Pyrolysis Reaction of Carpronium Chloride and its Structurally Related Compounds

2—A Mass Spectrometric Study of The Lactonization Mechanism

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The mechanism of the pyrolysis reaction of carpronium chloride [$(CH_3)_3N^+$—$(CH_2)_3$—$COOCH_3Cl^-$] leading to γ-butyrolactone and tetramethylammonium chloride was investigated by means of thermal analysis, pyrolysis gas chromatography mass spectrometry and field desorption mass spectrometry, using deuterium labelling. The results indicated that carpronium chloride pyrolysed to yield equimolar amounts of γ-butyrolactone and tetramethylammonium chloride, methyl transfer occurred between N and O during the pyrolysis process. The mechanism is discussed on the basis of the experimental results, and with the aid of the theoretical results calculated by the CNDO/2 method. The mechanism presented is as follows. γ-Butyrolactone is formed by the intramolecular migration of the π-orbital of C=O to the carbon adjacent to $[(CH_3)_3N]^+$ via a 5-membered ring transition state, accompanied by a bimolecular reaction between $[(CH_3)_3N]^+$ and the CH_3 of O—CH_3, resulting in the formation of tetramethylammonium chloride in an amount equimolar with γ-butyrolactone.

INTRODUCTION

Previous papers[1–3] have presented the pyrolysis features of a parasympathomimetic agent carponium chloride leading predominantly to γ-butyrolactone (γ-BL). This characteristic reaction has been interpreted in terms of the electronic and steric contributions[3] in the molecule. A similar thermal lactonization reaction has been reported for some phosphoniocarboxylate betaines[4,5] and ammoniocarboxylate betaines.[5–9] The reaction mechanism[6] for these has been interpreted in terms of intramolecular attack of the carboxylic anion (COO^-) on the carbon atom adjacent to the quaternary nitrogen atom (N^+). In the case of carpronium chloride, the reaction was accompanied by the production of tetramethylammonium chloride (TMAC)[2,3] and other interesting phenomena.[1,10] These experimental results and theoretical considerations[3] have suggested that the lactonization reaction occurred by a specific mechanism involving complex reactions.

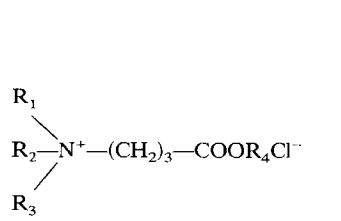
In order to clarify the reaction mechanism, it was essential to determine the correlation between the product ratios of γ-BL and TMAC, and to obtain information regarding the movement of the atoms and/or the functional groups under pyrolysis by using deuterium labelling. As an extension of our earlier work,[3] the lactonization mechanism was investigated by mean of thermal analysis, pyrolysis gas chromatography mass spectrometry (GC/MS) and field desorption (FD) mass spectrometry, using carponium chloride, its deuterated derivatives and its structural analogues.

This paper provides the experimental results and discusses the reaction mechanism with the aid of the molecular orbital calculations using the CNDO/2 method.

EXPERIMENTAL

Materials

Carponium chloride (**1**), its partially deuterated derivatives (**2,3,4**) and its structural analogues (**5,6,7**) were the quaternary ammonium compounds used. These compounds have been described previously,[1,3,10] their purity was tested by FD mass spectrometry. The chemical purity of all the compounds was 99% or above, and the isotopic purity of the deuterated derivatives was 98% or above against the indicated labelling amount. The trace amounts of impurities seemed to be negligible for the purposes of this study.



1: $R_1 = R_2 = R_3 = R_4 = CH_3$
2: $R_1 = R_2 = R_3 = CH_3$, $R_4 = CD_3$
3: $R_1 = R_2 = R_3 = CD_3$, $R_4 = CH_3$
4: $R_1 = R_2 = R_3 = R_4 = CD_3$
5: $R_1 = R_2 = R_3 = CH_3$, $R_4 = H$
6: $R_1 = R_2 = R_3 = CH_3$, $R_4 = CH_2CH_3$
7: $R_1 = R_2 = R_3 = CH_3$, $R_4 = CH(CH_3)_2$

Methyl *N,N*-dimethyl-γ-aminobutyrate (**8**) was synthesized by the method presented previously.[1,10]

Electron impact (EI) mass spectrometry

An Hitachi RMU-6M mass spectrometer was used. The ion generation was recorded by total ion monitoring (TIM), and the mass spectra were generally measured under the following conditions. The temperature

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of the chamber heater was held at 160 °C, and ionizing, accelerating and ion multiplier voltages were 70 eV, 3.2 kV and 1.5 kV, respectively. The sample heater was gradually increased from 80 °C to 300 °C by a manual operation. The sample solutions were prepared at a concentration of about 50 $\mu g\,\mu l^{-1}$ for each compound using CH_3OH or CD_3OD. Each sample solution (10 μl) was introduced via a direct inlet probe, and the measurement was carried out in the usual manner after removal of the solvent.

Field desorption mass spectrometry

FD mass spectrometry was carried out with a JMS-01SG double focusing mass spectrometer equipped with an EI/FI/FD ion source (JEOL Co. Ltd, Japan). FD mass specta were recorded using a JMA-2000 data processing system (JEOL Co. Ltd, Japan) over the mass range of m/z 50–400 at a rate of 20 s per scan. Emitters used were 10 μm diameter tungsten wires activated by benzonitrile. The anode voltage and cathode voltage were set at +10 kV and −2 kV, respectively. The emitter current was increased gradually from 0 to 23 mA by manual operation. The sample solutions were prepared at a concentration of 5 $\mu g\,\mu l^{-1}$ for each compound, using a mixture of H_2O and the appropriate alcohol corresponding to each ester group (1:1) or H_2O for **5**. The sample size was 1 μl for each sample solution using a syringe technique.

Thermal analysis

Differential thermal analysis (DTA) and thermogravimetry (TG) were used for the determination of the product ratio of TMAC and for the preparation of TMAC submitted to FD mass spectrometry. A Shimadzu DT-30 thermal analyser was generally operated, unless otherwise noted, at the heating rate of 10 °C min^{-1} under an atmosphere of nitrogen at 30 ml min^{-1}. About 10 mg of each compound in an open sample holder was heated up to 400 °C. The progress of the reaction was monitored by both DTA and TG. The product ratio of TMAC was calculated from the TG curve. TMAC submitted to FD mass spectrometric measurement was prepared under the same conditions as those presented above, except for the heating temperature. Each compound was heated to 250 °C at the rate of 20 °C min^{-1}, held isothermally for 10 min, and then cooled.

Others

Pyrolysis GC/MS carried out with the same apparatus[1–3,10] and under the same conditions[3] as presented previously. The atomic populations of C, H, N^+ and O, and the conformational energies were calculated for **1**, **6** and **7** by the CNDO/2 method with a Burroughs 7800 computer, using the same values of the bond length and the bond angle as presented in a preceding paper.[3] The abundance of the isotopic TMAC produced from each compound was calculated in the usual way[11] with a Burroughs 7800 computer.

RESULTS AND DISCUSSION

Preliminary examinations of the pyrolysis of **1**, **2**, **3** and **4** were made by EI mass spectrometry using the direct inlet method. The TIM profiles of these compounds indicated ion generation with two steps depending upon the temperature of the sample heater. Figure 1 shows a typical TIM profile and the mass spectra corresponding to the ion *b* generated from **1**, **2**, **3** and **4**. The presence of volatile products such as γ-BL, methyl *N,N*-dimethyl-γ-aminobutyrate and methyl γ-chlorobutyrate corresponding to each original compound was presumed in the mass spectra of ion *a* for **1**, **2**, **3** and **4**. These products have already been identified[1,2] by means of pyrolysis GC/MS. It was noteworthy that the mass spectra suggested no incorporation of deuterium in the γ-BL produced.

On the other hand, the mass spectra of ion *b* indicated that the presence of 'TMAC' resulted from the pyrolysis of **1**, **2**, **3** and **4**. As seen in Fig. 1(a), the mass spectrum of ion *b* for **1** has an intense peak at m/z 59 and the base peak at m/z 58. By comparison with the mass spectrum of authentic $(CH_3)_4N^+Cl^-$, these peaks were assigned as the molecular ion $[(CH_3)_3N]^{+\cdot}$ (found 59.0708, calc. 59.0734) and the fragment ion $[(CH_3)_2N{=}CH_2]^+$ (found 58.0623, calc. 58.0656) due to trimethylamine arising from the thermal decomposition of $(CH_3)_4N^+Cl^-$. The mass spectra of ion *b* for **2**, **3** and **4** indicate remarkable features as seen in Fig. 1(b–d). When compared with the mass spectrum of $(CH_3)_4N^+Cl^-$ in Fig. 1(a), it is apparent that the 'TMAC' produced from these, especially from **2** and **3**, is composed of abundant isotopic species other than $(CH_3)_3CD_3N^+Cl^-$ for **2** and

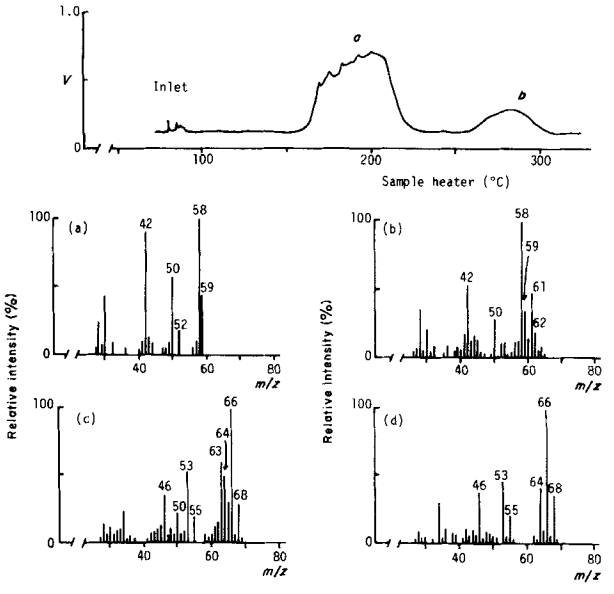


Figure 1. Typical TIM profile of compounds **1**, **2**, **3** and **4** in EI mass spectra and mass spectra corresponding to ion *b* of (a) compound **1**, (b) compound **2**, (c) compound **3** and (d) compound **4**.

$(CD_3)_3CH_3N^+Cl^-$ for **3**. The phenomena, which suggest that an intermolecular CD_3/CH_3 scrambling is occurring under pyrolysis, are of interest in connection with the lactonization mechanism. This will be clarified by means of FD mass spectrometry in a later section.

Correlation between product ratios γ-BL and TMAC

Determination of the product ratio of TMAC was essential for the clarification of the lactonization mechanism for **1**. It was also necessary to reveal whether the lactonization reaction of **1** was based on the pathway via **5**, which largely converted into γ-BL at 90% molar or above.[2] Thermal analysis techniques were applied to solve these problems. Figure 2 shows the typical DTA and TG curves for **1** and **5**. As seen in Fig. 2(a), the DTA curve for **1** indicates the endothermic peaks at *c.* 70 °C and *c.* 120 °C. These peaks were assigned as those due to the elimination of the adsorbed water for the former and the melting of **1** for the latter, respectively. The broad peak with complicated endothermic and exothermic variation is observed over the temperature range of *c.* 180–260 °C. When referring to the TG curve, it is apparent that these thermal phenomena are due to the pyrolysis of **1** progressing with complex reaction over the temperature range. In addition, the endothermic peaks at *c.* 270 °C and *c.* 330 °C were assigned as the changes due to the phase transition (not melting but polymorphism) of the TMAC produced and its thermal decomposition, respectively. The TG curve indicates that the weight decrease takes place in two steps, that is, the first weight decrease begins at *c.* 180 °C and ends at *c.* 270 °C, and the second occurs between *c.* 280–360 °C. When taking account of the thermal behaviour of **1** in EI mass spectrometry, it is readily supposed that the first is caused by the pyrolysis of intact **1** and the second by pyrolysis of the TMAC produced from **1**. The TMAC produced was confirmed by elementary analysis, DTA and TG curves, the infrared spectrum and the FD mass spectrum, compared with those of authentic TMAC. The amount of TMAC recorded on the TG curve was about 70% molar ratio, almost regardless of the sampling weight (2–20 mg) and the heating rate (1–20 °C min^{-1}).

Attempts to apply this thermal analysis technique to the determination of the production ratio of γ-BL failed, because the apparatus used was mechanically unsuitable for application to volatile compounds. When taking account of the evidence[1,2] on the conversion ratio of **1** into γ-BL (*c.* 70–75% molar), the molar ratio of the TMAC produced agreeds well with that of γ-BL obtained from **1** by means of pyrolysis GC/MS. The formation of γ-BL and TMAC seems to occur stoichiometrically regardless of the pyrolysis conditions.

Similar DTA and TG curves were obtained from **6** and **7**, and the results indicated that **6** and **7** gave rise to tetraalkylammonium chloride by pyrolysis at the degrees of *c.* 25% molar for **6** and *c.* 10% molar for **7**, respectively. These molar ratios were similar to those[2] of γ-BL produced from **6** and **7**. From these results, it was considered that the formation of γ-BL and tetraalkylammonium chloride from **1**, **6** and **7** proceeded stoichiometrically.

In the case of **5**, both the DTA curve and TG curve are simple as seen in Fig. 2(b). The DTA curve indicates the endothermic peak at *c.* 220 °C due to the melting of **5**, and the broad endothermic peak at *c.* 225 °C due to the pyrolysis of **5**. The TG curve indicates the simple weight decrease due to the pyrolysis of **5**. Compared with the TG curve for **1**, it appears that the pyrolysis of **1** occurs at lower temperature where the pyrolysis of **5** does not begin. Compound **6** and **7** also pyrolysed at lower temperatures, similar to the pyrolysis of **1**. Table 1 shows the comparison of the pyrolysis features for **1**, **5**, **6** and **7**. It is noteworthy that the ester compounds **1**, **6** and **7** all pyrolyse in the molten state, in contrast with the pyrolysis of **5** which progresses in the solid state. This evidence indicates reduced possibility for such a pyrolysis pathway as **1** (or **6** or **7**) → **5** → γ-BL.

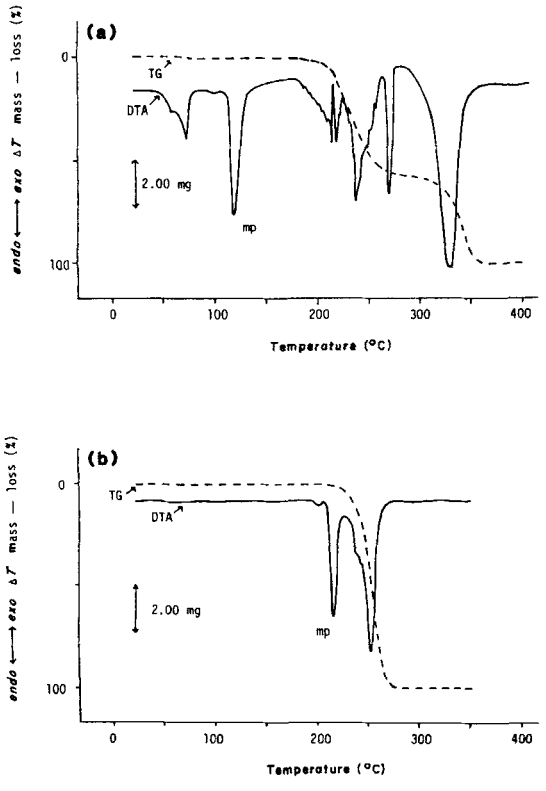


Figure 2. DTA and TG curves of (a) compound **1** and (b) compound **5** at the heating rate of 10 °C min^{-1} under an atmosphere of nitrogen (30 ml min^{-1}).

Table 1. Thermal properties of compounds 1, 5, 6 and 7

Compounds	m.p. (°C)	Heating rate (°C min^{-1})	Decomposition temp. (°C) Initial	Half	Final
1	122	1	152	206	234
		10	180	232	278
5	218	1	197	228	248
		10	218	261	300
6	132	1	156	206	235
		10	185	240	279
7	152	1	157	209	231
		10	183	242	269

Isotopic aspects of pyrolysis products

The preliminary observation that γ-BL produced from **2**, **3** and **4** did not incorporate deuterium in the molecule, was confirmed by pyrolysis GC/MS. The mass spectra of γ-BL produced from each of the deuterated compounds did not indicate the incorporation of deuterium. From these results it was concluded that neither the $[(CH_3)_3N]^+$ or the CH_3 of O—CH_3 participated in γ-BL formation. It is certain that γ-BL is never formed by mechanisms such as C—C bond cleavage of the skeletal methylene chain of the original compounds.

On the other hand, in order to determine more information about CD_3/CH_3 scrambling of TMAC, further investigations were made by means of FD mass spectrometry. Figure 3 shows the FD mass spectra of the TMAC produced from **1**, **2**, **3** and **4**.

The FD mass spectra of TMAC produced from **2** and **3** each exhibit abundant isotopic ions $[(CH_3)_4N]^+$ (m/z 74) and $[(CH_3)_2(CD_3)_2N]^+$(m/z 80) for **2**, and $[(CH_3)_2(CD_3)_2N]^+$(m/z 80) and $[(CD_3)_4N]^+$(m/z 86) for **3**, despite the fact that no traces of corresponding isotopic species are present in either of the original compound. Furthermore, the FD mass spectra show the weak isotopic ions $[(CH_3)_2(CD_3)_2N]^+$(m/z 83) for **2** and $[(CH_3)_3CD_3N]^+$(m/z 77) for **3**. These FD ions appear to arise from the isotopic TMAC possessing one or two isotopic methyl species. It is considered that such isotopic TMAC results from intermolecular methyl rearrangement between *N*-methyl and *O*-methyl on the pyrolysis of **2** or **3**. In addition, the FD mass spectra of tetraalkylammonium chloride produced from **6** and **7** indicated interesting patterns, as shown in Fig. 4. The FD mass spectra have abundant characteristic ions $[(CH_3)_4N]^+$ (m/z 74) and $[CH_3)_2(C_2H_5)_2N^+$ (m/z 102) for **6**, and $[(CH_3)_4N]^+$(m/z 74) for **7**, besides the expected ions $[(CH_3)_3C_2H_5N]^+$(m/z 88) for **6** and $[(CH_3)_3C_3H_7N]^+$(m/z 102) for **7**. These unexpected ions must arise from $(CH_3)_4N^+Cl^-$ and $(CH_3)_2(C_2H_5)_2N^+Cl^-$ for **6**, and $(CH_3)_4N^+Cl^-$ for **7**. The ion $[(CH_3)_2(C_3H_7)_2]^+$(m/z 130) due to $(CH_3)_2(C_3H_7)_2N^+Cl^-$ was not observed in the FD mass spectrum of **7**. From these results, it became evident that in general intermolecular alkyl rearrangement between N and O occurred on pyrolysis of these trimethylaminocarboxylic acid esters used.

Meanwhile it remained unclear whether the alkylammonium chloride produced and the *N*-demethylation products (which were pyrolysis products[1,2,9] of the ammonium compounds **1**, **6** and **7**), participated in the alkyl rearrangement. In order to clarify this question, an equimolar mixture of **1** and **4**, **4** and **8**, **4** and $[(CH_3)_4N^+Cl^-]$, or $[(CH_3)_4N^+Cl^-]$ and $[(CD_3)_4N^+Cl^-]$ was heated at 250 °C for 10 min, and then submitted to FD mass spectrometry. Table 2 summarizes the relative abundance for the isotopic TMAC produced from each mixture sample, compared with that for the isotopic TMAC produced from **1**, **2**, **3** and **4**. As seen in Table 2, the equimolar mixture of **1** and **4** gives abundant TMAC-d_3 TMAC-d_6 and TMAC-d_9. In addition, the abundances of TMAC-d_0, TMAC-d_3, TMAC-d_9 and TMAC-d_{12} are almost equal, whereas the equimolar mixtures of **4** and $[(CH_3)_4N^+Cl^-]$ or $[(CD_3)_4N^+Cl^-]$ and $[(CH_3)_4N^+Cl^-]$ give TMAC-d_3, TMAC-d_6 and TMAC-d_9 scarcely or not at all. These results indicate that the methyl rearrangement occurs during the pyrolysis process of the original compounds **1**, **2**, **3** and **4**. The TMAC produced scarcely takes part in the methyl rearrangement. In addition, it is noteworthy that the TMAC produced from the mixture of **1** and **4** has an abundance of TMAC-d_6, despite the fact that the 'TMAC' produced from **2** and **3** scarcely has TMAC-d_9 for **2** and TMAC-d_3 for **3** respectively.

In the case of the equimolar mixture of **4** and **8**, the abundance of isotopic TMAC is greatly dependent on the pyrolysis conditions. When the pyrolysis is carried out in a sealed glass tube (c. 0.6 cm i.d. ×7 cm), the result indicates the presence of several kinds of isotopic TMAC, similar to that from the mixture of **1** and **4**. In contrast, the result obtained by the use of an

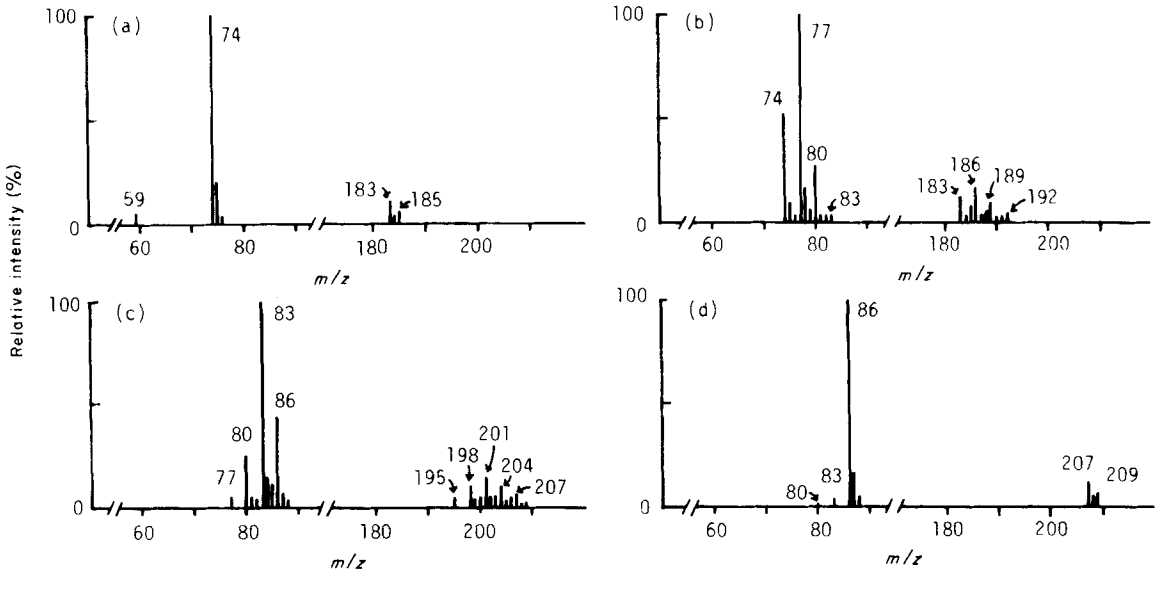


Figure 3. FD mass spectra of 'TMAC' produced from (a) compound **1**, (b) compound **2**, (c) compound **3** and (d) compound **4**, at the emitter current of 16–20 mA.

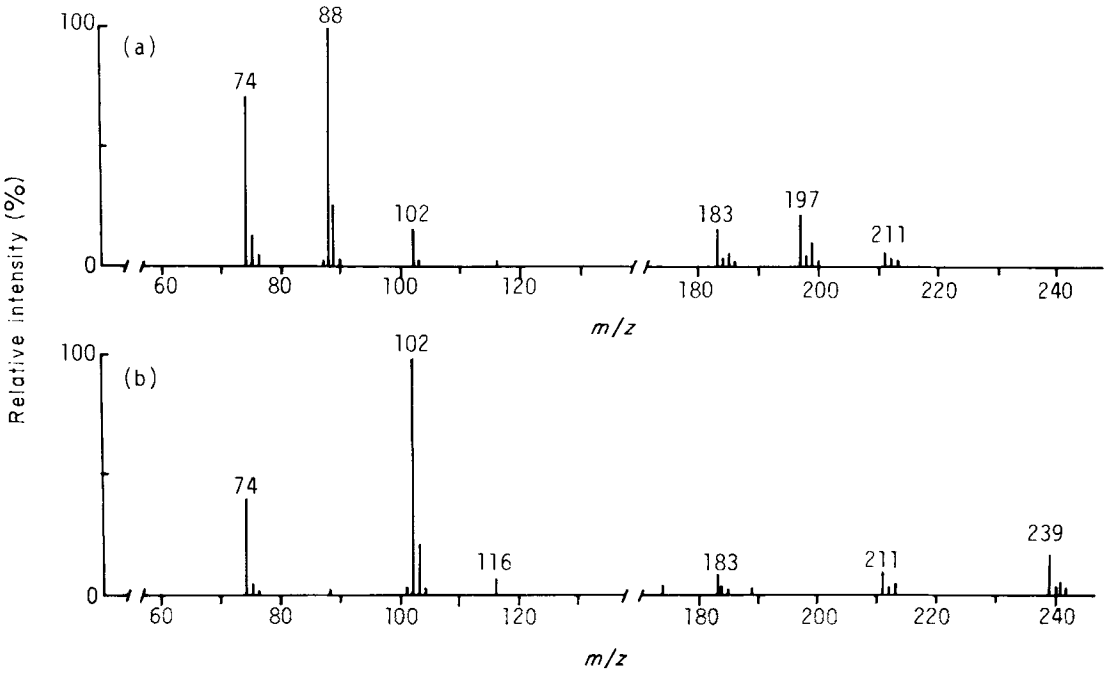


Figure 4. FD mass spectra of tetraalkylammonium chloride produced from (a) compound **6** and (b) compound **7**, at the emitter current of 16–20 mA.

open sample holder for thermal analysis barely gives isotopic TMAC, other than that from **4** only. These results would be due to the volatility of **8** (b.p. 59 °C per 9 Torr[12]); compound **8** presented with **4** in an open sample holder readily vaporizes to be removed from the reaction mixture, before beginning the pyrolysis of **4**. It is impossible from these results to estimate quantitatively the participation of **8** in the methyl rearrangement; however it is certain that **8** produced from **1** reacts in part with **1** during the pyrolysis of **1**, playing an important role in the methyl rearrangement.

Considering the methyl rearrangement on the basis of the evidence shown in Table 2, it was felt that the reaction occurred by two pathways via a zwitterionic intermediate[9] and methyl *N,N*-dimethyl-γ-aminobutyrate, as shown in Scheme 1. The first pathway converts **1** into a zwitterionic intermediate by *O*-demethylation via pairs of chloride anion, followed by the reconstitution of **1** by intermolecular methyl transfers from N to COO^-. The second pathway results when methyl *N,N*-dimethyl-γ-aminobutyrate is formed by the *N*-demethylation via ions involving chloride anion, followed by the intermolecular methyl transfer from O to N, giving reconstituted **1**. When the reconstitution of **1** is accomplished via both the pathways, two methyls of both N and O in the reconstituted **1** are replaced.

The mechanisms presented are applicable in general to the alkyl rearrangement between N and O to the pyrolysis of the other ester analogues **6** and **7**. Taking account of the absence of the FD ion $[(CH_3)_2(C_3H_7)_2N]^+$ (*m/z* 130) due to $[(CH_3)_2(C_3H_7)_2N^+Cl^-]$ in the pyrolysis of **7**, this appears to be caused by the stereochemical hindrance of the $CH(CH_3)_2$ group in the isopropyl transfer from O to N by pathway 2. The electronic and steric effects of the $(CH_3)_2$ of $CH(CH_3)_2$ group would prevent the access of N to the C of methine.

Table 2. Relative abundances of isotopic species of tetramethylammonium chloride (TMAC) produced from each original compound on heating at 250 °C for 10 min

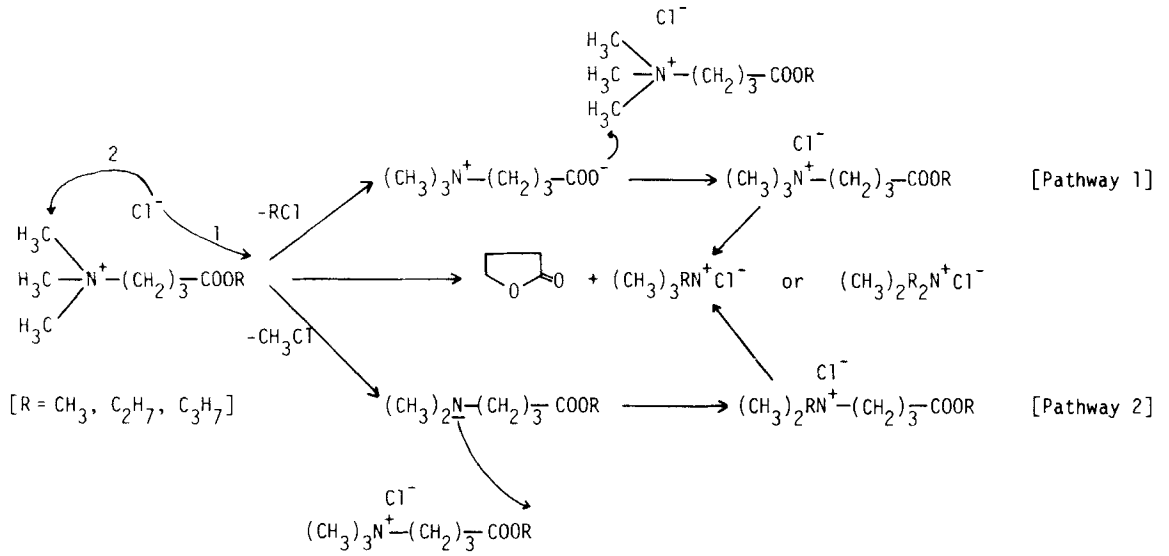
	Species of TMAC (%)				
Compounds (molar ratio)	d_0	d_3	d_6	d_9	d_{12}
1	100	0	0	0	0
2	28.9	56.3	13.5	1.3	0
3	0	2.1	15.3	57.6	25.0
4	0	0	0.4	2.5	97.1
1/4 = 1	23.4	22.6	10.2	22.0	21.8
4/8 = 1[a]	0.2	0.7	0.5	3.6	95.0
4/8 = 1[b]	5.8	12.3	14.5	15.2	52.2
4/$[(CH_3)_4N^+Cl^-]$ = 1	48.7	2.1	0.2	3.0	46.0
$[(CD_3)_4N^+Cl^-]/[(CH_3)_4N^+Cl^-]$ = 1	51.4	0	0	0.3	48.3

[a] In a open sample holder, the same as the others.
[b] In a sealed glass tube (*c.* 0.6 cm i.d.×7 cm).

Molecular orbital interpretation

Here and in the following sections, we use the following definition for the carbon atoms of the skeletal methylene chain; the carbon atom adjacent to trimethylamino group is α, the next β, etc., the same as the definition used in the preceding paper.[3]

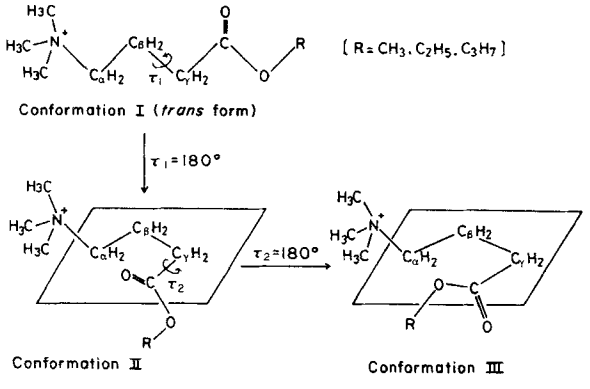
As described above, the behaviour noted on the pyrolysis of **1** became clear. However, it remained to be determined whether the driving force for the lactonization reaction was made by a nucleophilic attack of the carbonyl oxygen atom or that of the ester oxygen atom. The experimental distinction of both might be possible by the use of carpronium chloride labelled at either the carbonyl oxygen atom or the ester oxygen atom by stable isotope oxygen ^{18}O. The



Scheme 1. Presumed mechanism of transalkulation during the pyrolysis reaction of compounds **1**, **6** and **7**.

synthesis of such labelled compounds was considered to be very difficult or impossible. Taking account of the lactonization mechanism[13–17] for some carboxylic acid esters, and the E_i mechanism[18–20] for the formation of olefins from carboxylic acid esters, intramolecular attack by the carbonyl oxygen atom appeared to be more probable. This idea was supported by the electronic structure[3] calculated by the CNDO/2 method, using an assumed conformation I (presented in Scheme 2) in which the functional groups were all-*trans*.

In order to confirm this, the molecular orbital parameters were calculated by the CNDO/2 method, with two assumed conformations II and III, where the atoms C_α, C_β, C_γ, C and O of the carbonyl group or the atoms C_α, C_β, C_γ, C and O of the ester group lay on the same plane, as shown in Scheme 2. Rotation of the C_β—C_γ bond of the assumed conformation I about the axis for 180°, gives the assumed conformation II. Then, in the assumed conformation II, the rotation of the C_γ—C of COOR bond about the axis for 180° gives the assumed conformation III. These assumed conformations II and III appeared to reflect something of the transition state with reference to γ-BL formation, compared with the assumed conformation I which has already been discussed.[3] Table 3 summarizes the results as the net electronic charge of each atom and the conformation energy for II and III, compared with those for conformation I.



Scheme 2.

As seen in Table 3, conformation II appears reasonable for the transition probability rather than conformation III. It is apparent from the viewpoint of the electronic structure and conformational energy that conformation II is favored over conformation III. The same results were obtained from the other ester analogues **6** and **7**, as seen in Table 3. These results all indicate the ease of intramolecular nucleophilic access of the carbonyl oxygen atom to the C_α atom.

Mechanism

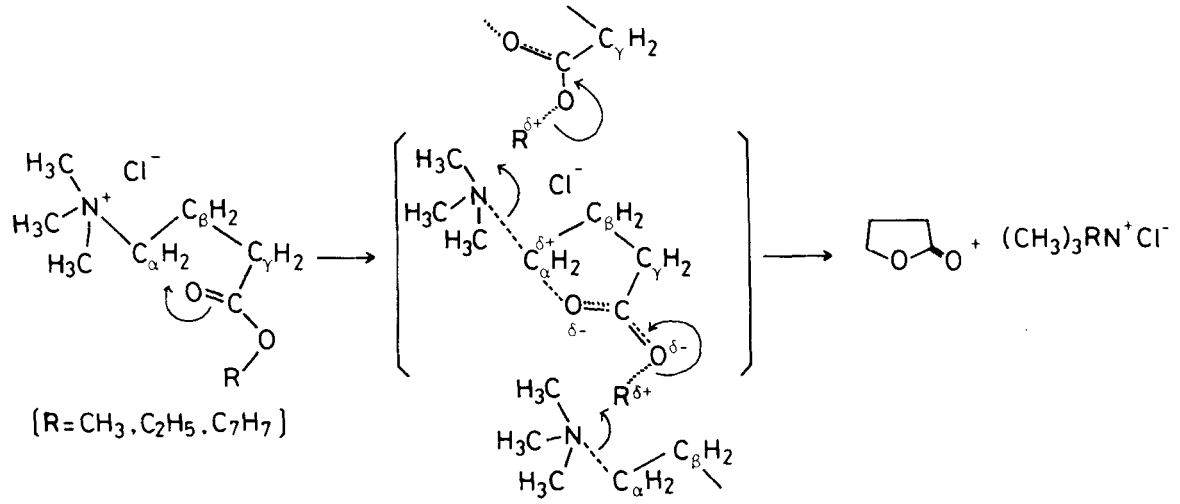
On the basis of the experimental results and the molecular orbital calculations, we assumed a mechanism for the conversion from carpronium chloride into γ-BL and TMAC. The driving force for the intramolecular nucleophilic access of the carbonyl oxygen atom to the C_α atom gives conformation II. In this structure the electron transfer of the π-orbital consisting of the C=O bond to the C_α atom begins to form a transition state with a 5-membered ring structure, accompanied by N^+—C_α and O—CH_3 bond breaking. In this electronic excitation, and electron of the π-orbital of C=O is removed from the π-orbital and placed in the σ-orbital between C_α and O. The completion of the σ-orbital forms γ-BL, followed by the intermolecular migration of a lone pair electron of N to a leaving CH_3, resulting in the formation of TMAC. The equimolar production ratios of γ-BL and TMAC are consistent with this assumed mechanism, and all of the other observations in Table 2 can be explained by this assumed mechanism (Scheme 3) in connection with the alkyl rearrangement mechanism shown in Scheme 1.

In contrast to this, if an intramolecular mechanism for the formation of 'TMAC' is assumed, the abundance of TMAC-d_9 from **2** and/or that of TMAC-d_3 from **3** ought to be nearly equal to that of TMAC-d_6 from the equimolar mixture of **1** and **4**. The experimental results were in conflict with this assumption. In

Table 3. Net total ($\sigma+\pi$) electronic charges and total energies in conformations I, II and III of compounds 1, 6 and 7 (the plus sign denotes net positive charge; the minus sign denotes net negative charge).

Compounds	Conformations	Net electronic charges[a] (electron units × 10^2)																	Total energies (eV)
		$(CH_3)_2N^+-$			$-(CH_2)_3-$						$=C=O$		$-O-R^b$						
		C	H	N^+	C_α	H_α	C_β	H_β	C_γ	H_γ	C	O	O	$C_{\alpha'}$	$H_{\alpha'}$	$C_{\beta'}$	$H_{\beta'}$	$C_{\beta''}$	$H_{\beta''}$	
	I	+5.38	+5.36	+9.21	+7.90	+3.74	+0.79	+2.56	−4.71	+4.07	+38.62	−30.82	−21.37	+15.61	−0.83	—	—	—	—	−32.41.327
1	II	+5.57	+4.98	+7.75	+8.64	+5.97	+0.60	+1.67	−5.36	+5.53	+39.70	−34.47	−20.54	+15.52	−0.73	—	—	—	—	−3241.002
	III	+5.48	+5.11	+8.11	+8.10	+5.54	+0.22	+1.74	−5.13	+5.79	+37.14	−26.91	−25.27	+14.72	+0.12	—	—	—	—	−3240.703
	I	+5.39	+5.34	+9.21	+7.89	+3.71	+0.80	+2.46	−4.76	+3.95	+38.32	−31.07	−22.33	+18.50	−1.66	−4.24	+2.16	—	—	−3477.820
6	II	+5.57	+4.98	+7.74	+8.64	+6.00	+0.64	+1.58	−5.42	+5.41	+39.39	−34.72	−21.54	+18.52	−1.84	−4.27	+2.44	—	—	−3477.505
	III	+5.48	+5.10	+8.10	+8.09	+5.57	+0.24	+1.68	−5.16	+5.70	+36.98	−27.75	−26.09	+17.30	−0.35	−4.34	+1.52	—	—	−3477.181
	I	+5.39	+5.34	+9.21	+7.89	+3.73	+0.80	+2.43	−4.80	+4.00	+38.72	−31.73	−23.47	+19.72	−1.26	−5.30	+1.83	−5.30	+1.83	−3713.927
7	II	+5.57	+4.99	+7.72	+8.66	+5.95	+0.60	+1.60	−5.45	+5.45	+39.79	−35.22	−22.67	+19.59	−0.61	−5.18	+2.12	−5.18	+2.05	−3713.592
	III	+5.23	+5.08	+8.06	+8.10	+5.68	+0.26	+1.64	−5.21	+5.64	+37.32	−28.13	−27.47	+19.17	−3.15	−5.39	+2.28	−5.39	+2.28	−3713.340

[a] The values represent the mean of each atom in the functional groups.
[b] The definition used for the atoms of the ester groups is as follows; the carbon atom adjacent to oxygen atom is α', next β', etc.



Scheme 3. Presumed mechanism for the formation of γ-butyrolactone and tetraalkylammonium chloride.

addition to the above discussion, an intramolecular electron migration from the N^+—C_α bond to CH_3 in conformation II appears to be impossible from the spatial viewpoint, because the atomic distance (5.925 Å calc.) between the N^+ and the C_α would be too great for the migration of the electron. The rotation of the C_α—C_β bond in conformation II brings the atoms N^+ and C of O—CH_3 close; however, such a conformation would be less probable because of the electronic repulsion and steric hindrance due to the other atoms in the molecule.

As described above, the pyrolysis of carpronium chloride leading to γ-BL and TMAC occurs according to the basic mechanism of Scheme 3. Under the reaction process the methyl rearrangement between N and O occurs according to the mechanisms via a zwitterionic intermediate and methyl *N,N*-dimethyl-γ-aminobutyrate (**8**), as shown in Scheme 1. These reaction features would be responsible for the electronic and steric structure characteristic of carpronium chloride. All of the experimental results described in this paper can be interpreted sufficiently in terms of the present mechanisms.

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