Thermal Ion-Molecule Reactions in Oxygen-Containing Molecules. Condensation-Elimination Reactions in Dimethyl Ether-Trioxane Mixtures

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Thermal ion-molecule reactions in dimethyl ether — trioxane mixtures have been studied with a time-of-flight mass spectrometer. The appearance potentials and ionization efficiency curves of product and major fragment ions were measured by an RPD technique. The product ions, having a linear structure such as CH$_3$OCH$_3$(CH$_2$O)$_n$H$^+$, CH$_3$OCH$_3$(CH$_2$O)$_n$H$^+$, CH$_3$OCH$_2$(CH$_2$O)$_n$H$^+$, and CH$_3$OCH$_3$(CH$_2$O)$_n$H$^+$ ($n = 1 — 3$), are formed by condensation-elimination reactions of CH$_3$OCH$_3$ and CH$_3$OCH$_2$ with trioxane. The formation of the product ions involves the dissociation of an intermediate-complex, which has a linear structure. It was found that homo-elimination of neutral products occurs preferentially from the trioxane molecule site in the complex. Extensive scrambling does not take place. The rate constants for the ions formed in dimethyl ether (or dimethyl-$d_4$ ether) — trioxane mixtures are obtained, and a small isotope effect is observed. The rate constants of the condensation-elimination reactions of CH$_3$OCH$_2$ with trioxane are compared with those with dimethyl ether.

Introduction

Thermal ion-molecule reactions in cyclic ethers using a time-of-flight mass spectrometer and the consecutive-association and condensation-eliminations involving oxygen-containing reactant ions have been investigated previously. In gas phase ion chemistry it is important to identify the structure of the product ions resulting from ion-molecule reactions. Frequently, it is possible to evaluate the mechanisms of the reactions. In general, the reactions of poly-atomic ions (ABCD$^+$) with neutral molecules (EFGH) lead to the formation of various product ions as follows,

$$\text{ABCD} + \text{EFGH} \rightarrow \text{AB} - \text{GH} + \text{CD} - \text{EF}$$  \hspace{1cm} (2)

$$\text{ABCD} + \text{EFGH} \rightarrow \text{ABCD} - \text{EFH}^-$$  \hspace{1cm} (3)

The Condensation (Addition) reaction (1) releases energy and requires collisional stabilization. The energy release in condensation-elimination reactions (2 and 3) occurs by the elimination of neutral products.

Condensation-elimination reactions are observed frequently, although the general mechanism of the elimination has not been extensively studied. Henis et al. studied the mechanism of hydrogen elimination from Carbon-Silicon ion-molecule reaction intermediates. The elimination of other groups and the associated mechanisms for some other ion-molecule reactions have also been studied. We are interested in clarifying how the neutral product is eliminated in the reactions involving cyclic oxygen-containing molecules and have studied. The ion-molecule reactions in dimethyl ether alone have been studied by several workers. The reactions in binary mixtures of dimethyl ether and cyclic ethers such as trioxane (1,3,5-trioxane) will be reported here. Since both dimethyl ether and trioxane incorporate the ether skeleton, it seems a favorable system to determine the effects of structure in the reactions.

Experimental

The instrument used was a Bendix Model 12-101 time-of-flight mass spectrometer, which has been modified to study ion-molecule reactions as described elsewhere. The modified ion source permitted operation under elevated pressures and at long delay times. The pulse electronics circuits of the instrument were also modified to obtain a variable delay of the time between the end of the ionizing pulse and the onset of the ion withdrawal pulse. During the time delay the entire ionization chamber...
is field-free, so that ion-molecule reactions during this time interval occur under thermal conditions. The retarding potential differential technique (RPD)\textsuperscript{13} was adopted for measurements of the appearance potential and the ionization efficiency curve. Ionization efficiency curves of two ions (reactant and product ion) were obtained simultaneously with a two-channel ion detection technique. The two components of the mixture were introduced individually into the ionization chamber through two separate leaks from separate reservoirs. The partial pressure of each component was measured with an MKS Baratron 90-X RP-2 capacitance manometer and the pressure was also calibrated by the known rate of CH\textsubscript{3}\textsuperscript{+} formation in the ion-molecule reaction of methane\textsuperscript{2}.

The following reagents were used: trioxane (Celanese Chemical), dimethyl ether, and dimethyl-d\textsubscript{6} ether (Merck Sharp and Dohme of Canada), each purified by vacuum distillation.

**Results and Discussion**

**Delay Time Dependence**

The variation of the ion intensities of the fragment and the product ions with the delay time in a 1 : 1 mixture of dimethyl ether and trioxane at $5.45 \times 10^\text{13}$ molecules cm\textsuperscript{-3} and 70 eV is shown in Figures 1—3. The major fragment ions from dimethyl ether are \(m/e\) 46 (CH\textsubscript{3}OCH\textsubscript{3}\textsuperscript{+}), 45 (CH\textsubscript{3}OCH\textsubscript{2}\textsuperscript{+}), 29 (CHO\textsuperscript{+}), and 15 (CH\textsubscript{3}\textsuperscript{+}), while those from trioxane are \(m/e\) 89 (C\textsubscript{3}H\textsubscript{5}O\textsubscript{3}\textsuperscript{+}), 61 (C\textsubscript{2}H\textsubscript{5}O\textsubscript{2}\textsuperscript{+}), 31 (CH\textsubscript{3}O\textsuperscript{+}), and 29 (CHO\textsuperscript{+}). The molecular ion from trioxane was less abundant, and its ion intensity was comparable to the ion intensity of the $^{13}$C isotope fraction from \(m/e\) 89\textsuperscript{13}. Since the formation reactions of the product ions formed in trioxane have been described previously\textsuperscript{1}, these ions are not shown in Figures 1—3. In the mixtures, new product ions (\(m/e\) 47, 61, 75, 76, 77, 91, 105, 106, 107, 135, 136, and 137) resulting from cross-reactions (reactions between ions of one compound and the molecules of the other) were observed.

In order to clarify the structure and formation mechanism of the product ions, the ion-molecule reactions in dimethyl-d\textsubscript{6} ether-trioxane mixtures were studied under the same conditions as for dimethyl ether-trioxane. The delay time dependence of product and major fragment ions is shown in Figures 4—6. The ions formed in dimethyl-d\textsubscript{6} ether itself.

**Ionization Efficiency Curves**

The appearance potentials and ionization efficiency curves of the product and major fragment ions were measured to determine the precursors of the product ions. The ionization efficiency curves of the ions in dimethyl-d\textsubscript{6} ether-trioxane mixtures are shown in Figures 7 and 8. The onsets of the ionization efficiency curves of CD\textsubscript{3}OCD\textsubscript{3}D\textsuperscript{+}, CD\textsubscript{3}OCD\textsubscript{3}CD\textsubscript{2}, CD\textsubscript{3}OCD\textsubscript{2}, and CD\textsubscript{2}OCD\textsubscript{3}CD\textsubscript{2} were the ions formed in the ion-molecule reactions of dimethyl-d\textsubscript{6} ether itself.

![Fig. 1. Delay time dependence of fragment and product ions in dimethyl ether-trioxane mixtures.](image-url)
Fig. 2. Delay time dependence of product ions in dimethyl ether-trioxane mixtures.
△ m/e 75, ○ m/e 105 (×10), □ m/e 135 (×50).

Fig. 3. Delay time dependence of product ions in dimethyl ether-trioxane mixtures.
△ m/e 76, ○ m/e 77, □ m/e 106 (×10), △ m/e 107 (×10), ○ m/e 136 (×200).

Table 1. Product ions of the ion-molecule reactions in dimethyl ether (or dimethyl-d₆ ether)-trioxane mixtures.

<table>
<thead>
<tr>
<th>Dimethyl ether-Trioxane</th>
<th>Dimethyl-d₆ ether-Trioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/e</td>
<td>Product ions</td>
</tr>
<tr>
<td>-----</td>
<td>--------------</td>
</tr>
<tr>
<td>47</td>
<td>CH₂OCH₃H⁺</td>
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<tr>
<td>61</td>
<td>CH₂OCH₃CH₃⁺</td>
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<tr>
<td>75</td>
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<tr>
<td>76</td>
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<td>CH₂OCH₂OCH₃⁺</td>
</tr>
<tr>
<td>91</td>
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</tr>
<tr>
<td>93</td>
<td>(CH₂O)₃H⁺</td>
</tr>
<tr>
<td>105</td>
<td>(CH₂O)₂CH₃⁺</td>
</tr>
<tr>
<td>106</td>
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</tr>
<tr>
<td>107</td>
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<tr>
<td>136</td>
<td>CH₂OCH₂OCH₂OCH₂OCH₂⁺</td>
</tr>
<tr>
<td>137</td>
<td>CH₂OCH₃(CH₂O)₂H⁺</td>
</tr>
<tr>
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</tr>
</tbody>
</table>
Fig. 4. Delay time dependence of fragment and product ions in dimethyl-d$_6$ ether-trioxane mixtures.

- $m/e$ 18
- $m/e$ 31 ($\times 1/4$)
- $m/e$ 50 ($\times 1/2$)
- $m/e$ 52
- $m/e$ 53
- $m/e$ 54
- $m/e$ 61
- $m/e$ 92 ($\times 100$)
- $m/e$ 143 ($\times 1000$)

Fig. 5. Delay time dependence of product ions in dimethyl-$d_6$ ether-trioxane mixtures.

- $m/e$ 70
- $m/e$ 80 ($\times 1/2$)
- $m/e$ 81 ($\times 10$)
- $m/e$ 110
- $m/e$ 140 ($\times 10$)
- $m/e$ 102 ($\times 10$)

All the ionization efficiency curves of CD$_3$OCD$_3$OCH$_3^+$, CD$_3$OCD$_3$OCH$_2^+$, CD$_3$OCD$_2$OCH$_2$OCH$_3^+$, and CD$_3$OCD$_3$(CH$_2$O)$_2$OCH$_3^+$ coincide at their onset and have similar shapes as well. The onsets of the ionization efficiency curves of these product ions agreed with the ionization potential of dimethyl-$d_6$ ether (CD$_3$OCD$_3^+$), indicating that CD$_3$OCD$_3^+$ is the precursor of the product ions. In the ionization efficiency curves of CD$_3$OCD$_2$OCH$_2^+$ and CD$_3$OCD$_2$OCH$_3^+$, CD$_3$OCD$_2$OCH$_2$OCH$_2$OCH$_3^+$, and CD$_3$OCD$_3$(CH$_2$O)$_2$OCH$_3^+$, the break points corresponding to the second appearance potentials were observed and agreed with the onsets of the curves of CH$_3$O$^+$ and C$_2$H$_5$O$^+$, respectively. Hence it is found that CH$_3$O$^+$ and C$_2$H$_5$O$^+$ are also the precursors of CD$_3$OCD$_3$OCH$_3^+$ and CD$_3$OCD$_3$OCH$_2$OCH$_3^+$.

The onsets of the ionization efficiency curves of CD$_3$OCD$_2$OCH$_2^+$, CD$_3$OCD$_2$OCH$_3^+$, CD$_3$OCD$_2$OCH$_2$OCH$_2^+$, CD$_3$OCD$_2$OCH$_2$OCH$_3^+$, CD$_3$OCD$_2$CH$_3$(CH$_2$O)$_n$H$^+$, and CH$_3$OCH$_2$(CH$_2$O)$_n$H$^+$ (n = 1, 2, 3) agreed with each other, and they agreed with the appearance potential of CD$_3$OCD$_2^+$ (Figure 8).

**Reaction Mechanism and Ion Structures**

The measurement of the ionization efficiency curves of the fragment and product ions confirmed that CH$_3$OCH$_3^+$ and CH$_3$OCH$_2^+$ are dominant reactant ions in dimethyl ether-trioxane mixtures. From the distribution of isotopic product ions in dimethyl-$d_6$ ether-trioxane mixtures and the correspondence of the product ions in both mixtures (dimethyl ether-trioxane, dimethyl-$d_6$ ether-trioxane), the structures of the ions can be proposed. The general formulas of the major product ions are described to be CH$_3$OCH$_3$(CH$_2$O)$_n^+$, CH$_3$OCH$_3$(CH$_2$O)$_n$H$^+$, CH$_3$OCH$_2$(CH$_2$O)$_n^+$, and CH$_3$OCH$_2$(CH$_2$O)$_n$H$^+$ (n = 1, 2, 3).
CH₃OCH₃H⁺, CH₃OCH₂⁺, CH₃OCH₂CH₃⁺, and CH₃OCH₃CH₃OCH₂⁺ result from the following reactions of dimethyl ether,

$$\begin{align*}
\text{CH}_3\text{OCH}_3^+ + \text{CH}_3\text{OCH}_3 &\rightarrow \text{CH}_3\text{OCH}_2\text{H}^+ + \text{CH}_3\text{OCH}_2, \\
\text{CHO}^+ + \text{CH}_3\text{OCH}_3 &\rightarrow \text{CH}_3\text{OCH}_2\text{H}^+ + \text{CO}, \\
\text{CH}_3^+ + \text{CH}_3\text{OCH}_3 &\rightarrow \text{CH}_3\text{OCH}_2^+ + \text{CH}_4, \\
\text{CH}_3\text{OCH}_2^+ + \text{CH}_3\text{OCH}_3 &\rightarrow \text{CH}_3\text{OCH}_3\text{CH}_3\text{OCH}_2^+, \\
&\rightarrow \text{CH}_3\text{OCH}_3\text{CH}_3^+ + \text{CH}_2\text{O}.
\end{align*}$$

Protonated molecular ions, CH₃OCH₃H⁺, (CH₂O)₃H⁺, and CH₃OCH₃(CH₂O)₃H⁺, are formed by cross-reactions,

$$\begin{align*}
\text{C}_3\text{H}_5\text{O}_3^+ + \text{CH}_3\text{OCH}_3 &\rightarrow \text{CH}_3\text{OCH}_3\text{H}^+ + \text{C}_3\text{H}_4\text{O}_3, \\
\text{CH}_3\text{OCH}_2^+ + \text{CHO}^+ &\rightarrow \text{CH}_3\text{OCH}_3\text{H}^+ + \text{CH}_2\text{O}.
\end{align*}$$

Fig. 6. Delay time dependence of product ions in dimethyl-ether-trioxane mixtures.

A: m/e 82, O m/e 83(×1/2), □ m/e 111(×10), ■ m/e 112(×10), ▲ m/e 113(×10), ● m/e 142(×10).

Fig. 7. Ionization efficiency curves of major fragment and product ions in dimethyl-d₆ ether-trioxane mixtures.
A: CD₃OCD₃⁺, B: C₂H₅O₂⁺, C: CH₃O⁺, D: CD₃OCD₃OCH₂⁺, E: CD₃OCD₃OCH₃⁺, F: CD₃OCD₃OCH₂OCH₂⁺, G: CD₃OCD₃OCH₂OCH₃⁺, H: CD₃OCD₃OCH₂OCH₃OCH₂⁺.

Fig. 8. Ionization efficiency curves of major fragment and product ions in dimethyl-d₆ ether-trioxane mixtures.
A: CD₃OCD₃⁺, B: CD₃OCD₂OCH₃⁺, C: CD₃OCD₂OCH₄⁺, D: CD₃OCD₂OCH₃⁺, E: CD₃OCD₂OCH₄⁺, F: CD₃OCD₂OCH₂OCH₂⁺, G: (CH₂O)₃CD₃⁺.
In dimethyl-d$_6$ ether-trioxane mixtures, CD$_3$OCD$_3$OCH$_2^+$, CD$_3$OCD$_3$OCH$_3^+$, CD$_3$OCD$_2$OCH$_2$OCH$_3^+$, CD$_3$OCD$_2$OCH$_3$, and CD$_3$OCD$_2$(CH$_2$O)$_3$ result from condensation-elimination reactions:

$$
\text{CD}_3\text{OCD}_3^+ + \text{CH}_2\text{O} \rightarrow \text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_2^+, \quad (12)
$$

$$
\text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_3^+ + \text{CH}_2\text{O} \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2 + \text{CHO}, \quad (13)
$$

$$
\text{CD}_3\text{OCD}_2\text{OCH}_3^+ + \text{CHO} \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_2 + 2 \text{CH}_2\text{O}, \quad (14)
$$

$$
\text{CD}_3\text{OCD}_2\text{OCH}_3^+ + \text{CH}_2\text{O} + \text{CHO}. \quad (15)
$$

From the ionization efficiency curves it results that CD$_3$OCD$_2$OCH$_2$OCH$_3^+$ and CD$_3$OCD$_2$OCH$_3^+$ were also formed by condensation reactions:

$$
\text{CH}_3\text{OCH}_2\text{O}^+ + \text{CD}_3\text{OCD}_3 \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_3^+, \quad (17)
$$

$$
\text{CH}_3\text{O}^+ + \text{CD}_3\text{OCD}_3 \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_3^+. \quad (18)
$$

CD$_3$OCD$_2^+$ reacts with trioxane to form an intermediate-complex and a part of the complex is stabilized. The other part dissociates to product ions (reactions 13—16) in which one or more molecules of formaldehyde or CHO are eliminated. CD$_3$OCD$_3$OCH$_2$OCH$_3^+$, CD$_3$OCD$_3$OCH$_2$OCH$_3^+$, CD$_3$OCD$_2$OCH$_2^+$, and CD$_3$OCD$_2$OCH$_3^+$ must be ions of a linear structure type. So it is proposed that the complex (I) has a linear structure:

$$
\begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array}
$$

From the ionization efficiency curves it results that CD$_3$OCD$_2$OCH$_2$OCH$_3^+$ and CD$_3$OCD$_2$OCH$_3^+$ were also formed by condensation reactions:

$$
\text{CH}_3\text{OCH}_2\text{O}^+ + \text{CD}_3\text{OCD}_3 \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_3^+, \quad (17)
$$

$$
\text{CH}_3\text{O}^+ + \text{CD}_3\text{OCD}_3 \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_3^+. \quad (18)
$$

CD$_3$OCD$_2^+$ reacts with trioxane to form an intermediate-complex and a part of the complex is stabilized. The other part dissociates to product ions (reactions 13—16) in which one or more molecules of formaldehyde or CHO are eliminated. CD$_3$OCD$_3$OCH$_2$OCH$_3^+$, CD$_3$OCD$_3$OCH$_2$OCH$_3^+$, CD$_3$OCD$_2$OCH$_2^+$, and CD$_3$OCD$_2$OCH$_3^+$ must be ions of a linear structure type. So it is proposed that the complex (I) has a linear structure:

$$
\begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array}
$$

The formation of CD$_3$OCD$_2$OCH$_2^+$ and CD$_3$OCD$_2$OCH$_3^+$ results from the cleavage of the C—O bond ((A)-position) in the complex (I), and CD$_3$OCD$_2$OCH$_2$OCH$_2^+$ and CD$_3$OCD$_2$OCH$_2$OCH$_3$ result from that of the C—O bond ((B)-position). The formation reaction of CD$_3$OCD$_2$OCH$_2$OCH$_3^+$ and CD$_3$OCD$_2$OCH$_3^+$ involves a rearrangement of the hydrogen atom.

$$
\text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+ \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+, \quad (19)
$$

$$
\text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+ + \text{CH}_2\text{O} \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+ + \text{CH}_2\text{O}, \quad (20)
$$

$$
\text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+ + \text{CHO} \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+ + \text{CHO}, \quad (21)
$$

$$
\text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+ + \text{CHO} \rightarrow \text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+ + \text{CHO}, \quad (22)
$$

$$
\text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+ + \text{CH}_2\text{O} + \text{CHO}. \quad (23)
$$

CD$_3$OCD$_2^+$ reacts with trioxane to form an intermediate-complex and a part of the complex is stabilized. The other part dissociates to product ions (reactions 13—16) in which one or more molecules of formaldehyde or CHO are eliminated. CD$_3$OCD$_3$OCH$_2$OCH$_3^+$, CD$_3$OCD$_3$OCH$_2$OCH$_3^+$, CD$_3$OCD$_2$OCH$_2^+$, and CD$_3$OCD$_2$OCH$_3^+$ must be ions of a linear structure type. So it is proposed that the complex (I) has a linear structure:

$$
\begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_3^+
\end{array}
$$

The condensation-eliminations of CD$_3$OCD$_2^+$ with trioxane an similar to those of CD$_3$OCD$_3^+$ with trioxane. Again it appears from the product ions in reactions (19)—(23) that the intermediate-complex has a linear structure as follows:

$$
\begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_2^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_2^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_2^+
\end{array} \quad \begin{array}{c}
\text{CD}_3\text{OCD}_3\text{OCH}_2\text{OCH}_2^+
\end{array}
$$

The rate constants of the condensation-elimination reactions in dimethyl ether (dimethyl-d$_6$ ether)-trioxane mixtures were measured and are summarized in Table 2. Since CH$_3$OCH$_3$OCH$_2$OCH$_3^+$ and CH$_3$OCH$_2$OCH$_3^+$ were formed by concurrent reactions, their rate constants were obtained with the ratio-plot technique. As seen in Table 2, an isotope
Table 2. Rate constants of the condensation-elimination reactions in dimethyl ether (or dimethyl-d₄ ether)-trioxane mixtures.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$k_{X-H} \times 10^{10}$ cm³ molecule⁻¹ s⁻¹</th>
<th>$k_{X-D} \times 10^{10}$ cm³ molecule⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{OCH}_3^+$ + $\text{CH}_2\text{O}$</td>
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<td>1.89</td>
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<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$</td>
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<tr>
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<td>16.7</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$</td>
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<td>0.186</td>
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<td>1.12</td>
</tr>
<tr>
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<td>0.0041</td>
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<tr>
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<td>0.0108</td>
</tr>
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<td>0.0120</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$</td>
<td>0.0168</td>
<td>0.0164</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$</td>
<td>1.21</td>
<td>1.16</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$</td>
<td>1.88</td>
<td>1.83</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$</td>
<td>3.23</td>
<td>3.12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$</td>
<td>1.75</td>
<td>1.60</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$</td>
<td>1.93</td>
<td>1.89</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$</td>
<td>1.93</td>
<td>1.89</td>
</tr>
</tbody>
</table>

X denotes H or D atom.

Effect is observed. It is of interest to discuss a relationship between the rate constant for the formation of the product ion and the structure of the reactant ion. In the condensation-elimination reactions of both CH₃OCH₃⁺ and CH₃OCH₂⁺ with trioxane similar product ions were formed, but the rate constants differed. The rate constants for the formation of CH₃OCH₂OCH₂OCH₂OCH₂⁺ and CH₃OCH₂OCH₂OCH₂OCH₂⁺ were larger than those for CH₃OCH₃OCH₂OCH₂⁺ and CH₂OCH₂OCH₂⁺. On the other hand, the rate constants for the formation of CH₃OCH₂OCH₂OCH₃⁺ and CH₃OCH₂OCH₃⁺ were smaller than those for CH₃OCH₃OCH₂OCH₂⁺ and CH₂OCH₂OCH₂⁺. The formation reaction of the ion involving the cleavage of the C—O bond in the reactant ion (CD₃OCD₃⁺ or CD₃OCD₂⁺) was minor, that is, only (CH₂O)₃CD₃⁺ was observed. This suggests that the dissociation energy of the C—O bond in CD₃OCD₂⁺ is higher than that in trioxane molecule. The product ions observed in the mixtures contain almost the molecular structure of the reactant ion,

CH₃OCH₃⁺ and CH₃OCH₂⁺ with trioxane extensive scrambling does not take place. The rate constants for the formation of CD₃OCD₂OCH₂OCH₂⁺ and CD₃OCD₂OCH₂⁺ are larger than those for CD₃OCD₂OCH₃OCH₃⁺ and CD₃OCD₂OCH₃⁺, indicating that the dissociation channels of the complex involve minor rearrangement. The rate constant for the formation of CD₃OCD₂OCH₂⁺ is larger than that for CD₃OCD₂OCH₂OCH₂⁺. This indicates that the cleavage of the C—O bond ((C)-position) in the complex (II) takes place preferentially as compared with that of the C—O bond ((D)-position). Similarly, the rate constant for the formation of CD₃OCD₂OCH₂⁺ is larger than that for CD₃OCD₂OCH₂OCH₂⁺. The formation reaction of the ion involving the cleavage of the C—O bond in the reactant ion (CD₃OCD₃⁺ or CD₃OCD₂⁺) was minor, that is, only (CH₂O)₃CD₃⁺ was observed. This suggests that the dissociation energy of the C—O bond in CD₃OCD₂⁺ is higher than that in trioxane molecule. The product ions observed in the mixtures contain almost the molecular structure of the reactant ion,
indicating that the preferential process is homo-
elimination of a neutral product (formaldehyde) 
from the trioxane molecule site in the complex. 
This observation is one of the most striking 
features in this work. CH$_3$OCH$_3$\(^+\) and CH$_3$OCH$_2$\(^+\) (from dimethyl ether) and CH$_3$OCH$_2$O\(^+\) (from trioxane) 
are reactive and stable ions. These ions react with 
trioxane and subsequently can open the ring of 
a trioxane molecule. It is known that -CH$_2$-O-CH$_3$\(^+\) 
is a propagating ion in the polymerization of 
trioxane\(^{14}\).

The rate constants of the reactions of CH$_3$OCH$_3$\(^+\), 
CH$_3$OCH$_2$\(^+\), CH$_3$\(^+\), and CHO\(^+\) with dimethyl ether 
are also given in Table 2. The rate constants for the 
formation of CH$_3$OCH$_3$H\(^+\), CH$_3$OCH$_3$CH$_3$\(^+\), and 
CH$_3$OCH$_2$\(^+\) are in good agreement with the results 
reported earlier by Blair and Harrison\(^{11}\). The rate 
constant for CH$_3$OCH$_3$CH$_3$OCH$_2$\(^+\) resulting from 
the condensation reaction of CH$_3$OCH$_3$\(^+\) with di-
methyl ether is larger than that for 
CH$_3$OCH$_3$OCH$_2$OCH$_2$OCH$_2$\(^+\) 
or CH$_3$OCH$_2$OCH$_2$OCH$_2$OCH$_2$\(^+\) 
from the reaction of CH$_3$OCH$_3$\(^+\) or CH$_3$OCH$_2$\(^+\) with 
trioxane. Also the rate constant for the formation of 
CH$_3$OCH$_3$CH$_3$\(^+\) is larger than that for 
(CH$_2$O)$_3$CH$_3$\(^+\), suggesting that the methylation re-
action by CH$_3$OCH$_2$\(^+\) involving elimination of 
mormaldehyde depends on the property of the 
neutral molecule. The proton affinity of dimethyl 
ether has been reported to be 205 \( \pm \) 3 kcal mol\(^{-1}\) 
(Ref. \(^{15}\)), which would be larger than that of tri-
oxane. In fact it is known that the basicity of ether 
is larger than that of trioxane\(^ {16}\). Thus it is pre-
sumed that the methylation reaction by CH$_3$OCH$_2$\(^+\) 
is affected by the proton affinity of the neutral 
molecule.

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