Substituent Effect on Fragmentations and Ion-Molecule Reactions of Ionized Alkyn Alcohols

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The fragmentation patterns and ion-molecule reactions of two alkyn alcohols, 2-propyn-1-ol ($HC\equiv CCH_2OH$) and 2-methyl-3-butyn-2-ol ($HC\equiv CC(CH_3)_2OH$), were investigated using Fourier transform mass spectrometry (FTMS). The most abundant fragment ions formed from the molecular ions were $[M\text{-}H]^+$ for 2-propyn-1-ol and $[M\text{-}CH_3]^+$ for 2-methyl-3-butyn-2-ol. The dehydrated ion, $[M\text{-}H_2O]^+$ was formed only from 2-propyn-1-ol in which α-hydrogen atoms were available for α,α-elimination reaction. The protonated molecules were dissociated into $[M\text{+}H\text{-}H_2O]^+$ and $[M\text{+}H\text{-}C_2H_2]^+$ through dehydration and deacetylenylation processes. The formations of $[M\text{+}H\text{-}H_2O]^+$ and $[M\text{+}H\text{-}C_2H_2]^+$ from 2-methyl-3-butyn-2-ol were more favorable than those from 2-propyn-1-ol due to stabilization by two methyl groups at α-carbon. Ion-neutral complexes formed at long ion trapping time gave dehydrated and/or deacetylenylated ion products by further dissociation.

Key Words : Dehydration, Deacetylenylation, Ion-molecule reaction, 2-Propyn-1-ol, 2-Methyl-3-butyn-2-ol

Introduction

Fourier transform mass spectrometry (FTMS) has been widely used to study gas phase chemistry.[1-5] Its capability of trapping ions and high resolution has motivated researchers to utilize FTMS as one of the premier methods for exploring gas-phase ion-molecule chemistry. Molecules with specific functional groups undergo typical fragmentation patterns, which can be used to obtain structural information.[6-15] The typical example is the formation of prominent ions of general formula, $C_nH_{2n}O^{+\bullet}$, observed in the mass spectra of alcohols and ethers.[9,10] The relative abundances of fragment ions and their fragmentation patterns depend on the functional groups of ionized molecule.[13-15] In the precedent work[14] analyzing the chemical ionization of geometrical isomers of ROOCCR'=CHCOOR (R and R'=H, CH_3, C_2H_5), the relative abundances of typical ions such as $[M\text{+}H]^+$ and $[M\text{+}H\text{-}ROH]^+$ were different depending on the functional groups.

In the present work, we investigated the patterns of fragmentation and ion-molecule reactions of alkyn alcohols using FTMS. Two alkyn alcohol compounds were used in our experiment; 2-propyn-1-ol ($HC\equiv CCH_2OH$) and its derivative having dimethyl substituents at α-carbon, 2-methyl-3-butyn-2-ol ($HC\equiv CC(CH_3)_2OH$). Since 2-methyl-3-butyn-2-ol has no hydrogen atoms at α-carbon, its ionized molecule would show different fragmentation patterns compared with ionized 2-propyn-1-ol. We investigated fragmentation patterns of these two ionized alkyn alcohols by varying ion trapping times. Ions trapped in the ICR cell react with neutral molecules for the trapping time. The ion trapping time is the ion-molecule reaction time. This paper focuses on the dehydration and deacetylenylation reactions of ionized 2-propyn-1-ol and 2-methyl-3-butyn-2-ol. In addition, the origination of the ions with molecular weight heavier than the molecular ion and their fragmentation patterns were also analyzed.

Experimental Section

All the experiments were carried out on an Extrel FTMS 2000 Fourier transform ion cyclotron resonance (FT/ICR) mass spectrometer. The instrument is equipped with two diffusion pumps attached to dual ion trapping cells aligned collinearly within a superconducting magnet of 3.1 Tesla. The cells are 2 inch cubic and a conductance limit is shared between the two cells. The nominal value of background pressure is measured with nude ion gauge, and was lower than 1×10^{-8} Torr. Samples were introduced into the cell through a heated batch inlet. The sample pressure was about 10^{-6} Torr and the ion trapping time was 1.0 - 1.0×10^4 ms. The electron impact energy was 50 eV and time of ionization pulse applied by electron impact was 1.0 ms. Each spectrum was recorded with 64 K data points and subjected to one zero fill before Fourier transformation.

2-Propyn-1-ol and 2-methyl-3-butyn-2-ol were purchased from Aldrich Co., and used without further purification. The empirical formulas of product ions generated from ion-molecule reactions were obtained by comparisons between observed mass and calculated mass of plausible empirical formula. The mechanisms for the formations of product ions generated from ion-molecule reactions were elucidated with the empirical formulas obtained from mass spectra.

Results and Discussion

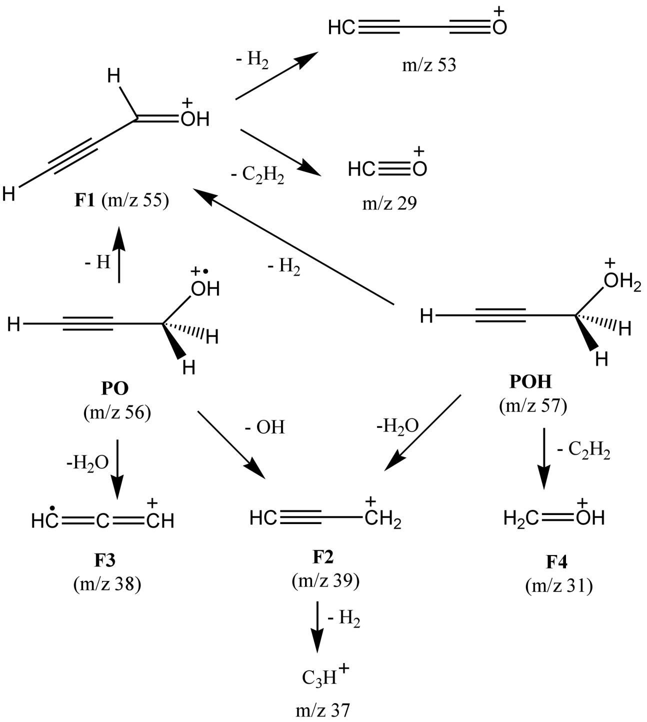
$HC\equiv CCH_2OH^{+\bullet}$ **PO**

$HC\equiv CCH_2OH_2^+$ **POH**

$HC\equiv CC(CH_3)_2OH^{+\bullet}$ **MBO**

$HC\equiv CC(CH_3)_2OH_2^+$ **MBOH**

Fragmentation of Ionized 2-Propyn-1-ol. Major fragment ions of the ionized 2-propyn-1-ol, which have more than 10% of the relative abundance in Figure 1(a), are $C_3H_3O^+$ (m/z 55), C_3HO^+ (m/z 53), $C_3H_3^+$ (m/z 39), $C_3H_2^+$ (m/z 38), C_3H^+ (m/z 37), HCO^+ (m/z 29), $C_2H_4^+$ (m/z 28), and $C_2H_3^+$ (m/z 27). Fragmentation mechanism of ionized 2-propyn-1-ol is demonstrated in Scheme 1. The $C_3H_3O^+$ (**F1**) is the most abundant fragment ion and formed by loss of α-hydrogen atom from the molecular ion (**PO**). The $C_3H_3^+$ (**F2**) is formed by direct C-O bond breaking and loss of OH radical, while the $C_3H_2^+$ (**F3**) is formed by rearrangement and loss of H_2O. **F1**, **F2**, and **F3** are the primary fragment ions formed directly from **PO**. **F1** is further dissociated into HCO^+ and $HC\equiv CCO^+$ by loss of C_2H_2 and H_2, respectively, while **F2** is further dissociated into C_3H^+ by loss of a hydrogen molecule. The protonated molecule (**POH**) can be also decomposed into smaller ions, **F1**, **F2** and **F4** as shown in Scheme 1. Among them, **F4** (CH_3O^+, m/z 31) peak was observed only at the long ion trapping time of 80 ms, not at the very short ion trapping time of 1 ms (Figure 1). This observation suggests that **F4** is formed only from **POH** because the relative ion intensity of **POH** increases as the ion trapping time increases (Figures 1 and 2). In the other side, unlike **POH**, the relative ion abundances of $C_3H_2^+$ (**F3**), CH_3O^+ (**F4**), and CHO^+ are decreased as the ion



Scheme 1. Fragmentations of the molecular ion (**PO**) and the protonated molecule (**POH**) of 2-propyn-1-ol.

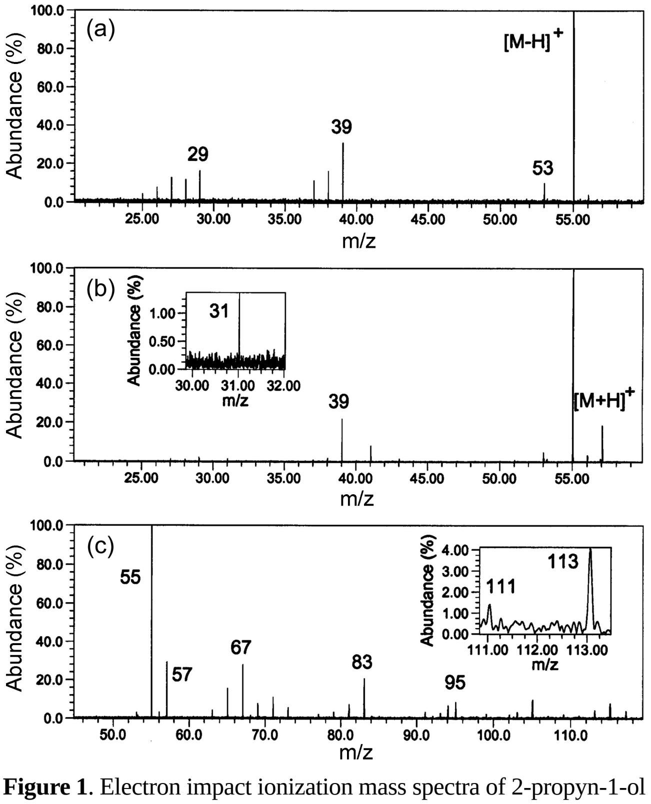


Figure 1. Electron impact ionization mass spectra of 2-propyn-1-ol at 50 eV of the electron impact energy. The sample pressure and ion trapping time are 1.8×10^{-6} Torr/1 ms (a), 5.4×10^{-6} Torr/80 ms (b), and 5.8×10^{-6} Torr/4 s (c).

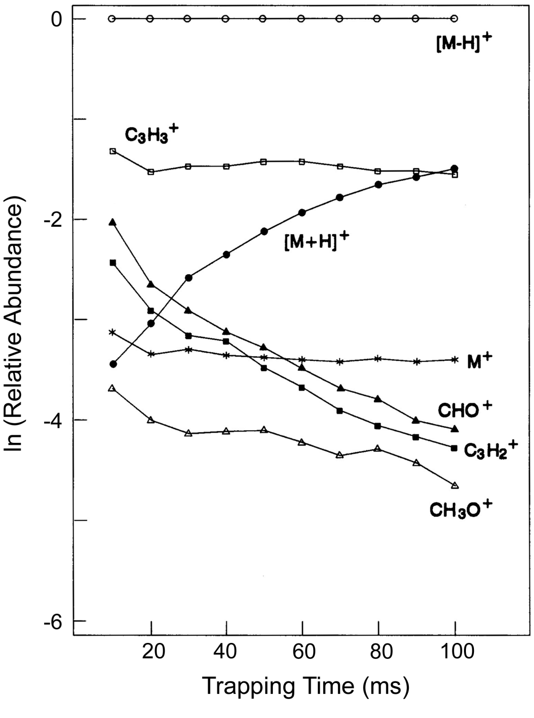


Figure 2. Temporal variation of the ion abundances for the fragmentation of 2-propyn-1-ol at 50 eV of the electron impact energy and 5.4×10^{-6} Torr of the sample pressure.

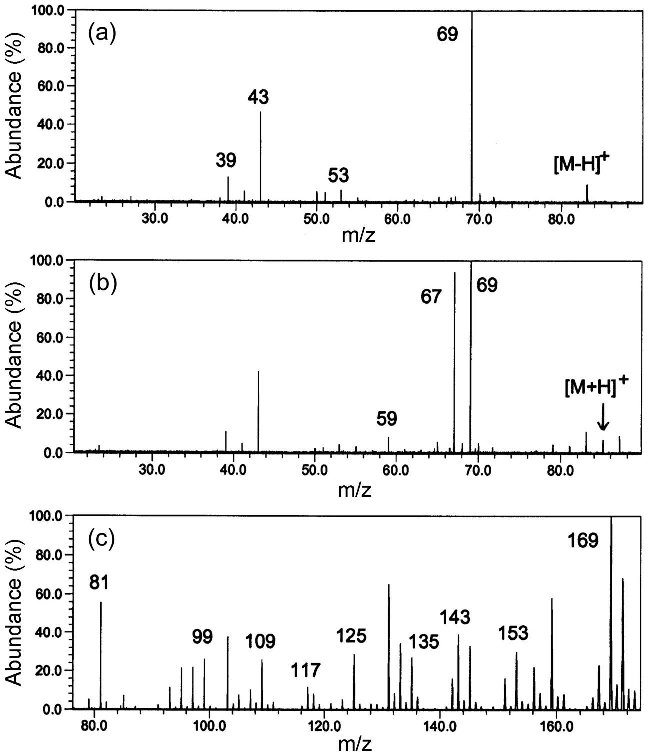
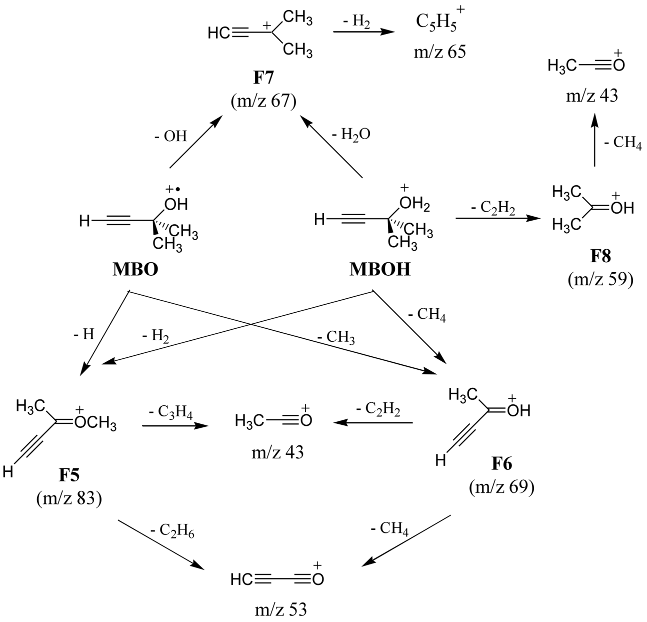


Figure 3. Electron impact ionization mass spectra of 2-methyl-3-butyn-2-ol at 50 eV of the electron impact energy. The sample pressure and ion trapping time are 1.7×10^{-6} Torr/1 ms (a), 4.2×10^{-6} Torr/80 ms (b), and 4.1×10^{-6} Torr/4 s (c).

trapping time increases. The dehydrated form (**F3**) of **PO** is notably decreased while **F4** formed from **POH** is slightly decreased (Figure 2). **F1** is still the most abundant ion regardless ion trapping time.

Fragmentation of Ionized 2-Methyl-3-bytyn-2-ol. Figure 3 shows fragment ions of the ionized 2-methyl-3-butyn-2-ol and the fragmentation mechanism is demonstrated in Scheme 2. Among the fragment ions, the $C_4H_5O^+$ (**F6**) is the most abundant fragment ion. It is noticeable that the molecular ion (**MBO**) was not observed even at the short ion trapping time of 1 ms (Figure 3) while **PO** was observed even at the very long ion trapping time (Figure 1). This observation suggests that **MBO** is very easily dissociated into fragment ions.

The primary fragment ions of **MBO** are $C_5H_7O^+$ (**F5**), $C_4H_5O^+$ (**F6**), and $C_5H_7^+$ (**F7**) generated by direct bond cleavages of C-H, C-C, and C-O, respectively. They can be further dissociated into smaller ions. **F5** is dissociated into $H_3CC{\equiv}O^+$ (m/z 43) and $HC{\equiv}CCO^+$ (m/z 53) by loss of $HC{\equiv}CCH_3$ and CH_3CH_3, respectively, **F6** is dissociated into $H_3CC{\equiv}O^+$ (m/z 43) and $HC{\equiv}CCO^+$ (m/z 53) by loss of $HC{\equiv}CH$ and CH_4, respectively, and **F7** is dissociated into $C_5H_5^+$ (m/z 65) by loss of a hydrogen molecule. Like **POH**, the protonated molecule (**MBOH**) is increased as the ion trapping time increases. **MBOH** is also dissociated into smaller ions, **F5**, **F6**, **F7**, and **F8** by loss of H_2, CH_4, H_2O, and C_2H_2, respectively (Scheme 2). **F8** ($C_3H_7O^+$) was observed at a long ion trapping time but not at a short ion trapping time. This observation coincides with the increase of **MBOH** as the ion trapping time increases and indicates that **F8** is actually formed only from **MBOH** by loss of C_2H_2. **F7**, **F8**, and **MBOH** remarkably increase as the ion trapping time increases from 10 to 100 ms, and **F7** becomes the most abundant ion after 90 ms of the ion trapping time (Figure 4). **F7** can be formed from both of **MBOH** and **MBO**. From the experimental results of the coincident



Scheme 2. Fragmentations of the molecular ion (**MBO**) and the protonated molecule (**MBOH**) of 2-methyl-3-butyn-2-ol.

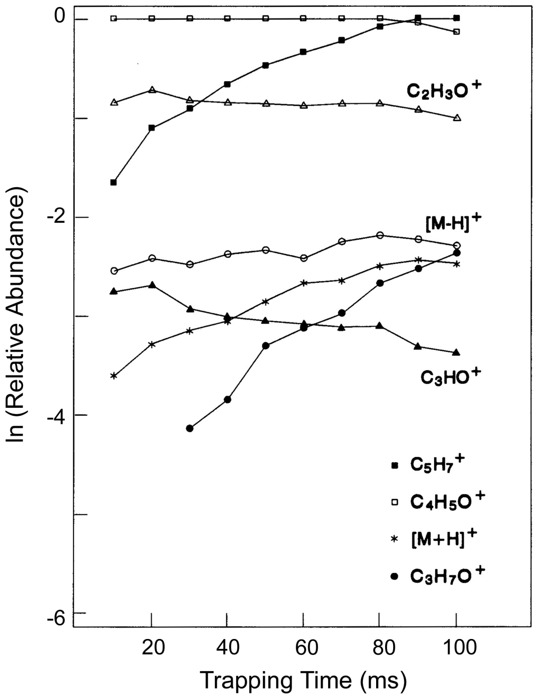


Figure 4. Temporal variation of the ion abundances for the fragmentation of 2-methyl-3-butyn-2-ol at 50 eV of the electron impact energy and 4.2×10^{-6} Torr of the sample pressure.

increases of **F7** and **MBOH**, we can say that **F7** is mainly formed from **MBOH** not **MBO**. **F6** is the most abundant ion at a short ion trapping time but its relative intensity decreases after 80 ms of the ion trapping time. This is an evidence that **F6** is mainly formed from **MBO** not **MBOH**.

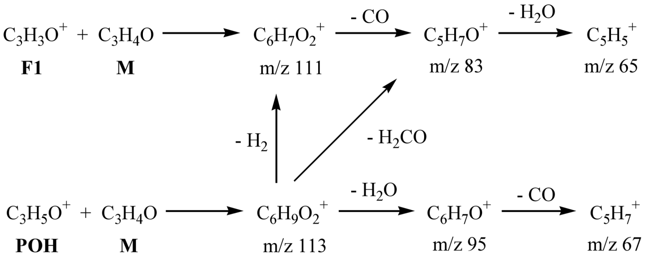
Effects of Methyl Groups at α-Carbon on the Fragmentation Patterns. 2-Methyl-3-butyn-2-ol (HC≡CC-$(CH_3)_2OH$) is a derivative of 2-propyn-1-ol (HC≡CCH_2OH), in which two methyl groups are substituted for two hydrogen atoms at α-carbon of 2-propyn-1-ol. **F3**, [**PO**-H_2O]$^{+\bullet}$ is formed from **PO** by a,a-elimination of H_2O as shown in Scheme 1. For **MBO**, however, neither [**MBO**-H_2O]$^{+\bullet}$ (m/z 66) nor [**MBO**-CH_3OH]$^{+\bullet}$ (m/z 54) was observed in the mass spectra because of absence of α-hydrogen atoms for the α,α-elimination of H_2O or CH_3OH.

F1 can be formed from **PO** with loss of a hydrogen atom by direct C-H or O-H bond cleavage. Which one is the major process? The answer can be inferred from the analysis of fragment ions formed from **MBO** and their abundances. While **F6** is formed from **MBO** by direct C-CH_3 bond breaking, **F5** is formed from **MBO** by direct O-H bond cleavage. However, **F5** is much less abundant than the **F6** as shown in Figure 3(a). Therefore, it can be suggested that the major process of the formation of **F1** from **PO** is the direct C-H bond breaking, not O-H cleavage.

F2 and **F7** can be formed from the protonated molecules (**POH** and **MBOH**, respectively) by dehydration process (Schemes 1 and 2). **F7** is notably increased as increasing the ion trapping time, while **F2** is slightly decreased as shown in Figures 2 and 4, respectively. The relative ion intensity ratios of **F2**/**POH** and **F7**/**MBOH** at 80 ms of the ion trapping time are 1.17 and 13.57, respectively. This observation means that the dehydration process is more favorable in **MBOH** than in **POH** mainly due to the stabilization of the positive charge in **F7** by two methyl groups.

F4 and **F8** are also formed from the protonated molecules (**POH** and **MBOH**, respectively) by deacetylenylation process (Schemes 1 and 2). **F8** is strikingly increased, while **F4** is slightly decreased by increasing the ion trapping time (Figures 2 and 4). The relative ion intensity ratios of **F4**/**POH** and **F8**/**MBOH** at 80 ms of the ion trapping time are 0.07 and 1.18, respectively. The more favorable deacetylenylation process occurred in **MBOH** can be also ascribed to the stabilization effect of two methyl groups at α-carbon in **MBOH**.

Ion-Molecule Reactions. For 2-propyn-1-ol, at the long ion trapping time, the product ions with molecular weight heavier than the molecular ion, such as m/z 65, 67, 83, 95, 111, and 113 were observed (Figure 1(c)). Since **F1** and **POH** have an acidic hydrogen atom and are more abundant than the other fragment ions, the ion-molecule reaction between **POH** and a neutral molecule (**M**) occurs to generate a protonated dimer ($[2M+H]^+$, $C_6H_9O_2^+$), and $C_6H_7O_2^+$ is formed from the same reaction between **F1** and **M** (Scheme 3). These product ions can be also dissociated into smaller ions, and the details of their fragmentation patterns are shown in Scheme 3. The empirical formulas of observed mass peaks are obtained from comparisons between the observed and calculated masses (Table 1).



Scheme 3. Ion-molecule reactions of 2-propyn-1-ol.

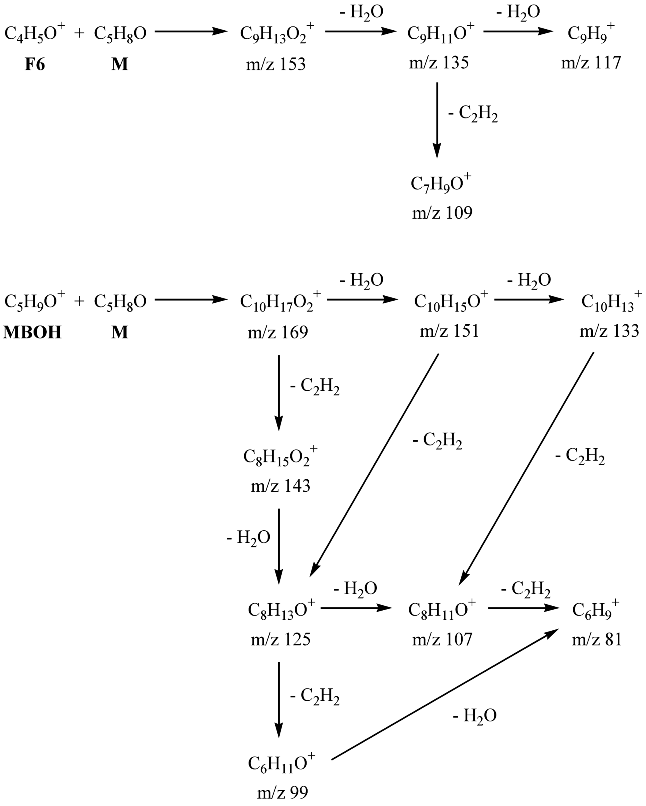
Table 1. Observed product ions generated from ion-molecule reactions of 2-propyn-1-ol and their empirical formulas

Observed mass (m/z)	Empirical formula	Calculated mass (m/z)
113.061054	$C_6H_9O_2^+$	113.059708
111.045196	$C_6H_7O_2^+$	111.044060
95.049216	$C_6H_7O^+$	95.049149
83.049160	$C_5H_7O^+$	83.049149
67.054274	$C_5H_7^+$	67.054230
65.038574	$C_5H_5^+$	65.038574
57.033616	$C_3H_5O^+$	57.033489
55.017852	$C_3H_3O^+$	55.017841

For 2-methyl-3-butyn-2-ol, the product ions with molecular weight heavier than the molecular ion were also observed from ion-molecule reactions (Figure 3(c)). Among the ion-molecule reactions, we focus on the ion-molecule reactions of **F6** or **MBOH** with a neutral molecule because **F6** and **MBOH** are the most abundant ions at the short and long ion trapping times, respectively. The empirical formulas of product ions are obtained from comparisons between the observed and calculated masses (Table 2). The fragmentation mechanisms of product ions formed by the ion-molecule reactions of **F6** or **MBOH** are shown in Scheme 4. **MBOH** reacts with a neutral molecule to generate the protonated dimer ($[2M+H]^+$, $C_{10}H_{17}O_2^+$) which

Table 2. Observed product ions generated from ion-molecule reactions of 2-methyl-3-butyn-2-ol and their empirical formulas

Observed mass (m/z)	Empirical formula	Calculated mass (m/z)
169.126319	$C_{10}H_{17}O_2^+$	169.122314
153.075750	$C_9H_{13}O_2^+$	153.091003
151.121131	$C_{10}H_{15}O^+$	151.111740
143.110766	$C_8H_{15}O_2^+$	143.106659
135.080444	$C_9H_{11}O^+$	135.081183
133.105490	$C_{10}H_{13}^+$	133.101181
125.100321	$C_8H_{13}O^+$	125.096085
117.066205	$C_9H_9^+$	117.069878
109.093307	$C_7H_9O^+$	109.101173
107.088542	$C_8H_{11}^+$	107.085526
99.082230	$C_6H_{11}O^+$	99.080444
85.066828	$C_5H_9O^+$	85.064789
81.070932	$C_6H_9^+$	81.069878



Scheme 4. Ion-molecule reactions of 2-methyl-3-butyn-2-ol.

is successively dissociated into $C_{10}H_{15}O^+$ and $C_{10}H_{13}^+$ by loss of one and two H_2O molecules, respectively. **F6** reacts with a neutral molecule to generate $C_9H_{13}O_2^+$ which is dissociated into $C_9H_{11}O^+$ by loss of H_2O. The $C_9H_{11}O^+$ can be further dissociated into $C_9H_9^+$ and $C_7H_9O^+$ by loss of H_2O and C_2H_2, respectively. The further dissociation of these ions is detailed in Scheme 4.

Conclusion

The fragmentation patterns of two alkyn alcohol compounds (2-propyn-1-ol and its derivative, 2-methyl-3-butyn-2-ol) were analyzed in details. The dehydrated ion (**F3**), $[M-H_2O]^+$ was formed only from 2-propyn-1-ol in which α-hydrogen atoms were available for α,α-elimination reaction. Both of protonated molecules (**POH**, **MBOH**) were dissociated into $[M+H-H_2O]^+$ and $[M+H-C_2H_2]^+$ through dehydration and deacetylenylation processes. The formations of $[M+H-H_2O]^+$ and $[M+H-C_2H_2]^+$ from 2-methyl-3-butyn-2-ol were more favorable than those from 2-propyn-1-ol due to stabilization by two methyl groups at α-carbon. **F1** and **POH** having an acidic hydrogen atom underwent ion-molecule reaction with a neutral molecule (**M**) to give ion-neutral complexes, however, only dehydration reactions was observed in further dissociation of these complexes. The complexes formed from the reactions of **F6** or **MBOH** with a neutral molecule showed both dehydration and deacetylenylation reactions in fragmentation processes.

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