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# Estimation of the Thermal Yields in the Reaction with Methanes of $^{80}$Br Activated by (n, $\gamma$) Process

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The Estrup-Wolfgang Kinetic theory has been applied to the results obtained from the reactions of $^{80}$Br activated by the (n,$\gamma$) process with two methanes, $CH_4$ and $CD_4$. With suitable assumptions, the most probable kinetic parameters, $I$'s and $\alpha$'s have been obtained. The thermal yields of the products have been estimated as a function of the m.f. of the Kr moderator as the differences between the yields predicted by the kinetic theory with these kinetic parameters and those experimentally obtained. The thermal $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$ yields are strongly affected by the m.f. of Kr in such a way that they are not important in the range from zero to around 0.7 m.f. of Kr, but become significant over 0.7 m.f. of Kr. On the other hand, the thermal $CH_2{}^{80}BrBr$ and $CD_2{}^{80}BrBr$ yields are much less sensitive to the m.f. of Kr and are almost constant at 0.5% over the whole moderator range of Kr.

In the recoil chemistry of the gaseous phase, the excess kinetic energy processes are depressed by the addition of an inert gas as a kinetic energy moderator to the reaction system. At 1.0 m.f. of an inert gas moderator, the yields of the energetic processes should be extrapolated to zero. If the extrapolated value is finite, the value is usually considered to be the yield of the kinetic-energy-independent processes in an unmoderated system. In our recent work on the reaction with $CH_4$ of $^{80}$Br activated by the (IT) process, however, we found that the addition of a large excess of inert gases to a reaction system sometimes causes an increase in the yield.[1] In such a case, it is necessary for a detailed analysis of the data to establish how the kinetic energy-independent-processes are affected by the addition of inert gases.

This complex phenomenon is primarily due to the charges imparted to the $^{80}$Br atom at the time of the nuclear reaction; it is also due to the relatively low ionization potential of Br. Thus, it could also be anticipated in the reaction of $^{80}$Br activated by the (n,$\gamma$) process with methane.

Rack and Gordus have examined the above reaction and reached the conclusion that the $^{80}$Br atom from the (n,$\gamma$) activation reacts with $CH_4$ principally *via* energetic processes in the whole m.f. range of the moderators.[2] However, a detailed examination of the same reaction system using Kr as the additive has clearly shown that the kinetic-energy-independent process also contributes to the observed organic yields.[3]

In this paper we will apply the Estrup-Wolfgang kinetic theory[4,5] to the data obtained in the reaction of $^{80}$Br activated by the (n,$\gamma$) process with two methanes, $CH_4$ and $CD_4$; with suitable assumptions, the most probable kinetic parameter $I$'s and $\alpha$'s will be determined. The thermal yields of the products have, then, been determined as a function of the m.f. of the Kr moderator as the differences between the yields predicted by the kinetic theory and those experimentally determined.

## Experimental and Results

The experimental procedure has been described in detail in a previous paper.[3] Samples were prepared in 18.5 ml silica ampoules. In all cases, the $Br_2/CH_4$ or $CD_4$ ratio was 0.02, and the total pressure was kept constant at 500±10 mmHg. Energetic $^{80}$Br was formed by irradiating the samples for 5—60 sec in a JRR-4 reactor. The thermal neutron flux at the irradiation port was $2\times10^{12}$ n/cm$^2$/sec.

The present experimental data, as well as those in Ref. 3, have been used for the present kinetic treatment. The agreements between them are reasonably good. A small difference, however, can be seen in the yield of $CH_3{}^{80}Br$ at a high moderation. All the results are included in Figs. 1 and 2. The most sig-

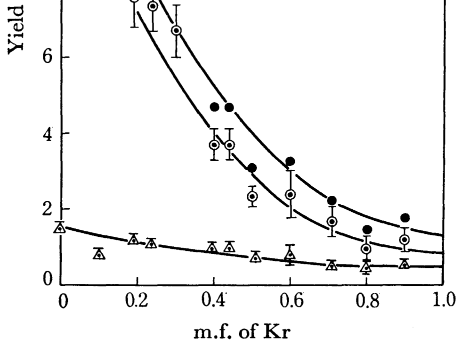

Fig. 1. Product distributions from the reaction system, $^{80}Br+CH_4+Kr$.
●: total organic yield, ⊙: $CH_3{}^{80}Br$, △: $CH_2{}^{80}BrBr$.

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[1] K. Numakura, M. Saeki, and E. Tachikawa, This Bulletin, **46**, 1 (1973).

[2] E. P. Rack and A. A. Gordus, *J. Phys. Chem.*, **65**, 944 (1961).

[3] M. Saeki, K. Numakura, and E. Tachikawa, This Bulletin, **45**, 1715 (1972).

[4] P. J. Estrup and R. Wolfgang, *J. Amer. Chem. Soc.*, **82**, 2665 (1960).

[5] R. Wolfgang, *J. Chem. Phys.*, **39**, 2983 (1963).

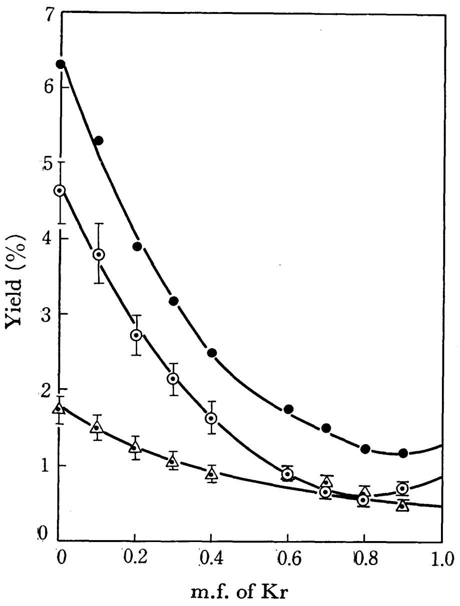

Fig. 2. Product distributions from the reaction system, $^{80}Br+CD_4+Kr$.
●: total organic yield, ⊙: $CH_3{}^{80}Br$, △: $CH_2{}^{80}BrBr$.

nificant error in the present data has been introduced in the measurement of the total $^{80}Br$ activities; it amounts to ±10% in some cases. The uncertainties in the figures indicate the standard deviations among the several measurements.

## Application of Kinetic Theory

Estrup and Wolfgang have developed a kinetic theory of hot atom reactions partially based on the mathematics of neutron-cooling processes.[4,5] Although the exact solutions for the kinetic theory must be valid only for highly restricted special cases, they can furnish appropriate forms for the treatment of the experimental data. Three assumptions are involved in this kinetic treatment.[5] The first is that the energy loss occurs by collisions, in which the collision partners can be treated as elastic spheres. The second is that the initial energy of the atom, $E_0$, is sufficiently large so that the atom has made a number of collisions before reaching the upper limit of the reaction zone, $E_2$, thus providing a statistically well-defined distribution of energies for the hot atoms in the region of interest. The third is that the minimum energy required for the reaction, $E_1$, is still large compared to the thermal energies. The validity of these assumptions has been discussed in various systems, and the theory has been successfully applied to the hot atom reactions of halogens[2,6-8] as well as tritium.[5,9]

In the present systems, difficulties arise for at least two reasons. One is related to the initial energy of the $^{80}Br$ atom, in connection with the second assumption. Since the present knowledge of the spectrum of $\gamma$-rays emitted after the neutron capture of $^{79}Br$ is not sufficient, we only known that the maximum initial kinetic energy of $^{80}Br$ is 179 eV, which is low compared with those of (n,p)-activated tritium atoms (in the order of $10^5$ eV). Thus, it can be considered that an appreciable fraction of the $^{80}Br$ atoms will be born with a low kinetic energy, in or near the reactive zone.[10] Rack and Gordus applied this theory to the reaction of $^{80}Br$ with gaseous methane.[2] Later, its application was extended further to the reaction of $^{80}Br$[11,12] or $^{82}Br$[6] activated by isomeric transition in various systems. These successful applications in both gaseous and liquid phases[8] can be taken as indicating that this assumption is reasonably justified in our present system. The other concerns the fact that no information is available about the Br-to-HBr abstraction reaction probability for the present reaction system, since no experimental procedure can serve for measuring $H^{80}Br$. Because of the low organic yield in the $^{80}Br+CH_4$ system, we could expect the inorganic yield to be comparable, causing no difficulty in the use of the kinetic theory treatment for a case of low reactivity.

According to the developed kinetic theory, the total energetic yields, $P$, in the moderator experiments have been expressed in terms of two kinetic parameters, $I$, reactivity integral and, $\alpha$, average logarithmic energy loss, as follows:

$$-\frac{1}{\ln(1-P)} = \frac{\alpha_{\mathrm{react}}}{I} + \frac{\alpha_{\mathrm{mod}}}{I}\cdot\frac{1-f}{f} \tag{1}$$

When the total probability of a hot reaction, $P$, is low, as in the present case, the developed equation for the yield of individual products from the hot reaction with a reactant in the moderated system, $P_i$ (hot), can be simply expressed as:

$$P_i(\mathrm{hot}) = (I_i/\alpha_{\mathrm{react}})(1+\alpha_{\mathrm{mod}}/\alpha_{\mathrm{react}}(1/f-1))^{-1} \tag{2}$$

If we know the values of $I_i/\alpha_{\mathrm{react}}$ and $\alpha_{\mathrm{react}}/\alpha_{\mathrm{mod}}$, we can calculate $P$ over the whole range of moderators using Eq. (1).

In the actual application of the kinetic theory to the results shown in Figs. 1 and 2, we have to consider the contribution of the thermal yield involved. It is possible to express the observed yield of individual products as the summation of the yields due to the energetic process and the thermal process at any m.f. of Kr. Thus, the following equation can be derived:

$$P_i = (I_i/\alpha_{\mathrm{CH_4}})(1+\alpha_{\mathrm{Kr}}/\alpha_{\mathrm{CH_4}}(1/f-1))^{-1} + P_{i(\mathrm{thermal})} \tag{3}$$

The first term is for the energetic yield, and the second, for the thermal yield. It is known only that $P_{i(\mathrm{thermal})}$ is equal to the extrapolated value, $P^{\infty}_{i(\mathrm{thermal})}$, at 1.0 m.f. of Kr. Three cases can be considered, depending upon how the $P_{i(\mathrm{thermal})}$ varies with the m.f. of Kr:

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[6] J. B. Nicholas and E. P. Rack, *J. Chem. Phys.*, **48**, 4058 (1968).

[7] E. P. Rack and A. A. Gordus, *ibid.*, **34**, 1855 (1961).

[8] M. Milman, *Radiochim. Acta*, **2**, 180 (1964).

[9] R. T. K. Baker, M. Silbert, and R. Wolfgang, *J. Chem. Phys.*, **52**, 1120 (1970).

[10] Using the random-walk equations, Rack *et al.* tried to calculate the kinetic energy spectra for (n,$\gamma$)-activated $^{128}I$ atoms, which have the maximum initial kinetic energy of 194 eV. The results showed that an appreciable fraction of the $^{128}I$ species are born with kinetic energy, near the reaction zone. M. Yoog, Y. C. Pao, and E. P. Rack, COO-1617-30 (1971).

[11] E. Tachikawa and K. Yanai, *Radiochim. Acta*, **17**, 138 (1972).

[12] K. Numakura and E. Tachikawa, This Bulletin, **46**, 346 (1972).

Case 1. $P_{i(\text{thermal})}$ is constant over the whole m.f. range of Kr. In this case, $P_{i(\text{thermal})}$ is simply equal to $P^{\infty}_{i(\text{thermal})}$ and can be experimentally found.

Case 2. $P_{i(\text{thermal})}$ is zero with no additive, but rises with an increase in the m.f. of Kr.

Case 3. This involves both cases, 1 and 2. $P_{i(\text{thermal})}$ increases with the m.f. of Kr from a non-zero value to $P^{\infty}_{i(\text{thermal})}$.

In the first case, the addition of an inert gas simply reduces the average kinetic energy of the $^{80}$Br atom, resulting in a reduction of the energetic yiled without influencing the thermal yield. This is the case which is usually expected in recoil chemistry. In the other cases, however, the physical properties other than the kinetic energy of the recoil atom, such as the charge or electronic excitation energy state, are also affected by the addition of an inert gas, and the extrapolated value, $P_{i(\text{thermal})}$, at 1.0 m.f. of Kr does not reflect the true thermal yield in the unmoderated system.

Unfortunately, without any *a priori* basis to know which category the present case belongs to, we can only assume that the thermal yield does not exceed the $P^{\infty}_{i(\text{thermal})}$-value at any m.f. of Kr. Thus, the contribution of the total thermal yield ($P_{\text{thermal}}=\sum P_{i(\text{thermal})}$) to the observed yield ($P$) is probably not significant at low m.f. values of Kr. As a first step to the kinetic treatment, therefore, the total organic yields obtained from zero to about 0.4 m.f. of Kr were subjected to Eq. (1), with the assumptions that, in this range of the m.f. of Kr, the total thermal yield is of only minor importance and that practically all the products are formed *via* energetic processes. The results obtained were shown graphically in Figs. 3 and 4 for the $^{80}$Br–CH$_4$–Kr and $^{80}$Br–CD$_4$–Kr systems. The ratio of the intercept to the slope gives $\alpha_{\text{CH}_4}/\alpha_{\text{Kr}}=0.33$ in Fig. 3 and $\alpha_{\text{CD}_4}/\alpha_{\text{Kr}}=0.37$ in Fig. 4.

If the $I_i/\alpha_{\text{react}}$ values are obtained by subtracting the thermal yield, $P^0_{i(\text{trermal})}$, from the observed yield, $P_i$, in an unmoderated system, we can calculate the energetic yield of the individual products at any m.f. of Kr using Eq. (2). Then, the difference ($\Delta P_i$) between the calculated yield and the experimentally-obtained yield can be assumed to be the kinetic-energy-independent yield. Without a knowledge of the true $P^0_{i(\text{thermal})}$ value, however, we can choose any value from zero to the limiting yield at 1.0 m.f. of Kr, $P^{\infty}_{i(\text{thermal})}$. If a proper value is taken for $P^0_{i(\text{thermal})}$, $\Delta P_i$ as a function of the m.f. of Kr should belong to one of three classes, depending upon the Cases 1, 2, or 3 discussed above. In Case 1, $\Delta P_i$ will be equal to the chosen value at any m.f. of Kr, while in Case 2 or 3 $\Delta P_i$ will increase with the m.f. of Kr from zero or a non-zero value to the $P^{\infty}_{i(\text{thermal})}$. A set of calculations with the results for CH$_3$$^{80}$Br and CD$_3$$^{80}$Br show that when we use a $P^0_{i(\text{thermal})}$ value other than zero the $\Delta P_i$ value obtained always shows a concave curve *vs.* the m.f. of Kr and has a minimum around 0.5 m.f. of Kr. Such a behavior of the thermal yield is very unrealistic, since the thermal process yield should not be reduced by the addition of an inert gas. On the other hand, when $P^0_{i(\text{thermal})}$ is set as zero, the $\Delta P_i$ converges from around zero up to 0.7 m.f. of Kr. This $\Delta P_i$ curve shows a behavior consistent with the Case 2, indicating that the thermal yields of CH$_3$$^{80}$Br and CD$_3$$^{80}$Br in the present system are not important in the range from zero to around 0.7 m.f. of Kr, but become significant at a higher moderation.

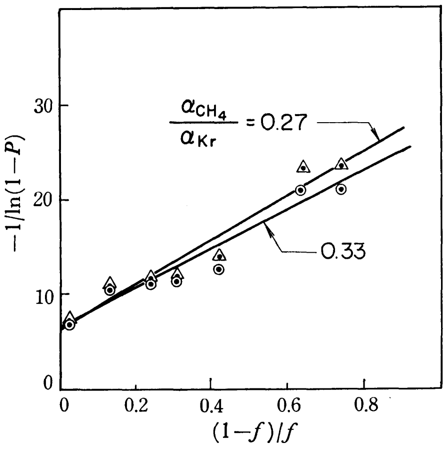

Fig. 3. Plot corresponding to equation 1) for the reaction system, $^{80}$Br+CH$_4$+Kr.
⊙: calculated with the total organic yields, △: calculated with the values subtracted 0.5% from the total organic yields.

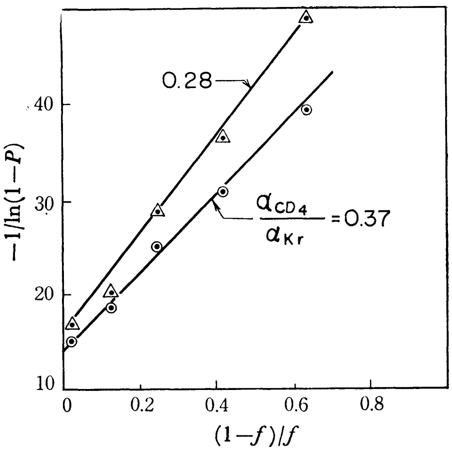

Fig. 4. Plot corresponding to equation 1) for the reaction system, $^{80}$Br+CD$_4$+Kr.
⊙: calculated with the total organic yields, △: calculated with the values subtracted 0.5% from the total organic yields.

A similar treatment of the results for CH$_2$$^{80}$BrBr and CD$_2$$^{80}$BrBr leads to the conclusions that, when $P^0_{i(\text{thermal})}$ is chosen as 0.5%, $\Delta P_i$ is almost constant at 0.5 any mole fraction of Kr. This accords with the results expected in Case 1.

Those results were fed back to the recalculation of $\alpha_{\text{react}}/\alpha_{\text{mod}}$ using Eq. (1). In this feed-back calculation, the total organic yields less 0.5% were used as the $P$ values. The results obtained are also plotted in Figs. 3 and 4 in the $-1/\ln(1-P)$ *vs.* $(1-f)/f$ relation. The ratio of the intercept to the slope of the lines gives $\alpha_{\text{CH}_4}/\alpha_{\text{Kr}}=0.27$ for the CH$_4$–Kr system and $\alpha_{\text{CD}_4}/\alpha_{\text{Kr}}=0.28$ for the CD$_4$–Kr system. Using new values for $\alpha_{\text{react}}/\alpha_{\text{mod}}$, the calculation of the energetic yields of the individual products were performed in a manner similar to that described above. The results are summarized in Fig. 5 for methyl bromides, CH$_3$$^{80}$Br and CD$_3$$^{80}$Br, and in Fig. 6 for methylene bromide, CH$_2$-

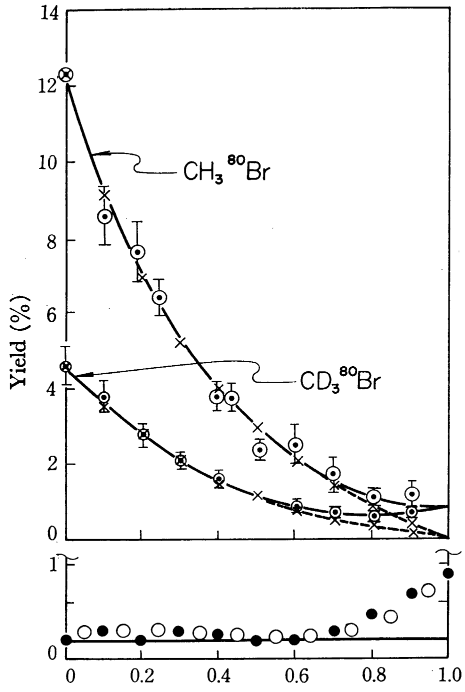

Fig. 5. Difference between the experimental yields and calculated ones of CH$_3$$^{80}$Br and CD$_3$$^{80}$Br: estimation of their thermal yields.
in the upper figure.
⊙: experimental yields of CH$_3$$^{80}$Br or CD$_3$$^{80}$Br
× : calculated yields of CH$_3$$^{80}$Br or CD$_3$$^{80}$Br
in the lower figure
●: estimated thermal yields of CH$_3$$^{80}$Br
○: estimated thermal yields of CD$_3$$^{80}$Br

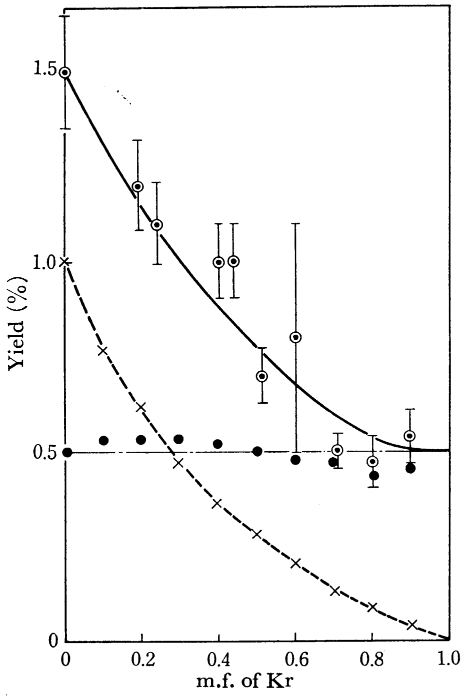

Fig. 6. Difference between the experimental yields and calculated ones of CH$_2$$^{80}$BrBr.
estimation of the thermal yields.
⊙: experimental yields of CH$_2$$^{80}$BrBr
× : calculated yields of CH$_2$$^{80}$BrBr
●: estimated thermal yields of CH$_2$$^{80}$BrBr

$^{80}$BrBr. The calculated energetic yields are shown by broken lines, in comparison with the experimental data, which are expressed by circles, with the experimental error and are connected by a solid line. The differences between two lines are assumed to be the thermal yields and are shown in the same figures by solid circles for CH$_3$$^{80}$Br and CH$_2$$^{80}$BrBr and by open circles for CD$_3$$^{80}$Br. The thermal yields of CD$_2$$^{80}$BrBr obtained by a similar treatment, which are not included in the figure, were just the same as that obtained for CH$_2$$^{80}$BrBr, showing no significant difference in the contribution of the thermal process to the observed yield between CH$_2$$^{80}$BrBr and CD$_2$$^{80}$BrBr.

It can be said that the thermal yield of methyl bromide is not significant and that it is substantially zero in the m.f. range of Kr from zero to around 0.7, but it starts to rise with a further increase in the m.f. of Kr and can reach to around 0.8% at 1.0 m.f. of Kr. On the other hand, the thermal yield of methylene bromide, CH$_2$$^{80}$BrBr or CD$_2$$^{80}$BrBr, is almost constant at 0.5% over the whole m.f. range of Kr and no noticeable effect has been observed upon the addition of Kr.

In order to confirm the above hypotheses, a further investigation has been carried out on the isotope effect in CH$_3$$^{80}$Br/CD$_3$$^{80}$Br. The following assumptions have been introduced:

1) The thermal yield of the methyl bromide is related to the m.f. of Kr in the form of $X_{\mathrm{Kr}}^n$ ($X_{\mathrm{Kr}}$ is the m.f. of Kr, and $n$ is a constant), and no isotope effect exists in the CH$_3$$^{80}$Br/CD$_3$$^{80}$Br system as far as the thermal yields are concerned.
2) The values of the isotope effect in the energetic yield do not vary significantly from 2.7 over the whole moderator range of interest.

The first assumption is primarily based on the findings of the above kinetic treatments of the results. Although any other possible function might be used, it is convenient to use the present simple function, since there is almost no knowledge about the dependence of the thermal yield on the concentration of Kr except the present results. The non-existence of the isotope effect on the thermal processes has also been noticed in the reaction of $^{80}$Br activated by the isomeric transition.[11] Thus, this is a reasonable starting assumption for the subsequent considerations. The second assumption is a rather crude one. Strictly speaking, this assumption is well justified only in a situation where the possible reaction energy range is the same for both reactions to form CH$_3$$^{80}$Br and CD$_3$$^{80}$Br and where the ratio of the probability of a successful reaction per collision for CH$_3$$^{80}$Br relative to that for CD$_3$$^{80}$Br is constant over the whole reaction energy range. This situation is a case of the reactivity integral isotope effect. However, the distinction of this situation from the others is not possible, and we can only assume this is the case.

On these assumption, the following equation can be derived for the isotopic variation in the yield of methyl bromide:

$$Y_{(n)}=\frac{(I_{\mathrm{i}}/\alpha_{\mathrm{CH_4}})(1+\alpha_{\mathrm{Kr}}/\alpha_{\mathrm{CH_4}}(1/f-1))^{-1}+X_{\mathrm{Kr}}^{n}A}{(I_{\mathrm{i}}/\alpha_{\mathrm{CD_4}})(1+\alpha_{\mathrm{Kr}}/\alpha_{\mathrm{CD_4}}(1/f-1))^{-1}+X_{\mathrm{Kr}}^{n}A'} \tag{4}$$

If $n$=zero, Eq. (4) can be simplified to;

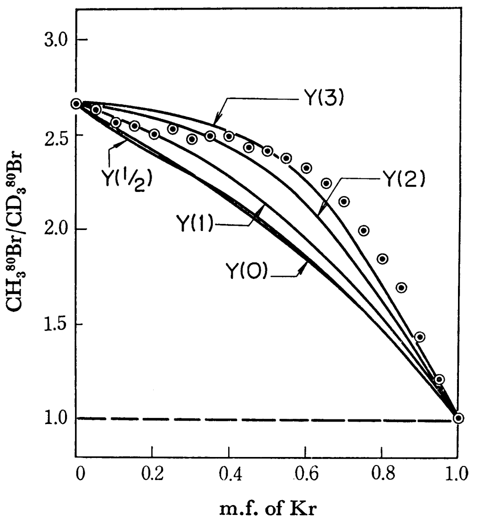

Fig. 7. Plot corresponding to Eqs. (4) and (5) with the experimental values. (details in the text.)

$$Y_{(n)} = \frac{(I_i/\alpha_{CH_4} - A)(1+\alpha_{Kr}/\alpha_{CH_4}(1/f-1))^{-1}+A}{(I_i/\alpha_{CD_4} - A')(1+\alpha_{Kr}/\alpha_{CD_4}(1/f-1))^{-1}+A'} \quad (5)$$

At the limiting condition at 1.0 m.f. of Kr, A$=P^{\infty}_{CH_3{}^{80}Br\,(thermal)}$ and $A'=P^{\infty}_{CD_3{}^{80}Br\,(thermal)}$. Since the limiting yield is roughly equal to 0.85% for both $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$, $A'=A$. On the other hand, at zero m.f. of Kr, $I_i/\alpha_{CH_4}$ and $I_i/\alpha_{CD_4}$ are equal to $P^0_{CH_3{}^{80}Br}$ and $P^0_{CD_3{}^{80}Br}$ and are 12.3 and 4.6% respectively. Figure 7 shows Eq. (4) (for $n$ equal to 1/2, 1, or 2) and Eq. (5) (for $n$ equal to zero). The plots of the $CH_3{}^{80}Br/CD_3{}^{80}Br$ ratio obtained from the interpolated curves in Figs. 1 and 2 for $CH_3{}^{80}Br$ and $CD_3{}^{80}Br$ are also shown in the same figure. It is obvious that the experimental curve is far from the prediction for $n$=zero, although it does not show a good fit with either of the calculated cruves.

In view of the limits, accuracy of the present experimental results, it is very hard to discuss the results quantitatively and to find a function to fit the experimental results. One conclusion we can draw from the present calculations is that the contribution of the thermal process in producting methyl bromide is affected by the concentration of Kr. This conclusion accords with the finding in the early part of this paper.

*Comparison of the Kinetic Parameter. I.* Here it is interesting to evaluate the $I$ value in the present reaction system and to compare it with those found in other reaction systems, such as in the reaction with the methane of $^{80}$Br activated by isomeric transition.[1] This comparison will provide qualitative information concerning the reactivity of the recoil atom activated by various nuclear reactions.

By expanding Eq. (1), the following can be obtained:

$$P = (f/\alpha)I - (f/\alpha)^2K + (f/\alpha)^3L \cdots \quad (6)$$

In the case of a low reactivity, the total probability, $P$, may be well approximated by the first two terms, because these series will converge rapidly. A plot of $(\alpha/f)P$ *vs.* $f/\alpha$ should give a straight line, with an intercept of $I$ and a slope of $K$. The values for $I$ obtained by the plots are tabulated in Table 1, with along the $\alpha_{CH_4}$ and $\alpha_{CD_4}$ values. The $I_i$ values obtained using Eq. (2) were also included. Those are all expressed in units of $\alpha_{Kr}$.

Nicholas and Rack have also applied the kinetic theory to the total organic yield in the reaction of $^{82}$Br activated by the (IT) process with $CH_4$.[6] In their calculation, the kinetic energy yield was obtained simply by subtracting the limiting yield at 1.0 m.f. of the moderator from the observed yield at various m.f. values of the moderator; $\alpha_{CH_4}=0.098$ $\alpha_{Kr}$ and $I_{CH_3{}^{82}Br}=0.004$ $\alpha_{Kr}$ were thus obtained.

However, a recent detailed examination of the reaction of $^{80}$Br activated by the (IT) process with $CH_4$[1,14] has revealed that an additional yield due to the kinetic-energy-independent process becomes noticeable at a high moderation. A similar trend can also be expected in Rack's experiment. We consider that these reported values are strongly affected by the kinetic-energy-independent yield.

Although the $\alpha$ value should be an energy-dependent term, it is not conceivable that the value changes drastically in the reaction of the (IT)-induced $^{80}$Br or $^{82}$Br atom. The treatment of the results in Ref. (1) using the $\alpha$ value obtained in this work, $\alpha_{CH_4}=0.27$ $\alpha_{Kr}$, gave $I_{CH_3{}^{80}Br}=0.018$ $\alpha_{Kr}$, which is also included in Table 1. The $I_{CH_3{}^{80}Br}$ value in the (n,$\gamma$)$^{80}$Br–$CH_4$ system is roughly three times that in the $^{80m}$Br–$CH_4$ system under the present kinetic treatment.

## Discussion

The above calculations show that, within the limits of experimental error, the kinetic theory appears to be applicable to the present system as far as the energetic reactions are concerned; it also seems to be an adequate

TABLE 1. PARAMETERS OF KINETIC THEORY
(expressed in units $\alpha_{Kr}$)

| Reaction system | $\alpha$ | $I$(total) | $I$(product) | Reference |
|---|---|---|---|---|
| $^{79}Br(n,\gamma)^{80}Br+CH_4$ | $\alpha_{CH_4}=0.266$ | 0.043 | $I_{CH_3{}^{80}Br}=0.04$ | Present work |
| | $(\alpha_{CH_4}=0.3)^{a)}$ | 0.057 | …… | Ref. 2 |
| $^{79}Br(n,\gamma)^{80}Br+CD_4$ | $\alpha_{CD_4}=0.280$ | 0.020 | $I_{CD_3{}^{80}Br}=0.015$ | Present work |
| $^{80m}Br(IT)^{80}Br+CH_4$ | $\alpha_{CH_4}=0.266$ | …… | $I_{CH_3{}^{80}Br}=0.018$ | Ref. 1 |
| $^{82m}Br(IT)^{82}Br+CH_4$ | $\alpha_{CH_4}=0.098$ | …… | $I_{CH_3{}^{80}Br}=0.004$ | Ref. 6 |

a ) calculation with Kr moderation data in Ref. 2.
b ) calculation based on the present $\alpha$ value.

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13) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids" John Wiley & Sons, Inc., New York (1954), p. 1110.

14) E. Tachikawa and T. Kahara, This Bulletin, **43**, 1293 (1970).

framework for the entire range of data. In other words, it appears that the assumptions of the kinetic theory are reasonably satisfied, in that the treatment is sufficiently insensitive to the approximations that are inherent in these assumptions.

However, some question still remains as to the value used as the total energetic yield. The abstraction of hydrogen by the recoil atom is a very common reaction mode; it must also be taken into account in the present system. In the recoil tritium reactions, the ratio of the hydrogen-abstraction yield to the hydrogen-substitution-reaction yield has been well established as 0.79 for $CH_4$,[15] and it tends to increase with the number of carbon atoms in the reactant molecule.[16] Recently Root *et al.* examined the energetic F-to-HF abstraction yield in the reaction of recoil $^{18}F$ with $CH_3CF_3$ and reported the value of 51% for the primary yield.[17]

Without any available experimental data for the Br-to-HBr abstraction reaction, we assigned various yields for this abstraction yield and tried to determine the trend shown by the results drawn from the kinetic treatment. Assuming, for example, that the energetic $H^{80}Br$ yield is equal to the total organic yield, the kinetic treatment gave $\alpha_{CH_4}/\alpha_{Kr}=0.26$, which is quite similar to the value found in the preceeding calculation. Thus, the conclusion reached above is hardly affected by a correction for the total organic yield, considering the energetic $H^{80}Br$ yield.

The identity of the thermal processes is primarily ascribed to the thermal ionic processes, considering the physical state of $^{80}Br$ at the time of formation from the nuclear reaction. However, when we compared the limiting yield at 1.0 m.f. of Kr between the present case and the $^{80m}Br$–$CH_4$,[1] a similar value was found for $CH_3{}^{80}Br$ but not for $CH_2{}^{80}BrBr$. This can not be easily explained with the presently available knowledge, as has been suggested in an earlier report of this series,[18] the role of interaction between $^{80}Br$ and Kr might also be considered.

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