Rate constants and branching ratios for the dissociative recombination of $\text{C}_3\text{D}_7^+$ and $\text{C}_4\text{D}_9^+$


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14. ABSTRACT
The dissociative recombination of $\text{C}_3\text{D}_7^+$ was measured in the ion storage ring CRYRING. The higher mass separation offered from the deuterated species provided more accurate branching ratios than the data obtained previously for $\text{C}_3\text{H}_7^+$. We obtained rate constants of $2.3 \pm 0.4 \times 10^{-11}$ cm$^3$ s$^{-1}$ for $\text{C}_3\text{D}_7^+$ and $5.8 \pm 1.1 \times 10^{-11}$ for $\text{C}_4\text{D}_9^+$.

15. SUBJECT TERMS
Hydrocarbon ions
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<table>
<thead>
<tr>
<th>a. REPORT</th>
<th>b. ABSTRACT</th>
<th>c. THIS PAGE</th>
<th>d. NUMBER OF PAGES</th>
</tr>
</thead>
<tbody>
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The dissociative recombination (DR) of hydrocarbon ions has been studied extensively at ion storage rings the past couple of years.\textsuperscript{1-9} These studies have allowed complete product branching ratios to be determined in addition to thermal rate constants, which can also be obtained by means of afterglow techniques.\textsuperscript{10,11} There are several reasons for this recent activity. There is a need for DR product branching ratios for hydrocarbon ions in several different areas of applied research. These include plasma assisted combustion,\textsuperscript{12} thermonuclear reactor divertors,\textsuperscript{13} and interstellar\textsuperscript{14-16} and planetary astrophysics.\textsuperscript{17} The studies carried out thus far demonstrate that the electron recombination induces considerably more molecular dissociation than expected, which results in the production of more free radicals per recombination event than previously believed. The grid technique developed at ion storage rings\textsuperscript{3} has allowed the study of increasingly complex molecular ions.

In this note, we report data for the DR of $\text{C}_3\text{D}_7^+$ and $\text{C}_4\text{D}_9^+$ obtained in the ion storage ring CRYRING. In an earlier study, the rate coefficient and product branching ratios for the dissociative recombination of $\text{C}_3\text{H}_7^+$ was measured at CRYRING.\textsuperscript{5} The analysis of the branching ratios was complicated, and we had reasons to believe that a study of one of the isotopomers $\text{C}_3\text{D}_7^+$ would provide more accurate branching ratios because of the higher mass separation offered from the deuterated species. This turned out to be correct.

In conjunction with this experiment, $\text{C}_4\text{D}_9^+$ was also studied. The hope was to be able to extract information on not only the C-C fission which had been studied elsewhere,\textsuperscript{7} but also the deuterium release channels. This turned out to be impracticable, and we report here on the C-C bond breaking only, in addition to the thermal rate constant.

The experiments were carried out at the ion storage ring CRYRING, operated by the Manne Siegbahn Laboratory of Stockholm University. The grid technique applied to branching ratio measurements in CRYRING has been described in detail\textsuperscript{1,3,4} and we give only a brief description here. By a suitable choice of precursor molecules, deuterated 1-bromopropane (secondary-$\text{C}_3\text{D}_7$-Br) and t-butylbromide (tertiary-$\text{C}_4\text{D}_9$-Br), s-$\text{C}_3\text{D}_7^+$ and t-$\text{C}_4\text{D}_9^+$ isomers were produced using a Nielsen hot-cathode discharge ion source. The ions were injected into CRYRING and stored at the maximum energies possible, 1.9 MeV and 1.45 MeV, respectively. Dissociative recombination reaction products were generated in the 0.85 m interaction region, where the ions were merged with a collinear electron beam. The neutral products were detected $\approx$4 m downstream from the interaction region by an energy-resolving surface barrier detector. Branching ratios were measured by placing a grid of known transmission in front of the surface barrier detector. Figure 1 shows a pulse-height spectrum for $\text{C}_3\text{D}_7^+$ taken with this configuration. Without the grid, all combinations of DR products

![FIG. 1. Pulse-height spectrum for $\text{C}_3\text{D}_7^+$ with the grid placed in front of the surface barrier detector.](image)
from the ASTRID ion storage while a had to settle with only determining the amount of which is likely to be an isotope effect. The disagreement with the two-step normalization of the signal, might have introduced a larger error than anticipated at the time. A prerequisite for the determination of an absolute cross section is that the ion current can be measured, which is difficult with small intensity hydrocarbon ion beams. The procedure used in Ref. 3, which was based on a two-step normalization of the signal, might have introduced a larger error than anticipated at the time. The two-step normalization procedure was unique to the C2H7 experiment due to a malfunctioning piece of equipment. In contrast, a new and very sensitive integrating current transformer was used in the present experiment.

In Table II the branching ratios for DR of C2D7 and C2H7 are given. The higher resolution afforded by the deuterated isotopomer made it possible to determine all decay channels. The disagreement with C2H7 concerning the single HD-atom loss channel is due to the inferior resolution for C2H7. The carbon bond breaking fractions, which can be measured with the same accuracy for the two isotopomers, differ slightly, which is likely to be an isotope effect.

The complete branching fractions could not be determined for C2D7 due to the resolution of the detector, and we had to settle with only determining the amount of C-C bond breaking. All three carbon bonds are preserved in 61% of the recombination events, while a CD3-molecule is ejected in 39% of the events. This is in excellent agreement with results from the ASTRID ion storage ring.7

A.A.V. and S.T.A. were supported by the United States Air Force of Scientific Research under Project No. 2303EP4, and A.E. was supported by the European Office of Aerospace and Development under Contract No. F61775-02-C4032. This project was also supported by the Swedish Research Council and the IHP Program of the EC under Contract Nos. HPRN-CT-2000-00142 and HPMT-CT-2001-00226.

Table I. Thermal rate constants for C2D5 and C2D6.

<table>
<thead>
<tr>
<th>Species</th>
<th>Rate Constant at 300 K (10^-7 cm^3 s^-1)</th>
<th>Other 300 K results (10^-7 cm^3 s^-1)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-C2D5</td>
<td>2.3±0.4</td>
<td>0.73 (19.8)</td>
<td>3, 22</td>
</tr>
<tr>
<td>t-C2D6</td>
<td>5.8±1.1</td>
<td>0.59 (19.8)</td>
<td>3</td>
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</tbody>
</table>

4Results for the hydrogenated isotopomers.

Table II. Product branching ratios in the dissociative recombination of C2D5 and C2H7.

<table>
<thead>
<tr>
<th>Product channels for C2D5</th>
<th>C2D5 (%)</th>
<th>C2H7 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2D5+D</td>
<td>13±5</td>
<td>42</td>
</tr>
<tr>
<td>C2D5+D2</td>
<td>12±5</td>
<td></td>
</tr>
<tr>
<td>C2D5+D+D</td>
<td>22±8</td>
<td>11</td>
</tr>
<tr>
<td>C2D5+D2+D</td>
<td>9±2</td>
<td>9</td>
</tr>
<tr>
<td>C2D5+CD3</td>
<td>3±2</td>
<td></td>
</tr>
<tr>
<td>C2D5+CD2+D</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>C2D5+CD4</td>
<td>2±2</td>
<td></td>
</tr>
<tr>
<td>C2D5+CD+D</td>
<td>15±4</td>
<td>19</td>
</tr>
<tr>
<td>C2D5+CD4+D</td>
<td>3±3</td>
<td></td>
</tr>
<tr>
<td>C2D5+CD2+D2</td>
<td>21±4</td>
<td>11</td>
</tr>
<tr>
<td>C2D5+CD</td>
<td>0</td>
<td>&lt;5</td>
</tr>
<tr>
<td>C2D5+CD2</td>
<td>0</td>
<td></td>
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<tr>
<td>Total C-C breaking</td>
<td>44</td>
<td>34–39</td>
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</table>

Reference 3.

156101-2 Larsson et al.


