888	0.5±0.1	1.2±0.1
^{82m}Br-CH_4					
5.0	0.0	45.9	0.0	5.0±0.5	1.0±0.1
4.0	9.9	37.4	0.193	4.0±0.4	0.9±0.1
3.0	21.2	27.1	0.413	2.6±0.2	1.2±0.1
2.0	30.6	18.1	0.603	1.6±0.2	1.1±0.1
1.0	41.1	9.6	0.795	1.0±0.1	1.1±0.1

$CH_3{}^{80}Br$ and $CH_3{}^{82}Br$ are moderator-sensitive, and both are extrapolated to $0.5\pm0.3\%$ at 1.0 mol fraction of Ar. On the other hand, both $CH_2{}^{80}BrBr$ and $CH_2{}^{82}BrBr$ are constant within range of experimental uncertainty over the whole range of mole fractions of Ar.

Discussions

Reaction of Br with CH_4. The most convenient way to differentiate the energetic reaction from the kinetic enregy-independent (thermal ionic) reactions is through the addition of inert gas as an energy sink of the energetic Br atom. Judging from the ionization potentials of the inert gas and the Br atom, the charge transfer from the Br^{+1} atom to the inert gas molecule seems not to be important.

Thus, if a product is formed *via* the kinetic energy process, its yield should be reduced by the addition of inert gas. The conclusion drawn from the results shown in Table 2 is that $3.5\%-0.5\%=3.0\%$ for $CH_3{}^{80}Br$ and $5.0\%-0.5\%=4.5\%$ for $CH_3{}^{82}Br$ are moderator-sensitive and formed *via* an energetic process, probably through the direct substitution reaction of hydrogen by energetic ^{80}Br and ^{82}Br, neutral or ionic.[2] One-half per cent of $CH_3{}^{80}Br$ and $CH_3{}^{82}Br$ and 1.1% of $CH_2{}^{80}BrBr$ and $CH_2{}^{82}BrBr$ are formed *via* thermal ionic processes.

Nicholas and Rack have discussed the nature of the thermal ionic reaction and suggested the following equation:[8]

$$CH_4 + Br^{+1} \longrightarrow CH_3Br^{+1} + H \qquad (1)$$

However, the formation of CH_2Br_2 can hardly be explained by this equation. Instead, we suggest the formation of CH_4Br^{+1*} through the ion-molecule reaction of thermal Br^{+1}:

$$CH_4 + Br^{+1} \longrightarrow CH_4Br^{+1*} \qquad (2)$$

Such a reaction is very favored energetically and more probable for the CH_2Br_2 formation.[9,10]

Comparison of the Reactions of ^{80}Br and ^{82}Br. The finding that similar reaction mechanisms are involved in the two systems is rather to be expected, since the orginal physical properties of ^{80}Br and ^{82}Br are similar. However, the importance of a careful inspection of the results is that there is an isotope effect between ^{80}Br and ^{82}Br on the energetic reaction (1.5 ± 0.2), but not on the thermal inoic reactions.

Nicholas and Rack[8] measured the total organic yield from the recation of ^{82}Br with CH_4 and compared it with the value found by Spicer and Gordus[11] in the ^{80m}Br-CH_4 system. They attemped to conclude the same organic yield from the reaction of the (I.T.)-induced ^{80}Br and ^{82}Br with CH_4, based upon the value (1.1 ± 0.1) for the ratio. A possible explanation for the discrepancy between the present results and the reported results is that the ratio of the total organic yields ($CH_3Br+CH_2Br_2$) from the present systems turns out to be 1.3 ± 0.2, instead. This indicates that the comparison of the total organic yields makes the difference between them less significant. Furthermore, under the conditions adopted by Spicer and Gordus, containing a smaller amount of Br_2 as a scavenger, the yield increases[8,12] considerable and the ratio between them is closer to unity. In addition, the differences in the experimental procedure might be at least partly responsible for this discrepancy.

The same yields for the thermal ionic process in both systems are consistent with the previous conclusion[2,3] that the ionization potential of the reactant relative to that of Br is the most important controlling factor in the thermal ionic process.

Among the explanations for the isotope effect in the energetic reaction which must be considered is that CH_4 shows a different efficiency in the energy degradation for ^{80}Br and ^{82}Br.[13,14] Thus, the spectrum of the Br atom in the energetic reaction range could be different in ^{80m}Br-CH_4 and in ^{82m}Br-CH_4. Under the present conditions, no precise information concerning the encrgy degradation of the Br atom is available. As a crude evaluation, however,[14] the average logarithmic energy loss, α, of ^{80}Br and ^{82}Br in collision with CH_4 can be calculated using the atom-molecule elastic collision model. The value of 1.03 has been obtained for the $\alpha_{^{80}Br-CH_4}/\alpha_{^{82}Br-CH_4}$ ratio.

It is well known that the actual collisions of the recoil atom are generally of a highly inelastic nature,[15] with a strong bond coupling of the atoms in the molecule attacked. Thus, the above gives only qualitative information concerning the difference in the energy degradation between the two systems. It is very unlikely, therfore, to explain the observed isotope effect.

Here it will be very interesting to check the decay schemes[7] of ^{80m}Br and ^{82m}Br precisely (see Fig. 1). The γ-transition of ^{82m}Br to the ground

8) J. Nicholas and E. P. Rack, *J. Chem. Phys.*, **48**, 4085 (1968).

9) Neutralization[10] of the CH_4Br^{+1*} probably takes place *via* the charge transfer and results in decomposition to fragments, such as CH_3Br, CH_2Br, and so on. The formed CH_2Br radical could be scavenged by Br_2 to form CH_2Br_2.

10) E. P. Rack and A. A. Gordus, *J. Chem. Phys.*, **34**, 1855 (1961).

11) L. D. Spicer and A. A. Gordus, "Chemical Effects of Nuclear Transformation," Vol. I, IAEA, Vienna (1965), p. 185.

12) J. A. Merrigan, W. K. Ellgren, Jr., and E. P. Rack, *J. Chem. Phys.*, **44**, 174 (1966).

13) E. K. C. Lee, G. Miller and F. S. Rowland, *J. Amer. Chem. Soc.*, **87**, 190 (1965).

14) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

15) J. W. Root and F. S. Rowland, *J. Chem. Phys.*, **46**, 4299 (1967).

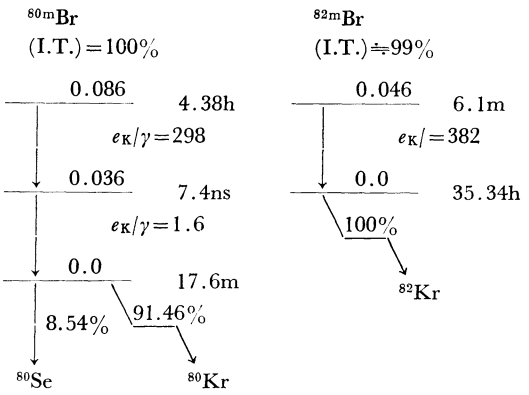

Fig. 1

state is attained in a single transition, the internal conversion ratio of which is 382. This means that 99.7% of the ^{82m}BrBr explodes,[16] to result in the highly-charged ^{82}Br atom with excess kinetic energy. On the other hand, ^{80m}Br is converted to the gronud state by two successive γ-transitions. The first transition (49 keV) is fully converted, while the second transition (37 keV) is partly converted (62%). The time required for the completion of the charging process initiated by nuclear internal conversion ranges from 10^{-15} to 10^{-16} sec.[17]

The charge and kinetic energy distributions on the excited ^{80}Br resulting from the molecular explosion of ^{80m}BrBr will be identical with those on ^{82}Br. However, the excited ^{80}Br has a successive transition to the ground state with a hilf-life of 7.4×10^{-9} sec. Thus, there are two possibilities, depending upon the length of the lifetime in the excited state relative compared to the time required for the atom to have a chemical reaction with the surrounding molecules: 1) the lifetime is too short for the atom to have a chemical reaction prior to the transition to the ground state or 2) the lifetime is long enough for the atom to react chemically with its environment during that period.

In Case 1, the following internal conversion leads to an additional build-up of the charge on the free atom, but it does not affect the kinetic energy of the atom. Most of the freshly built charges are also neutralized in the subsequent collisions with the environment.[5] The chemical consequences of the atom will, thus, be essentially the same as if the atom had not undergone the second internal conversion. As a result, if this is the case, it is probable that no isotope effect appears between ^{80}Br and ^{82}Br.

In Case 2, the kinetic energy achieved on the ^{80}Br atom in the chemical combination as a result of the γ-emission is of an order of a few-hundredths eV;[5,18] this energy is not sufficient to break any bond in the molecule, only to produce a little excitation of it. On the other hand, the ^{80}Br ion freed *via* the molecular explosion following the internal conversion has a kinetic energy which is very much dependent on the remainder of the molecule containing the Br atom.[16] If the excited ^{80}Br atom is in a chemical combination with surrounding atoms other than ^{80}BrBr*, then it is probable that the kinetic energy achieved on the ^{80}Br in the molecular explosion is different from that on the ^{82}Br freed from ^{82m}BrBr and that an isotope effect between them might appear on the energetic reaction, whereas the thermal ionic yields are more or less the same in both systems as long as the reaction occurs with the thremal Br^{+1} atom.

Most of the physicochemical stage, such as the energy-transfer, dissociation and ion-molecule reactions, terminated before 10^{-9} to 10^{-10} sec.[19] This also suggests that at least a part of the ^{80}Br in the excited state reacts chemically with the surrounding molecules. Thus, alternatively, the present results might be understood to indicate that the time scale of the reaction of the recoil Br atom is less than the order of 10^{-8} sec, the life-time of the excited ^{80}Br atom.

It is tempting to ascribe the yield of $CH_3{}^{80}Br$, which is lower than that of $CH_3{}^{82}Br$, to these differences in kinetic energy. Gordus and Willard[20] measured the total organic yields from the reaction of ^{80}Br in different parent compounds with CH_4. They showed that the yield increases with an increase in the mass of the residue to which ^{80m}Br is orginaly attached, that is, in the following order: $HBr < CH_3Br < C_2H_5Br < Br_2 < CCl_3Br < CHBr_3$. Qualitatively, this is in the same order as the increasing kinetic energy achieved on ^{80}Br in the molecular explosion.

Generally the reaction schemes[21,22] of the recoil halogen atom are very similar to those of the recoil tritium atom as far as the energetic reactions are concerned. One of the most important reactions of the recoil tritium is well known to be a hydrogen abstraction reaction to form HT.[23] As the present results show, the total organic yield in the reaction

16) T. A. Carlson and R. M. White, "Chemical Effects of Nuclear Transformation," Vol. I, IAEA, Vienna (1965), p. 23.
17) S. Wexler, *ibid.*, Vol. I (1961), p. 115.
18) C. Hsiung and A. A. Gordus, *ibid.*, Vol. II (1965), p. 461.
19) J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Willey & Sons, Inc., New York (1964), p. 252.
20) A. A. Gordus and J. E. Willard, *J. Amer. Chem. Soc.*, **79**, 4609 (1957).
21) C. M. Wai and F. S. Rowland, *ibid.*, **90**, 3638 (1968).
22) Yi-N. Tang, T. Smail and F. S. Rowland, *ibid.*, **91**, 2130 (1969).
23) E. Tachikawa and F. S. Rowland, *ibid.*, **90**, 4767 (1968).

of the Br atom with CH_4 is less than 10%. It can reasonably assumed that the hydrogen abstraction reaction of the excited ^{80}Br freed from the molecular explosion of the $^{80m}BrBr$ is very popular. The kinetic energy achieved on the Br atom as a result of the explosion of the $H^{80}Br^*$ will be in the range of a few electron volts, which will already be in the range for the energetic reaction. On the other hand, the initial kinetic energy of the Br atom, resulting from the explosion of Br_2, as in the ^{82m}Br-CH_4 system, could be of the order of 100 eV. The atom having such a high kinetic energy shows a complete spectrum over the entire range of the energetic reaction. This implies that the average number of possible collisions of atom in the reaction range is smaller for the ^{80}Br atom than for the ^{82}Br atom; that is, the flux of the ^{80}Br atom in the energetic reaction range is greately reduced compared to that of the ^{82}Br atom.

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