Bull. Chem. Soc. Jpn., **60**, 2727—2735 (1987)

Ion/Molecule Reactions in Gaseous Isopropyl Alcohol

Kenzo Hiraoka,* Hajime Takimoto, and Shinichi Yamabe†,*
Faculty of Engineering, Yamanashi University, Takeda-4, Kofu 400
†Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630
(Received December 25, 1986)

The ion/molecule reactions observed in 4 Torr CH_4 containing known small amounts of i-C_3H_7OH or i-C_3H_7OH/H_2O mixture were studied over the temperature range 40—400 °C. The experiments were carried out using a pulsed electron beam mass spectrometer. At low temperatures (<150 °C), the major ions are i-$C_3H_7OH_2^+(i\text{-}C_3H_7OH)_n$. By increasing the temperature, the slow growth of ions with m/z=59, 85, and 101 is observed. These ions are assigned to $(CH_3)_2COH^+$, $(CH_3)_2CHC^+(CH_3)_2$, and $C_6H_{13}O^+$, respectively. They are probably produced from reactions of i-$C_3H_7^+$ with isopropyl alcohol. The $(CH_3)_2COH^+$ ion may be produced from the electrophilic attack of i-$C_3H_7^+$ onto the secondary carbon atom of i-C_3H_7OH. At high temperatures (≈400 °C), the $(CH_3)_2COH^+$ ion becomes dominant. Acid-catalyzed dehydration of isopropyl alcohol, $i\text{-}C_3H_7OH_2^+ + H_2O \rightarrow H_3O^+(H_2O) + C_3H_6$, is also observed. Ion/molecule reactions involved in the present experiment are discussed according to the frontier-orbital theory.

The kinetics of the gas-phase ion/molecule reactions of aliphatic alcohols have been studied in various respects. The condensation reactions of protonated alcohols ROH_2^+ leading to the formation of protonated ethers R_2OH^+have been observed.[1–7]

$$ROH_2^+ + ROH \rightarrow R_2OH^+ + H_2O \qquad (1)$$

The γ-radiation-sensitized pyrolysis of isopropyl alcohol vapor has been studied by Freeman and coworkers.[7–9] At temperatures about 250 °C, chain reactions were found to be important in isopropyl alcohol vapor. Four modes of radiation-induced chain decomposition were found.[9] The stoichiometric representation of the modes, with G values at 380 °C are $2i\text{-}C_3H_7OH \rightarrow H_2O + (i\text{-}C_3H_7)_2O$, 300; $i\text{-}C_3H_7OH \rightarrow H_2O + C_3H_6$, 1200; $i\text{-}C_3H_7OH \rightarrow CH_4 + CH_3CHO$, 43; $i\text{-}C_3H_7OH \rightarrow H_2 + (CH_3)_2CO$, 600. For the formation of diisopropyl ether, radiation-induced cationic chain reactions 2—4 have been proposed.[8]

$$i\text{-}C_3H_7OH_2^+ + i\text{-}C_3H_7OH \rightarrow (i\text{-}C_3H_7)_2OH^+ + H_2O \qquad (2)$$

$$(i\text{-}C_3H_7)_2OH^+ + i\text{-}C_3H_7OH \rightarrow (i\text{-}C_3H_7)_2OH^+(i\text{-}C_3H_7OH) \qquad (3)$$

$$(i\text{-}C_3H_7)_2OH^+(i\text{-}C_3H_7OH) + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7OH_2^+(i\text{-}C_3H_7OH) + (i\text{-}C_3H_7)_2O \qquad (4)$$

Reaction 2 has the mechanism of the bimolecular nucleophilic substitution (S_N2). Reaction 3 is the standard clustering, and reaction 4 is the displacement reaction.

Van der Linde and Freeman[9] suggested the radical chain reactions 5—8 for the formation of H_2, $(CH_3)_2CO$, and C_3H_6.

$$H + i\text{-}C_3H_7OH \longrightarrow H_2 + (CH_3)_2\dot{C}OH \qquad (5)$$

$$(CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2CO + H \qquad (6)$$

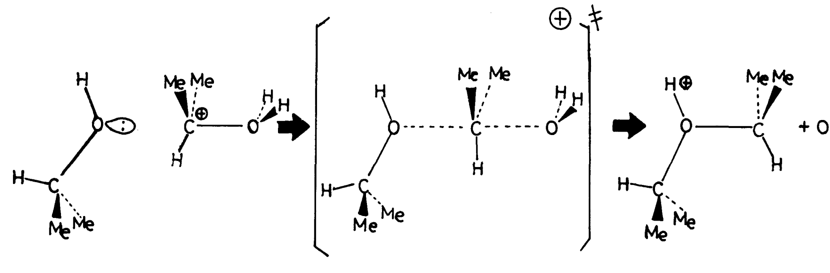
$$OH + i\text{-}C_3H_7OH \longrightarrow H_2O + \left.\begin{array}{l}\dot{C}H_2\\ CH_3\end{array}\right\rangle CHOH \qquad (7)$$

$$\left.\begin{array}{l}\dot{C}H_2\\ CH_3\end{array}\right\rangle CHOH \longrightarrow C_3H_6 + OH \qquad (8)$$

Hiraoka and Kebarle found the acid-catalyzed dehydration reaction 9 of t-butyl alcohol in the gas phase.[10] It is a unimolecular elimination (E1).

$$t\text{-}C_4H_9OH_2^+ + H_2O \rightarrow H_3O^+(H_2O) + i\text{-}C_4H_8 \qquad (9)$$

So far the gas-phase ion/molecule reactions in isopropyl alcohol have not been studied before. In the present work, some detailed examination of the same reactions were done using a pulsed electron beam mass spectrometer. It was found that several unique ions were produced from the ion/molecule reactions in isopropyl alcohol such as i-$C_3H_7^+$, $(CH_3)_2COH^+$, $C_6H_{13}^+$, $C_6H_{11}O^+$, $C_6H_{13}O^+$, $(i\text{-}C_3H_7)_2OH^+$, and $C_6H_{13}O_2^+$ in addition to the proton-bound cluster ions $i\text{-}C_3H_7OH_2^+$ $(i\text{-}C_3H_7OH)_n$. The mechanisms for the



Back side attack of i-PrOH to cation

S_N2

formation of these ions were proposed on the grounds of the thermochemical data and the frontier-orbital theory. The evidence for the occurrence of the acid-catalysed dehydration reaction analogous to reaction 9 was obtained for isopropyl alcohol.

Experimental

The measurements were made with the pulsed electron beam mass spectrometer which has been described previously.[11–13] A small amount of isopropyl alcohol or isopropyl alcohol/water vapor mixture was introduced into 4 Torr[14] CH_4 carrier gas through stainless steel capillaries.

Two keV electron beam was pulsed on for 100 μs and off for 3 ms. The electron beam entered the ion source through the electron entrance slit made of stainless steel razor blades. The width and the length of the slit were 15 μm and 1 mm, respectively. The incident electron current at non-pulsed mode was about 5×10^{-9} A. The ions produced were sampled through an ion exit slit made of razor blades. The width and the length of the slit were the same as those of the electron entrance slit. Under the present experimental conditions, the mean free paths of ions and molecules are greater than the slit width. Thus the ions pass through the slit by molecular flow and the adiabatic cooling of the escaping gas is negligible. The lifetime of ions due to the diffusive loss to the wall was more than a few ms under the present experimental conditions. They were dependent on the ion source temperature and the gas pressure. The loss of ions due to the electron-positive ion recombination reaction is negligible under the present experimental conditions. About 2 ms after the electron pulse, a short positive pulse (+25 V) was applied to the ion repeller electrode in order to annihilate all ions produced in the ion source. The ions escaping from the field-free ion source into an evacuated region were mass analysed by a quadrupole mass spectrometer (ULVAC MSQ-400) and collected in a multichannel analyser as a function of their arrival time after the electron pulse. The intensities of all ions are normalized on the measurements so that they correspond to their relative concentrations in the ion source. The ion counts collected in a multichannel analyser were transferred to the microcomputer and the time profiles of the calculated per cent of the total ionization of observed ions were recorded on the x-y plotter.

Structural data were obtained by the ab initio MO calculation with the 3-21G and STO-3G basis sets. The GAUSSIAN 80 program was used.[15]

Results

When the ion source temperature is low (<150 °C), the observed major ions are $i\text{-}C_3H_7OH_2^+(i\text{-}C_3H_7OH)_n$. That is, the standard clustering reaction takes place. When the ion source temperature is raised, several new ions are formed. Figure 1 shows the temporal profile of ions observed in 4.05 Torr of CH_4 containing 2.3 mTorr of $i\text{-}C_3H_7OH$ and 0.116 Torr of H_2O at 302.0 °C. The primary ion H_3O^+ is produced from reactions of the added H_2O with CH_5^+ and $C_2H_5^+$. These major ions are produced from the methane ion/molecule reactions. The rapid increase of $H_3O^+(H_2O)$ (mass 37) and $i\text{-}C_3H_7^+$ (mass 43) is observed at the expense of the H_3O^+ ion. The onsets of appearance of ions with m/z=59 and higher masses are slower than those of $H_3O^+(H_2O)$ and $i\text{-}C_3H_7^+$ ions. This indicates that the ions with m/z=59 and higher masses are the

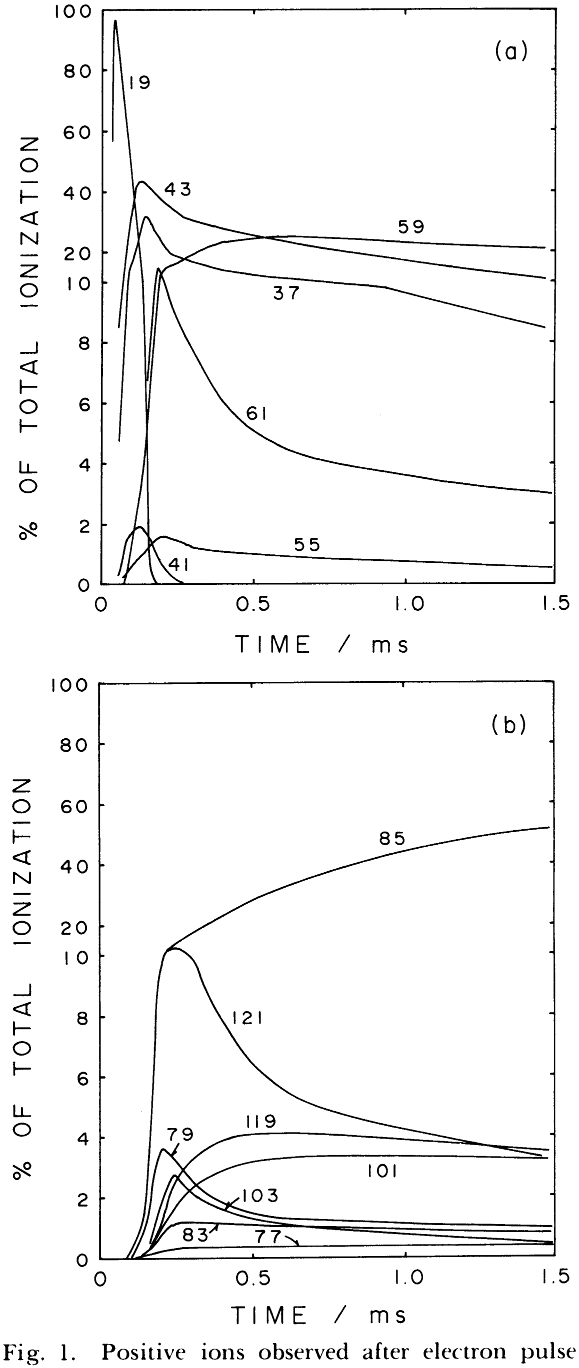


Fig. 1. Positive ions observed after electron pulse ionization in a gas mixture containing 4.05 Torr of CH_4, 0.116 Torr of H_2O, and 2.3 mTorr of $i\text{-}C_3H_7OH$ at 302.0 °C.
(a) Mass 19: H_3O^+, mass 37: $H_3O^+(H_2O)$, mass 41: $C_3H_5^+$, mass 43: $i\text{-}C_3H_7^+$, mass 55: $H_3O^+(H_2O)_2$, mass 59: $(CH_3)_2COH^+$, mass 61: $i\text{-}C_3H_7OH_2^+$.
(b) Mass 77: $(CH_3)_2COH^+(H_2O)$, mass 79: $i\text{-}C_3H_7OH_2^+(H_2O)$, mass 83: $C_6H_{11}^+$, mass 85: $C_6H_{13}^+$, mass 101: $C_6H_{13}O^+$, mass 103: $(i\text{-}C_3H_7)_2OH^+$, mas 119: $(CH_3)_2COH^+(i\text{-}C_3H_7OH)$, mass 121: $i\text{-}C_3H_7OH_2^+(i\text{-}C_3H_7OH)$.

secondary ions mainly produced from $H_3O^+(H_2O)_n$ or i-$C_3H_7^+$ as precursor ions.

Figure 2 shows the temporal profiles of ions observed in 4.08 Torr of CH_4 and 2.0 mTorr of i-C_3H_7OH at 307.3 °C. The CH_5^+ (mass 17) and $C_2H_5^+$ (mass 29) ions which are the primary ions produced from the ion/molecule reactions in methane are quickly converted to ions with m/z=41, 43, and 61. The slower onsets of appearance of ions with m/z=83 and higher masses suggest that these ions are secon-

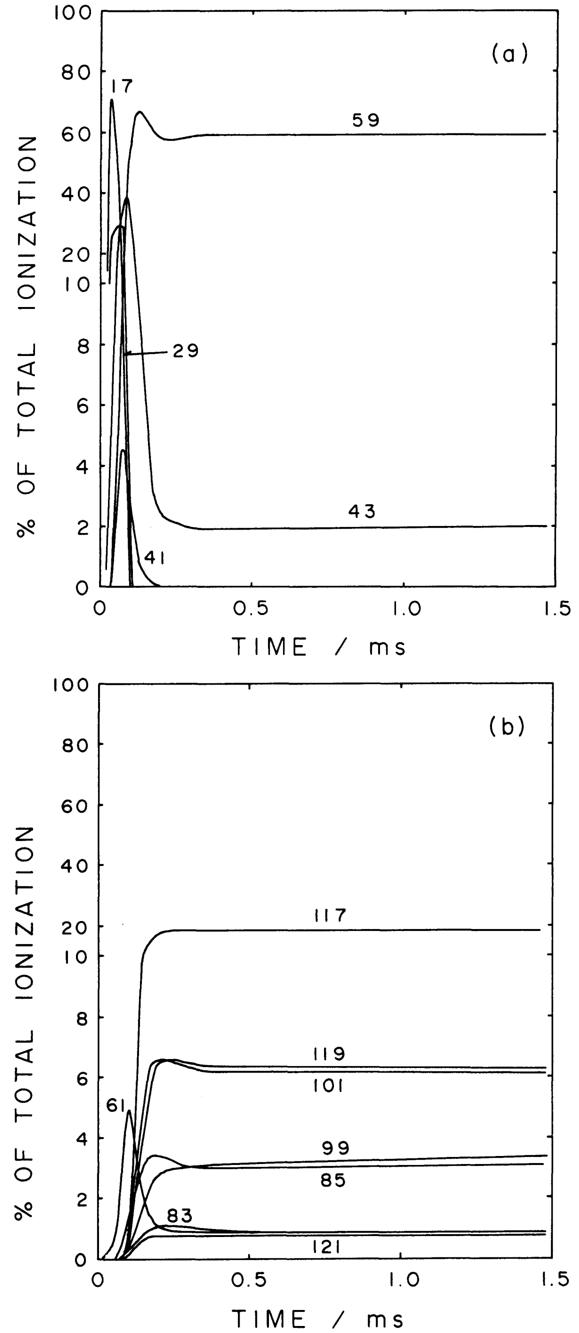


Fig. 2. Positive ions observed after electron pulse ionization in a gas mixture containing 4.08 Torr of CH_4 and 2.0 mTorr of i-C_3H_7OH at 307.3 °C.
(a) Mass 17: CH_5^+, mass 29: $C_2H_5^+$, mass 41: $C_3H_5^+$, mass 43: i-$C_3H_7^+$, mass 59: $(CH_3)_2COH^+$.
(b) Mass 61: i-$C_3H_7OH_2^+$, mass 83: $C_6H_{11}^+$, mass 85: $C_6H_{13}^+$, mass 99: $C_6H_{11}O^+$, mass 101: $C_6H_{13}O^+$, mass 117: $(CH_3)_2COH^+((CH_3)_2CO)$, mass 119: $(CH_3)_2COH^+(i$-$C_3H_7OH)$, mass 121: i-$C_3H_7OH_2^+(i$-$C_3H_7OH)$.

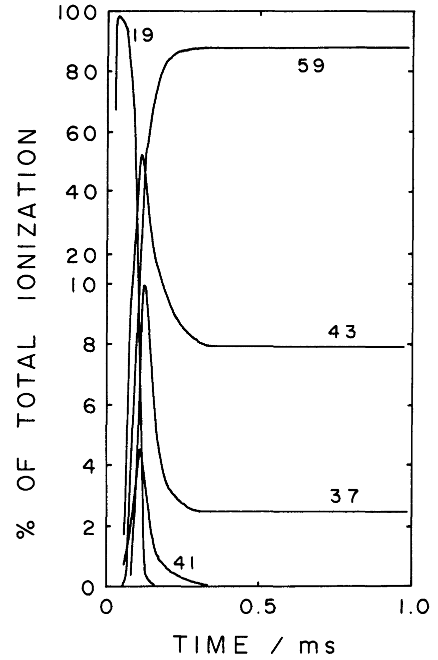


Fig. 3. Positive ions observed after electron pulse ionization in a gas mixture containing 4.06 Torr of CH_4, 0.12 Torr of H_2O, and 2.4 mTorr of i-C_3H_7OH at 413.0 °C.
Mass 19: H_3O^+, mass 37: $H_3O^+(H_2O)$, mass 41: $C_3H_5^+$, mass 43: i-$C_3H_7^+$, mass 59: $(CH_3)_2COH^+$.

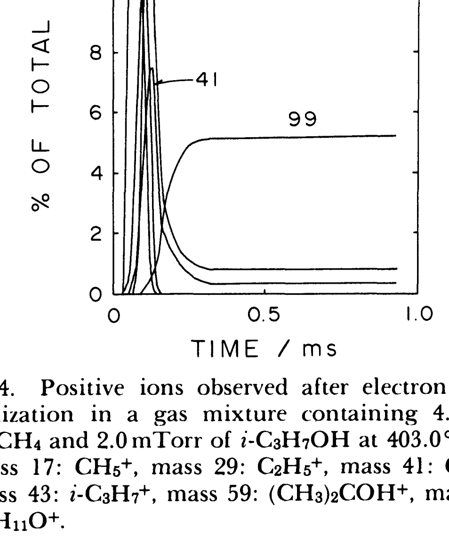


Fig. 4. Positive ions observed after electron pulse ionization in a gas mixture containing 4.1 Torr of CH_4 and 2.0 mTorr of i-C_3H_7OH at 403.0 °C.
Mass 17: CH_5^+, mass 29: $C_2H_5^+$, mass 41: $C_3H_5^+$, mass 43: i-$C_3H_7^+$, mass 59: $(CH_3)_2COH^+$, mass 99: $C_6H_{11}O^+$.

dary product ions in gaseous *i*-PrOH. The ions with m/z=99 and 117 are formed which are not detected in Fig. 1. The H_2O vapor seems to suppress the formation of these ions.

Figure 3 shows the temporal profiles of ions observed in 4.06 Torr of CH_4, 0.12 Torr of H_2O, and 2.4 mTorr of *i*-PrOH at 413 °C. The strong growth of the ion with m/z=59 is observed.

In Fig. 4 are shown the temporal profiles of ions observed in 4.1 Torr of CH_4 and 2.0 mTorr of *i*-PrOH at 403.0 °C. In this case, the ion with m/z=99 as well as that with m/z=59 are observed as major product ions.

Discussion

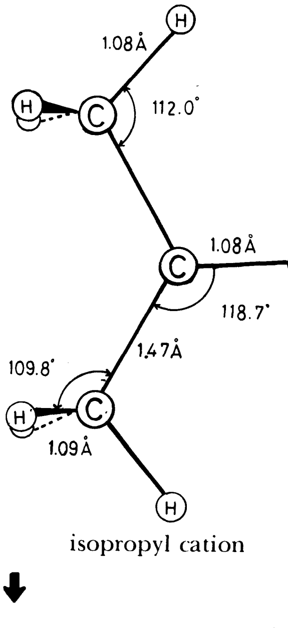
$C_3H_7^+$ Ion m/z=43. In Fig. 1, the rapid increase of the i-$C_3H_7^+$ ion, at the expense of the H_3O^+ ion is observed. This indicates that the i-$C_3H_7^+$ ion is produced by reaction 10.

$$H_3O^+ + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7^+ + 2H_2O \quad \Delta H^\circ = -0.9\ \text{kcal mol}^{-1} \quad (1\ \text{cal}=4.184\ \text{J}) \tag{10}$$

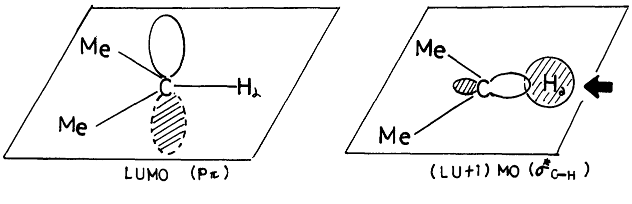
The thermochemically estimated bond energy of the species i-$C_3H_7^+ \cdots OH_2$ is 23.8 kcal mol^{-1}. Since the proton transfer reaction 11

$$H_3O^+ + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7OH_2^+ + H_2O \quad \Delta H^\circ = -24.7\ \text{kcal mol}^{-1} \tag{11}$$

is exothermic by −24.7 kcal mol^{-1}, the protonated isopropyl alcohol produced from reaction 11 has more than enough energy to dissociate toward i-$C_3H_7^+$ and OH_2.

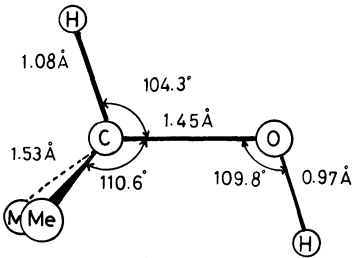


isopropyl cation

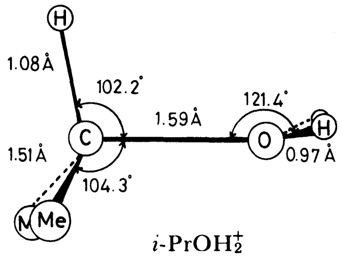


As is shown later in reactions 13, 16, 17, and 23, i-$C_3H_7^+$ reacts with *i*-PrOH in various patterns. It is of interest to examine its electronic structure with the theoretically optimized geometry. *i*-PrOH and *i*-$PrOH_2^+$ are also investigated. Three carbon atoms and H_α are in the common plane. As an electrophile, i-$C_3H_7^+$ has two reactive sites. The reactivity is demonstrated by the shape of the lowest unoccupied MO (LUMO) and the next lowest unoccupied one (LU+1)MO. Anions or bases attack $C_3H_7^+$ potentially from two directions. These are indicated by bold arrows in the figure above.

Geometries of *i*-PrOH and *i*-$PrOH_2^+$ are shown below.

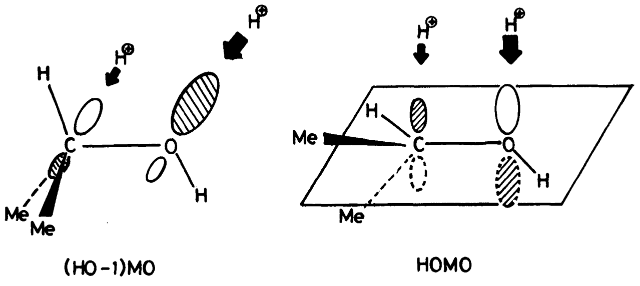


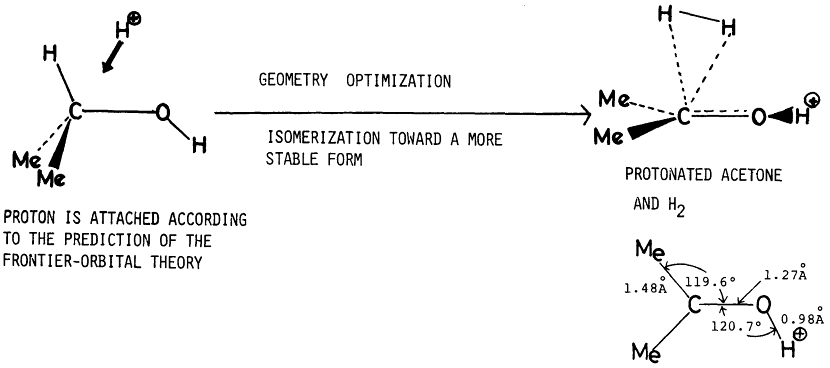
i-PrOH



i-$PrOH_2^+$

By protonation of *i*-PrOH, the C-O bond is elongated, 1.45 Å→1.59 Å. The decrease of the C-O bond population, 0.24→0.05, is remarkable. This bond weakening suggests that the thermal decomposition of i-$PrOH_2^+$ to i-$C_3H_7^+$ and H_2O in reaction 15 shown later is likely as well as the proton transfer in reaction 11. It is natural that the proton should attack the oxygen atom of *i*-PrOH. However, it is a question whether the attacking pattern is exclusive or not. To examine this, the shape of the highest occupied MO, HOMO, and the next highest occupied MO, (HO−1)MO of *i*-PrOH is drawn. The shape indicates that the oxygen lone-pair electron is the best target for an electrophile (e.g., proton) and the next favorable site is the secondary carbon atom. The carbon may be





attacked by a proton. In the next sub-section, this reactivity is described.

$(CH_3)_2COH^+$ Ion m/z=59. The production of the ion m/z=59 from the ion/molecule reaction of *i*-PrOH is stated. As the case of *i*-$C_3H_7^+$, the initial rapid increase of this ion is due to the proton transfer reaction. What kind of species is formed by the protonation on the secondary carbon of *i*-PrOH? To answer this question, the geometry of the species is optimized with the MO of the 3-21G basis set. A following isomerization reaction is found during the optimization. That is, two C-H bonds begin to be cleaved to give a hydrogen molecule. This geometric change occurs without the energy barrier. The secondary carbon gets the electronic density from two methyl groups through the hyperconjugation and pushes out H_2 by the exchange repulsion. Thus, the ion m/z=59 is the protonated acetone. Three reactions, 12—14, are possible to form the protonated acetone. Their difference lies in the source of the proton.

$$H_3O^+ + i\text{-}C_3H_7OH \rightarrow (CH_3)_2COH^+ + H_2 + H_2O \quad \Delta H^\circ = -17\ \text{kcal mol}^{-1} \quad (12)$$

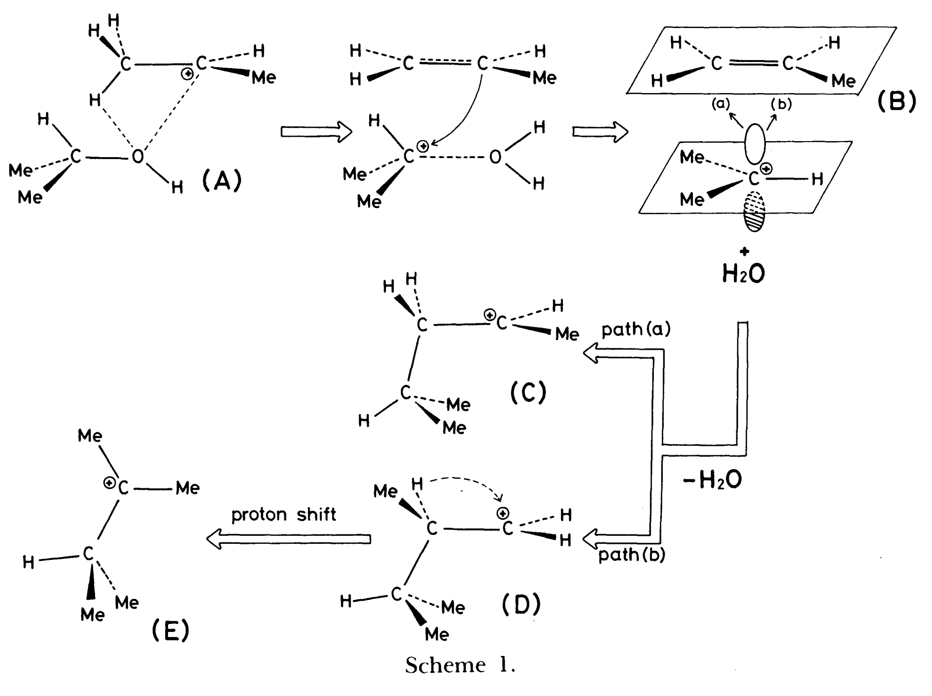
$$i\text{-}C_3H_7^+ + i\text{-}C_3H_7OH \rightarrow (CH_3)_2COH^+ + H_2 + C_3H_6 \quad \Delta H^\circ = -3.9\ \text{kcal mol}^{-1} \quad (13)$$

$$i\text{-}C_3H_7OH_2^+ + i\text{-}C_3H_7OH \rightarrow (CH_3)_2COH^+ + H_2 + i\text{-}C_3H_7OH \quad \Delta H^\circ = 7.3\ \text{kcal mol}^{-1} \quad (14)$$

Reaction 12 is more exothermic than reaction 10, however, the frontier orbital [(HO—1)MO or HOMO] of *i*-PrOH suggests that reaction 10 is more favorable than reaction 12. The ion-permanent dipole interaction between H_3O^+ and *i*-PrOH also favors reaction 10. This explains the greater initial increase of *i*-$C_3H_7^+$ than $(CH_3)_2COH^+$ (Fig. 1,a). Since reaction 14 is endothermic by 7.3 kcal mol^{-1}, the contribution of the reaction for the formation of protonated acetone is negligible under the present experimental conditions.

The gradual increase of the m/z=59 ion following the initial rapid growth is also observed (Fig. 1,a). Since the reactive ion which survives after 0.2 ms is *i*-$C_3H_7^+$, this ion is a possible precursor for the gradual formation of the m/z=59 ion in reaction 13.

The gradual decrease of *i*-$C_3H_7OH_2^+$ (mass 61) and *i*-$C_3H_7OH_2^+$ (*i*-C_3H_7OH) (mass 121) may be due to the consumption of these ions by the unimolecular decomposition reaction 15 of *i*-$C_3H_7OH_2^+$ at high temperatures.



Scheme 1.

$$i\text{-}C_3H_7OH_2^+ \rightarrow i\text{-}C_3H_7^+ + OH_2 \qquad \Delta H° = 23.8 \text{ kcal mol}^{-1} \quad (15)$$

$C_6H_{13}^+$ Ion m/z=85. The gradual growth of the m/z=85 ion, probably $C_6H_{13}^+$, is also observed as shown in Fig. 1,b. As in the case of the m/z=59 ion, no other probable candidates are conceivable for the precursor ions except for the i-$C_3H_7^+$ ion. It seems likely that the reaction of i-$C_3H_7^+$ with i-C_3H_7OH produces the $C_6H_{13}^+$ ion.

$$i\text{-}C_3H_7^+ + i\text{-}C_3H_7OH \rightarrow C_6H_{13}^+ + H_2O \qquad \Delta H° = -27 \text{ kcal mol}^{-1} \quad (16)$$

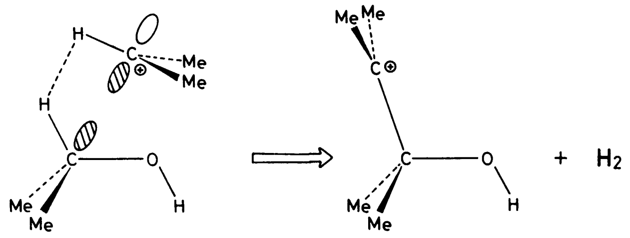
The mechanism for the $C_6H_{13}^+$ formation by reaction 16 may be described in Scheme 1. In the process of the elimination of H_2O in the associated complex **A**, the intermediate complex may have the structrure **B** in which i-$C_3H_7^+$ is interacting with propylene. According to the Markownikov rule, the less substituted sp^2 carbon in propylene may be attacked by the cation, i.e., the path (a). This leads to the formation of the secondary carbonium ion **C**. The enthalpy change of reaction 16 leading to the formation of **C** is calculated to be -9.7 kcal mol^{-1}. Here, the heat of formation of **C** is estimated to be 174 kcal mol^{-1} by the method proposed by Nakata and Kobayashi.[16)] The species **C** has the structure of protonated 4-methyl-1-pentene, CH_2=CH-CH_2-$CH(CH_3)_2$. The proton affinity of this compound is expected to be much lower than that of i-PrOH.[17)] Thus the rate constant of the proton transfer reaction $C_6H_{13}^+ + i\text{-PrOH} = i\text{-PrOH}_2^+ + C_6H_{12}$ may be of the order of 10^{-9} cm^3/molecule·s. From this value, the lifetime of the decay of the $C_6H_{13}^+$ ion due to the proton transfer reaction can be calculated to be ≈20 μs under the present experimental conditions. Since the condensation reactions such as reaction 16 are usually much slower than the collision rate (≈10^{-9} cm^3/molecule·s), the steady state concentration of the ion **C** would become very low under the present experimental conditions. However, as shown in Fig. 1,b, $C_6H_{13}^+$ shows a gradual increase. This indicates that $C_6H_{13}^+$ has a much more stable structure than **C**. If the central sp^2 carbon of propylene is attacked by i-$C_3H_7^+$ and the hydrogen atom on it migrates to the terminal sp^2 carbon of propylene (path b), the tertiary carbonium ion **E** would be formed. From the calculated heat of formation of **E**, 156.7 kcal mol^{-1},[16)] the enthalpy change of reaction 16 can be estimated to be -27 kcal mol^{-1}. **E** is about 17 kcal mol^{-1} more stable than **C**. **E** has the structure of protonated 2,3-dimethyl-1-butene, CH_2=$C(CH_3)CH(CH_3)_2$. Since the proton transfer reaction of $C_6H_{13}^+$(**E**) with i-PrOH is endothermic by about 7 kcal mol^{-1}, the long lifetime of $C_6H_{13}^+$(**E**) can be expected under the present experimental conditions. This explains the time profile of $C_6H_{13}^+$ shown in Fig. 1,b. Thus we would like to conclude that $C_6H_{13}^+$ has the structure **E**. It would be worthwhile noting that the nominal Markownikov rule may not be applied to the reactions of propylene (or terminal olefins) with the secondary carbonium ions. The rule is concerned usually with the orientation of the proton (electrophilic) addition to the double bond. However, when the electrophile is a large species with the secondary carbon, the rule would become exceptionally invalid. The present reaction seems to favor the formation of thermochemically more stable tertiary carbonium ions (by the anti-Markownikov rule) through the hydrogen migration in the intermediate complex.

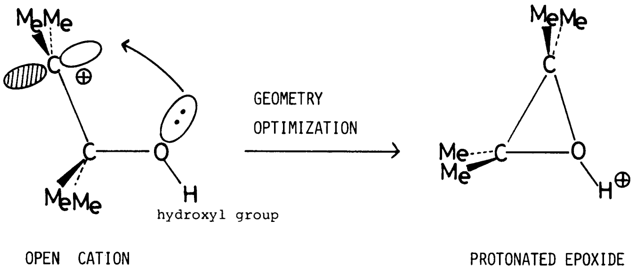
The $C_6H_{13}^+$ ion starts to be observed at ≈180 °C and becomes a dominant ion at ≈300 °C. At higher temperature, its intensity decreases and becomes nil at ≈400 °C. Some finite lifetime for the intermediate complex of (i-$C_3H_7^+ \cdots i$-C_3H_7OH)* seems indispensable for the formation of $C_6H_{13}^+$ in the condensation reaction 16.

$C_6H_{13}O^+$ Ion m/z=101. The slow production of the m/z=101 ion in Figs. 1 and 2 may be explained by reaction 17.

$$i\text{-}C_3H_7^+ + i\text{-}C_3H_7OH \rightarrow C_6H_{13}O^+ + H_2 \quad (17)$$

Reaction 17 would consist of two steps. One is the H_2 elimination leading to the formation of the tertiary carbonium ion, $(CH_3)_2C^+$-$C(CH_3)_2OH$. The other is the closure of the epoxide ring. During the optimization, the open cation is found to be converted smoothly to the protonated epoxide. The hydroxyl group cannot stay alone due to the intramolecular charge transfer.



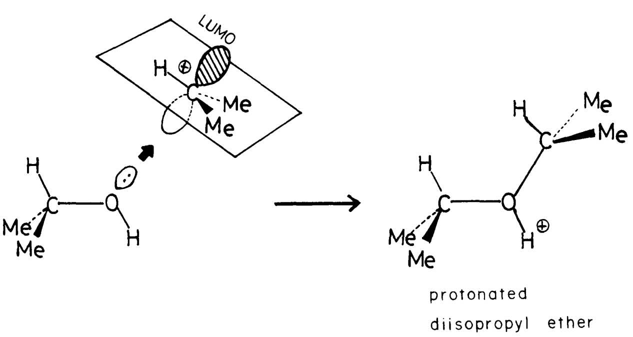


The minor product ion with m/z=83 may be produced from the dehydration of $C_6H_{13}O^+$.

$$C_6H_{13}O^+ \rightarrow C_6H_{11}^+ + H_2O \quad (18)$$

$(i\text{-}C_3H_7)_2OH^+$ Ion m/z=103. The $(i\text{-}C_3H_7)_2OH^+$ ion (mass 103) shows the initial rapid increase which is followed by the slow decrease (Fig. 1,b). Freeman[8)] proposed the cationic chain reactions 2—4 for the formation of diisopropyl ether. The obtained experimental results can be interpreted by the Freeman's proposal. The initial rapid increase of the $(i\text{-}C_3H_7)_2OH^+$ ion may be mainly due to reaction 2 and partly to reaction 19.

$$i\text{-}C_3H_7^+ + i\text{-}C_3H_7OH \xrightarrow{M} (i\text{-}C_3H_7)_2OH^+ \qquad (19)$$



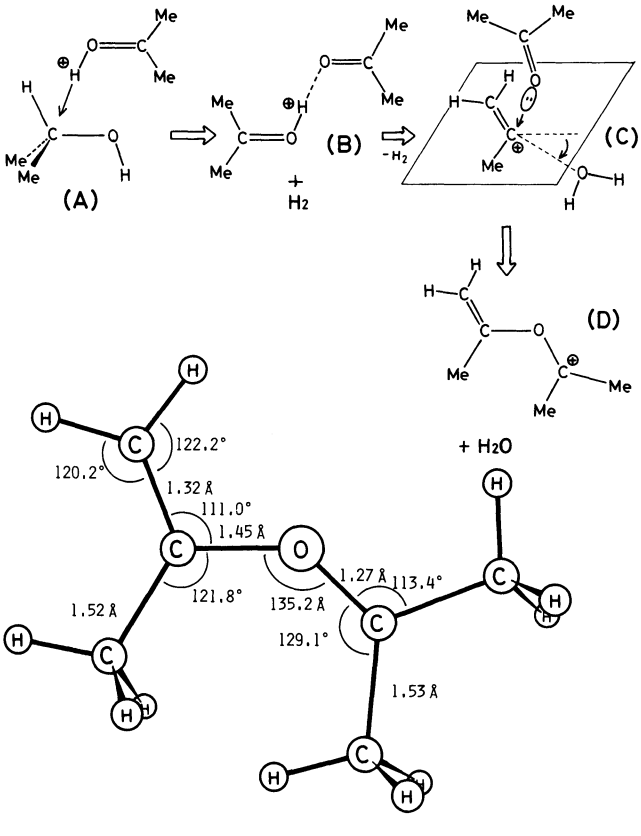
The slow decrease of $(i\text{-}C_3H_7)_2OH^+$ may be due to reactions 3 and 4. The contribution of the direct proton transfer reaction 20 may be negligible, because the reaction is highly endothermic.

$$(i\text{-}C_3H_7)_2OH^+ + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7OH_2^+ + (i\text{-}C_3H_7)_2O$$
$$\Delta H^\circ = 15.2\ \mathrm{kcal\,mol^{-1}} \qquad (20)$$

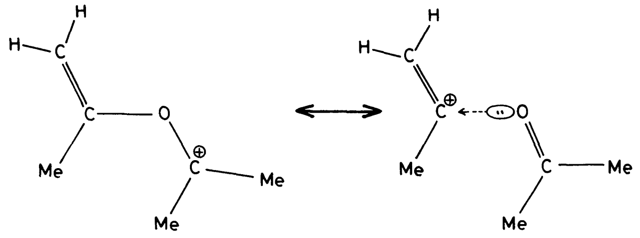
$C_6H_{13}O_2^+$ and $C_6H_{11}O^+$ Ions m/z=117 and 99. Strong growths of m/z=117 and 99 ions are observed in Fig. 2,b. The $(CH_3)_2COH^+$ ion as a precursor may explain the formation of these ions.

$$(CH_3)_2COH^+ + i\text{-}C_3H_7OH \rightarrow C_6H_{13}O_2^+ + H_2 \qquad (21)$$

$$(CH_3)_2COH^+ + i\text{-}C_3H_7OH \rightarrow C_6H_{11}O^+ + H_2 + H_2O \qquad (22)$$



The attack of the secondary carbon of i-PrOH by the protonated acetone yields the proton-held acetone dimer cation (m/z=117) (**A**→**B**). This reaction may be followed by the dehydration to give the m/z=99 ion. The dehydration involves two mechanisms. One is the keto-enol isomerization of the protonated acetone. The other is the subsequent attack of acetone onto the unsaturated carbon of the enol form in **C**. The latter reaction is similar to the nucleophilic displacement on the carbonyl carbon. It is well known that the $C_6H_{11}O^+$ ion with m/z=99 is formed from the ion/molecule reactions in gaseous acetone.[18–20] We think that this ion D is produced by the same mechanism as shown above. It is noteworthy that the length of the C^+-O bond is 1.27 Å in the optimized geometry of D. The double bond makes the cationic nature small, leading to the stability of the species. The geometry of the m/z=99 ion is described by the resonance structure.



Freeman[8,9] found that the isopropyl alcohol vapor starts to suffer the thermal decomposition on the wall of the reaction vessel above ≈300 °C. It would be possible that $(CH_3)_2COH^+$ (mass 59) and $(CH_3)_2COH^+ \cdots OC(CH_3)_2$ (mass 117) ions observed in Fig. 2 originate from the acetone produced from the thermal decomposition of i-PrOH in the reaction chamber. If this was the case, acetone should exist in the system regardless of the presence or absence of the H_2O vapor. However, the m/z=117 ion could not be detected in Fig. 1 where the H_2O vapor is present in the system. This clearly indicates that the m/z=59 and 117 ions in Fig. 2 are produced from the ion/molecule reactions in gaseous i-PrOH. In Figs. 3 and 4, the situation is more serious since the ion source temperature is high (≈400 °C). If an appreciable amount of acetone were produced, all the protonated species should be quickly converted to the protonated acetone due to the high proton affinity of acetone. However, the steady concentrations of ions such as $H_3O^+(H_2O)$ and $i\text{-}C_3H_7^+$ are established in Fig. 3. It is likely that the thermal decomposition of i-PrOH toward acetone is negligible under the present experimental conditions.

It is of interest to note that the $C_6H_{11}O^+$ ion (mass 99) is observed in Fig. 4, but not in Fig. 3. The presence of H_2O vapor seems to suppress the formation of this ion. It is described that the $C_6H_{11}O^+$ ion is produced through the formation of several intermediate complexes such as **A**—**C**. When such intermediate complexes are formed in the atmosphere of highly polar H_2O vapor, the neutral species in the complex may suffer the displacement reaction with an H_2O molecule. For example, the loose complex of $(CH_3)_2COH^+\cdots i\text{-}C_3H_7OH$ (A) may be converted to $(CH_3)_2COH^+\cdots OH_2$ by the displacement reaction, $(CH_3)_2COH^+\cdots i\text{-}C_3H_7OH+H_2O\rightarrow(CH_3)_2COH^+\cdots OH_2+i\text{-}C_3H_7OH$. Such reactions of intermediate complexes may interrupt the formation of the $C_6H_{11}O^+$ ion. This also explains the absence of the m/z=99 and 117 ions in Fig. 1. This kind of reactions may become important when the lifetimes of the intermediate complexes are long enough that the complexes suffer multiple collisions with third-body gas molecules. The destruction of the complex, A, B, or C by a water molecule may be regarded as a solvent effect in the gas-phase ion/molecule reactions.

$C_3H_7^+$ Ion Re-Visited. After the rapid decrease, the intensity of $i\text{-}C_3H_7^+$ becomes time-independent as shown in Figs. 1—4. The rapid consumption of the ion is mainly due to reaction 23, proton transfer.

$$i\text{-}C_3H_7^+ + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7OH_2^+ + C_3H_6 \qquad \Delta H^\circ = -11.7\ \text{kcal mol}^{-1} \tag{23}$$

The contribution of reactions 13, 16, 17, and 19 may be relatively minor compared to that of reaction 23. The lifetime of $i\text{-}C_3H_7^+$ due to reaction 23 is estimated to be less than 20 μs under the present experimental conditions. Since the steady-state concentration is established for $i\text{-}C_3H_7^+$, the rate of the regeneration of $i\text{-}C_3H_7^+$ by reaction 15 must be comparable to that of the consumption by reaction 23.

Van der Linde and Freeman[9)] proposed the radical chain reactions 5—8 for the formation of H_2, $(CH_3)_2CO$, and C_3H_6 in the γ-radiation-sensitized pyrolysis of gaseous *i*-PrOH. In the present experiments, the strong growth of $(CH_3)_2COH^+$ is observed at high temperatures in ion/molecule reactions in gaseous *i*-PrOH. Alternative cationic chain reactions 13, 24, and 15 may be possible for the formation of $(CH_3)_2CO$ and H_2 in the γ-radiation-sensitized pyrolysis of gaseous *i*-PrOH.

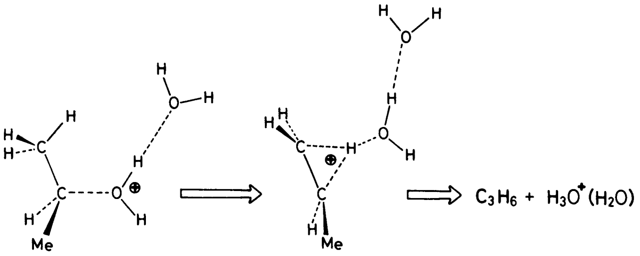
$$(CH_3)_2COH^+ + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7OH_2^+ + (CH_3)_2CO \qquad \Delta H^\circ = 5.5\ \text{kcal mol}^{-1} \tag{24}$$

Besides, the rapid chain reactions 23 and 15 for the formation of C_3H_6 are established at high temperatures in gaseous *i*-PrOH. The formation of C_3H_6 in the γ-radiation-sensitized pyrolysis of *i*-PrOH could also be accounted for by the cationic chain reactions 23 and 15.

It would be of great interest to measure the temperature dependences of the rate constants of reactions 13, 16, etc., and determine the energy barriers for the corresponding reactions. However, the measurements of the rate constants for these reactions are difficult due to the regeneration of the $i\text{-}C_3H_7^+$ ion by reaction 15. Besides, the product ions such as $(CH_3)_2COH^+$ and $C_6H_{13}^+$ are slowly consumed by the proton transfer reactions with *i*-PrOH. This also makes the kinetic measurements difficult. Thus we are discouraged to perform the detailed measurements of rate constants to obtain the meaningful information on the reaction kinetics.

Acid-Catalyzed Dehydration Reaction of *i*-C_3H_7OH. It should be noted that the steady-state concentration of $H_3O^+(H_2O)$ (m/z=37) is established in Fig. 3. If the $H_3O^+(H_2O)$ ion establishes the equilibrium with H_3O^+, the concentration ratio of $H_3O^+(H_2O)/H_3O^+$ can be estimated to be about 3 to 1 under the present experimental conditions. Thus, the $H_3O^+(H_2O)_n$ ions should be rapidly converted to $i\text{-}C_3H_7OH_2^+$ by the proton transfer reaction 11. The expected lifetime of $H_3O^+(H_2O)_n$ is less than 100 μs under the present experimental conditions. The steady appearance of $H_3O^+(H_2O)$ indicates that the $H_3O^+(H_2O)$ ion is quickly reproduced from some ion/molecule reactions. The regeneration of $H_3O^+(H_2O)$ may be due to reaction 25.

$$i\text{-}C_3H_7OH_2^+ + H_2O \rightarrow H_3O^+(H_2O) + C_3H_6 \qquad \Delta H^\circ = 2\ \text{kcal mol}^{-1} \tag{25}$$

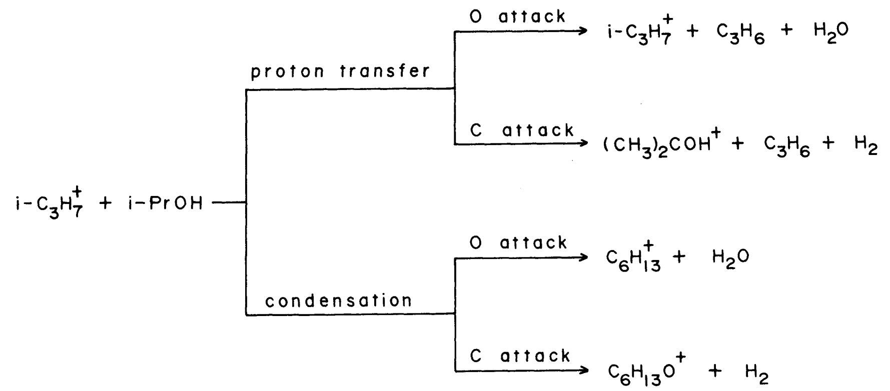


The $i\text{-}C_3H_7OH_2^+$ ion produced from reaction 23 decomposes unimolecularly to produce $i\text{-}C_3H_7^+$. When the $i\text{-}C_3H_7OH_2^+$ ion collides with an H_2O molecule within its lifetime, the dehydration of $i\text{-}C_3H_7OH_2^+$ may take place. Since the product ion $H_3O^+(H_2O)$ from reaction 25 reproduces the $i\text{-}C_3H_7OH_2^+$ ion by reaction 11, H_2O acts as a catalyst for the formation of propylene. Reaction 25 is analogous to acid-catalyzed dehydration of alcohols in solution. A similar reaction is also found for *t*-butyl alcohol in the gas phase.[10)]

Summary and Conclusion

The positive ion/molecule reactions in gaseous isopropyl alcohol were studied in detail. The new information obtained in the present work may be summarized as follows.

1) The isopropyl alcohol has two reactive sites for the nucleophilic reactions, i.e., the oxygen atom and the secondary carbon atom. The protonations onto the O and s-C atom yield $i\text{-}C_3H_7^+$ and $(CH_3)_2COH^+$ ion, respectively. The condensation reactions of $i\text{-}C_3H_7^+$ with *i*-PrOH leads to the formation of $C_6H_{13}^+$ and $C_{16}H_{13}O^+$ ion. The reactions of $i\text{-}C_3H_7^+$ with *i*-PrOH may be summarized as the Scheme 1.



2) The condensation reactions of the secondary product ion $(CH_3)_2COH^+$ with *i*-PrOH produce $C_6H_{13}O_2^+$ and $C_6H_{11}O^+$ ion. The $C_6H_{13}O_2^+$ ion may have the structure of the proton-bound acetone dimer cations. The dehydration of $C_6H_{13}O_2^+$ yields $C_6H_{11}O^+$ through the keto-enol isomerization of the protonated acetone molecule in the complex $C_6H_{13}O_2^+$. The $C_6H_{11}O^+$ ion (m/z=99) is known to be one of the major product ions from the gas-phase ion/molecule reactions in acetone.[18–21] We think that this ion has the same structure as the one produced in the present system. It was found that the presence of H_2O in the system greatly suppresses the formation of $C_6H_{13}O_2^+$ and $C_6H_{11}O^+$ ion. This may be due to the displacement reactions of the intermediate ions with the H_2O molecule. This may be regarded as the solvent effect in the gas-phase ion/molecule reactions.

3) The acid-catalyzed dehydration reaction, $i\text{-}C_3H_7OH_2^+ + H_2O \rightarrow H_3O^+(H_2O) + C_3H_6$, was observed. The similar reaction has also been observed for $t\text{-}C_4H_9OH$ but at much lower temperature.[10]

4) Acetone and propylene are produced with high G values from the γ-radiation-sensitized pyrolysis of *i*-PrOH vapor.[7–9] The formation of these compounds may be explained by the cationic chain reactions 13, 24, 23, and 15. The radical chain reactions 5—8 suggested by van der Linde and Freeman[9] for the formation of these compounds are not unique because the rate constants of hydrogen abstraction reactions such as reactions 5 and 7 are relatively small.[22]

5) The Markownikov rule may not be applied to the reactions of terminal olefins with the secondary carbonium ions. When the electrophile is a large secondary carbonium ion, the reaction seems to favor the formation of thermochemically more stable tertiary carbonium ion through the hydrogen migration in the intermediate complex.

One of the authors (KH) thanks Mr. Yukio Chino of the Yamanashi University for making the ion source used in this experiment. The financial supports of the Grant-in-Aid from the Ministry of Education and of the 1st Morino Trust for Molecular Science are gratefully acknowledged.

MO calculations were carried out on the FACOM M-382 computer at the Data Processing Center of Kyoto University and on the HITAC M-200H computer at the Institute for Molecular Science.

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