Reactions of Hot \((n, \gamma)\)-Produced \(^{80}\text{Br}\) with CH\(_3\)Br. Comparison with the Reactions between Hot \(^{35}\text{Cl}\) and CH\(_3\)Cl, and Calculation of the Excitation Functions\(^*\)

Zeev B. Alfassi,† Saadia Amir, and Michael Baer†

Nuclear Chemistry Department, Soreq Nuclear Research Centre, Yavne, Israel

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The reactions of hot \((n, \gamma)\)-produced 17.6 m \(^{80}\text{Br}\) with methyl bromide were studied in the presence of He and Kr as moderators. The survival probability of the reaction products was found to be the same in both moderators, suggesting that no observable decomposition took place upon moderation (within a 15% error). The reactivity integral for halogen displacement in the reaction was found to be equal to that in the system \(^{35}\text{Cl} + \text{CH}_3\text{Cl}\), which seems reasonable since the activation energies and steric factors are almost equal. The ratio of hydrogen displacement to halogen displacement was smaller in the case of \(^{80}\text{Br}\) than in that of \(^{35}\text{Cl}\), as can be predicted on the basis of the translational inertial factor. From the reactivity integrals and the activation energies the excitation functions for halogen displacement were calculated by the energy-dependent hard potential model of Baer and Amir.

I. INTRODUCTION

In a system containing hot \(^{80}\text{Br}\) atoms (* denoted radioactive) and methyl bromide molecules the following hot reactions can occur: \(^{*}\)

1. displacement of a halogen atom:

\[^{*}\text{Br} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3[^{*}\text{Br}] + \text{Br}; \quad [\text{I}]\]

2. displacement of a hydrogen atom:

\[^{*}\text{Br} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3[^{*}\text{Br}] + \text{Br} + \text{H}; \quad [\text{II}]\]

3. displacement of both a hydrogen atom and a halogen atom:

\[^{*}\text{Br} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3[^{*}\text{Br}] + \text{H} + \text{Br}\) (or \(\text{HBr}\)); \quad [\text{III}]

4. displacement of two hydrogen atoms:

\[^{*}\text{Br} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3[^{*}\text{Br}] + \text{H} + \text{H}\) (or \(\text{H}_2\)). \quad [\text{IV}]

This study is concerned with the study of the yields of these reactions, their dependence on the concentration of the moderators (He and Kr), and the parameters of the kinetic theory derived from this dependence.

The \((n, \gamma)\) reaction with bromine forms two isomers from each of the naturally occurring isotopes \(^{79}\text{Br}\) and \(^{81}\text{Br}\), of natural abundances of 50.54% and 49.64%, respectively; from \(^{79}\text{Br}\) are formed 4.44 h \(^{80}\text{Br}\) (25%) and 17.6 m ground state \(^{80}\text{Br}\) (75%); from \(^{81}\text{Br}\) are formed 6.2 m \(^{80}\text{Br}\) (9%) and 35.4 h ground state \(^{80}\text{Br}\) (91%). The metastable isomers of both \(^{80}\text{Br}\) and \(^{82}\text{Br}\) decay into their corresponding ground state by isomeric transition (I.T.). The energy of recoil due to the I.T. (arising from the electrostatic breakup of the parent molecule) is much smaller than that of the same nuclide produced directly by \((n, \gamma)\) reaction. Since it is the higher energy which is of interest, care should be taken that there will be no considerable contribution from the I.T. to the studied nuclide. By choosing appropriate time intervals between the irradiation and the separation of the mixture of the irradiated gases, the chemical reactions of the hot \(^{80}\text{Br}\) produced directly by the \((n, \gamma)\) reaction and the chemical reactions of hot \(^{80}\text{Br}\) originating from isomeric transition can be studied separately.

II. EXPERIMENTAL

The reactions of hot bromine atoms with methyl bromide were studied using \(^{80}\text{Br}\) recoiling from \(^{79}\text{Br}\) \((n, \gamma)\) \(^{80}\text{Br}\) reaction, induced by reactor neutrons. The experimental procedure was the same as described previously for \(^{35}\text{Cl}\). Essentially this procedure involves the irradiation near the reactor core of a quartz ampule containing a mixture of gases and the separation of the irradiated gaseous mixture by gas chromatography in a 1.5 m column containing 15% tricresyl phosphate on Sil-O-Cel firebrick 50–60 mesh, at 105°, and eluting with helium at a flow of 80–140 ml/min at STP with T.C. scanning a thermistor and radioactivity scan by NaI(Tl) detector. A representative radioisotope chromatogram is given in Fig. 1. The different fractions were collected on short columns of active charcoal. The kather of 17.6 m \(^{80}\text{Br}\) atoms in the unbroken irradiated ampule and in the different separated fractions, on the columns of the active charcoal, were assayed by measuring the 618 keV gamma rays of \(^{80}\text{Br}\) by a 3 in. NaI(Tl) scintillator connected to 100 channel analyzer.

A time interval between the irradiation (ranging between 15–60 sec) and the last counting not exceeding 30 min was chosen to keep the contribution of \(^{80}\text{Br}\) produced by the isomeric transition of \(^{80}\text{Br}\) below 5%.

The ratio of the concentrations of the scavenger to the reactant was increased with increasing mole fraction of the moderator. This procedure, the same as used previously in the case of \(^{35}\text{Cl}\), was employed to take care of a possible increase of the fraction of the thermal atoms and ions.

III. RESULTS

A. Scavengers

The efficiencies of Br\(_2\) and I\(_2\) as scavengers for studying the reactions of hot bromine atoms were
determined by measuring the yield of the reaction

\[
{}^{80}\text{Br} + \text{CH}_2\text{Br} \rightarrow \text{CH}_2{}^{80}\text{Br} + \text{Br}
\]

in the presence of different concentrations of Br$_2$ and I$_2$. The results of these measurements are given in Table I. It is seen that both Br$_2$ and I$_2$ are satisfactory scavengers. This was verified by the unchanged yield when ethylene (which scavenges thermal halogen atoms and ions\textsuperscript{1,9}) was added. The same behavior was previously found for $^{35}$Cl$^1$.

Use of Br$_2$ is more convenient, since the low vapor pressure of I$_2$ required a corresponding low pressure of CH$_2$Br (up to 30 torr). However, Br$_2$ as a scavenger has the disadvantage that the product of substitution of a hydrogen atom (Reaction [II]) is the same as the product of a double displacement of both a bromine atom and a hydrogen atom (Reaction [III]) since the CH$_2{}^{80}$Br$^\cdot$ radical reacts with Br$_2$ to produce CH$_2$BrBr:

\[
\text{CH}_2{}^{80}\text{Br}^\cdot + \text{Br}_2 \rightarrow \text{CH}_2{}^{80}\text{Br} + \text{Br}_2.
\]

In the case of I$_2$ these reactions are distinguishable, the first producing CH$_2$BrBr and the second CH$_2{}^{80}$BrI. Br$_2$ was used to study the dependence of the yields on the moderator concentration while I$_2$ was used to study the yields of Reactions [II] and [III] separately, in the absence of moderators.

### B. Reaction Yields

Table II summarizes the measured hot reaction yields of CH$_2{}^{80}$Br and CH$_2$BrBr in the presence of He and Kr as moderators and Br$_2$ as a scavenger. Each result is an average of 6–12 repeated experiments and the standard deviation of the average value is 6%–12%. Varying the pressure in the range of 200–800 torr had no effect on the yields (within the experimental error), when the samples were of constant composition (cf. Table III).

From the last column of Table II it can be seen that the ratio of the yields of CH$_2{}^{80}$BrBr to CH$_2$Br remains constant, within the experimental error, and is independent of the concentration and type of moderator, as predicted by the kinetic theory for systems with low yields\textsuperscript{10}.

The separate contributions of Reactions [II] and [III] to the yield of CH$_2$BrBr were measured using I$_2$ as a scavenger. These measurements were made only in the absence of moderators. The ratio of the yields of these two reactions may be assumed to be independent of the presence of a moderator, as was found for the ratio between CH$_2$BrBr and CH$_2$Br. The yield of CH$_2{}^{80}$BrBr (Reaction [II]) was found to be 0.27% of the total $^{80}$Br atoms, and the yield of CH$_2$Br (Reaction [III]) 0.66%. (The sum of these two results is slightly less, but within experimental error, than the CH$_2$BrBr yield of 1.00% found when Br$_2$ was used as scavenger.)

Another product obtained from the interaction of hot

### Table I. Yields of the reaction $^{80}$Br + CH$_2$Br $\rightarrow$ CH$_2$Br in the presence of varying concentrations of different scavengers.

<table>
<thead>
<tr>
<th>Mole fraction of scavenger</th>
<th>Ethylene (±const Br$_2$)</th>
<th>Ethylene (±const I$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>12.8</td>
<td>3.2</td>
</tr>
<tr>
<td>0.003</td>
<td>10.6</td>
<td>2.8</td>
</tr>
<tr>
<td>0.004</td>
<td>6.9</td>
<td>4.6</td>
</tr>
<tr>
<td>0.005</td>
<td>3.2</td>
<td>3.4</td>
</tr>
<tr>
<td>0.010</td>
<td>2.9</td>
<td>3.1</td>
</tr>
<tr>
<td>0.020</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>0.050</td>
<td>3.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* The relative error is <10%.

$^a$ 0.010 mole fraction of I$_2$ and varying concentrations of ethylene.

$^b$ 0.020 mole fraction of Br$_2$ and varying concentrations of ethylene.
$^{80}\text{Br}$ with $\text{CH}_2\text{Br}$ in the presence of $\text{Br}_2$ is $\text{CH}^{80}\text{BrBr}_2$, which could be formed in two ways:

(a) by the reaction of the radical $\text{CH}^{80}\text{Br}^+$, produced by the displacement of two hydrogen atoms (Reaction [IV]), with a $\text{Br}_2$ molecule:

$$\text{CH}^{80}\text{Br}^+ + \text{Br}_2 \rightarrow \text{CH}^{80}\text{BrBr}_2 + \text{Br}$$  \[VI\]

![Diagram](image)

Fig. 2. The kinetic theory plots for the yields of $\text{CH}_2^{80}\text{Br}$ and $\text{CH}_2^{80}\text{BrBr}$ in the presence of He and Kr as moderators. The collision cross sections were calculated from the collision diameters derived from Lennard-Jones potentials fitted to viscosity data. The following collision diameters were used: $\text{He} = 2.58$ Å, $\text{Br} = \text{Kr} = 3.61$ Å. The diameter of $\text{CH}_2\text{Br}$ was calculated from that of $\text{CH}_3\text{Cl}$ ($3.38$ Å) and from the difference in the covalent radii of a bromine atom and a chlorine atom (1.14 Å and 0.99 Å, respectively); the value obtained was $3.38 + 2(0.15) = 3.68$ Å.

(b) by the elimination of HBr from $\text{CH}_2^{80}\text{BrBr}^{11,12}$ and the reaction of the produced carbene diradical, $\text{CH}^{80}\text{Br}$: with a $\text{Br}_2$ molecule:

$$\text{CH}_2^{80}\text{BrBr}^{*} \rightarrow \text{CH}^{80}\text{Br}^+ + \text{HBr}$$

$$\text{CH}^{80}\text{Br}^+ + \text{Br}_2 \rightarrow \text{CH}^{80}\text{BrBr}_2$$  \[VII\]

The yield of $\text{CH}_2^{80}\text{BrBr}_2$ is low and because of this

<p>| Table II. Yields of $\text{CH}_2^{80}\text{Br}$ and $\text{CH}_2^{80}\text{BrBr}$ in the reaction $^{80}\text{Br}^+ + \text{CH}_2\text{Br}$. |
|-----------------|-----------------|-----------------|-----------------|
| Mole fraction  | Yields (in percents of total $^{80}\text{Br}$)* | Ratio of yields |</p>
<table>
<thead>
<tr>
<th>of $\text{CH}_2\text{Br}$</th>
<th>$\text{CH}_2^{80}\text{Br}$</th>
<th>$\text{CH}_2^{80}\text{BrBr}$</th>
<th>$\text{CH}_2^{80}\text{BrBr}/\text{CH}_2^{80}\text{Br}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Moderated by helium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>3.00</td>
<td>1.00</td>
<td>0.33</td>
</tr>
<tr>
<td>0.36</td>
<td>2.78</td>
<td>0.91</td>
<td>0.33</td>
</tr>
<tr>
<td>0.25</td>
<td>2.30</td>
<td>0.80</td>
<td>0.32</td>
</tr>
<tr>
<td>0.18</td>
<td>2.32</td>
<td>0.77</td>
<td>0.33</td>
</tr>
<tr>
<td>0.14</td>
<td>2.27</td>
<td>0.82</td>
<td>0.36</td>
</tr>
<tr>
<td>0.11</td>
<td>2.08</td>
<td>0.73</td>
<td>0.35</td>
</tr>
<tr>
<td>0.08</td>
<td>1.82</td>
<td>0.56</td>
<td>0.31</td>
</tr>
<tr>
<td>Average:</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. Moderated by krypton</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>3.00</td>
<td>1.00</td>
<td>0.33</td>
</tr>
<tr>
<td>0.33</td>
<td>1.72</td>
<td>0.61</td>
<td>0.35</td>
</tr>
<tr>
<td>0.25</td>
<td>1.49</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>0.22</td>
<td>1.18</td>
<td>0.41</td>
<td>0.35</td>
</tr>
<tr>
<td>0.20</td>
<td>1.09</td>
<td>0.37</td>
<td>0.34</td>
</tr>
<tr>
<td>0.165</td>
<td>1.00</td>
<td>0.37</td>
<td>0.36</td>
</tr>
<tr>
<td>0.145</td>
<td>0.86</td>
<td>0.28</td>
<td>0.33</td>
</tr>
<tr>
<td>Average:</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The standard deviation of the mean is 6%–9% for helium results and 6%–12% for krypton results.

and due also to the long separation time (elution of about 20 min in the gas chromatograph), it could be determined only in the absence of a moderator. The presence of a moderator decreases the yield and the detection is subject to relatively large error. The yield (in the absence of a moderator) found was 0.3 (±0.1)%; this value is expressed as percent of the total $^{80}\text{Br}$ atoms. This determination is based on a measurement made ~45 min after the irradiation, at which time about 10% of the $^{80}\text{Br}$ present could be ascribed to the isomeric transition.

Figures 214, 214 and 3 show the kinetic theory plots10

<p>| Table III. Pressure dependence of the yield of $\text{CH}_2^{80}\text{Br}$ and $\text{CH}_2^{80}\text{BrBr}$ in an unmoderated system.* |
|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Yields (in percents of total $^{80}\text{Br}$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.95</td>
</tr>
<tr>
<td>420</td>
<td>2.72</td>
</tr>
<tr>
<td>630</td>
<td>3.00</td>
</tr>
<tr>
<td>800</td>
<td>3.27</td>
</tr>
</tbody>
</table>

* In the presence of 0.025 mole fraction of $\text{Br}_2$.

b Each figure represents the average of 6–8 measurements. The standard deviation of the mean is 6%–10%.
TABLE IV. Results of the kinetic-theory plots.

<table>
<thead>
<tr>
<th>Noble gas moderator</th>
<th>Product</th>
<th>Slope</th>
<th>Intercept</th>
<th>Reactivity integral&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$\alpha_{\text{Br}^-\text{CH}_{3}\text{Br}}$&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;BBr</td>
<td>2.42±0.12</td>
<td>33.4±1.5</td>
<td>0.41±0.03</td>
<td>13.8±1.3</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;BrBr</td>
<td>7.70±1.30</td>
<td>99.1±15.2</td>
<td>0.13±0.03</td>
<td>12.9±4.1</td>
</tr>
<tr>
<td></td>
<td>Sum</td>
<td>1.83±0.13</td>
<td>24.0±1.7</td>
<td>0.54±0.04</td>
<td>13.7±1.9</td>
</tr>
<tr>
<td>Kr</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;BBr</td>
<td>13.7±0.6</td>
<td>32.4±4.4</td>
<td>0.073±0.003</td>
<td>2.34±0.42</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;BrBr</td>
<td>39.6±3.9</td>
<td>96.7±18.3</td>
<td>0.025±0.002</td>
<td>2.44±0.71</td>
</tr>
<tr>
<td></td>
<td>Sum</td>
<td>10.5±0.7</td>
<td>23.7±3.9</td>
<td>0.095±0.006</td>
<td>2.61±0.38</td>
</tr>
</tbody>
</table>

<sup>a</sup> In units of $\alpha_{\text{bromine-moderator}}$.

for the yields of the different products and the total yields ($\sim$ sum of CH<sub>3</sub>BBr and CH<sub>3</sub>BrBr) in the presence of He and Kr as moderators. Table IV gives the slopes and intercepts of the lines in Figs. 2 and 3, the values of the reactivity integrals $I$ and the average logarithmic energy decrements $\alpha$ calculated from them.

The survival probabilities of the products when colliding with krypton, $(1 - J_{Kr})$, are given in Table V. These values were calculated both from the slopes and from the intercepts, using the following expressions:

For the slopes<sup>5,15</sup>

$$1 - J_{Kr} = \frac{(\alpha_{Kr}/\alpha_{He})_{\text{theor}}}{\text{slope}_{Kr}/\text{slope}_{He}},$$

(1)

where<sup>11,16</sup>

$$\frac{(\alpha_{Kr}/\alpha_{He})_{\text{theor}}}{\text{slope}_{Kr}/\text{slope}_{He}} = (1 - \beta_{Kr-He})/(1 - \beta_{Br-He}),$$

(2)

$$\beta = \left[\frac{(m_1 - m_2)}{(m_1 + m_2)}\right]^2,$$

(3)

$m_1$ and $m_2$ are the masses of the hot atom and the moderator atom, respectively.

For the intercepts

$$1 - J_{Kr} = \frac{\text{intercept}_{He}}{\text{intercept}_{Kr}},$$

(4)

The values calculated from the slopes are the more reliable ones, as the errors in the slopes are smaller than those in the intercepts.

The reactivity integrals for the reaction products are shown in Table VI, while Table VII shows the average logarithmic energy decrements in the collision of hot bromine atoms with CH<sub>3</sub>Br molecules, ($\alpha_{Br^-\text{CH}_{3}\text{Br}}$). The values for the He-moderated system were normalized to units of the Kr-moderated system<sup>5</sup> so as to permit comparison of the results for the two systems and subsequently derive an average value.

![Fig. 3. The kinetic theory plots for the sum of CH<sub>3</sub>BBr + CH<sub>3</sub>BrBr ($\sim$ total yield) in the presence of He and Kr as moderators.](image)

### Table V. Survival probabilities of CH<sub>3</sub>BBr and CH<sub>3</sub>BrBr in collision with krypton atoms.

<table>
<thead>
<tr>
<th>Product</th>
<th>$\text{Slope}<em>{Kr}/\text{slope}</em>{He}$</th>
<th>The survival probability $(I - J_{Kr})$ from the slope&lt;sup&gt;a&lt;/sup&gt;</th>
<th>The survival probability $(I - J_{Kr})$ from the intercepts&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;BBr</td>
<td>5.66±0.53</td>
<td>0.98±0.09</td>
<td>1.03±0.19</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;BrBr</td>
<td>5.12±1.38</td>
<td>1.09±0.29</td>
<td>1.03±0.35</td>
</tr>
<tr>
<td>Total</td>
<td>5.74±0.80</td>
<td>0.97±0.13</td>
<td>1.05±0.28</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from the equation

$$1 - J_{Kr} = \frac{(\alpha_{Kr}/\alpha_{He})_{\text{theor}}}{\text{slope}_{Kr}/\text{slope}_{He}},$$

where $(\alpha_{Kr}/\alpha_{He})_{\text{theor}} = 5.56$.

<sup>b</sup> Calculated from the equation $1 - J_{Kr} = \text{intercept}_{He}/\text{intercept}_{Kr}$. 

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TABLE VI. Reactivity integrals for the different products of the reaction of $^{89}$Br with CH$_3$Br normalized to units of $\alpha_{Br-Kr}$.

<table>
<thead>
<tr>
<th>Moderator \ Product</th>
<th>CH$_3^{89}$Br</th>
<th>CH$_3^{89}$BrBr + CH$_3^{89}$BrBr</th>
<th>Sum of CH$_3^{89}$Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.074</td>
<td>0.024</td>
<td>0.097</td>
</tr>
<tr>
<td>Kr</td>
<td>0.073</td>
<td>0.025</td>
<td>0.095</td>
</tr>
<tr>
<td>Average</td>
<td>0.074</td>
<td>0.025</td>
<td>0.096</td>
</tr>
</tbody>
</table>

IV. DISCUSSION

The total yield of organic products (CH$_3^{89}$Br, CH$_3^{89}$BrBr, and CH$_2^{89}$BrBr$_2$) when measured without moderator: 4.3 (±0.4)% is in full agreement with the finding of Rack and co-workers, who have reported this yield to be 4.3%. This is in disagreement with the value of 2.8 (±0.2)% found by Spicer and Gordus. The lower yield found by Spicer and Gordus may be due to an incomplete extraction of the products by the organic phase.

A. Survival Probability of the Products

The results in Table V show that the CH$_3^{89}$Br and CH$_3^{89}$BrBr formed by the reaction of $^{89}$Br with CH$_3$Br survive completely (within a certainty of 10%-15%) when colliding with krypton atoms. This conclusion is based on the assumption that collision with helium atoms does not cause decomposition of the products. Complete survival was found recently also for CH$_3^{89}$Cl formed by the reaction of (n, γ) produced $^{89}$Cl with CH$_3$Cl in the presence of Kr and Ar molecules. A similarity between hot Br and Cl reactions is not necessarily to be expected since there are some factors which favor the decomposition of CH$_3^{89}$Br and others which favor the decomposition of CH$_3^{89}$Cl. For example, CH$_3^{89}$Br can be formed with higher energies than CH$_3^{89}$Cl, which would be expected to lead to a higher probability of decomposition of CH$_3$Br. On the other hand, the fraction of kinetic energy transferred to internal energy is higher when CH$_3$Cl collides with a krypton atom than when a collision of CH$_3$Br with a krypton atom does; thus the decomposition of CH$_3$Cl is then more likely.

The nonrupture of the newly formed molecules can be caused by two factors: (a) the energy of the reactive hot atom is not high enough; (b) the conversion of the translational energy of the product into its internal energy is inefficient.

B. Double Displacement

The radical CH$_3^{89}$Br$^*$ resulting from the displacement of both a bromine and a hydrogen atom from CH$_3$Br can be formed either in a single step by the simultaneous displacement of the two atoms, or in two steps, with one atom being displaced to form a molecule which then decomposes to the radical and the second atom. In the case of the two-step process there are two ways in which the newly formed molecule can decompose: by unimolecular decomposition of the internally excited molecule, or by collisional decomposition in which the translational energy of the molecule is converted into vibrational and rotational modes. The first mechanism of decomposition can be ruled out since the yields of the products are independent of the total pressure. The second mechanism should be excluded by the fact that the survival probability of the newly formed CH$_3^{89}$Br is not less than a unity, and that of CH$_3^{89}$BrBr is not greater than a unity. Further evidence against the latter mechanism is that the ratio of the yields of the two products is independent of the type and concentration of the moderator. Thus, by elimination, we conclude that the radical CH$_3^{89}$Br$^*$ should be formed by a single-step mechanism. The same arguments hold for the formation of CH$_3^{89}$Cl$^*$ in the system $^{89}$Cl + CH$_3$Cl.

C. Comparison of the Kinetic Theory Parameters for $^{35}$Cl + CH$_3$Cl and $^{89}$Br + CH$_3$Br

(a) The reactivity integrals for hot displacement reaction of chlorine and bromine are equal within experimental error (0.074$\alpha_{Br-Kr}$ for $^{89}$Br+CH$_3$Br and 0.073$\alpha_{Cl-Ar}$ for $^{35}$Cl+CH$_3$Cl; $\alpha_{Br-Kr}$ and $\alpha_{Cl-Ar}$ are taken to be almost equal[15,16]). This should be expected in view of the similarity of the reaction parameters which determine the yield: viz., the activation energies in the center of mass system, the steric factors and the ratios of the masses of the incoming atoms and the displaced ones. Although the energy range for displacement of a bromine atom extends to higher values than that for displacement of a chlorine atom, yet since the reactivity integral is defined as

$$I = \int_0^\infty \frac{P(E)}{E} dE,$$

(i.e., the energy term is in the denominator), then the major contribution to the integral comes from the lower energies, and thus I for CH$_3^{89}$Br formation is not expected to be substantially higher than I for CH$_3^{35}$Cl formation.

(b) The average logarithmic energy decrement of a bromine atom colliding with a CH$_3$Br molecule,

TABLE VII. $\sigma_{Br-CH_3 Br}$ calculated from the yields of the different products normalized to units of $\sigma_{Br-Kr}$.

<table>
<thead>
<tr>
<th>Moderator</th>
<th>CH$_3^{89}$Br</th>
<th>CH$_3^{89}$BrBr + CH$_3^{89}$BrBr</th>
<th>Sum of CH$_3^{89}$Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.48</td>
<td>2.32</td>
<td>2.46</td>
</tr>
<tr>
<td>Kr</td>
<td>2.34</td>
<td>2.44</td>
<td>2.36</td>
</tr>
</tbody>
</table>

* Average of all the results = 2.40.
The observation that the Translational Inertial factor and the bond energies are sufficient in explaining the changes of the ratio of hydrogen displacement to halogen displacement only when the projectile and the displaced halogen atom are the same and insufficient if they are different is puzzling at this stage.

**D. Excitation Functions of the Reactions**

$$^{80}\text{Br} + \text{CH}_2\text{Br} \rightarrow \text{CH}_2^{80}\text{Br} + \text{Br} \quad \text{and} \quad ^{35}\text{Cl} + \text{CH}_2\text{Cl} \rightarrow \text{CH}_2^{35}\text{Cl} + \text{Cl}$$

The excitation functions of the following reactions

$$^{80}\text{Br} + \text{CH}_2\text{Br} \rightarrow \text{CH}_2^{80}\text{Br} + \text{Br}, \quad \text{[VIII]}$$

$$^{35}\text{Cl} + \text{CH}_2\text{Cl} \rightarrow \text{CH}_2^{35}\text{Cl} + \text{Cl}, \quad \text{[IX]}$$

were calculated by the energy dependent hard potential model of Baer and Amiel.\(^{22,23}\) Two parameters of the interaction potentials of each of the reactions were adjusted by trial and error, as will be shown below, to fit the activation energies and reactivity integrals of the respective reactions.

**1. The Model**

Recently an energy-dependent hard potential model was presented\(^{22,23}\); it permits computation of the cross section for rearrangement reactions of the type

$$\text{ZXY} + \text{X} \rightarrow \text{ZX} + \text{Y}, \quad \text{[X]}$$

where X and Y are isotopes and Z is an atom or a group of atoms which behaves as a single particle.

The cross sections obtained according to this model were compared with those derived by the more accurate model of Karplus, Porter, and Sharma (soft potentials)\(^{24}\) for the reactions

$$\text{H}_2 + \text{T} \rightarrow \text{HT} + \text{T}, \quad \text{[XI]}$$

$$\text{D}_2 + \text{T} \rightarrow \text{DT} + \text{D}. \quad \text{[XI]}$$

The fit was found to be satisfactory. The fit with experiment was tested by examining the reaction integral $$R$$,\(^{25}\) which is defined as

$$R = \int_0^\infty \sigma(E) \, dE, \quad (5)$$

where $$\sigma(E)$$ is the reaction cross section and $$E$$ is the kinetic energy of the projectile X in the laboratory system, whereas the target molecule ZY is assumed to be stationary. Seewald, Gersh, and Wolfgang\(^{26}\) determined experimentally the ratio $$R_{\text{HT}}/R_{\text{DT}}$$ for the Reactions [XI] and Wolfgang and Seewald\(^{27}\) determined the ratio $$R_{\text{HT}}/R_{\text{DT}}$$ for the reactions:

$$\text{HD} + \text{T} \rightarrow \text{HT} + \text{D} \rightarrow \text{DT} + \text{H}. \quad \text{[XII]}$$

In both cases the values calculated by the “hard” model were in good agreement with the experimental results.
This hard potential is composed of four terms:

\( V_z(r_x, r_y) \) — the interaction of \( Z \) and \( X \),
\( V_y(r_x, r_y) \) — the interaction of \( Z \) and \( Y \),
\( V_{x,y}(r_x, r_y) \) the attenuation of \( Z-Y \) attraction when \( X \) is approaching \( Z \) and vice versa, the attenuation of the \( Z-X \) attraction when \( Y \) is approaching \( Z \), and
\( V_{zy}(r_y) \) — the repulsion between \( X \) and \( Y \).

\[
V(r_x, r_y) = V_z(r_x, r_y) + V_y(r_x, r_y) + V_{x,y}(r_x, r_y) + V_{zy}(r_y),
\]
where \( r_x \) and \( r_y \) is the distance between \( Z \) and \( X \) and between \( Z \) and \( Y \), respectively; \( r_{zy} \) is the distance between \( X \) and \( Y \). \( V_{0z} \) and \( V_{0y} \) are the bond energies of \( Z-X \) and \( Z-Y \) respectively. The details of these potentials are:

\[
\begin{align*}
V_z(r_x, r_y) &= 0, & r_x > R_z; & \text{for every } r_y \\
&= -V_{0z}, & R_z > r_x > \rho_z; & r_y > R_y \\
&= \infty, & r_x > \rho_z; & \text{for every } r_y,
\end{align*}
\]
\[
\begin{align*}
V_y(r_x, r_y) &= 0, & r_y > R_y; & \text{for every } r_x \\
&= -V_{0y}, & R_y > r_y > \rho_y; & r_x > R_x \\
&= \infty, & r_y > \rho_y; & \text{for every } r_x,
\end{align*}
\]
\[
\begin{align*}
V_{x,y}(r_x, r_y) &= -V_0, & R_x > r_x > \rho_x; & r_y > R_y \\
&= \infty, & \rho_x > r_x; & \text{elsewhere,}
\end{align*}
\]
\[
V_{zy}(r_y) = \infty, & \rho_y > r_y \\
= 0, & r_{zy} > \rho_y.
\]

An example of the graphic representation of this potential is seen in Fig. 4 which shows the potential energy surface for a linear configuration of \( Y-R-X \). The details of the model have been discussed in full elsewhere.

In the present study some changes were introduced to adapt the model for the systems investigated in Reactions [VIII] and [IX]. These systems differ from those previously studied in that \( Z \) is now a \( CH_4 \) radical (assumed to behave as a single particle) rather than a single atom (\( H \) or \( D \)). For the system \( CH_3Cl+^{35}Cl \) the following numerical values were used:

\[
V_0 = V_{0z} = V_{0y} = 2.5 \text{ eV;}^{21}
\]
\[
\gamma = 1.67 \text{ Å}^{-1};^{28} \quad R = 5 \text{ Å};
\]
\[
L = 1.78 \text{ Å};^{29} \quad R_y = 2.22 \text{ Å};^{30}
\]
\[
\rho_y = 1.34 \text{ Å};^{30} \quad E_{35} = 1.10 \text{ eV};^{31}
\]

and for the system \( CH_3Br+^{80}Br \):

\[
V_0 = V_{0z} = V_{0y} = 2.92 \text{ eV;}^{21}
\]
\[
\gamma = 1.72 \text{ Å}^{-1};^{28} \quad R = 5 \text{ Å};
\]
\[
L = 1.93 \text{ Å};^{29} \quad R_y = 2.36 \text{ Å};^{30}
\]
\[
\rho_y = 1.50 \text{ Å};^{30} \quad E_{80} = 0.97 \text{ eV};^{31}
\]

The missing parameters are \( r_0, \rho_x, \) and \( R_y \). Of these, \( r_0 \) is not independent, and for a given \( R_x, r_0 \) is determined so as to yield the correct threshold energy of the reaction \( r_0 \approx R_x + L \), see Ref. 23. \( R_x \) and \( \rho_x \) are chosen so as to be equally spaced on both sides of the values of the bond length of \( C-X \). The value of the width of the potential well \( (R_x - \rho_x) \) is adjusted to yield the correct value of the reaction integral.

To fit the calculations to the experimental results, several changes were made in the model. Previously it was assumed that since \( Y \) and \( X \) are isotopes, \( R_y \) must be equal to \( R_x \). However, this gave \( R \) values which were far too large, and thus \( R_x \) had to be assumed to be much smaller than \( R_y \). The physical reason for this is probably that the radical \( CH_4 \) is actually not a single particle, and the three hydrogens, which lie between the carbon and the incoming halogen, reduce the radius of
attraction. The second change concerns the parameter $r_s$, which was originally assumed to be energy dependent. This caused the reaction integral values in the present case to be too large, and consequently $r_s$ was assumed to be constant. The third change is connected with the conditions required for a reaction to occur. In the original description of the model it was stated that a reaction will occur if $Y$ reaches the boundary of attraction before $X$ does, and if the internal energy $E_{ZX}$ of $ZX$ fulfills the condition

$$E_{ZX} < V_{a_{0}} / \cos^{2} \eta,$$  \hspace{1cm} (6)$$

where $V_{a_{0}}$ is the depth of the potential well and $\eta$ is the angle between the trajectory of the reduced particle $ZX$ and the radius of the square well at the point of contact. For the present case this condition [Eq. (6)] was replaced by

$$E_{ZX} < V_{a_{0}}.$$ \hspace{1cm} (7)$$

This was necessary because of the type of potential used, the square well, which considers mainly the vibrational component of the energy and does not allow for bond stretching (and hence, rupture) by the centrifugal force of the rotation. Under these circumstances, Equation (6) permits accumulation of an infinite amount of energy in the rotational mode at high energies (> 20 eV), and as a result the cross sections become too high, since de-excitation by centrifugal decomposition cannot take place. Condition (7), on the other hand, prevents accumulation of an infinite amount of internal energy by the newly formed molecule, a situation which is common to all soft attractive potentials.

Out of the entire set of parameters needed to describe the potential surface, only one, namely, $R_s - \rho_s$, is still unknown. This parameter is fixed in such a way as to obtain the experimental value of $R$.

2. Analysis of the Experimental Results

The reactivity integrals found experimentally for Reactions [VIII] and [IX] are

$I$ for $^{35}$Cl + CHCl → CH$^{35}$Cl + CHCl $\equiv I_{CI} = 0.073 \alpha_{CI-Ar}$,

$I$ for $^{86}$Br + CH$^{35}$Br → CH$^{86}$Br + Br$^{35}$Br $\equiv I_{Br} = 0.074 \alpha_{Br-Kr}$.

To find the absolute values of $I_{CI}$ and $I_{Br}$ one must know $\alpha_{CI-Ar}$ and $\alpha_{Br-Kr}$. These parameters are unknown, but their values can be estimated by assuming the interaction between the hot atom and the noble gas to be purely elastic. It has been shown that if the potential governing the interaction is of the form:

$$V(r) = \alpha_{1} / r^6 + \alpha_{2} / r^8,$$ \hspace{1cm} (8)$$

where $\alpha_{1} > 0$ and $S_1 > S_2 > 0$, the values of $\alpha$ are in the range

$$0.12 < \alpha < 0.33$$

for the case where the mass $m$ of the hot atom is 135 and the mass $M$ of the inert atom is 82. In order to derive the range of $\alpha$ for the present case, we use the following equation:

$$\alpha_{1} / \alpha_{2} = (1 - \beta_{1}) / (1 - \beta_{2}),$$ \hspace{1cm} (9)$$

where $\beta_i$ is given by [Eq. (3)]

$$\beta_{i} = [ (m_i - M_i) / (m_i + M_i) ].$$

Consequently,

$$0.13 < \left( \frac{\alpha_{CI-Ar}}{\alpha_{Br-Kr}} \right) < 0.35.$$ 

Substituting these boundary values, we get for $I_{CI}$ and $I_{Br}$ the values:

$$0.010 < I_{CI} < 0.026,$$

$$0.010 < I_{Br} < 0.026.$$
The reaction integral $R$ is defined as the product of the geometrical cross section, for collision between the hot atom and the reactant, and the reactivity integral. The range for the respective $R$ values [in atomic units, 1 a.u. = (1 Bohr radius)$^2$ = $(0.53 \times 10^{-8})^2$ cm$^2$] is

$$1.30 < R_{Cl} < 3.38,$$

$$1.49 < R_{Br} < 3.88.$$  

In Figs. 5 and 6, the reaction cross sections (in atomic units) are given as a function of the energy of the projectile. In each figure there are two curves, one referring to the lower limit of $R$ and the other to the upper limit; the values of the respective $\rho_1$, $R_1$, and $r_0$ are given in the figure caption.

The excitation functions of the two reactions are closely related, the main difference being that the reaction $^{85}$Br$\rightarrow$CH$_2$Br$\rightarrow$CH$_3$Br$\rightarrow$Br$\rightarrow$ extends to higher energies than $^{35}$Cl$\rightarrow$CH$_2$Cl$\rightarrow$CH$_3$Cl$\rightarrow$Cl. Thus, the conclusion is that the effective range of displacemen reactions extends to higher energies as the mass of X and Y is larger.

The verification of such a conclusion is possible only by measuring cross sections at the given energies by beam techniques.

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† Present address: Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, Calif. 94025.

‡ Presently on leave, at the Department of Chemistry, Houston University, Houston, Tex.