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Kinetic and Theoretical Study on the Ion/Molecule Reactions of Methoxymethyl Cation with Ammonia

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Abstract: The reaction between $C_2H_5O^+$ and NH_3 is investigated by using the ion-trapping technique. Rate constants of reactions 3, 4, and 5 are determined. Their potential energy profiles are sought by use of the ab initio MO calculation. Reaction 3 gives the products methanol and protonated methylenimine. It is composed of the nucleophilic addition of NH_3 to the carbonyl carbon and the subsequent 1,3-proton shift. Reaction 4 gives formaldehyde and protonated methylamine. It is of the S_N2 type. Reaction 5 gives ammonium ion and ethylene oxide. The last reaction is of the specific pattern in the gas phase, although the reverse reaction involves the popular mechanism of the electrophilic ring cleavage.

Ion/molecule reactions in the gas phase have an important role to elucidate the mechanism of organic chemistry. It is an attractive subject to study whether the solvent-free reaction has the same pattern as that in the condensed phase or not. It is a goal to separate the intrinsic reactivity of the substrate from the solvent effect.

The reaction of the methoxymethyl cation $CH_3OCH_2^+$ with a base is known to give several products.[2-7] However, it is not yet solved what kind of process is involved. In this work, kinetics of the reaction between methoxymethyl cation and ammonia are studied by using the ion-trapping technique.[8-11] To investigate the reaction process, an ab initio MO calculation is also made. The aim of this work is to judge whether reactions of $CH_3OCH_2^+$ with NH_3 involve the established mechanism of organic chemistry or the specific pattern in the gas phase.

Experimental Section

The reactions have been studied by using the technique for ion trapping in the ion source of a mass spectrometer described by Bourne and Danby.[8] This technique has been used to study the ion/molecule reactions by Harrison[9,10] and Ryan.[11] Ions were produced during the short pulse (1 μs) of an ionizing electron of suitable energy (15–25 eV). The ions were trapped in the negative space charge created by an electron beam whose energy is insufficient to cause ionization. The ions trapped were left to react successively further. A small negative bias was applied to repeller plates to obtain efficient ion trapping. The ions were removed for the mass analysis by applying a positive pulse of 2-μs duration and 10-V amplitude to the repeller plates. Ion currents were detected by a 16-stage electron multiplier as a function of delay time (up to 1.8 ms) between the ionizing pulse and the ion removal pulse.

Table I. Rate Constants for the Reactions of CH_3O^+ with CH_3OCH_3 and NH_3

reaction	$10^{-10}k$, $cm^3/(molecule{\cdot}s)$ this work (433 K)	$10^{-10}k$, $cm^3/(molecule{\cdot}s)$ other works
(1) $CH_3O^{+a} + CH_3OCH_3 \xrightarrow{k_1} CH_3OCH_2^+ + CH_3OH$	9.6 ± 1	11.6 ± 1.5[b]
(2) $CH_3O^+ + NH_3 \xrightarrow{k_2} NH_4^+ + CH_2O$	8 ± 1	8.57[c]

[a] m/z 31. [b] Reference 2. [c] Reference 5.

Source concentrations of the reaction gases were not measured directly but were related to the concentration in the inlet system from measurements of the disappearance rate of the CH_4^+ in pure methane. A rate constant of 1.1×10^{-9} $cm^3/(molecule{\cdot}s)$ for the reaction[12] $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ was used. All experiments were carried out at an ion source temperature, 433 K.

The ammonia and methane used were of Takachiho Research grade. Dimethyl ether and ammonia-d_3 solution were from Wako Pure Chemicals and purified by vacuum distillation before use. Mass spectrometric analysis of ammonia-d_3 gas revealed 90% ND_3 and 10% ND_2H.

Figure 1 shows the semilogarithmic plots of normalized ion intensities of major ions observed in the CH_3OCH_3–NH_3 system. The reactant ion was mainly $C_2H_5O^+$. The initial increase of the $C_2H_5O^+$ ion at less than

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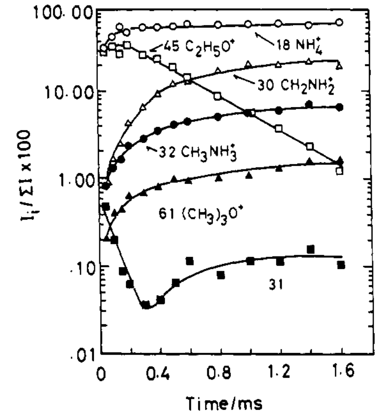

Figure 1. Normalized ion intensities vs. reaction time observed in the CH_3OCH_3-NH_3 system. $[CH_3OCH_3]/[NH_3] = 0.36$, total ion source concentration = 1.26×10^{13} molecule/cm^3, ion source temperature = 433 K, and electron energy = 20 eV.

0.15 ms would be attributed to H^- abstraction reactions of ions[2] NH_2^+, CH_3^+, and CH_3O^+ with CH_3OCH_3. There are three stable isomers of the $C_2H_5O^+$ ion. They are methoxymethyl cation $CH_3OCH_2^+$, protonated ethylene oxide $\overset{\ulcorner OH^+ \urcorner}{CH_2—CH_2}$, and protonated acetaldehyde CH_3CHOH^+. Three species have been identified experimentally.[14] It has been shown in several works[2-6,13] that the $C_2H_5O^+$ ion derived from CH_3OCH_3 by electron impact and the H^- abstraction reaction is the methoxymethyl cation. The experimental[15] and theoretical studies[16] of the $C_2H_5O^+$ potential energy surface have shown that the isomerization from $CH_3OCH_2^+$ to CH_3CHOH^+ ion proceeds through $\overset{\ulcorner OH^+ \urcorner}{CH_2—CH_2}$ as an intermediate. However, the process of the isomerization from $CH_3OCH_2^+$ to $\overset{\ulcorner OH^+ \urcorner}{CH_2—CH_2}$ ion may have a very high barrier estimated to be $\Delta H^\ddagger = \sim 97$ kcal/mol[15] or 89.7 kcal/mol.[16] These facts support that the ion involved in this study is mainly $CH_3OCH_2^+$, although the $CH_3OCH_2^+$ ion would have various internal energies.

An initial decrease of CH_3O^+ (time = ~0.3 ms) in Figure 1 would be due to the reactions with CH_3OCH_3 and NH_3 shown in reactions 1 and 2. The rate constants measured are presented in Table I. The

$$\underset{(m/z\ 31)}{CH_3O^+} + CH_3OCH_3 \xrightarrow{k_1} CH_3OCH_2^+ + CH_3OH \qquad (1)$$

$$CH_3O^+ + NH_3 \xrightarrow{k_2} NH_4^+ + CH_2O \qquad (2)$$

increase of m/z 31 at a longer (>0.3 ms) reaction time is shown in the figure. Two ions, CH_2OH^+ and $CH_3NH_2^+$, formed by the reaction between $CH_3OCH_2^+$ and NH_3 are conceivable. CH_2OH^+ may be ruled out due to the subsequent rapid reaction with NH_3 [$k_{ADO}(CH_2OH^+ + NH_3) = 1.60 \times 10^{-9}$ cm^3/(molecule·s) at 433 K]. $CH_3NH_2^+$ appears to be most likely. But the ion species m/z 31 was not clearly identified, because the relative ion intensity was very small. The rate constants for the reactions of CH_3O^+ with CH_3OCH_3 and NH_3 are in agreement with that obtained by Harrison[2] and that determined in our previous study,[5] respectively.

The ion species of m/z 30 and 32 in Figure 1 were assigned to be $CH_2NH_2^+$ and $CH_3NH_3^+$ by using ND_3 instead of NH_3. This result is in agreement with that reported by Kinter and Bursey.[7] The sum of relative ion intensities of $CH_2ND_2^+$ and $CH_3ND_3^+$ in m/z 30–35 obtained in the CH_3OCH_3-ND_3 system was ~94%. This result shows that the H and D in the intermediate complex formed by the ion/molecule reaction of $CH_3OCH_2^+$ with NH_3 hardly scramble. Although there are two structural isomers,[17-19] CH_3NH^+ and $CH_2NH_2^+$, as the m/z 30 ion, the formation of CH_3NH^+ is excluded. This is because the enthalpy change of reaction for the formation of this ion is endothermic ($\Delta H_r = 12.96$ kcal/mol). The reactions of $CH_3OCH_2^+$ with NH_3 at a longer time than 0.2 ms can be described by reactions 3–6.

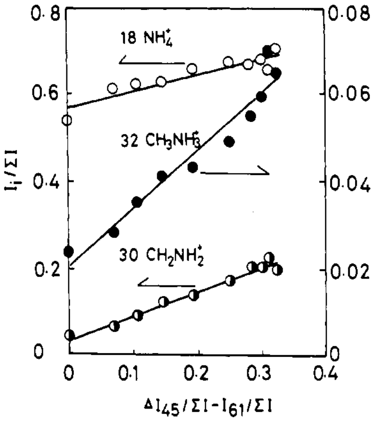

Figure 2. Normalized ion intensites vs. $\Delta I_{45} - I_{61}$. The same experimental conditions as in Figure 1 are used.

$$CH_3OCH_2^+ + NH_3 \xrightarrow{k_3} CH_2NH_2^+ + CH_3OH \qquad (3)$$

$$CH_3OCH_2^+ + NH_3 \xrightarrow{k_4} CH_3NH_3^+ + CH_2O \qquad (4)$$

$$CH_3OCH_2^+ + NH_3 \xrightarrow{k_5} NH_4^+ + C_2H_4O \qquad (5)$$

$$CH_3OCH_2^+ + NH_3 \xrightarrow{k_6} m/z\ 31 \qquad (6)$$

In Figure 1, the m/z 61 ion was observed at the same time scale. This ion is known to be $(CH_3)_3O^+$, formed by the ion/molecule reaction of $CH_3OCH_2^+$ with CH_3OCH_3 in only the dimethyl ether system,[2] as is given by reaction 7. The disappearance rate constant of $CH_3OCH_2^+$

$$CH_3OCH_2^+ + CH_3OCH_3 \xrightarrow{k_7} (CH_3)_3O^+ + CH_2O \qquad (7)$$

obtained was $(1.4 \pm 0.6) \times 10^{-11}$ cm^3/(molecule·s), which is in agreement with $(1.16 \pm 0.15) \times 10^{-11}$ cm^3/(molecule·s) reported by Harrison.[2]

The overall disappearance rate constant of $CH_3OCH_2^+$ may be expressed by eq 8 in consideration of reactions 3–7. I_{45} is the normalized ion intensity of $C_2H_5O^+$ (m/z 45). $[NH_3]$ and $[CH_3OCH_3]$ are the concentrations of reactant molecules, t is the reaction time, and C is a constant.

$$\log I_{45} = -(\sum_{j=3}^{6} k_j[NH_3] + k_7[CH_3OCH_3])t + C \qquad (8)$$

Each rate constant, k_i, was determined from the ΔI plot[20] by using eq 9, where I_{si} is the normalized intensity of the secondary ion si, k_i is the rate constant leading to the disappearance of $CH_3OCH_2^+$, and $\sum_{j=3}^{6} k_j$ is the rate constant for the reaction of $CH_3OCH_2^+$ with NH_3. $\Delta I_{45} =$

$$I_{si} = \frac{k_i}{\sum_{j=3}^{6} k_j}(\Delta I_{45} - I_{61}) \qquad (9)$$

$I_{45}^0 - I_{45}$, where I_{45}^0 is the normalized intensity of I_{45} extrapolated to reaction time, 0.2 ms. I_{61} is the normalized ion intensity of $(CH_3)_3O^+$ (m/z 61). The linear portion of a semilogarithmic plot for $CH_3OCH_2^+$ gives the overall rate constant for the reaction of $CH_3OCH_2^+$ with NH_3 and CH_3OCH_3. The rate constant, $\sum_{j=3}^{6} k_j$, was determined to be $(2.30 \pm 0.1) \times 10^{-10}$ cm^3/(molecule·s) by the use of eq 8, as the rate constant, k_7, was previously measured in only the CH_3OCH_3 system.

Figure 2 shows a plot of $I_{18}(NH_4^+)$, $I_{30}(CH_2NH_2^+)$, and $I_{32}(CH_3NH_3^+)$ as a function of $\Delta I_{45} - I_{61}$. The straight lines are observed. The average slopes of five runs which give $k_i/\sum_{j=3}^{6} k_j$ were 0.58 ± 0.07, 0.16 ± 0.02, 0.25 ± 0.08, and ~0.004, respectively. These data for k_3, k_4, k_5, and k_6 were obtained independently over the electron energy between 15 and 25 eV (not corrected).

More recent results[7] have indicated that the relative intensities of ions formed in reactions 3 and 4 decrease with increasing ion kinetic energy

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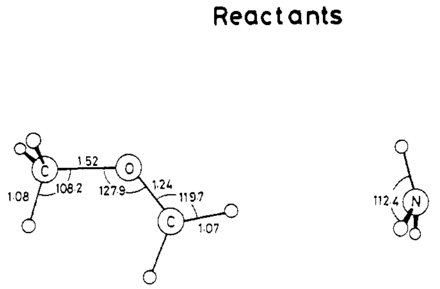


Figure 3. Geometries of methoxymethyl cation ($C_2H_5O^+$) and ammonia optimized with the 3-21G basis set. Bond lengths are in Å and the angles are in deg. Empty small circles denote hydrogen atoms.

Table II. Rate Constants and Enthalpy Changes for the Reactions of $CH_3OCH_2^+$ with NH_3

reaction	$10^{-10}k_i$, $cm^3/(molecule{\cdot}s)$ exptl	$10^{-10}k_i$, $cm^3/(molecule{\cdot}s)$ calcd ADO[b]	ΔH_r,[a] kcal/mol
$CH_3OCH_2^+ + NH_3 \xrightarrow{k_3} CH_2NH_2^+ + CH_3OH$	$1.3_3 \pm 0.2$	16.8	−16 (−20)[c]
$CH_3OCH_2^+ + NH_3 \xrightarrow{k_4} CH_3NH_3^+ + CH_2O$	0.37 ± 0.05		−28 ± 3[d]
$CH_3OCH_2^+ + NH_3 \xrightarrow{k_5}$	$0.5_8 \pm 0.2$		
$NH_4^+ + \overset{O}{CH_2{-}CH_2}$			−8 ± 3[d]
(CH_3CHO)[e]			−35 ± 3[d]
$CH_3OCH_2^+ + NH_3 \xrightarrow{k_6} m/z\ 31$	~0.01		

[a] $\Delta H_f^{298}(CH_3OCH_2^+)$ = 157 kcal/mol from ref 13. $\Delta H_f^{298}(CH_2NH_2^+)$ = 178 and 174 kcal/mol from ref 18 and 19. $\Delta H_f^{298}(CH_3NH_3^+)$ = 146 kcal/mol is calculated by using $\Delta H_f^{298}(CH_3NH_2)$ = −5.49 kcal/mol from ref 21. $\Delta H_f^{298}(H^+)$ = 367.7 kcal/mol is taken from ref 22. $PA(CH_3NH_2)$ = 214.1 kcal/mol is taken from ref 22. $\Delta H_f^{298}(NH_4^+)$ = 150.68 kcal/mol is calculated by using $\Delta H_f^{298}(NH_3)$ = −11.02 kcal/mol from ref 21. $PA(NH_3)$ = 204 kcal/mol is taken from ref 22. $\Delta H_f^{298}(CH_3OH)$ = −47.96 kcal/mol, $\Delta H_f^{298}(CH_2O)$ = −28 kcal/mol, $\Delta H_f^{298}(\overset{O}{CH_2{-}CH_2})$ = −12.58 kcal/mol, and $\Delta H_f^{298}(CH_3CHO)$ = −39.72 kcal/mol are from ref 21. [b] Calculated by using the ADO theory.[23] [c] $\Delta H_f^{298}(CH_2NH_2^+)$ = 174 kcal/mol is used.[19] [d] Deviation was that of $PA(NH_3)$.[22] [e] The ΔH_r value for this product is −35 ± 3[d] kcal/mol.

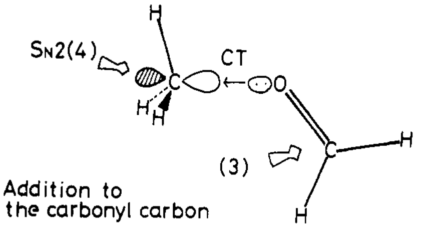
and that reaction 5 has the threshold energy, ΔH_r = 55.32 kcal/mol (center of mass). It has been pointed out[7] that reaction 5 is not expected at low ion kinetic energies. As electron energies ≥15 eV were used in this study to generate $CH_3OCH_2^+$ from CH_3OCH_3, reaction 5 can be observed. Therefore, the $CH_3OCH_2^+$ ions formed would have enough of the internal energies[3] needed for reaction 5.

The individual rate constants and enthalpy changes for the reaction of $CH_3OCH_2^+$ with NH_3 are obtained and are presented in Table II. The collision rate constant calculated by average dipole orientation (ADO) theory[23] is also shown in Table II.

Computations

To identify the product and to elucidate the route of reactions between methoxymethyl cation and ammonia, reactions 3, 4, and 5, an ab initio MO calculation is made. The geometries of reactants, ion–dipole complexes, and transition states are searched for by the optimization with the 3-21G basis set. Energies and electronic distributions are obtained by the single-point calculation of 6-31G* (6-31G*//3-21G). All calculations are carried out using the GAUSSIAN 80 program.[24]

In Figure 3, geometries of $C_2H_5O^+$ and NH_3 are shown. Theoretical studies of methoxymethyl cation have been made extensively.[16,25] However, the structural picture is not clear yet. The most stable isomer of $C_2H_5O^+$ is regarded as a Mulliken charge-transfer (CT) complex between formaldehyde and methyl cation. In the picture below, two reactive sites for the nucleophile may be indicated by bold empty arrows.

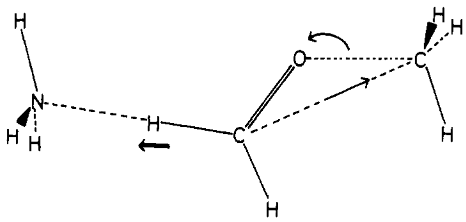


When the carbonyl carbon of formaldehyde is attacked by NH_3, reaction 3 takes place. In Figure 4, the reaction process is exhibited. When NH_3 collides with $C_2H_5O^+$, a stable intermediate called the ion–dipole complex I is formed. It is another strong (->N → >C=) CT complex. After the complex is generated, the reaction proceeds by the ammonia–proton migration. In the transition state, bridge O···H and H···N bonds are found. The more electronegative oxygen atom pulls the proton away from the nitrogen atom. Then, the second stable intermediate II is generated, followed by product formation (methanol and protonated methylenimine). Reaction 3 is composed of the nucleophilic addition onto the unsaturated carbon and the subsequent proton migration between two heteroatoms.

When the back side of the methyl cation of methoxymethyl cation is attacked by NH_3, the S_N2-type reaction 4 occurs. In Figure 5, the reaction process is exhibited. First, NH_3 is captured by the methyl hydrogen to form the intermediate I. Second, at the transition state (TS), the bond interchange (N···C–O → N–C···O) and the Walden inversion take place. Third, the intermediate II is formed. Products are formaldehyde (leaving group of S_N2) and protonated methylamine.

The reaction patterns of 3 and 4 are readily predictable in terms of the shape of the methoxymethyl cation, $CH_3^+{\cdots}O{=}CH_2$. In contrast, it is somewhat difficult to say what kind of reaction mechanism is involved in reaction 5. To give NH_4^+ as a product, a proton should be removed from $CH_3^+{\cdots}O{=}CH_2$. To diminish the large destabilization caused by the scission of the tight C–H σ bond, a new bond formation is required. According to this criterion, the reaction path of reaction 5 is sought. The result is shown in Figure 6. The intermediate I is common to that of reaction 4. At TS, the proton shift and the C–C bond formation (ring closure) occur concertedly. After the intermediate II is generated, products (ammonium ion and ethylene oxide) are given. Thus, the ethylene oxide formation is found by the calculation.

As an alternative product, acetaldehyde is considered. The enthalpy changes for the formation of ethylene oxide and acetaldehyde are −8 ± 3 and −35 ± 3 kcal/mol, respectively. Since the CH_3CHO formation is more exothermic, the route to it appears to be more likely than to ethylene oxide as reaction 5. However, by the potential energy search, we cannot find any reasonable path leading to CH_3CHO. The C–H bond of formaldehyde is too tight to break. Although the reaction (reaction 5) for the ethylene oxide is unfamiliar, the reverse reaction is the standard organic chemical reaction. The reverse reaction gives the electrophilic ring cleavage of the epoxide, where the similar ring opening of the cyclopropane derivatives is well-known.



Total energies (E_T's) of species appearing in Figures 3, 4, 5, and 6 are computed with the 6-31G* basis set and are shown in Table III. The theoretical enthalpy change ΔH_r is approximately given by the difference of E_T's between reactants and products.[26]

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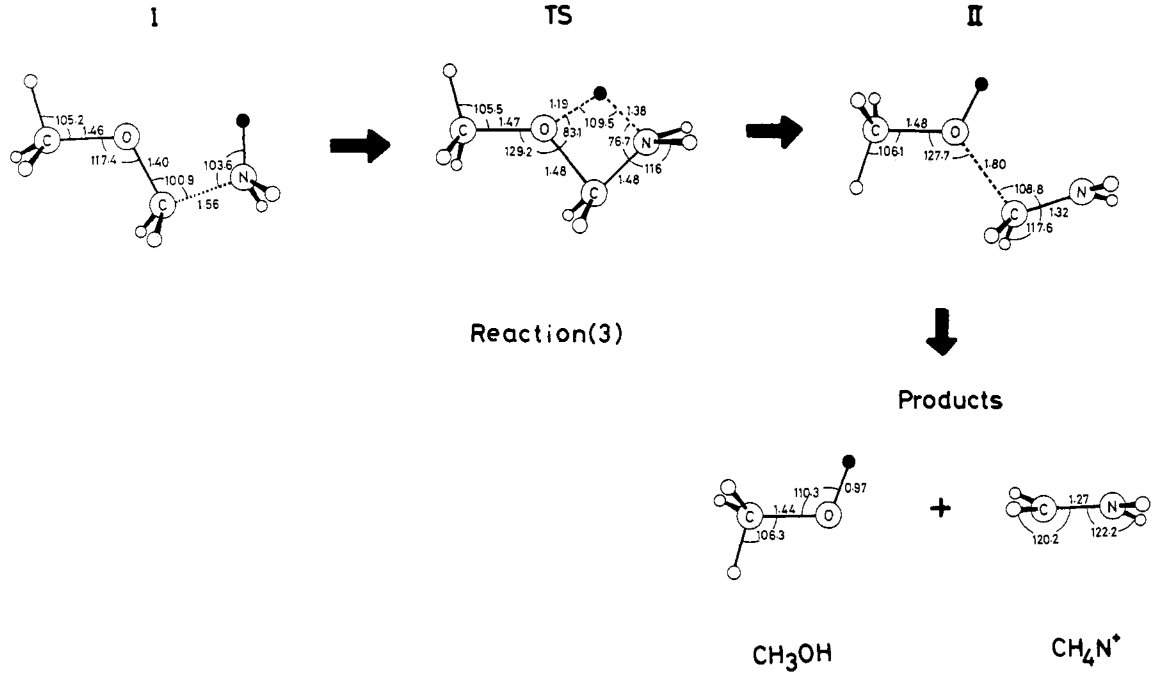


Figure 4. Geometries of two ion–dipole complexes (I and II), the transition state (TS), and the product in reaction 3. A black circle is the proton to be migrated.

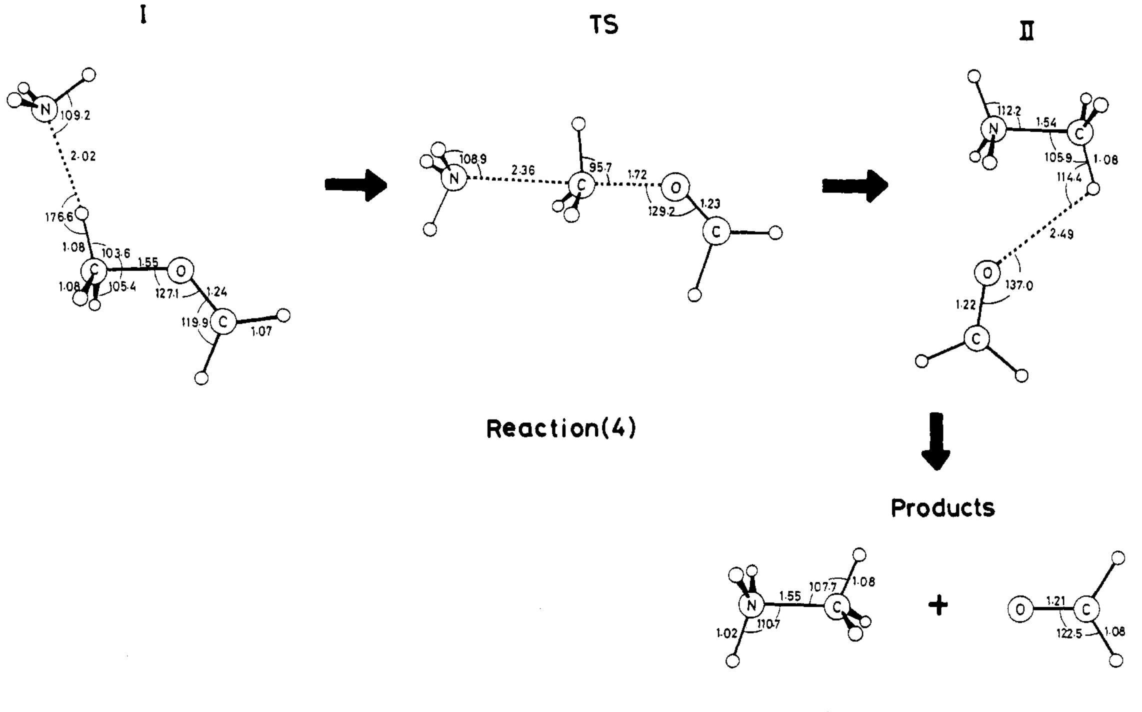
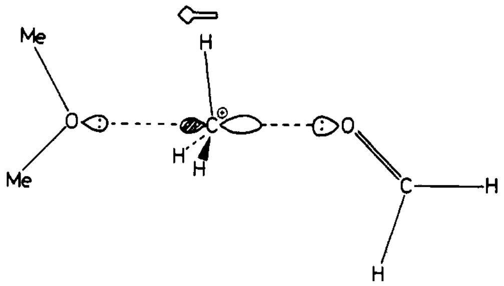


Figure 5. Geometries of two ion–dipole complexes (I and II), the transition state (TS), and the product in reaction 4.

Calculated and estimated (exptl) ΔH_r's of reactions 3 and 4 are in good agreement, but those of reaction 5 are somewhat different. One reason for this discrepancy lies in the choice of the heat of formation.

In Figure 7, E_T's are displayed. Three curves of reactions 3, 4, and 5 show the typical Braumann's double-well potential. The intermediate I of reaction 3 gets the large (−40.83 kcal/mol) stability due to CT. The large activation energy barrier of reaction 5 is also noticeable, which is needed for the C–H bond cleavage.

Reaction 7 is composed of the methyl cation shift between two bases (formaldehyde and dimethyl ether). The migration is a ready process, as is understandable by the difference of the proton affinities, PA(CH_2O) = 171.7 vs. PA(CH_3OCH_3) = 192.1 kcal/mol.[22]



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(26) The difference of theoretical ΔE_T and theoretical ΔH_r is known to be small (~ 1 or 2 kcal/mol).

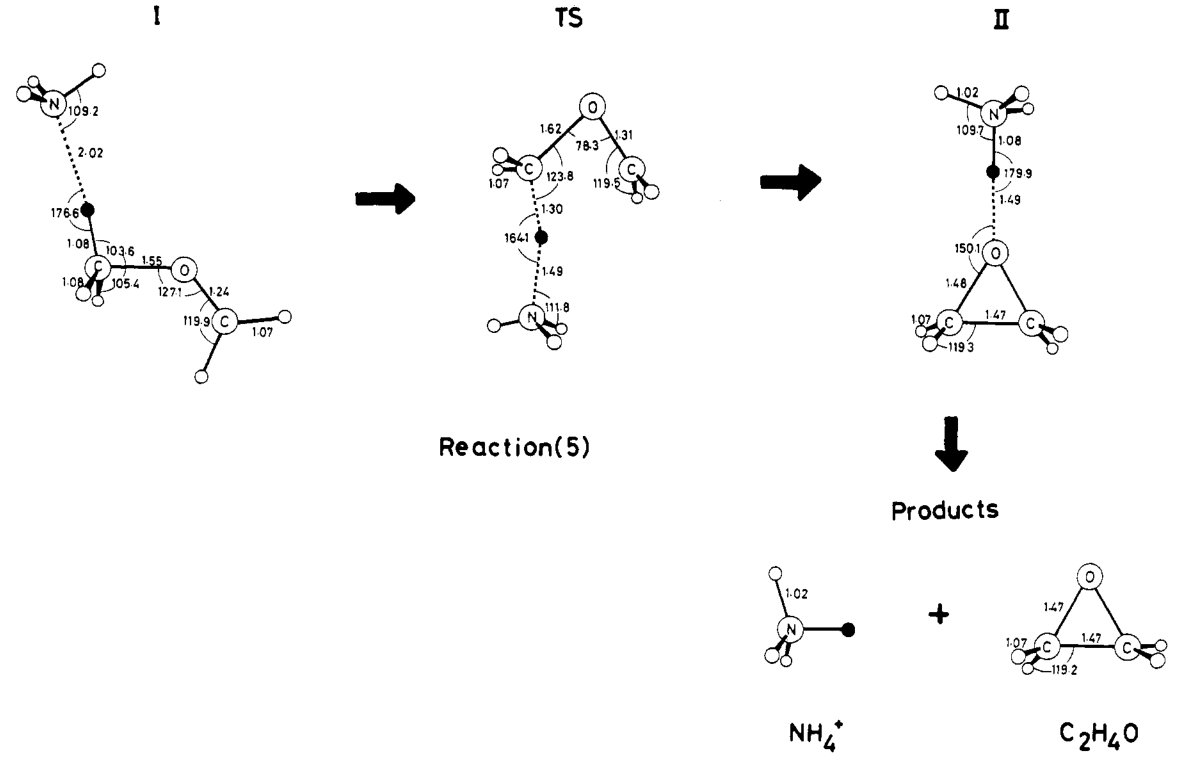


Figure 6. Geometries of two ion–dipole complexes (I and II), the transition state (TS), and the product in reaction 5. The small black circle denotes the proton to be migrated.

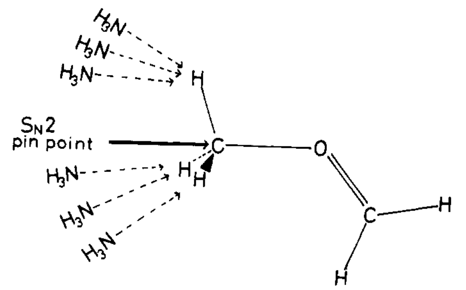
Table III. Total Energies (E_T's) and Exothermicities (ΔH_r's) of Reactions 3, 4, and 5[a]

		E_T, hartree				ΔH_r, kcal/mol	
reactants	reaction	ion–dipole complex I	TS	ion–dipole complex II	products	calcd	exptl[b]
NH_3, −56.182 499	3	−209.449 207	−209.386 494	−209.429 923	CH_3OH, −115.033 753 CH_4N^+, −94.383 056	−20.50	−16 (−20)[c]
	4	−209.400 017	−209.395 498	−209.464 232	CH_2O, −113.865 299 CH_6N^+, −95.572 598	−33.73	−28 ± 3[d]
$C_2H_5O^+$, −153.201 642	5	−209.400 017	−209.321 097	−209.428 131	$\overset{\ulcorner O \urcorner}{CH_2{-}CH_2}$, −152.861 878 CH_3CHO, −152.913 362 CH_2CHOH, −152.884 013 NH_4^+, −56.530 551	−5.20 −37.52 −19.10	−8 ± 3[d] −35 ± 3[d]

[a] 1 hartree = 627.566 kcal/mol. [b] Experimental data are those shown in Tabve II. [c] $\Delta H_f^{298}(CH_2NH_2^+)$ = 174 kcal/mol[19] is used. [d] Deviation was that of $PA(NH_3)$.[22]

Discussion

Reactions 3, 4, and 5 are examined kinetically and theoretically. Rate constants in Table II are in the order $k_3 > k_5 > k_4$. In view of the potential energy profiles in Figure 7, it seems strange that reaction 5 is faster than reaction 4. Two reactions have the common intermediate I. It is noteworthy that the gas-phase reaction has a peculiar reactivity, when the methyl hydrogen is attacked by a nucleophile. The reaction channel of reaction 4, i.e., S_N2, is sterically quite narrow. The S_N2 path is just a pinpoint. If the approaching NH_3 misses it, only the elastic collision takes place. The isomerization of the intermediate I to the net S_N2 is not so likely under the present large internal energy (the electron energies of ≥15 eV were used to generate $CH_3OCH_2^+$ from CH_3OCH_3). Thus, the pinpoint penetration is of a small probability, leading to the small Arrhenius factor in spite of the low activation barrier. Reactions 3 and 5 do not suffer from the block of the methyl hydrogens.



Kinter and Bursey[7] have studied the same ion/molecule reaction with the triple-quadrupole instrument where the kinetic analysis has not been made. Their spectral data, translational energy vs. ion yields, may be discussed in terms of the present result. The ion intensity of $CH_2NH_2^+$ produced by reaction 3 is not so affected by the magnitude of the ion kinetic energy (1.5–7 eV).[7] The deep potential well of the intermediate I is thought to hold a probability of the nonelastic collision effectively. Next, the intensity of the product ion NH_4^+ is reported[7] to increase monotonically as the ion kinetic energy is enlarged, with the threshold value = 55 ± 5 kcal/mol. This energy is somewhat larger than our activation barrier, 39.56 kcal/mol, of reaction 5. Interestingly, the energy of 55 ± 5 kcal/mol is found to be almost the same as our barrier, 49.52 kcal/mol (=39.56 + 9.56 kcal/mol), relative to the energy of the intermediate I. Therefore, the product (ethylene oxide, not $\cdot CH_2{-}O{-}CH_2\cdot$ which they assumed) of the *exothermic* reaction 5 is confirmed by this agreement. The ion intensity of $CH_3NH_3^+$ of reaction 4 is decayed as the kinetic energy increases.[7] Reactions

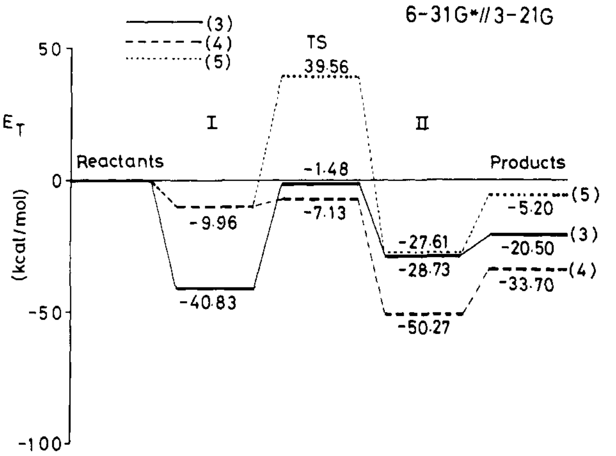


Figure 7. Potential energy profiles of reactions 3, 4, and 5. I and II denote ion–dipole complexes, and TS means the transition state. Energies in the figure stand for the stabilizing (<0) or destabilizing (>0) values relative to those of reactants.

4 and 5 are competitive, holding the intermediate I in common. By the larger kinetic energy, reaction 4 becomes minor as reaction 5 with the larger activation barrier becomes dominant. The large kinetic energy gives either the simple elastic collision (no S_N2) between the methyl hydrogen of $CH_3OCH_2^+$ and NH_3 or reaction 5.

Concluding Remarks

In this work, the kinetics of the three gas-phase reactions, reactions 3, 4, and 5, between methoxymethyl cation and ammonia has been determined at 433 K. The result in Table II shows the similar rate constants where the rank is $k_3 > k_5 > k_4$. An ab initio MO calculation has given the potential energy profile of the three reactions. Reaction 3 consists of the nucleophilic attack of NH_3 to the carbonyl carbon and the 1,3-proton shift from the nitrogen to the oxygen atom. The kinetic efficiency of reaction 3 is ascribed to the substantial stability of the intermediate I (i.e., the long-lived collision complex). Reaction 4 is of the S_N2 type and is not efficient due to the short-lived intermediate I and the pinpoint target of the back-side attack. Reaction 5 is composed of the concerted motion of the proton shift and the ring closure. Although reaction 5 has a large activation barrier, it is more efficient than reaction 4 through the effective conversion[7] of the translation energy to the internal energy and the absence of the methyl hydrogen block.

Reactions 3 and 4 involve the representative mechanisms of organic chemistry. Reaction 5 is a characteristic gas-phase process under the abundant translation energy. The methyl hydrogen may be hardly abstracted in the mild conditions of the aqueous media.

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Registry No. $MeOCH_2^+$, 23653-97-6; NH_3, 7664-41-7.

Infrared Spectra of Alkali Metal Atom–Ammonia Complexes in Solid Argon

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Abstract: One-to-one complexes between Li, Na, K, and Cs atoms and NH_3 have been studied by using matrix IR spectroscopy. New bands at 1133, 1079, 1064, and 1049 cm^{-1} are assigned to perturbed ν_2 modes, and bands at 3277, 3294, 3292, and 3287 cm^{-1} are assigned to the perturbed ν_1 ammonia submolecule modes of the Li--NH_3, Na--NH_3, K--NH_3, and Cs--NH_3 complexes, respectively. The corresponding bands for K and $^{15}NH_3$, NH_2D, NHD_2, and ND_3 complexes are also assigned. The intensity ratios of ν_1 to ν_2 for the ammonia submolecule modes in the Li, Na, K, and Cs complexes are larger by factors of 15, 20, 30, and 35, respectively, than the corresponding ratio for isolated ammonia. The intensification and position of ν_1 in the complex and the alkali metal–ammonia interaction are consistent with calculations of a very small ammonia → metal charge transfer where the alkali atom acts as a weak Lewis acid for Li and Na. The increased ammonia interaction with K and Cs may suggest a possible acid–base role reversal for the heavier alkali complexes. At higher metal/ammonia concentrations higher aggregate bands of $(M)_n$--NH_3 nature are also observed.

Solutions of alkali metal in liquid ammonia have been the subject of numerous studies dating back more than a century.[1-3] The well-known reactions of alkali metals with liquid water and ammonia are highly exothermic, and solvation of the alkali cation and electron formed provide major contributions to the exothermicity of the reaction. At the molecular level in the gas phase, however, the reactivity is expected to be greatly reduced. Ab initio SCF calculations[4,5] predict a 14.5 kcal/mol binding energy for Li--NH_3 but only 6.0 kcal/mol for Na--NH_3, as compared to 33 and 29 kcal/mol, respectively, for the corresponding ion-molecule complexes Li^+--NH_3 and Na^+--NH_3 observed by high-pressure mass spectrometry in the gas phase.[6] No calculations exist for larger alkali atom complexes, but experimentally measured binding energies decrease steadily going down the series for the cation–ammonia complexes. The ESR spectrum of the Li--NH_3 complex in solid argon indicates a reduced spin density localized in the lithium 2s orbital.[7] Although chemical intuition

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