# Unimolecular Reactions of Isolated Organic Ions: Some Isomers of $C_6H_{14}^{+\cdot}$

By **Jens F. Wendelboe, Richard D. Bowen,** * and **Dudley H. Williams,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The slow unimolecular reactions of the four isomers of $C_6H_{14}^{+\cdot}$ which do not contain a quaternary carbon atom are reported. The results are discussed in terms of a general mechanism involving species comprising a partially formed carbonium ion co-ordinated to an incipient radical. Such species are accessible from the parent $C_6H_{14}^{+\cdot}$ radical-cation by simply stretching a given C–C bond. In many cases, rearrangement of the partially formed carbonium ion occurs to give thermodynamically more stable isomers. The proposed mechanism also accounts for previously reported energy measurements and ^{13}C-labelling data. Further evidence in support of the mechanism is furnished by [2]H-labelling experiments.

THE unimolecular reactions of ionised alkanes have been the subject of extensive research.[1-21] Complex behaviour is often observed, even for relatively small $C_nH_{2n+2}^{+\cdot}$ species, and the chemistry of alkane molecular ions appears to be rich in unexpected reactions. Thus, for example, alkyl radical loss, which is a common decomposition process, frequently involves atoms within the original chain in addition to the elimination of an intact terminal radical.[15-18] These results, taken together with energy measurements,[3,4] suggest that isomerisation precedes or accompanies the dissociation of at least some ionised alkane isomers. In particular, radical elimination from larger n-$C_nH_{2n+2}^{+\cdot}$ species gives rise to daughter ions having a secondary cationic site; for example, $\cdot$CH$_3$ loss from n-$C_4H_{10}^+$ gives $(CH_3)_2CH^+$ as the product ion.[17]

A variety of mechanisms have been advanced to explain the behaviour of ionised alkanes; some of the processes involved (for example, the 'extrusion' of internal methylene groups in methyl radical loss [17,18]) have not in the past been understood in terms of accepted concepts of mechanistic organic chemistry. More recently, a general mechanism has been proposed that involves both reactions and intermediates which are acceptable from energetic and mechanistic standpoints.[21]
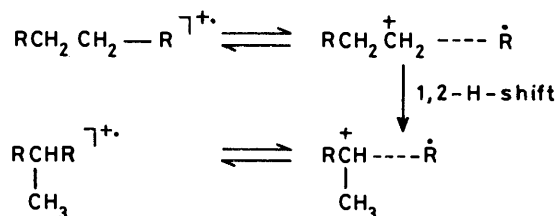
SCHEME 1

This mechanism involves the stretching of a given carbon–carbon bond, so that a species consisting of an incipient carbonium ion co-ordinated to a radical is produced. Rearrangement of the incipient carbonium ion may then occur, to give an isomerised radical cation; alternatively, dissociation can take place to yield a product ion having a structure not available by direct cleavage of the original radical cation. The mechanism

is illustrated, in general terms, in Scheme 1, which shows how secondary carbonium ions can be formed by radical loss from alkane molecular ions. It is envisaged that the species in which a very weak bond is represented by a dashed line in Scheme 1 are bound by virtue of polarisation of the radical by the charge on the incipient carbonium ion.

Application of this mechanism to $C_4H_{10}^{+\cdot}$ and $C_5H_{12}^{+\cdot}$ ion systems can explain the observed reactions in some detail.[21] Moreover, the explanation is more satisfying than the earlier rationalisations involving 'extrusion' processes. This paper seeks to extend the analysis to $C_6H_{14}^{+\cdot}$; the four isomers of hexane that do not contain a quaternary carbon atom were selected for detailed study.

RESULTS AND DISCUSSION

The slow unimolecular reactions of ionised n-hexane, 2- and 3-methylpentane and 2,3-dimethylbutane are given in Table 1.

TABLE 1

Slow unimolecular reactions of isomeric $C_6H_{14}^{+\cdot}$ ions

| Ion structure	Neutral lost [a]				
	CH$_3$	CH$_4$	C$_2$H$_5$	C$_2$H$_6$	C$_3$H$_8$
$(CH_3)_2CHCH(CH_3)_2^{+\cdot}$ (1)	84	8			8
$(CH_3CH_2)_2CHCH_3^{+\cdot}$ (2)	<1	2	6	92	
$(CH_3)_2CHCH_2CH_2CH_3^{+\cdot}$ (3)	9	13	47	31	
$CH_3CH_2CH_2CH_2CH_2CH_3^{+\cdot}$ (4)	5	3	18	73	1

[a] Values determined by B/E scans using an AEI–KRATOS MS 50 double-focusing mass spectrometer; the relative abundances were measured by peak heights and normalised to a total of 100 units.

For reasons which become apparent as the discussion develops, it is instructive to consider the most branched isomers first.

$(CH_3)_2CHCH(CH_3)_2^{+\cdot}$.—It is immediately obvious from the data of Table 1 that ionised 2,3-dimethylbutane is unique in undergoing no $C_2H_5^\cdot$ or C_2H_6 loss; in contrast, the other three isomers of $C_6H_{14}^{+\cdot}$ lose $C_2H_5^\cdot$ and C_2H_6 in high abundance (78—98% of the total metastable ion current from $C_6H_{14}^{+\cdot}$). This may be explained by the lack of an intact ethyl group in $(CH_3)_2CHCH-(CH_3)_2^{+\cdot}$ (1); consequently, the stretching of carbon–

carbon bonds in (1) produces only incipient methyl and propyl radicals (Scheme 2). Energy data relevant to the dissociation of (1) are given in Table 2. In Table 2 and subsequent Tables containing energy data, the

threshold (880 kJ mol^{-1}) expected for formation of the 1,2-dimethylpropyl cation. This result indicates that $\cdot CH_3$ loss does not proceed via simple cleavage in (1), at least for low energy ions; rearrangement of the incipient
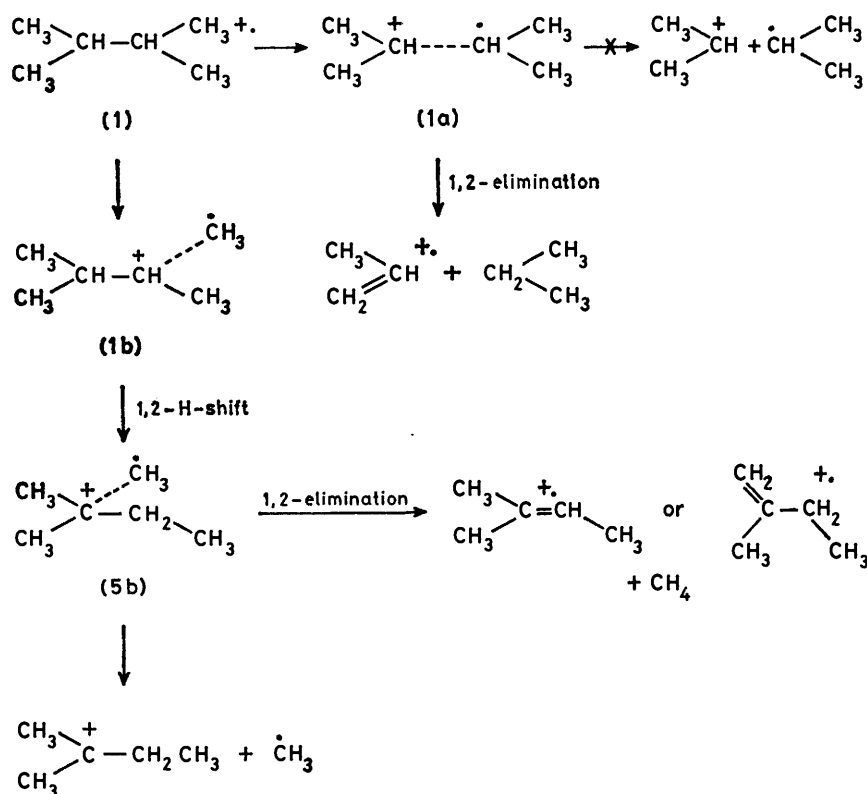
SCHEME 2

column headed $\Sigma \Delta H_f$ gives the total heat of formation of the hypothetical product combination under consideration. Since the actual transition state energy is available from appearance potential measurements, certain product combinations can be excluded on the grounds that $\Sigma \Delta H_f$ for these products lies significantly above the measured transition state energy. Small differences of up to 10 kJ mol^{-1} are not considered significant (for example, Table 2 line 2 and Table 3 line 2) and can be interpreted simply in terms of experimental errors inherent in the energy data. It is apparent that the transition state energies for elimination of C_3H_8, $\cdot CH_3$, and CH_4 lie within the range 830—850 kJ mol^{-1}. These decomposition channels have the lowest activation energies and consequently are the main reactions observed for metastable $(CH_3)_2CHCH(CH_3)_2^{+\cdot}$ ions. However, elimination of $\cdot C_3H_7$ proceeds via a transition state of higher energy (910 kJ mol^{-1}) and is not observed at low internal energies. The complex (1a), formed by stretching the central carbon–carbon bond in (1), undergoes a 1,2-elimination to give the energetically more favourable products $C_3H_6^{+\cdot}$ and C_3H_8. Loss of $\cdot CH_3$ occurs via a transition state having a significantly lower energy (850 kJ mol^{-1}) than the thermochemical

secondary carbonium ion occurs to give a more stable tertiary cation [(1) ⟶ (1b) ⟶ (5b)]. Methane loss can give rise to a number of ionic products, ionised 2-

TABLE 2

Energy data relevant to the dissociation of
$(CH_3)_2CHCH(CH_3)_2^{+\cdot}$

| Reaction	Possible product structures and $\Delta H_f{}^a$	$\Sigma \Delta H_f{}^a$	Measured transition state energy ^{a,b}
$\cdot C_3H_7$ loss	$(CH_3)_2CH^+ + (CH_3)_2CH^\cdot$ 805[22] 70[23]	875	910
C_3H_8 loss	$CH_3CH=CH_2^{+\cdot} + CH_3CH_2CH_3$ 960[24] $+$ $-105[23]$	855	845
$\cdot CH_3$ loss	$\begin{cases} (CH_3)_2C\overset{+}{C}H_2CH_3 + \cdot CH_3 \\ 675[25] \quad + \quad 140[23] \\ (CH_3)_2CH\overset{+}{C}HCH_3 + \cdot CH_3 \\ 740\,^c \qquad\qquad 140[23] \end{cases}$	815 880	850 850
CH_4 loss	$\begin{cases} (CH_3)_2C=CHCH_3^{+\cdot} + CH_4 \\ 790[24] \qquad\quad {}^{+\cdot}\; -75[23] \\ CH_2=C(CH_3)CH_2\overset{+}{C}H_3 + CH_4 \\ 850[24] \qquad\qquad -75[23] \end{cases}$	715 775	830 830

^{a} All values in kJ mol.$^{-1}$ ^{b} Appearance potential measurements [3] using photoionisation. ^{c} Value estimated by analogy with lower homologues.

methylbut-2-ene and ionised 2-methylbut-1-ene being plausible candidates. These two radical cations arise by hydrogen abstraction, by the incipient methyl radical in

(5b), from either methyl group or the methylene group adjacent to the cationic site. Other products could be formed by analogous 1,2-eliminations in (1b) or related species. In any case, a mixture of isomeric $C_5H_{10}^{+\bullet}$ products is by no means impossible: similar ionic reactions, involving isolated cations, are known to give mixtures

direct cleavage in (1) and the actual transition state energy (850 kJ mol^{-1}). However, this can be regarded only as a rough figure because it represents the small difference in two large values, each of which may contain errors of 10 kJ mol^{-1} or more.

$(CH_3CH_2)_2CHCH_3^{+\bullet}$.—The major slow reaction of
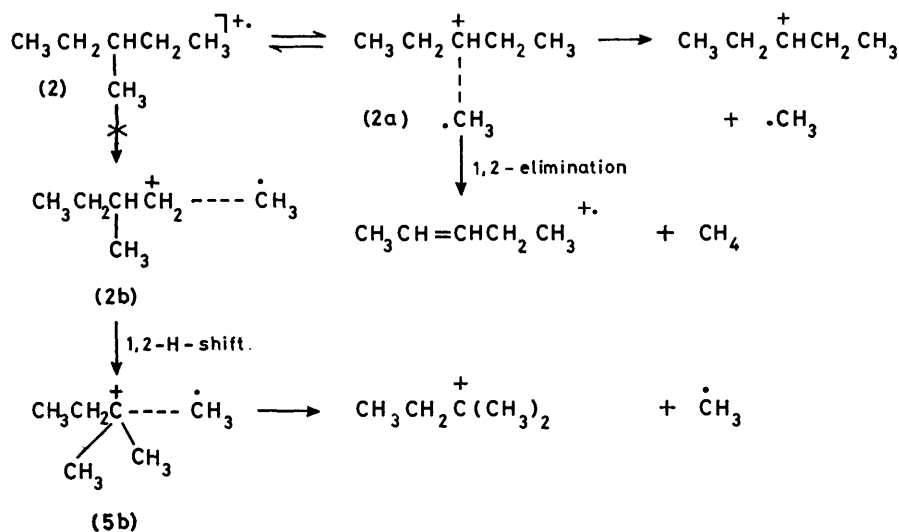
SCHEME 3

of eliminated neutral species;[26,27] in addition, acid-catalysed dehydration of tertiary alcohols in solution often yields more than one isomeric olefin.[28] A final point in connection with $^{\bullet}CH_3$ and CH_4 loss from (1) is that $^{\bullet}CH_3$ elimination dominates, despite possessing a higher transition state energy. This result is somewhat surprising and may reflect a kinetic preference for $^{\bullet}CH_3$ loss, which might reflect the less stringent geometrical requirement associated with $^{\bullet}CH_3$ loss compared to elimination of CH_4. Each of these processes proceed via transition states having energies significantly higher than the total heat of formation of the products; therefore, it is probable that rearrangement steps occur prior to dissociation. Since CH_4 loss involves more extensive rearrangement than $^{\bullet}CH_3$ loss, the latter dominates. This effect appears to be fairly general for ionised alkanes which undergo rate-determining rearrangement of the incipient carbonium ion. Thus, for example, n-$C_6H_{14}^{+\bullet}$ eliminates more $^{\bullet}CH_3$ than CH_4; in this case, the isomerisation involves an incipient primary carbonium ion rearranging to a secondary structure. However, when $^{\bullet}CH_3$ and CH_4 loss can occur without prior rearrangement of the incipient carbonium ion (for example, from ionised 3-methylpentane, see later), the effect is less marked or not evident at all. Moreover, the measured transition state energy (850 kJ mol^{-1}) for $^{\bullet}CH_3$ loss from (1) allows an estimate to be made for the binding energy in (1b). Assuming that (1b) corresponds to the highest energy species en route to $^{\bullet}CH_3$ loss, the binding energy (30 kJ mol^{-1}) is given by the difference between the energy (880 kJ mol^{-1}) needed to effect

ionised 3-methylpentane is C_2H_6 elimination, with a minor amount of $^{\bullet}C_2H_5$ loss; $^{\bullet}CH_3$ and CH_4 losses together account for only ca. 2% of the total metastable ion current from $C_6H_{14}^{+\bullet}$ (Table 1). Relevant energy data for these reactions are summarised in Table 3.

TABLE 3

Energy data relevant to the dissociation of $(CH_3CH_2)_2CHCH_3^{+\bullet}$

Reaction	Possible product structures and $\Delta H_f{}^a$	$\Sigma \Delta H_f{}^a$	Measured transition state energy^{a,b}
$^{\bullet}CH_3$ loss	$CH_3CH_2(CH_3)\overset{+}{C}HCH_2 + {}^{\bullet}CH_3$ 805^c 140^{23}	945	875
	$(CH_3CH_2)_2\overset{+}{C}H + {}^{\bullet}CH_3$ 745^c 140^{23}	885	875
	$CH_3CH_2\overset{+}{C}(CH_3)_2 + {}^{\bullet}CH_3$ 675^{25} 140^{23}	815	875
CH_4 loss	$C_5H_{10}^{+\bullet}$ (various isomers) + CH_4 790—895^{24} -75^{23}	715—820	860
$^{\bullet}C_2H_5$ loss	$CH_3CH_2\overset{+}{C}HCH_3 + {}^{\bullet}C_2H_5$ $^{\bullet}C765^{22}$ 105^{23}	870	885
$^{\bullet}C_2H_6$ loss	$CH_3CH=CHCH_3^{+\bullet} + C_2H_6$ 875^{24} -85^{23}	790	850
	$CH_3CH_2CH=CH_2^{+\bullet} + C_2H_6$ 925^{24} -85^{23}	840	850

^{a} All values in kJ mol^{-1}. ^{b} Appearance potential [3] measurements using photoionisation. ^{c} Values estimated by analogy with lower homologues.

There are two plausible mechanisms for $^{\bullet}CH_3$ loss (Scheme 3): either simple cleavage of the 3-methyl group, forming the secondary 1-ethylpropyl cation, (2) ⟶ (2a) ⟶ products; or loss of a methyl group from an ethyl chain, with an associated 1,2-hydride

shift in the incipient primary carbonium ion, to form a tertiary cation, (2) —→ (2b) —→ (5b) —→ products. Two pieces of evidence indicate that the former mechanism operates. First, ^{13}C-labelling studies reveal that the 3-methyl group is specifically lost, at least in fast reactions, when ·CH_3 is expelled from (2).[8] Secondly, energy data are consistent with the formation of the 1-ethylpropyl cation,[3] although the 1,1-dimethylpropyl cation could conceivably be produced with excess energy.

Given that ·CH_3 loss gives rise to a 1-ethylpropyl cation, the most logical pathway for CH_4 elimination would be via (2a); a 1,2-elimination yields ionised pent-2-ene and methane, with a total heat of formation (755 kJ mol^{-1}) which would be easily accessible. However, other product ion structures cannot be excluded rigorously on this basis. Nevertheless, support for the proposed mechanism for methane loss can be found from the results of [2]H-labelling experiments (Table 4). The

TABLE 4

Slow unimolecular reactions of $(CH_3CD_2)_2CHCH_3^{+·}$

Mass of neutral lost [a]	Probable structure of neutral lost	Relative abundance [b]
15	CH_3	0
16	CH_4 (CH_2D)	≪1
17	CH_3D	2
29	C_2H_5	0
30	C_2H_6 (C_2H_4D)	0
31	$C_2H_3D_2$	1
32	$C_2H_4D_2$ ($C_2H_2D_3$)	10
33	$C_2H_3D_3$ (C_2HD_4)	88

[a] Values given to the nearest dalton. [b] Values determined by B/E scans using an AEI-KRATOS MS 50 double-focusing mass spectrometer; the relative abundances were measured by peak heights and normalised to a total of 100 units.

methane lost from $(CH_3CD_2)_2CHCH_3^{+·}$ consists essentially exclusively of CH_3D; this result is consistent with the mechanism of Scheme 3. It is significant that CH_4 loss dominates over ·CH_3 loss starting from (2), as expected from the lower transition state energy asso-

associated activation energies for dissociation. However, additional kinetic factors have to be considered in the reactions of (1).

The energy data of Table 3 show that ·C_2H_5 loss from (2) is interpretable in terms of a simple cleavage of an ethyl group, producing the 1-methylpropyl cation (Scheme 4). Furthermore, 1,2-eliminations in the complex (2c) can result in C_2H_6 loss and formation of either ionised but-1-ene or but-2-ene. This mechanism is supported by the results for $(CH_3CD_2)_2CHCH_3^{+·}$ decomposition: ethyl radical and ethane eliminations are seen to involve specifically the original ethyl groups, no ·C_2H_5 or C_2H_6 loss being detected. Indeed, almost no ethyl radical loss is observed: this suppression of $CH_3\dot{C}D_2$ loss, relative to $CH_3\dot{C}H_2$ loss from the unlabelled compound, may originate in a secondary deuterium isotope effect. Ethane elimination from $(CH_3CD_2)_2$-$CHCH_3^{+·}$ comprises mainly CH_3CD_3, with a minor amount of CH_3CHD_2. These data show that, on the basis of Scheme 4, there is a preference for selecting the hydrogen atom, needed to complete the ethane molecule, from the methylene group in the incipient carbonium ion in (2c). Consequently, although both ionised but-1-ene and but-2-ene occur in the ionic products, mainly the latter is formed. This result may be understood in energetic terms on the reasonable assumption that the transition state leading to ionised but-2-ene has the lower heat of formation, as would be expected on the basis of product ion stability. Moreover, the energetic preference over-rides any primary deuterium isotope effect in this case: CH_3CD_3 loss is nine times more abundant than CH_3CHD_2 loss, even though a C–D bond must be broken to form CH_3CD_3, whereas only a C–H bond is cleaved in CH_3CHD_2 elimination.

$(CH_3)_2CHCH_2CH_2CH_3^{+·}$.—Table 5 gives energy data relevant to the decomposition of ionised 2-methylpentane. Several conclusions emerge from a consideration of these data. First, the dominant reaction, ·C_2H_5

SCHEME 4

ciated with the latter process, whereas a trend in the opposite direction is observed for the decomposition of (1). This apparent contradiction can be explained because ·CH_3 and CH_4 loss from (2) can occur without rearrangement of the incipient carbonium ion; in contrast, these eliminations from (1) require isomerisation of the incipient carbonium ion. Therefore, when (2) decomposes via elimination of ·CH_3 or CH_4, the relative abundances of these processes reflect primarily the

loss (Table 1), cannot lead to the 2-methylpropyl cation because the estimated transition state energy (935 kJ mol^{-1}) is far in excess of the experimental energy threshold (860 kJ mol^{-1}) required for ·C_2H_5 loss. The results are best interpreted in terms of a 1,2-hydride shift in the incipient primary carbonium ion, (3b) —→ (5a), thus resulting in the eventual formation of a tertiary cation. An analogous rearrangement has previously been shown to occur when ·C_3H_7 is eliminated from

ionised 2-methylhexane.[12] On this basis (Scheme 5) C_2H_6 loss ought to produce ionised 2-methylpropene. This product combination (total heat of formation 790

TABLE 5

Energy data relevant to the dissociation of $(CH_3)_2CHCH_2CH_2CH_3^{+\bullet}$

Reaction	Possible product structures and $\Delta H_f{}^a$	$\Sigma \Delta H_f{}^a$	Measured transition state energy ^{a,b}
$^\bullet C_2H_5$ loss	$(CH_3)_2CH\overset{+}{C}H_2 + {}^\bullet C_2H_5$ 830^{22}　　105^{23}	935	860
	$(CH_3)_3C^+ + {}^\bullet C_2H_5$ 700^{22}　105^{23}	805	860
C_2H_6 loss	$(CH_3)_2C=CH_2^{+\bullet} + C_2H_6$ 875^{24}　　　-85^{23}	790	855
$^\bullet CH_3$ loss	$CH_3\overset{+}{C}HCH_2CH_2CH_3 + {}^\bullet CH_3$ 750^{25}　　　　140^{23}	890	875
CH_4 loss	$CH_2=CHCH_2CH_2CH_3^{+\bullet} + CH_4$ 895^{24}　　　　　-75^{23}	820	870
	$CH_3CH=CHCH_2CH_3^{+\bullet} + CH_4$ 850^{24}　　　　　-75^{23}	775	870
$^\bullet C_3H_7$ loss	$(CH_3)_2\overset{+}{C}H + {}^\bullet CH_2CH_2CH_3$ 805^{22}　　80^{23}	885	

^{a} All values in kJ mol^{-1}. ^{b} Appearance potential measurements [3] using photoionisation.

kJ mol^{-1}) is easily accessible at the thermochemical threshold (855 kJ mol^{-1}) for C_2H_6 elimination; however, other structures for the $C_4H_8^{+\bullet}$ daughter ion cannot be excluded unequivocally. Secondly, $^\bullet CH_3$ loss can plausibly be explained in terms of simple bond cleavage involving elimination of a methyl radical in the isopropyl group of (3).

Although the reaction occurs with a transition state energy some 15 kJ mol^{-1} below the thermochemical

threshold for formation of 1-methylbutyl cation and a methyl radical, this discrepancy probably lies within the experimental errors in the energy measurements. In any case, ^{13}C-labelling results indicate that, at least for fast reactions, the methyl radical eliminated originates essentially exclusively from the isopropyl group of (3).[8] Moreover, [2]H-labelling experiments (Table 6) show that this behaviour persists at energies appropriate to the decomposition of metastable ions.

The [2]H-labelling data are worthy of further discussion.

TABLE 6

Slow unimolecular reactions of $(CH_3)_2CDCH_2CH_2CH_3^{+\bullet}$ and $(CD_3)_2CHCH_2CH_2CH_3^{+\bullet}$

Neutral lost		Relative abundance ^{b}	
Mass ^{a}	Probable structure	$(CH_3)_2CDCH_2CH_2CH_3^{+\bullet}$	$(CD_3)_2CHCH_2CH_2CH_3^{+\bullet}$
15	CH_3	20	
16	CH_4 (CH_2D)	31	
17	CH_3D	2	
18	CD_3		4
19	CHD_3		3
20	CD_4		1
29	C_2H_5	25	61
30	C_2H_6	17	12
31	C_2H_5D	5	16
32	$C_2H_2D_3$		2
33	$C_2H_3D_3$		1

^{a} Values given to the nearest dalton. ^{b} Values determined by B/E scans using an AEI-KRATOS MS 50 double-focusing mass spectrometer; the relative abundances were measured by peak heights and normalised to a total of 100 units.

In broad outline, the results show that methyl radical and methane losses involve specifically the isopropyl group in (3), whereas ethyl radical and ethane eliminations proceed with involvement of only the original
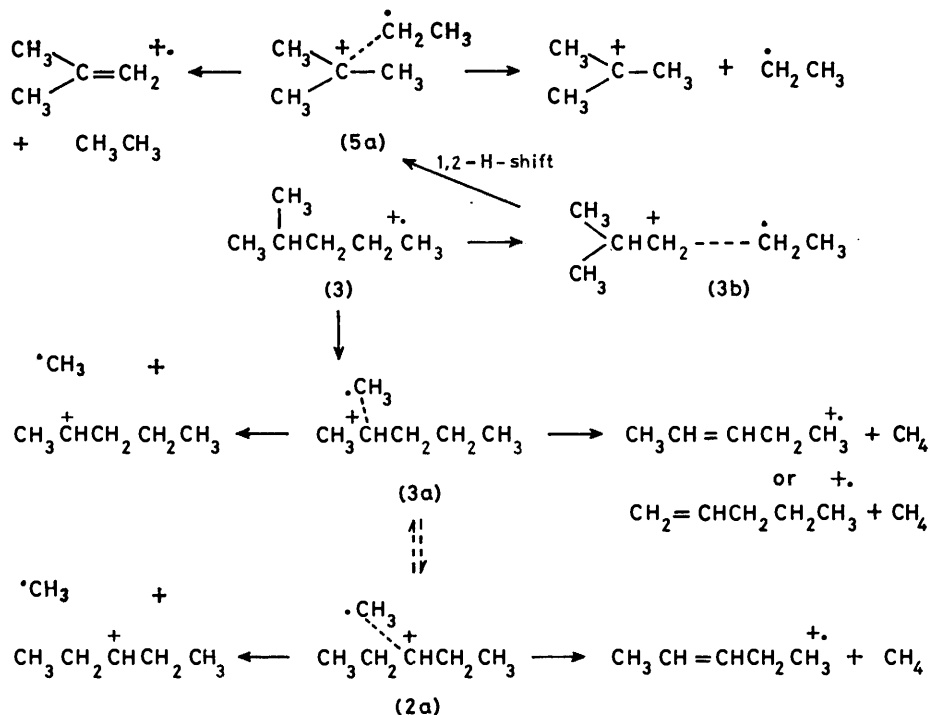
SCHEME 5

ethyl group. An interesting overall isotope effect can be discerned in the relative total abundances of methyl radical plus methane and ethyl radical plus ethane losses. The unlabelled compound eliminates C_1 and C_2 fragments in the ratio 22 : 78; however, $(CH_3)_2CDCH_2CH_2CH_3^{+\cdot}$ and $(CD_3)_2CHCH_2CH_2CH_3^{+\cdot}$ expel C_1 and C_2 fragments in the ratio 53 : 47 and 8 : 92, respectively. These results can be explained, in terms of isotope effects, on the basis of Scheme 5. Ethyl radical and ethane losses occur via (3b) and (5a); a 1,2-hydride shift must occur (or, at least, begin to occur) before dissociation can take place. This 1,2-hydride shift necessitates the breaking of the C–H bond, in the original methine group in (3), in the rate-determining step. No comparable effect operates for methyl radical or methane eliminations from (3). Consequently, when the appropriate C–H bond is replaced by a C–D bond, in $(CH_3)_2CDCH_2CH_2$-$CH_3^{+\cdot}$, a primary deuterium isotope effect discriminates against (3b) $\longrightarrow$ (5a). Therefore, the total abundance of ethyl radical and ethane losses is reduced, relative to the total abundance of methyl radical and methane eliminations, for dissociation of $(CH_3)_2CDCH_2CH_2CH_3^{+\cdot}$. A similar effect has been reported previously for ionised isoheptane.[12] The preference exhibited by $(CD_3)_2$-$CHCH_2CH_2CH_3^{+\cdot}$ for eliminating C_2 fragments may be interpreted as arising from a secondary isotope effect. Loss of methyl radical or methane from (3) involves stretching a CH_3–C bond, (3) $\longrightarrow$ (3a); this process should be rate-determining and be more difficult when the CH_3–C bond is replaced by CD_3–C, in $(CD_3)_2CHCH_2$-$CH_2CH_3^{+\cdot}$. Such secondary deuterium isotope effects can occur in neutral species [29] and have been detected previously in the unimolecular reactions of ionised alkanes.[12,17,21] For instance, the preference of CD_3-$(CH_2)_2CD_3^{+\cdot}$ for loss of CH_4, rather than CHD_3, can be ascribed to a secondary deuterium isotope effect.[17] Similar effects operate in the decomposition of ionised t-butylbenzene and 4-t-butylpyridine.[30]

Finally, the observation of a minor amount of CH_3D loss from $(CH_3)_2CDCH_2CH_2CH_3^{+\cdot}$, and small quantities of $\cdot C_2H_2D_3$ and $C_2H_3D_3$ losses from $(CD_3)_2CHCH_2$-$CH_2CH_3^{+\cdot}$, can be explained. Rearrangement of the incipient 1-methylbutyl cation to the 1-ethylpropyl structure [(3a) $\longrightarrow$ (2a)] may occur for a small number of ions; subsequent decomposition can then account for these observed minor decay channels. The isomerisation (3a) $\longrightarrow$ (2a) does not release much potential energy, both cations being secondary and of comparable heats of formation; consequently, (3a) $\longrightarrow$ (2a) does not occur for many ions generated as (3). In contrast, (3b) $\longrightarrow$ (5a) is very exothermic (primary to tertiary incipient cations) and occurs with great facility.

$CH_3(CH_2)_4CH_3^{+\cdot}$.—Ionised n-hexane eliminates predominantly $\cdot C_2H_5$ and C_2H_6, together with minor amounts of $\cdot CH_3$ and CH_4 (Table 1); only a very small quantity of C_3H_8 loss is detectable. The four processes involving loss of C_1 or C_2 fragments proceed via transition states of closely similar energies (895 ± 5 kJ mol^{-1}).[3] These data indicate that $\cdot CH_3$ and $\cdot C_2H_5$ losses must
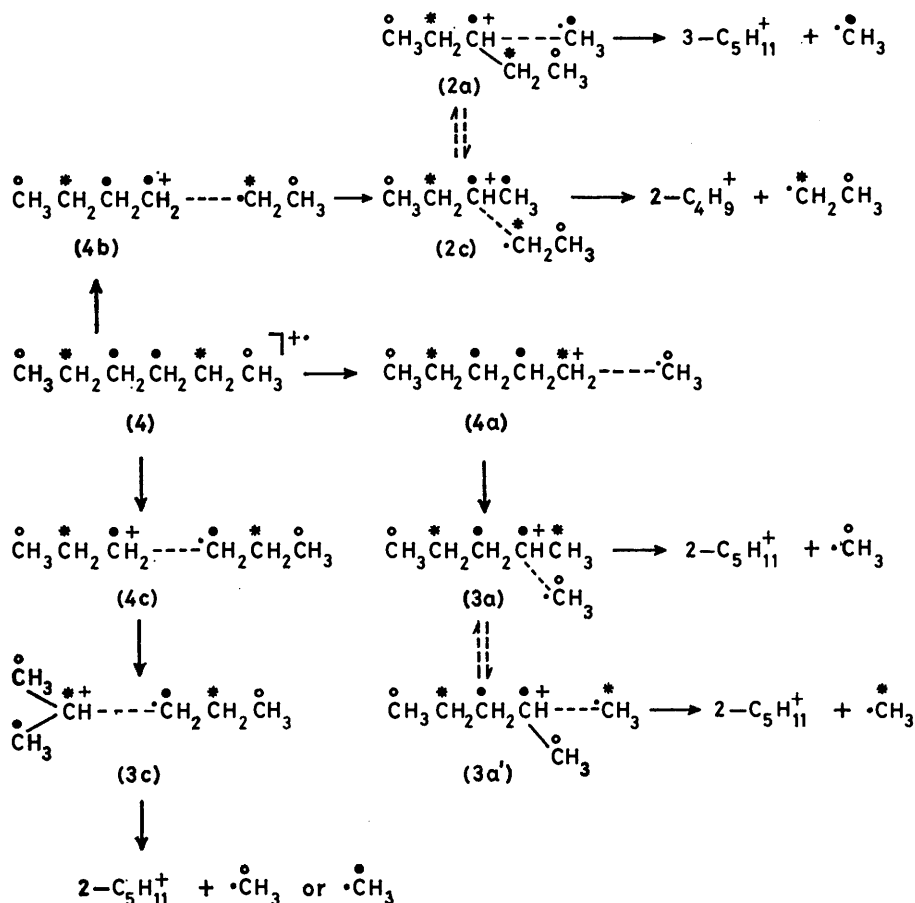
give rise to $C_5H_{11}^{+}$ and $C_4H_9^{+}$ daughter ions, respectively, having secondary cationic sites. Thus, $\cdot C_2H_5$ and 1-methylpropyl cation have a total heat of formation of 870 kJ mol^{-1}, and $\cdot CH_3$ and 1-methylbutyl cation have a total heat of formation of 890 kJ mol^{-1}. Formation of primary cations can be ruled out from energetic considerations. Tertiary daughter ion structures could be produced in principle, but this is unlikely in view of the extensive rearrangement required and the good agreement between the thermochemical data and the formation of secondary carbonium ions in radical loss.

Extensive ^{13}C-labelling experiments have been performed on ionised n-alkanes,[8,16,18,31] including n-$C_6H_{14}^{+\cdot}$. It is found that methyl radical elimination involves only the carbon atoms in the 1- and 3-positions. The discrimination against loss of the 2-carbon atom is also observed for higher homologues, especially for ions with low internal energies.[16,31] An explanation of this curious phenomenon has been advanced for n-$C_6H_{16}^{+\cdot}$ [21] and a similar analysis is presented in Scheme 6 for n-$C_6H_{14}^{+\cdot}$. Starting from (4), stretching of the appropriate bond can lead to complexes [(4a—c), respectively] containing an incipient methyl, ethyl, and propyl radical. In each case, rearrangement of the incipient primary carbonium ion can occur to give an isomeric secondary cation. Loss of the terminal methyl group can take place via (4) $\longrightarrow$ (4a) $\longrightarrow$ (3a) $\longrightarrow$ 2-$\overset{+}{C}_5H_{11}$ + $\cdot CH_3$; in order to eliminate a methyl radical containing the original 2-carbon atom, further changes (3a) $\longrightarrow$ (3a') must occur. Such a pathway should be unfavourable, especially if (4a) $\longrightarrow$ (3a) is the rate-determining step; consequently (3a) prefers to lose $\cdot\overset{o}{C}H_3$ rather than lose $\cdot\overset{*}{C}H_3$. Even when 1,2-ethyl and 1,2-propyl shifts are considered, it transpires that no plausible mechanism exists whereby the 2-carbon atom can be expelled as a methyl radical. In contrast, the 3-carbon atom can be lost in a methyl radical following (4) $\longrightarrow$ (4b) $\longrightarrow$ (2c) $\longrightarrow$ 3-$\overset{+}{C}_5H_{11}$ + $\cdot CH_3$ or (4) $\longrightarrow$ (4c) $\longrightarrow$ (3c) $\longrightarrow$ 2-$\overset{+}{C}_5H_{11}$ + $\cdot CH_3$. Of these two routes, that involving an ethyl radical shift [(4) $\longrightarrow$ (4b) $\longrightarrow$ (2c)] is more likely; this is because (4) undergoes substantial $\cdot C_2H_5$ and C_2H_6 losses, which must involve species such as (4b), but virtually no $\cdot C_3H_7$ and C_3H_8 losses. The preference for forming (4b), rather than (4c) may be interpreted in energetic terms since the energies of these complexes ought to reflect the total heat of formation of the corresponding separated cation and radical. Ethyl radical and butyl cation have a total heat of formation of $840^{22} + 105^{25} = 945$ kJ mol^{-1}, whereas the total heat of formation for propyl radical and propyl cation is $870^{22} + 90^{25} = 960$ kJ mol^{-1}; consequently, (4) $\longrightarrow$ (4b) should require less energy than (4) $\longrightarrow$ (4c). Moreover, methyl radical and pentyl cation have a total heat of formation of $810^{22} + 140^{25} = 950$ kJ mol^{-1}, which is comparable to that of ethyl radical and butyl cation. It is evident that the complexes (4a—c) have closely similar energies and that small differences in thermochemistry can cause

significant changes in the relative abundances of competing dissociations of n-$C_nH_{2n+2}^{+\cdot}$ ions.

Although the bulk of (2c) ions, produced by rearrangement of (4b), decompose *via* $\cdot C_2H_5$ or C_2H_6 loss, a small fraction may undergo $\cdot CH_3$ or CH_4 elimination by reform-

the expected ratios of $C_1 : C_2 : C_3$ fragment losses are 9 : 73 : 18; the experimental values are 4 : 85.5 : 10.5.[20] Moreover, the expected ratios for eliminating the 1-, 2-, 3-, and 4-carbon atoms in the methyl loss reaction are 24 : 1 : 20 : 8; the experimental result is 26 : 3 : 18 : 6.[16]

$$CH_3CH_2CH\cdots\cdots CH_3 \longrightarrow 3\text{-}C_5H_{11}^+ + \cdot CH_3$$
$$\text{(2a)} \quad CH_2CH_3$$

$$CH_3CH_2CH_2CH_2\cdots\cdots\cdot CH_2CH_3 \longrightarrow CH_3CH_2CHCH_3 \longrightarrow 2\text{-}C_4H_9^+ + \cdot CH_2CH_3$$
$$\text{(4b)} \qquad\qquad\qquad\qquad \text{(2c)} \quad \cdot CH_2CH_3$$

$$[CH_3CH_2CH_2CH_2CH_2CH_3]^{+\cdot} \longrightarrow CH_3CH_2CH_2CH_2CH_2\cdots\cdots CH_3$$
$$\text{(4)} \qquad\qquad\qquad\qquad\qquad \text{(4a)}$$

$$CH_3CH_2CH_2\cdots\cdots CH_2CH_2CH_3 \qquad CH_3CH_2CH_2CHCH_3 \longrightarrow 2\text{-}C_5H_{11}^+ + \cdot CH_3$$
$$\text{(4c)} \qquad\qquad\qquad\qquad\qquad \text{(3a)} \quad \cdot CH_3$$

$$\begin{array}{c} CH_3 \\ CH\cdots\cdots CH_2CH_2CH_3 \\ CH_3 \end{array} \qquad CH_3CH_2CH_2CH\cdots\cdots CH_3 \longrightarrow 2\text{-}C_5H_{11}^+ + \cdot CH_3$$
$$\text{(3c)} \qquad\qquad\qquad\qquad\qquad \text{(3a')} \quad CH_3$$

$$2\text{-}C_5H_{11}^+ + \cdot CH_3 \text{ or } \cdot CH_3$$

SCHEME 6

ation of the stretched C–C_2H_5 bond and fission of the C–CH_3 bond [(2c) $\longrightarrow$ (2a) $\longrightarrow$ 3-$\overset{+}{C_5}H_{11}$ + $\cdot CH_3$]. A very simple model can account for the experimental facts: one sixteenth of ions generated as (4) isomerise to (3a) *via* (4a), whilst the rest rearrange to (2c) *via* (4b); in the complexes (2c) and (3a) thus formed, a preference of 19 : 1 operates in favour of cleaving the bond which is already stretched. According to this model (4) ought to eliminate C_1 and C_2 fragments in the ratio (90 – 4.5) : (6 + 4.5) $\approx$ 8 : 1; the experimental figure is 11 : 1. Furthermore, the expected ratios for eliminating the 1-, 2-, and 3-carbon atoms in the methyl loss reaction are (6 – 0.3) : 0.3 : 4.5 = 28 : 1.5 : 22; the measured values are 31 : 0 : 19.[31] A similar model can be used to interpret the behaviour of ionised n-heptane. On the assumption that complexes involving methyl, ethyl, and propyl radicals are formed in the ratio 1 : 16 : 3 and that a similar preference of 19 : 1 operates in favour of cleaving the stretched bond in the rearranged complexes,

These data again reflect a slight energetic preference for forming a complex involving an ethyl radical.

Apart from the energy measurements, which show that radical losses from (4) give rise to secondary cations, and the above ^{13}C-labelling data, two other types of experimental evidence can be cited in support of Scheme 6. First, the mechanism requires that the isomerisations of (4a—c) be the rate-determining steps *en route* to products. This ought to be evidenced by increased average kinetic energy releases for dissociation of (4), compared to the analogous process starting from (2) or (3). Such an effect is observed for ethane loss from (2)—(4), for which the average [32] kinetic energy releases are 5.4, 6.7, and 7.7 kJ mol^{-1}, respectively; the errors (±0.5—0.6 kJ mol^{-1}) involved in these measurements are less than the differences observed. Secondly, [2]H-labelling results (Table 6) also furnish evidence in favour of Scheme 6. Thus $CH_3CH_2CH_2CD_2CH_2CH_3^{+\cdot}$ eliminates a significant amount of $CH_3D/\dot{C}HD_2$ and a small quantity of CH_2D_2; in contrast, $CH_3CH_2CH_2CH_2CD_2CH_3^{+\cdot}$

eliminates no CH_2D_2 and only a minor (0.5%) amount of $CH_3D/\dot{C}HD_2$, which can be interpreted as comprising only CH_3D. These data indicate that the hydrogen atoms on the 3-carbon atom are selected, in the eliminated methyl radical and methane, to a far greater

ing the original $CD_3\text{-}C_5H_{11}{}^{+\cdot}$ bond. For ethyl radical and ethane losses, the data of Table 7 reveal a lower probability of selecting the hydrogen atoms on the 3-carbon atom, compared to those on the 2-carbon atom and especially those on the 1-carbon atom, in the

TABLE 7

Slow unimolecular reactions of $CH_3CH_2CH_2CD_2CH_2CH_3{}^{+\cdot}$, $CH_3CH_2CH_2CH_2CD_2CH_3{}^{+\cdot}$ and $CH_3CH_2CH_2CH_2CH_2CD_3{}^{+\cdot}$

Mass [a]	Neutral lost Probable structure	Relative abundance [b] $CH_3CH_2CH_2CD_2CH_2CH_3{}^{+\cdot}$	$CH_3CH_2CH_2CH_2CD_2CH_3{}^{+\cdot}$	$CH_3CH_2CH_2CH_2CH_2CD_3{}^{+\cdot}$
15	CH_3	3	4	4
16	CH_4 or CH_2D	2	2	2
17	CH_3D or CHD_2	1.5	0.5	0
18	CH_2D_2 or CD_3	0.5	0	0.5
19	CHD_3			0.5
29	C_2H_5	15	11.5	10.5
30	C_2H_6 (C_2H_4D)	57	31	41
31	C_2H_5D or $C_2H_3D_2$	13	24	4.5
32	$C_2H_4D_2$ or $C_2H_2D_3$	7	27	7
33	$C_2H_3D_3$			30

[a] Values given to the nearest dalton. [b] Values determined by B/E scans using an AEI-KRATOS MS 50 double-focusing mass spectrometer; the relative abundances were measured by peak height and normalised to a total of 99 units.

extent than are those on the 2-carbon atom. Moreover, $CH_3CH_2CH_2CH_2CH_2CD_3{}^{+\cdot}$ loses $\cdot CH_3$, CH_4 (possibly $\cdot CHD_2$), $\cdot CD_3$ (possibly CH_2D_2), and CHD_3 but no $CH_3D/\dot{C}HD_2$. All these results can be accommodated by Scheme 6. The observation that $CH_3CH_2CH_2CH_2\text{-}CH_2CD_3{}^{+\cdot}$ loses much more $\cdot CH_3$ than $\cdot CD_3$ can be ascribed, at least in part, to the operation of a secondary deuterium isotope effect discriminating against stretch-

eliminated neutral species. This behaviour is consistent with Scheme 6.

Conclusions.—The unimolecular reactions of four $C_6H_{14}{}^{+\cdot}$ isomers can be understood in terms of species involving incipient carbonium ions and radicals. Rearrangement of the incipient carbonium ion frequently occurs, to give thermodynamically more stable isomers; however, these rearrangements are irreversible and are

$$(CH_3CH_2)_2 C=O \xrightarrow[\text{repeat}]{D_2O-cat} (CH_3CD_2)_2 C=O \xrightarrow{CH_3MgBr} (CH_3CD_2)_2 C(OH)CH_3$$

$$\xrightarrow[0°C]{HBr(g)} (CH_3CD_2)_2 CBrCH_3 \xrightarrow{Bu_3SnH} (CH_3CD_2)_2 CHCH_3 \qquad (1)$$

$$(CH_3)_2 CBrCH_2CH_2CH_3 \xrightarrow{Bu_3SnD} (CH_3)_2 CDCH_2CH_2CH_3 \qquad (2)$$

$$(CD_3)_2 C=O \xrightarrow{CH_3CH_2CH_2MgBr} (CD_3)_2 C(OH)CH_2CH_2CH_3 \xrightarrow[0°C]{HBr(g)}$$

$$(CD_3)_2 CBrCH_2CH_2CH_3 \xrightarrow{Bu_3SnH} (CD_3)_2 CHCH_2CH_2CH_3 \qquad (3)$$

$$CH_3CH_2CH_2COCH_2CH_3 \xrightarrow{LiAlD_4} CH_3CH_2CH_2CD(OH)CH_2CH_3$$

$$\xrightarrow[Br_2]{Ph_3P} CH_3CH_2CH_2CDBrCH_2CH_3 \xrightarrow{Bu_3SnD} CH_3CH_2CH_2CD_2CH_2CH_3 \qquad (4)$$

$$CH_3CH_2CH_2CH_2COCH_3 \xrightarrow{LiAlD_4} CH_3CH_2CH_2CH_2CD(OH)CH_3 \xrightarrow[Br_2]{Ph_3P}$$

$$CH_3CH_2CH_2CH_2CDBrCH_3 \xrightarrow{Bu_3SnD} CH_3CH_2CH_2CH_2CD_2CH_3 \qquad (5)$$

$$n\text{-}C_5H_{11}CO_2CH_3 \xrightarrow{LiAlD_4} n\text{-}C_5H_{11}CD_2OH \xrightarrow[Br_2]{Ph_3P} n\text{-}C_5H_{11}CD_2Br$$

$$\xrightarrow{Bu_3SnD} n\text{-}C_5H_{11}CD_3 \qquad (6)$$

SCHEME 7

probably the rate-determining steps for decomposition. Detailed analysis explains the results of earlier energy measurements, ^{13}C-labelling studies, and new [2]H-labelling experiments.

EXPERIMENTAL

All mass spectra were obtained using either an AEI-KRATOS MS 902 or MS 50 double-focusing mass spectrometer. Samples were admitted to the source using the all-glass heated inlet system (AGHIS) and ionisation was effected by bombardment with an electron beam having a nominal energy of 70 eV. Typical source pressures and temperatures were 10^{-6} Torr (MS 902), 10^{-7} Torr (MS 50), and 120 °C, respectively. The average [32] kinetic energy releases were determined from the widths at half-height of the corresponding metastable peaks in the normal mass spectra (MS 902). The quoted values are the means of at least five measurements; no correction was applied for the width of the main beam. Since comparisons were to be made between the kinetic energy released upon dissociation of isomeric ions, the appropriate compounds were run consecutively under identical operating conditions. The daughter ions arising from decomposition of a given parent ion were recorded (MS 50) by scanning the electric and magnetic fields, simultaneously, such that their ratio remained constant $(B/E$ scan).[33]

Unlabelled C_6H_{14} compounds were available commercially or else synthesised by routine procedures. The [2]H-labelled compounds were prepared by the routes in Scheme 7; details of these procedures have been given elsewhere [21] for [2]H-labelled analogues of $C_5H_{12}^{+\cdot}$.

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