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 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 \( \text{CH}_3\text{OCH}_2(\text{CH}_2\text{O})_n^+ \), \( \text{CH}_3\text{OCH}_2(\text{CH}_2\text{O})_n^+\text{H}^+ \), \( \text{CH}_3\text{OCH}_2(\text{CH}_2\text{O})_n^+ \), and \( \text{CH}_3\text{OCH}_2(\text{CH}_2\text{O})_n\text{H}^+ \) (\( n = 1 \cdots 3 \)), are formed by condensation-elimination reactions of \( \text{CH}_3\text{OCH}_2 \) and \( \text{CH}_3\text{OCH}_2^- \) 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_5 ether) — trioxane mixtures are obtained, and a small isotope effect is observed. The rate constants of the condensation-elimination reactions of \( \text{CH}_3\text{OCH}_2^+ \) 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-elimination involving oxygen-containing reactant ion 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,

\[
\begin{align*}
\text{ABCD} - \text{EFGH}^+ & : (1) \\
\text{ABCD}^+ + \text{EFGH} & \rightarrow \text{AB} - \text{GH}^+ + \text{CD} - \text{EF} : (2) \\
& \rightarrow \text{ABCD} - \text{E}^+ + \text{FGH} : (3)
\end{align*}
\]

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. \(^6\) 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. \(^7\text{–}9\) 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. \(^10\text{–}12\) 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. \(^2\) 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}+ 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 $5.45 \times 10^{13}$ molecules cm\textsuperscript{-3} and 70 eV is shown in Figures 1—3. The major fragment ions from dimethyl ether are m/e 46 ($\text{CH}_3\text{OCH}_3^+$), 45 ($\text{CH}_3\text{OCH}_2^+$), 29 ($\text{CHO}^+$), and 15 ($\text{CH}_3^+$), while those from trioxane are m/e 89 ($\text{C}_3\text{H}_5\text{O}_3^+$), 61 ($\text{C}_2\text{H}_5\text{O}_2^+$), 31 ($\text{CH}_3\text{O}^+$), and 29 ($\text{CHO}^+$). 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, trioxane mixtures are given in Table 1 together with those in dimethyl ether-trioxane. CD\textsubscript{3}OCD\textsubscript{3}D\textsuperscript{+}, CD\textsubscript{3}OCD\textsubscript{2}CD\textsubscript{3}\textsuperscript{+}, CD\textsubscript{3}OCD\textsubscript{2}D\textsubscript{2}\textsuperscript{+}, and CD\textsubscript{3}OCD\textsubscript{2}CD\textsubscript{3}OCD\textsubscript{2}\textsuperscript{+} were the ions formed in the ion-molecule reactions of 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{+} and CD\textsubscript{3}OCD\textsubscript{2}D\textsubscript{2}\textsuperscript{+} from dimethyl-d\textsubscript{6} ether were obtained to be $10.06 \pm 0.05$ and $11.18 \pm 0.05$ eV, respectively.

The appearance potentials of C\textsubscript{3}H\textsubscript{5}O\textsubscript{3}+, C\textsubscript{2}H\textsubscript{5}O\textsubscript{2}+, and CH\textsubscript{3}O+ from trioxane were $10.59 \pm 0.05$, $10.79 \pm 0.05$, and $11.49 \pm 0.05$ eV, respectively.
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 m/e</th>
<th>Product ions</th>
<th>Dimethyl-d₆ ether-Trioxane m/e</th>
<th>Product ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>CH₃OCH₃H⁺</td>
<td>53</td>
<td>CD₂OCD₂H⁺</td>
</tr>
<tr>
<td>61</td>
<td>CH₃OCH₂CH₃⁺</td>
<td>54</td>
<td>CD₂OCD₂D⁺</td>
</tr>
<tr>
<td>75</td>
<td>CH₃OCH₂OCH₃⁺</td>
<td>70</td>
<td>CD₂OCD₂CD₂⁺</td>
</tr>
<tr>
<td>76</td>
<td>CH₃OCH₂OCH₃⁺</td>
<td>80</td>
<td>CD₂OCD₂OCH₂⁺</td>
</tr>
<tr>
<td>77</td>
<td>CH₃OCH₂OCH₃⁺</td>
<td>81</td>
<td>CD₂OCD₂OCH₃⁺</td>
</tr>
<tr>
<td>91</td>
<td>(CH₂O)₂H⁺</td>
<td>82</td>
<td>CD₂OCD₂OCH₂⁻</td>
</tr>
<tr>
<td></td>
<td>CH₃OCH₂CH₃OCH₂⁺</td>
<td>83</td>
<td>CD₂OCD₂OCH₃⁺</td>
</tr>
<tr>
<td>93</td>
<td>(CH₃OCH₃)₂H⁺</td>
<td>92</td>
<td>(CH₂O)₃D⁻</td>
</tr>
<tr>
<td>105</td>
<td>(CH₂O)₂CH₃⁺</td>
<td>102</td>
<td>CD₂OCD₂CD₂OCD₂⁺</td>
</tr>
<tr>
<td>106</td>
<td>CH₃OCH₂OCH₂OCH₂⁻</td>
<td>105</td>
<td>(CD₂OCD₂)₂H⁺</td>
</tr>
<tr>
<td>107</td>
<td>CH₃OCH₂OCH₂OCH₃⁻</td>
<td>108</td>
<td>(CH₂O)₃Cd⁺</td>
</tr>
<tr>
<td>135</td>
<td>CH₃OCH₂OCH₂OCH₂OCH₂⁺</td>
<td>110</td>
<td>CD₂OCD₂OCH₂OCH₂⁺</td>
</tr>
<tr>
<td>136</td>
<td>CH₃OCH₂OCH₂OCH₂OCH₂⁺</td>
<td>111</td>
<td>CD₂OCD₂OCH₂OCH₃⁺</td>
</tr>
<tr>
<td>137</td>
<td>CH₃OCH₃(CH₂O)₂H⁺</td>
<td>112</td>
<td>CD₂OCD₂OCH₂OCH₂⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>113</td>
<td>CD₂OCD₂OCH₂OCH₃⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140</td>
<td>CD₂OCD₂OCH₂OCH₂OCH₂⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>142</td>
<td>CD₂OCD₂OCH₂OCH₂OCH₂⁺</td>
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<tr>
<td></td>
<td></td>
<td>143</td>
<td>CD₂OCD₂(CH₂O)₂H⁺</td>
</tr>
</tbody>
</table>
All the ionization efficiency curves of CD₃OCD₃OCH₃⁺, CD₃OCD₃OCH₂⁺, CD₃OCD₃OCH₂OCH₂⁺, and CD₃OCD₃(CH₂O)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-d₆ ether (CD₃OCD₃⁺), indicating that CD₃OCD₃⁺ is the precursor of the product ions. In the ionization efficiency curves of CD₃OCD₂OCH₃⁺ and CD₃OCD₂OCH₂OCH₃⁺, the break points corresponding to the second appearance potentials were observed and agreed with the onsets of the curves of CH₃O⁺ and C₂H₅O₂⁺, respectively. Hence it is found that CH₃O⁺ and C₂H₅O₂⁺ are also the precursors of CD₃OCD₂OCH₃⁺ and CD₃OCD₂OCH₂OCH₃⁺.

The onsets of the ionization efficiency curves of CD₃OCD₄OCH₃⁺, CD₃OCD₄OCH₂⁺, CD₃OCD₄OCH₂OCH₂⁺, CD₃OCD₄OCH₂OCH₃⁺, CD₃OCD₂(CH₂O)₃⁺, and (CH₂O)₃CD⁺ agreed with each other, and they agreed with the appearance potential of CD₃OCD₂⁺ (Figure 8).

**Reaction Mechanism and Ion Structures**

The measurement of the ionization efficiency curves of the fragment and product ions confirmed that CH₃OCH₃⁺ and CH₃OCH₂⁺ are dominant reactant ions in dimethyl ether-trioxane mixtures. From the distribution of isotopic product ions in dimethyl-d₆ ether-trioxane mixtures and the correspondence of the product ions in both mixtures (dimethyl ether-trioxane, dimethyl-d₆ ether-trioxane), the structures of the ions can be proposed. The general formulas of the major product ions are described to be CH₃OCH₃(CH₂O)ₙ⁺, CH₃OCH₃(CH₂O)ₙH⁺, CH₃OCH₂(CH₂O)ₙ⁺, and CH₃OCH₂(CH₂O)ₙH⁺ (n = 1, 2, 3).
CH₃OCH₃H⁺, CH₃OCH₂⁺, CH₃OCH₂CH₃⁺, and CH₃OCH₂CH₃OCH₂⁺ result from the following reactions of dimethyl ether,

\[
\begin{align*}
\text{CH₃OCH₃}^+ + \text{CH₃OCH₃} & \rightarrow \text{CH₃OCH₃H}^+ + \text{CH₃OCH₂}^- , \\
\text{CHO}^+ + \text{CH₃OCH₃} & \rightarrow \text{CH₃OCH₃H}^+ + \text{CO}^- , \\
\text{CH₃}^+ + \text{CH₃OCH₃} & \rightarrow \text{CH₃OCH₂}^+ + \text{CH₄}^- , \\
\text{CH₃OCH₂}^+ + \text{CH₃OCH₃} & \rightarrow \text{CH₃OCH₃CH₃OCH₂}^+ , \\
& \rightarrow \text{CH₃OCH₂CH₃}^+ + \text{CH₂O}^- .
\end{align*}
\]

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

\[
\begin{align*}
\text{C₃H₅O}^+ & + \text{CH₃OCH₃} \rightarrow \text{CH₃OCH₃H}^+ + \text{C₃H₄O}_3 \\
\text{CH₃OCH₂}^+ & + \text{CH₄} \rightarrow \text{CH₃OCH₃CH₃OCH₂}^+, \\
\text{CH₃OCH₃}^+ & + \text{CHO}^+ \rightarrow \text{CH₃OCH₃CH₃OCH₂}^+ + \text{CH₂O}.
\end{align*}
\]
In dimethyl-d₆ ether-trioxane mixtures, CD₃OCD₃OCH₂⁺, CD₃OCD₃OCH₃⁺, CD₃OCD₃OCH₂OCH₂⁺, and CD₃OCD₃(OCH₂O)₃⁺ result from condensation-elimination reactions:

\[
\text{CD₃OCD₃⁺ + CH₂O₀₀₁ -CH₂CH₂₀₀₂ -CH₂CH₂₀₀₃ -CH₂CH₂₀₀₄ \rightarrow CD₃OCD₃OCH₂OCH₂OCH₂⁺, (12)}
\]

\[
\text{CD₃OCD₃OCH₂OCH₂OCH₂⁺ + CH₂O \rightarrow CD₃OCD₃OCH₂OCH₂OCH₂⁺ + CH₂O⁻, (13)}
\]

\[
\text{CD₃OCD₃OCH₂OCH₂OCH₂⁺ + CHO \rightarrow CD₃OCD₃OCH₂OCH₂OCH₂⁺ + CHO⁻, (14)}
\]

\[
\text{CD₃OCD₃OCH₂OCH₂OCH₂⁺ + 2 CH₂O \rightarrow CD₃OCD₃OCH₂OCH₂OCH₂⁺ + 2 CH₂O⁻, (15)}
\]

\[
\text{CD₃OCD₃OCH₃⁺ + CH₂O + CHO \rightarrow (CH₂O)₃CD₃⁺ + CD₂O⁻, (16)}
\]

The condensation-eliminations of CD₃OCD₂⁺ with trioxane are similar to those of CD₃OCD₃⁺ with trioxane. Again it appears from the product ions in reactions (19)—(23) that the intermediate-complex has a linear structure as follows:

\[
\text{CD₃OCD₂⁺ + CH₂O₀₀₁ -CH₂CH₂₀₀₂ -CH₂CH₂₀₀₃ -CH₂CH₂₀₀₄ \rightarrow CD₃OCD₂OCH₂OCH₂OCH₂⁺, (19)}
\]

\[
\text{CD₃OCD₂OCH₂OCH₂OCH₂⁺ + CH₂O \rightarrow CD₃OCD₂OCH₂OCH₂OCH₂⁺ + CH₂O⁻, (20)}
\]

\[
\text{CD₃OCD₂OCH₂OCH₂OCH₂⁺ + CHO \rightarrow CD₃OCD₂OCH₂OCH₂OCH₂⁺ + CHO⁻, (21)}
\]

\[
\text{CD₃OCD₂OCH₂OCH₂OCH₂⁺ + 2 CH₂O \rightarrow CD₃OCD₂OCH₂OCH₂OCH₂⁺ + 2 CH₂O⁻, (22)}
\]

\[
\text{CD₃OCD₂OCH₃⁺ + CH₂O + CHO \rightarrow (CH₂O)₃CD₃⁺ + CD₂O⁻, (23)}
\]

CD₃OCD₃OCH₂⁻ and CD₃OCD₃OCH₃⁻ result from the cleavage of the C—O bond ((A)-position) in the complex (I), and CD₃OCD₃OCH₂OCH₂⁺ and CD₃OCD₃OCH₂OCH₃ result from that of the C—O bond ((B)-position). The formation reaction of CD₃OCD₃OCH₂OCH₃⁻ and CD₃OCD₃OCH₂⁺ involves a rearrangement of the hydrogen atom.

\[
\text{CD₃OCD₃OCH₂OCH₂OCH₂⁺ \rightarrow CD₃OCD₃OCH₂OCH₂OCH₂⁻ + CHO⁻, (24)}
\]

The formation of CD₃OCD₃OCH₂⁻ and CD₃OCD₃OCH₃⁻ results from the cleavage of the C—O bond ((A)-position) in the complex (I), and CD₃OCD₃OCH₂OCH₂⁺ and CD₃OCD₃OCH₂OCH₃ result from that of the C—O bond ((B)-position). Reactions (20)—(24) again involve the elimination of formaldehyde or CHO.

The rate constants of the condensation-elimination reactions in dimethyl ether (dimethyl-d₆ ether)-trioxane mixtures were measured and are summarized in Table 2. Since CH₃OCH₃OCH₂OCH₃⁺ and CH₃OCH₃OCH₃⁻ were formed by concurrent reactions, their rate constants were obtained with the ratio-plot technique². As seen in Table 2, an isotope
### Table 2. Rate constants of the condensation-elimination reactions in dimethyl ether (or dimethyl-d₆ ether)-trioxide mixtures.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$k_{X-H}$</th>
<th>$k_{X-D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}^+$ + $\text{CH}_3\text{OCH}_2\text{O}^+$</td>
<td>0.0121</td>
<td>0.0120</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}^+$ + $\text{CH}_3\text{O}$</td>
<td>1.21</td>
<td>1.16</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}^+$ + 2$\text{CH}_3\text{O}$</td>
<td>1.88</td>
<td>1.83</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}^+$ + $\text{CH}_3\text{O} + \text{CHO}$</td>
<td>3.23</td>
<td>3.12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}^+$ + $\text{CH}_3\text{O} + \text{CHO}$</td>
<td>1.75</td>
<td>1.60</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}^+$ + $\text{CH}_3\text{O}$</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 $\text{CH}_3\text{OCH}_3^+$ and $\text{CH}_3\text{OCH}_2^+$ with trioxane similar product ions were formed, but the rate constants differed. The rate constants for the formation of $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_2^+$ and $\text{CH}_3\text{OCH}_2\text{OCH}_2^+$ were larger than those for $\text{CH}_3\text{OCH}_3\text{OCH}_2\text{OCH}_2^+$ and $\text{CH}_3\text{OCH}_3\text{OCH}_2^+$.

On the other hand, the rate constants for the formation of $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_3^+$ and $\text{CH}_3\text{OCH}_2\text{OCH}_3^+$ were smaller than those for $\text{CH}_3\text{OCH}_3\text{OCH}_2\text{OCH}_3^+$ and $\text{CH}_3\text{OCH}_3\text{OCH}_3^+$.

These are poly-ether ions probably having a linear structure and result from simple condensation-elimination reactions of $\text{CH}_3\text{OCH}_2^+$ with trioxane. In the complex (I) and (II) formed in the reactions of $\text{CH}_3\text{OCH}_3^+$ and $\text{CH}_3\text{OCH}_2^+$ with trioxane extensive scrambling does not take place. The rate constants for the formation of $\text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+$ and $\text{CD}_3\text{OCD}_2\text{OCH}_2^+$ are larger than those for $\text{CD}_3\text{OCD}_2\text{OCH}_3^+$ and $\text{CD}_3\text{OCD}_2\text{OCH}_3^+$, indicating that the dissociation channels of the complex involve minor rearrangement. The rate constant for the formation of $\text{CD}_3\text{OCD}_2\text{OCH}_2^+$ is larger than that for $\text{CD}_3\text{OCD}_2\text{OCH}_2^+$.

Similarly, the rate constant for the formation of $\text{CD}_3\text{OCD}_3\text{OCH}_2^+$ is larger than that for $\text{CD}_3\text{OCD}_2\text{OCH}_2\text{OCH}_2^+$.

The formation reaction of the ion involving the cleavage of the C—O bond of $\text{CD}_3\text{OCD}_2\text{OCH}_2^+$ in the reactant ion $\text{CD}_3\text{OCD}_2\text{OCH}_2^+$ or $\text{CD}_3\text{OCD}_2\text{OCH}_2^+$ was minor, that is, only $\text{CD}_3\text{OCD}_2\text{OCH}_2^+$ was observed. This suggests that the dissociation energy of the C—O bond in $\text{CD}_3\text{OCD}_2\text{OCH}_2^+$ 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 homoe
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. CH₃OCH₃⁺ and CH₃OCH₂⁺ (from
dimethyl ether) and CH₃OCH₂O⁺ (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 -CH₂-O-CH₃⁺
is a propagating ion in the polymerization of
trioxane.\(^{14}\)

The rate constants of the reactions of CH₃OCH₃⁺,
CH₃OCH₂⁺, CH₃⁺, and CHO⁺ with dimethyl ether
are also given in Table 2. The rate constants for the
formation of CH₃OCH²H⁺, CH₃OCH₂CH₃⁺, and
CH₃OCH₂⁺ are in good agreement with the results
reported earlier by Blair and Harrison.\(^{11}\) The rate
constant for CH₃OCH₃CH₃OCH₂⁺ resulting from
the condensation reaction of CH₃OCH₂⁺ with di-
methyl ether is larger than that for
CH₃OCH₃OCH₂OCH₂OCH₂⁺
or
CH₃OCH₂OCH₂OCH₂OCH₂⁺
from the reaction of CH₃OCH₃⁺ or CH₃OCH₂⁺ with
trioxane. Also the rate constant for the formation of
CH₃OCH₃CH₃⁺ is larger than that for
(CH₂O)₃CH₃⁺, suggesting that the methylation re-
action by CH₃OCH₂⁺ involving elimination of
mormaldehyde depends on the property of the
neutral molecule. The proton affinity of dimethyl
ether has been reported to be 205 ± 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 CH₃OCH₂⁺
is affected by the proton affinity of the neutral
molecule.

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