Ion-Molecule Reactions in the Binary Mixture of Acetaldehyde and Trioxane. I. Hydrogen Atom and Proton Transfer Reactions

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(Received May 19, 1977)

The formation reactions of protonated molecular ions in acetaldehyde–trioxane mixtures have been studied with a modified time-of-flight mass spectrometer. From the analysis of the fine structure of the ionization efficiency curves of fragment and product ions obtained by means of the retarding potential differential technique using acetaldehyde-d_4, the precursors of the product ions were determined. Protonated acetaldehyde is formed by the hydrogen atom transfer reaction of acetaldehyde molecular ion with trioxane, and protonated trioxane by the proton transfer reaction of CHO^+ generated from acetaldehyde with trioxane. The rate constants of the formation reactions of the product ions in acetaldehyde (or acetaldehyde-d_4)–trioxane mixtures were determined and isotope effect was observed. The CHO^+ generated from acetaldehyde participated predominantly in the proton transfer reaction as compared with that generated from trioxane. From the proton transfer reaction involving thermal ion CHO^+ generated from acetaldehyde it was found that the proton affinity of trioxane is smaller than that of acetaldehyde.

In studies on the ion-molecule reactions in the binary mixture of ethylene oxide and trioxane (1,3,5-trioxane) it was found that protonated ethylene oxide and trioxane are formed by cross-reaction.[1] In the ion-molecule reactions of ethylene oxide[2] and acetaldehyde,[3] the CHO^+ plays an important role in the formation of protonated molecular ions. The ion-molecule reactions in acetaldehyde have been studied by several workers.[4–8] However, the ion-molecule reaction of acetaldehyde in the mixture involving cyclic ether molecule of a large member ring such as trioxane does not seem to have been reported. In the present work, the ion-molecule reactions in the binary mixture of acetaldehyde and trioxane were studied in order to clarify the formation mechanism of protonated molecular ions. Highly strained three member ring molecule such as ethylene oxide could be isomerized under appropriate conditions into more stable isomer (acetaldehyde). A relative abundance pattern of the fragment ions from acetaldehyde in electron impact fragmentation resembles that from ethylene oxide.[3] Some oxygen-containing fragment ions of a similar structure were also produced from acetaldehyde, ethylene oxide, and trioxane. A study of the ion-molecule reactions involving the structural isomer ions in acetaldehyde–trioxane mixtures is important in connection with elementary process in radiation and ion chemistry.

Experimental

A Bendix Model 12-101 time-of-flight mass spectrometer modified with a closed ionization chamber was used.[2] Substituted ion source permitted operation under elevated pressures at long delay times. The pulse electronic circuits of the apparatus were also modified. The variable delay time circuit permitted a variation of time between the end of the ionizing pulse and the onset of the ion withdrawal pulse.[1] During the delay time the entire ionization chamber is field-free, ion-molecule reactions occurring during the time interval thus being under purely thermal conditions. The retarding potential differential technique (RPD)[9] was adopted for appearance potential and ionization efficiency curve measurement. Measurement of the ionization efficiency curves of two ions (reactant and product ion) was simultaneously performed by the two-channel ion detection technique. The gas-sample inlet-system consisting of a dual-leak and dual-reservoir was used. Two kinds of samples were introduced separately 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 known rate constant (1.11×10^{-9} cm^3 molecule^{-1} s^{-1}) of CH_5^+ in the ion-molecule reaction of methane.[2]

The following reagents were used: trioxane (Celanese Chemical), acetaldehyde, and acetaldehyde-d_4 (Merck Sharp and Dohme of Canada). The samples were used after vacuum distillation several times.

Results and Discussion

Delay Time Dependence. The delay time dependence of major fragment ions in a 1 : 1 mixture of acetaldehyde and trioxane at pressure of 1.67×10^{13} molecules cm^{-3} and electron energy of 70 eV is shown in Fig. 1. The *m/e* 44 (CH_3CHO^+), 43 (CH_3CO^+), 29 (CHO^+) are fragment ions from acetaldehyde, while *m/e* 89 ($C_3H_5O_3^+$), 61 ($C_2H_5O_2^+$), 31 (CH_3O^+), and a part of *m/e* 29 are those from trioxane. The molecular ion from trioxane was relatively less abundant, its ion intensity being comparable with the ion intensity of ^{13}C atom of *m/e* 89.[9] The variation of ion intensity of the fragment ions with delay time was investigated. The ion intensity of the fragment ions of low mass numbers decreased markedly with increasing delay time as compared with that of high mass numbers. The decrease was mainly due to a mass discrimination effect though a part of the ions was lost by ion-molecule reactions. It is presumed that the CHO^+ ions play an important role in proton transfer reactions.

The delay time dependence of product ions is shown in Fig. 2. The formation of protonated acetaldehyde (CH_3CHOH^+) is remarkable as compared with that of protonated trioxane ($C_3H_6O_3H^+$). The ion intensity ratio of protonated acetaldehyde to protonated trioxane is *ca.* 7 at delay time 1.0 μs. Protonated molecular ions are formed in acetaldehyde as well as in trioxane,[2,10] but further formation of these ions was observed in the mixture. This suggests that the protonat-

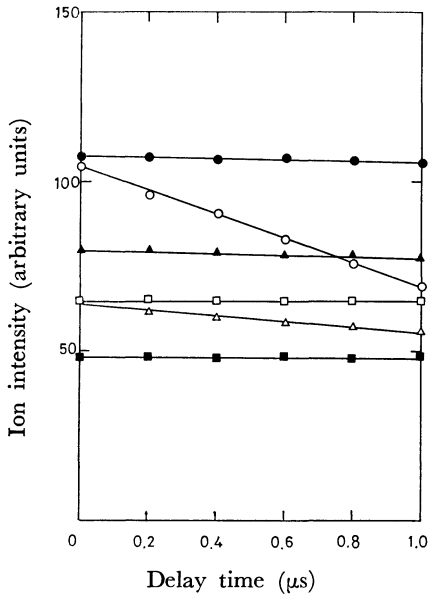


Fig. 1. Delay time dependence of fragment ions in acetaldehyde–trioxane mixtures.
▲: CH_3CHO^+, ■: CH_3CO^+, ○: CHO^+ (X1/5), □: $C_3H_5O_3^+$, ●: $C_2H_5O_2^+$, △: CH_3O^+(X1/5).

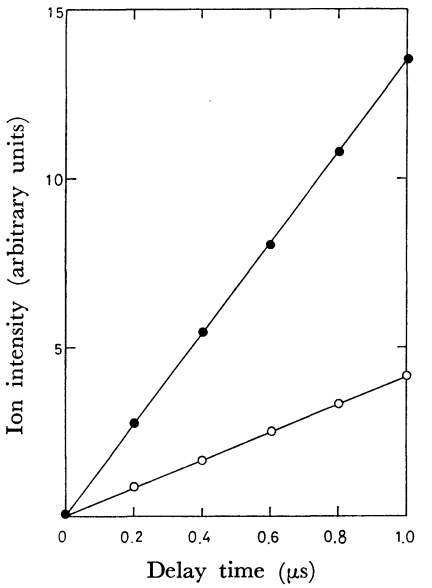


Fig. 2. Delay time dependence of protonated molecular ions in acetaldehyde–trioxane mixtures.
●: CH_3CHOH^+, ○: $C_3H_6O_3H^+$ (X2).

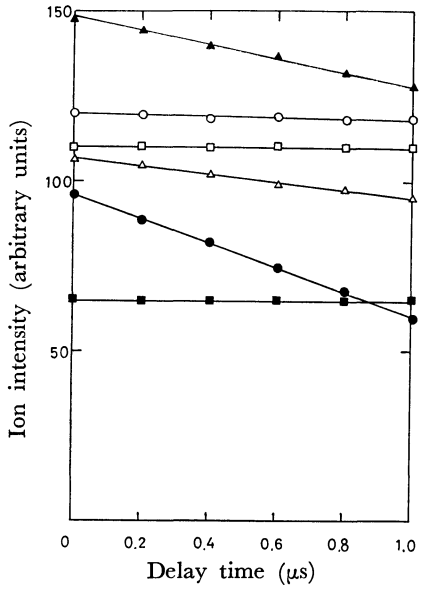


Fig. 3. Delay time dependence of fragment ions in acetaldehyde-d_4–trioxane mixtures.
○: CD_3CDO^+, ■: CD_3CO^+, ▲: CDO^+, □: $C_3H_5O_3^+$, △: CH_3O^+ (X1/5), ●: CHO^+ (X1/2).

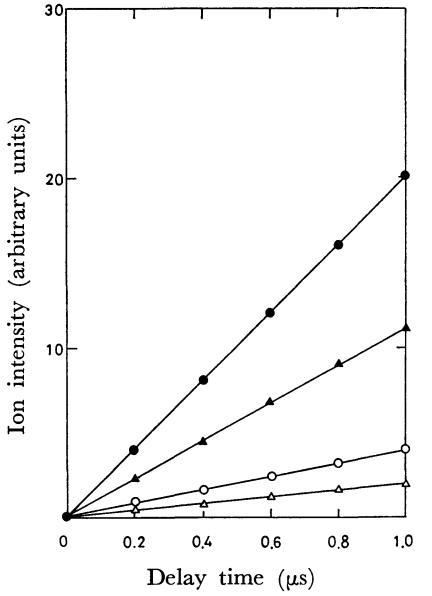


Fig. 4. Delay time dependence of protonated and deuteronated molecular ions in acetaldehyde-d_4–trioxane mixtures.
●: CD_3CDOH^+, ▲: CD_3CDOD^+, ○: $C_3H_6O_3H^+$. △: $C_3H_6O_3D^+$ (X5).

ed molecular ions are formed by cross-reactions. Studies in the mixture using deuterated acetaldehyde were carried out to elucidate the formation mechanism of the protonated molecular ions under the same conditions as unlabeled acetaldehyde mixture. The delay time dependence of major fragment and product ions in acetaldehyde-d_4–trioxane mixtures is shown in Figs. 3 and 4. The CHO^+ ions from both molecule were separated into CHO^+ and CDO^+. The isotopic distribution of product ions is given in Fig. 4. The *m/e* 49 (CD_3CDOH^+) and 50 (CD_3CDOD^+) are protonated and deuteronated acetaldehyde-d_4, and *m/e* 91 ($C_3H_6O_3H^+$) and 92 ($C_3H_6O_3D^+$) protonated and deuteronated trioxane, respectively. The CD_3CDOH^+ and $C_3H_6O_3D^+$ are cross-reaction product ions in acetaldehyde-d_4–trioxane mixtures. The ion intensity ratio of CD_3CDOH^+ to CD_3CDOD^+ and $C_3H_6O_3D^+$ to $C_3H_6O_3H^+$ were *ca.* 2 and 0.1 at delay time of 1.0 μs. It is suggested that the cross-reaction of proton or hydrogen atom transfer occurs in the mixture. These observations give important information on the reactivity of ionic and neutral reactants in the mixture.

Pressure Dependence. The ion intensity variation of the product ions with pressure in each molecule was

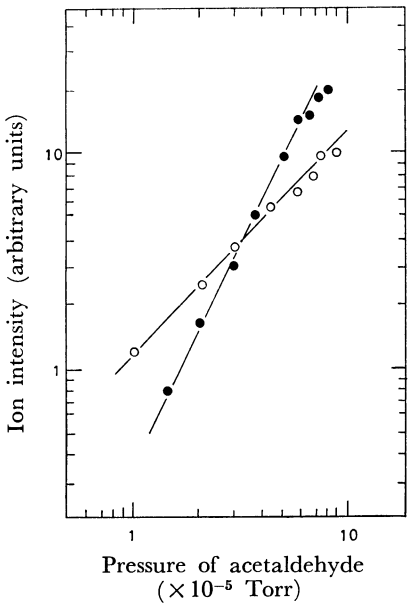


Fig. 5. Dependence of protonated molecular ions on pressure of acetaldehyde.
●: CH_3CHOH^+, ○: $C_3H_6O_3H^+$.

examined in order to clarify the contribution of acetaldehyde and trioxane. The pressure dependence of the protonated molecular ions on acetaldehyde (Fig. 5) was obtained by pressure variation of acetaldehyde using the dual leak at a fixed pressure (8.2×10^{12} molecules cm^{-3}) of trioxane and delay time of 1.0 μs. Protonated acetaldehyde shows a dependence of second order on the pressure of acetaldehyde, protonated trioxane showing one of first order. This suggests that the formation of protonated trioxane is correlated with acetaldehyde. The pressure dependence of protonated molecular ions on trioxane at a fixed pressure (8.2×10^{12} molecules cm^{-3}) of acetaldehyde is shown in Fig. 6. Protonated trioxane and acetaldehyde show

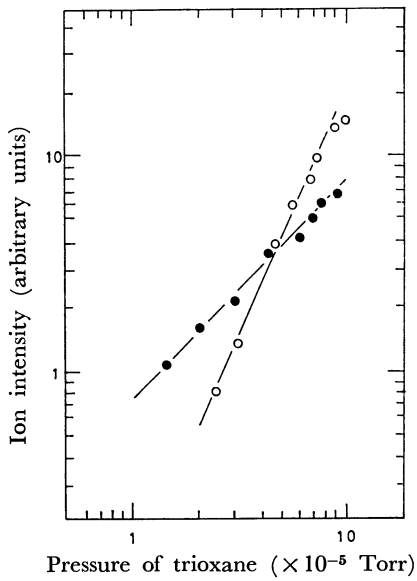


Fig. 6. Dependence of protonated molecular ions on pressure of trioxane.
●: CH_3CHOH^+, ○: $C_3H_6O_3H^+$.

a dependence of second and first order, respectively, on trioxane pressure.

Ionization Efficiency Curves. The ionization efficiency curves of major fragment and product ions in acetaldehyde-d_4–trioxane mixtures were obtained in order to determine the precursors of the product ions at delay time of 1.0 μs. The ionization efficiency curves of CD_3CDOH^+, CD_3CDO^+, and $C_3H_5O_3^+$ are shown in Fig. 7 and those of $C_3H_6O_3D^+$, CD_3CO^+, CDO^+, and CD_3^+ in Fig. 8. The ionization potential of acetaldehyde and the appearance potential of $C_3H_5O_3^+$ from trioxane are 10.32±0.05 and 10.59±0.05 eV, respectively.[9]

The onset and fine structures of the ionization efficiency curves of both CD_3CDOH^+ and CD_3CDO^+ agree. The onset of the ionization efficiency curve of CD_3CDOH^+ approaches that of $C_3H_5O_3^+$, no agreement being observed in the fine structures of the curves of both ions. In fact, the second appearance potentials of CD_3CDOH^+ and $C_3H_5O_3^+$ did not agree, the second and third appearance potential of CD_3CDOH^+ showing a good agreement with those of CD_3CDO^+ in Fig. 7. The appearance potentials (*m/e* 61: 10.79±0.05, 31: 11.49±0.05, and 29: 13.59±0.05 eV) of other fragment ions (*m/e* 61, 31, and 29) from trioxane were higher than that of CD_3CDOH^+, the break points of

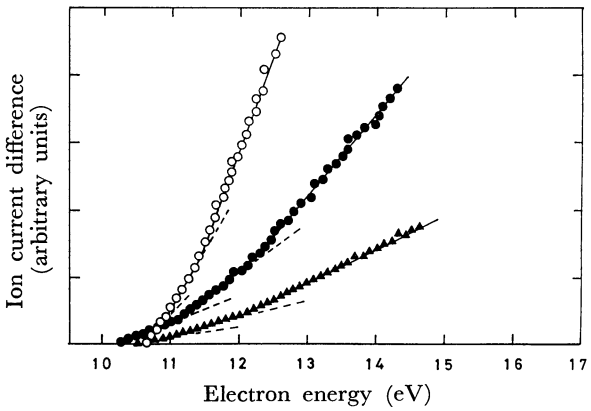


Fig. 7. Ionization efficiency curves of CD_3CDO^+ (●), CD_3CDOH^+ (▲), and $C_3H_5O_3^+$ (○) in acetaldehyde-d_4–trioxane mixtures.

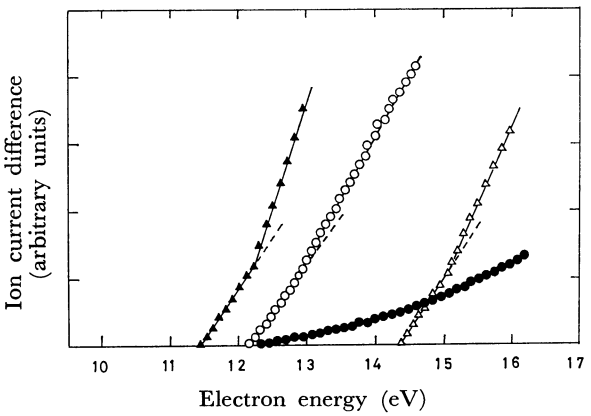


Fig. 8. Ionization efficiency curves of CD_3^+ (△), CDO^+ (○), CD_3CO^+ (▲), and $C_3H_6O_3D^+$ (●) in acetaldehyde-d_4–trioxane mixtures.

the ionization efficiency curve of CD_3CDOH^+ and these fragment ions not agreeing. Thus, it was concluded that CD_3CDO^+ is the sole precursor of CD_3CDOH^+. The onset of the ionization efficiency curve of $C_3H_6O_3D^+$ agreed with that of CDO^+. The appearance potentials of CD_3CO^+ and CD_3^+ which are abundant fragment ions from acetaldehyde-d_4 were 11.42±0.05 and 14.32±0.05 eV, respectively, deviating considerably from the onset of the ionization efficiency curve of $C_3H_6O_3D^+$. The onset of the ionization efficiency curves of both $C_3H_6O_3D^+$ and CD_3CDO^+ did not agree either. It was thus found that the precursor of $C_3H_6O_3D^+$ is CDO^+ from acetaldehyde-d_4.

Reaction Mechanism. The product ions resulting from the reactions in pure acetaldehyde were observed also in acetaldehyde (or acetaldehyde-d_4)–trioxane mixtures.

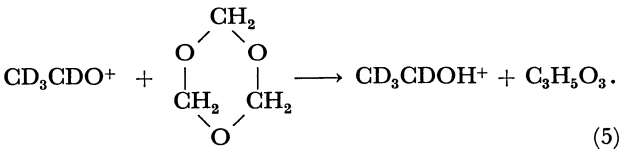
$$CH_3CHO^+ + CH_3CHO \longrightarrow CH_3CHOH^+ + CH_3CO, \quad (1)$$

$$CHO^+ + CH_3CHO \longrightarrow CH_3CHOH^+ + CO, \quad (2)$$

$$CD_3CDO^+ + CD_3CDO \longrightarrow CD_3CDOD^+ + CD_3CO, \quad (3)$$

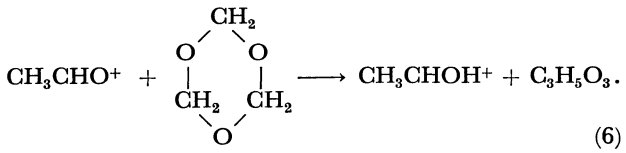
$$CDO^+ + CD_3CDO \longrightarrow CD_3CDOD^+ + CO. \quad (4)$$

It is evident from the ionization efficiency curve measurements that CD_3CDOH^+ in acetaldehyde-d_4–trioxane mixtures is formed by hydrogen atom transfer reaction as follows:



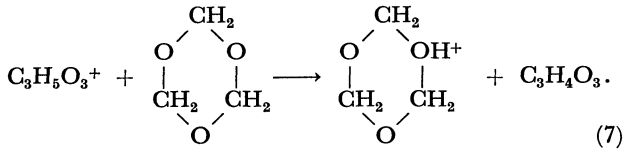
(5)

Similarly, CH_3CHOH^+ in acetaldehyde–trioxane mixtures is mainly formed by the following reaction:



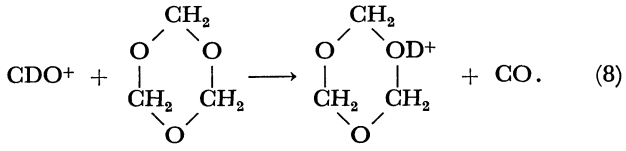
(6)

On the other hand, protonated trioxane shows a dependence of the second order on the pressure of trioxane. Thus the formation of protonated trioxane occurs in the mixture as follows.



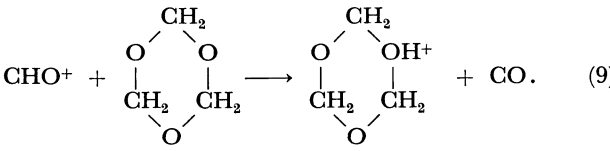
(7)

A slight increase in the ion intensity of $C_3H_6O_3D^+$ with delay time was observed (Fig. 4). The results in the ionization efficiency curve measurements confirm the view that $C_3H_6O_3D^+$ in acetaldehyde-d_4–trioxane mixtures is formed by deuteron transfer from CDO^+ to trioxane.



(8)

The contribution of other fragment ions from acetaldehyde for the formation of $C_3H_6O_3D^+$ is negligible since the onset and the fine structures of the ionization efficiency curves of these ions and $C_3H_6O_3D^+$ did not agree with each other. Since the ion intensity of trioxane molecular ion is very low, this ion could not be considered as the main precursor. Protonated trioxane in acetaldehyde–trioxane mixtures results mainly from the following reaction:



(9)

Rate Constants and Reactivity. Protonated acetaldehyde in acetaldehyde–trioxane mixtures was formed by Reactions 1, 2, and 6. Thus the rate constant of Reaction 6 is obtained by subtracting the contribution of Reactions 1 and 2. The rate constant of Reaction 9 is obtained in the same way as for k_6. The rate constants of Reactions 3 and 4 which are concurrent are obtained with a ratio plot technique.[2,3] The rate constants obtained are summarized in Table 1. The rate constant ratio k_4/k_3 is 1.68 which is nearly equal to that of k_2/k_1. The ratios k_1/k_3, k_2/k_4, and k_9/k_8 are 1.23, 1.24, and 1.14, respectively. Thus appreciable isotope effect was observed. The striking feature in the mixture is a predominant hydrogen atom transfer reaction (Reactions 5 and 6). The rate constant of Reaction 6 is smaller than that in ethylene oxide–trioxane mixtures by a factor of 1.2, suggesting that ability of hydrogen atom abstraction of acetaldehyde is lower than one of ethylene oxide. The rate constant of hydrogen atom transfer depends on the proton affinity and/or the hydrogen affinity of neutral molecule. Here, the proton affinity of acetaldehyde is 183±2[11] and 182[12] kcal mol^{-1}, and that of ethylene oxide 183 kcal mol^{-1},[11,13] the proton affinity of both molecules thus being almost equal. It is suggested that the hydrogen affinity of acetaldehyde is smaller than that of ethylene oxide.

TABLE 1. RATE CONSTANTS

Acetaldehyde–Trioxane		Acetaldehyde-d_4–Trioxane	
Reaction	$k\times10^9$ cm^3 molecule^{-1} s^{-1}	Reaction	$k\times10^9$ cm^3 molecule^{-1} s^{-1}
1	1.80[a]	3	1.46
2	3.04[a]	4	2.45
6	3.47	5	3.35
7	1.15[a]		
9	0.137	8	0.120

a) Ref. 3.

The rate constant of Reaction 2 is considerably larger than that of Reaction 9, indicating that the proton affinity of trioxane is smaller than that of acetaldehyde. CHO^+ belongs to proton donor ion among oxygen-containing ions. However, CHO^+ from trioxane did not contribute to the formation reaction of protonated molecular ions as major reactant ion in

acetaldehyde–trioxane mixtures. The effect of the translational and internal energy of reactant ions on ion-molecule reactions is important. In the measurement of translational energies of oxygen-containing ions, it was demonstrated that the energy of CHO^+ from trioxane is considerably higher than that of acetaldehyde.[14] Futrell *et al.*[15] report that the internal energy of CHO^+ depends on the source molecule and that CHO^+ from acetaldehyde has lowest internal energy among the CHO^+ ions from various oxygen-containing molecules. The difference in reactivity of the CHO^+ ions from acetaldehyde and trioxane observed in this work could be explained by an energy effect of reactant ion for proton transfer reaction.

The authors express cordial thanks to Dr. I. Kuriyama for helpful advice and encouragement during the course of the work.

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