The Concept of a Hierarchy of Unimolecular Reactions in a Homologous Series. Prediction of the Unimolecular Chemistry of Some Saturated Carbenium Ions

By **Richard D. Bowen** and **Dudley H. Williams,*** University Chemical Laboratory, Cambridge CB2 1EW

The unimolecular chemistry of the saturated cations C_nH_{2n+1} (n = 2—12) is examined on the basis that such ions, when produced by electron impact, undergo (in slow reactions) decomposition over the lowest available energy surfaces. There is no evidence for any isolated states which could, in principle, undergo slow reactions ($\log_{10} k$ = 4—6) from high energy states. Elimination of neutral molecules (H_2, CH_4) with σ-bond formation is found for the lower homologues ($C_2H_5^+$, $C_3H_7^+$, $C_4H_9^+$). In higher homologues ($C_5H_{11}^+$—$C_{12}H_{25}^+$), only olefin eliminations are observed in slow reactions. With only the assumptions that (*a*) the various possible olefin eliminations compete one against the other and (*b*) the reverse reactions (combination of an olefin and a carbenium ion) have zero, or near zero, activation energies, the unimolecular chemistry of the C_5—C_{12} saturated carbenium ions can be either accounted for or predicted.

IF ions are generated in the mass spectrometer and their unimolecular reactions observed as metastable transitions, then in such relatively slow reactions (occurring some 10^8 vibrations after generation of the ion) the excess energy in the transition state is normally relatively small (say 0—20 kcal mol^{-1}),† [1] and the ability of one reaction path to compete with another is critically dependent on the relative activation energies for the two pathways.[2] Such simple energetic criteria will not of course apply when isolated excited states are involved. Although clearly defined examples of the intervention of isolated states in unimolecular gas-phase reactions exist,[3] such processes may well be the exception rather than the rule, and it is the purpose of the present work to show that the comparative unimolecular chemistry of the ions $C_nH_{2n+1}^+$ (n = 2—12) is in accord with reactions over the lowest available energy surfaces in the slow dissociations.

DISCUSSION

The basic assumption is that only the lowest activation energy processes will be observed to give abundant metastable transitions; competition between two possible pathways to give abundant metastable transitions will require similar activation energies.

The quoted metastable transitions are those observed

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† Units of kcal mol^{-1} are used throughout this paper; multiplication by 4.18 gives values in kJ mol^{-1}.

[1] R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, ' Metastable Ions,' Elsevier, Amsterdam, 1973.

[2] H. M. Rosenstock, V. H. Dibeler, and F. N. Harlee, *J. Chem. Phys.*, 1964, **40**, 591.

[3] I. G. Simm, C. J. Danby, and J. H. D. Eland, *J.C.S. Chem. Comm.*, 1973, 832.

irrespective of the type of precursor ion (primary, secondary, or tertiary bromides or iodides). For various $C_nH_{2n+1}^+(n=2—8)$ precursors, the quoted metastable ratios were within 20% of the values given.

The ion $C_2H_5^+$. This species undergoes only one significant metastable transition, namely H_2 loss, and the reaction occurs without a specific release of kinetic energy.[4] The relevant energy parameters (present work; see also refs. 5 and 6) are given in Table 1 (along with those to be discussed subsequently). The decomposition to ionised ethylene and a hydrogen radical must have a transition state energy which is at least 20 kcal mol^{-1} higher than that leading to the vinylium ion and H_2, and is therefore not observed (Figure 1). For similar reasons, metastable transitions for the formation of CH_3^+, CH_2^+, and CH^+ are not observed (Figure 1).

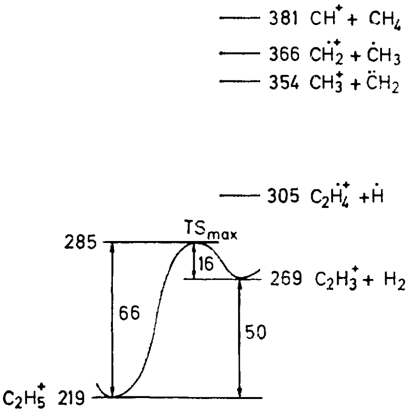

FIGURE 1 Possible and observed reactions of the ethyl cation; $TS_{max.}$ indicates the maximum transition state energy, but the true value could be lower (see Table 1)

The ion $C_3H_7^+$. The only metastable transition observed is for reaction (1), but in contrast to the

$$C_3H_7^+ \longrightarrow C_3H_5^+ + H_2 \qquad (1)$$

corresponding loss of H_2 from the ethyl ion, the reaction occurs with a specific release of kinetic energy (8—9 kcal mol^{-1};[5,6] 5 kcal mol^{-1} [7]) and the product is the allyl ion.[5,8] The smaller kinetic energy release (5 kcal mol^{-1}) is in accord with the appearance potential[9] of $C_3H_5^+$ from the sec-C_3H_7 radical which gives an energy excess above the thermochemical limit (for formation of the allyl ion and H_2) of 5.5 kcal mol^{-1}.[7] Whereas allyl ion formation requires 1,2-elimination from the n-propyl ion or 1,3-elimination from the isopropyl ion, vinylium ion formation from $C_2H_5^+$ is believed to proceed as a 1,1-elimination.[5] We conclude that an analogous 1,1-elimination from n-$C_3H_7^+$ is, for energetic reasons, unable to compete with the observed allyl ion formation. The most energetically favourable (hypothetical) 1,1-elimination would presumably occur from n-$C_3H_7^+$ to give the 1-methylvinyl ion (ΔH_f 243 kcal mol^{-1}).[10] The transition state energy (231.5 kcal mol^{-1}) for formation of the allyl ion from $C_3H_7^+$ is thus less than the energy (243 kcal mol^{-1}) required to produce the 1-methylvinyl ion (Figure 2).

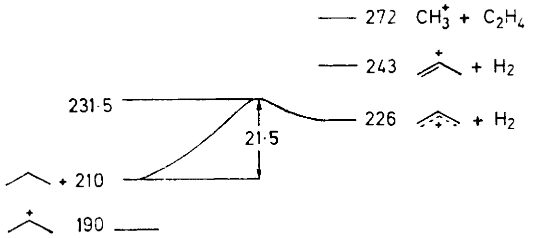

FIGURE 2 Possible and observed reactions of the propyl cation

Moreover, production of CH_3^+ and C_2H_4 would require a minimum of 272 kcal mol^{-1} [ΔH_f (CH_3^+) = 260, ΔH_f (C_2H_4) = 12 kcal mol^{-1}] [11] and is therefore not observed. It is noteworthy that the symmetry-forbidden production of the allyl ion is preferred to the symmetry-allowed production of the 1-methylvinyl ion. The above data clearly indicate that n- and iso-propyl ions, ΔH_f 210 and 190 kcal mol^{-1}, respectively, will be equilibrated prior to slow unimolecular decomposition, in accord with previous experimental findings.[12]

The ion $C_4H_9^+$. Irrespective of their method of generation (*e.g.* from primary, iso-, secondary, or tertiary C_4 structures), in metastable transitions butyl ions undergo almost exclusively methane loss [reaction (2)].[13] A

$$C_4H_9^+ \longrightarrow C_3H_5^+ + CH_4 \qquad (2)$$

small fraction of the metastable ion current (*ca.* 5%) is due to reaction (3). However, this process appears to be

$$C_4H_9^+ \longrightarrow C_2H_5^+ + C_2H_4 \qquad (3)$$

at least in part collision-induced, since its percentage contribution to the total metastable ion current can be reduced by lowering the residual pressure in the field-free region. The important points in the present context are (i) that the threshold for $C_2H_5^+$ production does not seem to be far above that for $C_3H_5^+$ production and (ii) why, in contrast to the behaviour of $C_3H_7^+$, is H_2 loss not observed from $C_4H_9^+$?

The relevant energetics are summarised in Figure 3 and Table 1. The most stable product which could be formed by H_2 loss from $C_4H_9^+$ is 1-methylallyl (ΔH_f

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[4] C. Lifshitz and R. Sternberg, *Internat. J. Mass Spectrometry Ion Phys.*, 1969, **2**, 303.

[5] D. H. Williams and G. Hvistendahl, *J. Amer. Chem. Soc.*, 1974, **96**, 6755.

[6] M. L. Vestal in ' Fundamental Processes in Radiation Chemistry,' ed. P. Ausloos, Wiley–Interscience, New York, 1968, ch. 2.

[7] J. L. Holmes and G. Weese, *Org. Mass Spectrometry*, 1974, **9**, 618.

[8] G. Hvistendahl and D. H. Williams, *J.C.S. Perkin II*, 1975, 881.

[9] F. P. Lossing, *Canad. J. Chem.*, 1971, **49**, 357.

[10] L. Radom, P. C. Hariharan, J. A. Pople, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 6531.

[11] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, ' Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions,' National Bureau of Standards, Washington, D.C., 1969.

[12] G. Hvistendahl and D. H. Williams, *J.C.S. Chem. Comm.*, 1975, 4.

[13] B. Davis, D. H. Williams, and A. N. H. Yeo, *J. Chem. Soc.* (*B*), 1970, 81.

204 kcal mol^{-1}), which is appreciably more stable than 2-methylallyl (ΔH_f 211 kcal mol^{-1}).[14] A lower limit to the transition state energy for reaction (4), occurring

$$C_4H_9^+ \longrightarrow MeCH\cdots\overset{+}{C}H\cdots CH_2 + H_2 \qquad (4)$$

through the same geometry as the observed loss of H_2 from $C_3H_7^+$ [reaction (1)] can be estimated on the assumption that all the stabilisation (22 kcal mol^{-1}) that the methyl substituent of 1-methylallyl confers relative to the allyl ion is retained in the transition state, *i.e.* the reverse activation energy for reaction (4) could be as low as that (5.5 kcal mol^{-1}) observed for reaction (1) (Table 1). In reality, some of the hyperconjugative stabilisation of 1-methylallyl by the methyl group will certainly be lost in the transition state and the transition state energy of 209.5 kcal mol^{-1} will represent an unlikely lower limit. At the other extreme, one might consider that an inserted CH_2 residue would provide only ' spectator stabilisation ' in comparing transition state energies for reactions (1) and (4), *i.e.*, that a CH_2 group provides only the stabilisation observed on passing up a homologous series of saturated hydrocarbons. In this ' other extreme ' model, the assumption is that the transition state for reaction (4) would be stabilised by only 5 kcal mol^{-1} for each added CH_2 group.[15] Thus an upper boundary for the transition state energy for H_2 loss from $C_4H_9^+$ is 226.5 kcal mol^{-1}.

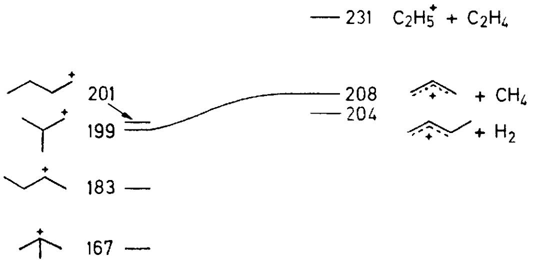

FIGURE 3 Possible and observed unimolecular reactions of butyl cations

TABLE 1

Energy parameters for some observed and possible unimolecular reactions of C_2—C_5 saturated carbenium ions (E_f = forward and E_r = reverse activation energy)

Reactant	Products	ΔH [a]	E_f	E_r	Observed
$C_2H_5^+$	$C_2H_3^+ + H_2$	50	56—66	6—16 [b]	Yes
$C_2H_5^+$	$C_2H_4 + \overset{+}{H}\cdot$	86	⩾86		No
n-$C_3H_7^+$	$CH_2\cdots\overset{+}{C}H\cdots CH_2 + H_2$	16	21.5	5.5	Yes
n-$C_3H_7^+$	$CH_2{=}\overset{+}{C}Me + H_2$	33	⩾33		No
n-$C_3H_7^+$	$CH_3^+ + C_2H_4$	62			No
n-$C_4H_9^+$	$CH_2\cdots\overset{+}{C}H\cdots CH_2 + CH_4$	7	7	*ca.* 0	Yes
n-$C_4H_9^+$	$MeCH\cdots\overset{+}{C}H\cdots CH_2 + H_2$	3			No
n-$C_4H_9^+$	$C_2H_5^+ + C_2H_4$	30			Yes
iso-$C_5H_{11}^+$	$Me_2CH^+ + C_2H_4$		6	6—15 [b]	Yes
iso-$C_5H_{11}^+$	$MeCH\cdots\overset{+}{C}H\cdots CH_2 + CH_4$	−10			No
iso-$C_5H_{11}^+$	$Me_2C\cdots\overset{+}{C}H\cdots CH_2 + H_2$	−12			No
iso-$C_5H_{11}^+$	$C_2H_5^+ + C_3H_6$	28			No

[a] Energy levels are (arbitrarily) quoted relative to the primary carbenium ion. All values are kcal mol^{-1}. [b] The upper limits of these reverse activation energies are computed from the mean values of appearance potential measurements on the daughter ions (see Table 5, Appendix 1); the lower limits are computed from the lowest reproducible appearance potential values determined on metastable peaks or daughter ions.

The measured transition state energy for the observed reaction of $C_4H_9^+$ [reaction (2)] is 208 kcal mol^{-1},[16] which is less than that estimated for H_2 loss (see above). Therefore, according to the basic postulate of competition among the available surfaces, H_2 loss should not be observed, or should occur as a minor reaction only. The experimental results are in accord with this conclusion. Alternatively, if one takes the viewpoint of accepting the basic postulate of competition (as first proposed in the quasi-equilibrium theory of mass spectrometry) [17] then the conclusion must be that the transition state energy for the hypothetical loss of H_2 from $C_4H_9^+$ must lie near the upper boundary (226.5 kcal mol^{-1}) estimated above, since excess energy opens up the channel to $C_2H_5^+$ plus C_2H_4 (requiring at least 231 kcal mol^{-1}) and not to $C_4H_7^+$ and H_2. Although it is normally the rule that the lowest activation energy process gives rise to the most abundant metastable peak, an interesting case where an ' entropy ' effect is important even after allowing 10^8 vibrations before reaction has recently been uncovered;[18] the relative abundances (areas) of the metastable peaks for H and H_2 losses from $C_3H_6^+$ are *ca.* 10 : 1, even though the activation energy for the latter fragmentation is lower by some 6—10 kcal mol^{-1}. Convincing evidence is presented to support the case

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[14] F. P. Lossing, *Canad. J. Chem.*, 1972, **50**, 3973.

[15] J. L. Franklin, *Ind. and Eng. Chem.*, 1949, **41**, 1070; *J. Chem. Phys.*, 1953, **21**, 2029; see also Appendix 2, p. 285 of ref 11.

[16] J. L. Holmes, A. D. Osborne, and G. M. Weese, *Org. Mass Spectrometry*, 1975, **10**, 867.

[17] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U.S.A.*, 1952, **38**, 667.

[18] J. L. Holmes and J. K. Terlouw, *Org. Mass Spectrometry*, 1975, **10**, 787.

that the rate of H_2 loss (k) rises exceptionally slowly with energy, so that even for $\log_{10} k = 4$—6 (metastable transitions) H loss is more rapid than H_2 loss, notwithstanding the lower activation energy for the latter process. A similar effect could also be operating in discriminating against H_2 loss from $C_4H_9^+$; given similar activation energies for H_2 and C_2H_4 loss from $C_4H_9^+$, an 'entropy' effect might discriminate against H_2 loss (rearrangement reaction, ordered transition state) relative to C_2H_4 loss (single bond cleavage in the n-$C_4H_9^+$ configuration; Figure 3).

The data summarised in Figure 3 do of course demand that n-, iso-, sec-, and t-butyl ions should undergo rapid equilibration prior to unimolecular decomposition, and this is borne out by the occurrence of the same reactions (2) and (3) in similar ratios irrespective of the precursor structure, and the scrambling of isotopic ^2H and ^{13}C labels in various butyl ions prior to decomposition.[13]

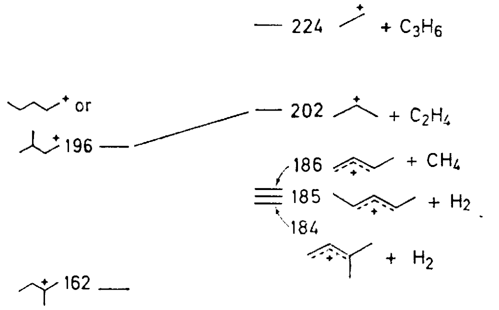
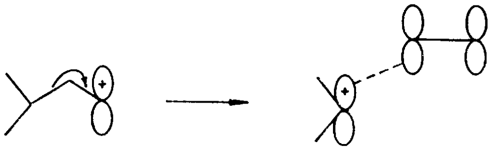


FIGURE 4 Possible and observed unimolecular reactions of the ions C_5H_{11}

The ion $C_5H_{11}^+$. Metastable transitions undergone by the ions $C_5H_{11}^+$ to $C_8H_{13}^+$ were known, prior to this study, to involve only neutral olefin eliminations;[19] loss of neutral species with concomitant σ-bond formation (*e.g.* H_2, CH_4, C_2H_6) is not observed. Since such reactions could lead to thermodynamically more stable product combinations (see, for example, Figure 4),[20] within a model assuming competition among reactions over the lowest available surfaces, one can only rationalise that the reverse reactions (*e.g.* addition of H_2 to dimethylallyl ion) involve considerable activation energy (around 20 kcal mol^{-1} in Figure 4). However, a model in which olefin eliminations from the cations C_nH_{2n+1} (n = 5—12) occur without reverse activation energy successfully accounts in some detail for the observed unimolecular chemistry. The model seems a plausible one, since the reverse reactions are allowed, gas-phase, Friedel–Crafts alkylations, *e.g.* reaction (5).



(5)

On the basis of the model, only ethylene elimination should be observed from $C_5H_{11}^+$, since the formation of a primary (ethyl) cation and propene requires a further 22 kcal mol^{-1} (Figure 4). Ethylene loss is in fact the sole reaction observed in unimolecular metastable transitions of $C_5H_{11}^+$, the reacting configuration presumably being the 3-methylbutyl ion [reaction (5)].

Appearance potential measurements on daughter ions formed in this reaction give a transition state energy of 213 ± 3 kcal mol^{-1}, while that computed on the assumption of no reverse activation energy is 202 kcal mol^{-1}. We believe that the true reverse activation energy for this process may be anywhere in the 0—11 kcal mol^{-1} range, with values near zero being more probable, since with increasing molecular size of the precursor ion, appearance potential measurements in conventional mass spectrometers will tend to give values which are too high. This situation arises because, with increasing molecular size, the probability of fluctuating all the vibrational energy of the ion into the reaction co-ordinate decreases and decomposition is only likely to occur within 10^{-6} s in the presence of significant excess energy. This problem is expected to be more severe in the C_6—C_8 ions (see below).

The ion $C_6H_{13}^+$. The relevant energy levels which are derived *via* use of the same criteria as for $C_5H_{11}^+$ are summarised in Figure 5. The analysis indicates that the rate-limiting step in the formation of t-butyl ion and ethylene is attainment of the reacting configuration of the 3,3-dimethylbutyl ion (Figure 5). The energy required to attain this configuration (*ca.* 191 kcal mol^{-1}) is very similar to that required (195 kcal mol^{-1}) to produce an isopropyl ion and propylene (without excess energy). Thus the analysis leads to the conclusion that $C_6H_{11}^+$ ions will undergo competitive loss of C_2H_4 and C_3H_6 [production of an ethyl cation and *trans*-but-2-ene (or equally isobutene) would require in the region of a further 20 kcal mol^{-1} (Figure 5)].

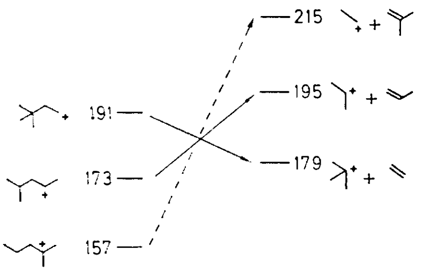


FIGURE 5 Possible and observed unimolecular reactions of the ions $C_6H_{13}^+$

$$C_6H_{13}^+ \begin{cases} \longrightarrow Me_3C^+ + C_2H_4 & (6) \\ \longrightarrow Me_2CH^+ + C_3H_6 & (7) \end{cases}$$

In fact, these are the only two metastable transitions

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[19] See, for example, D. H. Williams and I. Howe, 'Principles of Organic Mass Spectrometry,' McGraw-Hill, 1972, p. 110; W. G. Cole and D. H. Williams, *Chem. Comm.*, 1969, 784.

[20] The ΔH_f values of the dimethylallyl cations were reported by Professor F. P. Lossing at the A.S.M.S. meeting, Houston, 1975.

which are observed for decomposition of $C_6H_{13}^+$ ions,[2] C_2H_4 and C_3H_6 losses occurring in the abundance ratio 1 : 1.6.[2] The importance of considering the heats of formation of the reacting configuration is seen in understanding what otherwise might have appeared to be the inexplicable formation of a secondary ion in competition with a tertiary ion. Although appearance potential measurements were made for the observed reactions, the results for the C_6—C_8 compounds are not quoted in the text, since although they provide broad support for our conclusions, the values are certainly too high owing to the large kinetic shifts anticipated for precursor ions containing 19—25 atoms. The data are summarised in Appendix 1.

The ion $C_7H_{15}^+$. The appropriate data are summarised in Figure 6. In the $C_6H_{13}^+$ case, formation of a secondary cation was able to compete with formation of a tertiary cation and ethylene only because the reacting configuration for the latter process was a primary cation. This competition is neatly avoided in the $C_7H_{15}^+$ case since although the same balance potentially exists (Figure 6), both routes are pre-empted by the fact that a secondary reacting configuration can now lead to the t-butyl ion and propene *via* a reaction pathway which is nearly thermoneutral. Thus the analysis indicates that the only observed reaction should be propene elimination, and experimentally this is precisely the situation found for metastable transitions.

$$C_7H_{15}^+ \longrightarrow Me_3C^+ + C_3H_6 \qquad (8)$$

The ion $C_8H_{17}^+$. In the case of the $C_7H_{15}^+$ ion, there is only one way in which a relatively stable reacting configuration (*i.e.* a secondary ion) can lead to a tertiary product ion and therefore only a single decomposition route is observed. In the case of the $C_8H_{17}^+$ ion, two such possibilities exist (Figure 7): either (i) a secondary reacting configuration can lead to a tertiary ion plus propene or (ii) a tertiary reacting configuration can lead to a tertiary ion plus isobutene (this reaction could be expressed in terms of a secondary reacting configuration leading to the t-butyl ion plus *trans*-butene, but this is of no consequence since the product combination is only 1 kcal mol^{-1} higher in energy). The pathways (i) and (ii) lead to products which are separated only by *ca.* 4 kcal mol^{-1} in energy (Figure 7). Thus $C_8H_{17}^+$ should decompose either exclusively to $C_4H_9^+$, or competitively to $C_4H_9^+$ and $C_5H_{11}^+$. Experimentally, these are the only ions formed from $C_8H_{17}^+$ in metastable transitions, $C_5H_{11}^+$ and $C_4H_9^+$ being formed in the ratio 1.5 : 1.0.[19]

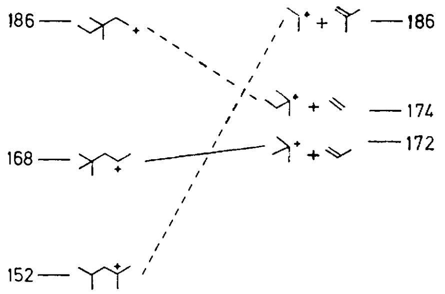

FIGURE 6 Possible and observed unimolecular reactions of the ions $C_7H_{15}^+$

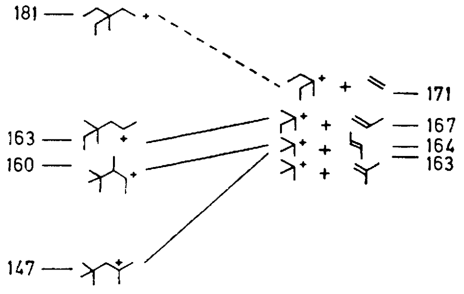

FIGURE 7 Possible and observed unimolecular reactions of the ions $C_8H_{17}^+$

$$C_8H_{17}^+ \longrightarrow \begin{cases} Me_3C^+ + C_4H_8 & (9) \\ Me_2\overset{+}{C}Et + C_3H_6 & (10) \end{cases}$$

The ions $C_9H_{19}^+$ *to* $C_{12}H_{25}^+$. Since no detailed study of the metastable transitions undergone by the C_9—C_{12} saturated cations has been reported, we have made predictions as to the number and types of slow reactions which these ions should undergo, and subsequently subjected these predictions to experimental test.

$C_9H_{19}^+$. Relevant thermochemical data, available from the literature or estimated by the method outlined in Appendix 2, are shown in Table 2.

TABLE 2

Thermochemical data (kcal mol^{-1}) for threshold unimolecular reactions of the ions $C_9H_{19}^+$ [a]

ΔH_f Reacting configuration	Process	ΔH_f Products	$\Sigma\Delta H_f$ Products
$Et_3CCH_2\overset{+}{C}H_2$ (176 *)	$-C_2H_4$	$Et_3C^+ + CH_2{=}CH_2$ 152 * 12	164
$Et_2CMeCH_2\overset{+}{C}HMe$ (158 *)	$-C_3H_6$	$Et_2\overset{+}{C}Me + CH_2{=}CHMe$ 157 * 5	162
$Me_2CEtCH_2\overset{+}{C}Me_2$ (142 *)	$-C_4H_8$	$Me_2\overset{+}{C}Et + CH_2{=}CMe_2$ 162 * −4	158
$Me_3CCHMe\overset{+}{C}Me_2$ (142 *)	$-C_5H_{10}$	$Me_3C^+ + MeCH{=}CMe_2$ 167 −11	156
$Me_2CHC(Me)_2\overset{+}{C}Me_2$ (142 *)	$-C_6H_{12}$	$Me_2CH^+ + Me_2C{=}CMe_2$ 190 −16	174

[a] Values indicated by an asterisk are estimated by the method given in Appendix 2.

From Table 2, it is evident that the favoured slow unimolecular reactions of $C_9H_{19}^+$ should be competitive loss of C_3H_6, C_4H_8, and C_5H_{10}. The loss of ethylene is precluded by a high energy reacting configuration, while C_6 olefin loss is precluded by the relatively high heat of formation of the isopropyl cation.

The predictions were tested not only by observing metastable peaks for the decomposition of $C_9H_{19}^+$ in the normal mass spectrum, but also by confirming the appropriate transitions, and their relative abundances, by use of the metastable refocussing technique.[21] The results are given in Table 3.

The results are in accord with the predictions, C_6H_{12} loss not being observed, and first field-free region transition for C_2H_4 loss being two orders of magnitude less than those for C_3H_6, C_4H_8, and C_5H_{10} losses.

TABLE 3

Slow reactions undergone by the ions $C_9H_{19}^+$

Process	Relative abundance [a]	*m*/*e* Value of metastable peak
$-C_2H_4$	5	(77.2) [b]
$-C_3H_6$	739	56.9
$-C_4H_8$	1 000	39.7
$-C_5H_{10}$	350 [c]	25.6
$-C_6H_{12}$	Not obs.	(14.6) [b]

[a] Normalised to 1 000 units for the most abundant metastable peak; for a given precursor of $C_9H_{19}^+$, the individual relative abundances are reproducible within 20% of the values quoted. [b] Metastable peaks not observed in normal spectrum. [c] Estimated relative abundance from the normal spectrum, since this transition could not be refocused ($m_2 < m_1/2$).

The ions $C_{10}H_{21}^+$, $C_{11}H_{23}^+$, *and* $C_{12}H_{25}^+$. The procedure adopted for these ions does not differ in principle from that described for $C_9H_{19}^+$, and in each case it is predicted that (*a*) C_2H_4 loss should not be significant because of the high ΔH_f value of the reacting configuration (primary cation), and (*b*) $C_{n-3}H_{2(n-3)}$, $C_{n-2}H_{2(n-2)}$, and $C_{n-1}H_{2(n-1)}$ olefins should not be eliminated in slow reactions to a significant extent from $C_nH_{2n+1}^+$ precursors owing to the relatively high ΔH_f values of $C_3H_7^+$, $C_2H_5^+$, and CH_3^+.[11] Thus, the C_{10}, C_{11}, and C_{12} saturated carbenium ions are predicted to competitively eliminate C_3—C_6, C_3—C_7, and C_3—C_8 olefins (respectively) in slow reactions. The experimental data for these cations are summarised in Table 4.

TABLE 4

Slow reactions undergone by the cations $C_{10}H_{21}^+$, $C_{11}H_{23}^+$, and $C_{12}H_{25}^+$ †

Cation	Process	Abundance [a]
$C_{10}H_{21}^+$	$-C_2H_4$	7 [b]
	$-C_3H_6$	567
	$-C_4H_8$	1 000
	$-C_5H_{10}$	822
	$-C_6H_{12}$	220 [c]
	$-C_7H_{14}$	Not obs.
$C_{11}H_{23}^+$	$-C_2H_4$	2 [b]
	$-C_3H_6$	440
	$-C_4H_8$	960
	$-C_5H_{10}$	1 000
	$-C_6H_{12}$	670 [c]
	$-C_7H_{14}$	220 [c]
	$-C_8H_{16}$	Not obs.
$C_{12}H_{25}^+$	$-C_2H_4$	5 [b]
	$-C_3H_6$	456
	$-C_4H_8$	964
	$-C_5H_{10}$	1 000
	$-C_6H_{12}$	750
	$-C_7H_{14}$	170 [c]
	$-C_8H_{16}$	80 [c]
	$-C_9H_{18}$	Not obs.

† The superscripts *a*—*c* have the same significance as in Table 3.

As predicted, the main threshold unimolecular reactions of the saturated C_{10}, C_{11}, and C_{12} cations are elimination of C_3—C_6, C_3—C_7, and C_3—C_8 olefins, respectively. In view of the success of the approach towards olefin eliminations it appears likely that our original basic assumptions that (i) reactions occur over the lowest available energy surfaces with competition between the possible reaction channels and (ii) the olefin eliminations proceed with a zero or small reverse activation energy, are correct.

Our approach requires that secondary and tertiary cations will, in general, undergo interconversion prior to unimolecular decomposition. This requirement is consistent with studies of collision-induced decompositions of the cations $C_nH_{2n+1}^+$.[22]

With regard to the lower saturated cations, it is particularly satisfying that the existence of 1, 2, and 1 channels for the threshold decomposition of $C_5H_{11}^+$, $C_6H_{13}^+$, and $C_7H_{15}^+$ (respectively) is naturally accommodated.

APPENDIX 1

In order to test that the transition state energies for olefin eliminations from saturated carbenium ions were not inconsistent with these processes occurring with small or negligible reverse activation energies, appearance potential (A.P.) measurements have been made for some representative reactions. These measurements were made on daughter ions and the data were evaluated by using semi-log plots.[23] The results may well be subject to systematic (as well as random) errors since (i) the normalisation procedure used in semi-log plots is rather arbitrary, and (ii) in cases where the precursor ion has many atoms, the kinetic shift [24] will tend to produce results which are systematically high. *Thus our apparent reverse activation energies computed from A.P. measurements may be subject to large (positive) errors and can only crudely support our postulate insofar as (i) they should not be negative and (ii) a positive value should not be larger than one which might reasonably be ascribed to a kinetic shift.*

The A.P.s were measured on numerous isomeric alkyl bromides and iodides and the results are summarised in Table 5.

TABLE 5

Apparent reverse activation energies (E_r) for unimolecular reactions of $C_nH_{2n+1}^+$ ($n = 5$—8)

Ion	Fragments	No. of determinations	Mean E_r (kcal mol^{-1})	Est. random error [a] (kcal mol^{-1})
$C_5H_{11}^+$	$C_3H_7^+ + C_2H_4$	8	11	3
$C_6H_{13}^+$	$C_3H_7^+ + C_3H_6$	14	9	5
$C_6H_{13}^+$	$C_4H_9^+ + C_2H_4$	14	17	5
$C_7H_{15}^+$	$C_4H_9^+ + C_3H_6$	10	11	5
$C_8H_{17}^+$	$C_4H_9^+ + C_4H_8$	8	22	6
$C_8H_{17}^+$	$C_5H_{11}^+ + C_3H_6$	12	14	6

[a] These errors are the random ones for the spread of E_r obtained from the various precursors; a positive systematic error will also be present (see text).

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[21] M. Barber and R. M. Elliott, 12th Annual Conference on Mass Spectrometry and Allied Topics, Committee E.14 A.S.T.M., Montreal, June 1964.

[22] For work on isomerisation of the cations $C_nH_{2n+1}^+$ following collisional activation, see K. Levsen, *Org. Mass Spectrometry*, 1975, **10**, 43.

[23] F. P. Lossing, A. W. Tichner, and W. A. Bryce, *J. Chem. Phys.*, 1951, **19**, 1254.

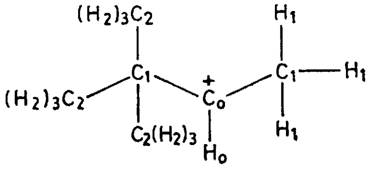
[24] W. A. Chupka, *J. Chem. Phys.*, 1959, **30**, 191.

Owing to the relatively large errors that may be associated with this type of A.P. measurement, we feel that the results support our approach only insofar as they satisfy the criteria (i) and (ii) given above.

APPENDIX 2

Heats of Formation of the Ions $C_nH_{2n+1}^+$.—At the time our work was carried out, reliable heats of formation were available only for the cations CH_3^+, $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$.[11,25] For higher members of the series ($C_5H_{11}^+$ to $C_{12}H_{25}^+$), the following procedure was employed to give ΔH_f values.

The appropriate butyl cation (primary, secondary, or tertiary) is considered, and the carbon atom carrying the positive charge designated C_0, the adjacent carbon atom (or atoms) as C_1 and so on. Similarly, the hydrogen atom (or atoms) attached to C_n are designated H_n. This scheme is illustrated in formula (1).



(1)

The following adjustments are then made to the known heats of formation of the butyl cation, depending on the type of $-CH_2-$ insertion performed. (*a*) Insertion of a $-CH_2-$ residue between C_1 and H_1 produces a stabilization of 8 kcal mol^{-1} for primary or secondary cations, but only 5 kcal mol^{-1} for tertiary cations. (*b*) Insertion of a $-CH_2-$ residue between C_2 and H_2, or between higher labelled carbon and hydrogen atoms produces a stabilization of 5 kcal mol^{-1}, irrespective of the nature of the cation considered. The basis for these increments is to be found in Franklin's method of group equivalents,[15] in which a $-CH_2-$ group is allotted a value of 5 kcal mol^{-1}. The use of 8 kcal mol^{-1} for cases where the insertion is carried out close to a primary or secondary carbenium ion centre is based upon the extra hyperconjugative and polarization stabilisation available in these cases. Some values estimated in this manner are given in Table 6. Subsequent to our use of these estimates, values for various cations $C_5H_{11}^+$, $C_6H_{13}^+$, and $C_7H_{15}^+$ became available through the work of Lossing[26] and of Solomon and Field;[27] their values are also given in Table 6 for comparison.

TABLE 6

Heats of formation (kcal mol^{-1}) of some cations $C_nH_{2n+1}^+$

Structure	Est.	Ref. 26	Ref. 27[b]
$Me[CH_2]_3CH_2^+$	196	194	
$Me_3CCH_2^+$	191	188	
$Me[CH_2]_2\overset{+}{C}HMe$	178	179	
$Et\overset{+}{C}Me_2$	162[a]	161	161
$Me[CH_2]_4CH_2^+$	191	189	
$Me[CH_2]_3\overset{+}{C}HMe$	173	173	
$Me[CH_2]_2\overset{+}{C}Me_2$	157	155	156
$Et_2\overset{+}{C}Me$	157		155
$Me_2CH\overset{+}{C}Me_2$	157		153
$Me[CH_2]_5CH_2^+$	186	183	
$Me[CH_2]_4\overset{+}{C}HMe$	168	168	
$Me[CH_2]_3\overset{+}{C}Me_2$	152	150	

[a] *Cf.* value (164 kcal mol^{-1}) obtained from photoionization studies on 2,2-dimethylbutane (B. Steiner, C. F. Giese, and M. G. Ingrham, *J. Chem. Phys.*, 1961, **34**, 189). [b] Values are rounded to the nearest kcal mol^{-1}.

For those values given in Table 6, the average difference between our estimated values and those from refs. 26 and 27 is 1.7 kcal mol^{-1}. For values used in Figures 4—7, the largest difference is 3 kcal mol^{-1}, and such small values are of course of no consequence for our present purposes. Our procedure for estimating the ΔH_f values is strongly supported by the new data.[26,27]

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