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 $CH_3OCH_3(CH_2O)_n^+$, $CH_3OCH_3(CH_2O)_nH^+$, $CH_3OCH_2(CH_2O)_n^+$, and $CH_3OCH_2(CH_2O)_nH^+$ $(n = 1 - 3)$, are formed by condensation-elimination reactions of $CH_3OCH_3^+$ and $CH_3OCH_2^+$ 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_6 ether) — trioxane mixtures are obtained, and a small isotope effect is observed. The rate constants of the condensation-elimination reactions of $CH_3OCH_2^+$ with trioxane are compared with those with dimethyl ether.

Introduction

Thermal ion-molecule reactions in cyclic ethers using a time-of-flight mass spectrometer[1-3] and the consecutive-association[1] and condensation-eliminations[4] 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,

$$ABCD^+ + EFGH \begin{cases} \rightarrow ABCD - EFGH^+ & (1) \\ \rightarrow AB - GH^+ + CD - EF & (2) \\ \rightarrow ABCD - E^+ + FGH & (3) \end{cases}$$

The Condensation (Addition) reaction (1) releases energy and requires collisional stabilization[5]. 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[7-9]. 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[10-12]. The reactions in binary mixtures of dimethyl ether and cyclic ethers such as trioxane (1,3,5-trioxane) will be reorted 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.

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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)[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_5^+ formation in the ion-molecule reaction of methane[2].

The following reagents were used: trioxane (Celanese Chemical), dimethyl ether, and dimethyl-d_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 5.45×10^{13} molecules cm^{-3} and 70 eV is shown in Fugures 1—3. The major fragment ions from dimethyl ether are *m/e* 46 ($CH_3OCH_3^+$), 45 ($CH_3OCH_2^+$), 29 (CHO^+), and 15 (CH_3^+), while those from trioxane are *m/e* 89 ($C_3H_5O_3^+$), 61 ($C_2H_5O_2^+$), 31 (CH_3O^+), and 29 (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[13]. Since the formation reactions of the product ions formed in trioxane have been described previously[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_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_6 ether-

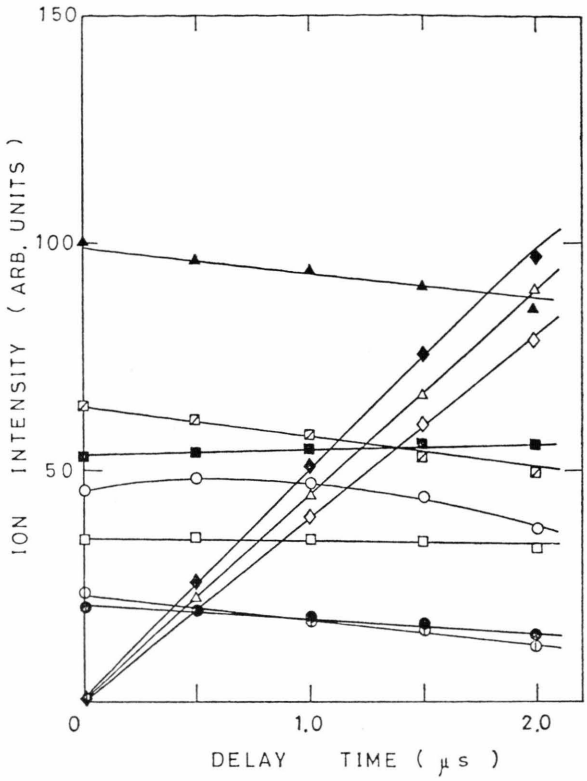


Fig. 1. Delay time dependence of fragment and product ions in dimethyl ether-trioxane mixtures.
ⓘ *m/e* 15, ▨ *m/e* 29, ▲ *m/e* 31(×1/2), ○ *m/e* 45, ● *m/e* 46, ◆ *m/e* 47(×10), ■ *m/e* 61, □ *m/e* 89, ◇ *m/e* 91(×40), △ *m/e* 137(×2000).

trioxane mixtures are given in Table 1 together with those in dimethyl ether-trioxane. $CD_3OCD_3D^+$, $CD_3OCD_3CD_3^+$, $CD_3OCD_2^+$, and $CD_3OCD_3CD_3OCD_2^+$ were the ions formed in the ion-molecule reactions of dimethyl-d_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_6 ether-trioxane mixtures are shown in Figures 7 and 8. The onsets of the ionization efficiency curves of $CD_3OCD_3^+$ and $CD_3OCD_2^+$ from dimethyl-d_6 ether were obtained to be 10.06 ± 0.05 and 11.18 ± 0.05 eV, respectively.

The appearance potentials of $C_3H_5O_3^+$, $C_2H_5O_2^+$, and CH_3O^+ from trioxane were 10.59 ± 0.05, 10.79 ± 0.05, and 11.49 ± 0.05 eV, respectively.

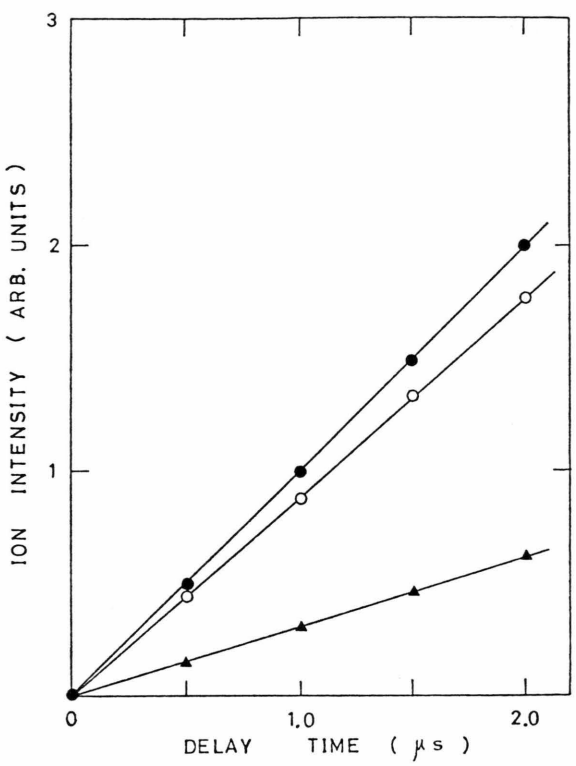


Fig. 2. Delay time dependence of product ions in dimethyl ether-trioxane mixtures.
▲ *m/e* 75, ● *m/e* 105(×10), ○ *m/e* 135(×50).

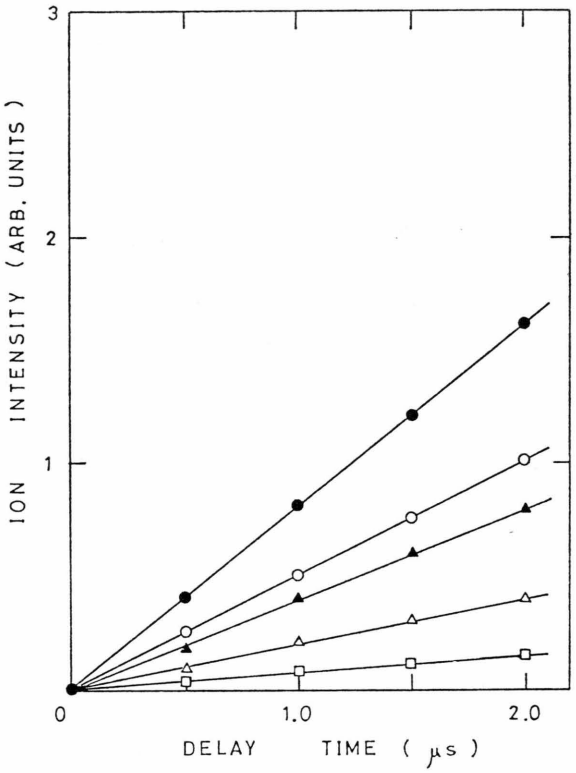


Fig. 3. Delay time dependence of product ions in dimethyl ether-trioxane mixtures.
△ *m/e* 76, ○ *m/e* 77, □ *m/e* 106(×10),
▲ *m/e* 107(×10), ● *m/e* 136(×200).

Table 1. Product ions of the ion-molecule reactions in dimethyl ether (or dimethyl-d_6 ether)-trioxane mixtures.

Dimethyl ether-Trioxane		Dimethyl-d_6 ether-Trioxane	
m/e	Product ions	*m/e*	Product ions
47	$CH_3OCH_3H^+$	53	$CD_3OCD_3H^+$
		54	$CD_3OCD_3D^+$
61	$CH_3OCH_3CH_3^+$	70	$CD_3OCD_3CD_3^+$
75	$CH_3OCH_2OCH_2^+$	80	$CD_3OCD_2OCH_2^+$
76	$CH_3OCH_2OCH_3^+$	81	$CD_3OCD_2OCH_3^+$
	$CH_3OCH_3OCH_2^+$	82	$CD_3OCD_3OCH_2^+$
77	$CH_3OCH_3OCH_3^+$	83	$CD_3OCD_3OCH_3^+$
91	$(CH_2O)_3H^+$	92	$(CH_2O)_3D^+$
	$CH_3OCH_3CH_3OCH_2^+$	102	$CD_3OCD_3CD_3OCD_2^+$
93	$(CH_3OCH_3)_2H^+$	105	$(CD_3OCD_3)_2H^+$
105	$(CH_2O)_3CH_3^+$	108	$(CH_2O)_3CD_3^+$
	$CH_3OCH_2OCH_2OCH_2^+$	110	$CD_3OCD_2OCH_2OCH_2^+$
106	$CH_3OCH_3OCH_2OCH_2^+$	111	$CD_3OCD_2OCH_2OCH_3^+$
		112	$CD_3OCD_3OCH_2OCH_2^+$
107	$CH_3OCH_3OCH_2OCH_3^+$	113	$CD_3OCD_3OCH_2OCH_3^+$
135	$CH_3OCH_2OCH_2OCH_2OCH_2^+$	140	$CD_3OCD_2OCH_2OCH_2OCH_2^+$
136	$CH_3OCH_3OCH_2OCH_2OCH_2^+$	142	$CD_3OCD_3OCH_2OCH_2OCH_2^+$
137	$CH_3OCH_3(CH_2O)_3H^+$	143	$CD_3OCD_3(CH_2O)_3H^+$

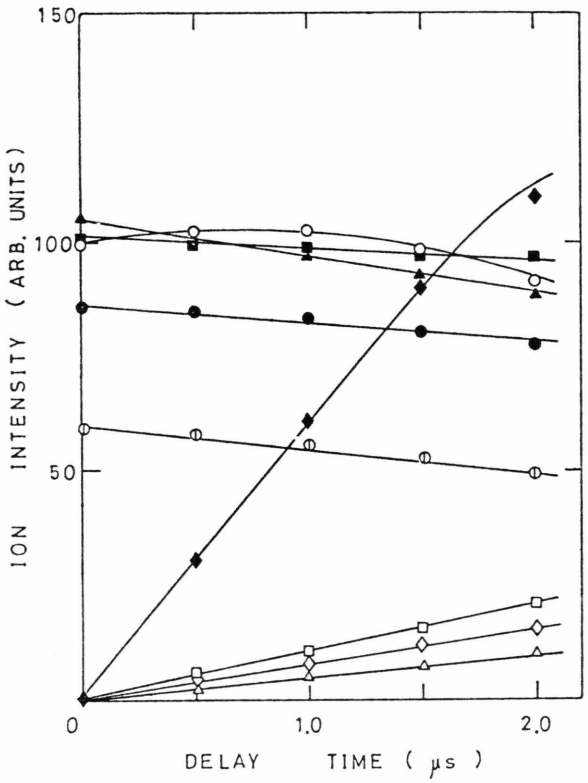


Fig. 4. Delay time dependence of fragment and product ions in dimethyl-d_6 ether-trioxane mixtures.
ⓘ *m/e* 18, ▲ *m/e* 31(×1/4), ○ *m/e* 50(×1/2), ● *m/e* 52, ▨ *m/e* 53, △ *m/e* 54, ■ *m/e* 61, ◆ *m/e* 92(×100), ◇ *m/e* 143(×1000).

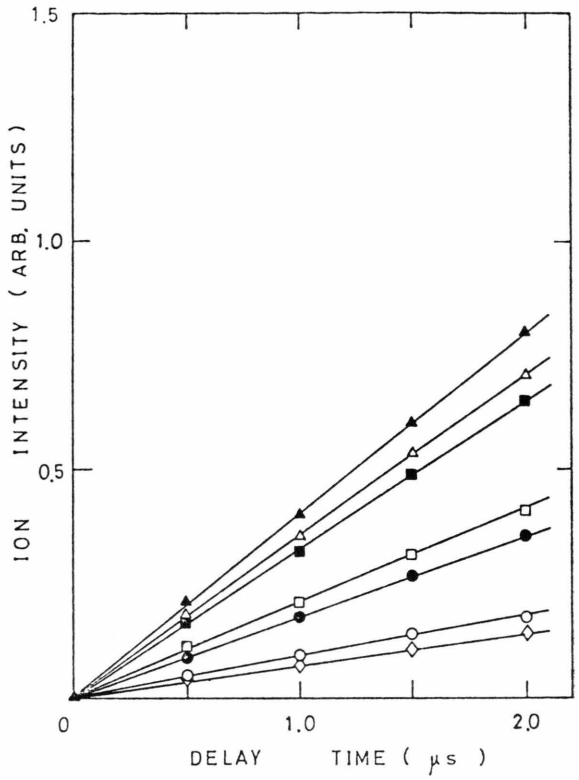


Fig. 5. Delay time dependence of product ions in dimethyl-d_6 ether-trioxane mixtures.
□ *m/e* 70, ▲ *m/e* 80(×1/2), △ *m/e* 81(×10), ● *m/e* 110, ○ *m/e* 140(×10), ■ *m/e* 102(×10).

All the ionization efficiency curves of $CD_3OCD_3OCH_2^+$, $CD_3OCD_3OCH_3^+$, $CD_3OCD_3OCH_2OCH_2^+$, $CD_3OCD_3OCH_2OCH_3^+$, and $CD_3OCD_3(CH_2O)_3^+$ 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 ($CD_3OCD_3^+$), indicating that $CD_3OCD_3^+$ is the precursor of the product ions. In the ionization efficiency curves of $CD_3OCD_3OCH_3^+$ and $CD_3OCD_3OCH_2OCH_3^+$, the break points corresponding to the second appearance potentials were observed and agreed with the onsets of the curves of CH_3O^+ and $C_2H_5O_2^+$, respectively. Hence it is found that CH_3O^+ and $C_2H_5O_2^+$ are also the precursors of $CD_3OCD_3OCH_3^+$ and $CD_3OCD_3OCH_2OCH_3^+$.

The onsets of the ionization efficiency curves of $CD_3OCD_2OCH_2^+$, $CD_3OCD_2OCH_3^+$, $CD_3OCD_2OCH_2OCH_2^+$, $CD_3OCD_2OCH_2OCH_3^+$, $CD_3OCD_2(CH_2O)_3^+$, and $(CH_2O)_3CD_3^+$ agreed with each other, and they agreed with the appearance potential of $CD_3OCD_2^+$ (Figure 8).

Reaction Mechanism and Ion Structures

The measurement of the ionization efficiency curves of the fragment and product ions confirmed that $CH_3OCH_3^+$ and $CH_3OCH_2^+$ 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 $CH_3OCH_3(CH_2O)_n^+$, $CH_3OCH_3(CH_2O)_nH^+$, $CH_3OCH_2(CH_2O)_n^+$, and $CH_3OCH_2(CH_2O)_nH^+$ ($n = 1, 2, 3$).

$CH_3OCH_3H^+$, $CH_3OCH_2^+$, $CH_3OCH_3CH_3^+$, and $CH_3OCH_3CH_3OCH_2^+$ result from the following reactions of dimethyl ether,

$$CH_3OCH_3^+ + CH_3OCH_3 \rightarrow CH_3OCH_3H^+ + CH_3OCH_2\,, \tag{4}$$

$$CHO^+ + CH_3OCH_3 \rightarrow CH_3OCH_3H^+ + CO\,, \tag{5}$$

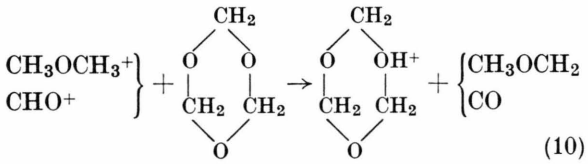
$$CH_3^+ + CH_3OCH_3 \rightarrow CH_3OCH_2^+ + CH_4\,, \tag{6}$$

$$CH_3OCH_2^+ + CH_3OCH_3 \rightarrow CH_3OCH_3CH_3OCH_2^+, \tag{7}$$

$$\rightarrow CH_3OCH_3CH_3^+ + CH_2O\,. \tag{8}$$

Protonated molecular ions, $CH_3OCH_3H^+$, $(CH_2O)_3H^+$, and $CH_3OCH_3(CH_2O)_3H^+$, are formed by cross-reactions,

$$\left.\begin{matrix}C_3H_5O_3^+\\CH_3O^+\end{matrix}\right\} + CH_3OCH_3 \rightarrow CH_3OCH_3H^+ + \begin{cases}C_3H_4O_3\\CH_2O\end{cases} \tag{9}$$



$$\left.\begin{matrix}CH_3OCH_3^+\\CHO^+\end{matrix}\right\} + \text{(1,3-dioxane)} \rightarrow \text{(1,3-dioxan-5-ol)} + \begin{cases}CH_3OCH_2\\CO\end{cases} \tag{10}$$

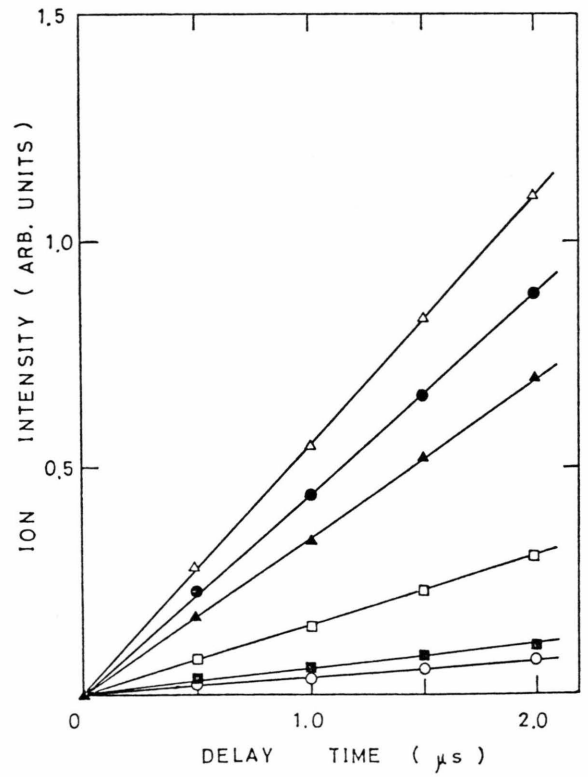


Fig. 6. Delay time dependence of product ions in dimethyl-d_6 ether-trioxane mixtures.
△ *m/e* 82, ○ *m/e* 83(×1/2), □ *m/e* 111(×10),
■ *m/e* 112(×10), ▲ *m/e* 113(×10), ● *m/e* 142(×10).

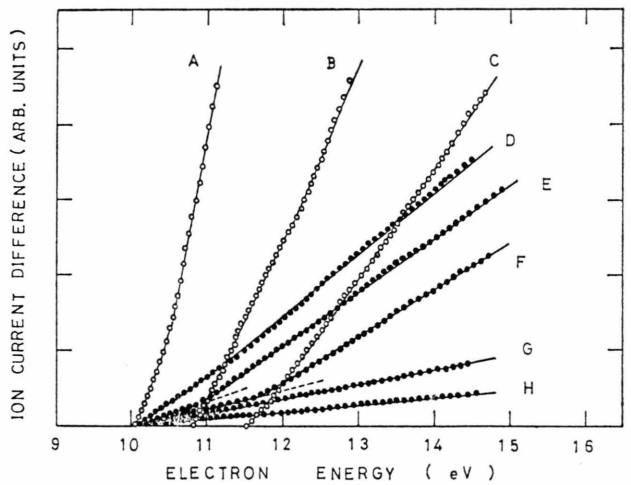


Fig. 7. Ionization efficiency curves of major fragment and product ions in dimethyl-d_6 ether-trioxane mixtures.
A: $CD_3OCD_3^+$, B: $C_2H_5O_2^+$, C: CH_3O^+,
D: $CD_3OCD_3OCH_2^+$, E: $CD_3OCD_3OCH_3^+$,
F: $CD_3OCD_3OCH_2OCH_3^+$, G: $CD_3OCD_3OCH_2OCH_2^+$,
H: $CD_3OCD_3OCH_2OCH_2OCH_2^+$.

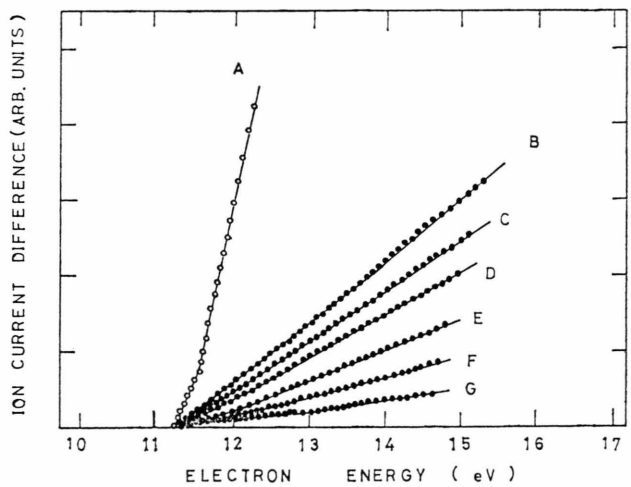
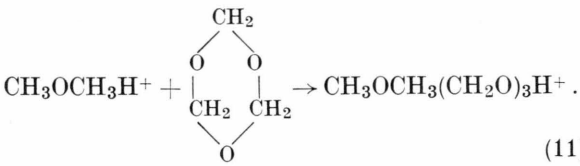
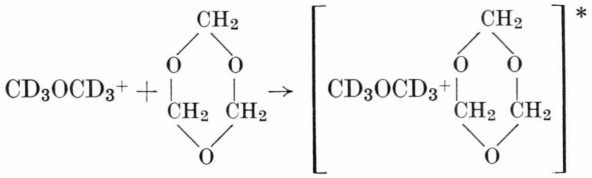


Fig. 8. Ionization efficiency curves of major fragment and product ions in dimethyl-d_6 ether-trioxane mixtures.
A: $CD_3OCD_2^+$, B: $CD_3OCD_2OCH_2^+$,
C: $CD_3OCD_2OCH_2OCH_2^+$, D: $CD_3OCD_2OCH_3^+$,
E: $CD_3OCD_2OCH_2OCH_3^+$,
F: $CD_3OCD_2OCH_2OCH_2OCH_2^+$, G: $(CH_2O)_3CD_3^+$.



$$CH_3OCH_3H^+ + \text{trioxane} \rightarrow CH_3OCH_3(CH_2O)_3H^+ . \quad (11)$$

In dimethyl-d_6 ether-trioxane mixtures,
$CD_3OCD_3OCH_2^+$, $CD_3OCD_3OCH_3^+$,
$CD_3OCD_3OCH_2OCH_2^+$, $CD_3OCD_3OCH_2OCH_3$,
and $CD_3OCD_3(CH_2O)_3^+$ result from condensation-elimination reactions:



$$CD_3OCD_3^+ + \text{trioxane} \rightarrow [CD_3OCD_3^+ \cdot \text{trioxane}]^*$$

$$\rightarrow CD_3OCD_3OCH_2OCH_2OCH_2^+ , \quad (12)$$

$$\rightarrow CD_3OCD_3OCH_2OCH_2^+ + CH_2O , \quad (13)$$

$$\rightarrow CD_3OCD_3OCH_2OCH_3^+ + CHO , \quad (14)$$

$$\rightarrow CD_3OCD_3OCH_2^+ + 2\,CH_2O , \quad (15)$$

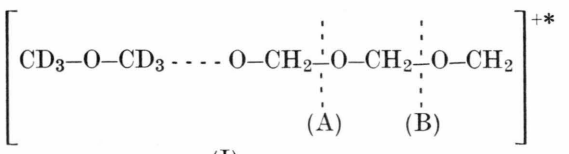
$$\rightarrow CD_3OCD_3OCH_3^+ + CH_2O + CHO . \quad (16)$$

From the ionization efficiency curves it results that $CD_3OCD_3OCH_2OCH_3^+$ and $CD_3OCD_3OCH_3^+$ were also formed by condensation reactions:

$$CH_3OCH_2O^+ + CD_3OCD_3 \rightarrow \rightarrow CD_3OCD_3OCH_2OCH_3^+ , \quad (17)$$

$$CH_3O^+ + CD_3OCD_3 \rightarrow CD_3OCD_3OCH_3^+ . \quad (18)$$

$CD_3OCD_3^+$ 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. $CD_3OCD_3OCH_2OCH_2^+$, $CD_3OCD_3OCH_2OCH_3^+$, $CD_3OCD_3OCH_2^+$, and $CD_3OCD_3OCH_3^+$ must be ions of a linear structure type. So it is proposed that the complex (I) has a linear structure:



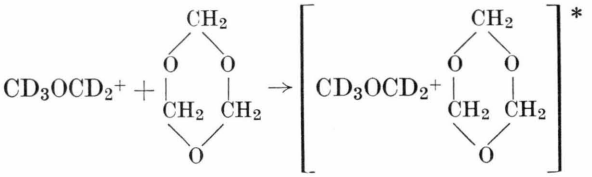
$$[CD_3{-}O{-}CD_3 \cdots O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2]^{+*}$$

(A) (B)

(I)

The formation of
$CD_3OCD_3OCH_2^+$ and $CD_3OCD_3OCH_3^+$
results from the cleavage of the C—O bond ((A)-position) in the complex (I), and
$CD_3OCD_3OCH_2OCH_2^+$ and $CD_3OCD_3OCH_2OCH_3$ result from that of the C—O bond ((B)-position). The formation reaction of $CD_3OCD_3OCH_2OCH_3^+$ and $CD_3OCD_3OCH_3^+$ involves a rearrangement of the hydrogen atom.

$CD_3OCD_2OCH_2OCH_2OCH_2^+$,
$CD_3OCD_2OCH_2OCH_2^+$, $CD_3OCD_2OCH_3^+$,
$CD_3OCD_2OCH_2^+$, $CD_3OCD_2OCH_3^+$,
and $(CH_2O)_3CD_3^+$ are formed by the following condensation-elimination reactions:



$$CD_3OCD_2^+ + \text{trioxane} \rightarrow [CD_3OCD_2^+ \cdot \text{trioxane}]^*$$

$$\rightarrow CD_3OCD_2OCH_2OCH_2OCH_2^+ , \quad (19)$$

$$\rightarrow CD_3OCD_2OCH_2OCH_2^+ + CH_2O , \quad (20)$$

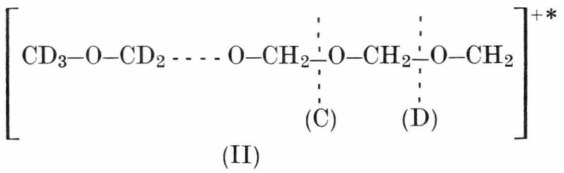
$$\rightarrow CD_3OCD_2OCH_2OCH_3^+ + CHO , \quad (21)$$

$$\rightarrow CD_3OCD_2OCH_2^+ + 2\,CH_2O , \quad (22)$$

$$\rightarrow CD_3OCD_2OCH_3^+ + CH_2O + CHO , \quad (23)$$

$$\rightarrow (CH_2O)_3CD_3^+ + CD_2O . \quad (24)$$

The condensation-eliminations of $CD_3OCD_2^+$ with trioxane an similar to those of $CD_3OCD_3^+$ with trioxane. Again it appears from the product ions in reactions (19)—(23) that the intermediate-complex has a linear structure as follows:



$$[CD_3{-}O{-}CD_2 \cdots O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2]^{+*}$$

(C) (D)

(II)

$CD_3OCD_2OCH_2^+$ and $CD_3OCD_2OCH_3^+$ result from the cleavage of the C—O bond ((C)-position) in the complex (II), and $CD_3OCD_2OCH_2OCH_2^+$
$CD_3OCD_2OCH_2OCH_3^+$ from that of the C—O bond ((D)-position). Reactions (20)—(24) again involve the elimination of formaldehyde or CHO.

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 $CH_3OCH_3OCH_2OCH_3^+$ and $CH_3OCH_3OCH_3^+$ were formed by concurrent reactions, their rate constants were obtained with the ratio-plot technique[2]. As seen in Table 2, an isotope

Table 2. Rate constants of the condensation-elimination reactions in dimethyl ether (or dimethyl-d_6 ether)-trioxane mixtures.

Reactions	$\times 10^{10}$ cm^3 molecule^{-1} s^{-1} $k_{X=H}$	$k_{X=D}$
 $CX_3OCX_3^+ +$ $\rightarrow CX_3OCX_3OCH_2OCH_2OCH_2^+$	0.0121	0.0120
$\rightarrow CX_3OCX_3OCH_2OCH_2^+ + CH_2O$	0.0168	0.0164
$\rightarrow CX_3OCX_3OCH_2OCH_3^+ + CHO$	1.21	1.16
$\rightarrow CX_3OCX_3OCH_2^+ + 2\,CH_2O$	1.88	1.83
$\rightarrow CX_3OCX_3OCH_3^+ + CH_2O + CHO$	3.23	3.12
$CH_3O^+ + CX_3OCX_3 \rightarrow CX_3OCX_3OCH_3^+$	1.75	1.60
$CH_3OCH_2O^+ + CX_3OCX_3 \rightarrow CX_3OCX_3OCH_2OCH_3^+$	1.93	1.89
 $CX_3OCX_2^+ +$ $\rightarrow CX_3OCX_2OCH_2OCH_2OCH_2^+$	0.0163	0.0150
$\rightarrow CX_3OCX_2OCH_2OCH_2^+ + CH_2O$	0.190	0.186
$\rightarrow CX_3OCX_2OCH_2OCH_3^+ + CHO$	0.0170	0.0159
$\rightarrow CX_3OCX_2OCH_2^+ + 2\,CH_2O$	1.24	1.12
$\rightarrow CX_3OCX_2OCH_3^+ + CH_2O + CHO$	0.046	0.041
$\rightarrow (CH_2O)_3CX_3^+ + CX_2O$	0.0116	0.0108
$CX_3OCX_3^+ + CX_3OCX_3 \rightarrow CX_3OCX_3X^+ + CX_3OCX_2$	15.3	15.0
$CXO^+ + CX_3OCX_3 \rightarrow CX_3OCX_3X^+ + CO$	17.1	16.7
$CX_3^+ + CX_3OCX_3 \rightarrow CX_3OCX_2^+ + CX_4$	19.8	17.6
$CX_3OCX_2^+ + CX_3OCX_3 \rightarrow CX_3OCX_3CX_3OCX_2^+$	0.0364	0.0352
$\rightarrow CX_3OCX_3CX_3^+ + CX_2O$	2.15	2.10

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 $CH_3OCH_3^+$ and $CH_3OCH_2^+$ with trioxane similar product ions were formed, but the rate constants differed. The rate constants for the formation of $CH_3OCH_2OCH_2OCH_2OCH_2^+$ and $CH_3OCH_2OCH_2OCH_2^+$ were larger than those for $CH_3OCH_3OCH_2OCH_2OCH_2^+$ and $CH_3OCH_3OCH_2OCH_2^+$.

On the other hand, the rate the constants for the formation of

$CH_3OCH_2OCH_2OCH_3^+$ and $CH_3OCH_2OCH_3^+$

were smaller than those for

$CH_3OCH_3OCH_2OCH_3^+$ and $CH_3OCH_3OCH_3^+$.
$CH_3OCH_2OCH_2OCH_2OCH_2^+$ and $CH_3OCH_2OCH_2OCH_2^+$

are poly-ether ions probably having a linear structure and result from simple condensation-elimination reactions of $CH_3OCH_2^+$ with trioxane. In the complexes (I) and (II) formed in the reactions of $CH_3OCH_3^+$ and $CH_3OCH_2^+$ with trioxane extensive scrambling does not take place. The rate constants for the formation of $CD_3OCD_2OCH_2OCH_2^+$ and $CD_3OCD_2OCH_2^+$ are larger than those for $CD_3OCD_2OCH_2OCH_3^+$ and $CD_3OCD_2OCH_3^+$, indicating that the dissociation channels of the complex involve minor rearrangement. The rate constant for the formation of $CD_3OCD_2OCH_2^+$ is larger than that for $CD_3OCD_2OCH_2OCH_2^+$. 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 $CD_3OCD_3OCH_2^+$ is larger than that for $CD_3OCD_3OCH_2OCH_2^+$.

The formation reaction of the ion involving the cleavage of the C—O bond in the reactant ion ($CD_3OCD_3^+$ or $CD_3OCD_2^+$) was minor, that is, only $(CH_2O)_3CD_3^+$ was observed. This suggests that the dissociation energy of the C—O bond in $CD_3OCD_2^+$ 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 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. $CH_3OCH_3^+$ and $CH_3OCH_2^+$ (from dimethyl ether) and $CH_3OCH_2O^+$ (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 $-CH_2-O-CH_2^+$ is a propagating ion in the polymerization of trioxane[14].

The rate constants of the reactions of $CH_3OCH_3^+$, $CH_3OCH_2^+$, CH_3^+, and CHO^+ with dimethyl ether are also given in Table 2. The rate constants for the formation of $CH_3OCH_3H^+$, $CH_3OCH_3CH_3^+$, and $CH_3OCH_2^+$ are in good agreement with the results reported earlier by Blair and Harrison[11]. The rate constant for $CH_3OCH_3CH_3OCH_2^+$ resulting from the condensation reaction of $CH_3OCH_2^+$ with dimethyl ether is larger than that for

$$CH_3OCH_3OCH_2OCH_2OCH_2^+$$

or

$$CH_3OCH_2OCH_2OCH_2OCH_2^+$$

from the reaction of $CH_3OCH_3^+$ or $CH_3OCH_2^+$ with trioxane. Also the rate constant for the formation of $CH_3OCH_3CH_3^+$ is larger than that for $(CH_2O)_3CH_3^+$, suggesting that the methylation reaction by $CH_3OCH_2^+$ involving elimination of mormaldehyde depends on the property of the neutral molecule. The proton affinity of dimethyl ether has been reported to be 205 ± 3 kcal mol^{-1} (Ref. [15]), which would be larger than that of trioxane. In fact it is known that the basicity of ether is larger than that of trioxane[16]. Thus it is presumed that the methylation reaction by $CH_3OCH_2^+$ is affected by the proton affinity of the neutral molecule.

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