Survival Probability of Products of Hot Reactions of (n, γ)-Produced 38Cl with CH2Cl in the Gas Phase*

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(Received 20 July 1970)

The hot reactions of (n, γ)-produced 38Cl with CH2Cl have been studied in the presence of three noble-gas moderators: He, Ar, and Kr, using Br2 as a scavenger. The main purpose of this work was to study the extent of decomposition of the newly formed products upon collision with Ar and Kr. Applying the method of Baer and Amiel, it was established that the average survival probability of the various hot products in Ar and Kr is 100%, within the experimental error. Kinetic parameters for the three hot products, CH235Cl, CH237Cl, and CH236ClBr were determined as well.

I. INTRODUCTION

The possible effect of the medium on the survival of molecules produced by hot atom reactions in the gas phase was mentioned in several recent papers. Since the molecules are produced by energetic displacement reactions, they may possess high translational and internal energies and may decompose upon collision with the particles of the medium. The extent of decomposition will depend on the medium. The survival probability, \( P_s(u) \), then appears as a determining factor in the yield equation of the hot reaction:\(^1\)

\[
P = \int n(E) P_c(E) P_s(u) \, dE \, du,
\]

where \( P_c(E) \) is the probability that a reaction with a hot atom possessing kinetic energy \( E \) will occur, and \( P_s(u) \) is the probability that the newly formed molecule will survive during the moderation process; here \( u \) stands for one or more variables of the molecule and medium. Spicer and Wolfgang\(^6\) (henceforth SW) derived the decomposition probability for the energetic CH2Cl\(^*\) produced by the reaction of 38Cl with methane in an argon medium [the 38Cl was obtained by the (γ, p) reaction in argon]. The probability for decomposition of the newly formed molecules when colliding with argon atoms was found to be 38%.

Wahl and Rowland\(^4\) (WR) measured the yields of CH3\(^*\)Cl and CH2\(^*\)Cl\(^*\) from the hot reaction of (n, γ)-produced 38Cl with CH2Cl in the presence of neon and helium. An analysis of their results based on the method reported by Baer and Amiel\(^9\) leads to the conclusion that the decomposition probability of the newly formed CH2\(^*\)Cl in neon and helium is the same. Now, since the decomposition probability is dependent on the mass of the medium, it should increase when using neon instead of helium, unless it is practically zero in both cases. We thus conclude that this probability is indeed negligibly small in these media. The present work is an attempt to find if in heavier noble-gas moderators (argon and krypton) the newly formed products which result from the reaction of (n, γ)-produced 38Cl with CH2Cl will decompose.

II. EXPERIMENTAL

The hot reactions of chlorine with methyl chloride were studied using CI recoiling from the reaction 38Cl(n, γ)38Cl\(^*\) produced by reactor neutrons. The scavenger used in the experiment was usually bromine, but
### Table I. Yields of CH$_2$Cl, CH$_3$Cl, and CH$_2$Br in the reaction $^{35}$Cl+CH$_2$Cl moderated by helium, with Br$_2$ scavenger.

<table>
<thead>
<tr>
<th>Mole fraction of CH$_2$Cl</th>
<th>Yields (%)$^a$</th>
<th>Ratio of yields</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_2$Cl</td>
<td>CH$_3$Cl</td>
</tr>
<tr>
<td>1.0</td>
<td>3.4</td>
<td>0.50</td>
</tr>
<tr>
<td>0.420</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>0.355</td>
<td>2.66</td>
<td>0.40</td>
</tr>
<tr>
<td>0.258</td>
<td>2.22</td>
<td>0.36</td>
</tr>
<tr>
<td>0.205</td>
<td>2.13</td>
<td>0.36</td>
</tr>
<tr>
<td>0.171</td>
<td>1.97</td>
<td>0.32</td>
</tr>
<tr>
<td>0.112</td>
<td>1.55</td>
<td>0.26</td>
</tr>
<tr>
<td>0.075</td>
<td>1.36</td>
<td>0.22</td>
</tr>
<tr>
<td>Mean:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The standard deviation is 6%-8% up to 85% concentration of the moderation, and 8%-10% in the highly moderated systems.

$^b$ Percentage of total $^{35}$Cl.

in some cases a mixture of cis-1, 2 dichloroethylene with bromine was used; both gave identical results.

The samples were prepared by condensing into a quartz ampoule, at liquid air temperature, measured amounts of bromine and methyl chloride. Then an estimated amount of inert gas was introduced, after which the ampoule was sealed and irradiated. After irradiation the ampoule was broken and its contents expanded into a known volume. The accurate amount of the inert gas was determined by measuring the pressure and subtracting the amount of bromine and methyl chloride. The condensable components of the irradiated sample, at liquid air temperature, together with known amounts of CH$_2$Cl, and CH$_2$Br, were transferred to a gas chromatograph for separation. The percentage yields of the different reaction products were obtained by measuring the radioactivity of the $^{35}$Cl in the ampoule before breaking, and the individual fractions separated by the chromatograph. The details of this procedure are reported separately.  

### III. RESULTS AND DISCUSSION

#### A. Experimental Results

Tables I–III summarize the measured hot reaction yields of CH$_2$Cl, CH$_3$Cl, and CH$_2$Br in the presence of He, Ar, and Kr used as moderators. (The Br-containing product results from the addition of Br$_2$ as a scavenger for thermal atoms and radicals.) Each yield is an average of 6–12 repeated experiments. The standard deviation is about 5% for CH$_2$Cl Cl and CH$_2$Br and 8% for CH$_3$Cl. For highly moderated systems (more than 85%) the error is slightly higher.

The effectiveness of the scavenger was checked at high moderator concentrations, where thermalization is very efficient. The check was made by increasing the bromine-to-methyl chloride ratio, up to about 0.4. Only a slight variation of the reaction yields was observed, (cf. Table IV) thus indicating that the scavenging was nearly complete. The procedure was to increase the bromine-to-methyl chloride ratio along with the increase

### Table II. Yields of CH$_2$Cl, CH$_3$Cl, and CH$_2$Br in the reaction $^{35}$Cl+CH$_2$Cl moderated by argon, with Br$_2$ scavenger.

<table>
<thead>
<tr>
<th>Mole fraction of CH$_2$Cl</th>
<th>Yields (%)$^*$</th>
<th>Ratio of yields</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_2$Cl</td>
<td>CH$_3$Cl</td>
</tr>
<tr>
<td>1.0</td>
<td>3.4</td>
<td>0.60</td>
</tr>
<tr>
<td>0.485</td>
<td>1.85</td>
<td>0.30</td>
</tr>
<tr>
<td>0.355</td>
<td>1.65</td>
<td>0.28</td>
</tr>
<tr>
<td>0.263</td>
<td>1.50</td>
<td>0.27</td>
</tr>
<tr>
<td>0.212</td>
<td>1.30</td>
<td>0.25</td>
</tr>
<tr>
<td>0.149</td>
<td>0.81</td>
<td>0.16</td>
</tr>
<tr>
<td>0.117</td>
<td>0.77</td>
<td>0.15</td>
</tr>
<tr>
<td>0.085</td>
<td>0.55</td>
<td>0.11</td>
</tr>
<tr>
<td>Mean:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^*$ See Footnotes to Table I.
in the moderator concentration, e.g., in the unmoderated system the ratio was 0.02 and in highly moderated systems the ratio was between 0.10 and 0.20.

Varying the pressure in the range 250–1000 torr had no effect on the yields when the samples were of constant composition (cf. Table V).

From the 5th and 6th columns of Tables I–III it can be seen that the ratios CH₂⁺⁺Cl/CH₂⁺⁺Cl and CH₂⁺⁺ClBr/CH₂⁺⁺Cl remain constant and do not depend on the concentration of the moderator. Moreover, as to the ratio CH₂⁺⁺ClBr/CH₂⁺⁺Cl, only slight differences, which are within the experimental error, are observed when different noble gases are used as moderators. These facts are in agreement with the kinetic theory, which predicts that in systems with small yield the ratios of the products are independent of the concentration and type of moderator.⁵ For the ratio CH₂⁺⁺ClBr/CH₂⁺⁺Cl a slight dependence on the type of the moderator is observed (cf. Tables I, III). This dependence, if not an artifact, may be due to incomplete scavenging of CH₂⁺⁺Cl as can be seen from Table IV where it is observed that the yield of CH₂⁺⁺ClBr is relatively more dependent on the concentration of the scavenger than the yield of the other products.

Table IV. The effect of the ratio Br₂/CH₂Cl on the yields of the products of the reaction ^³⁺⁺Cl + CH₂Cl moderated by 88% krypton.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Yields (%) a, b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br₂/CH₂Cl</td>
<td>CH₂⁺⁺Cl</td>
</tr>
<tr>
<td>0.03</td>
<td>0.90</td>
</tr>
<tr>
<td>0.05</td>
<td>0.87</td>
</tr>
<tr>
<td>0.10</td>
<td>0.88</td>
</tr>
<tr>
<td>0.15</td>
<td>0.85</td>
</tr>
<tr>
<td>0.20</td>
<td>0.83</td>
</tr>
<tr>
<td>0.30</td>
<td>0.85</td>
</tr>
<tr>
<td>0.40</td>
<td>0.82</td>
</tr>
</tbody>
</table>

a The standard deviation of the mean is 8%–10%.
b Percentage of total ^³⁺⁺Cl.

Spicer and Wolfgang have studied a similar system, namely CH₂⁺⁺Cl⁺⁺Cl in an argon moderator, with ethylene + I₂ as a scavenger [the ^³⁺⁺Cl was produced by the (γ, p) reaction in argon]. They measured the yields of CH₂⁺⁺Cl, CH₂⁺⁺ClCl, and CH₂⁺⁺ClBr at 60% moderator concentration and obtained the results 0.80 and 0.59 for the ratios CH₂⁺⁺ClCl/CH₂⁺⁺Cl and CH₂⁺⁺ClBr/CH₂⁺⁺Cl respectively. The second ratio is in agreement with the corresponding one obtained by us (0.62), but the first differs appreciably from our value of 0.18 (see Table II).

WR,⁴ who studied the same reaction but with 1, 2 cis-dichloroethylene + O₂ as scavenger and He and Ne as moderators,⁴ found the first ratio to be in the range 0.23–0.41, which is in between our result and that of SW.⁷

SW⁷ did not study the dependence of the yields on the concentration and type of moderator. However WR⁴ did, and found a distinct dependence. They attributed this result, which is in contradiction to the theory mainly to possible interference by the scavengers. It seems that the large differences observed for the ratio of CH₂⁺⁺ClCl/CH₂⁺⁺Cl as observed by SW, WR, and by us are closely connected with the efficiency of the scavenging of CH₂⁺⁺ClCl (in all cases different scavengers were used).

Table V. The effect of the total pressure on the yield of the products of the reaction ^³⁺⁺Cl + CH₂Cl in an unmoderated system. a

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Yields (%) b, c</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂⁺⁺Cl</td>
<td>CH₂⁺⁺ClCl</td>
</tr>
<tr>
<td>270</td>
<td>3.4</td>
</tr>
<tr>
<td>480</td>
<td>3.6</td>
</tr>
<tr>
<td>750</td>
<td>3.3</td>
</tr>
<tr>
<td>975</td>
<td>3.4</td>
</tr>
</tbody>
</table>

a Similar results were obtained also for the systems 26% CH₂Cl and 74% Ar, and 35% CH₂Cl and 65% He.
b The standard deviation of the mean is 6%–8%.
c Percentage of total ^³⁺⁺Cl.
B. Decomposition of Hot Reaction Products

The yield \( P_j \) of the product \( j \) in a hot reaction is given by:\(^6\)

\[
P_j(E) = \int_{E_0}^{E} \frac{F(E') p_{o_{j}}(E') dE'}{\alpha(E') E'[1-f(E') p_{o_{j}}(E')]}
\times \exp \left[ - \int_{E'}^{E} \frac{f(E'') p_{o_{j}}(E'') dE''}{\alpha(E'') E''\left[1-f(E''') p_{o_{j}}(E''')\right]} \right],
\]

where \( \alpha(E) \) is the mean energy decrement per collision, \( f(E) \) is the fraction of collisions that the hot atom makes with the reactant, \( p_{o_{j}}(E) \) is the probability for a hot atom of energy \( E \) to yield a stable product \( j \), \( p_{o_{j}}(E) \) is the probability for a hot atom to enter into any stable chemical combination, and \( E \), the upper limit of the integration, is the kinetic energy with which the hot atom is formed.

Performing the summation over all the products one obtains the expression for the total yield:

\[
\hat{p}(E) = 1 - \exp \left[ - \int_{E_0}^{E} \frac{f(E') p_{o_{j}}(E') dE'}{\alpha(E') E'[1-f(E') p_{o_{j}}(E')]} \right].
\]

Assuming \( f(E) \) and \( \alpha(E) \) to be energy independent and \( f(E') p_{o_{j}}(E') \ll 1 \), the well-known Estrup–Wolfgang equations\(^6,9\) can then be derived:

\[
P(E) = 1 - \exp \left[ -(f/\alpha) I(E) \right],
\]

where \( I(E) \) is the reactivity integral:

\[
I(E) = \int_{E_0}^{E} \frac{p_{o_{j}}(E') dE'}{E'}. \tag{4}
\]

In the case of a medium-dependent decomposition of the newly formed molecule, it was shown\(^2\) that the reactivity integral appearing in Eqs. (4) and (5) depends on the medium, and can be expressed as follows:

\[
I(E) = I_0(E) \left[ 1 - f' J_r(E) - (1-f') J_m(E) \right], \tag{5}
\]

where \( f' \) is the fraction of collisions the hot molecule makes with the reactant, \( I_0(E) \) is the reactivity integral, assuming no decomposition has taken place, and \( J_r(E) \) and \( J_m(E) \) are closely related to the collision breakup probabilities of the hot molecule upon colliding with the reactant and the moderator respectively; \( J_r(E) \) and \( J_m(E) \) will be termed accordingly the average collisional decomposition probabilities. Substituting Eq. (5) in Eq. (3) and rearranging, one obtains

\[
-\ln(1-P) = I_0^{-1} \frac{\alpha_r + \alpha_m [(1-f)/f]}{1-J_m} \times \left[ 1 + f' \frac{J_m-J_r}{1-J_m} \right]^{-1}, \tag{6}
\]

where \( \alpha \) is replaced by

\[
\alpha = f \alpha_r + (1-f) \alpha_m, \tag{7}
\]

in which \( \alpha_r \) and \( \alpha_m \) refer to collisions of the hot atom with the reactant and the moderator, respectively.

---

**Fig. 1.** Kinetic theory plot for the system CH₃Cl-³⁵Cl with a helium moderator.

Equation (6) refers to the total hot yield. However, when the total yield is small, i.e., \( P(E) \ll 1 \), similar equations can be derived for each hot product separately. Since the exponential function which appears under the integral sign in Eq. (1) is bounded by

\[
1 - P(E) \leq \exp \left[ - \int_{E'}^{E} \frac{f(E'') p_{o_{j}}(E'') dE''}{\alpha(E'') E''[1-f(E''') p_{o_{j}}(E''')] \right] \leq 1,
\]

we obtain for \( P_j(E) \) that

\[
[1-P(E)] \int_{E_0}^{E} \frac{f(E') p_{o_{j}}(E') dE'}{\alpha(E') E'[1-f(E') p_{o_{j}}(E')]} < P_j(E) < \int_{E_0}^{E} \frac{f(E') p_{o_{j}}(E') dE'}{\alpha(E') E''[1-f(E'') p_{o_{j}}(E'')]}.
\]

Consequently if \( P(E) \ll 1 \), \( P_j(E) \) can be written as:

\[
P_j(E) = \int_{E_0}^{E} \frac{f(E') p_{o_{j}}(E') dE'}{\alpha(E') E'[1-f(E') p_{o_{j}}(E')]}.
\]

Assuming again that \( f(E) \) and \( \alpha(E) \) are energy independent and \( f(E) p_{o_{j}}(E) \ll 1 \), one derives that

\[
P_j(E) = (f/\alpha) I_j(E).
\]

Going through the same arguments as before, we arrive at the expression

\[
P_j^{-1} = I_0^{-1} \frac{\alpha_r + \alpha_m [(1-f)/f]}{1-J_m} \times \left[ 1 + f' \frac{J_m-J_r}{1-J_m} \right]^{-1}.
\]
masses of the moderator and the hot atom, respectively. Thus the ratio of the slopes and the ratio of the intercepts yield independent values of \((1-J_{m_{ij}})/(1-J_{m_{ij}})\). In order to extract the value of \(J\) for one moderator one has to assume a known \(J_f\) for a reference moderator. It was shown recently\(^2\) that if the mass ratio \(m_i/(M_f+m_i)\) is close to zero (\(m_i\) and \(M_f\) are the masses of the moderator and the newly formed molecule, respectively), the amount of translational energy that might be transferred into the internal modes of the molecule upon collision is negligible, thus reducing to zero the possibility for decompositional breakup. Consequently, if a hot heavy product is moving in a moderated system composed of relatively light particles the expected value of \(J_{m_{ij}}\) is close to zero. In the cases under consideration each of the hot products contains at least one chlorine atom, so that when He is the moderator the mass ratio is small, leading to a negligible value for \(J_{Hej}\). Thus the values of \(J_{Arj}\) and \(J_{Krj}\) can be computed directly for each product by comparison with He as a reference moderator.

Although in theory, both the ratios of the intercepts and the ratios of the slopes can be used to determine \(J_{Arj}\) and \(J_{Krj}\), in practice the experimental errors for the intercepts were too large to give significant results, and

**Fig. 2.** Kinetic theory plot for the system CHCl₃⁻¹⁻Cl with an argon moderator.

From Eqs. (6) and (10) it is seen that the dependence of \(1/P\) and \(1/P_f\) on \((1-f)/f\) becomes linear for small values of \(f\) (and consequently small values of \(f'\)) i.e., high moderator concentrations. Thus,

\[
P^{-1} = I_0^{-1} \frac{\alpha_r + \alpha_m [(1-f)/f]}{1-J_m} \quad (6')
\]

\[
P_f^{-1} = I_0^{-1} \frac{\alpha_r + \alpha_m [(1-f)/f]}{1-J_{m_{ij}}} \quad (10')
\]

The average collisional decomposition probability of products formed via high-energy reactions of \(^{35}\text{Cl}\) can thus be found by plotting \(1/P_f\) vs \((1-f)/f\) for every product. The plots are given in Figs. 1-3.\(^{20}\) The straight lines were computed by the least squares method (weighting each point equally). For each plot the computed slope yields the value of \(\alpha_m/I_0(1-J_m)\) and the intercept the value of \(\alpha_r/I_0(1-J_{m_{ij}})\). The results are summarized in Table VI.

The ratio of the two slopes for a product \(j\) in two moderators is \((\alpha_m/\alpha_{m'}) [(1-J_{m_{ij}})/(1-J_{m_{ij}})]\) and the ratio of the two intercepts is \((1-J_{m_{ij}})/(1-J_{m_{ij}})\). Now \(\alpha_{m1}/\alpha_{m2}\) is given by\(^{21}\):

\[
\alpha_{m1}/\alpha_{m2} = (1-\beta_1)/(1-\beta_2),
\]

where \(\beta_i = [(m_i-m)/(m_i+m)]^2\), and \(m_i\) and \(m\) are the

**Fig. 3.** Kinetic theory plot for the system CHCl₃⁻¹⁻Cl with a krypton moderator.
HOT REACTIONS OF \((n, \gamma)\) PRODUCED \(^{38}\text{Cl}\)

TABLE VI. Results of the kinetic theory plots.

<table>
<thead>
<tr>
<th>Noble gas</th>
<th>Product</th>
<th>Slope</th>
<th>Intercept</th>
<th>(\alpha\text{Cl}/\alpha\text{He})_{\text{ theor}}^a</th>
<th>1 - J_{m}^b</th>
<th>(I_{n}) reactivity integral(^e)</th>
<th>(\alpha_{\text{H},\text{Cl}-\text{Cl}}^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>CH(_3)(^{38}\text{Cl})</td>
<td>4.94(\pm)0.38</td>
<td>30.6(\pm)4.8</td>
<td>2.72(\pm)0.36</td>
<td>2.90</td>
<td>1.06(\pm)0.17</td>
<td>0.075(\pm)0.004</td>
</tr>
<tr>
<td></td>
<td>CH(_3)(^{38}\text{Cl})Cl</td>
<td>28.5(\pm)2.3</td>
<td>197(\pm)29</td>
<td>2.20(\pm)0.26</td>
<td>2.90</td>
<td>1.31(\pm)0.18</td>
<td>0.016(\pm)0.001</td>
</tr>
<tr>
<td></td>
<td>CH(_3)(^{38}\text{Cl})Br</td>
<td>7.92(\pm)1.0</td>
<td>56.0(\pm)12</td>
<td>2.83(\pm)0.64</td>
<td>2.90</td>
<td>1.03(\pm)0.28</td>
<td>0.045(\pm)0.002</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>2.70(\pm)0.27</td>
<td>18.7(\pm)3.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>CH(_3)(^{38}\text{Cl})</td>
<td>13.4(\pm)0.75</td>
<td>33.0(\pm)11</td>
<td>2.72(\pm)0.36</td>
<td>2.90</td>
<td>1.06(\pm)0.17</td>
<td>0.075(\pm)0.004</td>
</tr>
<tr>
<td></td>
<td>CH(_3)(^{38}\text{Cl})Cl</td>
<td>62.9(\pm)4.6</td>
<td>210(\pm)71</td>
<td>2.20(\pm)0.26</td>
<td>2.90</td>
<td>1.31(\pm)0.18</td>
<td>0.016(\pm)0.001</td>
</tr>
<tr>
<td></td>
<td>CH(_3)(^{38}\text{Cl})Br</td>
<td>22.4(\pm)1.5</td>
<td>50.6(\pm)23</td>
<td>2.83(\pm)0.64</td>
<td>2.90</td>
<td>1.03(\pm)0.28</td>
<td>0.045(\pm)0.002</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>7.46(\pm)0.45</td>
<td>18.1(\pm)7.0</td>
<td>2.76(\pm)0.49</td>
<td>2.90</td>
<td>1.05(\pm)0.23</td>
<td>0.13(\pm)0.01</td>
</tr>
<tr>
<td>Kr</td>
<td>CH(_3)(^{38}\text{Cl})</td>
<td>11.7(\pm)0.64</td>
<td>25.5(\pm)7.1</td>
<td>2.36(\pm)0.31</td>
<td>2.44</td>
<td>1.03(\pm)0.16</td>
<td>0.086(\pm)0.005</td>
</tr>
<tr>
<td></td>
<td>CH(_3)(^{38}\text{Cl})Cl</td>
<td>55.5(\pm)5.5</td>
<td>124(\pm)61</td>
<td>1.95(\pm)0.39</td>
<td>2.44</td>
<td>1.25(\pm)0.31</td>
<td>0.018(\pm)0.002</td>
</tr>
<tr>
<td></td>
<td>CH(_3)(^{38}\text{Cl})Br</td>
<td>20.4(\pm)1.7</td>
<td>40.2(\pm)19</td>
<td>2.58(\pm)0.64</td>
<td>2.44</td>
<td>0.94(\pm)0.32</td>
<td>0.049(\pm)0.005</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>6.55(\pm)0.32</td>
<td>13.6(\pm)5.5</td>
<td>2.42(\pm)0.40</td>
<td>2.44</td>
<td>1.01(\pm)0.20</td>
<td>0.15(\pm)0.01</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from the equation \(\alpha_{\text{Cl}}/\alpha_{\text{He}} = (1 - \beta_{\text{Cl}})/(1 - \beta_{\text{He}})\).

\(^b\) Calculated from the equation \((\alpha_{\text{Cl}}/\alpha_{\text{He}})_{\text{ theor}} = (\text{slope}(\text{He})_{\text{ theor}})/(\text{slope}(\text{Cl})_{\text{ theor}})\).

\(^e\) In units of \(\alpha_{\text{moderator}}\) - chlorine.

the computations were performed only from the slope ratios:

\[J_{m,j} = 1 - \left[\frac{\text{slope}(\text{He})_{\text{ theor}}}{\text{slope}(m_{j})_{\text{ theor}}} \right] (1 - \beta_{m_{j}})/(1 - \beta_{\text{He}})\]

From Table VI it can be seen that the values of \(J_{m,j}\) for all the cases under consideration are zero within the experimental errors. In other words, the hot molecules CH\(_3\)\(^{38}\text{Cl}\), CH\(_3\)\(^{38}\text{Cl}\)Cl, and CH\(_3\)\(^{38}\text{Cl}\)Br formed by the reaction of \(^{38}\text{Cl}\) with CH\(_3\)Cl have a negligible probability of breaking up upon colliding with argon and krypton atoms.\(^{12}\)

This conclusion (of complete survival of CH\(_3\)\(^{38}\text{Cl}\)) is different from the results obtained by SW\(^3\) who found the decomposition probability for hot CH\(_3\)\(^{38}\text{Cl}\) formed by the reaction of \(^{38}\text{Cl}\) + CH\(_3\)I to be 38\%\(\pm\)11\%. The difference could be due to two reasons:

(i) The hot methyl chloride molecules formed by the reaction CH\(_3\)I + \(^{38}\text{Cl}\) might have higher translational energies than those produced by the reaction CH\(_3\)I + CH\(_3\)I. This could happen if: (a) the reactive zones of the two reactions extend to energies higher than the initial energy of the \(^{38}\text{Cl}\) (a few hundred eV) but less than the initial energy of the \(^{38}\text{Cl}\) (several hundreds of keV); (b) the reactive zone for the reaction CH\(_3\)I + \(^{38}\text{Cl}\) is located at relatively higher energies than of the reaction CH\(_3\)Cl + \(^{38}\text{Cl}\). This is supported by the fact that the first reaction is endothermic by 0.9 eV, whereas for the second one the energetic of the reaction is zero; (c) the hot atom loses more energy while interacting with CH\(_3\)I than with CH\(_3\). As for the CH\(_3\)I system the conservation laws demand that the CH\(_3\)ICl product carry a dominant share of the center-of-mass momentum of the incoming ClI, while in contrast there is no such requirement for the CH\(_3\)ICl formed by substitution in CH\(_3\)Cl. The first possibility seems unlikely in the light of the findings of WR\(^4\) which show that the ratios of the product yields for the reactions of CH\(_3\)I and cis-1,2-C\(_2\)H\(_4\)I with \(^{38}\text{Cl}\) are the same as with \(^{38}\text{Cl}\). On the other hand, upon comparing our \(^{38}\text{Cl}\) results with the \(^{38}\text{Cl}\) of SW (in 60\% argon in both cases) the latter yields are consistently higher (2.4 vs 1.7 for CH\(_3\)I, 1.2 vs 0.29 for CH\(_3\)Cl, and 1.4 for CH\(_3\)ClI vs 1.07 for CH\(_3\)ClBr). This discrepancy could be attributed to the different scavengers used, but other possibilities due to the difference in the energies of the chlorines cannot be ignored. As to possibilities (b) and (c), there is no experimental evidence to support or exclude them.

(ii) The mathematical approach used to derive the decomposition probability was different in the work of SW\(^3\) and in the present work, and this might lead to the discrepancy. SW based their method on the second term in the series expansion\(^6\)\(^9\)

\[P_j = (f/\alpha)I_j - (f/\alpha)^3K_j.\]

This method could not be applied in the present case because of the uncertainty involved in the estimation of \(K_{\text{CH,Cl}}\): (a) The value of \(I_j\) is about 40\% smaller than in the case treated by SW thus yielding a 2\(\%\) value which is about 60\% smaller than this of SW. (b) In order to extract the value of \(K_{\text{CH,Cl}}\) the \(K\) values of the other products have to be estimated. Since in our
Table VIII. Unnormalized and normalized values of $\alpha_{\text{CHCl}-\text{Cl}}^*$ for the different moderators.

<table>
<thead>
<tr>
<th>Moderator</th>
<th>$\alpha_{\text{CHCl}-\text{Cl}}^*$ in units of $\alpha_{\text{H}}$</th>
<th>$\alpha_{\text{CHCl}-\text{Cl}}^*$ in units of $\alpha_{\text{Ar}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>6.8</td>
<td>2.3</td>
</tr>
<tr>
<td>Ar</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Kr</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>2.3</td>
</tr>
</tbody>
</table>

case three products are involved in contrast to the two involved in the case of SW the uncertainty in the estimation of $K_{\text{CHCl}}$ is much larger. It should be noted, however, that the present method, which is based on using two moderators, cannot be applied to the results of SW since they used only one moderator (argon).

C. Kinetic Theory Parameters

The results derived from the kinetic theory plots are summarized in Table VI. Utilizing the fact that the ratio between the $\alpha$ values for two media is given by $(1-\beta_1)/(1-\beta_2)$, it is possible to “normalize” the results for helium and krypton in terms of argon. The “normalized” values are summarized in Table VII. Only slight differences appear between the three moderators.

In the last column of Table VI the values of $\alpha_{\text{CHCl}-\text{Cl}}$ are given in units of the $\alpha$ values of each of the three different moderators. The errors are relatively large, especially in the case of krypton and argon (35%−55%), with a slightly smaller error in the case of helium (20%−30%); the reason for the larger errors in Ar and Kr is that the slopes of the lines for these moderators are larger than in He, thus increasing the uncertainty in the value of the intercept. In Table VIII, column 2 shows the average values of $\alpha_{\text{CHCl}}$ in units of $\alpha_{\text{He}}$, $\alpha_{\text{Ar}}$, and $\alpha_{\text{Kr}}$, and column 3 shows the corresponding values after normalization, in units of $\alpha_{\text{Ar}}$. Thus the value of $\alpha_{\text{CHCl}}$ will be taken as 2.3$\alpha_{\text{Ar}}$. For the reaction CH$_4$+Cl, moderated in argon, SW obtained for $\alpha_{\text{Cl}}$−CH$_4$ the value 0.63$\alpha_{\text{Ar}}$, which is about one-fourth of the value obtained in this work. This large difference accounts for most of the difference found in the yields of CHCl from the reactions of hot chlorine with methane on the one hand and with methyl chloride on the other. For 10% argon, SW obtained a CHCl yield of 20% in the reaction Cl*+CH$_4$, vs 3.2% obtained in this work for the reaction Cl*+CH$_4$. This large ratio (6.3) originates from two factors: the effect of moderation, which is the principal one and is given by $\alpha_{\text{CHCl}}/\alpha_{\text{CH}}$=3.5, and the efficiency of the reaction, expressed by

$I_{\text{CHCl}}/I_{\text{CH}}=1.8$.

Regarding the replacement of a hydrogen by a hot chlorine, this substitution is about 10 times more efficient in CH$_4$ than in CH$_2$Cl (0.13 for CH$_3$Cl vs 0.015 for CH$_2$Cl(Cl)). The only case for which the $I$ value of CHCl is higher than that of CH$_4$ is when two atoms in the molecule are replaced (0.044 for CH$_2$ClBr vs 0.035 for CH$_2$Cl(Cl)). The difference becomes greater if relative magnitudes are taken, namely $I_{\text{double}}/I_{\text{total}}$ (0.34 vs 0.21). Since hot chlorine, upon collision, transfers much more energy to CHCl than to CH$_4$, as is verified by the ratio $\alpha_{\text{CHCl}}/\alpha_{\text{CH}}$=3.5, the above-mentioned result supports the assumption that in a double replacement reaction relatively larger amounts of energy are involved than in a single replacement one.

* This is part of a study for a Ph.D. degree by Z. B. Alfassi to be submitted to the Feinberg Graduate School, Weizmann Institute of Science, Rehovoth, Israel.
† Present address: Department of Chemistry, University of Houston, Houston, Texas 77004.
‡ S. Amiel and Y. Pais, Third International Hot Atom Chemistry Symposium, Purdue, Indiana, 1966; and Fourth International Hot Atom Chemistry Symposium, Kyoto, Japan, 1967.
9 The collision cross sections were calculated from the collision radii based on Leonard-Jones potentials fitted to viscosity data: He, 2.58 Å; Cl(=Ar), 3.49 Å; Kr, 3.61 Å and CHCl, 3.38 Å. See J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1954), pp. 1100-1112.
11 The decomposition of the products which may take place prior to their first collision with the medium is included in the formation cross section of the products which are independent of the medium. In this paper we deal with the fate of the products only during the moderation process.
12 The value of $\alpha_{\text{Cl}}/\alpha_{\text{H}}$ in units of $\alpha_{\text{Cl}}$−CH$_4$ was found previously by Wai and Rowland (Ref. 4) to be 7.4 which is rather close to the present value, i.e., 6.8, showing the reproducibility of the data from one laboratory to another.