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The Reactions of ^{80}Br Activated by Isomeric Transition in the Gaseous Phase. The Isotopic Variation between CH_4 and CD_4

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The roles of the excess kinetic energy and the thermal ionic processes in the reaction of the ^{80}Br from the isomeric transition of ^{80m}Br in gaseous CH_4 and CD_4 were investigated using a rare gas additive. A possible isotope effect has appeared on the substitution reaction of the energetic Br atom to form $CH_3{}^{80}Br$ or $CD_3{}^{80}Br$, but not on the thermal processes to form $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ or their isotopic alternatives. At a zero mole fraction of moderator, the $CH_3{}^{80}Br/CD_3{}^{80}Br$ ratio for the energetic process was found to be 2.7 ± 0.3. This is consistent with the moderator and/or probability integral isotope effects. However, in a highly moderated system the results indicated that the former effect is more important than the latter. Furthermore it can be inferred from the total pressure effects on the energetic reaction products that the excited primary products are able to decompose unimolecularly due to internal excitation.

Many investigations concerning the target isotope effect on the reactions of recoil atoms have been performed using the recoil tritium atom.[1,2] However, only a few papers have appeared on the recoil Br atom. Spicer and Gordus[3] observed the isotopic variations in the total organic yield between CH_4 and CD_4 in the reaction of ^{80}Br activated by the (I.T.) process. A different attitude was taken by Nicholas and Rack,[4] who concluded that there was same dependence in kinetic energy for (I.T.)-induced ^{82}Br reactions with CH_4 and CD_4.

Experimental evidence shows that both ^{80}Br and ^{82}Br react with CH_4 *via* the energetic process to form CH_3Br and *via* the thermal ionic process to form CH_3Br and CH_2Br_2.[5] These findings, along with the results on the target isotope effect between CH_4 and CD_4 using ^{82}Br reported in a previous paper,[6] have led to these tentative conclusions: a) a target isotope effect appears in the energetic process, but not in the thermal process. b) the yield from the energetic process is higher for ^{82}Br than for ^{80}Br, while the thermal ionic reaction yield is similar for the two species.

In this paper we will deal with the target isotope effect between CH_4 and CD_4 as well as with the pressure effect using ^{80}Br activated by the (I.T.) process, since a comparative study of ^{80}Br and ^{82}Br can provide further knowledge concerning the chemical consequences of the recoil Br atom.

Experimental

The general experimental procedure is the standard one for recoil Br atom reactions, involving the formation of the ^{80}Br atom from the $^{80m}Br(I.T.)^{80}Br$ and the analysis of the radioactive products by radio gaschromatography.[5] The neutron irradiations were carried out in the JRR-4 in JAERI under a neutron flux of 10^{13}n/cm^2/sec. The total pressure was always kept at 51 ± 1 cmHg throughout the series of moderator experiments. The ratio of Br_2 as a scavenger, relative to CH_4 or CD_4 was 0.11 ± 0.01.

Materials. The CH_4 was supplied by the Takachiho Chemical Co., and CD_4, by the Merck Sharp and Dohm Co. Their nominal purities were 99.995 and 99.8% respectively, and they were used without further purification. The rare gas, xenon, was obtained from the Takachiho Chemical Co., its nominal purity was 99.995%.

Sample Processing. The inorganic bromides were isolated from the organic bromides by the insertion of a short glass column packed with potassium ferrocyanide into the gas stream ahead of the organic separation column. The gas-chromatographic separations were carried out in a column containing the celite and coated with dioctyl sebacate (15% by weight).

Correction and Experimental Error. All of the data obtained have been corrected using the half-lives 4.38 hr and 17.6 min for ^{80m}Br and ^{80}Br respectively. In most cases, the activity of the products was large enough to reduce the standard deviation of counting to

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[1] E. K. C. Lee, J. W. Root and F. S. Rowland, "Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Vienna (1965), p. 55.

[2] R. Wolfgang, *Progr. in Reaction Kinetics*, Vol. 3 (1965), p. 97.

[3] L. D. Spicer and A. A. Gordus, "Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Vienna (1965), p. 185.

[4] J. B. Nicholas and E. P. Rack, *J. Chem. Phys.*, **48**, 4085 (1968).

[5] E. Tachikawa, This Bulletin, **43**, 63 (1970).

[6] E. Tachikawa, *ibid.*, **42**, 2404 (1969).

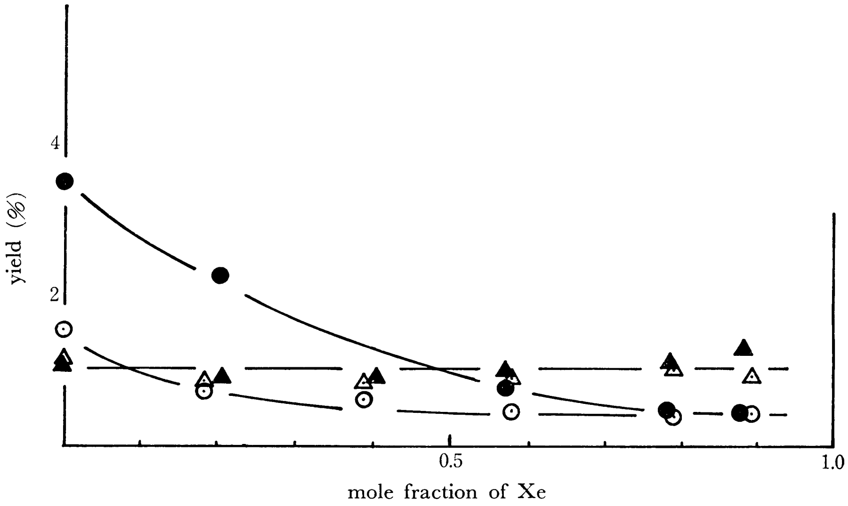

Fig. 1. Moderator curve at 50 cmHg total pressure for the reaction, $CH_4+^{80}Br$ and $CD_4+^{80}Br$, using xenon moderator.
● $CH_3{}^{80}Br$ ▲ $CH_2{}^{80}BrBr$ ⊙ $CD_3{}^{80}Br$ △ $CD_2{}^{80}BrBr$

a small percentage. The most serious error results from the correction of the results to the percentage yield, relative to the total activity. The product activities were measured in the flow system on radio gas chromatography. However, the total activities were measured under stationary conditions. The 17.6-min half-life is too short to obtain the correction factor between the different counting methods with a precision better than ±5%. Thus, the accuarcy of the present data is usually limited to ±5%. Moreover, in some cases where the total organic yield is relatively small, as in the case of the highly-moderated systems, the standard deviation of counting amounts to 15—20%.

Results and Discussion

Moderator Effect. The organic products observed in the reaction of gaseous CH_4 or CD_4 with the (I.T.)-activated ^{80}Br were CH_3 ^{80}Br and $CH_2{}^{80}BrBr$ or their isotopic products. The moderator effects of Xe on these are graphically displayed in Fig. 1. The following things can be noticed in the figure. Firstly, both $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$ are moderatorsensitive, although the effect of the additive is not the same, the former decreasing from $3.5\pm0.3\%$ to $0.5\pm0.3\%$, and the latter, from $1.6\pm0.2\%$ to $0.5\pm0.3\%$, with an increase in the mole fraction of Xe. Secondly, both $CH_2{}^{80}BrBr$ and $CD_2{}^{80}BrBr$ show a constant yield of $1.1\pm0.2\%$ over the whole range of the mole fractions of the moderator. Under the present experimental conditions, the yield is $3.5-0.5=3.0\%$ for $CH_3{}^{80}Br$ and $1.6-0.5=1.1\%$ for $CD_3{}^{80}Br$ as formed *via* the energetic Br for H and Br for D processes respectively. Thus, the isotopic variation between them is obtained as 2.7 ± 0.3, a value which is very consistent with the value, 2.8 ± 0.2, found using ^{82}Br instead of ^{80}Br.[6] These results imply that the overall isotope effect between CH_4 and CD_4 is 2.7 ± 0.3 for the energetic reaction of both ^{80}Br and ^{82}Br, although the absolute yield is always higher for ^{82}Br than for ^{80}Br by a factor of 1.5 ± 0.2.[5]

In a previous paper[5] we attempted to ascribe the difference in the absolute yields between ^{82}Br and ^{80}Br to the difference in kinetic energies between them. The γ-transition of ^{82m}Br to the ground state is attained in a single transition, whereas ^{80m}Br is converted by two successive transitions. If the excited ^{80}Br resulting from the first transition enters into a chemical combination with the surrounding molecules within its lifetime, a kinetic energy achieved on ^{80}Br in the successive transition of the excited ^{80}Br is very much dependent upon the remainder of the molecule.[7,8]

From the results, the thermal yields are found to be $0.5\pm0.3\%$ for $CH_3{}^{80}Br$ or $CD_3{}^{80}Br$ and $1.1\pm 0.2\%$ for $CH_2{}^{80}BrBr$ or $CD_2{}^{80}BrBr$. The ratio between them is 0.45 ± 0.08. Again, these results are in good agreement with those found using ^{82}Br,[5] suggesting that the relative ionization potential of the reactant is the main factor controlling the thermal ionic reactions. Thus, as long as the difference in the ionization potentials between CH_4 (13.12 eV) and CD_4 (13.26 eV)[9] or between ^{80}Br and ^{82}Br is small enough to be ignored, compared to that between CH_4 and Br, it seems that no isotope effect appears as either a target or as a reacting one in the thermal ionic process.

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[7] A. A. Gordus and J. E. Willard, *J. Amer. Chem. Soc.*, **79**, 4609 (1967).

[8] A. R. Kazanjian and W. F. Libby, *J. Chem. Phys.*, **42**, 2778 (1965).

[9] F. H. Field and J. L. Franklin, "Electron Impact Phenomena and The Properties of Gaseous Ions," Appendix, Academic Press, New York (1957).

Spicer snd Gordus[3] observed the isotopic variations of the total organic yields between CH_4 and CD_4 as 1.4±0.2. This value is not directly compared with the present value of $(3.5+1.1)/(1.6+1.1)=1.7\pm0.2$, since the amounts of Br_2 added as a scavenger are greatly different between their system and ours. However, the qualitative conclusion that the target isotope effect exists between CH_4 and CD_4 in the reaction of Br activated by the (I.T.) process can be drawn from both experiments. Contrarily, Nicholas and Rack observed no difference in the total organic yields from CH_4 and CD_4 using ^{82}Br, within the range of experimental uncertainty.[4] Unfortunately, it is not immediately possible to explain this contradiction.

Origin for the Isotope Effects. Extensive research into the isotope effects on the energetic reactions has been made using the recoil tritium atom. Several possible sources have been suggested for the variations in the yields measured for isotopic molecules.[10-12] If the energy losses in non-reacting collisions are not same for the two molecules, the isotopic variation can be observed. These differences are called "moderator isotope effects." On the other hand, the isotopic variation may still be expected if the reactivity integrals are not identical for the isotopic molecules. They can be grouped as "probability integral isotope effects." Another possible source is the"average-energy effect" resulting from the differences in the average energy for the reactions. All three effects may influence the energetic reaction of the Br atom and produce the observed differences in the yields from CH_4 and CD_4 molecules. However, the similar CH_3Br/CD_3Br ratios in the energetic processes for both ^{80}Br and ^{82}Br imply that the observed isotopic variations result from the same origins.

The "average-energy isotope effect" may be excluded, since it is only considered when the energetic *Br for H* and *Br for D* reactions compete with each other in the same reaction system. In such a system, the flux of the recoil Br atom surviving to lower energies can be noticeably diminished by a higher-energy reaction. Therefore, fewer energetic reaction may be observed with the lower-energy process than with the higher one.

Thus, the present results are consistent only with the "moderator isotope effect" and/or the "probability" one. One of the experimental approaches for distinguishing the "moderator isotope effect" from the "probability integral effect" is to use a single molecule containing both protium and deuterium. In this way, the same energy spectrum of the energetic Br atom can be used for both reactions; therefore, the "moderator isotope effect" is excluded. The second approach is to control the Br spectrum experimentally by the addition of a large excess of the third molecule.[13] In the limiting case of this type of approach, the reactant represents a negligible fraction of each sample. Therefore, the energetic reaction with a reactant would represent a negligible fraction of the total reaction and the non-reacting energetic Br collisions with the molecule would be completely unimportant. In such an ideal system, the reactant molecules would introduce only infinitely small perturbations to the total Br flux at each energy level, the total energetic yiels would, then, be a direct measure of the ease of the reactions.

Table 1. Yields of products from the reaction of ^{80}Br with CH_4 or CD_4 at high moderation with Xe

Br_2 (cmHg)	CH_4 (cmHg)	Xe (cmHg)	$CH_3{}^{80}Br$ (%)	$CH_2{}^{80}BrBr$ (%)
5.0	5.4	41.1	0.53±0.03	0.71±0.04
5.0	5.3	40.7	0.46±0.02	0.65±0.03
			av. 0.50±0.04	0.68±0.03
Br_2	CD_4	Xe	$CD_3{}^{80}Br$	$CD_2{}^{80}BrBr$
5.0	5.2	40.0	0.39±0.02	0.71±0.04
5.0	5.2	39.9	0.34±0.02	0.68±0.03
			av. 0.37±0.03	0.70±0.03

Table 1 shows the yields from the systems consisting of 0.8 m.f. of Xe, 0.1 m.f. of Br_2, and 0.1 m.f. of CH_4 or CD_4. The experiments are quite far from the ideal because the total reaction with a reactant is not negligible and the flux perturbation cannot be ignored. However, these conditions are the closest that we could attain experimentally. Thus, if the calculations are carried out as though the samples were actually of this ideal limiting type, a difference has been noticed between $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$, but not between $CH_2{}^{80}BrBr$ and $CD_2{}^{80}BrBr$. By assuming that the $CH_3{}^{80}Br$ or $CD_3{}^{80}Br$ formed *via* the thermal ionic process is 45% of the total $CH_2{}^{80}BrBr$ or $CD_2{}^{80}BrBr$ (see Fig. 1), the thermal yield of the mono-substituted products can be extimated to be $0.69\times0.45=0.31$ (%). Thus, the yields of $0.50\%-0.31\%=0.19\%$ for $CH_3{}^{80}Br$ and of $0.37\%-0.31\%=0.06\%$ for $CD_3{}^{80}Br$ are assigned to the energetic process. The ratio between them is 3.2±0.3; this is in the range of the value (2.7±0.3) found in the system containing no moderator. Thus, it can be concluded that the isotope effect observed in the energetic reaction results mostly from the "probability integral isotope effect."

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[10] E. K. C. Lee and F. S. Rowland, *J. Amer. Chem. Soc.*, **85**, 2907 (1963).

[11] H. C. Jurgeleit and R. Wolfgang, *ibid.*, **85**, 1057 (1963).

[12] E. K. C. Lee, G. Miller and F. S. Rowland, *ibid.*, **87**, 190 (1965).

[13] E. Tachikawa and F. S. Rowland, *ibid.*, **90**, 4767 (1968).

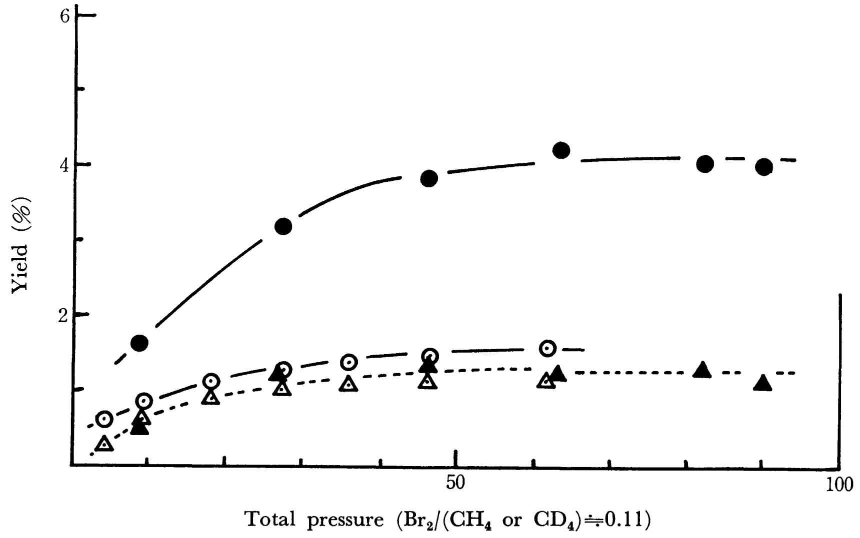

Fig. 2. Pressure dependence of the products from the reaction, $CH_4+{}^{80}Br$ and $CD_4+{}^{80}Br$.

● $CH_3{}^{80}Br$ ▲ $CH_2{}^{80}BrBr$ ⊙ $CD_3{}^{80}Br$ △ $CD_2{}^{80}BrBr$

Reaction Mechanisms Resulting in Isotopic Variations. The "probability integral isotope effect" observed in the replacement of the H or D atom by the Br atom could be either the result of the isotopic difference between the atoms replaced (the primary isotope effect) or between the CH_3 and CD_3 residues with which the Br atom then combines (the secondary isotope effect). The bond strength of C–H and C–D have been reported to be 4.45+0.02 eV and 4.56+0.03 eV respectively.[14] The C–H bond-dissociation energy has been shown to be correlated with the abstraction reaction of the recoil tritium atom,[13,15] but no definite correlation of it with the substitution reaction has yet been reported.[16] Instead, Rowland *et al.*[1] have suggested that the more rapid relaxation of the H atoms than D atoms into positions favorable for the successful bonding of the T atom is responsible for the observed isotopic variation in the recoil tritium substitution reactions. Moreover, the tendency in hot halogen reactions with alkanes for the reactivity of halogen atoms to decrease as the size of the halogen increases[17] has been ascribed to the ease with which the atoms can change direction in response to a newly-available chemical composition.[18] Thus, by analogy with this concept, it is possible that the fact the relaxation time for a new chemical bond is a controlling factor is also responsible for the present results. However, more work is required to clarify the reaction mechanisms of the substitution reaction of the energetic Br atom in detail.

Pressure Dependency of Products. The substitution of an energetic atom into a molecule is usually accompanied by a high excitation of the products. The excited molecule is able to undergo a secondary decomposition or isomerization, as detected by a pressure-dependent competition between the collisional stabilization and the secondary reaction, as in recoil tritium and other halogen experiments.[18-20] Recently, Spicer and Wolfgang[17]

TABLE 2. THE ESTIMATED YIELDS OF $CH_3{}^{80}Br$ AND $CD_3{}^{80}Br$ FROM THE ENERGETIC PROCESS IN THE REACTION OF ^{80}Br WITH CH_4 AND CD_4

Total Pressure (cmHg)	$CH_3{}^{80}Br$ (%)	$CD_3{}^{80}Br$ (%)
10	1.42±0.20	0.55±0.05
20	(1.97±0.20)*	0.69±0.07
30	2.61±0.20	0.82±0.08
40	(3.06±0.20)*	0.91±0.09
50	3.20±0.20	0.95±0.10
70	3.63±0.20	1.09±0.10
90	3.43±0.20	—
100	3.43±0.20	—

* Yields were estimated from the curve shown in Fig. 2.

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[14] J. Root, Ph. D. Thesis, The Univ. of Kansas, 1964.

[15] J. Root, W. Breckenridge and F. S. Rowland, *J. Chem. Phys.*, **43**, 3694 (1965).

[16] R. Cipollini and G. Stöcklin, *Radiochim. Acta*, **9**, 105 (1968).

[17] L. Spicer and R. Wolfgang, *J. Chem. Phys.*, **50**, 3466 (1969).

[18] C. M. Wai and F. S. Rowland, *J. Amer. Chem. Soc.*, **90**, 3638 (1968).

[19] Y. N. Tang, E. K. C. Lee and F. S. Rowland, *ibid.*, **86**, 1280 (1964).

[20] Y. N. Tang and F. S. Rowland, *J. Phys. Chem.*, **71**, 4576 (1967).

obtained negative evidence for a unimolecular decomposition of the $CH_3{}^{39}Cl$ and $CH_2{}^{39}Cl\cdot$ formed by the reaction of recoil ^{39}Cl with CH_4 and suggested that a collisional decomposition of hot molecules was involved.

Thus, it seemed that it would be very interesting to examine the pressure effects of the products from the present system. If a unimolecular decomposition of the excited $CH_3{}^{80}Br$ or $CD_3{}^{80}Br$ occurs, the splitting of the C–Br bond is most probable, since it is the weakest bond in the molecule (2.93 eV). However, in our radiochemical method of approach, a decomposition reaction is traced only through the fragment containing the radioactive atom. Under these conditions, no experimental procedures are available to trace the decomposition reaction of $CH_3{}^{80}Br$ or $CD_3{}^{80}Br$.

The results of a series of measurements of the yields *vs.* the total pressure is shown in Fig. 2. The results provide evidence for the pressure dependency of both $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$. Pressure effects are also noticed on both $CH_2{}^{80}BrBr$ and $CD_2{}^{80}BrBr$. This suggests that the observed pressure dependency of $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$ is partly due to the increase in the thermal ionic yields with an increase in the pressure. As an approximation, by assuming that the thermal ionic yields of these mono-substituted methanes are 45% of the $CH_2{}^{80}BrBr$ or $CD_2{}^{80}BrBr$ throughout the pressure range, $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$ from the energetic process are estimated to be as is shown in Table 2. The yields increase with the pressure at the beginning and then tend to flatten out, suggesting that the excited $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$ are stabilized through the collisional removal of the excitation energy. At low pressures, a considerable fraction of the energetic substitution products seems to decompose. The observed pressure dependency indicates the life-time of these species in the 10^{-8}—10^{-9} sec range. Furthermore, from the smaller significance of the pressure effect on the higher pressure side, it can be inferred that, at pressures of more than 50 cmHg, the excited $CH_3{}^{80}Br$ or $CD_3{}^{80}Br$ can be stabilized well. However, no highly-excited molecules having a life-time much shorter than 10^{-9} sec will be subjected to the present pressure effects.

On the other hand, the behavior of the thermal products in response to the pressure are consistent with either the increase in the collisional frequency of CH_4Br^{+1*} and CD_4Br^{+1*},[21] the plausible primary reaction products ($Br^{+1}+CH_4$ or $CD_4 = CH_4Br^{+1*}$ or CD_4Br^{+1*}), with their surroundings or the collisional stabilization of the products. Unfortunately, on the basis of the present experiments alone it is impossible to distinguish which process is involved here.

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21) E. Tachikawa and J. Okamoto, *Radiochim. Acta*, (in press).