JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 3, 301–308 (1990)

DESTABILIZED CARBENIUM IONS: α-CARBAMOYL-α,α-DIMETHYLMETHYL CATIONS

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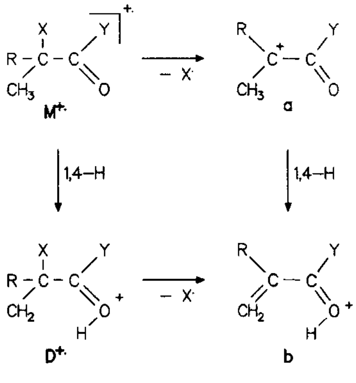
The formation and unimolecular reactions of the especially electron-deficient α-carbamoyl carbenium ions $[(CH_3)_2CCONH_2]^+$ (a_1) and $[(CH_3)_2CCON(CH_3)_2]^+$ (a_2) have been studied by mass spectrometric techniques. The ions a are formed by electron impact-induced dissociation from the relevant isobutyric amides α-substituted by I, Br and Cl, respectively, but the carbonyl protonated methacrylamides b_1 and b_2 are cogenerated. A similar mixture of ions a and b is obtained by CI(CH_4) of the corresponding methacyrlamides. The metastable ions decompose by the loss of CO exhibiting in particular a large kinetic energy release (KER) and by the elimination of NH_3 and $HN(CH_3)_2$, respectively. It is shown that isomeric ions of structures a and b interconvert prior to decomposition and that the energy barrier separating the isomeric ions is small. Hence the kinetic stability of the tertiary α-carbamoyl-α,α-dimethylmethylcations is reduced compared with other types of α-acyl carbenium ions. This effect can be attributed to the increased proton affinity of the amide group.

INTRODUCTION

Recently, destabilized carbenium ions carrying an electron-withdrawing substituent at the positive centre have been the object of many experimental and theoretical studies.[1] In particular, the subgroup of the α-acyl carbenium ions $^+CR_2COY$($Y = H, H_3C, HO, RO, R_2N$) has found much interest,[2] and there is an ongoing debate about the importance of the π-conjugative electron donation of these acyl substituents as opposed to their σ-withdrawing effect and about the carbonyl oxygen participation during solvolysis. In this connection, the investigation of destabilized carbenium ions in the gas phase by mass spectrometric techniques can give valuable additional information about the properties of these species in the absence of any stabilizing effects by solvation. We have shown in a systematic study of the properties of α-acyl carbenium ions that tertiary α-acyl carbenium ions[3] ($R = CH_3$) and benzylic α-acyl carbenium ions[4] ($R = C_6H_5$) with keto and ester groups, respectively, ($Y = H_3CCO, C_6H_5CO, H_3COCO$) as the destabilizing substituent are kinetically stable species in the gas phase, in contrast to the behaviour of the α-formyl methyl cation[5] and of primary α-acyl carbenium ions.[3a]

The α-acyl carbenium ions **a** were formed mass spectrometrically most conveniently by an electron impact-induced dissociation of a suitable α-substituent of the precursor molecule (Scheme 1) and were identified with tandem mass spectrometry[6] by their unique mass spectra obtained after collisional activation (CA spectra). The typical unimolecular reaction of these α-acetyl-, α-benzoyl and α-carbomethoxy carbenium ions corresponds to a 1,2-shift of Y and conconmitant loss of a CO molecule to form stable $^+CR_2Y$ ions. This reaction is accompanied by a very large and non-statistical kinetic energy release (KER) reflecting the gain in potential energy of the system by the increased stability of the product ions. A second reaction observed for the α-acyl carbenium ions with a CH_3 substituent at the carbenium centre is a rearrangement



Scheme 1

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0894–3230/90/050301–08$05.00

Received 16 May 1989
Revised 18 December 1989

by a 1,4-proton shift to the thermodynamically much more stable isomer **b** with the structure of a protonated α,β-unsaturated carbonyl compound (Scheme 1). Both spontaneous reactions of the gaseous α-acyl carbenium ions exhibit some analogies to the solution chemistry of these species, although the main reaction is usually the trapping of the ions by the nucleophilic solvent.[1] Nonetheless, rearrangements (1,2-shifts in **a**) and eliminations (deprotonation of **b**) are observed during the solvolysis in non-nucleophilic solvents.[2d,h]

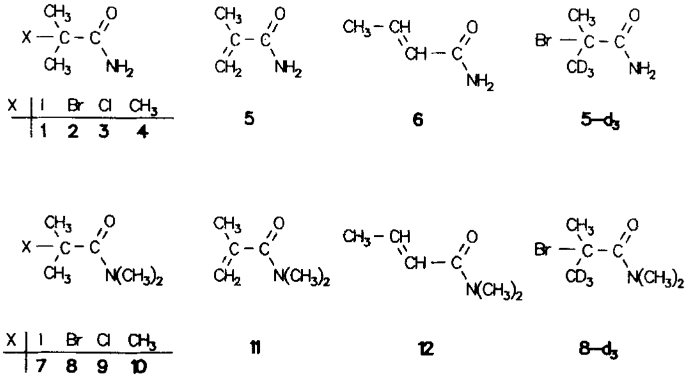
However, in the mass spectrometer the stable fragment ion **b** may be formed directly from the molecular ion $M^{+\cdot}$ if a 1,4-hydrogen shift precedes the loss of the α-substituent; a reaction which was observed for some carbonyl compounds[7] and which is explained by the exceptional stability of the intermediary ion $D^{+\cdot}$ representing a distonic ion[8] in which the charge and the radical site are localized separately in different parts of the species. The competition between fragmentation of the molecular ions $M^{+\cdot}$ straight into the α-acyl carbenium ion **a** and via the distonic ion $D^{+\cdot}$ into the more stable ion **b** depends crucially on the relationship between the dissociation energy of the α-substituent and the activation energy of the 1,4-H shift to the distonic ion $D^{+\cdot}$. The latter energy will be expected to decrease with an increasing basicity (or proton affinity, PA) of the COY group which is the terminus of the hydrogen migration. The activation energy of the 1,4-proton shift **a** → **b** is similarly affected by the PA of the group COY. Hence the tendency of formation of the α-acyl carbenium ions **a** and their kinetic stability in the gas phase is a function of the capability of COY to accept a proton and therefore should decrease in the series $YCO = RCO > CH_3OCO > H_2NCO > (CH_3)_2NCO$. Recently we have shown that tertiary α-carbamoyl benzyl cations are still stable species in the gas phase,[9] in spite of the increased PA of the amide group. This may be due to the extraordinary stability of benzyl cations outweighing the destabilizing effect of the carbamoyl substituents. Here we report on the formation and on the unimolecular reactions of tertiary α-carbamoyl-α,α-dimethylmethyl cations ($R = H_3C$, $Y = H_2N$ and $(H_3C)_2N$, respectively) lacking the benzylic stabilization. In the first part the formation of the relevant ions in the mass spectrometer and their structure(s) as determined by the CA spectra will be discussed, followed by the results of an investigation of the interconversion **a** $\leftrightharpoons$ **b** by deuterium labelling.

RESULTS AND DISCUSSION

Structures of isomeric $[C_3H_6CONH_2]^+$ and $[C_3H_6CON(CH_3)_2]^+$

Ions of the expected structure $\mathbf{a_1}$ (Scheme 1, $R = CH_3$, $Y = CONH_2$) and $\mathbf{a_2}$ [$R = CH_3$, $Y = CON(CH_3)_2$], will conceivably arise from the molecular ions of the α-substituted primary amides **1**–**4** and of the tertiary amides **7**–**10** (Scheme 2), respectively. $[C_3H_6CONH_2]^+$ ions $\mathbf{b_1}$ and $\mathbf{c_1}$ isomeric with $\mathbf{a_1}$ can be independently generated from methacrylamide **5** and crotonamide **6** by protonation in a chemical ionization (CI) experiment. Similarly, the ions $\mathbf{b_2}$ and $\mathbf{c_2}$ arise from the corresponding *N,N*-dimethylamides **11** and **12** under these conditions. These isomeric ions of type **b** and **c** would arise from the corresponding α-substituted amides by a preceding 1,4-H shift and by a 1,4-H shift followed by a skeletal rearrangement,[7] respectively.

The partial mass spectra shown in Table 1 reveal that the loss of the α-substituent gives rise to the base peak in the spectra of the primary amides **1** (X = I) and **2** X = Br) and is still an important fragmentation in the case of the chloroamide **3**, whereas the loss of an α-methyl group is only a minor process in the 70-eV mass spectrum of **4**. This shows conclusively the effect of an increasing activation energy for the loss of the α-substituent due to an increasing dissociation energy of the C—X bond. Note however, that this influence of the dissociation energy has to be expected for a direct dissociation to **a** (Scheme 1) as well as for the formation



Scheme 2

Table 1. Partial EI-mass spectra (70 eV) of the amides **1**–**4** and **7**–**10** (relative intensity as % of base peak)

Compound	$M^{+\cdot}$	$[M-X]^+$	$[M-X-CO]^+$	$(CH_3)_2C^+X$	R_2NCO^+	$[C_3H_5]^+$
$(CH_3)_2C(X)CONH_2$:						
1, X = I	1.5	100	32	2	37	49
2, X = Cl	5.5	100	12	31	80	15
3, X = Br	2.5	49	10	51	100	54
4, $X = CH_3$	18	6	7	14	100	50
$(CH_3)_2C(X)CON(CH_3)_2$:						
7, X = I	2.5	92	60	9	78	100
8, X = Br	5.0	8	5	5	100	16
9, X = Cl	7.0	8	5	4	100	2
10, $X = CH_3$	29	7	5	62	100	24

of **b** if in the latter case the 1,4-shift is *not* rate determining as supposed.[7a,b] In the case of the *N,N*-dimethylamides **7**–**10** an intense peak due to the loss of the α-substituent is only observed in the 70-eV mass spectrum of the iodide **7** and the main process in all spectra is the formation of $^+CON(CH_3)_2$ ions, *m/z* 72, by the usual α-cleavage. Nevertheless, the more selectively reacting metastable molecular ions of **1**–**3** and **7**–**9** investigated by mass analysed ion kinetic energy (MIKE) spectroscopy[10,11] decompose exclusively by loss of the α-substituent. Thus, under low-energy conditions, this is the energetically most favourable reaction path of the molecular ions of the halogenated amides.

The structural information about these fragment ions is obtained by comparing their CA spectra with those of the protonated unsaturated amides **5**, **6**, **11** and **12**, respectively. The CA spectra of the $[C_3H_6CONH_2]^+$ ions are summarized in Figure 1. The spectra of the ions derived from the α-substituted amides **1**–**4** are similar with the exception of an additional signal of ions $C_3H_7^+$ at *m/z* 43 in the spectrum of the bromo derivative **3**. It is not known where the propyl cations come from, but they do not interfere with the structure elucidation of the other ions {the CA spectrum of $[C_3H_6CONH_2]^+$ ions formed from protonated **2** (same batch!) by HBr loss during CI is lacking these ions of *m/z* 43 but otherwise identical with that in Figure 1}. The characteristic features of these CA spectra are a peak at *m/z* 85 (loss of H) and *m/z* 69 (loss of NH_3) and a broad dish-topped peak *m/z* 58 (loss of CO). However, the intensities of these signals differ in the individual spectra, in particular the relative intensity of the peak at *m/z* 69 is increasing and that at *m/z* 58 is decreasing in the sequence **1**–**4**, i.e. with an increasing activation energy for a direct loss of the α-substituent. Exceptional within this series is also the maximum of the peak intensity at *m/z* 85 in the spectrum of the ions derived from the chloro derivative **3**. These intensity differences in the CA spectra of the $[C_3H_6CONH_2]^+$ ions derived from **1**–**4** give evidence unequivocally that these spectra are due to at least three structurally different ions and that these isomeric ions are formed in very different amounts from the individual precursors.

A comparison with the CA spectra (Figure 1) of the protonated methacrylamide **5H**$^+$ and crotonamide **6H**$^+$, respectively, shows that the ions $\mathbf{c}_1$ do not lose CO but primarily NH_3 on collisional activation. Hence the large signal at *m/z* 69 and the small signal at *m/z* 58 in the CA spectrum of the ions generated by loss of CH_3 for $\mathbf{4}^{+\cdot}$ are suggestive of a preponderance of ions $\mathbf{c}_1$ also in this case. This would be expected if the $[C_3H_6CONH_2]^+$ ions arise from the molecular ions by a 1,4-H shift and subsequent skeletal rearrangement.[7] Obviously, the activation energy for the loss of CH_3 and the formation of the destabilized ion $\mathbf{a}_1$ is too large to compete with the rearrangement pathway resulting eventually in a very stable fragment ion (Scheme 3).

Surprisingly, the CA spectrum of **5H**$^+$ is interchangeable with that of the $[C_3H_6CONH_2]^+$ ions from **3** and very similar to the spectrum obtained from **2** (for *m/z* 43, see above), although protonation of **5** should give rise only to ions $\mathbf{b}_1$. All spectra, however, exhibit a broad and dished peak of moderate intensity for the loss of CO which is expected for the destabilized α-acyl carbenium ions $\mathbf{a}_1$. Hence these CA spectra represent not exclusively ions b_1 but also an admixture of ions $\mathbf{a}_1$. In line with this is the increased intensity for the CO loss in the CA spectra of the iodo derivative **1**; the facile loss of the α-iodo substituent from $\mathbf{1}^{+\cdot}$ increases the concentration of $\mathbf{a}_1$ within the mixture of isomeric $[C_3H_6COCH_2]^+$ ions.

The same results with respect to the generation and structures of the ions $\mathbf{a}_2$, $\mathbf{b}_2$ and $\mathbf{c}_2$ are deduced from the CA spectra of the $[C_3H_6CON(CH_3)_2]^+$ ions formed from **7**–**12** (Figure 2). Again, the characteristic features of the CA spectrum of ions $\mathbf{c}_2$ generated by protonation of **12**, i.e. a large peak due to the loss of $(CH_3)_2NH)$, an additional peak at *m/z* 46 and the absence of a signal for the loss of H, are found in the CA spectrum of the ions derived from $\mathbf{10}^{+\cdot}$. This confirms excessive rearrangements accompanying the elimination of the α-methyl substituent.[7] The relatively small intensity of the broad peak for the loss of CO indicates the admixture

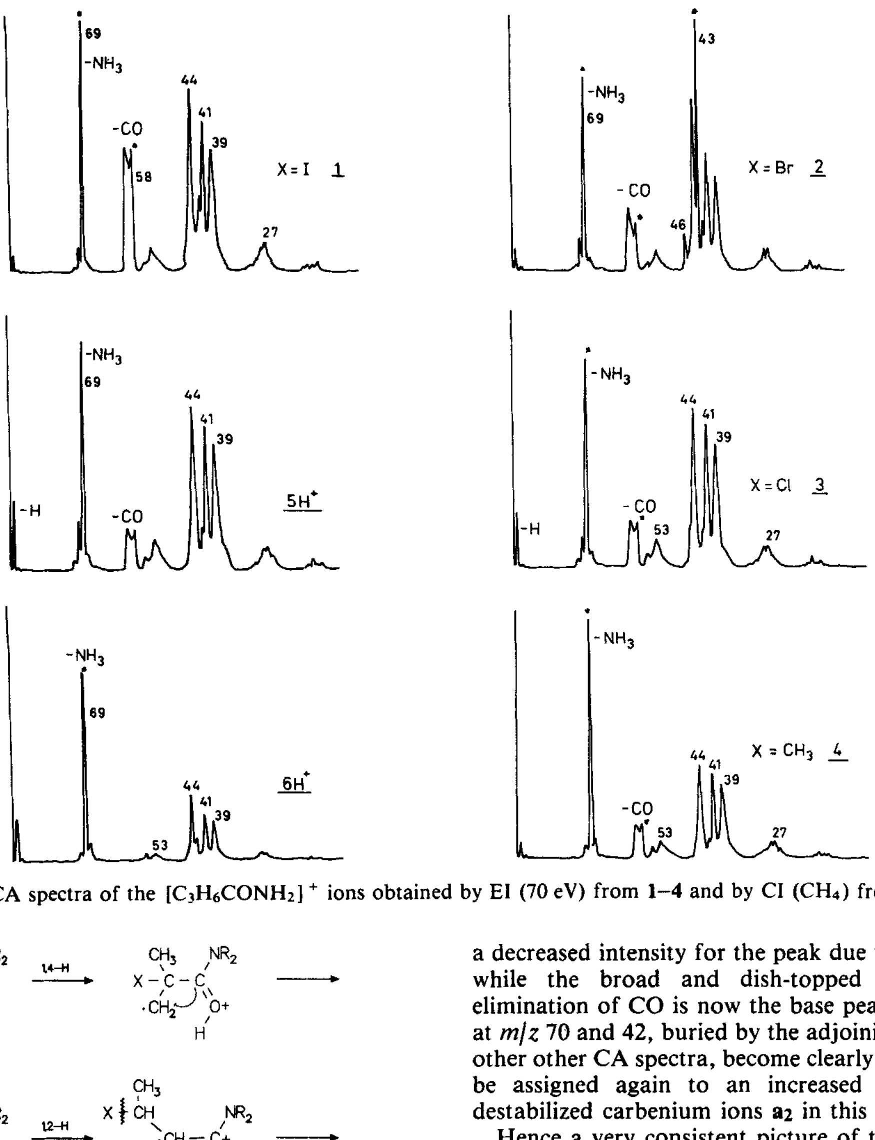
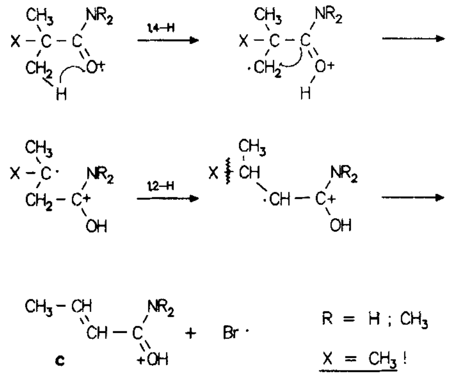


Figure 1. CA spectra of the $[C_3H_6CONH_2]^+$ ions obtained by EI (70 eV) from **1**–**4** and by CI (CH_4) from **5** and **6**



Scheme 3

of only a small amount of ions **a₂**. The CA spectra of the $[C_3H_6CO(NCH_3)_2]^+$ ions obtained from **8**, **9** and **11** are superimposable, obviously representing identical mixtures of the ions **a₂** and **b₂**. The CA spectrum of ions generated by the facile loss of I˙ from $7^{+\cdot}$ exhibits a decreased intensity for the peak due to the loss of H, while the broad and dish-topped signal for the elimination of CO is now the base peak and the peaks at *m*/*z* 70 and 42, buried by the adjoining signals in the other other CA spectra, become clearly visible. This can be assigned again to an increased amount of the destabilized carbenium ions **a₂** in this mixture.

Hence a very consistent picture of the formation of ions **a**, **b** and **c** arises from these results. Firstly, the large activation energy necessary for a direct loss of an α-methyl group obstructs the formation of the α-carbamoyl carbenium ion **a** and favours the formation of the stable isomer **c** by an initial 1,4-H shift followed by a skeletal rearrangement (Scheme 3). Secondly, and in contrast, the small dissociation energy of the C—I bond opens the reaction path for a direct generation of ion **a** for $1^{+\cdot}$ and $7^{+\cdot}$, respectively, and this can be detected by a characteristic elimination of CO from the fragment ions. However, ions of structure **b** are cogenerated, and obviously their contribution increases with the activation energy for the loss of the α-substituent in the series **1**, **2** and **3** and **7**, **8** and **9**,

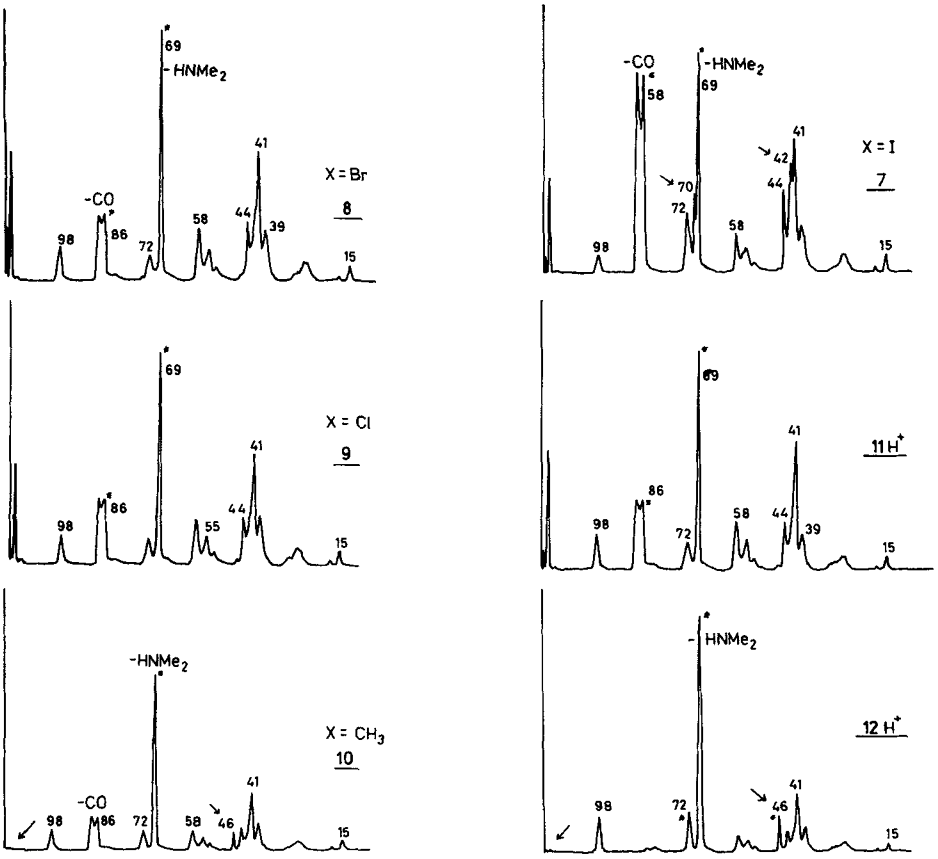


Figure 2. CA spectra of the $[C_3H_6CON(CH_3)_2]^+$ ions obtained by EI (70 eV) from **7**–**10** and by CI (CH_4) from **11** and **12**

respectively. Hence there is a close analogy between the formation of the α-carbamoyl-α, α-dimethylmethyl cations from the appropriate precursors and of the corresponding α-carbamoylbenzyl cations[9] and even of the tertiary α-carbomethoxy carbenium ions.[3c]

Unimolecular reactions of $[C_3H_6CONH_2]^+$ and $[C_3H_6CON(CH_3)_2]^+$

By definition, a kinetically stable species is separated from its isomers and the products of its spontaneous fragmentations by energy barriers corresponding to the activation energies of the reactions. For gaseous ions the energetically most favourable spontaneous decompositions determining the kinetic stability can be most conveniently explored by MIKE spectrometry.[11] The $[C_3H_6CONH_2]^+$ (Table 2) and $[C_3H_6CON(CH_3)_2]^+$ (Table 3) ions fragment metastably by loss of CO and elimination of NH_3 and $HN(CH_3)_2$, respectively.

The CO loss occurs by 1,2-shift of the NH_2 and $N(CH_3)_2$, respectively, and is associated with an extraordinary large KER, exceeding even that observed for the same fragmentation of α-carbamoylbenzyl cations.[9] Undoubtedly, the energy released reflects the large gain in potential energy by the formation of the very stable tertiary immonium ion by this rearrangement reaction of ions **a**$_1$ and **a**$_2$ (Scheme 4), but the non-statistical distribution identified by the broad and strongly dish-topped peak shape (see Figures 1 and 2) proves the existence of an extra energy barrier[12]

Table 2. MIKE spectra of $[C_3H_6CONH_2]^+$ ions (relative intensity as % of base peak)

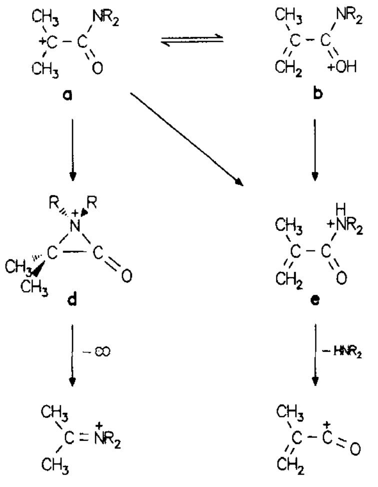
Precursor	Ionization	m/z 69 —NH_3	m/z 58 —CO	T_{50} (kJ mol^{+1})	m/z 43
1	EI, 70 eV	100	30	1090	3
2	EI, 70 eV	100	20	990[a]	335
3	EI, 70 eV	100	28	1025	2
5	CI (CH_4)	100	23	1085	—
6	CI (CH_4)	100	—	—	—

[a] Composite peak due to an additional sharp signal at m/z 59.

Table 3. MIKE spectra of $[C_3H_6CON(CH_3)_2]^+$ ions (relative intensity as % of base peak)

Precursor	Ionization	m/z 86 —CO	T_{50} (kJ mol^{-1})	m/z 69 —$HN(CH_3)_2$	m/z 46
7	EI, 70 eV	56	910	100	—
8	EI, 70 eV	28	1010	100	—
9	EI, 70 eV	27	1000	100	—
11	CI (CH_4)	31	990	100	—
12	CI (CH_4)	—	—	100	69

[a] Additional signals at m/z 39 (2%), 41 (6%) and 70 (4%).



Scheme 4

and of a tight transition state in accord with the α-lactam structure depicted in Scheme 4. Hence there is no doubt that the ground-state ions **a₁** and **a₂** are kinetically stable with respect to the rearrangement and the loss of CO, in line with the behaviour of α-carbamoylbenzyl cations[9] and of other α-acyl carbenium ions.[3,4]

However, the situation is less clear for the second process in the MIKE spectra, i.e. the elimination of NH_3 and $HN(CH_3)$. The elimination requires a hydrogen migration, and *a priori* one would expect protonated amide structures similar to **b₁** and **b₂** as precursors. The $[C_3H_6CONH_2]^+$ and $[C_3H_6CON(CH_3)_2]^+$ ions generated by electron impact-induced dissociation of **1**–**3** and **7**–**9** are mixtures of **a₁** and **b₁** and of **a₂** and **b₂**, respectively, which may arise either by a preceding rearrangement of the molecular ions or by a subsequent 1,4-H shift within the fragment ions (see Scheme 1). Although the former cannot be excluded entirely, the latter is conclusively shown by the identical or very similar ion mixtures obtained via a protonation of the α,β-unsaturated amides **5** and **11**. Then, the variation in the compositions of the ion mixtures are attributed to a variation of the internal energy of equilibrating ions **a₁** and **b₁** or **a₂** and **b₂** with the dissociation energy of the α-substituent of the molecular ions making an energy barrier between these ions questionable. Thus, in spite of the fact that the total amine elimination reaction of the metastable ions must possess an activation energy similar to that of the competing CO loss,[13] the aliphatic α-carbamoyl carbenium ions **a** may not be kinetically stable in the gas phase because of easy isomerization into the stable isomers **b** prior to their spontaneous reactions observed in the MIKE spectra. Clearly, this would be an effect of the increased PA of the amide group.

The interconversion between ions of structure **a** and **b** has been further examined using the deuterated bromides **2**-d_3 and **8**-d_3 (Scheme 2), and by the deuteronation of the unsaturated amides **5** and **11** in the gas phase by CI(CD_4). The results are given in Table 4.

In all cases, the interconversion between ions **a** and **b** results in the elimination of NH_3 and NH_2D and $HN(CH_3)_2$ and $DN(CH_3)_2$, respectively. Note that no elimination of NHD_2 is observed for **2**-d_3, so at least the H/D migration onto the N atom of the $CONH_2$ group is not reversible. The direct deuteriation of the amide group at the N atom[13] would also explain the increased loss of NH_2D and $DN(CH_3)_2$, respectively, in the CI(CD_4) experiment with **5** and **11** (saturated amides[13] and α,β-unsaturated amides[14] are protonated in the gas phase preferentially at the carbonyl O atom. However, the high gas-phase acidity of CH_5^+ (CD_5^+) allows also at least some *N*-protonation). In the case of the α-carbomethoxy carbenium ions[3c,4b] and the α-carbamoylbenzyl cations,[9] the energy barrier of the isomerization has been detected by isotope effects operating on the elimination reaction in the deuterated ions and increasing the relative intensity of the CO loss in the MIKE spectra. A similar effect is seen in the MIKE spectrum of **2**-d_3 (Table 4) exhibiting an increase of the relative intensity of the CO loss from 20 to 28% (note that there is also an isotope effect on the

Table 4. Comparison of the MIKE spectra of some deuterated and undeuterated ions **a** and **b**

Precursor	Ionization	− CO	− NH_3	− NH_2D
2	EI, 70 eV	20	80	—
2-d_3	EI, 70 eV	38	43	19
5	CI (CH_4)	23	77	—
5	CI(CD_4)	26	34	40
		− CO	− $NH(CH_3)_2$	− $DN(CH_3)_2$
8	EI, 70 eV	28	72	—
8-d_3	EI, 70 eV	29	41	30
11	CI (CH_4)	31	69	—
11	CI (CD_4)	32	21	47

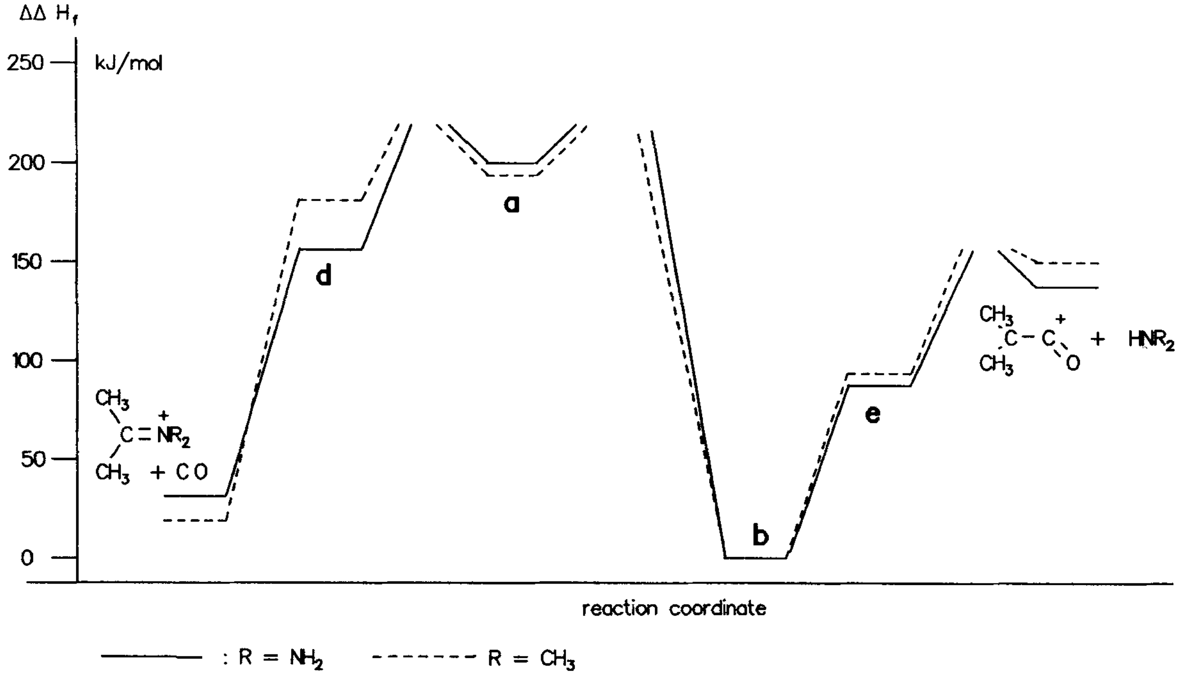


Figure 3. Schematic reaction energy profile of the unimolecular reactions of the $[C_3H_6CONH_2]^+$ and $[C_3H_6CON(CH_3)_2]^+$ ions

elimination of ammonia and dimethylamine, respectively, in the MIKE spectra of **2**-d_3 and **8**-d_3. $k_H/k_D = 2{\cdot}2$ and $1{\cdot}35$ are calculated assuming irreversible *N*-protonation). This is distinctly less than the effect observed for the α-carbamoylbenzyl cation.[9] Moreover, no increase in the relative intensity for the CO loss is noticed in the MIKE spectrum of **8**-d_3 (Table 4). Consequently, and in contrast with the α-carbamoylbenzyl cations, the energy barrier separating the isomeric ions **a** and **b** is distinctly below the activation energies of the spontaneous fragmentations of ions $\mathbf{a_1}$ and of no importance for the ions $\mathbf{a_2}$. This result demonstrates unequivocally the decreased kinetic stability of the tertiary aliphatic α-carbamoyl carbenium ions vs the corresponding benzyl cations and the effect of an increasing PA of the amide group on the barrier of the 1,4-H shift converting the destabilized α-carbamoyl carbenium ions into the stable protonated α,β-unsaturated amides **b**.

The experimental results of the study of the fragmentations and isomerizations of the $[C_3H_6CONH_2]^+$ and $[C_3H_6CON(CH_3)_2]^+$ ions, respectively, of structures **a** and **b** have been supported by a MNDO[15] calculation of the ΔH_f of the relevant ions. The results are shown in the schematic reaction energy profile of Figure 3, in which the ΔH_f's have been normalized to the ΔH_f of the most stable isomer $\mathbf{b_1}$ and $\mathbf{b_2}$, respectively ($\Delta H_f(\mathbf{b_1}) = 527\ \mathrm{kJ\,mol^{-1}}$ and $\Delta H_f(\mathbf{b_2}) = 541\ \mathrm{kJ\,mol^{-1}}$ by MNDO). The experimental ΔH_f of **5** and **11** are not known. 'Semi-experimental' values of 509 and $514\ \mathrm{kJ\,mol^{-1}}$ for $\mathbf{b_1}$ and $\mathbf{b_2}$, respectively, have been obtained from the PA (**5**, $878\ \mathrm{kJ\,mol^{-1}}$, **11**, $907\ \mathrm{kJ\,mol^{-1}}$, ref. 13) and the ΔH_f values (**5**, $-134\ \mathrm{kJ\,mol^{-1}}$; **11**, $-106\ \mathrm{kJ\,mol^{-1}}$, both by MNDO). The exothermic fragmentation of **a** by loss of CO is expected, but by MNDO the α-lactam structure **d** is more stable than **a**. This is very likely an artefact of MNDO which gives too small ΔH_f values for cyclic structures[16] and which is not seen for the corresponding benzyl cations.[9] Another unique feature is an exothermic elimination of NH_3 and $HN(CH_3)_2$ from $\mathbf{a_1}$ and $\mathbf{a_2}$, respectively, again not observed in the case of the α-carbamoylbenzyl cations[9] and for the corresponding reactions of other α-acyl carbenium ions.[3,4] The activation energies for the unimolecular fragmentations cannot be obtained reliably by MNDO, but the low ΔH_f values of **d** and in particular of **b** and **e** and the exothermic amine elimination indicate that the energy barriers surrounding the potential energy well of $\mathbf{a_1}$ and $\mathbf{a_2}$ cannot be high.

EXPERIMENTAL

Materials. The primary amides **1**–**6** were prepared by the reaction of the corresponding carboxylic acid chlorides with aqueous ammonia (25%) at −10 °C.[17] The reaction of a solution of these acid chlorides in dichloroethane with $HN(CH_3)_2.HCl$ in aqueous NaOH

(20%) at −10 °C yielded the tertiary amides **7–12**.[18] 2-Iodoisobutyric acid was obtained by a direct iodination of isobutyric acid in the presence of $SOCl_2$.[19] 2-Bromoisobutyric acid was synthesized by the reaction of isobutyric acid with $P-Br_2$ and 2-chloroisobutyric acid was obtained by the treatment of isobutyric acid with SO_2Cl_2 as described.[20] The other acid chlorides were prepared by standard techniques of organic chemistry.

All amides were purified by column chromatography and their structures were verified by ^1H NMR, spectroscopy.

Mass spectrometry. The EI mass spectra were obtained with a MAT 311A mass spectrometer combined with a SS200 data system under the following conditions: electron energy 70 eV, electron emission 2 mA, accelerating voltage 3 kV and ion source temperature *ca* 200 °C. Solid samples were introduced by the direct inlet probe and liquid samples by the HTE-leak system at 180 °C.

The MIKE and CA spectra were measured on a VG ZAB 2F mass spectrometer using either EI or CI. EI was performed at an electron energy of 70 eV, an electron trap current of 100 μA an acceleration voltage of 6 kV and an ion source temperature of *ca* 200 °C. Solid samples were introduced by the direct heated inlet probe and samples of a sufficiently high vapour pressure by a direct heated inlet system with a variable leak at 120 °C. The CI experiments were performed by introducing CH_4 or CD_4 until a pressure of *ca* 10^{-5} Torr was attained, measured at the ionization gauge at the pump exit of the ion source housing, and by using 100-eV electrons for primary ionization and an accelerating voltage of 6 kV. For the measurement of the MIKE and CA spectra the relevant ions were magnetically focused into the first field-free region and the reaction products were analysed by scanning the deflecting voltage of the electrostatic analyser. Collisional activation was achieved by the introduction of He into the collision cell of the first field-free region at a rate such that the intensity of the main beam had dropped to about 30%.

ACKNOWLEDGEMENTS

The support of this work by a grant from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank the Fond der Chemischen Industrie for additional financial support.

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