Chemical Ionization Mass Spectra of Urethanes

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Chemical ionisation mass spectra using methane as the reagent gas are reported for 33 urethanes of general structure $RNHCO_2C_2H_5$ [R = H, C_nH_{2n+1} (n = 1–8), $CH_2CH{=}CH_2$, cyclo-C_6H_{11}, Ph, $PhCH_2$, $PhCH_2CH_2$, and $Ph(CH_3)CH$] and $R_2NCO_2C_2H_5$ [R = C_nH_{2n+1} (n = 1–4)]. Abundant MH^+ ions are present in all the spectra, accompanied by satellite peaks corresponding to $[M + C_2H_5]^+$ and $[M + C_3H_5]^+$. Four classes of fragment ions are of general importance in the spectra. Two of these, $[MH - C_2H_4]^+$ and $[MH - C_2H_5OH]^+$, are associated with the $CO_2C_2H_5$ group. The other two, corresponding to alkane and alkene elimination from MH^+, arise from the RNH or R_2N function. The mechanisms whereby these fragment ions are formed are discussed and their analytical utility is illustrated by reference to the spectra of the four isomeric $C_4H_9NHCO_2C_2H_5$ and the eight isomeric $C_5H_{11}NHCO_2C_2H_5$ compounds. The results of ^2H-labelling studies are presented and a comparison is made between the methane and ammonia chemical ionisation spectra of selected urethanes.

Relatively little attention has been given to the mass spectra of urethanes. Early work described the fragmentation patterns of a selection of urethanes after ionisation by 70 eV electrons[1] and a ^2H-labelling study on the behaviour of ionised $C_2H_5NHCO_2C_2H_5$ and $PhNHCO_2C_2H_5$.[2] More recently, the chemical ionisation mass spectra (c.i.m.s.) of a number of urethanes having pesticidal properties were reported.[3,4] A study of the 12.1 eV 75 °C electron ionisation mass spectra of the homologous series of urethanes $RNHCO_2C_2H_5$ and $R_2NCO_2C_2H_5$ has established the analytical value of these low-energy spectra.[5] In view of these developments, a systematic survey of the c.i.m.s. of urethanes, and a comparison of the usefulness of the c.i.m.s. and low-energy e.i.m.s., is of interest.

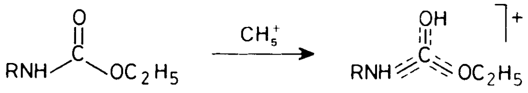
Results and Discussion

The c.i.m.s. of 33 urethanes of general structure $RNHCO_2C_2H_5$ and $R_2NCO_2C_2H_5$, obtained using methane as the reagent gas, are given in Tables 1–6. Bar-graph representations of the spectra of the four isomeric $C_4H_9NHCO_2C_2H_5$ compounds are shown for purposes of illustration in the Figure. These data may be discussed under two headings.

(a) *MH^+ and Related Ions.*—All of the 33 urethanes display abundant MH^+ ions formed by proton transfer; indeed, MH^+ usually accounts for the base peak in these spectra. Apart from proton transfer, a minor amount of ionisation occurs by capture of $C_2H_5^+$ or $C_3H_5^+$ by the urethane. These processes result in formation of $[M + 29]^+$ and $[M + 41]^+$ peaks, which become steadily more important on ascending the homologous series of urethanes. Although these $[M + C_2H_5]^+$ and $[M + C_3H_5]^+$ peaks are of relatively low intensity, they provide useful confirmation of the molecular mass information furnished by the large MH^+ peaks. The presence of $[M + C_2H_5]^+$ adducts in the methane c.i.m.s. of several of the carbamates having pesticidal activity has been reported.[3,4] By analogy with the related $[M + \text{ethyl}]^+$ adducts of ethyl acetate and ethylbenzene, which have been shown to contain a relatively strong M–ethyl bond,[6] it is probable that these species are better described as covalently bonded, rather than as weak ion–dipole complexes.

It is noticeable that the relative abundance of MH^+ and the related $[M + C_2H_5]^+$ and $[M + C_3H_5]^+$ ions are diminished in the spectra of $RNHCO_2C_2H_5$ compounds containing tertiary alkyl groups, R, compared with the corresponding ions in the spectra of isomeric urethanes in which the alkyl group has a primary or secondary structure. This trend reflects the greater ease of fragmentation of MH^+ by alkene (R–H) loss when R is a tertiary alkyl group. The origin of this phenomenon is discussed in more detail below under alkene loss. From the analytical point of view, the reduction in the relative abundance of MH^+ coupled with the rise in the relative intensity of the peak at m/z 90, identifies urethanes of structure $RNHCO_2C_2H_5$ in which R is tertiary. This information is complementary to that supplied by the low-energy e.i.m.s.,[5] in which the $M^{+\bullet}$ peak is characteristically very intense for $RNHCO_2C_2H_5$ compounds with primary alkyl groups, but only of moderate or low intensity when R is secondary or tertiary.

The high abundance of the MH^+ ions raises the question of the site of protonation of the urethanes. Protonation on the carbonyl oxygen reaction (1) would be expected to be



$$RNHC(=O)OC_2H_5 \xrightarrow{CH_5^+} [RNH\text{⋯}C(\text{⋯}OH)\text{⋯}OC_2H_5]^+ \qquad (1)$$

thermodynamically most favourable since the positive charge in the resultant cation should be effectively delocalised over the three heteroatoms and the central carbon atom. The gas phase basicity of ethyl N-methylcarbamate (R = CH_3) is relatively high (843–846) kJ mol^{-1}.[7] An early compilation of proton affinities[8] revealed that the proton affinity of ethyl N,N-dimethylcarbamate (884 kJ mol^{-1}) was slightly higher than that (875 kJ mol^{-1}) of dimethylformamide. The proton affinity of methane is only 545[9] kJ mol^{-1}; consequently proton transfer from CH_5^+ to $RNHCO_2C_2H_5$ or $R_2NCO_2C_2H_5$ releases *ca.* 300 kJ mol^{-1} or more energy. Although at least part of this energy would be dissipated by collisional quenching of the resultant MH^+ ion, the high abundance of the MH^+ ions nevertheless indicates the stability of these species towards fragmentation. In view of the large differences in the proton affinities of urethanes and methane, it is possible that some MH^+ ions are produced by protonation on the nitrogen atom or the oxygen atom of the ethoxy group. Alternatively, proton

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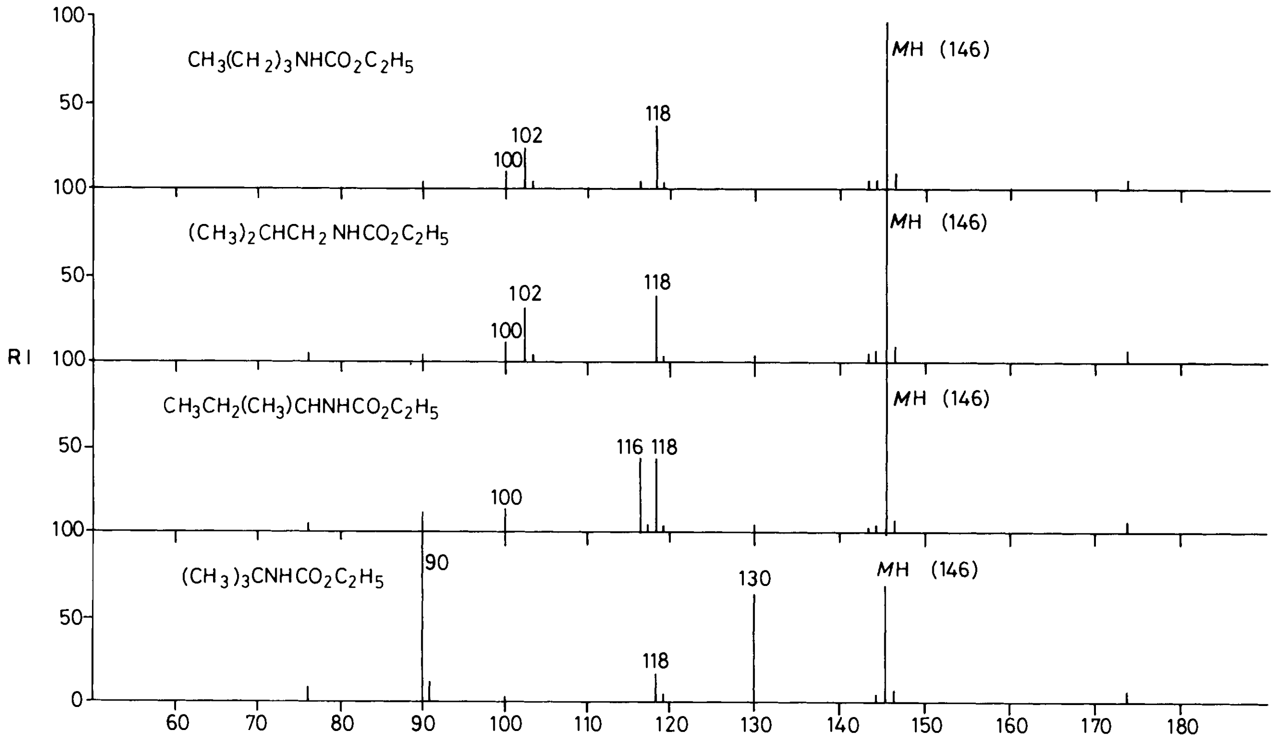


Figure.

Table 1. Methane c.i.m.s. of $RNHCO_2C_2H_5$ ($R = C_nH_{2n+1}$; n = 0–3) compounds.

(1) R = H		(2) R = CH_3		(3) R = C_2H_5		(4) R = n-C_3H_7		(5) R = i-C_3H_7		
m/z	RI[a]	m/z	RI[a]	m/z	RI[a]	m/z	RI[a]	m/z	RI[a]	Assignment[b]
						160	4	160	4	$[M + C_2H_5]^+$
91	4	105	5	119	7	133	7	133	8	
90	100	104	100	118	100	132	100	132	100	MH^+
89	1	103	5	117	<4	131	4	131	<1	$M^{+\cdot}$
						130	5	130	3	$[M - H]^+$
						118	8			
				102	7			116	21	$[MH - CH_4]^+$
						105	2	105	2	
62	19	76	84	90	60	104	45	104	52	$[MH - C_2H_4]^+$
				88	15	102	16			$[MH - C_2H_6]^+$
						90	8	90	7	$C_3H_8NO_2^+$
44	3	58	23	72	20	86	9	86	9	$[MH - C_2H_5OH]^+$
						62	7	62	5	

[a] Intensities normalised to a value of 100 units for the base peak; reagent ion peaks and peaks of intensity lower than 3 units are omitted. [b] The presentation of data in the Table is such that corresponding ions are arranged on the same horizontal row.

transfer between the heteroatoms might occur, probably at a relatively slow rate, thus forming a MH^+ species other than that which is thermodynamically most stable. Behaviour of this kind has been reported for protonated carboxylic acids, from which water loss occurs from the $RCOOH_2^+$ structure, though $RC(OH)_2^+$ is unquestionably lower in energy.[10,11]

(b) *Daughter Ions.*—(*i*) $[MH - C_2H_4]^+$. This ion, which is present in almost all the spectra, corresponds to ethylene expulsion from MH^+. Apart from the parent compound, $H_2NCO_2C_2H_5$, which shows an unusually small $[MH - C_2H_4]^+$ peak in its spectrum, the relative intensity of this peak decreases steadily on ascending the homologous series of urethanes. Thus, in the spectra of n-$C_nH_{2n+1}NHCO_2C_2H_5$, the relative abundance of $[MH - C_2H_4]^+$ is reduced from 76% for n = 1, to 39% for n = 4, and to 8% for n = 8. A similar trend is found for the disubstituted series $R_2NCO_2C_2H_5$: $[MH - C_2H_4]^+$ declines from 59% in the spectrum of $(CH_3)_2NCO_2C_2H_5$ to 8% in that of $(C_4H_9)_2NCO_2C_2H_5$. In contrast, provided tertiary alkyl groups are excluded, the relative abundance of $[MH - C_2H_4]^+$ depends only marginally on the structure of the alkyl group in isomeric $RNHCO_2C_2H_5$ and $R_2NCO_2C_2H_5$ compounds. This is strong evidence that the ubiquitous $[MH - C_2H_4]^+$ ion originates from the $CO_2C_2H_5$ group. Support for this proposal is found in the spectra of n-$C_5H_{11}NHCO_2CH_3$ and $(CH_3)CCH_2NHCO_2CH_3$: the relative abundance of m/z 118 $\{[MH - C_2H_4]^+\}$ is <2%. In addition, the spectrum of $(CH_3)_3C(CD_3)_3NCO_2C_2H_5$ contains a peak at m/z 135 (15%) $[MH - C_2H_4]^+$, but no significant peak at m/z 134 corresponding to C_2H_3D from MH^+.

Table 2. Methane c.i.m.s. of $RNHCO_2C_2H_5$ ($R = C_4H_9$) compounds.

	RI[a]				
m/z	**(6)** (n-C_4H_9)	**(7)** (i-C_4H_9)	**(8)** (s-C_4H_9)	**(9)** (t-C_4H_9)	Assignment[b]
174	5	6	6	1	$[M + C_2H_5]^+$
147	8	10	10	6	
146	100	100	100	71	MH^+
145	6	8	<3	<2	$M^{+\bullet}$
144	4	5	3		$[M - H]^+$
130		4	4	66	$[MH - CH_4]^+$
119	2	3	3	3	
118	39	41	45	23	$[MH - C_2H_4]^+$
117			3		
116	3		46		$[MH - C_2H_6]^+$
103	2	2			
102	24	30			$[MH - C_3H_8]^+$
100	8	10	13	3	$[MH - C_2H_5OH]^+$
91				9	
90	3	5	11	100	$C_3H_8NO_2^+$
76		3	5	7	

[a,b] The footnotes have the same significance as those to Table 1.

Table 3. Methane c.i.m.s. of $C_5H_{11}NHCO_2C_2H_5$ compounds.

	RI[a]								
m/z	**(10)**[c]	**(11)**[c]	**(12)**[c]	**(13)**[c]	**(14)**[c]	**(15)**[c]	**(16)**[c]	**(17)**[c]	Assignment[b]
188	5	9	10	7	13	7	9		$[M + C_2H_5]^+$
161	8	9	9	9	13	12	9	3	
160	100	100	100	100	100	100	100	35	MH^+
159	4	3	4	1	1	<2	1	<1	$M^{+\bullet}$
158	5	4	6	3	5	5	6	2	$[M - H]^+$
144		3	2	6	4		6	6	$[M - CH_4]^+$
132	31	21	20	22	20	25	24		$[M - C_2H_4]^+$
131							5	2	
130	2	1	3	1	2	71	2	39	$[M - C_2H_6]^+$
117							2	2	
116	2	2	1	1	38		33	1	$[M - C_3H_8]^+$
114	8	8	8	5	9	9	5	2	$[M - C_2H_5OH]^+$
104			2	5	1		5	1	
103	2	3	2	8					
102	22	19	20	8	1	3	3	1	$[M - C_4H_{10}]^+$
91								4	
90	4	8	5	4	13	18	15	100	$C_3H_8NO_2^+$
71	6	10	14	6	15	20	22	29	$C_5H_{11}^+$

[a,b] The footnotes have the same significance as those to Table 1.[c] See Scheme 1 for structures of **(10)**–**(17)**.

$n\text{-}C_5H_{11}NHCO_2C_2H_5$ **(10)**

$(CH_3)_2CHCH_2CH_2NHCO_2C_2H_5$ **(11)**

$CH_3CH_2(CH_3)CHCH_2NHCO_2C_2H_5$ **(12)**

$(CH_3)_3CCH_2NHCO_2C_2H_5$ **(13)**

$CH_3CH_2CH_2(CH_3)CHNHCO_2C_2H_5$ **(14)**

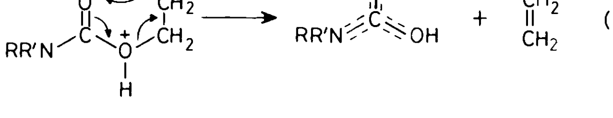
$(CH_3CH_2)_2CHNHCO_2C_2H_5$ **(15)**

$(CH_3)_2CH(CH_3)CHNHCO_2C_2H_5$ **(16)**

$CH_3CH_2(CH_3)_2CNHCO_2C_2H_5$ **(17)**

Scheme 1.

Given that ethylene loss from MH^+ occurs from the ethoxy group, a plausible mechanism for this process is provided by reaction (2). This route requires that a fraction of the urethane molecules ionised by proton transfer are initially protonated on the oxygen atom of the ethoxy group, or that proton transfer to this atom from the carbonyl oxygen atom precedes ethylene expulsion. As indicated previously, these hypotheses (particularly the latter) are quite reasonable in the light of the reported[11] mechanisms of water loss from protonated carboxylic acids.



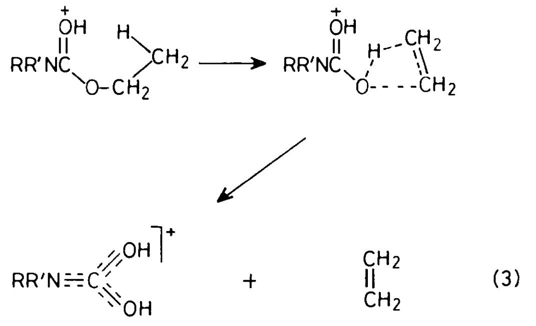
(2)

There is evidence that alkene expulsion from several types of closed-shell ions occurs *via* ion–molecule complexes and/or species containing incipient cations.[12–14] Although such a

Table 4. Methane c.i.m.s. of $RNHCO_2C_2H_5$ compounds.

R: n-C_6H_{13} m/z	RI[a]	n-C_7H_{15} m/z	RI[a]	n-C_8H_{17} m/z	RI[a]	$CH_2 = CHCH_2$ m/z	RI[a]	c-C_6H_{11} m/z	RI[a]	Assignment[b]
214	2	228	2	242	2			212	1	$[M + C_3H_5]^+$
202	8	216	14	230	12	158	<3	200	7	$[M + C_2H_5]^+$
175	10	189	13	203	13	131	6	173	14	
174	100	188	100	202	100	130	76	172	100	MH^+
173	4	187	6	201	7	129	10	171	6	$M^{+\cdot}$
172	8	186	16	200	21			170	9	$[M - H]^+$
158	6	172	2	186	3					$[MH - CH_4]^+$
146	19	160	10	174	8	102	100	144	10	$[MH - C_2H_4]^+$
144	3	158	4	172	5	100	14	142	3	$[MH - C_2H_6]^+$
130	1	144	2	158	2	86	11	128	8	$[MH - C_3H_8]^+$
128	6	142	9	156	7	84	16	126	4	$[MH - C_2H_5OH]^+$
116		130	1	144	2					$[MH - C_4H_{10}]^+$
102	24	116	1	130	1			100	1	$[MH - C_5H_{12}]^+$
		103	2	113	1					
		102	23							$[M - C_6H_{14}]^+$
				103	3					
				102	28					$[M - C_7H_{16}]^+$
		99	2	99						$C_7H_{15}^+$
90	4	90	6	90	9			90	13	$C_3H_8NO_2^+$
85	5	85	1	85						$C_6H_{13}^+$
83	1	83	1	83	1			83	6	$C_6H_{11}^+$

[a,b] The footnotes have the same significance as those to Table 1.

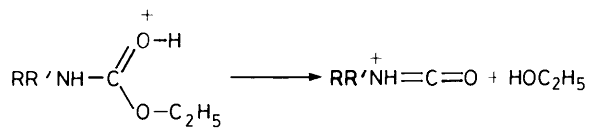

(3)

mechanism, reaction (3), would allow ethylene loss to take place from the carbonyl-protonated form of MH^+, it seems less likely than reaction (2).

(*ii*) $[MH - C_2H_5OH]^+$. The trends in the relative abundance of this ion show several features common to those discussed above for $[MH - C_2H_4]^+$. Thus, a peak corresponding to ethanol loss from MH^+ is present in all the spectra. This peak decreases in relative intensity from 23% in the spectrum of $CH_3NHCO_2C_2H_5$ to 7% in that of n-$C_8H_{17}NHCO_2C_2H_5$. Similarly, the relative abundance of this ion is largely unaffected by changes in the structure of the alkyl group R in $RNHCO_2C_2H_5$ or $R_2NCO_2C_2H_5$, provided tertiary alkyl groups are not considered. Ethanol loss from MH^+ generally occurs to a slightly lesser extent than ethylene elimination, though the resultant daughter ions are usually of comparable abundance. The spectra of the disubstituted urethanes, $R_2NCO_2C_2H_5$, are an exception to this rule of thumb. In these spectra, the importance of $[MH - C_2H_5OH]^+$ declines less rapidly than that of $[MH - C_2H_4]^+$, so that for $(C_3H_7)_2NCO_2C_2H_5$ and $(C_4H_9)_2NCO_2C_2H_5$ the peak produced by ethanol loss is more intense.

As with ethylene loss from MH^+, it is logical to associate the $[MH - C_2H_5OH]^+$ peak with the ethoxy group because of its general occurrence throughout the set of urethane spectra. Furthermore, $(CH_3CD_2)CHNHCO_2C_2H_5$ shows predominantly $[MH - C_2H_5OH]^+$ at m/z 118 in peaks attributable to ethanol loss from MH^+. This explanation is also supported by the observation that the spectra of n-$C_5H_{11}NHCO_2CH_3$ and $(CH_3)_3CCH_2NHCO_2CH_3$ contain ions at m/z 114 $[MH - CH_3OH]^+$ but not at m/z 100 $[M - C_2H_5OH]^+$. Moreover, the fact that methanol and ethanol losses occur from MH^+ in the c.i.m.s. of $C_5H_{11}NHCO_2CH_3$ and $RR'NCO_2C_2H_5$, respectively, suggests that $[MH - C_2H_5OH]^+$ arises by expulsion of ethanol rather than by successive loss of ethylene and water. This two-step alternative would be less likely on energetic grounds since it would be unusual for the primary daughter ions to be formed with enough internal energy to undergo secondary reactions.

Two possible mechanisms can be advanced for ethanol loss: a 1,2-elimination from the carbonyl-protonated from of MH^+, reaction (4), or simple cleavage of the ethoxy protonated isomer, equation (5). The second alternative is somewhat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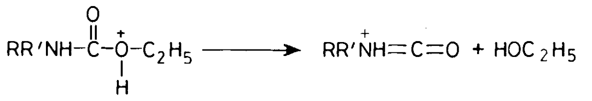


$$RR'NH-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{+}{O}}-C_2H_5 \longrightarrow RR'\overset{+}{N}H{=}C{=}O + HOC_2H_5 \quad (5)$$

more likely, bearing in mind the similar behaviour of protonated carboxylic acids.[11] The ethoxy-protonated isomer of MH^+ could be produced during ionisation or by rearrangement of the carbonyl protonated form.

Despite the difficulty in elucidating the precise mechanisms of ethylene and ethanol expulsion from MH^+, the analytical value of the peaks formed by these processes is clear. They indicate the presence of a $CO_2C_2H_5$ group in the urethane. This information is complementary to that provided by low-energy e.i.m.s., in

Table 5. Methane c.i.m.s. of aromatic $RNHCO_2C_2H_5$.

R								
Ph		$PhCH_2$[c]		$PhCH_2CH_2$		$Ph(CH_3)CH$[c]		
m/z	RI[a]	*m/z*	RI[a]	*m/z*	RI[a]	*m/z*	RI[a]	Assignment[b]
				234	1			$[M + C_3H_5]^+$
194	4	208	4	222	3			$[M + C_2H_5]^+$
167	11			195	14			
166	100	180	100	194	100	194	91	MH^+
165	10	179[c]	0	193	2	193[c]	0	$M^{+\bullet}$
		178	5	192	1	192	2	$[M - H]^+$
						180	19	
150				178		178	15	$[MH - CH_4]^+$
138	21	152	18	166	2	166	2	$[MH - C_2H_4]^+$
120	4	134	3	148	6			$[MH - C_2H_5OH]^+$
				116		116	20	$[MH - PhH]^+$
				106	2			
		105	5	105	27	105	99	$C_8H_9^+$
		102	58	102	8			$C_4H_8NO_2^+$
		91	45	91	2			$C_7H_7^+$
						90	100	$C_3H_8NO_2^+$

[a,b] The footnotes have the same significance as those to Table 1. [c] The residual e.i. component in these spectra remained large even at very low partial pressures of sample; these data were corrected using a background subtraction procedure.

Table 6. Methane c.i.m.s. of $R_2NCO_2C_2H_5$ compounds.

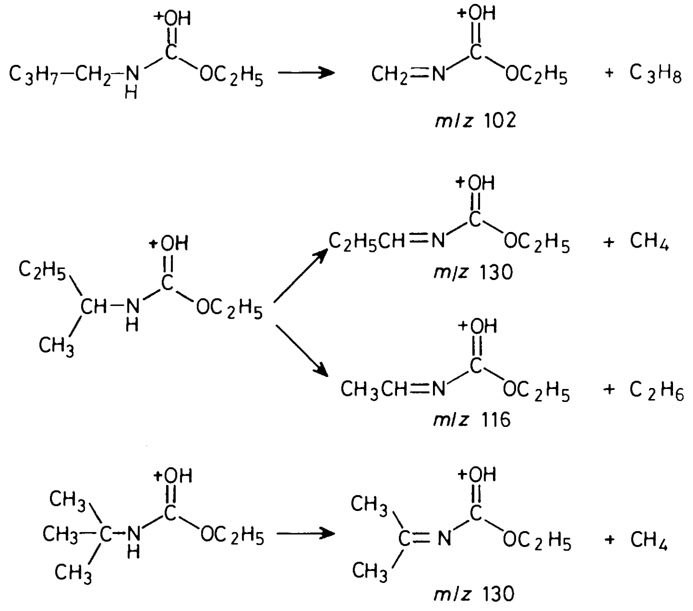
R														
CH_3		C_2H_5		n-C_3H_7		i-C_3H_7		n-C_4H_9		i-C_4H_9		s-C_4H_9		
m/z	RI[a]	*m/z*	RI[a]	*m/z*	RI[a]	*m/z*	RI[a]	*m/z*	RI[a]	*m/z*	RI[a]	*m/z*	RI[a]	Assignment[b]
		186	3	214	2	214	3	242	2	242	2	242	3	$[M + C_3H_5]^+$
146	3	174	11	202	9	202	14	230	10	230	11	230	21	$[M + C_2H_5]^+$
119	5	147	13	175	12	175	12	203	13	203	12	203	20	
118	100	146	100	174	100	174	100	202	100	202	100	202	100	MH^+
117	6	145	4	173	3	173	3	201	5	201	4	201	4	$M^{+\bullet}$
116	5	144	7	172	7	172	5	200	11	200	11	200	11	$[M - H]^+$
		130	14	158	3	158	22	186	3	186	11	186	16	$[MH - CH_4]^+$
90	59	118	33	146	14	146	9	174	8	174	6	174	6	$[MH - C_2H_4]^+$
								173		173		173	8	
		116	3	144	22	144	1	172	3	172	1	172	69	$[MH - C_2H_6]^+$
				132		132	7	160		160		160		$[MH - C_3H_6]^+$
				130	1	130	2	158	38	158	30	158		$[MH - C_3H_8]^+$
72	15	100	24	128	23	128	16	156	15	156	15	156	23	$[MH - C_2H_5OH]^+$
								146	1	146	6	146	16	$[MH - C_4H_8]^+$
								144		144		144	4	$[MH - C_4H_{10}]^+$
								116	5	116	1	116	21	
								100		100	1	100	11	

[a,b] The footnotes have the same significance as those to Table 1.

which the fragment ions are predominantly produced by fragmentation of the RR′NH function.

(*iii*) $[MH - C_mH_{2m+2}]^+$. The presence of one or more ions in the series *m/z* 102, 116, 130, 144, *etc.*, corresponds to alkane loss from MH^+. These ions establish the nature of the principal alkyl group, R, in the saturated urethanes $RNHCO_2C_2H_5$ ($R = C_nH_{2n+1}$). This fragmentation involves formal cleavage of the bond connecting the α- and β-carbon atoms in the urethane. Thus, for the isomeric urethanes $C_4H_9NHCO_2C_2H_5$, the n- and iso-C_4H_9 compounds show a sizeable peak at *m/z* 102 $[MH - C_3H_8]^+$, Scheme 2. The s-C_4H_9 isomer displays a peak at *m/z* 116 $[MH - C_2H_6]^+$ and a smaller peak at *m/z* 130 $[MH - CH_4]^+$. The spectrum of t-$C_4H_9NHCO_2C_2H_5$ is distinct in showing only $[MH - CH_4]^+$ at *m/z* 130 in reactions attributable to alkane loss. This allows the t- and s-$C_4H_9NHCO_2C_2H_5$ compounds to be distinguished from one another and from the n- and iso-$C_4H_9NHCO_2C_2H_5$ isomers. The n- and iso-butyl compounds can be differentiated by reference to the abundances of the subsidiary alkane loss arising by notional cleavage of the bond joining the β- and γ-carbon atoms. The spectrum of n-$C_4H_9NHCO_2C_2H_5$ contains a larger peak at *m/z* 116 $[MH - C_2H_6]^+$ and a smaller peak at *m/z* 130 $[MH - CH_4]^+$ than does the spectrum of iso-$C_4H_9NHCO_2C_2H_5$. These subsiduary ions, however, are of only low abundance, and their use for analytical purposes is less reliable than that of the more prominent C_α–C_β cleavage ions.

The analytical applications of the ions corresponding to alkane loss from MH^+ are further exemplified by the spectra of the eight isomeric $C_5H_{11}NHCO_2C_2H_5$ species, Table 3. Those containing primary alkyl groups show sizeable peaks at *m/z* 102 $[MH - C_4H_{10}]^+$ but only smaller peaks attributable to expulsion of C_3H_8 (*m/z* 116), C_2H_6 (*m/z* 130), and CH_4



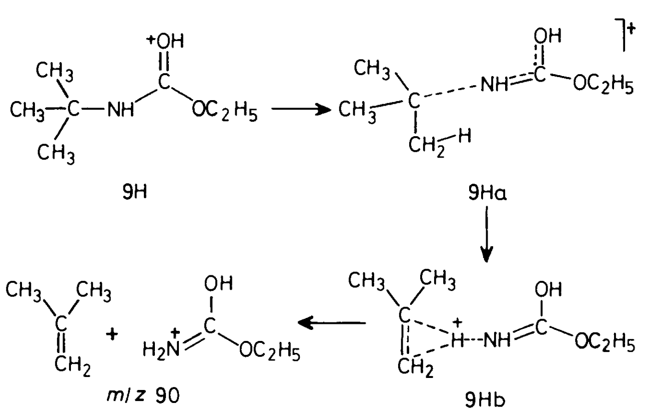
Scheme 2.

(m/z 144) from MH^+. The spectrum of n-$C_5H_{11}NHCO_2C_2H_5$ displays a smaller peak at m/z 144 than do those of $(CH_3)_2CHCH_2CH_2NHCO_2C_2H_5$, $CH_3CH_2(CH_3)CHCH_2NHCO_2C_2H_5$, and $(CH_3)_3CCH_2NHCO_2C_2H_5$. Furthermore, the abundances of the subsidiary ions corresponding to C_β–C_γ cleavage can be employed to distinguish each of these three branched isomers from the others. The $C_5H_{11}NHCO_2C_2H_5$ urethanes containing secondary pentyl groups give spectra showing $[MH - C_2H_6]^+$ for $(CH_3CH_2)_2CHNHCO_2C_2H_5$, but $[MH - C_3H_8]^+$ for $C_3H_7(CH_3)CHNHCO_2C_2H_5$ in the principal C_α–C_β cleavage process. In addition, the two $C_3H_7(CH_3)CHNHCO_2C_2H_5$ compounds also show a minor $[MH + CH_4]^+$ peak in their spectra. Thus, in common with the lower homologue s-$C_4H_9NHCO_2C_2H_5$, loss of the larger alkyl substituent from the branch point dominates in the C_α–C_β cleavage reaction. This trend persists in the spectrum of $C_2H_5(CH_3)_2CNHCO_2C_2H_5$, which shows a larger $[MH - C_2H_6]^+$ peak and a less intense $[MH - CH_4]^+$ peak. The structure of the eighth isomer is confirmed as t-$C_5H_{11}NHCO_2C_2H_5$ by the reduced importance of MH^+ and the abundant m/z 90 ion. In summary, most of the eight isomers of $C_5H_{11}NHCO_2C_2H_5$ are defined by their c.i.m.s.; only n-$C_3H_7(CH_3)CHNHCO_2C_2H_5$ and iso-$C_3H_7(CH_3)CHNHCO_2C_2H_5$ yield spectra that are so similar to one another that identification of the structure is not feasible.

Recent work[15] has established that alkane elimination from ions in the gas phase is not so unusual as was once thought. Indeed, $[MH - \text{alkane}]^+$ peaks occur in the c.i.m.s. of saturated alkylamines,[16] from which urethanes are derived by ethoxycarbonylation.

The main alkane loss can be represented as occurring by cleavage for the C_α–C_β bond, with elimination of the alkyl group and the hydrogen originally attached to nitrogen. This mechanism is probably an oversimplification, but it does lead to delocalised allylic daughter ions, Scheme 2, and it provides a working model for analytical purposes. The above discussion of alkane loss presupposes that the peaks corresponding to $[MH - \text{alkane}]^+$ are not actually $[M - \text{alkyl}]^+$ artefacts arising from a residual e.i. component in the ionisation process. A similar origin for the $[MH - C_2H_5OH]^+$ peaks as $[M - C_2H_5OH]^+$ might also be postulated. In certain circumstances, residual e.i. can cause confusion in c.i.m.s.[17] especially when large $M^{+\bullet}$ and specific fragment ions are produced under e.i. conditions.[18]

Residual e.i. cannot account for the $[MH - C_2H_5OH]^+$ peaks in the c.i.m.s. of these urethanes because $C_2H_5O^\bullet$ loss from $M^{+\bullet}$ is not of sufficient importance at 70 eV[1,2] or at 12.1 eV.[5] Unfortunately, however, the urethanes do show intense $M^{+\bullet}$ and $[M - \text{alkyl}]^+$ peaks in their 12.1 eV e.i.m.s.[5] It is likely, therefore, that the $[MH - \text{alkane}]^+$ ions in the spectra reported in Tables 1–6 arise at least in part from a residual e.i. component. Two observations support this interpretation. First, the e.i.m.s. of neopentyl urethanes show peaks at $[M - C_4H_9]^+$, $[M - C_4H_8]^{+\bullet}$ and $[M - C_4H_7]^+$; in the case of $C_5H_{11}NHCO_2C_2H_5$, these ions are at m/z 102, 103, and 104, respectively.[5] Such ions also are present (Table 3) under c.i. conditions. It is highly unlikely that all these ions arise by decomposition of $[MH]^+$; in particular, production of m/z 103 would constitute a violation[19] of the even-electron rule.[20] Similar remarks apply to the peaks at m/z 88, 89, and 90 in the spectra of neo-$C_5H_{11}NHCO_2CH_3$. Secondly, when the c.i.m.s. reagent gas is changed to ammonia, the relative abundance of the $[M - \text{alkane}]^+$ ions declines much less quickly than those of ions formed by other fragmentations. For instance, the relative intensities of the peaks at m/z 160 $[MH]^+$, 144 $[MH - CH_4]^+$, 130 $[MH - C_2H_6]^+$, and 90 $[MH - C_5H_{10}]^+$ are 100, 3, 25, and 3, respectively, in the ammonia c.i.m.s. of t-$C_5H_{11}NHCO_2C_2H_5$. The analogous figures in the methane c.i.m.s. are 35, 6, 39, and 100, respectively. These experiments involve a reduction in the exothermicity of protonation from *ca.* 300–350 kJ mol^{-1} (CH_5^+ reagent ion) to *ca.* 50–100 kJ mol^{-1} (NH_4^+ reagent ion). The abundances of the $[MH - CH_4]^+$ and $[MH - C_2H_6]^+$ ions decrease by a factor of about two with respect to the $[MH]^+$ abundance; the corresponding reduction for the $[MH - C_5H_{10}]^+$ ion is a factor of more than fifteen. Part of the difference between these factors might be caused by changes in the partial pressures of sample in the methane and ammonia c.i.m.s. Nevertheless, these trends suggest that the $[MH - \text{alkane}]^+$ peaks contain a contribution from $[M - \text{alkyl}]^+$ fragmentations produced by residual e.i. and, moreover, that the proportion of this contribution increases when the enthalpy of protonation is reduced. This conclusion does not, however, detract from the analytical value of these peaks.



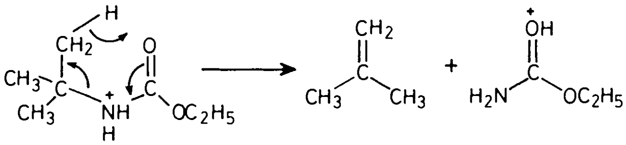
Scheme 3.

(*iv*) $[MH - C_nH_{2n}]^+$. The fourth general fragment ion in the spectra arises by expulsion of an alkene, C_nH_{2n}, derived by hydrogen abstraction from the principal alkyl group ($R = C_nH_{2n+1}$) in $RNHCO_2C_2H_5$. This yields an ion at *m*/*z* 90, which is almost certainly protonated ethyl carbamate acid. The importance of this ion increases only slowly and irregularly on ascending the homologous series of urethanes n-C_nH_{2n+1}-$NHCO_2C_2H_5$. There is, however, a good correlation between the relative intensity of the peak at *m*/*z* 90 and the structure of the principal alkyl group in the spectra of isomeric $RNHCO_2C_2H_5$ compounds. When R is primary, the relative abundance of the $C_3H_8NO_2{}^+$ ion is 8%, or less; when R is secondary, this figure increases to 11–18% (with the exception of 7% for iso-$C_3H_7NHCO_2C_2H_5$); but when R is tertiary, *m*/*z* 90 is the base peak in the spectrum. Consequently, this fragmentation is favoured by increased branching at the α-carbon atom in R, as would be expected if it involved a build up of positive charge on that site. This explanation is supported by the spectrum of $Ph(CH_3)CHNHCO_2C_2H_5$, which contains a large peak at *m*/*z* 90, reflecting the high stability of the incipient $[PhCHCH_3]^+$ ion. One possible mechanism for this reaction is depicted in Scheme 3.

Starting from 9H, stretching of the C–N σ-bond gives 9Ha, in which a partial positive charge has developed on the tertiary carbon atom. Proton transfer from the incipient t-butyl cation then results in expulsion of C_4H_8 and formation of $C_3H_8NO_2{}^+$; a proton bound dimer, such as 9Hb, may be an approximation to the transition state or intermediate in this hydrogen-transfer step. The involvement of species like 9Ha and 9Hb, some of which may be described as ion–molecule complexes, has previously been proposed in the decomposition of isolated organic ions.[12,13] Whilst the validity of this mechanistic approach has been questioned, very recent work[21–34] has shown that it is definitely important in numerous systems; a recent review[14] highlights the main features of the chemistry of these species.

The intervention of ion–molecule complexes in the production of protonated alcohols from protonated carbamates has already been suggested.[3,4] The mechanism of Scheme 3 offers a plausible rationalisation for the effect of substitution on the α-carbon atom on the abundance of alkene loss from MH^+. It also explains the high abundance of the *m*/*z* 90 ion in the spectrum of $Ph(CH_3)CHNHCO_2C_2H_5$, in that a particularly stable incipient cation $[PhCHCH_3]^+$ is involved. The corresponding protonated alkylamines, $RNH_3{}^+$, $RNH_2CH_3{}^+$, and $RNH(CH_3)_2{}^+$ also expel an alkene derived by hydride abstraction from R^+.[16,34] Ion–molecule complexes have been implicated in this process, and the abundance of alkene loss is again greatest when R is a tertiary alkyl group.

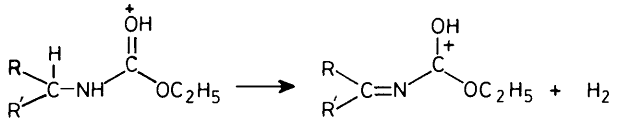
Other explanations for alkene loss, such as reaction (6) cannot be rigorously excluded, particularly since the reacting configuration of MH^+ remains uncertain. This alternative, however, does not so logically explain the effect of substitution on the α-carbon atom on the abundance of $[MH - \text{alkene}]^+$ ions.



(6)

Two other minor fragmentation processes deserve a brief mention. First, formation of R^+ cations from MH^+ produced from $RNHCO_2C_2H_5$ occurs in the spectra of the larger urethanes. These peaks are more important when a favourable cation is produced (for instance, *m*/*z* 91 $[C_7H_7]^+$ when $R = PhCH_2$). When $R = C_nH_{2n+1}$, these peaks are of little analytical value, but they do provide useful structural information when R contains a phenyl group.

Secondly, $[MH - H_2]^+$ ions appear in the spectra of many of the urethanes. These ions increase in abundance for higher members of the homologous series of urethanes, but they are of small or negligible abundance when the α-carbon atom in $RNHCO_2C_2H_5$ has no hydrogen atoms attached to it. In view of this latter trend, these ions may originate by H_2 elimination across the C_α–NH bond, thus producing allylic delocalised daughter ions, reaction (7). However, this cannot be the whole story, since $[MH - H_2]^+$ peaks are found in the spectra of disubstituted urethanes $R_2NCO_2C_2H_5$. In addition, it is known that $[MH - H_2]^+$ peaks often arise by hydride abstraction from *M*, rather than by H_2 elimination from MH^+;[17] thus, the origin of these ions cannot be elucidated with certainty.



(7)

Conclusion

Methane c.i.m.s. is applicable in elucidating the structures of urethanes of general formula $RR'NCO_2C_2H_5$. All these spectra contain intense $[MH]^+$ peaks. The presence of the $CO_2C_2H_5$ group is revealed by $[MH - C_2H_4]^+$ and $[MH - C_2H_5OH]^+$ peaks. In addition, structural information about the alkyl groups attached to nitrogen is accessible from the peaks corresponding to alkene and alkane loss from $[MH]^+$.

Experimental

The compounds required for this work were either commercial samples of high purity ($H_2NCO_2C_2H_5$, $C_2H_5NHCO_2C_2H_5$; obtained from Aldrich) or synthesised by condensation of the parent amine with the appropriate chloroformate ester at −50 to −20 °C in pyridine/dichloromethane solution, reaction (8).

$$RR'NH + ClCO_2R'' \xrightarrow[CH_2Cl_2]{\text{pyridine}} RR'NCO_2R'' \quad (8)$$

Crude urethanes were isolated by extraction into dichloromethane, after aqueous workup, and purified by fractional distillation or recrystallisation from hexane. ^2H-labelled urethanes were prepared using the routes outlined in reactions (9)–(10), Scheme 4. Further details of these procedures are available from the authors.

$$(CH_3)_3CNHCO_2C_2H_5 \xrightarrow[(ii)]{(i)} (CH_3)_3C(CD_3)NCO_2C_2H_5 \qquad (9)$$

$$(C_2H_5)_2CO \xrightarrow{(iii)} (CH_3CD_2)_2CO \xrightarrow{(iv)} (CH_3CD_2)_2C{=}NOD \xrightarrow{(v)}$$

$$(CH_3CD_2)_2CHNH_2 \xrightarrow{(vi)} (CH_3CD_2)_2CHNHCO_2C_2H_5 \qquad (10)$$

Scheme 4. *Reagents and conditions:* i, NaH, $(CH_3)_2SO$; ii, CD_3I; iii, $NaOD/D_2O$, $Bu_4N^+Br^-$ then repeat; iv, ND_2OD/K_2CO_3, D_2O, heat; v, $LiAlH_4/Et_2O$; vi, $ClCO_2C_2H_5$/pyridine/CH_2Cl_2, −30 °C.

The c.i.m.s. were recorded using a KRATOS MS 80 double-focusing mass spectrometer operating at an accelerating voltage of 4 kV. Samples were introduced into the methane plasma by probe insertion, with cooling when necessary for the more volatile urethanes. The energy of the ionising electrons was 100 eV and the nominal methane pressure was *ca.* 0.5 Torr.*

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* 1 Torr = (101 325)/760 Pa.

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