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Ion/Molecule Reactions in Gaseous Acetone

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The ion/molecule reactions in acetone were investigated which were induced by the electron impact. It was found that the protonated acetone reacts with an acetone molecule to produce the protonated diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) and the protonated mesityl oxide (4-methyl-3-penten-2-one) through the aldol condensation reaction. It was also found that the acetone molecule isomerizes from keto to enol form in the interaction with the chloride ion. The thermochemical data for the higher-order clustering reactions of the proton and chloride ion with acetone molecules were obtained.

In recent years a number of studies have been made of the gas-phase ion/molecule chemistry of acetone.[1–5] Through these experiments, the nature and rates of formation of several reaction products have become fairly well established. Like many ionic species, the ion/molecule chemistry of acetone centers around the formation of cluster ions. MacNeil and Futrell,[2] who ionized the acetone with an electron beam, as well as Sieck[3] and Wincel,[5] who employed photons as the ionizing agents, observed a number of cluster ions at relatively high pressures. Furthermore, the species corresponding to loss of a water molecule from $H^+(CH_3COCH_3)_n$ with $n \geqq 2$ have been observed.

Lau et al. measured the equilibria and van't Hoff plots for Reaction (1).[6]

$$H^+(CH_3COCH_3)_{n-1} + CH_3COCH_3 = H^+(CH_3COCH_3)_n \quad (n-1,\ n) \qquad (1)$$

They tried to measure the (2, 3) equilibria of Reaction (1). They found that the equilibrium "constants" were not independent of pressures but decreased when the pressure of third gas CH_4 and of acetone were increased. In our previous work,[7] we observed that the intensities of ions with m/z=157 and 175 increase gradually at the expense of the $H^+(CH_3COCH_3)_2$, m/z=117, ion. These results suggest the occurrence of some unique ion/molecule reactions in gaseous acetone. However, little information was obtained so far regarding the kinetics of ion/molecule reactions in gaseous acetone. In the present work, we made extensive kinetic measurements of ion/molecule reactions in gaseous acetone. We got some evidence that acid-catalysed keto-enol isomerization of the acetone molecule followed by the formation of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) and mesityl oxide (4-methyl-3-penten-2-one) take place in gaseous acetone. The keto-enol isomerization of the acetone molecule was also found to occur in the interaction of Cl^- with the acetone molecule.

Experimental

The measurements were made with the pulsed electron beam mass spectrometer which has been described previously.[7,8] The ion/molecule reactions observed in the gas mixtures of CH_3COCH_3/He, CH_3COCH_3/CH_4, $CH_3COCH_3/CCl_4/He$, and $CH_3COCH_3/CCl_4/CH_4$ were studied. Small amounts of CH_3COCH_3 and/or CCl_4 were introduced into the He or CH_4 carrier gas through stainless steel capillaries (0.1 mm×1 m). 2 keV electron beam (5×10^{-9} A) was pulsed on for 50 μs and off for 3 ms. 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 ion counts collected in a multichannel analyser were transferred to the microcomputer and the time profile of the calculated per cent of total ionization of observed ions were recorded on the x—y plotter.

Two kinds of gases, He and CH_4, were used as carrier gases in order to examine the third-body dependence on the ion/molecule reactions (see the following section). The positive ions produced in CH_3COCH_3/He and CH_3COCH_3/CH_4 are more or less the same except that the $CH_3CO^+(CH_3COCH_3)_n$ and $C_2H_5^+(CH_3COCH_3)_n$ ions are only detected in CH_3COCH_3/He and CH_3COCH_3/CH_4, respectively. Negative ions could not be detected in CH_3COCH_3/He and CH_3COCH_3/CH_4. On the contrary, strong signals of Cl^- and its clusters were observed in $CH_3COCH_3/CCl_4/He$ and $CH_3COCH_3/CCl_4/CH_4$. The Cl^- ion is yielded from the dissociative electron capture by CCl_4.

$$e + CCl_4 = Cl^- + CCl_3 \qquad (2)$$

No other negative ions originating from acetone could be detected.

Results and Discussion

1. Acetone Containing Mesityl Oxide and Diacetone Alcohol as Impurities. Positive Ions: Figure 1 shows the temporal profile of ions observed in 4.02 Torr (1 Torr=133.322 Pa) of He containing 86 mTorr of acetone at 33.7 °C.

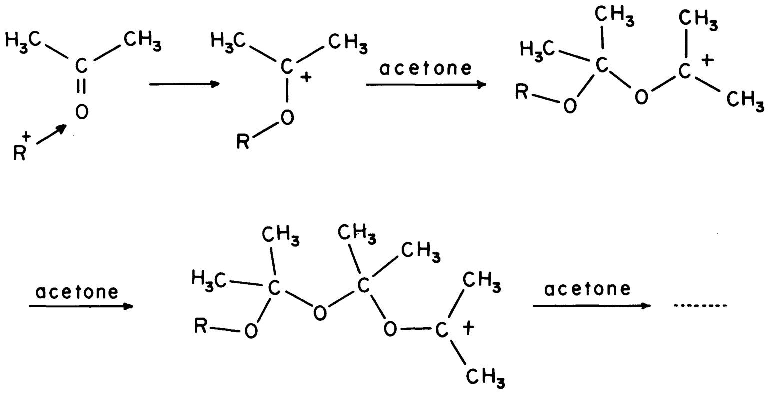
The m/z=73, 131, and 189 ions correspond to

$CH_3^+(CH_3COCH_3)_n$ with $n=1$ to 3. The rapid decay of the $m/z=73$ ion is completely accounted for by the increase of $m/z=131$ and 189 ions.

The ions with $m/z=159$ and 217, which correspond to $CH_3CO^+(CH_3COCH_3)_n$ with $n=2$ and 3, decrease rapidly. The rapid consumption of these ions may be due to the reactions of CH_3CO^+ with acetone molecules.[2] The ions $CH_3CO^+(CH_3COCH_3)_n$ were not detected when methane is used as a carrier gas. This indicates that CH_3CO^+ is yielded by the reaction of the primary ion $He^{+\cdot}$ with acetone molecule.

The ions with $m/z=155$ and 213 may be the cluster ions of $C_3H_3^+$ with acetone molecules, $C_3H_3^+(CH_3COCH_3)_n$ with $n=2$ and 3. The mechanism for the formation of $C_3H_3^+$ ion is not clear.

The results described above indicate that acetone has an ability to form large cluster ions with onium ions $R^+=CH_3^+$, CH_3CO^+, and $C_3H_3^+$. The sequence for the formation of cluster ions may be described as follows:



The reactions of onium ions with acetone molecules form polyethers. The reactions of onium ions with acetone molecules may be regarded as condensation reactions rather than clustering reactions.

The gradual increase of the ion $H_3O^+(CH_3COCH_3)_3$ with $m/z=193$ is observed which is yielded from water impurity. For aprotic solvent molecules B's such as acetone, acetonitrile, etc., the proton-held trimer ions $H^+(B)_3$ are known to be much less stable than the dimer ions $H^+(B)_2$.[9] Hence, the presence of a small amount of water impurity in aprotic solvents often yields quite a strong $H_3O^+(B)_3$ ion compared to $H^+(B)_3$ ion because H_3O^+ has three protic hydrogen atoms.

The gradual increase of ions with $m/z=157$ and 175 at the expense of the ion with $m/z=117$ is observed. It is evident that the ion $C_6H_{11}O^+(CH_3COCH_3)$ and some isomeric ion whose m/z is equal to the trimer ion $H^+(CH_3COCH_3)_3$ are formed from the dimer ion $H^+(CH_3COCH_3)_2$. In order to examine whether these ions are produced from acid (proton)-catalysed reactions of acetone or come from impurities contained in the acetone samples, we remeasured the ion/molecule reactions using the distilled and purified acetone samples. The apparent decrease in the growth rates of ions with $m/z=157$ and 175 were observed. This indicates that the gradual increase of ions with $m/z=157$ and 175 is due to the impurities present in the used acetone sample. It is known that under acidic or basic conditions, acetone produces diacetone alcohol and mesityl oxide by the aldol condensation reaction in the liquid phase.[10] The gradual increase in the intensities of ions with $m/z=157$ and 175 is likely to be due to the presence of mesityl oxide and diacetone alcohol contained in acetone as impurities.

Negative Ions: Figure 2 shows the temporal profile of negative ions observed in 4.09 Torr of He containing 0.790 Torr of acetone and 0.3 mTorr of CCl_4 at 38.9 °C.

The gradual decrease of Cl^- ($m/z=35$) and $Cl^-(CH_3COCH_3)$ ($m/z=93$) ions are observed. The decrease is compensated by the increase of $m/z=151$ and 209 ions. The used acetone sample contains diacetone alcohol as an impurity. As the diacetone alcohol molecule has a protic hydrogen atom, it can form a rather strong bond with Cl^- to yield $Cl^-\cdots HO(CH_3)_2CCH_2COCH_3$ ($m/z=151$) and its cluster with acetone ($m/z=209$). This explains the increase of $m/z=151$ and 209 ions at the expense of $m/z=35$ and 93 ions.

The cluster ion of Cl^- with mesityl oxide could not be detected under the present experimental conditions. This is because mesityl oxide does not have a protic hydrogen and it cannot form a strong bond with Cl^-.

The $m/z=53$, 111, and 169 ions correspond to $Cl^-(H_2O)(CH_3COCH_3)_n$ with $n=0$—2. In our previous paper,[8] we found that the third-order clustering reaction (3) with $n=1$ is particularly

$$Cl^-(H_2O)_{n-1} + H_2O + CH_4 = Cl^-(H_2O)_n + CH_4 \quad (3)$$

slow compared to higher order reactions ($n\geqq 2$). In

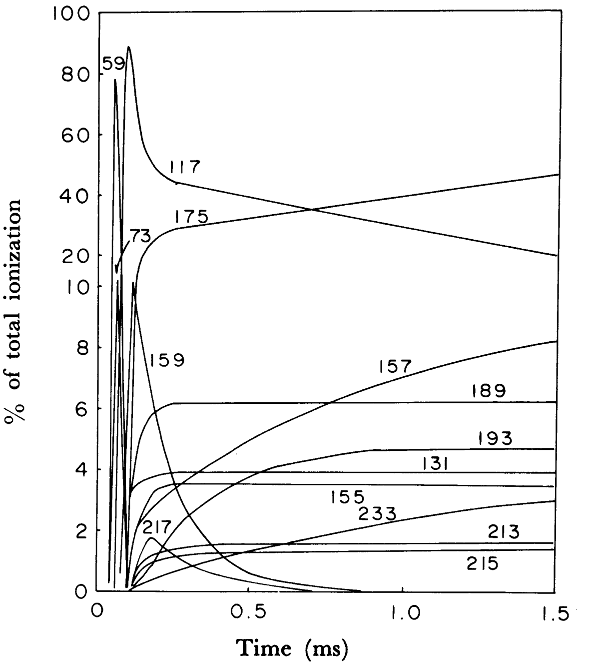


Fig. 1. Positive ions observed in a gas mixture containing 4.02 Torr of He and 86 m Torr of acetone at 33.7 °C. Acetone contains small amounts of mesityl oxide and diacetone alcohol as impurities. Mass 59 : $H^+(CH_3COCH_3)$, mass 117 : $H^+(CH_3COCH_3)_2$. The initial increase of mass 175 is due to the formation of $H^+(CH_3COCH_3)_3$. The gradual increase of mass 175 after 0.3 ms is due to the formation of $H^+((CH_3)_2C(OH)CH_2COCH_3)(CH_3COCH_3)$. Mass 233 : $H^+((CH_3)_2C(OH)CH_2COCH_3)_2$. Mass 159 : $CH_3CO^+(CH_3COCH_3)_2$, mass 217 : $CH_3CO^+(CH_3COCH_3)_3$. Mass 73 : $CH_3^+(CH_3COCH_3)$, mass 131 : $CH_3^+(CH_3COCH_3)_2$, mass 189 : $CH_3^+(CH_3COCH_3)_3$. Mass 157 : $H^+((CH_3)_2C{=}CHCOCH_3)(CH_3COCH_3)$, mass 215 : $H^+((CH_3)_2C{=}CHCOCH_3)(CH_3COCH_3)_2$. Mass 193 : $H_3O^+(CH_3COCH_3)_3$. Mass 155 : $C_3H_3^+(CH_3COCH_3)_2$, mass 213 : $C_3H_3^+(CH_3COCH_3)_3$.

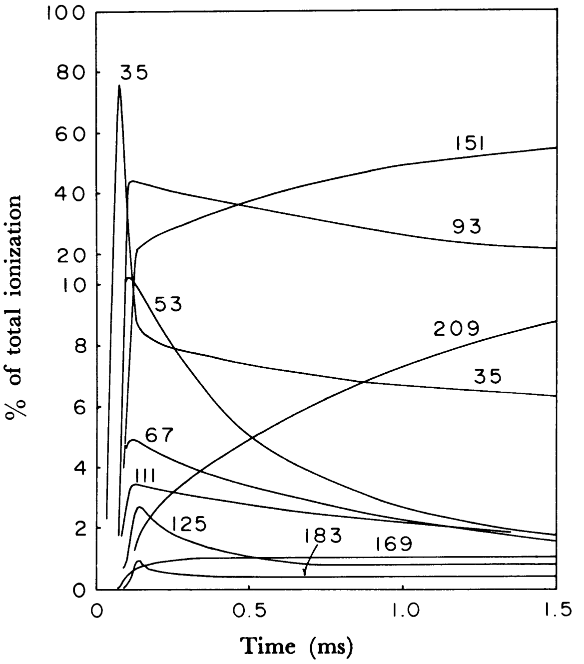


Fig. 2. Negative ions observed in a gas mixture containing 4.09 Torr of He, 0.79 Torr of acetone, and 0.3 mTorr of CCl_4 at 38.9 °C. Acetone contains small amounts of mesityl oxide and diacetone alcohol as impurities. Mass 35 : Cl^-, mass 93 : $Cl^-(CH_3COCH_3)$. The initial increase of mass 151 is due to $Cl^-(CH_3COCH_3)_2$. The gradual increase of mass 151 after 0.2 ms is due to the formation of $Cl^-((CH_3)_2C(OH)CH_2COCH_3)$. Mass 209 is mainly due to $Cl^-((CH_3)_2C(OH)CH_2COCH_3)(CH_3COCH_3)$. Mass 53 : $Cl^-(H_2O)$, mass 111 : $Cl^-(H_2O)(CH_3COCH_3)$, mass 169 : $Cl^-(H_2O)(CH_3COCH_3)_2$ and $Cl^-(H_2O)((CH_3)_2C(OH)CH_2COCH_3)$. Mass 67 : $Cl^-(CH_3OH)$, mass 125 : $Cl^-(CH_3OH)(CH_3COCH_3)$, mass 183 : $Cl^-(CH_3OH)(CH_3COCH_3)_2$ and $Cl^-(CH_3OH)((CH_3)_2C(OH)CH_2COCH_3)$.

Fig. 2, the rapid growth of $Cl^-(H_2O)$ is observed right after the electron pulse. Because the rate of reaction (3) with $n=1$ is slow, it is likely that $Cl^-(H_2O)$ is formed by switching Reaction (4).

$$Cl^-(CH_3COCH_3) + H_2O = Cl^-(H_2O) + CH_3COCH_3 \tag{4}$$

The ions $Cl^-(H_2O)$ and $Cl^-(H_2O)(CH_3COCH_3)$ are seen to be converted gradually to $Cl^-((CH_3)_2C(OH)CH_2COCH_3)(CH_3COCH_3)_n$ with $n=0$ and 1. This happens because the bond energy of $Cl^-(H_2O)$ is weaker than that of $Cl^-((CH_3)_2C(OH)CH_2COCH_3)$. The $m/z=169$ ion, whose intensity is independent on time, may be composed of not only $Cl^-(H_2O)(CH_3COCH_3)_2$ but also $Cl^-(H_2O)((CH_3)_2C(OH)CH_2COCH_3)$.

The $m/z=67$, 125, and 183 ions correspond to $Cl^-(CH_3OH)(CH_3COCH_3)_n$ with $n=0$—2. Methanol is a common impurity contained in acetone. The bond energies of $Cl^-\cdots CH_3OH$ and $Cl^-\cdots CH_3COCH_3$ are 17.4 and 12.4 kcal mol^{-1}(1 cal=4.184 J).[11] respectively, i.e., methanol has a greater chloride affinity than acetone. This is the reason why methanol can be readily detected by the present negative ion/molecule reactions. It should be noted that the methanol impurity could also be detected as the $CH_3OH_2^+(CH_3COCH_3)_2$ ion by the positive ion/molecule reactions when the ion source temperature was decreased. However, we found that the detection limit of methanol by positive ion/molecule reactions is about one order of magnitude lower than that by negative ion/molecule reactions under the present experimental conditions. This is because $H_3O^+(CH_3COCH_3)_3$ is thermochemically more stable than $CH_3OH_2^+(CH_3COCH_3)_2$ (i.e., the protic hydrogens of H_3O^+ are more acidic than those of $CH_3OH_2^+$) and the $H_3O^+(CH_3COCH_3)_3$ ion becomes dominant as an impurity ion under the present experimental conditions.

2. Ion/Molecule Reactions of Acetone. Positive Ions: As was described in the previous section, the used acetone contained diacetone alcohol and mesityl oxide as impurities. Although we tried to purify the sample by elaborate distillation, we could not decrease the contents of these impurities below the detection limit. We tried all available commercial acetone samples. We found that all samples measured contained detectable amounts of diacetone alcohol and mesityl oxide except the one purchased from Merck (Uvasol). The temporal profile of the positive ions observed in 4.16 Torr of CH_4 containing 0.259 Torr of acetone (Merck, Uvasol) at 46.7 °C is shown in Fig. 3. The intensities of m/z=157 and 175 ions are seen to be time-independent. This indicates that the contents of mesityl oxide and diacetone alcohol in the used acetone are below the detection limit.

The m/z=145 ion, which corresponds to $C_2H_5^+(CH_3COCH_3)_2$, is observed only when CH_4 is used as a carrier gas. The core ion $C_2H_5^+$ in the cluster may be the product ion from the ion/molecule reactions of methane.[12]

The m/z=157 ion may be the cluster ion of $C_6H_{11}O^+$ (m/z=99) with acetone. Since this ion is already produced right after the electron pulse, it may be yielded from the ion/molecule reactions induced by the primary electron irradiation. The core ion $C_6H_{11}O^+$ may have the structure $(CH_3)_2\overset{\oplus}{C}CH_2COCH_3$, which is different form that of the protonated mesityl oxide, $(CH_3)_2C{=}CH\overset{H\oplus}{C}OCH_3$ (see below).

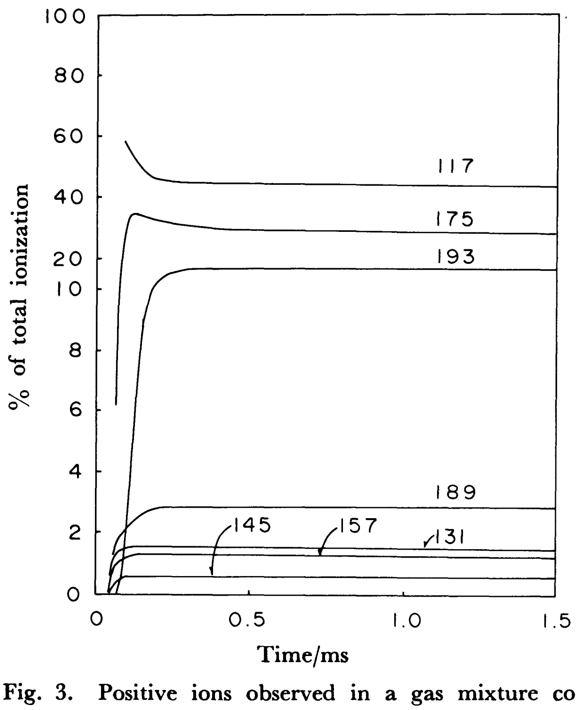


Fig. 3. Positive ions observed in a gas mixture containing 4.16 Torr of CH_4 and 0.259 Torr of acetone at 46.7 °C. Mass 117 : $H^+(CH_3COCH_3)_2$, mass 175 : $H^+(CH_3COCH_3)_3$. Mass 193 : $H_3O^+(CH_3COCH_3)_3$. Mass 131 : $CH_3^+(CH_3COCH_3)_2$, mass 189 : $CH_3^+(CH_3COCH_3)_3$. Mass 157 : $C_6H_{11}O^+(CH_3COCH_3)$. Mass 145 : $C_2H_5^+(CH_3COCH_3)_2$.

When the ion source temperature was increased, the gradual growth of m/z=157 and 175 ions starts to be observed. Figure 4 shows the ions observed in 4.92 Torr of CH_4 containing 0.365 Torr of acetone at 104 °C. The m/z=157 and 175 ions grow gradually at the expense of the m/z=117 ion. The observed growth may not be due to the impurities because intensities of these ions are time-independent at room temperature as shown in Fig. 3. The ions seem to be produced by some ion/molecule reactions of acetone. The increase of the growth rates at higher temperature suggests the existence of energy barrier for the formation of m/z=157 and 175 ions. The growth rates increase with temperature up to ≈100 °C. Above ≈100 °C, they start to decrease and the intensities of m/z=157 and 175 ions become weaker.

It was also found that as shown in Fig. 5, the growth rates increased when the pressure of the carrier gas was decreased. This indicates that the formation of m/z=157 and 175 ions is suppressed by the third-body collision. In order to examine the

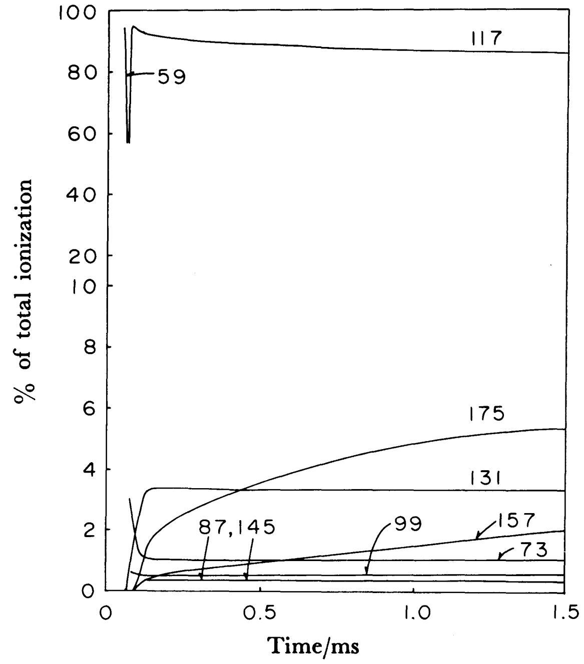


Fig. 4. Positive ions observed in a gas mixture contatining 4.92 Torr of CH_4 and 0.365 Torr of acetone at 104 °C. Mass 59 : $H^+(CH_3COCH_3)$, mass 117 : $H^+(CH_3COCH_3)_2$. Mass 73 : $CH_3^+(CH_3COCH_3)$, mass 131 : $CH_3^+(CH_3COCH_3)_2$. Mass 99 : $(CH_3)_2C^+CH_2COCH_3$. Mass 87 : $C_2H_5^+(CH_3COCH_3)$, mass 145 : $C_2H_5^+(CH_3COCH_3)_2$. The gradual increase of mass 157 and 175 may be due to the formation of $H^+((CH_3)_2C{=}CHCOCH_3)(CH_3COCH_3)$ and $H^+((CH_3)_2C(OH)CH_2COCH_3)(CH_3COCH_3)$, respectively, from the ion/molecule reactions of acetone (see text).

third-body dependence on the formation of these ions, the carrier gas was changed from CH_4 to He with keeping the ion source temperature and pressures of carrier gas and acetone constant. The apparent increase in the growth rates of these ions were observed. This may be due to the fact that helium is a less efficient third body than methane. It seems likely that m/z=157 and 175 ions are formed from the long-lived intermediate complex. The tentative reaction mechanisms for the formation of m/z=157 and 175 ions are given in Scheme 1, where M represents the third body. The clusters of species (IV) and (V) with acetone correspond to ions with m/z=175 and 157, respectively.

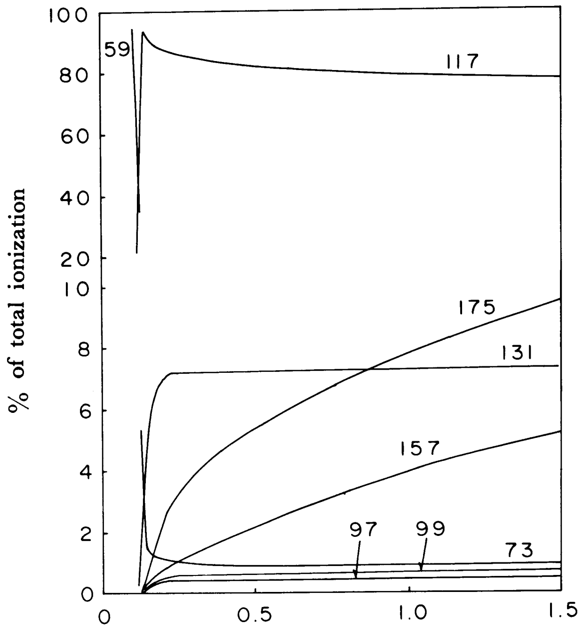
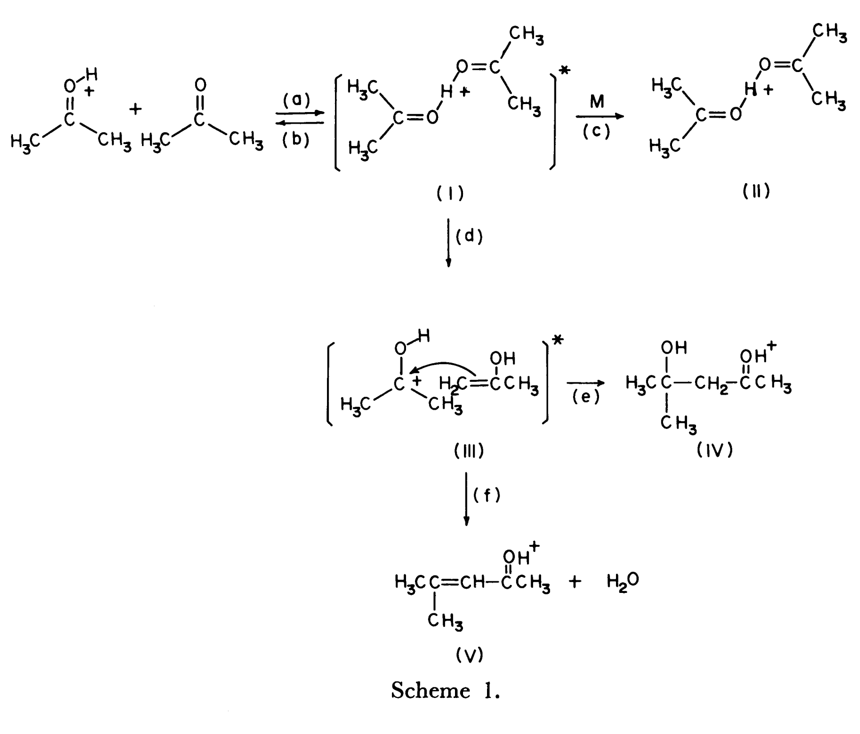


Fig. 5. Positive ions observed in a gas mixture containing 0.17 Torr of CH_4 and 0.33 Torr of acetone at 98 °C. Mass 59 : $H^+(CH_3COCH_3)$, mass 117 : $H^+(CH_3COCH_3)_2$. Mass 73 : $CH_3^+(CH_3COCH_3)$, mass 131 : $CH_3^+(CH_3COCH_3)_2$. Mass 99 : $(CH_3)_2C^+CH_2COCH_3$. Mass 97 : $C_3H_3^+(CH_3COCH_3)$. The increase of mass 157 and 175 are due to the formation of $H^+((CH_3)_2C{=}CHCOCH_3)(CH_3COCH_3)$ and $H^+((CH_3)_2C(OH)CH_2COCH_3)(CH_3COCH_3)$.

The bond energy of the proton-held acetone dimer ion is 29.6 kcal mol^{-1}.[13] Since the keto form of acetone is about 10 kcal mol^{-1} more stable than the enol form,[14] the complex (I) has more than enough internal energy for the isomerization of acetone from keto to enol form (Process (d)). The formation of the complex (III) may be followed by the formation of protonated diacetone alcohol (IV) or mesityl oxide (V). The formation of the latter species (V) is analogous to the aldol condensation reaction of acetone observed in the liquid phase.

With increase of ion source temperature (>≈150 °C), the back dissociation reaction (b) of the intermediate complex (I) becomes prominent. This explains the decrease in the rate of the formation of m/z=157 (or 99) and 175 ions at high temperatures.

As shown in Figs. 4 and 5, the steady growth of m/z=157 ion is observed, while the intensity of m/z=99 ion is time-independent. As described in the reaction scheme given above, the m/z=157 ion is suggested to have the structure of the cluster of protonated mesityl oxide (m/z=99) with acetone. Since the protonated mesityl oxide has a protic

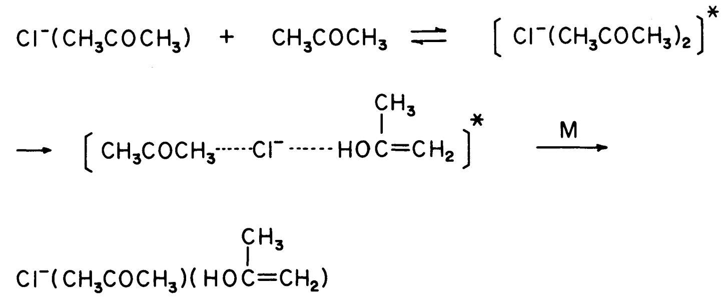


Scheme 1.

hydrogen atom, it can form a fairly strong hydrogen bond with acetone to give the *m/z*=157 ion. Since the intensity of the *m/z*=99 ion does not increase with time, this ion must have the different structure from the protonated mesityl oxide. We tentatively propose that the *m/z*=99 ion has the structure of $(CH_3)_2\overset{\oplus}{C}CH_2COCH_3$ which is produced during the primary electron irradiation. This ion is the tertiary carbonium ion and the bond of its cluster with acetone must be much weaker than that of protonated mesityl oxide with acetone.

Negative Ions: Figure 6 shows the negative ions observed in 4.07 Torr of CH_4 containing 0.287 Torr of acetone (Merck, Uvasol) and 0.2 mTorr of CCl_4. If the acetone sample contains diacetone alcohol as an impurity, the ion with *m/z*=151 (i.e. $Cl^-((CH_3)_2C(OH)CH_2COCH_3)$ as well as its clusters with acetone molecules would be produced gradually with time. The steady intensity of ions observed in Fig. 6 indicates that the content of diacetone alcohol in the acetone sample is lower than the detection limit in the present experimental conditions.

When the ion source temperature is increased, the *m/z*=151 ion starts to increase as shown in Fig. 7. As described in the previous paper,[2] we think that solvent acetone molecule isomerizes from keto to enol form during the clustering reaction, as shown in Scheme 2. This reaction may be regarded as the base (Cl^- ion)-catalysed keto-enol isomerization reaction of acetone in the gas phase. In our previous work,[7] we observed that for higher order clustering Reactions (5),



$$Cl^-(CH_3COCH_3) + CH_3COCH_3 \rightleftharpoons [Cl^-(CH_3COCH_3)_2]^*$$

$$\rightarrow [CH_3COCH_3\cdots\cdots Cl^-\cdots\cdots HO\overset{CH_3}{\overset{|}{C}}=CH_2]^* \xrightarrow{M}$$

$$Cl^-(CH_3COCH_3)(HO\overset{CH_3}{\overset{|}{C}}=CH_2)$$

Scheme 2.

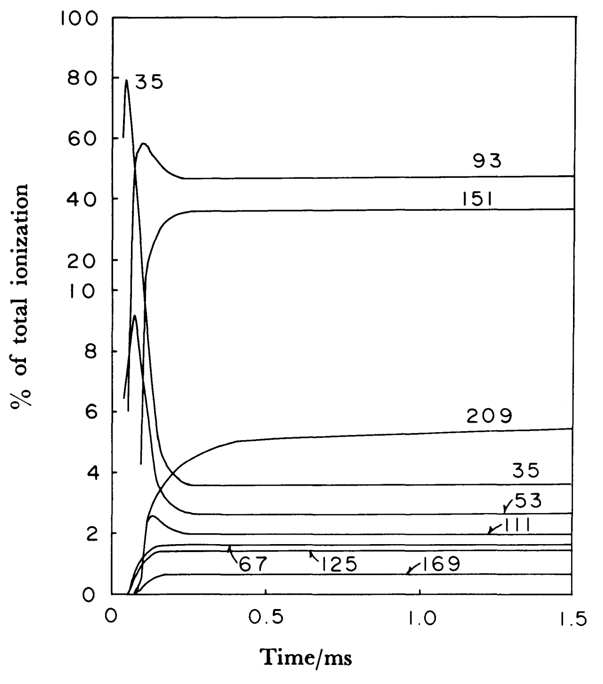


Fig. 6. Negative ions observed in a gas mixture containing 4.07 Torr of CH_4, 0.287 Torr of acetone, and 0.2 mTorr of CCl_4 at 30 °C. Mass 35 : Cl^-, mass 93 : $Cl^-(CH_3COCH_3)$, mass 151 : $Cl^-(CH_3COCH_3)_2$, mass 209 : $Cl^-(CH_3COCH_3)_3$. Mass 53 : $Cl^-(H_2O)$, mass 111 : $Cl^-(H_2O)(CH_3COCH_3)$, mass 169 : $Cl^-(H_2O)(CH_3COCH_3)_2$. Mass 67 : $Cl^-(CH_3OH)$, mass 125 : $Cl^-(CH_3OH)(CH_3COCH_3)$.

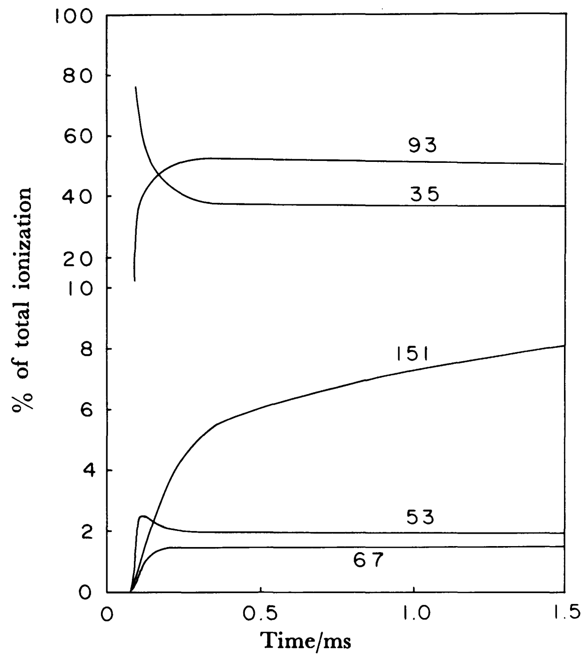


Fig. 7. Negative ions observed in a gas mixture containing 3.99 Torr of CH_4, 0.213 Torr of acetone, and 0.2 mTorr of CCl_4 at 80.5 °C. Mass 35 : Cl^-, mass 93 : $Cl^-(CH_3COCH_3)$. Mass 53 : $Cl^-(H_2O)$. Mass 67 : $Cl^-(CH_3OH)$. The initial increase of mass 151 is due to the formation of $Cl^-(CH_3COCH_3)_2$. The gradual increase of mass 151 after 0.3 ms may be due to the formation of $Cl^-(CH_3COCH_3)$ $(CH_2{=}C(OH)CH_3)$ by keto-enol isomerization of acetone.

$$Cl^-(CH_3COCH_3)_{n-1} + CH_3COCH_3 = Cl^-(CH_3COCH_3)_n \quad (5)$$

the decays of larger clusters were found to be slower at 15 °C (Fig. 8 in the Ref. 7). Since the gradual growth of larger clusters $Cl^-(CH_3COCH_3)_n$ were not observed at 30 °C in the present experiments (see Fig. 6), the acetone sample used in the previous work must contain diacetone alcohol as an impurity. We are now sure that the ions $Cl^-(CH_3COCH_3)_2$, $Cl^-(CH_3COCH_3)_3$, and $Cl^-(CH_3COCH_3)_4$ shown in Fig. 8 in Ref. 7 are more or less contaminated by $Cl^-((CH_3)_2C(OH)CH_2COCH_3)$, $Cl^-((CH_3)_2C(OH)CH_2COCH_3)(CH_3COCH_3)$, and $Cl^-((CH_3)_2C(OH)CH_2COCH_3)_2$, respectively.

The growth rate of m/z=151 ion becomes low at high ion source temperature (≈100 °C). The keto→enol isomerization reaction seems to be suppressed when the lifetime of the intermediate complex $[Cl^-(CH_3COCH_3)_2]^*$ gets short at high temperatures.

3. Equilibrium Measurements for Clustering Reactions of Proton and Chloride Ion with Acetone Molecules. Since the diacetone alcohol contained in the used acetone (Merck, Uvasol) is only a negligible amount, it was possible to measure clustering Reactions (1) and (5) without having the impurity problem. Figure 8 shows the van't Hoff plots for Reaction (1) with n=4 using the "pure" acetone sample. The van't Hoff plots of (1, 2) and (2, 3) were measured in our previous work.[7,13] The thermochemical data obtained from the van't Hoff plots are summarized in Table 1. There is a sudden decrease in the stabilities of clusters $H^+(CH_3COCH_3)_n$ between n=2 and 3. This indicates that the clusters $H^+(CH_3COCH_3)_n$ ($n \geqq 3$) are regarded as the shell $(CH_3)_2CO \cdots H^+ \cdots OC(CH_3)_2$ plus surrounding ligand acetone molecules. Yamabe et al. studied the gas-phase solvation of acetone toward the proton theoretically.[9] They predicted the structure of $H^+(CH_3COCH_3)_3$ in which the proton in $(CH_3)_2CO \cdots H^+ \cdots OC(CH_3)_2$ is attacked by the third molecule in the direction perpendicular to the shell plane.[9] This result suggests that the fourth acetone molecule may also approach to the proton perpendicularly from the other side of the shell plane.

Figure 9 shows the van't Hoff plots for Reaction (5) with n=2 and 3 obtained in the present work. The van't Hoff plots of (0, 1) was obtained in our previous work.[7] Contrary to the van't Hoff plots of reaction (1) (Fig. 8), the plots with n=1—3 are close with each other and the decrease in the enthalpy changes $-\Delta H^\circ_{n-1,n}$ is only gradual. This indicates that the interaction of Cl^- with ligand acetone molecules are

Table 1. Thermochemical Data for Clustering Reactions[a)]

Reaction	$-\Delta H^\circ$	$-\Delta S^\circ$
$H^+(CH_3COCH_3) + CH_3COCH_3$ $= H^+(CH_3COCH_3)_2$	29.6[b)] 30.1[c)]	29.3[b)] 30.4[c)]
$H^+(CH_3COCH_3)_2 + CH_3COCH_3$ $= H^+(CH_3COCH_3)_3$	12.2[d)]	23.0[d)]
$H^+(CH_3COCH_3)_3 + CH_3COCH_3$ $= H^+(CH_3COCH_3)_4$	8.5	17.0
$Cl^- + CH_3COCH_3 = Cl^-(CH_3COCH_3)$	12.4[d)]	17.1[d)]
$Cl^-(CH_3COCH_3) + CH_3COCH_3$ $= Cl^-(CH_3COCH_3)_2$	11.5	20.3
$Cl^-(CH_3COCH_3)_2 + CH_3COCH_3$ $= Cl^-(CH_3COCH_3)_3$	10.4	(22)[e)]

a) $-\Delta H^\circ$ in kcal mol^{-1} and $-\Delta S^\circ$ in cal mol^{-1} K (standard state 1 atm). b) Ref. 9. c) Ref. 1. d) Ref. 2. e) Entropy value assumed.

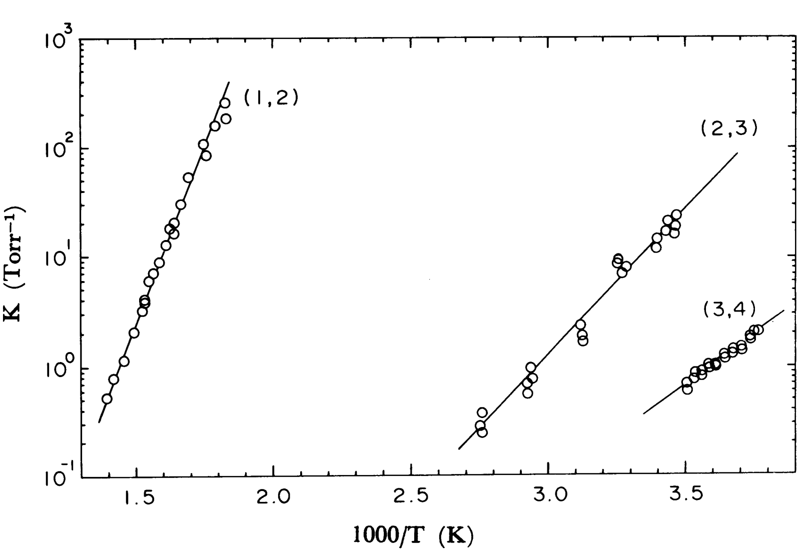


Fig. 8. The van't Hoff plots for clustering reactions: $H^+(CH_3COCH_3)_{n-1} + CH_3COCH_3 = H^+(CH_3COCH_3)_n$, ($n-1$, n).

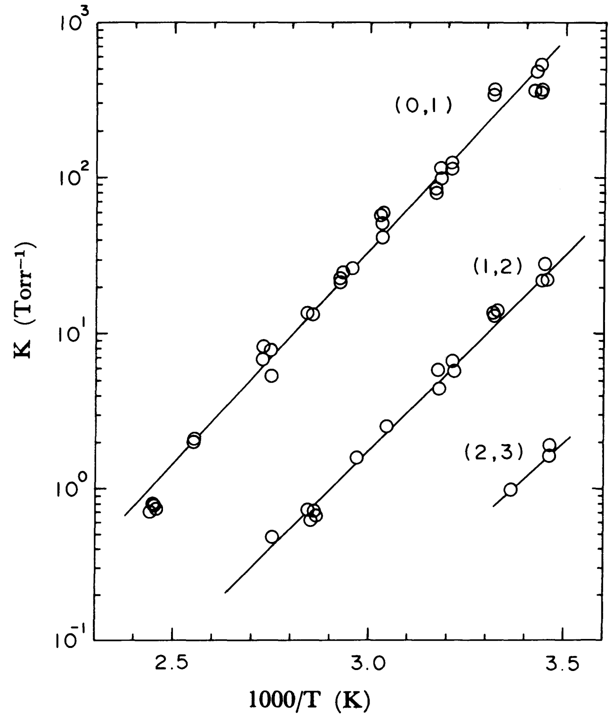
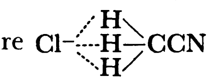


Fig. 9. The van't Hoff plots for clustering reactions: $\mathrm{Cl^-(CH_3COCH_3)_{\mathit{n}-1}+CH_3COCH_3{=}Cl^-(CH_3COCH_3)_{\mathit{n}}}$, $(n-1,\ n)$.

mainly electrostatic.

Yamabe and Hirao investigated the stability and structure of the cluster $\mathrm{Cl^-\cdots CH_3CN}$ by SCF computation.[15] They found that the most stable C_{3v} structure  $\mathrm{Cl^-\underset{H}{\overset{H}{\cdots}}H{-}CCN}$ is more stable than the C_s structure $\mathrm{Cl^-\cdots H\text{-}CH_2CN}$ by only$\leqq$1 kcal mol^{-1}. This suggests that the bond strength of the complex $\mathrm{Cl^-\cdots CH_3CN}$ is less affected by the change of the angle for the bending motion of $\mathrm{Cl^-}$ and $\mathrm{CH_3CN}$ species. Thus the cluster would show a considerable flexibility in the bending motion of the bond between $\mathrm{Cl^-}$ and $\mathrm{CH_3CN}$. By analogy with $\mathrm{Cl^-\cdots CH_3CN}$, $\mathrm{Cl^-\cdots CH_3COCH_3}$ would also be very flexible as already pointed out in our previous paper.[8] The great flexibility of the cluster $\mathrm{Cl^-\cdots CH_3COCH_3}$ means that the species in the cluster have appreciable freedoms of motion. This may explain the small entropy change $-\Delta S^\circ_{0,1}$ for Reaction (5).

Concluding Remarks

The reactions of protonated acetone and chloride ion with acetone molecules were investigated. It was found that mesityl oxide and diacetone alcohol which are contained as impurities in commercial acetone samples spoil the studies of ion/molecule reactions in acetone seriously. Using the relatively pure acetone, detailed kinetic studies of the positive and negative ion/molecule reactions were done. In the reactions of protonated acetone with acetone molecule, the formation of protonated mesityl oxide and diacetone alcohol are suggested. For the clustering reactions of chloride ion with acetone molecules, the equilibria could not be observed at high temperatures. We tentatively concluded that this is due to a keto-enol isomerization of the acetone ligand molecules. However, we feel that the evidences obtained in this work are suggestive rather than compelling.

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