

# Destabilized Carbenium Ions: $\alpha$ -Carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl Cations

Rainer Wolf and Hans-Fr. Grützmacher  
Fakultät für Chemie, Universität Bielefeld, FRG.

Tertiary  $\alpha$ -carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl cations *a* have been generated by electron impact induced fragmentation from the appropriately  $\alpha$ -substituted methyl isobutyrate 1-4. The destabilized carbenium ions *a* can be distinguished from their more stable isomers protonated methyl methacrylate *c* and protonated methyl crotonate *d* by MIKE and CA spectra. The loss of I<sup>•</sup> and Br<sup>•</sup> from the molecular ions of 1 and 2, respectively, predominantly gives rise to the destabilized ions *a*, whereas loss of Cl<sup>•</sup> from [3]<sup>+</sup> results in a mixture of ions *a* and *c*. The loss of CH<sub>3</sub><sup>•</sup> from [4]<sup>+</sup> favours skeletal rearrangement leading to ions *d*. The characteristic reactions of the destabilized ions *a* are the loss of CO and elimination of methanol. The loss of CO is associated by a very large KER and non-statistical kinetic energy release ( $T_{50} = 920$  meV). Specific deuterium labelling experiments indicate that the  $\alpha$ -carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl cations *a* rearrange via a 1,4-H shift into the carbonyl protonated methyl methacrylate *c* and eventually into the alkyl-O protonated methyl methacrylate before the loss of methanol. The hydrogen rearrangements exhibit a deuterium isotope effect indicating substantial energy barriers between the [C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>]<sup>+</sup> isomers. Thus the destabilized carbenium ion *a* exists as a kinetically stable species within a potential energy well.

## INTRODUCTION

$\alpha$ -Acylcarbenium ions carrying an acyl group -COR, a carboalkoxy group -COOR and a carbamoyl group -CONR<sub>2</sub>, respectively, at the carbenium ion centre are an important sub-group of the family of destabilized carbenium ions. These ions are reactive intermediates of solvolytic reactions and their chemistry in solution has been intensively investigated.<sup>1</sup> Theoretical calculations show that most electron withdrawing groups act still as  $\sigma$ -donors on the electron deficient primary carbenium ion, but in spite of this the primary  $\alpha$ -acyl carbenium ions collapse immediately into the more stable isomers.<sup>2-4</sup> The theoretical calculations also suggest that phenyl or methyl substituted  $\alpha$ -acylmethyl cations prefer the open structure instead of the structure of cyclic oxiranyl cations. This agrees well with the experimental evidence<sup>5,6</sup> that these secondary and tertiary  $\alpha$ -acylcarbenium ions with a 'push-pull' substitution are kinetically stable species in the gas phase.

In this paper we report the formation and the unimolecular reactions of the tertiary  $\alpha$ -carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl cations *a*, [C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>]<sup>+</sup>, which have been generated in the gas phase by the loss of a substituent X from the molecular ions of 2-substituted methyl isobutyrate.

Two problems are connected with an investigation of thermodynamically unstable ions of a large heat of formation. Firstly, the formation of these ions may be avoided by a rearrangement of the precursor ions yielding more stable isomers upon fragmentation. Such rearrangements have been observed for the loss of  $\alpha$ -substituents from the molecular ions of certain substituted aliphatic esters.<sup>7</sup> In the present case the competition between the formation of destabilized  $\alpha$ -

carbomethoxy carbenium ions *a* by a direct bond cleavage and of more stable isomers by rearrangement processes has been studied by varying the substituent of the  $\alpha$ -substituted methyl isobutyrate implying also a variation of the critical energy of the direct cleavage reaction. Secondly, the existence of an energy rich ion as a discrete species in the gas phase depends critically on the energy barriers separating it from the fragmentation products and from the more stable isomers. The stabilizing effect of the two  $\alpha$ -methyl groups of *a* is very likely less than the effect of the phenyl substituent of the  $\alpha$ -carbomethoxy benzyl cations studied previously.<sup>6</sup> Furthermore the proton affinity of an ester group exceeds that of the keto group<sup>8</sup> of  $\alpha$ -acetyl  $\alpha,\alpha$ -dimethyl-methyl cations.<sup>5</sup> Both effects increase the reactivity of ions *a* especially with respect to an isomerization into the much more stable carbonyl protonated methyl methacrylate *c* by a 1,4-hydride shift.

The energetically most favourable spontaneous fragmentations of *a* are easily detected in the MIKE spectra, but the isomerizations of *a* at small internal energies are more difficult to observe and have been investigated by deuterium labelling and CA mass spectrometry.

## RESULTS AND DISCUSSION

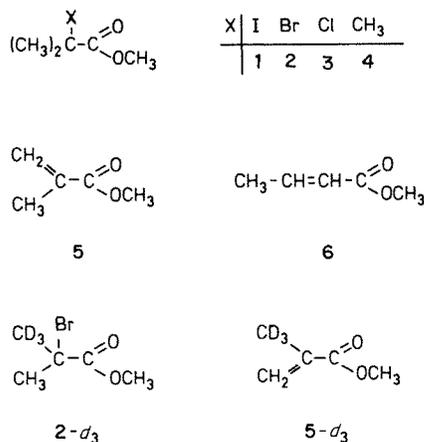
### CA spectra and structures of [C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>]<sup>+</sup>

The 70 eV mass spectra of 1 and 2 exhibit large peaks of [M - X]<sup>+</sup> ions, while the formation of these ions is much less intense in the mass spectra of 3 and 4 (Table 1). However, the loss of X<sup>•</sup> appears to be always ener-

**Table 1. Characteristic ions in the mass spectra (70 eV) of 1-4**

	X	M <sup>+</sup>	[M-X] <sup>+</sup>	[M-X-CO] <sup>+</sup>	[(CH <sub>3</sub> ) <sub>2</sub> CX] <sup>+</sup>	[OCOCH <sub>3</sub> ] <sup>+</sup>	[C <sub>3</sub> H <sub>6</sub> ] <sup>+</sup>
<b>1</b>	I	13.5	71.7	69.7	7.6	41.3	100.0
<b>2</b>	Br	5.2	98.6	74.4	40.0 <sup>a</sup>	31.7	100.0
<b>3</b>	Cl	1.5	10.9	20.0	123.3 <sup>a</sup>	27.7	100.0
<b>4</b>	CH <sub>3</sub>	4.2	3.3	10.4	100.0	6.5	45.9

<sup>a</sup> Sum of the intensity of Br and Cl isotopes, respectively.

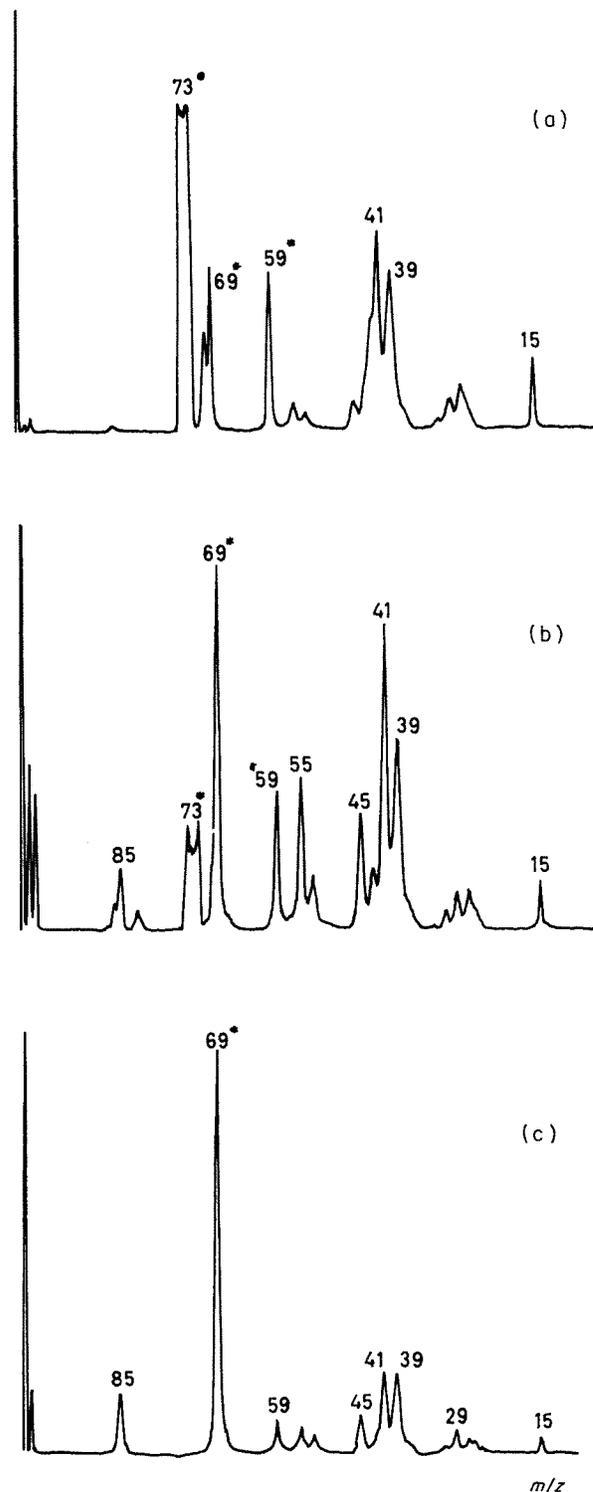


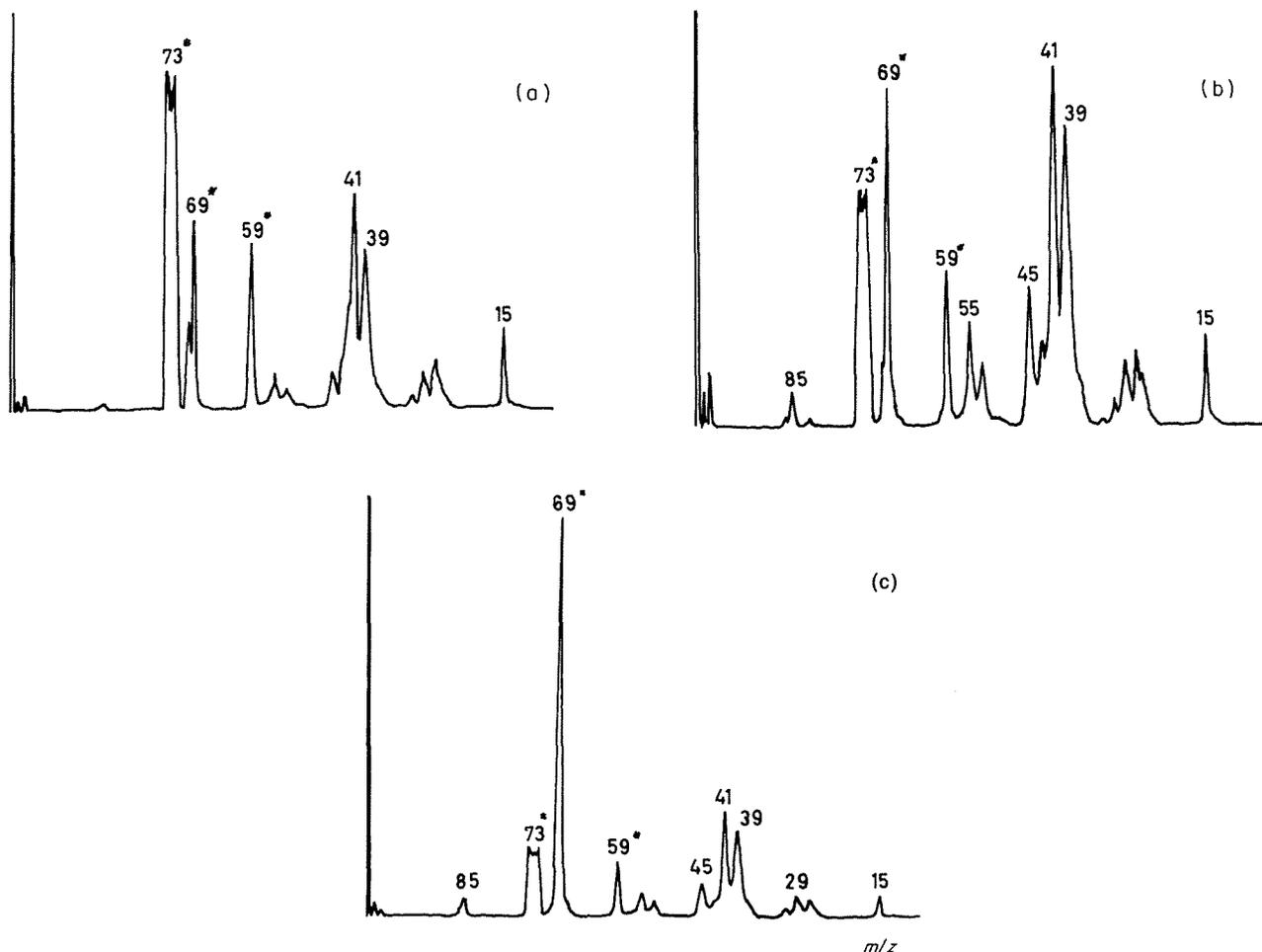
getically favourable, because this is the only spontaneous reaction observed for the metastable ions from **1** and **2**, respectively, and is still the predominant fragmentation in the MIKE spectra of [3]<sup>++</sup> and [4]<sup>+</sup> (Table 2). Narrow Gaussian shaped peaks are observed for the loss of X = I, Br and Cl, respectively, which agrees well with a direct bond cleavage (Table 2). The T<sub>50</sub>-value increases significantly for the loss of CH<sub>3</sub><sup>+</sup> from [4]<sup>+</sup>, however, so that in this case the loss of the α-substituent occurs probably not (only) by a direct bond cleavage.

The CA spectra of the [M - X]<sup>+</sup> ions from 1-4 and of the isomeric [C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>]<sup>+</sup> ions *c* and *d* arising by protonation of methyl methacrylate **5** and methyl crotonate **6**, respectively, are shown in Figs 1 and 2. The CA spectra of the [M - X]<sup>+</sup> ions from 1-4 are clearly different indicating that other processes than the direct bond cleavage are competing for the loss of X and that the structures of the [M - X]<sup>+</sup> ions depend distinctly on the critical energy of the direct bond cleavage. The largest critical energy within this series is needed for the loss of the methyl group (a 'bad leaving group') from the molecular ion of **4**. The CA spectrum of the resulting [C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>]<sup>+</sup> ions is very similar to the ions *d* arising from the protonation of **6**. Both spectra exhibit a very dominant peak at *m/z* 69 due to the loss of methanol.

**Table 2. MIKE spectra of molecular ions from 1-4 (relative intensity in % base peak) and kinetic energy release (meV) for loss of X**

X	-X <sup>+</sup>	T <sub>50</sub> (-X)	-HX	-C <sub>4</sub> H <sub>8</sub>	-C <sub>3</sub> H <sub>6</sub>
<b>1</b>	I	100.0	3	-	-
<b>2</b>	Br	100.0	3	-	-
<b>3</b>	Cl	100.0	6	3.3	-
<b>4</b>	CH <sub>3</sub>	100.0	76	-	11.5 10.9

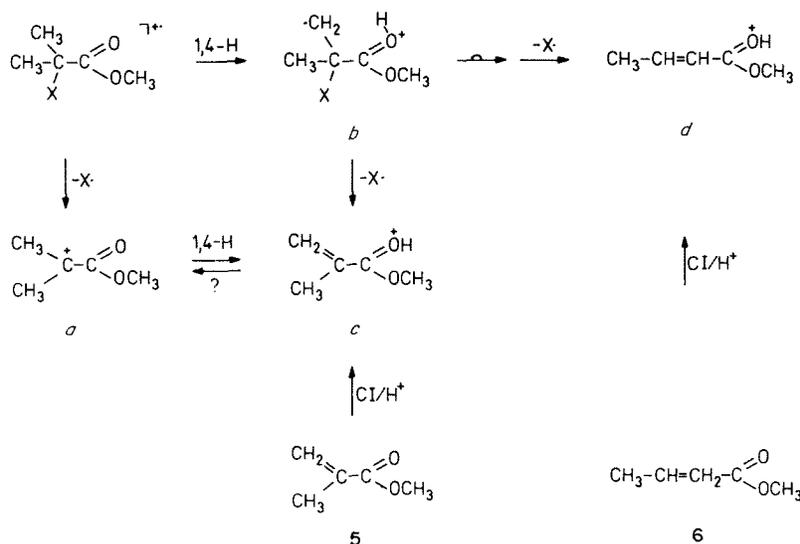
**Figure 1.** CA spectra of [C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>]<sup>+</sup> ions from (a) **1** (X = I), (b) [5H]<sup>+</sup> and (c) [6H]<sup>+</sup>. Peaks indicated with an asterisk are also observed as a result of spontaneous unimolecular decompositions.



**Figure 2.** CA spectra of  $[C_5H_9O_2]^+$  ions from (a) **2** ( $X = Br$ ), (b) **3** ( $X = Cl$ ) and (c) **4** ( $X = CH_3$ ). Peaks indicated with an asterisk are also observed as a result of spontaneous unimolecular decompositions.

The formation of ions *d* from **4** agrees with the skeletal rearrangement process (see Scheme 1 below) proposed by Schwarz and co-workers<sup>7</sup> for the loss of  $\alpha$ -alkyl substituents from aliphatic ester ions. However, the additional small peak at  $m/z$  73 for the loss of CO in the spectrum of the  $[M - CH_3]^+$  suggests the presence of at least a small amount of ions isomeric to *d*.

The elimination of CO associated with a large KER has been observed for other  $\alpha$ -acyl carbenium ions.<sup>5,6</sup> Indeed, the intensity of the characteristically dished-topped peak at  $m/z$  73 increases in the CA spectra with a decreasing dissociation energy of the C-X bond in **1-4** which should favour the formation of the  $\alpha$ -carbomethoxy ion *a*. The peak  $m/z$  73 is the base peak



**Scheme 1**

in the CA spectrum of  $[M - I]^+$  (Fig. 1) and  $[M - Br]^+$  (Fig. 2), respectively, and in fact both spectra are identical. The peak of  $[C_5H_9O_2]^+$  at  $m/z$  41 exceeds that at  $m/z$  73 in the CA spectrum of the  $[M - Cl]^+$  ions which contains, furthermore, additional signals at  $m/z$  55 and  $m/z$  45 typical of the CA spectrum of protonated methyl methacrylate *c* shown in Fig. 1. Thus, the CA spectra of the  $[M - X]^+$  ions show unequivocally that (at least) three isomeric  $[C_5H_9O_2]^+$  ions *a*, *c* and *d* arise from 1-4 by electron impact induced loss of the  $\alpha$ -substituent X depending on the nature of X. The intensity variation of the characteristic peaks in the CA spectra at  $m/z$  73 and  $m/z$  70 for *a*,  $m/z$  55,  $m/z$  45 and  $m/z$  41 for *c*, and  $m/z$  69 for *d*, respectively, shows that the  $[M - CH_3]^+$  ions are mainly ions *d*, and that 4 cannot be used as a precursor for the  $\alpha$ -carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl cations *a*. In contrast, the ions  $[M - I]^+$  and  $[M - Br]^+$  from 1 and 2, respectively, correspond to structure *a* with only small contributions from *c* and *d*. Finally, the  $[C_5H_9O_2]^+$  from the chloroester 3 are a mixture of ions *a* and *c*. The presence of some ions *d* in this mixture cannot be excluded but seems unlikely in view of the similarity between the CA spectra of the ions  $[M - Cl]^+$  and the ions *c* formed by protonation of 5. Note that the latter CA spectrum indicates clearly the formation of ions *a* by protonation of 5 which either means a protonation at the  $\beta$ -carbon atom of 5 or a rearrangement of the initially formed ions *c*.

The possible reactions leading to  $[C_5H_9O_2]^+$  ions of structures *a*, *c* and *d* from 2-substituted methyl isobutyrate are shown in Scheme 1. The loss of a substituent X' from the molecular ion of 2-substituted methyl isobutyrate by a direct bond cleavage gives rise to the formation of  $\alpha$ -carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl cation *a*. However, the loss of X' may also occur after a 1,4-hydrogen migration yielding the distonic ion *b*. Loss of X' from *b* would result in the formation of *c*, which corresponds to protonated methyl methacrylate, if protonation at the carbonyl group is assumed. The formation of the distonic ion *b* may be further followed by a 1,2-shift of the protonated carbomethoxy group, hydrogen rearrangement and loss of X' to give ion *d*, which corresponds to protonated methyl crotonate. Finally, ions *a* and *c* may interconvert mutually by a 1,4-H shift.

The observation that 1 and 2 form ions *a* by electron impact dissociation while 4 gives rise to ions *d* has some implications for the energy requirements of the competing mechanisms shown in Scheme 1 for the loss of  $\alpha$ -substituents from aliphatic ester ions. Clearly the dissociation energy for  $M^{+\cdot} \rightarrow a + X'$  is below the critical energy of the rearrangement pathway  $M^{+\cdot} \rightarrow b \rightarrow d + X'$  for X = I and Br, but larger for X = CH<sub>3</sub>. X = Cl is an intermediate case, and the mixture of ions *a* and *c* may arise from the molecular ions of 3 either by competing processes  $M^{+\cdot} \rightarrow a + X'$  and  $M^{+\cdot} \rightarrow b \rightarrow c + X'$  or by an isomerization  $a \rightleftharpoons b$  after the loss of X'. In the former case the last step  $b \rightarrow d + X'$  of the rearrangement process to *d* must be the rate determining step in contrast to the assumption by Schwarz and co-workers.<sup>7</sup> In the latter case ions *a* and *c* must be separated by an energy barrier and the  $[C_5H_9O_2]^+$  ions from 3 must contain more internal energy to over-

come this barrier than the corresponding ions from 1 and 2 which do not isomerize to a similar extent. This isomerization will be discussed below.

Finally it is of interest to compare the effects of the reaction energies of the formation of the  $\alpha$ -carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl cations *a* and the formation of other  $\alpha$ -carbomethoxy carbenium ions with different substituents at the carbenium centre. The loss of substituents from ionized  $\alpha$ -substituted methyl propionates has been shown to give rise to  $\alpha$ -carbomethoxy carbenium ions only in the case of X = I while already with X = Br a mixture of ions of different structures are formed.<sup>9</sup> This reflects a decreased (thermodynamic) stabilization of the  $\alpha$ -carbomethoxy carbenium ion by only one methyl substituent. In contrast the more stable  $\alpha$ -carbomethoxy benzyl cations arise from ionized 2-substituted methyl 2-phenylpropionates even in the case of X = CH<sub>3</sub>.<sup>6a</sup>

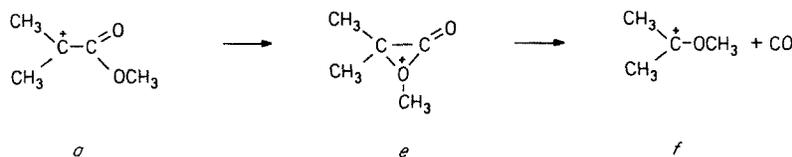
### Fragmentations and H/D-exchange of metastable $[C_5H_9O_2]^+$ ions

The spontaneous decomposition of metastable  $[C_5H_9O_2]^+$  ions formed by loss of X' from molecular ions from 1-4 under EI conditions are given in Table 3. Additionally Table 3 contains the unimolecular reactions of the isomeric metastable  $[C_5H_9O_2]^+$  ions formed by protonation of methyl methacrylate 5 and methyl crotonate 6 with CH<sub>4</sub> as CI gas. The main fragmentation reactions of metastable  $[C_5H_9O_2]^+$  ions from 1-4 and 5 are loss of CO ( $m/z$  73), elimination of methanol ( $m/z$  69) and formation of ions  $m/z$  59, respectively, while metastable  $[C_5H_9O_2]^+$  ions from 6 eliminate only methanol and no CO. The intensity variations of the fragmentations in the MIKE spectra agree very well with the formation of isomeric ions *a*, *c* and *d* from the different precursors as derived from the CA experiments. The  $[C_5H_9O_2]^+$  species predominantly arising from 1 and 2 by electron impact induced loss of I' and Br', respectively, lose CO as expected for ion *a*, the  $[C_5H_9O_2]^+$  ion mainly formed from 4 eliminates methanol as does the protonated methyl crotonate *d*, and the  $[C_5H_9O_2]^+$  ions derived from 3 and 5 are obviously a mixture of isomeric ions in which *a* and protonated methyl methacrylate *c* predominate.

The loss of CO from  $[C_5H_9O_2]^+$  ions formed by 1-4 and 5 is always associated with a very large and identical KER ( $T_{50} = 920 \pm 40$  meV, Table 3). This has been observed previously as a typical reaction for  $\alpha$ -acyl carbenium ions<sup>5,6</sup> and agrees well with the mechanism

Table 3. MIKE spectra of  $[C_5H_9O_2]^+$  ions (% relative intensity of base peak) and kinetic energy release (meV) for the loss of CO

	Precursor	-H	-CO	$T_{50}(-CO)$	-CH <sub>3</sub> OH	$m/z$ 59
1	I	2	100	878	28	29
2	Br	2	100	919	28	11
3	Cl	8	100	935	52	13
4	CH <sub>3</sub>	3	25	927	100	5
[5H] <sup>+</sup>			100	929	65	2
[6H] <sup>+</sup>		2	-	-	100	2



Scheme 2

outlined in Scheme 2, consisting of a CO elimination by a 1,2-shift of a methoxy group via a tight transition state of a large potential energy.

To get insight into the mechanisms of an isomerization between ions *a* and ions *c*, and of the hydrogen migration preceding the loss of methanol from  $[C_5H_9O_2]^+$  ions the deuterium distribution in the fragments of deuterated ions has been studied. These ions have been generated by  $Br^\cdot$  loss from **2-d<sub>3</sub>**, by deuteration of **5** during  $Cl(CD_4)$ , and by protonation of **5-d<sub>3</sub>** during  $Cl(CH_4)$ . The corresponding data are presented in Table 4 and the results will be discussed with the aid of the reactions shown in Scheme 3.

All deuterated metastable ions eliminate  $CH_3OH$  and  $CH_3OD$  although in a different ratio even after a correction for the different numbers of D-atoms within the ions. This excludes a complete scrambling of the D-labels which would be expected for an equilibration between ions *a* and *c* by many reversible 1,4-H(D) shifts.  $[5D]^+$  (one D at the carbonyl group) and  $[5-d_3H]^+$  (three D atoms at the methyl group) eliminate  $CH_3OH$  and  $CH_3OD$  in a ratio of 1:1.8 and 1:0.3, respectively, indicating that the  $H^+(D^+)$  added during the CI process is lost preferentially. Saturated aliphatic esters are protonated at the carbonyl group under CI conditions<sup>10</sup> and this has been observed also for some  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>11</sup> The alkyl-O protonated isomer *g* (Scheme 3) is an essential intermediate for the elimination of methanol. This isomer *g* is separated from the carbonyl-O protonated tautomer *c* by a large barrier<sup>12</sup> because a 1,3-shift of a proton is a symmetry forbidden reaction. However, the *PA* difference between methyl methacrylate **5** (843 kJ/mol<sup>11</sup>) and  $CH_4$  (546 kJ/mol<sup>13</sup>) is obviously large enough to generate the tautomer *g* either directly or via tautomer *c* during  $Cl(CH_4)$ . In any case the elimination of a considerable amount of  $CH_3OH$  from  $[5D]^+$  confirms an

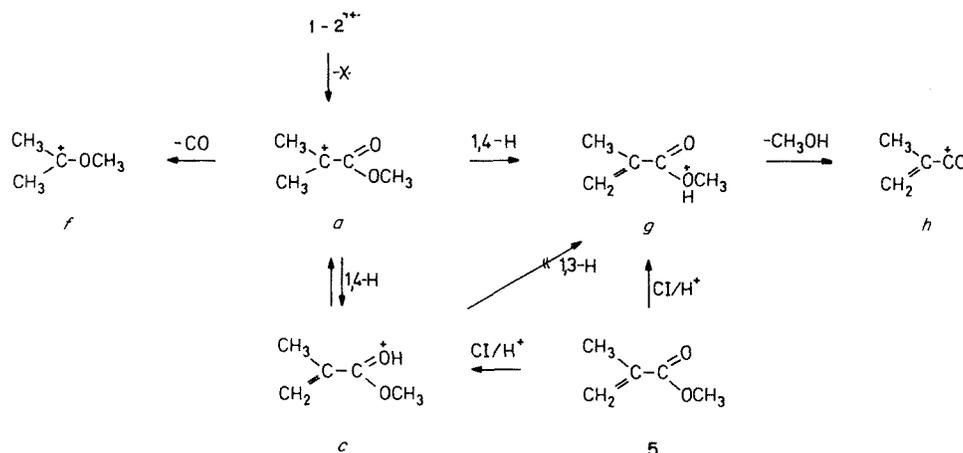
exchange of H(D) at the carbonyl group, and the methyl groups of tautomers *c* and *a*, but apparently without reaching an equilibrium distribution.

An important observation is the increase of *relative* intensity of the CO elimination in the MIKE spectra of the deuterated ions derived from **2-d<sub>3</sub>** as well as from **5** and **5-d<sub>3</sub>**. This is obviously due to an isotope effect of  $\sim 2$  on the competing elimination of methanol, which reduces the *relative* intensity of the latter reaction and which must be associated with the H(D) migration preceding the elimination. Thus the critical energies for the loss of CO and for the hydrogen migrations within the  $[C_5H_9O_2]^+$  ions eventually leading to methanol elimination have to be of similar heights.

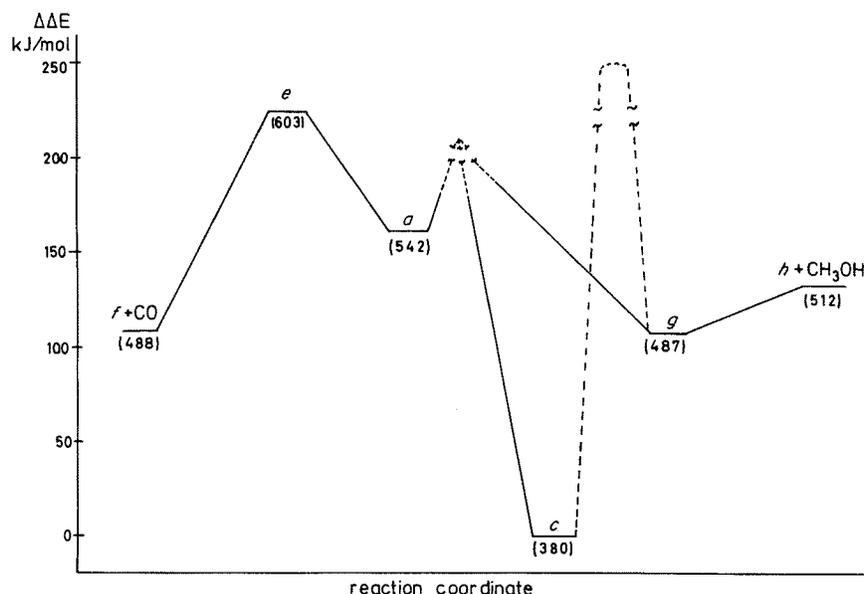
There are too many unknowns to estimate quantitatively the isotope effects and the compositions of the  $[C_5H_9O_2]^+$  ion mixtures by the isomers *a*, *c* and *g* (Scheme 3). Qualitatively, however, the data of Table 4 prove the absence of an equilibrium between ions *a* and *c* preceding the methanol elimination (compare the ratio for the loss of  $CH_3OH$  and  $CH_3OD$  for  $[C_5H_6D_3O_2]^+$  from **2-d<sub>3</sub>** and **5-d<sub>3</sub>**, respectively) and indicate that the observed isotope effect is not due to a rate determining 1,3-H shift  $c \rightarrow g$ . In the latter case one would observe no primary isotope effect in the MIKE spectrum of  $[5-d_3H]^+$ , protonated at the carbonyl group. In fact the isotope effect on the methanol elimination from metastable  $[5-d_3H]^+$  is larger than from metastable  $[5D]^+$  deuterated at the carbonyl group.

Table 4. MIKE spectra of deuterated compounds

Precursor	-CO	-CH <sub>3</sub> OH	-CH <sub>3</sub> OD	<i>m/z</i> 59	<i>m/z</i> 60	<i>m/z</i> 62
<b>2-d<sub>3</sub></b>	100	9.7	4.7	1.3	2.0	4.7
$[5D]^+$	100	14.0	25.0	5.6	9.4	-
$[5-d_3H]^+$	100	14.0	4.0	11.0	-	-



Scheme 3



**Figure 3.** MNDO reaction energy profile for the isomerization and fragmentation of ions *a* and *c*. (Values given refer to the heats of formation in kJ/mol.)

The observation that the isomerizations of ions *a*, *c* and *g* by H-shifts prior to the elimination of methanol need considerable critical energies proves that destabilized  $\alpha$ -carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl cations are distinct species within a potential energy well since the loss of CO, which is the second energetically favoured fragmentation of metastable ions *a*, has a large reverse critical energy as shown by the large KER. Figure 3 presents a schematic reaction energy profile with the heats of formation of relevant  $[\text{C}_5\text{H}_9\text{O}_2]^+$  ions calculated by MNDO.<sup>14,15</sup> Ions *c*, protonated at the C=O group, are thermodynamically more stable than the isomeric  $\alpha$ -acylcarbenium ions *a* by 162 kJ/mol, as expected. Ions *g*, protonated at the methoxy group, are 108 kJ/mol less stable than ions *c*. The loss of CO is the thermochemically most favoured fragmentation pathway and is exothermic for ions *a*. However the  $\alpha$ -lacton ion *e*, which very likely corresponds to the critical configuration of this process, imparts an activation barrier of  $\sim 160$  kJ/mol for this fragmentation. The height of critical barriers for the 1,3- and 1,4-hydrogen migrations are not known and cannot be calculated reliably by MNDO, but the barrier must be of a similar height as that for the loss of CO as indicated by the inverse isotope effect. The metastable ions *a* formed by electron impact induced loss of X from the molecular ions of 1–3 contain obviously excess energy sufficient for the elimination of CO and methanol, respectively. The protonation of the carbonyl group by  $\text{Cl}(\text{CH}_4)$  has a free enthalpy of reaction of about 300 kJ/mol. Thus ions *c* are formed also with enough excess energy to isomerize to ions *a* and to lose CO besides isomerization to ions *g* and eventually to eliminate methanol.

## CONCLUSION

The present results show that  $\alpha$ -carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl cations *a* can be formed in the gas phase by electron impact induced dissociation of  $\alpha$ -

substituted methyl isobutyrate. The spontaneous unimolecular reactions of metastable *a* are loss of CO by a 1,2-shift of the methoxy group and isomerization by H-shifts eventually followed by the elimination of methanol. Both reactions display a critical energy as shown by the large KER for the loss of CO and the isotope effects associated with the elimination of methanol. Hence the ion *a* exhibits the normal behaviour of a kinetically stable species in spite of the destabilizing  $\alpha$ -carbomethoxy substituent. However, the thermodynamic instability of this ion is clearly reflected by the limited tendency of formation from ionized 2-substituted isobutyrate. The structure *a* predominates among the  $[\text{C}_5\text{H}_9\text{O}_2]^+$  fragment ions only if the 'good leaving group' I and Br, respectively, is lost via a low energy pathway. If the dissociation energy for the loss of the substituent increases, the fragmentation of the 2-substituted isobutyrate molecular ions by rearrangement processes is preferred. Finally it has been shown that protonated methyl methacrylate *c* containing excess energy rearranges by a 1,4-H shift into the  $\alpha$ -carbomethoxy- $\alpha,\alpha$ -dimethyl-methyl cation *a* prior to decomposition.

## EXPERIMENTAL

The 70 eV mass spectra have been obtained with a MAT 311 A mass spectrometer connected to a data system SS200 at an ion source temperature of  $\approx 180^\circ\text{C}$  and by sample introduction via a heated inlet system at  $180^\circ\text{C}$ .

The MIKE and CA spectra were measured with a VG ZAB-2F mass spectrometer equipped with an EI and a CI source, respectively, using an accelerating voltage of 6 kV. The samples were introduced via a direct inlet system heated at  $120^\circ\text{C}$ . Ionization was performed either by 70 eV or by  $\text{Cl}(\text{CH}_4)$  and  $\text{Cl}(\text{CD}_4)$ , respectively, at an ion source pressure corresponding to a reading of  $\approx 0.5 \times 10^{-5}$  Pa at the ionization gauge

preceding the high vacuum pumps of the ion source housing. The mass-analysed ion kinetic energy (MIKE) spectra were obtained by focusing the relevant ions magnetically into the 2nd field-free region (2nd FFR) of the mass spectrometer and scanning the voltage across the electrostatic analyser. The CA spectra were measured in an analogous manner by introducing He as collision gas into the collision cell of the 2nd FFR at such a rate that the intensity of the main ion beam was reduced to  $\approx 30\%$  of its original value.

All compounds were purified by distillation and their structures have been verified by  $^1\text{H-NMR}$ .

2-Iodo methyl isobutyrate **1** was prepared by direct iodination of isobutyric acid in the presence of thionyl chloride,<sup>16</sup> followed by esterification with anhydrous methanol.

2-Bromo methyl isobutyrate **2** is synthesized by bromination of isobutyric acid with  $\text{P/Br}_2$  and subsequent addition of methanol to the reaction product.<sup>17</sup>

2-Chloro methyl isobutyrate **3** resulted from the reaction of isobutyryl chloride with  $\text{SO}_2\text{Cl}_2$ ,<sup>18</sup> followed by esterification in the usual manner.

Methyl pivaloate **4** has been obtained from the corre-

sponding acid by preparing the acid chloride and subsequent reaction with methanol.

The syntheses of the 2-trideuteromethyl 2-bromo methyl propionate **2-d<sub>3</sub>** was achieved in the same manner as for the unlabelled compound. The 2-trideuteromethyl propionic acid was prepared by alkylation of methyl diethylmalonate with  $\text{CD}_3\text{I}$  and  $\text{NaH}$  as base using standard methods of organic chemistry.

Methyl 3,3,3-trideuteromethacrylate **5-d<sub>3</sub>** results from elimination of  $\text{HBr}$  from the bromo derivate **2-d<sub>3</sub>** using DABCO as base besides 10% of **5-d<sub>2</sub>**.

Methyl methacrylate **5** was commercially available. Methyl crotonate **6** was prepared from the corresponding acid by esterification with methanol and hydrosulphuric acid by standard procedures.

### Acknowledgements

The financial support of this work by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Mr E. Gärtner, Universität Bielefeld, for his technical assistance of the mass spectrometric measurements.

### REFERENCES

- (a) P. G. Gassman and T. T. Tidwell, *Acc. Chem. Res.* **12**, 279 (1983). (b) T. T. Tidwell, *Angew. Chem.* **96**, 16 (1984). (c) J. P. Begue and M. Charpentier-Morize, *Acc. Chem. Res.* **13**, 207 (1984). (d) X. Creary, *J. Am. Chem. Soc.* **106**, 5568 (1984).
- R. H. Nobes, W. J. Bouma and L. Radom, *J. Am. Chem. Soc.* **105**, 309 (1983).
- M. H. Lien and H. C. Hopkinson, *J. Am. Chem. Soc.* **110**, 3788 (1988).
- M. A. Fox and R. C. Owen, *J. Am. Chem. Soc.* **102**, 6562 (1980).
- (a) H.-Fr. Grützmaier and A.-M. Dommröse, *Org. Mass Spectrom.* **18**, 601 (1983). (b) A.-M. Dommröse and H.-Fr. Grützmaier, *Org. Mass Spectrom.* **22**, 437 (1987). (c) A.-M. Dommröse, R. Wolf and H.-Fr. Grützmaier, *Int. J. Mass Spectrom. Ion Proc.*, **76**, 95 (1987).
- (a) R. Wolf, A.-M. Dommröse and H.-Fr. Grützmaier, *Org. Mass Spectrom.* **23**, 26 (1988). (b) H.-Fr. Grützmaier and R. Wolf, *New. J. Chem.* **12**, 865 (1988).
- T. Weiske, H. Halim and H. Schwarz, *Chem. Ber.* **118**, 495 (1985); and references cited therein.
- S. G. Lias, J. F. Liebman and R. L. Levin, *J. Phys. Chem. Ref. Data*, **13**, 695 (1984).
- P. C. Burgers, J. L. Holmes, F. P. Lossing, F. R. Povel and J. K. Terlouw, *Org. Mass Spectrom.* **18**, 335 (1983).
- (a) A. G. Harrison and H. I. Ichikawa, *Org. Mass Spectrom.* **19**, 394 (1984). (b) A. G. Harrison, *Can. J. Chem.* **59**, 2133 (1981).
- R. Wolf and H.-Fr. Grützmaier, 21. Diskussionstagung der AGMS, Würzburg, Germany, 1988; to be published.
- (a) M. A. Winnik, *Org. Mass Spectrom.* **9**, 920 (1974). (b) B. van Baar, H. Halim, J. K. Terlouw and H. Schwarz, *J. Chem. Soc., Chem. Commun.* 728 (1986).
- see A. G. Harrison, *Chemical Ionization Mass Spectrometry*, CRC Press, (1983), Chapt. 4.
- MNDO; W. Thiel, *OCPE* **4**, 397 (1979).
- For a discussion of the possible systematic errors of  $\Delta\text{H}_f$  calculated by MNDO see H. Halim, N. Heinrich, W. Kock, J. Schmidt and G. Frenking, *J. Comp. Chem.* **7**, 93 (1986). In spite of these possible errors the MNDO reaction energy profiles are still useful for the discussion of the *experimental* data for reactions of large organic ions.
- D. M. Harp, L. Q. Bao, C. J. Black, J. G. Gleason and R. A. Smith, *J. Org. Chem.* **40**, 3420 (1975).
- Houben-Weyl, Vol. 5/4, 4th Edition, p. 200 (1962).
- Houben-Weyl, Vol. 5/3, 4th Edition, p. 877 (1962).