Ion-Molecule Reactions in the Binary Mixture of Ethylene Oxide and Trioxane. II. Mechanism for Reaction of Ethylene Oxide Molecular Ion with Trioxane

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The ion-molecule reactions in the binary mixture of ethylene oxide and trioxane have been studied with use of a modified time-of-flight mass spectrometer. As cross-reaction product ions, $C_3H_5O_2^+$, $C_3H_6O_2^+$, and $C_3H_7O_2^+$ were observed under the conditions of long delay times and elevated pressure. It was found that these ions are formed by the dissociation of unstable intermediate-complex resulting from the reaction of ethylene oxide molecular ion with trioxane. It was proposed that the complex is of cyclic structure in which positive charge is delocalized. From the consideration of isotopic distribution of the prodoct ions in ethylene-d_4 oxide–trioxane mixtures, the skeletal structures of the product ions were investigated. The rate constants of the formation reactions of $C_3H_5O_2^+$, $C_3H_6O_2^+$, and $C_3H_7O_2^+$ in ethylene oxide–trioxane mixtures were found to be 2.20×10^{-10}, 2.61×10^{-10}, and 1.74×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively.

As part of our program dealing with radiation and ion chemistry of oxygen-containing molecules, studies were carried out on the ion-molecule reactions in ethylene oxide, trioxane (1,3,5-trioxane), and acetaldehyde.[1-3] The consecutive association reactions leading to the formation of the cluster ions were observed in trioxane and a study of the kinetics of the reactions was made. The ion-molecule reactions in oxygen-containing organic compounds are sensitive to the nature of the functional groups and the molecular structure of the ionic and neutral reactions.[1,4,5] The reaction pathway of oxygenated ions with cyclic oxygen-containing molecules seems to be of interest. So far the ion-molecule reaction in the mixture system of cyclic oxygen-containing molecules involving large member rings has not been studied, although a number of studies in the pure system of cyclic hydrocarbons have been made.[6-10] Since the formation mechanism of only protonated molecular ions by cross-reactions in the binary mixture of ethylene oxide and trioxane has been studied,[11] the present work deals with the formation of other product ions in the binary mixture under long delay times and elevated pressures. Various product ions were formed by the reaction of ethylene oxide molecular ion with trioxane. The present work was carried out in order to obtain mechanistic information on the ion-molecule reactions involving cyclic ion and neutral molecules.

Experimental

A Bendix Model 12-101 time-of-flight mass spectrometer was used. The ion source of the spectrometer was modified in order to permit operation under elevated pressures.[2] Some pulse electronic circuits of the apparatus were also modified.[11] A variable delay time circuit permitted a variation of time between the end of the ionizing pulse and the onset of the ion withdrawal pulse. During the delay time, the entire ionization chamber is field-free, so that ion-molecule reactions occurring during the time interval are under thermal conditions. The retarding potential differential technique (RPD)[12] was adopted for appearance potential and ionization efficiency curve measurement. Measurement of the ionization efficiency curves of two ions was simultaneously performed by a two-channel ion detection method. The gas-sample inlet-system consisting of dual-leak and dual-reservoir was used. Two kinds of samples are introduced individually into the ionization chamber through two separate leaks from separate reservoirs. The partial pressure of the two samples was indirectly measured with an MKS Baratron 90-X RP-2 capacitance manometer, the pressure being calibrated by the rate constant (1.11×10^{-9} cm^3 molecule^{-1} s^{-1}) of CH_5^+ in the ion-molecule reaction of methane.[13]

The following reagents were used: trioxane (Celanese Chemical), ethylene oxide (Nisso Yuka Industry Co., Ltd.), and ethylene-d_4 oxide (Merck Sharp and Dohme of Canada, deuterium atom purity, 98%). The samples were used after being subjected to vacuum distillation several times.

Results and Discussion

Delay Time Dependence. The delay time dependence of fragment and product ions in a 1 : 1 mixture of ethylene oxide and trioxane at 2.61×10^{13} molecules cm^3 is shown in Figs. 1 and 2. In Fig. 1, *m/e* 44 ($C_2H_4O^+$), 43 ($C_2H_3O^+$), and 29 (CHO^+) are

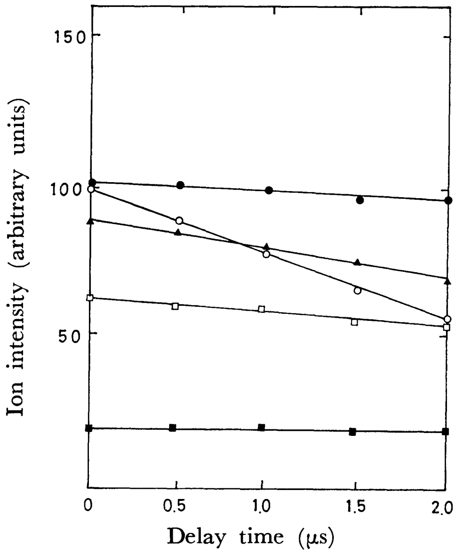


Fig. 1. Delay time dependence of fragment ions in ethylene oxide–trioxane mixtures.
▲: *m/e* 44, ■: *m/e* 43, ○: *m/e* 29 (×1/2), □: *m/e* 89, ●: *m/e* 61.

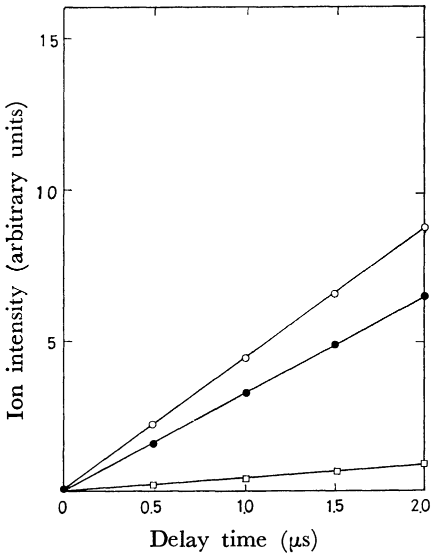


Fig. 2. Delay time dependence of product ions in ethylene oxide–trioxane mixtures.
○: *m/e* 73, □: *m/e* 74, ●: *m/e* 75.

major fragment ions from ethylene oxide, and *m/e* 89 ($C_3H_5O_3^+$), 61 ($C_2H_5O_2^+$), and a part of *m/e* 29 (CHO^+) are those from trioxane. Trioxane molecular ion is relatively less abundant, its ion intensity being comparable with the ion intensity of ^{13}C isotope of *m/e* 89.[12] The *m/e* 73, 74, and 75 were observed as new product ions in the mixture system as shown in Fig. 2. The plots of these ions are not shown, since the behavior of the protonated molecular ions and product ions formed in individual system has been described.[1,2,11] In order to elucidate the formation mechanism of the product ions in the mixture system, the ion-molecule reactions in ethylene-d_4 oxide–trioxane mixtures were studied under the same conditions as for ethylene oxide–trioxane mixtures. The delay time dependence of product ions is shown in Fig. 3. The isotopic product ions (*m/e* 73—79) correspond to the product ions (*m/e* 73—75) formed in ethylene oxide–trioxane mixtures.

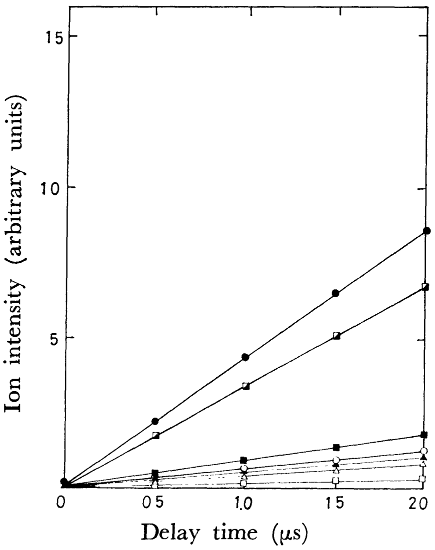


Fig. 3. Delay time dependence of product ions in ethylene-d_4 oxide–trioxane mixtures.
□: *m/e* 73, ▲: *m/e* 74, △: *m/e* 75, ◪: *m/e* 76, ■: *m/e* 77, ○: *m/e* 78, ●: *m/e* 79.

The pressure dependence of the product ions on each molecule was examined in order to determine the contribution of ethylene oxide and trioxane at delay time of 1.0 μs. The pressure dependence of the product ions in ethylene oxide–trioxane mixtures is shown in Figs. 4 and 5. The product ions show a dependence of the first order on the pressure of ethylene oxide and trioxane. The results indicate that the product ions are formed by cross-reactions.

Ionization Efficiency Curves and Reaction Mechanism. In order to identify the reactions with each of the prod-

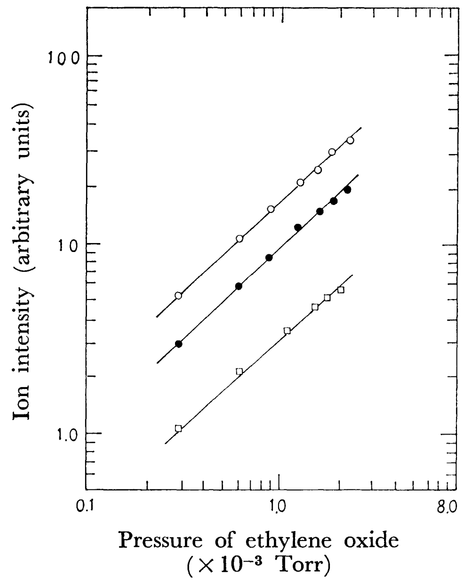


Fig. 4. Pressure dependence of product ions to ethylene oxide at 1.0 μs.
○: *m/e* 73, □: *m/e* 74, ●: *m/e* 75.

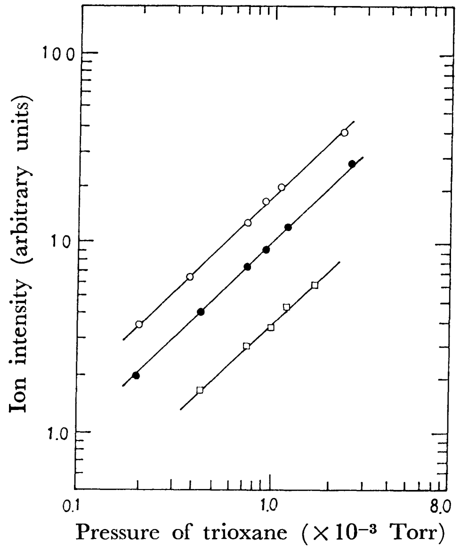


Fig. 5. Pressure dependence of product ions to trioxane at 1.0 μs.
○: *m/e* 73, □: *m/e* 74, ●: *m/e* 75.

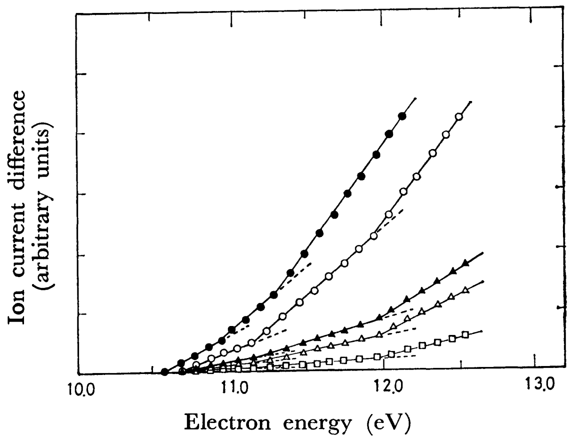
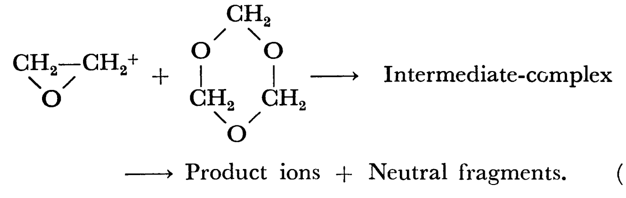


Fig. 6. Ionization efficiency curves of major fragment and product ions in ethylene oxide–trioxane mixtures. ○: *m*/*e* 44, ●: *m*/*e* 89, ▲: *m*/*e* 73, □: *m*/*e* 74, △: *m*/*e* 75.

uct ions, we measured the appearance potentials and the ionization efficiency curves of the product ions for comparison with those of the possible reactionts. The fragment ion whose appearance potential lies closest to that of product ion is taken to be the reactant ion (precursor), provided the reaction is energetically possible. If more than one fragment ion is responsible for the formation of a given product ion, a change in the slope of the ionization efficiency curve will often denote the onset of the reaction involving a different reactant ion.

The ionization efficiency curves of major fragment and product ions in ethylene oxide–trioxane mixtures are shown in Fig. 6. All the ionization efficiency curves of the product ions coincide in onset as well as shape. This suggests that the product ions are formed through a common precursor. The onset of the ionization efficiency curves of the product ions agrees with the ionization potential (10.64±0.1 eV) of ethylene oxide. The onset and fine structures in the ionization efficiency curves of the product ions do not agree with those of *m*/*e* 89 (trioxane). Furthermore, the appearance potentials, *m*/*e* 61 (10.79±0.05), 31 (11.49±0.05), 43 (12.06 ±0.1 eV),[2,12] of other abundant fragment ions (*m*/*e* 61, 31, and 43) from both trioxane and ethylene oxide are higher than those of the product ions. An agreement of the break points in the ionization efficiency curves between the product and the fragment ions was not observed. From the results of the ionization efficiency curve measurements of the fragment and the product ions, it is concluded that ethylene oxide molecular ion is the precursor of the product ions. Thus, it is suggested that the product ions result from the dissociation of unstable intermediate-complex.



(1)

The intermediate-complex resulting from the association reaction of ethylene oxide molecular ion with trioxane is very unstable. The ring opening of ethylene oxide and trioxane molecule would occur after the association of ethylene oxide molecular ion with trioxane. The ring strain energy of ethylene oxide is large (13 kcal mol⁻¹).[14] Furthermore, it is known that the bond dissociation energy of the C–O bond is lower than that of the C–C bond in ethylene oxide.[15]

Rate Constants and Ion Structures. Since the product ions in the mixture system are formed by a complex reaction mechanism, their rate constants are obtained by steady state treatment. The product ions are formed *via* certain dissociation channels of the intermediate-complex as in the following:

$$P_i^+ + M \xrightarrow{k_{1i}} P_iM^{+*}$$

$$P_iM^{+*} \xrightarrow{k_{2ij}} S_{ij}^+ + N_{ij},$$

where M, P^+, S^+, and P_iM^{+*} denote the concentration of neutral molecule and reactant, secondary product ion, and intermediate-complex, respectively. (P_iM^{+*}) and $(P_i{}^+)$ are expressed by

$$(P_iM^{+*}) = \frac{k_{1i}(P_i^+)(M)}{\sum_j k_{2ij}}, \tag{2}$$

$$(P_i^+) = (P_i^+)_0 \exp\left[-k_{1i}(M)t\right], \tag{3}$$

where t is delay time and $(P_i^+)_0$ is the concentration of (P_i^+) at $t=0$. $(S_{ij}{}^+)$ is determined by the equation

$$\frac{d(S_{ij}^+)}{dt} = k_{2ij}(P_iM^{+*}). \tag{4}$$

Integrating (4) and applying the condition $(S_{ij}{}^+)=0$ at $t=0$, we get

$$(S_{ij}^+) = \frac{k_{2ij}(P_i^+)_0}{\sum_j k_{2ij}}\{1-\exp\left[-k_{1i}(M)t\right]\}. \tag{5}$$

Assuming that the collection efficiencies are the same for both reactant and product ions, and expanding the exponential term, we have

$$\frac{I_{(S_{ij}^+)}}{I_{(P_i^+)_0}} = \frac{k_{2ij}k_{1i}(M)t}{\sum_j k_{2ij}}. \tag{6}$$

$I_{(P_i^+)_0}$ can be written as

$$I_{(P_i^+)_0} = I_{(P_i^+)} + \sum_i I_{(S_{ij}^+)} + I_{(P_iM^{+*})}. \tag{7}$$

Since $I_{(P_iM^{+*})} \approx 0$, Eq. 6 is simplified to

$$\frac{I_{(S_{ij}^+)}}{I_{(P_i^+)} + \sum_j I_{(S_{ij}^+)}} = \frac{k_{1i}k_{2ij}(M)t}{\sum_j k_{2ij}}. \tag{8}$$

Thus $k_{1i}k_{2ij}/\sum_j k_{2ij}$ is readily obtained by using Eq. 8. The rate constants obtained in ethylene oxide–trioxane and ethylene-d_4 oxide–trioxane mixtures are summarized in Table 1. The sum of the rate constants for the product ions (*m*/*e* 73—77) in ethylene-d_4 oxide–trioxane mixtures is nearly equal to that of the product ion (*m*/*e* 73) in ethylene oxide–trioxane mixtures. Similarly, the rate constants for *m*/*e* 78 and 79 in ethylene-d_4 oxide–trioxane mixtures are respectively comparable with those for *m*/*e* 74 and 75 in ethylene oxide–trioxane mixtures. The structures of the product ions proposed from the stoichiometric consideration for the product ions in both mixture systems are shown in Table 2.

Table 1. Rate constants

Ethylene oxide-Trioxane		Ethylene-d_4 oxide-Trioxane	
Product ion m/e	$k\times10^{10}$ cm^3 $molecule^{-1}$ s^{-1}	Product ion m/e	$k\times10^{10}$ cm^3 $molecule^{-1}$ s^{-1}
73	2.20	73	0.052
		74	0.195
		75	0.260
		76	1.13
		77	0.364
74	0.261	73	0.294
75	1.74	79	1.43

Table 2. Possible structures of products ions

Product ion[a)] m/e	Structure	Pıoduct ion[b)] m/e
73	CH_2-O-CH_2-O-CH^+	73
74	CX-O-CH_2-O-CH_2^+	
75	CX_2-O-CH_2-O-CH^+	
76	CX-CX_2-O-CH_2-O^+	
77	CX_2-CX_2-O-CH-O^+	
78	CX_2-CX_2-O-CH_2-O^+	74
79	CX_2-CX_2-O-CH_2-OH^+	75

a) Etylene-d_4 oxide-trioxane mixtures. b) Ethylene oxide-trioxane mixtures. X denotes H or D atom.

The skeletal structures of the product ions (m/e 74—79) consist of fragment molecules from ethylene oxide and trioxane, while the product ion at m/e 73 consists of fragment molecules derived only from trioxane. This indicates that positive charge is delocalized in the intermediate-complex having cyclic structure as shown in Fig. 7. From the structures of the product ions (Table 2), it is presumed that extensive scrambling in the complex does not occur.

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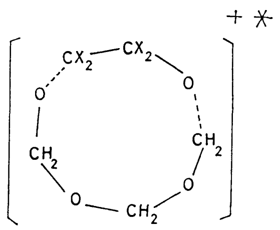

Fig. 7. Possible structure of intermediate-complex. X denotes H or D atom.

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