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Low-energy, Low-temperature Mass Spectra

10—Urethanes[1]

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The 12.1 eV, 75 °C electron impact mass spectra of 24 urethanes, $RNHCO_2C_2H_5$ [R = H, C_nH_{2n+1} (n = 1–8), $CH_2{=}CHCH_2$, Ph, $PhCH_2$ and $PhCH_2CH_2$], and seven symmetrically disubstituted urethanes $R_2NCO_2C_2H_5$ (R = C_nH_{2n+1} (n = 1–4)) are reported and discussed. All 31 spectra show appreciable molecular ion peaks. For n-C_nH_{2n+1} $NHCO_2C_2H_5$, $M^{+\cdot}$ usually is the most abundant ion in the spectrum. A peak at m/z 102 of comparable intensity also is present; this corresponds to formal cleavage of the bond connecting the α- and β-carbon atoms in the *N*-alkyl group, though it is unlikely that the daughter ion has the structure $[CH_2{=}NHCO_2C_2H_5]^+$. In the $RNHCO_2C_2H_5$ series, branching at the α-carbon atom enhances the relative abundance of the ion arising by notional α-cleavage at the expense of that of $M^{+\cdot}$. Formal cleavage of the bond between β- and γ-carbon atoms occurs to some extent for $[RNHCO_2C_2H_5]^{+\cdot}$ ions; this reaction provides information on the degree of branching at the β-carbon, especially if metastable molecular ions are considered. The higher n-$C_nH_{2n+1}NHCO_2C_2H_5$ (n = 5–8) urethanes exhibit two other significant ions in their mass spectra. First, there is a peak at $[M - C_2H_5]^+$. Secondly, a peak is present at m/z 90; the most plausible structure for this ion is $[H_2N(HO)COC_2H_5]^+$, arising by double hydrogen transfer from the alkyl group and expulsion of a $[C_nH_{2n-1}]^\cdot$ radical. Ions originating from secondary decomposition of the primary ionic species are generally of only very low abundance in these spectra.

INTRODUCTION

Recent work[1] has emphasized the advantages of low-energy, low-temperature electron impact (EI) mass spectra over their conventional 70 eV counterparts.[2] In particular, the relatively low abundance of ions arising from secondary decomposition of the primary daughter ions, taken together with the higher relative intensity of the molecular ion peak, results in simpler spectra which are easier to interpret than those recorded at 70 eV. Moreover, the relative abundances of analytically useful and mechanistically interesting ions formed by rearrangement reactions are often increased in the low-voltage spectra.

This paper reports the 12.1 eV, 75 °C EI spectra of 31 urethanes of general structure $R^1R^2NCO_2C_2H_5$ (R^1, R^2 = H, alkyl or phenyl). Such urethanes have received relatively little attention[3,4] from mass spectroscopists. In addition, the presence of both nitrogen and oxygen heteroatoms opens up new possibilities that were not available in the homologous series of compounds which were investigated in earlier papers in this series.

RESULTS AND DISCUSSION

The 12.1 eV, 75 °C EI mass spectra of 31 urethanes of general structure $R^1R^2NCO_2C_2H_5$ are presented in Figs 1–6. There are five general features of these spectra.

First, all the compounds studied in this work show significant molecular ions. Indeed, for n-$C_nH_{2n+1}NHCO_2C_2H_5$, $M^{+\cdot}$ either is itself the base peak or else it is of comparable relative intensity to the base peak. There is possibly some reduction in the relative abundance of $M^{+\cdot}$ compared to that of the ubiquitous ion at m/z 102 in the spectra of n-$C_nH_{2n+1}NHCO_2C_2H_5$ as n increases. However, this reduction is not pronounced. In contrast, the relative intensity of the $M^{+\cdot}$ peak declines quite sharply on ascending the homologous series of saturated alcohols n-$C_nH_{2n+1}OH$,[2] amines n-$C_nH_{2n+1}NH_2$,[5] and enols $CH_2{=}CH(CH_2)_mOH$,[6] especially for $n > 4$ and $m > 2$. The relative abundance of $M^{+\cdot}$ is considerably reduced by substitution at the α-carbon atom. Thus, $CH_3CH_2(CH_3)CHNHCO_2C_2H_5$ shows only a moderate $M^{+\cdot}$ peak. On the other hand, branching of the alkyl chain at the β-carbon atom has only a marginal effect on the relative abundance of $M^{+\cdot}$. This is illustrated by the spectra of $(CH_3)_2CHCH_2NHCO_2C_2H_5$ and $(CH_3)_3CCH_2NHCO_2C_2H_5$, both of which contain substantial $M^{+\cdot}$ peaks. The *N*-disubstituted urethanes $R_2NCO_2C_2H_5$ resemble the monosubstituted series in displaying abundant $M^{+\cdot}$ peaks; in this set of compounds, however, there is a sharp decline in the relative abundance of $M^{+\cdot}$ on progressing from $(CH_3)_2NCO_2C_2H_5$ to $(n\text{-}C_4H_9)_2NCO_2C_2H_5$. One possible conclusion is that decomposition of $[R_2NCO_2C_2H_5]^{+\cdot}$ ions is more facile than that of $[RNHCO_2C_2H_5]^{+\cdot}$ species because disubstitution

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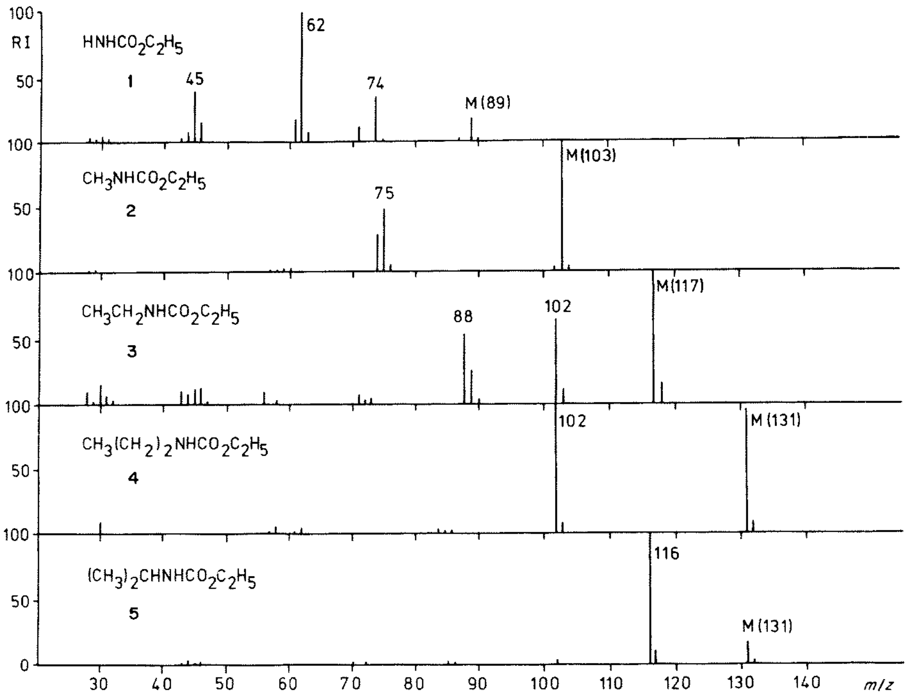


Figure 1. 12.1 eV, 75 °C EI mass spectra of **1**–**5**.

opens up a new mechanism for dissociation. Another difference between the disubstituted series and the monosubstituted series is that branching at the α-carbon atom apparently enhances the relative intensity of the $M^{+\bullet}$ peak for (iso-$C_3H_7)_2NCO_2C_2H_5$ compared to (n-$C_3H_7)_2NCO_2C_2H_5$. This trend does not persist in the spectra of the isomeric $(C_4H_9)_2NCO_2C_2H_5$ compounds (Fig. 6): the relative abundance of $M^{+\bullet}$ is greatest for (n-$C_4H_9)_2NCO_2C_2H_5$, slightly less for (iso-$C_4H_9)_2NCO_2C_2H_5$ and smallest for (sec-$C_4H_9)_2NCO_2C_2H_5$. One interpretation of this anomaly is that the intensity of the $M^{+\bullet}$ peak in the $R_2NCO_2C_2H_5$ series is strongly influenced by the length of the alkyl chain in the molecule. When R contains at least three contiguous carbon atoms connected at one end to the nitrogen atom, the abundance of $M^{+\bullet}$ ions is diminished, perhaps because hydrogen shifts to and from the carbon atoms become easier.

As might have been expected, conjugation of the urethane function with π-electrons elsewhere in the molecule greatly increases the relative abundance of $M^{+\bullet}$. Thus, the spectrum of $PhNHCO_2C_2H_5$ is dominated

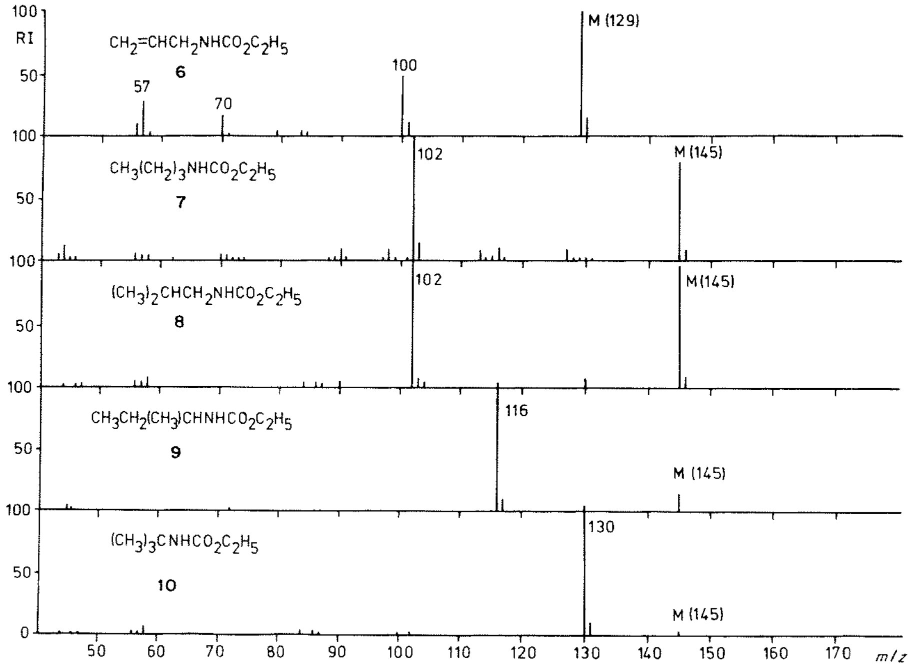


Figure 2. 12.1 eV, 75 °C EI mass spectra of **6**–**10**.

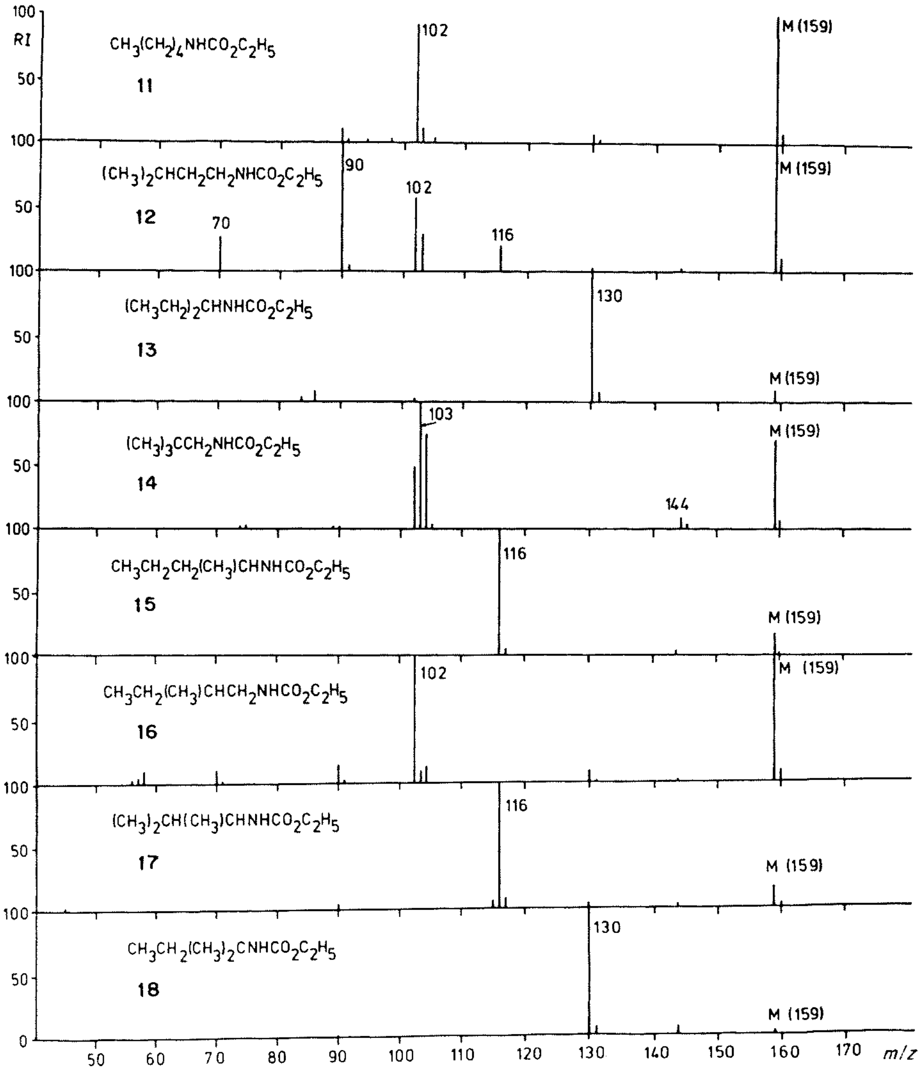


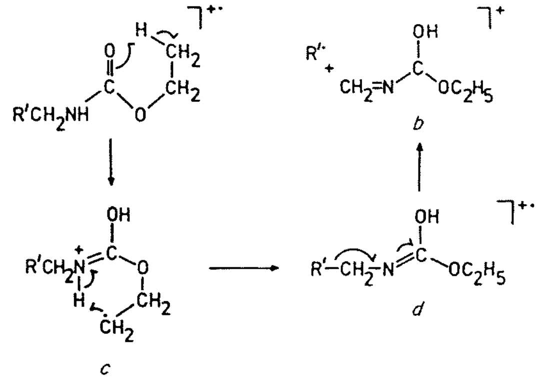
Figure 3. 12.1 eV, 75 °C EI mass spectra of **11**–**18**.

by the enormous $M^{+\cdot}$ ion, which accounts for most of the total ion current. The homologue, $PhCH_2NHCO_2C_2H_5$, also has a large $M^{+\cdot}$ in its spectrum, though intense peaks are present at *m/z* 133 and 150 (Fig. 4). This change reflects the interruption of conjugation by the extra $—CH_2—$ group in $PhCH_2NHCO_2C_2H_5$. The insertion of a second $—CH_2—$ group, to give $PhCH_2CH_2NHCO_2C_2H_5$, causes a reversion to normal behaviour: the spectrum is predominantly composed of $M^{+\cdot}$ and *m/z* 102 ions.

The second major trend in the spectra of the urethanes concerns the abundance of ions derived by formal α-cleavage of $M^{+\cdot}$. This process is evidently characteristic of ionized urethanes. All the $n\text{-}C_nH_{2n+1}NHCO_2C_2H_5$ compounds containing more than two carbon atoms in the *N*-alkyl group show abundant $[M - C_{n-1}H_{2n-1}]^+$ ions at *m/z* 102 in their spectra. Although this reaction could be rationalized as simple cleavage, Eqn (1), it is quite unlikely that this represents a true description of the process.

$$[R^1—CH_2NHCO_2C_2H_5]^{+\cdot} \rightarrow R^{1\cdot} + \underset{a}{[CH_2NHCO_2C_2H_5]^+} \quad (1)$$

The resultant daughter ion, $[CH_2NHCO_2C_2H_5]^+$, *a*, formed by simple cleavage, does not have any especially stabilizing structural features. The rearranged ion, *b*, produced by hydrogen migration from nitrogen to oxygen, represents a more attractive candidate. This species can be formed via a series of hydrogen transfers involving distonic[7] ions as intermediates (Scheme 1). Considerable precedent now exists for the intermediacy of distonic ions in the decomposition of radical cations of diverse functionality.[8–15] The mechanism postulated



Scheme 1

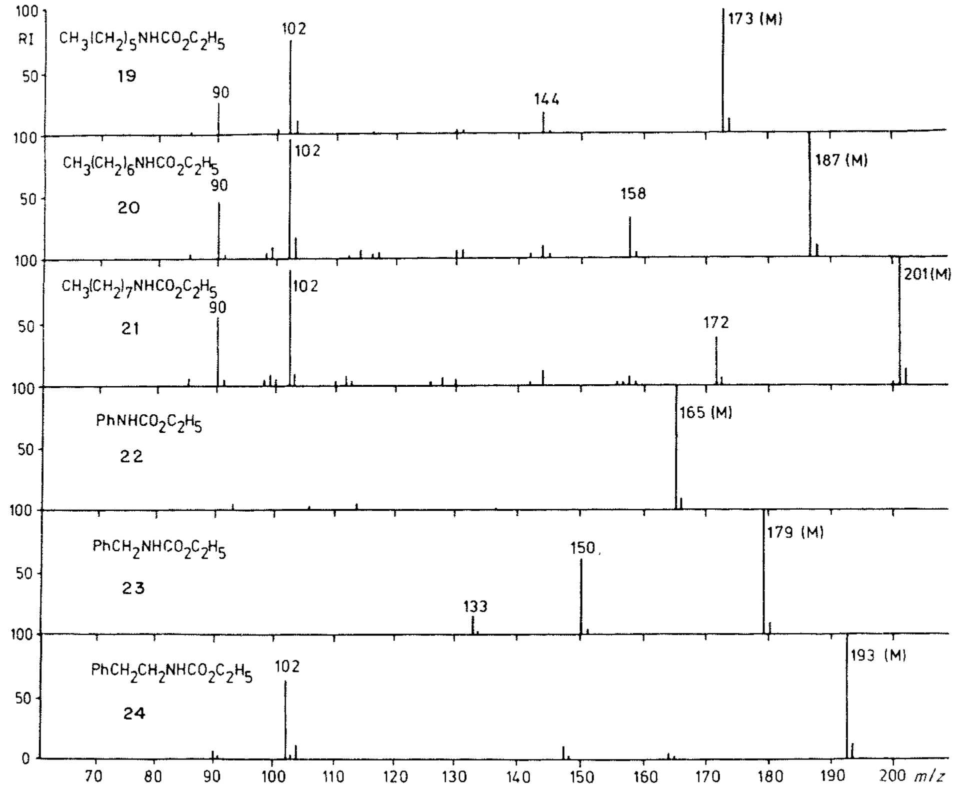
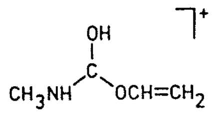
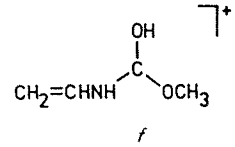


Figure 4. 12.1 eV, 75 °C EI mass spectra of **19–24**.

in Scheme 1 involves the formation of a radical site on the ethoxy group. This is necessary in the smaller $[n\text{-}C_nH_{2n+1}NHCO_2C_2H_5]^{+\cdot}$ species, but hydrogen migrations involving the *N*-alkyl group can achieve the same effect once $n \geqslant 3$. Other attractive daughter ion structures, *e* and *f*, may be devised for the $[C_4H_8NO_2]^+$ ion which is responsible for the peak at *m/z* 102.

Production of these ions necessitates further hydrogen migrations and, in the case of *f*, transfer of a carbon atom from the *O*-alkyl to the *N*-alkyl group. Some light is shed on this problem by the spectrum of


e


f

$n\text{-}C_5H_{11}NHCO_2CH_3$. An intense peak is present at *m/z* 88, analogous to that at *m/z* 102 in the spectrum of the higher homologue $n\text{-}C_5H_{11}NHCO_2C_2H_5$. This constitutes indirect evidence that *m/z* 102 in the spectrum of $n\text{-}C_5H_{11}NHCO_2C_2H_5$ is neither *e* nor *f*, since a corres-

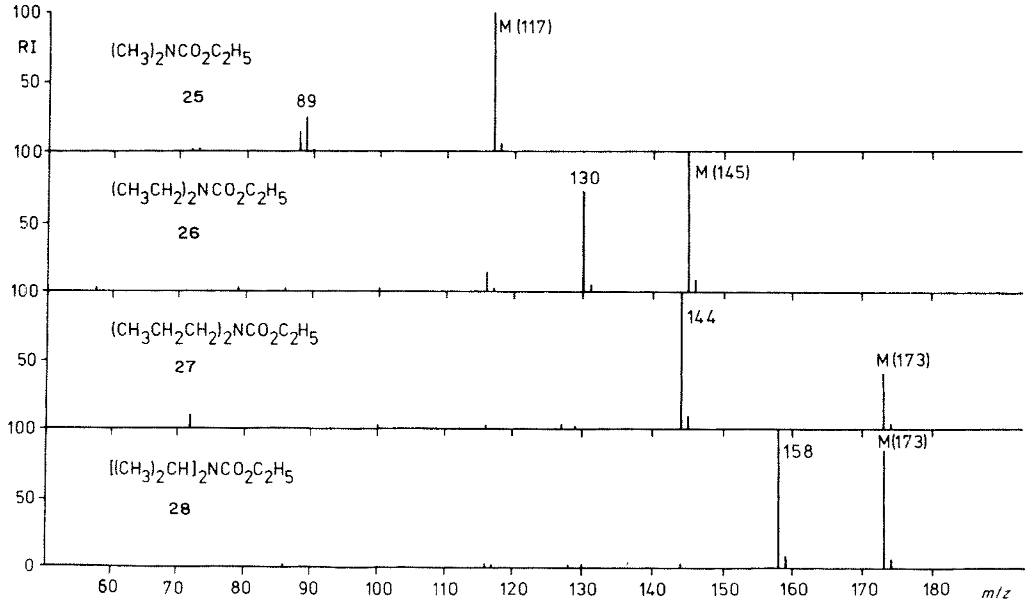


Figure 5. 12.1 eV, 75 °C EI mass spectra of **25–28**.

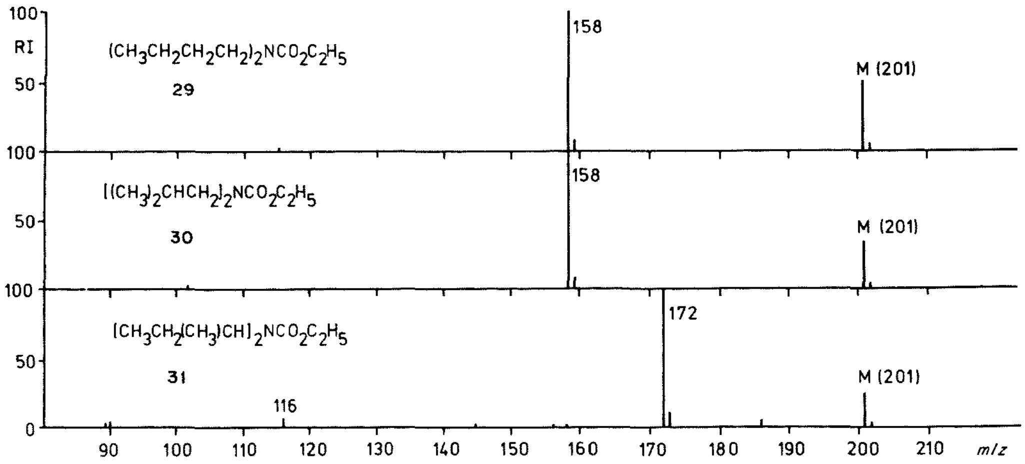


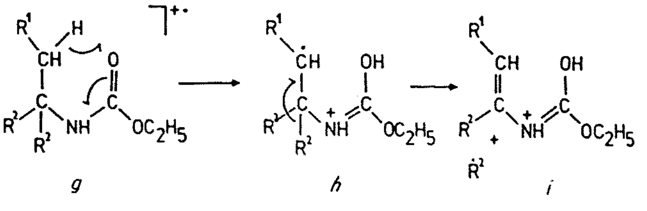
Figure 6. 12.1 eV, 75 °C EI mass spectra of **29–31**.

ponding ion of similar structure at *m/z* 88 could not be formed from $[n\text{-}C_5H_{11}NHCO_2CH_3]^{+\cdot}$. Thus, it would appear probable that the ions formed by nominal α-cleavage have the structures $[CH_2{=}NC(OH)OC_2H_5]^+$ and $[CH_2{=}NC(OH)OCH_3]^+$ (*m/z* 102 and 88, respectively.

This would provide an explanation for the differing trends in the relative abundances of $M^{+\cdot}$ and α-cleavage ions in the spectra of urethanes in the $RNHCO_2C_2H_5$ and $R_2NCO_2C_2H_5$ series. Formation of daughter ions containing the $>C{=}NC^+(OH)OC_2H_5$ moiety from $[R_2NCO_2C_2H_5]^{+\cdot}$ species would involve an alkyl shift from nitrogen to carbon. There is little or no precedent for such a step. It seems likely, therefore, that the α-cleavage processes in $[RNHCO_2C_2H_5]^{+\cdot}$ and $[R_2NCO_2C_2H_5]^{+\cdot}$ series may indeed proceed via different mechanisms.

The relative abundance of this α-cleavage reaction increases considerably with respect to the abundance of $M^{+\cdot}$ when the *N*-alkyl chain is branched at the α-carbon atom. This is well illustrated by the spectra of the isomeric $C_4H_9NHCO_2C_2H_5$ compounds (Fig. 2). The *n*- and isobutyl isomers contain $M^{+\cdot}$ and *m/z* 102 ions of similar abundances in their spectra. In contrast, *sec*-$C_4H_9NHCO_2C_2H_5$ has a spectrum showing only a moderate $M^{+\cdot}$ peak, accompanied by ions at $[M - CH_3]^+$ and $[M - C_2H_5]^+$ derived by notional α-cleavage of $M^{+\cdot}$. The base peak corresponds to expulsion of the larger alkyl radical, in this case $[C_2H_5]^\cdot$. This behaviour is general for higher $[RNHCO_2C_2H_5]^{+\cdot}$ radical cations in which the alkyl group has a secondary structure; thus both $CH_3CH_2CH_2(CH_3)CHNHCO_2C_2H_5$ and $(CH_3)_2CH(CH_3)CHNHCO_2C_2H_5$ have spectra showing $[M - C_3H_7]^+$ as the base peak at *m/z* 116 (Fig. 3). On progressing to *t*-$C_4H_9NHCO_2C_2H_5$, the relative abundance of $M^{+\cdot}$ is further reduced and the spectrum is dominated by the $[M - CH_3]^+$ ion at *m/z* 130. The preference for expelling the larger alkyl radical from $M^{+\cdot}$ persists for $[CH_3CH_2(CH_3)_2CNHCO_2C_2H_5]^{+\cdot}$, as shown by the huge $[M - C_2H_5]^+$ ion at *m/z* 130 and the much smaller $[M - CH_3]^+$ ion at *m/z* 144.

This characteristic 'α-cleavage' process in the spectra of $RNHCO_2C_2H_5$ compounds with branched alkyl groups could be envisaged as being a simple cleavage of the bond connecting the α- and β-carbon atoms (compare Eqn (1)). However, it is also plausible to interpret this reaction as occurring via hydrogen transfer to oxygen from one alkyl group, followed by loss of another alkyl group with production of the favourable delocalized daughter ion, *i* (Scheme 2). A third possibility is that this process takes place via a mechanism parallel to that postulated (Scheme 1) for the $[n\text{-}C_nH_{2n+1}NHCO_2C_2H_5]^{+\cdot}$ ions, producing $[R'CH_2(R^2)C{=}NC(OH)OC_2H_5]^+$ as the daughter ion.



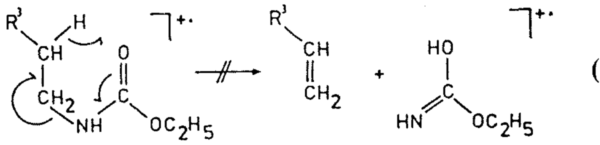
Scheme 2

Regardless of the exact mechanism(s) whereby the processes corresponding to α-cleavage in $[C_nH_{2n+1}NHCO_2C_2H_5]^{+\cdot}$ occur, it is clear that the peaks arising from these reactions are analytically most informative. The relative intensities of these peaks, compared to that of $M^{+\cdot}$, together with their *m/z* ratios, reveal whether the *N*-alkyl group has a primary, secondary or tertiary structure.

The mechanism of α-cleavage in ionized urethanes clearly merits further attention. It is significant that the process is blocked by unsaturation between the β- and γ-carbon atoms in the *N*-alkyl group. Thus, neither $[CH_2{=}CHCH_2NHCO_2C_2H_5]^{+\cdot}$ nor $[PhCH_2NHCO_2C_2H_5]^{+\cdot}$ show the reaction ($CH_2{=}CH^\cdot$ and $Ph^\cdot$ loss, respectively); abundant $[M - 29]^+$ ions appear instead in both of these spectra (Figs 2 and 4). However, $[PhCH_2CH_2NHCO_2C_2H_5]^{+\cdot}$ shows the normal α-cleavage, with only minimal $[C_2H_5]^\cdot$ loss. Expulsion of $[C_7H_7]^\cdot$ gives an abundant daughter ion at *m/z* 102 and it is responsible for a metastable peak at *m/z* 53.9 ($193^+ \rightarrow 102^+ + 91$) (Fig. 4). This 'abnormal' $[C_2H_5]^\cdot$ expulsion from $M^{+\cdot}$ in $[CH_2{=}CHCH_2NHCO_2C_2H_5]^{+\cdot}$ and

$[PhCH_2NHCO_2C_2H_5]^{+\cdot}$ probably involves the atoms of the ethoxy group. Similar remarks apply to $C_2H_5NHCO_2C_2H_5$, which also shows a prominent $[M - C_2H_5]^+$ peak in its spectrum (Fig. 1). Earlier ^{2}H-labelling experiments at 70 eV on this urethane revealed that methyl radical loss (here 'α-cleavage') involves specifically the *N*-ethyl group, whereas ethyl expulsion occurs almost exclusively from the *O*-ethyl group.[3]

It is evident that α-cleavage in ionized urethanes is a very facile process. Of the $RNHCO_2C_2H_5$ compounds studied in this work, only $CH_3NHCO_2C_2H_5$ and $C_2H_5NHCO_2C_2H_5$ show appreciable $[M - C_2H_4]^{+\cdot}$ peaks; moreover, none of the ionized urethanes expels an alkene derived from the *N*-alkyl group (Eqn (2)):



(2)

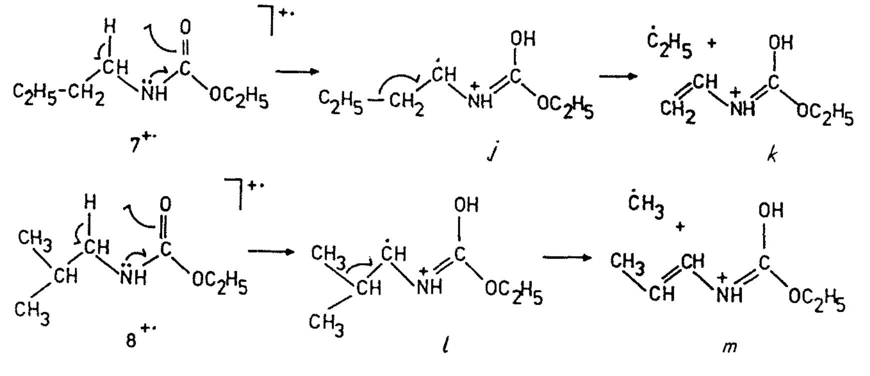
These rearrangement reactions involving six-membered ring transition states are commonly observed for ionized carbonyl compounds containing the $CO_2C_2H_5$ moiety. Consequently, the presence of the nitrogen atom in the ionized urethanes profoundly influences their chemistry.

Cleavage of the bond connecting the β- and γ-carbon atoms in the *N*-alkyl group is responsible for the third feature of the spectra of $RNHCO_2C_2H_5$ compounds. Whilst this 'β-cleavage' process produces only a small peak in the normal spectrum, it is diagnostically useful; furthermore, metastable $[RNHCO_2C_2H_5]^{+\cdot}$ radical cations frequently decompose via this route. Thus, *n*-$C_4H_9NHCO_2C_2H_5$ and iso-$C_4H_9NHCO_2C_2H_5$ may be distinguished by the relative intensity of the minor peaks at *m/z* 130 ($[CH_3]^\cdot$ loss) and 116 ($[C_2H_5]^\cdot$ loss) in their spectra. The former shows a significant $[M - C_2H_5]^+$ and only a smaller $[M - CH_3]^+$, whereas the latter displays a $[M - C_2H_5]^+$ peak of lower intensity and a larger $[M - CH_3]^+$ peak. The distinction persists for metastable $[C_4H_9NHCO_2C_2H_5]^{+\cdot}$ ions; both these radical cations expel $[C_3H_7]^\cdot$ (α-cleavage), as evidenced by a metastable peak at *m/z* 71.8 ($145^+ \rightarrow 102^+ + 43$). However, $[(CH_3)_2CHCH_2NHCO_2C_2H_5]^{+\cdot}$ eliminates $[CH_3]^\cdot$ [m^* at 116.5 ($145^+ \rightarrow 130^+ + 15$)], whereas $[CH_3CH_2CH_2CH_2NHCO_2C_2H_5]^{+\cdot}$ loses $[C_2H_5]^\cdot$ [m^* at 92.8 ($145^+ \rightarrow 116^+ + 29$)].

A plausible explanation for this process is shown in Scheme 3. Following hydrogen transfer from the α-carbon atom on to oxygen, fission of the C—C σ-bond results in formation of the delocalized daughter ions *k* and *m*. The distonic ions (*j* and *l*) involved in these reactions contain the $^\cdot CH-NH^+$ moiety; it is known that such ionized ylids are particularly stable.[9] Alternative structures, $[CH_3CH{=}NC(OH)OC_2H_5]^+$ and $[CH_3CH_2CH{=}NC(OH)OC_2H_5]^+$ for *k* and *m*, respectively, are thermodynamically attractive. Formation of these ions would require additional hydrogen shifts, however, and undermine the mechanistic interpretation of β-cleavage given in Scheme 3.

It should be noted that the behaviour of radical cations derived by ionization of compounds containing CO_2R groups is often far more complicated than appears at first sight. For example, expulsion of $I^\cdot$ from $[ICH_2CH_2CO_2CH_3]^{+\cdot}$ and $[CH_3CHICO_2CH_3]^{+\cdot}$ proceeds by simple cleavage; in contrast, $[CH_3]^\cdot$ loss from $[CH_3CH_2CH_2CO_2CH_3]^{+\cdot}$ and $[(CH_3)_2CHCO_2CH_3]^{+\cdot}$ yields $[CH_2{=}CHC(OH)OCH_3]^+$ in both cases.[16] Moreover, elimination of $[C_2H_5]^\cdot$ from $[n\text{-}C_5H_{11}CO_2H]^{+\cdot}$ affords protonated methacrylic acid $[CH_2{=}(CH_3)CC(OH)_2]^+$.[17,18] Loss of $[CH_3]^\cdot$ from $[(CH_3)_3CCO_2H]^{+\cdot}$ produces protonated crotonic acid, $[CH_3CH{=}CHC(OH)_2]^+$, whilst the apparently similar process of $[CH_3]^\cdot$ expulsion from $[CH_3CH_2(CH_3)CHCO_2H]^{+\cdot}$ gives protonated methacrylic acid.[19] The disparate reactions of $[(CH_3)_3CCO_2H]^{+\cdot}$ and $[CH_3CH_2(CH_3)CHCO_2H]^{+\cdot}$ are particularly interesting in that the respective daughter ions produced are the exact opposite of what might have been expected from a naive mechanistic analysis. Although the analogy between ionized urethanes and esters is not exact, the behaviour of these ionized esters serves to emphasize the need for caution in assigning daughter ion structures in the fragmentations of radical cations with CO_2R functions. Nevertheless, it seems highly unlikely that 'β-cleavage' occurs via simple rupture of the appropriate bond, which would lead only to thermodynamically unfavourable daughter ions such as $[CH_2CH_2NHCO_2C_2H_5]^+$.

This β-cleavage process is of some utility in determining the degree of branching at the β-carbon atom in $RNHCO_2C_2H_5$ urethanes of moderate size. For example, $(CH_3)_3CCH_2NHCO_2C_2H_5$ displays a minor $[M - CH_3]^+$ peak and



Scheme 3

$(CH_3)_2CHCH_2CH_2NHCO_2C_2H_5$ shows a sizeable $[M - C_3H_7]^+$ peak in their respective spectra (Fig. 3).

The corresponding n-$C_5H_{11}NHCO_2C_2H_5$ urethane does not show a significant peak attributable to β-cleavage ($[M - C_3H_7]^+$) in its spectrum; instead a minor ion is present at $[M - C_2H_5]^+$. This loss of ethyl radical constitutes the fourth general aspect of the reactions of the ionized urethanes $[n\text{-}C_nH_{2n+1}NHCO_2C_2H_5]^+$ for $n \geqslant 5$. A deep-seated rearrangement is probably responsible for the origin of this $[M - C_2H_5]^+$ ion, which becomes quite prominent in the spectra of n-hexyl, n-heptyl and n-octyl urethanes (Fig. 4). Unfortunately, this peak is of little analytical value, serving only to confirm the presence of a long alkyl chain in the $RNHCO_2C_2H_5$ molecule.

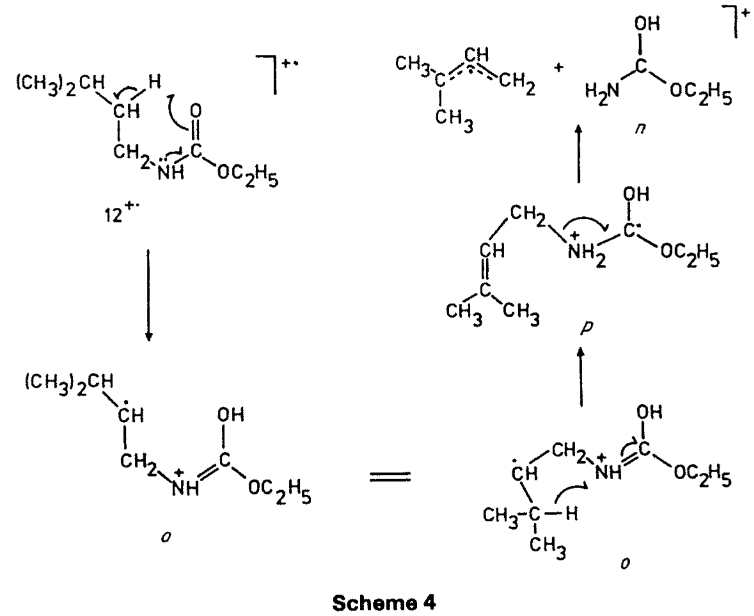
Ethyl radical loss from $[n\text{-}C_nH_{2n+1}NHCO_2C_2H_5]^{+\bullet}$ persists even for metastable molecular ions. It is interesting that expulsion of an ethyl radical is a surprisingly common process in the dissociation of various radical cations containing long alkyl chains. Thus, $[n\text{-}C_5H_{11}O(C_nH_{2n+1})]^{+\bullet}$ ($n = 1$–5)[20] and $[CH_2{=}CH(CH_2)_mOH]^{+\bullet}$ ($m = 2$–4)[6] show this reaction, especially at low internal energies.

The fifth feature of the spectra of the $C_nH_{2n+1}NHCO_2C_2H_5$ species is the appearance of a peak at m/z 90. Accurate mass measurements at higher resolving power indicate that this ion has the formula $[C_3H_8NO_2]^+$; this corresponds to elimination of $[C_nH_{2n-1}]^\bullet$ from $M^{+\bullet}$. This peak is present, though small, in the spectra of $RNHCO_2C_2H_5$ for R = n-C_4H_9, iso-C_4H_9 and n-C_5H_{11}. It is evidently associated with urethanes containing primary (unbranched at the α-carbon atom) R substituents, and it becomes noticeable in the spectra of n-hexyl, n-heptyl and n-octyl urethanes. A logical structure for the $[C_3H_8NO_2]^+$ daughter ion is protonated O-ethyl carbamate, n, which should be very stable on account of extensive delocalization of the positive charge on to the three heteroatoms. This may be formed by double hydrogen transfer from the N-alkyl group to the carbonyl oxygen and nitrogen atoms. A possible mechanism for this process is given in Scheme 4 for $[(CH_3)_2CHCH_2CH_2NHCO_2C_2H_5]^{+\bullet}$, for which production of m/z 90 is very favourable. Starting from **12**$^{+\bullet}$, hydrogen transfer from the β-carbon atom to the carbonyl oxygen atom leads to the delocalized distonic ion o, which can then undergo a second hydrogen transfer, this time from the γ-carbon atom to nitrogen, to form another distonic ion, p. Fission of the C—N bond in p results in production of n and expulsion of a dimethylallyl radical. Whilst this mechanism cannot be regarded as being firmly established in the absence of extensive ^{2}H-labelling experiments, it is consistent with the present facts and it is chemically sensible. In addition, the higher abundance of $[M - C_5H_9]^+$ in the spectrum of iso-$C_5H_{11}NHCO_2C_2H_5$, compared to that of n-$C_5H_{11}NHCO_2C_2H_5$, can be rationalized on the basis of the superior stability of p over the analogous distonic ion containing an unbranched C_5H_{10} alkenyl substituent.

The elimination of $[C_nH_{2n-1}]^\bullet$ radicals from the molecular ions of compounds containing large $[C_nH_{2n+1}]$ alkyl chains is by no means confined to urethanes. Thus, for example, early[21] work on the low-energy mass spectra of large dialkyl ethers such as $(n\text{-}C_{12}H_{25})_2O$ shows that these radical cations also undergo double hydrogen transfer and loss of a radical having one unit of unsaturation (here $[C_{12}H_{23}{}^\bullet]$).

It is significant that even the larger $RNHCO_2C_2H_5$ compounds display only a very small peak corresponding to R^+. Formation of R^+ almost certainly does not proceed by simple cleavage of the N—R bond, since this would give rise to an unstable primary carbenium ion. Rather, a 1,2-hydride shift would be expected to accompany cleavage of the N—R bond, particularly at or near the thermochemical threshold, thus producing a secondary carbenium ion.[22–24] Even allowing for this isomerization of the incipient carbenium ion, however, it is clear that charge retention by the hydrocarbon fragment remains an unfavourable decay route for ionized urethanes.

The relative abundances of ions derived by secondary decomposition of the primary daughter ions are usually low in these spectra. This is helpful from the analytical

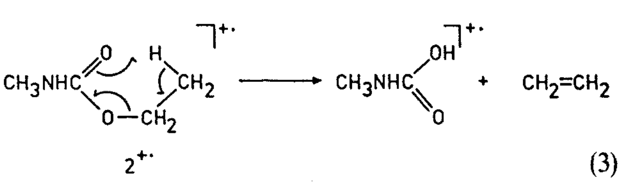


Scheme 4

point of view since it means that there is a good chance of associating the nature of the ions in the spectra with the structure of the molecular ions. Ths advantage of low-energy spectra over their 70 eV counterparts deserves emphasis.

Some of the urethanes studied in this work show peaks in their spectra which merit a brief discussion in their own right. Thus, the parent compound $H_2NCO_2CH_2CH_3$ displays a much smaller $M^{+\cdot}$ ion in its spectrum (Fig. 1) than would have been expected on a naive basis by extrapolation from the spectra of higher homologues. This enhancement of the relative abundances of $M^{+\cdot}$ ions by alkylation on the heteroatom is a normal phenomenon in low-energy spectra. It has been reported in the spectra of small alcohols and ethers,[2] n-$C_5H_{11}OR$ ($R = H$, alkyl) species,[20] and alkylamines;[5] however, a trend in the opposite sense has been found for n-$C_8H_{17}CO_2H$ and n-$C_8H_{17}CO_2R$ ($R = CH_3, C_2H_5$).[25] The base peak in the spectrum of $H_2NCO_2C_2H_5$ appears at m/z 62; this corresponds to either $[M - HCN]^+$ or $[M - C_2H_3]^+$. Accurate mass measurements at higher resolving power indicate that the latter is the correct explanation. An analogous peak appears at m/z 61 ($[C_2H_3]^\cdot$ loss) in the low-energy spectrum of $CH_3CO_2C_2H_5$.[26] This reaction must involve substantial rearrangement in $M^{+\cdot}$. The peak at m/z 45 can be attributed to $[M - C_2H_5OH]^+$ with $[NH{=}C{=}O]^{+\cdot}$ as the daughter ion), or $[M{-}H_2NCO]^+$ (with $[CH_3CHOH]^+$ as the probable daughter ion). Accurate mass measurements support the latter explanation. Other reactions undergone by $[H_2NCO_2C_2H_5]^{+\cdot}$ include $[CH_3]^\cdot$ loss (presumably from the OC_2H_5 group) and expulsion of H_2O to give m/z 71. In short, the behaviour of $[H_2NCO_2C_2H_5]^{+\cdot}$ shows many unique features which are not observed for the higher homologues.

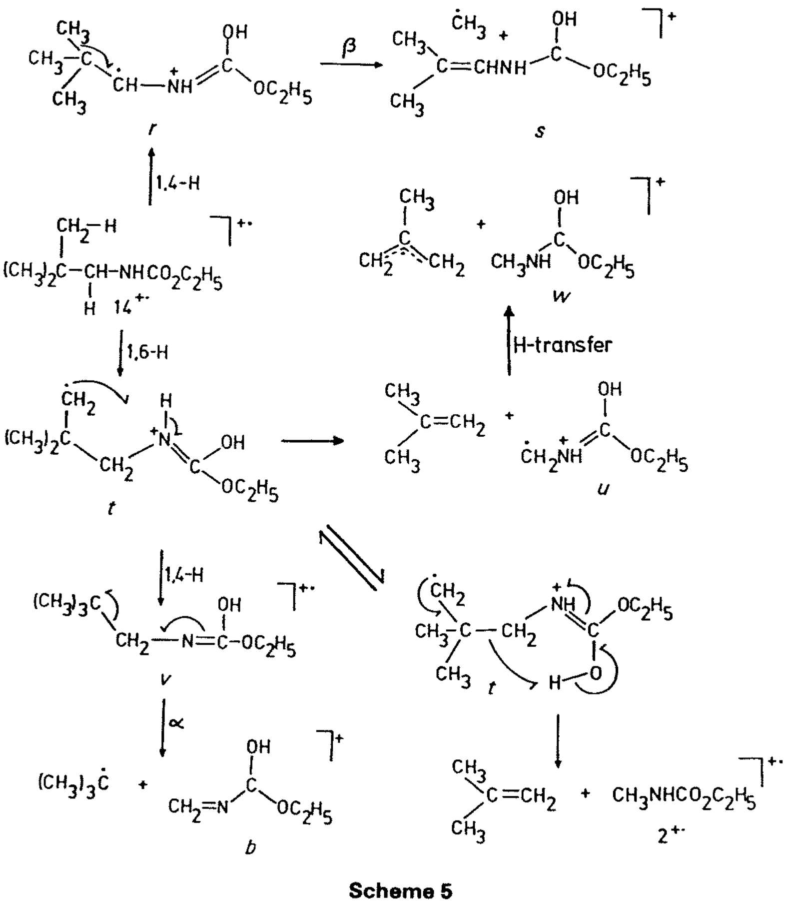
The only unusual feature of the spectrum of $CH_3NHCO_2C_2H_5$ is that loss of C_2H_4 from $M^{+\cdot}$ accounts for the principal daughter ion peak at m/z 75. This reaction, which also occurs for metastable molecular ions (m^* at 54.7, $103^+ \rightarrow 75^+ + 28$), can be explained using Eqn (3):



(3)

As mentioned previously, only the lower $[RNHCO_2C_2H_5]^{+\cdot}$ species undergo this apparently favourable process, which is pre-empted by alternative reactions for the higher homologues. Moreover, expulsion of an ethyl radical from $[CH_3NHCO_2C_2H_5]^{+\cdot}$ competes with ethene elimination, both in the production of daughter ions (m/z 74) in the ordinary spectrum and for metastable ions (m^* at 53.1, $103^+ \rightarrow 74^+ + 29$).

Loss of ethene from $M^{+\cdot}$ takes place to some extent in the spectra of $(CH_3)_2NCO_2C_2H_5$ (m/z 89, Fig. 5) and $C_2H_5NHCO_2C_2H_5$ (m/z 89, Fig. 1). However, even for $[C_2H_5NHCO_2C_2H_5]^{+\cdot}$, ethyl radical elimination is more important than ethene loss in both the normal spectrum (m/z 88) and for metastable molecular ions

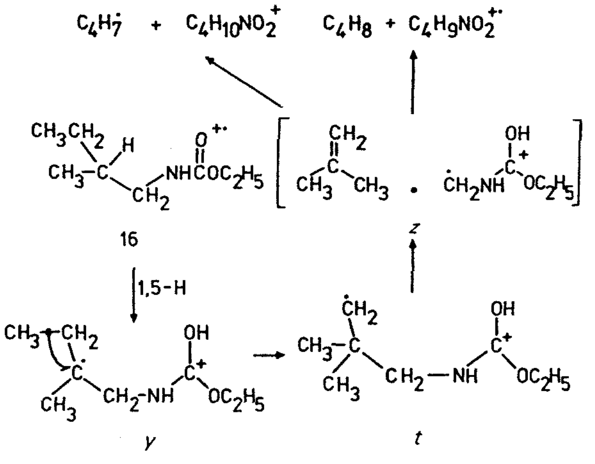


Scheme 5

(m^* at 66.1, $117^+ \rightarrow 88^+ + 29$). Thus, once the *N*-alkyl group contains a chain of two carbon atoms or more, $[M - C_2H_4]^{+\cdot}$ declines drastically in importance.

Finally, the spectrum of the *neo*-pentyl urethane, $(CH_3)_3CCH_2NHCO_2C_2H_5$, exhibits unusual peaks at *m/z* 103 (C_4H_8 loss) and *m/z* 104 ($[C_4H_7]^\cdot$ loss). Expulsion of $[C_4H_7]^\cdot$ from the molecular ions of several compounds containing the *neo*-pentyl group has been reported. Thus, for example, $[(CH_3)_3CCH_2NH_2]^{+\cdot}$ gives rise to a peak at *m/z* 32 in the normal mass spectrum and also loses $[C_4H_7]^\cdot$ in metastable transitions.[27,28] Elimination of C_4H_8 and production of $[C_4H_8]^{+\cdot}$ occurs in the 12.1 eV spectra of $(CH_3)_3CCH_2OH$ and $(CH_3)_3CCH_2OCH_3$.[27] Some or all of these reactions probably involve distonic ions.[28] In the present context, much of the chemistry of $[(CH_3)_3CCH_2NHCO_2C_2H_5]^{+\cdot}$ can be explained on the basis of Scheme 5. Loss of $[C_4H_9]^\cdot$ ('α-cleavage') and $[CH_3]^\cdot$ ('β-cleavage') can be rationalized in the usual fashion as occurring via *t*, and *v* and *r*, respectively. Butene elimination can take place by σ-cleavage in *t*, with formation of the distonic ion *u*; alternatively, $\mathbf{2}^{+\cdot}$ may be formed if σ-cleavage of *t* is accompanied by hydrogen transfer from oxygen to the α-carbon atom through a five-membered ring transition state. Production of $[C_4H_{10}NO_2]^+$ and $[C_4H_7]^\cdot$ is possible by hydrogen transfer between the developing products of butene loss. This hydrogen transfer may be interpreted as occurring in an ion–dipole or ion–molecule complex $[C_4H_9NO_2 \cdot C_4H_8]^{+\cdot}$. The intermediacy of these complexes in the unimolecular reactions of isolated organic ions is well established.[29–37] The driving force behind expulsion of a methylallyl radical is presumably the great stability of the daughter ion; a likely structure is *w*, in which the positive charge is extensively delocalized.

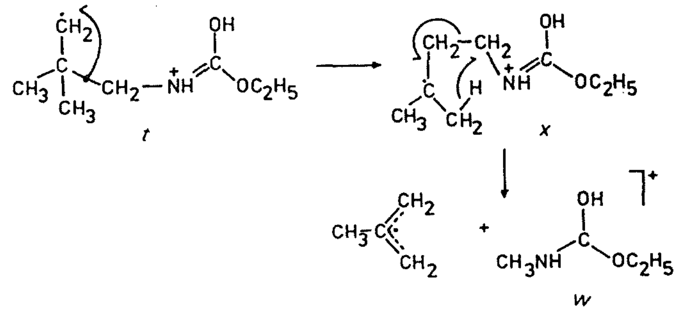
An alternative mechanism for $[C_4H_7]^{+\cdot}$ loss involves rearrangement of the hydrocarbon chain in *t* to give *x*, which then undergoes cleavage of the bond connecting the α- and β-carbon atoms with an associated 1,4-hydrogen shift, thus yielding *w*. One weakness of this explanation is that methylallyl radical loss does not occur from $[(CH_3)_2CHCH_2CH_2NHCO_2C_2H_5]^{+\cdot}$. In contrast, a minor amount of double hydrogen transfer does occur in the spectrum of **16**, $CH_3CH_2(CH_3)CHCH_2NHCO_2C_2H_5$. This may be interpreted using Scheme 7. A 1,5-hydrogen shift in $\mathbf{16}^{+\cdot}$ leads to *y*, which undergoes a 1,2-methyl shift to form *t*; dissociation of *t* by simple cleavage gives C_4H_8 loss, whereas hydrogen transfer between these incipient products accounts for $[C_4H_7]^\cdot$ expulsion.



Scheme 7

The details of the mechanism of $[C_4H_7]^\cdot$ elimination from ionized *neo*-pentyl compounds have been the subject of controversy.[27,28] Two points may, nevertheless, be made. First, it is clear that rapid interconversion of $[C_5H_{11}NHCO_2C_2H_5]^{+\cdot}$ species does not precede decomposition of these radical cations in the range of internal energies involved in this work. Loss of $[C_4H_7]^\cdot$ is associated principally with the *neo*-pentyl structure, and to a lesser degree with the $CH_3CH_2(CH_3)CHCH_2$ isomer. This is circumstantial evidence that the distonic ion *t* and the derived ion–molecule complex *z* are of crucial importance in $[C_4H_7]^\cdot$ elimination. Secondly, this process is energetically very favourable for ionized *neo*-pentyl compounds, as evidenced by a metastable peak at *m/z* 68.0 ($159^+ \rightarrow 104^+ + 55$) in the spectrum of *neo*-$C_5H_{11}NHCO_2C_2H_5$. It also occurs for *neo*-$C_5H_{11}NHCO_2CH_3$ and *neo*-$C_5H_{11}NHCOCH_3$; therefore, it is of analytical value in distinguishing *neo*-pentyl derivatives from their isomeric C_5H_{11} counterparts.

A similar double hydrogen transfer occurs to a limited extent in the chemistry of $[PhCH_2CH_2NHCO_2C_2H_5]^{+\cdot}$, which expels $[C_7H_5]^\cdot$ to produce *m/z* 104 and a metastable peak at *m/z* 56.0 ($193^+ \rightarrow 104^+ + 89$). This process takes place in competition with the usual $[C_7H_7]^\cdot$ loss in the ordinary spectrum (*m/z* 102) and for metastable molecular ions [m^* at 53.9 ($193^+ \rightarrow 102^+ + 91$)].



Scheme 6

CONCLUSIONS

The 12.1 eV mass spectra of urethanes are analytically useful and mechanistically interesting. Most of the 31 compounds investigated in this work are uniquely defined by their spectra. Thus, the four isomeric $C_4H_9NHCO_2C_2H_5$ urethanes are identified by their spectra, and most of the eight isomeric $C_5H_{11}NHCO_2C_2H_5$ compounds may be differentiated from each other on the basis of their spectra. These spectra are normally simple and easy to interpret on account of the general absence of ions produced by secondary decomposition of the primary daughter ions.

EXPERIMENTAL

The mass spectra were obtained using a modified AEI MS9 double-focusing mass spectrometer having a water-cooled source maintained at ~75 °C. Ionization was effected by bombardment of the vaporized sample at a source pressure of $\sim 2 \times 10^{-6}$ Torr, using electrons having an energy of 12.1 eV. Details of the experimental procedure, including the method for accurately calibrating the electron energy, have been published elsewhere.[2]

Apart from $H_2NCO_2C_2H_5$, $CH_3NHCO_2C_2H_5$ and $C_2H_5NHCO_2C_2H_5$, which were commercial samples of high purity, the urethanes were synthesized by condensation of the corresponding amines RNH_2 or R_2NH with ethyl chloroformate (Eqn 4):

$$R^1R^2NH + ClCO_2C_2H_5 \xrightarrow[<0\,^{\circ}C]{CH_2Cl_2/pyridine} R^1R^2NCO_2C_2H_5 \quad (4)$$

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