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The Reactions of ^{80}Br Activated by the (n, γ) Process with Methane

Masakatsu SAEKI, Kenshi NUMAKURA,* and Enzo TACHIKAWA
Division of Chemistry, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken

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The reactions of ^{80}Br activated by the (n,γ) process with CH_4 have been examined. By assuming that the limiting yields of products at 1.0 m.f. of the Kr-moderator is due to thermal ionic processes, the kinetic yields were tentatively determined to be the 12.4% for total organic, 11.4% for $CH_3{}^{80}Br$, and 1.0% for $CH_2{}^{80}BrBr$. A similar treatment of the results from the reactions with CD_4 gives 5.1% for total organic, 3.9% for $CD_3{}^{80}Br$, and 1.2% for $CD_2{}^{80}BrBr$. When the $CH_3{}^{80}Br$ yield was compared with that from the reactions of ^{80}Br from the (I.T.) activation, a noticeable difference was noticed; it was roughly 3 times as large as in the latter system. Furthermore, the pressure effects on the $CH_3{}^{80}Br$ show that a fraction of $CH_3{}^{80}Br$ is highly excited and is able to decompose even at a pressure of 1920 mmHg. This suggests that the distribution of ^{80}Br in the reaction energy range extends to a higher energy than in the case of ^{80}Br activated by the (I.T.) process.

The ^{80}Br atom activated by isomeric transition has a charge distribution ranging from +1 to +14, with a peak at +7 and an excess kinetic energy, as a result of a molecular explosion.[1,2] In previous papers[3-5] it was concluded that, in the reactions with CH_4, both kinetic-energy and kinetic-energy-independent processes are involved in the formation of organic products.

The (n,γ) activation process, on the other hand, results in ^{80}Br atoms and ions of a maximum kinetic energy equal to 358 eV when the ^{79}Br is a free atom. The maximum energy of ^{80}Br depends principally on the mass of the radical to which ^{79}Br is bonded.[6,7] However, the partial cancellation of prompt gamma-cascade momenta could result in a distribution of ^{80}Br from zero to the maximum, although most of the ^{80}Br energies will probably be formed with energies in a large excess of the reaction energy range, 18% of which is in a singly-charged state.[8] Thus, the study of the reactions of ^{80}Br from the (n,γ) activation is interesting with a view to comparing the reactivity of ^{80}Br activated by the (I.T.) process.

Rack and Gordus[9] investigated the reactions of ^{80}Br from the (n,γ) activation with gaseous CH_4 in an attempt to determine whether the reaction occurs principally because of the positive charge or because of the γ-recoil kinetic energy acquired by the ^{80}Br. The conclusion reached was that the reactions with CH_4 occur principally, if not completely, as a result of the recoil kinetic energy acquired by the atom in the activation. Later, Spicer and Gordus[10] conducted a gas-chromatographic analysis of the products and observed that 89% of the organic activity was due to $CH_3{}^{80}Br$, and 11%, to $CH_2{}^{80}BrBr$, and that the limiting organic yields at zero m.f. of Br_2 were 10.7% $CH_3{}^{80}Br$ and 1.3% $CH_2{}^{80}BrBr$.

However, in Rack's experiments,[9] the highest m.f. of

* On leave of absence from the Faculty of Engineering, Ibaraki University, Hitachi-shi, Ibaraki-ken.

1) S. Wexler and G. Anderson, *J. Chem. Phys.*, **33**, 850 (1960).
2) S. Wexler, *ibid.*, **36**, 1992 (1962).
3) E. Tachikawa and T. Kahara, This Bulletin, **43**, 1293 (1970).
4) M. Yagi, K. Kondo, and T. Kobayashi, *ibid.*, **44**, 580 (1971).
5) K. Numakura, M. Saeki, and E. Tachikawa, presented at the 15th discussion meeting on radiochemistry, Kyoto, 1971, and submitted to This Bulletin.
6) C. Hsiung and A. A. Gordus, *J. Chem. Phys.*, **36**, 947 (1962).
7) A. A. Gordus and C. Hsiung, *ibid.*, **36**, 945 (1962).
8) S. Wexler and T. Davies, *ibid.*, **20**, 1688 (1952).
9) E. P. Rack and A. A. Gordus, *J. Phys. Chem.*, **65**, 944 (1961).
10) L. D. Spicer and A. A. Gordus, "Chemical Effects of Nuclear Transformations," Vol. I, IAEA, Vienna, (1965), p. 185.

the moderator reached was 0.7. The previous work[5] in the (I.T.) experiments suggested that their extrapolation of the yields of the products to 1.0 m.f. of the moderator did not necessarily reflect the real yield-curve in highly-moderated systems.

The prime object of this paper is to examine the product-distribution from the reactions of ^{80}Br from the (n,γ) activation with CH_4 over the whole m.f. range of an inert moderator, Kr. The results obtained will be discussed in comparison with those in the (I.T.) experiments. Some experiments have also been performed on the isotopic variation between CH_4 and CD_4.

Experimental

The methane and Kr were supplied by the Takachiho Chemical Co., while the deuterated methane was supplied by Merck of Canada (its nominal purity was 99%). Those gases were used without purification.

Samples prepared in 18.5 m*l* silica bubblets usually contained about 1—10 mmHg of Br_2. The total pressure was kept constant at 500 ± 10 mmHg, except in the series of experiments where the yield variations of the products were measured as a function of the total pressure. Energetic (n,γ) activated ^{80}Br was formed by irradiating the samples for 5—60 sec in the JRR-4 reactor. The thermal neutron flux at the irradiation port was 2×10^{12} n/cm^2/sec. After irradiation, the ampoule was dipped into liq. N_2 within 1 min in order to stop further reactions; this was followed by the isomeric transition of ^{80m}Br. After the sample had been thawed by inserting it into warm water, it was divided into two portions using a vacuum-line technique. One portion was used to measure the decay of activities in the sample to obtain the total ^{80}Br activity involved. The other was directly injected into radio-gas chromatography. The relative yields of the individual products were obtained by dividing the activities in the radio-gas chromatograms by the total ^{80}Br activity.

The total organic yield was measured with samples with no additive. Separation into organic and inorganic fractions was achieved by the usual solvent extraction method.[5] The organic phase contained an activity, of which at least 98% was ^{80}Br, thus indicating that a proper chemical separation was achieved. After applying decay corrections, the total organic yield, O.Y.$=100\times$organic activity/(organic+inorganic activities), was calculated. All the relative yields of the individual products have been corrected to percentage yields, using a correction factor determined from the sum of the relative yields and the total organic yield found in the sample with no additive.

The concomitant irradiation of Kr added as a moderator yields various radioactive Kr-isotopes. However, the species which must be taken into account in the irradiation 5 to 60 sec in duration are ^{85m}Kr, ^{87}Kr, and ^{79}Kr, the relative activities of which are 1.00, 0.633, and 0.016. The uncertainty as to the total ^{80}Br activity caused by their simultaneous presence was not significant, less than a few percent.

A contamination of the results from the $^{80m}Br(I.T.)^{80}Br$ process can be anticipated. When the isomeric transition occurred while the sample was dipped in a liq. N_2 bath, the reaction of the newly-formed ^{80}Br with the reactant can be ignored because of the clamping effect.[11] Thus, the error resulting from the isomeric transition can be estimated to be less than 1%.

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

The most serious error in this work seems to result from the non-uniformity of the components among the two divided portions. The accuracy of the present results is usually limited to $\pm10\%$. For most of the samples, 2 to 3 samples were made and worked with. The data are usually consistent within the limits of experimental error.

Results

The radio-gas chromatographic analysis of samples has shown that the main products from the reactions of (n,γ)-activated ^{80}Br with CH_4 or CD_4 are $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ or their isotropic analogues, much as in the (I.T.) experiments.

Table 1. The total pressure effect on products from the ^{80}Br–CH_4 system

Total Pressure (mmHg)	$CH_3{}^{80}Br$ (%)	$CH_2{}^{80}BrBr$ (%)
55	11.1±1.1	1.1±0.1
110	11.5±1.2	1.1±0.1
210	10.5±1.1	1.2±0.1
310	—	1.5±0.2
500	12.3±0.4	1.6±0.3
710	12.9±0.4	1.8±0.2
890	—	2.5±0.3
930	13.8±1.4	1.9±0.2
1560	14.9±1.5	2.3±0.2
1920	15.8±0.6	2.1±0.2

Table 1 summarizes the yields of the individual products obtained under various total pressures. In all cases, the Br_2/CH_4 ratio is in the range from 0.02 to 0.03. The $CH_3{}^{80}Br$ yield increases with an increase in the total pressure, at least up to 1920 mmHg; $CH_2{}^{80}BrBr$ increases at the beginning, but a further increase in pressure has no measurable effect on it.

Table 2. The percentage yields of products from the Kr-moderated ^{80}Br–CH_4 and ^{80}Br–CD_4 systems

m.f. of Kr	Reactant CH_4		Reactant CD_4	
	$CH_3{}^{80}Br$ (%)	$CH_2{}^{80}BrBr$ (%)	$CD_3{}^{80}Br$ (%)	$CD_2{}^{80}BrBr$ (%)
0.00	12.3 ±0.4	1.5 ±0.4	4.6 ±0.4	1.7 ±0.2
0.10	8.5 ±0.9	0.82±0.07	3.8 ±0.4	1.5 ±0.15
0.19	9.4 ±0.9	1.4 ±0.2	2.0 ±0.2	0.87±0.09
0.24	6.4 ±0.6	0.95±0.10	—	—
0.30	6.7 ±0.7	—	1.6 ±0.2	0.80±0.08
0.42	3.7 ±0.4	0.96±0.10	1.6 ±0.2	0.90±0.09
0.51	2.2 ±0.2	0.66±0.07	—	—
0.60	1.7 ±0.6	0.81±0.28	0.88±0.09	0.88±0.09
0.71	1.1 ±0.1	0.51±0.05	0.69±0.07	0.83±0.08
0.80	0.78±0.08	0.47±0.05	0.60±0.06	0.64±0.06
0.90	0.93±0.10	0.54±0.08	0.72±0.07	0.47±0.05

The moderator effects of Kr in these products have been examined while keeping the Br_2/CH_4 ratio in the range from 0.02 to 0.05. The results obtained are summarized in Table 2. The yields of the total organic products and of the individual products in the ^{80}Br–CH_4 system were 13.8±0.6% total organic, 12.3±0.4% $CH_3{}^{80}Br$, and 1.5±0.2% $CH_2{}^{80}BrBr$. In the ^{80}Br–CD_4

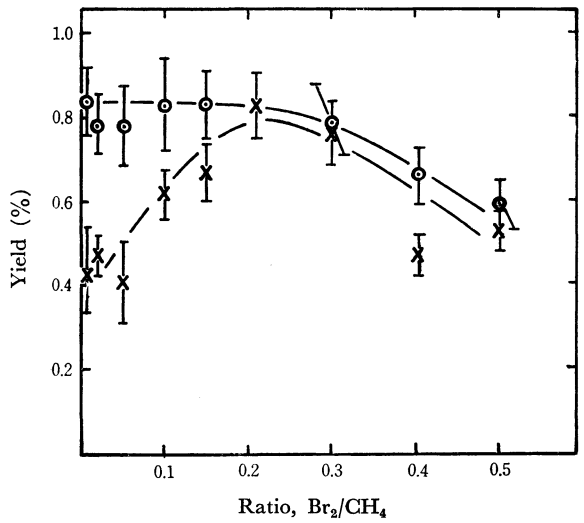

Fig. 1. Variations in $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ with the Br_2/CH_4 ratio in the reaction system in the constant presence of 100 mmHg of CH_4. (The total pressure was kept at 500±10 mmHg by adding Kr.)
⊙: $CH_3{}^{80}Br$, ×: $CH_2{}^{80}BrBr$

system, the yields were 6.3±0.6% total organic, 4.6±0.4% $CD_3{}^{80}Br$, and 1.7±0.2% $CD_2{}^{80}BrBr$. As the dilution of the reaction system by Kr proceeds, the yields decreased; the limiting values at 1.0 m.f. of Kr were 0.9±0.1% $CH_3{}^{80}Br$ and 0.5±0.1% $CH_2{}^{80}BrBr$, 0.7±0.1% $CD_3{}^{80}Br$ and 0.5±0.1% $CD_2{}^{80}BrBr$.

In order to make a comparison with the results obtained in the ^{80m}Br–CH_4 system,[5] the variation in $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ as a function of the ratio of Br_2/CH_4 has also been examined; the results are graphically depicted in Fig. 1. In all cases, the pressure of CH_4 was kept constant at 100 mmHg and Kr was added until the total pressure reached 500±10 mmHg. Under these conditions, the variation in Kr (400—350 mmHg) concomitantly with the increase in the Br concentration has no significant effect on the kinetic energy moderation of the energetic ^{80}Br, since Kr is as good a kinetic energy moderator as Br_2. Thus, the yield-curve of $CH_2{}^{80}BrBr$, showing a maximum, is related directly with the increase in Br_2, but not with the concomitant decrease in the amount of Kr in the system.

Discussion

The total organic yields found in the present work are in agreement with the values (12.0±1.0% from ^{80}Br–CH_4 and 6.4±1.0% ^{80}Br–CD_4) previously reported by Spicer and Gordus[10,12] and with the value of 13.3±0.5% from ^{80}Br–CH_4 reported by Rack and Gordus.[9,12] Furthermore, the percentage yields of individual products also show a reasonable agreement with the values,[10] 10.7% for $CH_3{}^{80}Br$ and 1.3% for $CH_2{}^{80}BrBr$, and 4.9% for $CD_3{}^{80}Br$ and 1.5% for $CD_2{}^{80}BrBr$. If one estimates the kinetic energy yield by simply subtracting the limiting yield at 1.0 m.f. of Kr from that obtained with no additive, 13.8−1.4=12.4% for the total organic products, 12.3−0.9=11.4% for $CH_3{}^{80}Br$, and 1.5−0.5=1.0% for $CH_2{}^{80}BrBr$ are obtained. A similar treatment of the results from the ^{80}Br–CD_4 system yields 6.3−1.2=5.1% for the total organic products, 4.6−0.7=3.9% for $CD_3{}^{80}Br$, and 1.7−0.5=1.2% for $CD_2{}^{80}BrBr$. The value of 12.3% for $CH_3{}^{80}Br$ is roughly 3 times that found in the (I.T.) experiments.[5] As has been discussed in a previous paper,[5] an additional formation of products due to the thermal ionic processes is possible in the highly Kr-moderated ^{80m}Br–CH_4 system. There is no "*a priori*" reason to believe that this additional formation does not occur in the present ^{80}Br–CH_4 or CD_4 systems. Thus, the values obtained for the kinetic energy yields in the above calculation should be taken to be minimum values.

Comparison of the Results with Those from the (I.T.) Experiments. The higher yield of $CH_3{}^{80}Br$ from the kinetic energy process in the (n,γ) experiment than in the (I.T.) experiments results from the difference in the physical nature of the ^{80}Br from the two types of activation. Since the ^{80}Br atom from the (n,γ) activation has a kinetic-energy distribution ranging up to E_{max}, while a fraction of the charged atom is of the order of 18%,[8] mostly singly-charged, the kinetic energy is a more important factor in the course of the reactions than is the positive charge. When products are formed *via* energetic processes, they are excited and so can undergo a secondary decomposition or isomerization, as detected by a pressure-dependent competition between the collisional deactivation and the unimolecular decomposition. The results in Table 1 agree with the above expectation, indicating that a fraction of $CH_3{}^{80}Br$ is highly excited and that it is subjected to a secondary decomposition, even under a total pressure of 1920 mmHg, although a large fraction is easily stabilized and is essentially pressure-independent. This is in great contrast with the results of the (I.T.) experiments, where $CH_3{}^{80}Br$ increases with the pressure at the beginning, but tends to level off at around 500 mmHg.[3] This is indicative that a fraction of the $CH_3{}^{80}Br$ in the (n,γ) experiment stays in somewhat higher excitation states than that in the (I.T.) experiment. Since the excitation energy of the products is a good measure of the energetic state of the reacting atom at the time of the reactions,[13] it may be pointed out that the possible collisions which can lead to energetic reactions of ^{80}Br are available to a higher energy in the present (n,γ) experiments, than in the (I.T.) experiments.

When one compares the $CH_2{}^{80}BrBr$ yield with that in the (I.T.) experiments, it is noticeable that a higher yield is obtained from the latter (2.1±0.2% in the (I.T.) experiments). This trend is very different from that found in $CH_3{}^{80}Br$ and implies that an appreciable amount of $CH_2{}^{80}BrBr$ is formed *via* a thermal ionic process in the (I.T.) experiments.

One attempt to evaluate the maximum yield of

12) These values were obtained by extrapolating to zero additive, while in the present work they are the percentage yields in the presence of 1—5 mmHg Br_2. However, the presence of this amount of Br_2 does not affect the yield beyond the range of experimental uncertainty. Thus, the direct comparison of the present values with the reported values is rather reasonable.

13) C. F. McKnight and J. W. Root, *J. Phys. Chem.*, **73**, 4430 (1971).

$CH_2{}^{80}BrBr$ in the (I.T.) experiments proceeds on the assumption that the energetic formations of $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ occur in the same energy range. On this assumption, the ratio of the yields of products, $CH_3{}^{80}Br/CH_2{}^{80}BrBr$, from the energetic reactions of ^{80}Br can be considered to be the same for both types of activation of ^{80}Br. The maximum value of the energetic yield of $CH_2{}^{80}BrBr$ in the (I.T.) experiments can, thus, be estimated by the calculation:

$$(CH_2{}^{80}BrBr/CH_3{}^{80}Br) \text{ in } (n,\gamma) \text{ work} \times (CH_3{}^{80}Br \text{ in (I.T.) work}) = (1.0/11.4) \times (3.9) = 0.34$$

The experimental uncertainty in the (I.T.) experiments[5] did not allow us to detect definitely the kinetic energy moderation of $CH_2{}^{80}BrBr$ by Kr, both because of its small yield and because of its additional formation in the Kr-moderated system. Although the above calculation does not involve any certainty, it may be considered that the kinetic energy formation of $CH_2{}^{80}BrBr$ is less important in the (I.T.) experiments.[4]

Another important observation regards the yields of products in the highly Kr-moderated system. While the limiting yields of $CH_3{}^{80}Br$ at 1.0 m.f. of Kr are $0.9\pm0.1\%$ for the (n,γ) activation and $0.5\pm0.1\%$ for the (I.T.) activation, a significant difference is noticed in the limiting yields of $CH_2{}^{80}BrBr$ between the two types of activations. In the (n,γ) activation, $CH_2{}^{80}BrBr$ decreases from 1.5% with the m.f. of Kr and can be extrapolated to 0.5% at 1.0 m.f. of Kr, but in the (I.T.) activation an additional, noticeable formation occurs when the m.f. of Kr exceeds 0.5 and can be extrapolated to 2.9%.[5]

The fraction of the charged ^{80}Br from the (n,γ) activation is mostly singly-charged. Thus, the thermal ionic yield of $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ must be due to the reactions of thermal Br^{1+}. If this species is also the most important reacting one in the limiting conditions of 1.0 m.f. of Kr in the (I.T.) experiments, there exists no plausible explanation of the higher yield of $CH_2{}^{80}BrBr$ and the lower yield of $CH_3{}^{80}Br$, relative to those in the (n,γ) experiments. A possible explanation, thus, would involve another kind of reacting species of ^{80}Br for the formation of products *via* kinetic-energy-independent processes in the (I.T.) experiments. This is very concievable when one considers that a large fraction of ^{80}Br is formed with multiple charges and little excess kinetic energy as a result of successive internal conversions.[14] As the dilution of the reaction system with Kr proceeds, the distribution of the charge and the energy tends to be controlled through collisions with Kr. At least the fractions of ^{80}Br may be in different charge and energy states from those in the (n,γ) experiments[15] and may react with CH_4 *via* a kinetic-energy-independent process. However, further study will be required before we can describe a real working process which can explain these results.

Formation of $CH_2{}^{80}BrBr$. The yield curve shown in Fig. 1 is very similar to that found in the (I.T.) experiments and can also be explained in terms of the competition of two types of reactions: 1) the formation of $CH_2{}^{80}BrBr$ through the reaction of $\cdot CH_2{}^{80}Br + Br_2 \rightarrow CH_2{}^{80}BrBr + Br$, and 2) the scavenging reaction of Br_2 for the reacting ^{80}Br atom.

However, the shift of the maximum from 0.08 to 0.2, a higher value of Br_2/CH_4 than in the (I.T.) experiments is indicative that the energy state of $\cdot CH_2{}^{80}Br$ is different in the two kinds of activation of ^{80}Br; $\cdot CH_2{}^{80}Br$ in the present (n,γ) activation is rather excited and is less sensitive to Br_2 than in the previous (I.T.) activation. This is possible if they are formed by different reaction processes. However, this is not the time to explore this problem further, although Kr may play a role in the formation of $\cdot CH_2{}^{80}Br$ in the (I.T.) activation.[16]

In the unmoderated systems, at least 2/3 of the $CH_2{}^{80}BrBr$ is formed *via* an energetic process of ^{80}Br. Thus, it is worthwhile to discuss its formation process on the basis of the model previously presented[17–19] by assuming that, in the energetic process, $\cdot CH_2{}^{80}Br$ exists as an intermediate in the formation of $CH_2{}^{80}BrBr$. Wolfgang[17] proposed a direct-double-displacement process to explain the formation of CH_2TI from the reaction of the recoil tritium atom with CH_4 in the iodine-scavenged systems. Later, Tang and Rowland[18] concluded that the process is of minor importance in the reaction of the recoil tritium atom. In the energetic reaction of ^{80}Br, however, the process is rather probable, since the greater the mass of the reacting species is, the larger is the linear momentum transfer into a product in collision, although some ambiguity concerning the time interval between the leaving of the two H atoms remains.[19] The following two reaction schemes can be suggested:

1) single-step double-replacement reaction

$$^{80}Br^* + CH_4 \longrightarrow \cdot CH_2{}^{80}Br + 2H$$

2) two-step single-replacement reaction

$$^{80}Br^* + CH_4 \longrightarrow (CH_3{}^{80}Br)^* + H$$
$$(CH_3{}^{80}Br)^* \longrightarrow \cdot CH_2{}^{80}Br + H$$

The implication of a double displacement occurring in a single step is that the entire reaction process is complete on a time scale comparable to that of the single-substitution processes, *i.e.*, $<10^{-13}$ sec. The two-step process, on the other hand, describes a situation in

14) E. Tachikawa, This Bulletin, **43**, 63 (1970).

15) This consideration is consistent with observations in the reactions of ^{80}Br and ^{82}Br activated by (I.T.) processes with CH_3Br. The moderator curve of the products from the reactions of ^{82}Br can be extrapolated to zero % at 1.0 m.f. of Kr, while those from the reaction of ^{80}Br can be extrapolated to some finite value. This difference can also be ascribed to the difference in the decay schemes of ^{80m}Br and ^{82m}Br: the latter decays to the ground state in a single transition, and the resulting ^{82}Br has a high excess kinetic energy as well as a high charge. Ref. T. Kobaysahi, unpublished data; J. Okamoto and E. Tachikawa, This Bulletin, **42**, 1504 (1969); D. W. Oates, R. L. Ayres, R. W. Helton, K. S. Schwartz, and E. P. Rack, *Radiochem. Radioanal. Lett.*, **4**, 123 (1970).

16) This is possible, since the ^{80}Br from the (I.T.) activation is highly ionized with a relatively low kinetic energy. In the ^{80m}Br–C_2H_6 system, the amount of one of the products, $CH_3{}^{80}Br$, very much depends upon the moderator used (see Ref. 21).

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

18) Y. N. Tang and F. S. Rowland, *J. Phys. Chem.*, **72**, 707 (1968).

19) R. T. K. Baker and R. L. Wolfgang, *ibid.*, **73**, 3478 (1969).

which the excited molecule formed in the first step has sufficient time for some vibrations and/or rotations of individual groups in the molecule on prior to the bond breaking. The two-step mechanism is normally determined through the pressure dependence of the yields of the decomposition products relative to that of the single-displacement products. In the present case, if $CH_2{}^{80}BrBr$ is mainly formed by a two-step mechanism, the ratio of $CH_2{}^{80}BrBr/CH_3{}^{80}Br$ must decrease with an increase in the total pressure. This is in great contrast to the results shown in Fig. 2, which

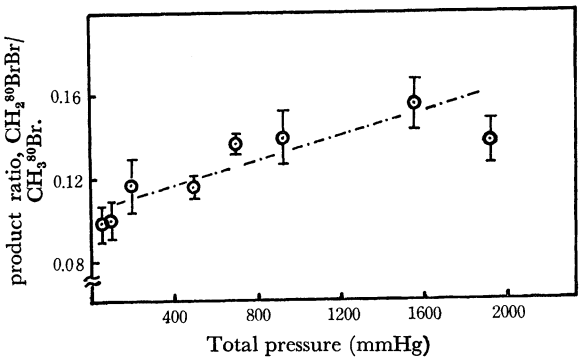

Fig. 2. The product ratio, $CH_2{}^{80}BrBr/CH_3{}^{80}Br$, as a function of the total pressure (Br_2/CH_4=0.02—0.03).

shows the plot of the $CH_2{}^{80}BrBr/CH_3{}^{80}Br$ ratio against the total pressure (using the results in Table 1). Although a quantitative treatment of the results requires a correct knowledge of the energetics of the individual reaction path as well as of a ^{80}Br-energy spectrum, qualitatively it is evident that the $\cdot CH_2{}^{80}Br$ radical is indeed formed largely by the one-step mechanism. However, the contribution, if any, by the two-step mechanism to the formation of this radical cannot be estimated.

Isotope Effect. The isotope effect has been observed in the $CH_3{}^{80}Br$–$CD_3{}^{80}Br$ pair; its value is 2.7 in the unmoderated system, decreases with the m.f. of Kr, and becomes close to unity when the m.f. of Kr becomes over 0.8. The difference in the yields between $CH_2{}^{80}BrBr$ and $CD_2{}^{80}BrBr$ does not exceed the experimental fluctuation over the range of the m.f. of Kr studied.

By tentatively identifying the kinetic energy yield of $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$ as 11.4% and 3.9%, the value of 2.9 ± 0.3 can be obtained as the kinetic isotope effect. When one compares these results with those obtained in the (I.T.) experiments, the ratio is found to be comparable with the 2.7 ± 0.3 for $CH_3{}^{80}Br/CD_3{}^{80}Br$ in the latter experiments.[3] Furthermore, the non-existence of any isotope variation between $CH_2{}^{80}BrBr$ and $CD_2{}^{80}BrBr$ within the range of experimental uncertainty shows an agreement between them.[3] The present isotope effect is due to the reactivity integral isotope effect,[20] and the contribution of the moderator isotope effect is not significant, as has been discussed previously.[3]

The results in Table 2 show that at least 2/3 of the $CH_2{}^{80}BrBr$ is formed *via* an energetic process. Thus, if a similar value of isotope effects presents in the energetic formation of $CH_2{}^{80}BrBr$, the present experimental method will provide a method of detecting the isotopic variation between $CH_2{}^{80}BrBr$ and its isotopic analogue, contrary to the experimental results. The current set of experiments in our laboratory shows that the kinetic isotope effect in C_2H_6–C_2D_6[21] and C_3H_8-isotopic analogues[22] ranges from 1.3 to 1.5. These results suggest that the chemical and/or physical natures of the residual and leaving groups play a role in the isotope effect. If the kinetic isotope effect in the present $CH_2{}^{80}BrBr$–$CD_2{}^{80}BrBr$ remains in this range, the difference in the yields might be overshadowed by the experimental fluctuation. This is possible, since their formations will involve the breaks of two C–H or D bonds. In conclusion, it can only be said that the isotope effect in $CH_2{}^{80}BrBr$–$CD_2{}^{80}BrBr$, if it exists, is much less than that in the $CH_3{}^{80}Br$–$CD_3{}^{80}Br$ pair.

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

21) K. Yanai and E. Tachikawa, presented at the 23rd annual meeting of the Chemical Society of Japan, Tokyo, 1970; *Radiochim. Acta*, in press.

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