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A PREDICTIVE MODEL FOR UNIMOLECULAR REACTIONS

REACTIONS OF UNSATURATED CARBONIUM IONS

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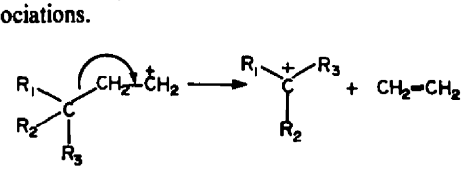
Abstract—The major slow unimolecular reactions undergone by $C_4H_7^+$, $C_5H_9^+$ and $C_6H_{11}^+$ are discussed in terms of a potential surface approach and the organic chemist's concept of mechanism. It is shown that the observed decompositions which do not involve σ-bond formation in the dissociation step are precisely those expected from the model. Further use of the model correctly predicts the slow reactions of $C_7H_{13}^+$ which have not previously been reported. The approach also permits useful limits to be set on the transition state energies for reactions involving σ-bond formation in the dissociation step (H_2,CH_4 loss). It is concluded that stepwise addition of ethylene to the allyl cation is preferred to a concerted 4-electron process which is symmetry forbidden.

In earlier work[1-4] we have shown how the slow unimolecular dissociations of ions which give rise to metastable peaks may be understood in terms of the potential surface approach. In this model, the relative energies of various reactant configurations, product combinations and plausible intermediates are considered. The resultant potential surface frequently explains the non-occurrence of mechanistically plausible reactions because there is insufficient energy to form the necessary intermediates or product combinations.[1] In favourable cases, the approach not only explains the slow reactions of ions which have previously been investigated but may be used to predict successfully the slow dissociations of ions as yet uninvestigated.[1,2] In the present work, we extend the approach to the slow reactions of some members of the series of unsaturated carbonium ions: $C_nH_{2n-1}^+$ ($n = 4$–7). It is found that the observed reactions which do not involve σ-bond formation in the dissociation step are precisely those expected in the cases $C_4H_7^+$, $C_5H_9^+$ and $C_6H_{11}^+$. In the case of $C_7H_{13}^+$ the approach correctly predicts the reactions undergone in metastable transitions.

The slow unimolecular dissociations of ions which give rise to metastable peaks occur after some 10^8 vibrations and the excess energy present in the transition state is normally small.[5] A consequence of this is that the ability of decomposition channels to compete against one another is critically dependent on the activation energies for the processes concerned.[6] Important evidence for this view is found in the frequent observation of isotope effects in the decomposition of labelled ions; these isotope effects span the entire range of those known for reactions occurring in solution, and in some cases[7,8] are spectacularly large.

In considering the decomposition of ions it is helpful to divide the reactions into two broad categories; namely those which involve σ-bond formation in the dissociation step (e.g. 1,2-eliminations of H_2 and CH_4) and those which do not. For reactions where σ-bond formation is involved in the dissociation step it is often difficult to obtain reliable values for the energy of the transition states involved. This usually prevents accurate predictions concerning the occurrence or non-occurrence of such reactions. For reactions corresponding to simple bond cleavage (e.g. radical or olefin loss) it is usually possible to obtain values for the heats of formation (ΔH_f) of the product combinations and also, by use of a modified isodesmic substitution,[9] good estimates for the heats of formation of the postulated reacting configurations. In some cases, the reacting configuration is lower in energy than the product combination; these reactions may therefore occur without reverse activation energy in the dissociation step. On the other hand, it is possible that the reacting configuration may be higher in energy than the product combination and so may dissociate exothermically. Thus, in considering a reaction involving σ-cleavage in the final step, it is important to note that the reacting configuration may approximate to the transition state for the process. Hence one must consider the possibility of a reverse activation energy for a dissociation which may proceed *via* simple σ-cleavage in the final step; the energies of both the product combination and reacting configuration must be taken into account. When this is done reliable predictions can usually be made, on a simple energetic basis, of which reactions are likely to occur in slow (metastable) dissociations.

The importance of considering the energy not only of product combinations, but also of reacting configurations may be illustrated by reference to the hypothetical loss of ethylene from higher members of the series of saturated alkyl ions $C_nH_{2n+1}^+$.[1] Although this process can lead to thermodynamically favourable products it must proceed *via* the high energy primary carbonium ion, 1, as reacting configuration. Since such high energy cations are inaccessible at energies appropriate to metastable transitions, ethylene loss is not observed in slow dissociations.



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As stated above, the competition of two or more decomposition pathways for a given ion demands that the transition state energies for these processes be similar.[6] Hence, when H_2 or CH_4 loss is observed in

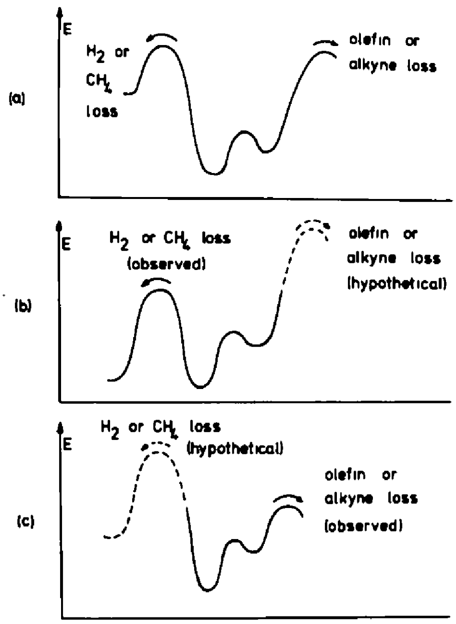


Fig. 1. Potential energy profile for possible competition between H_2 or CH_4 loss and olefin or alkyne loss; (a) both processes are observed, (b) only H_2 or CH_4 loss is observed, and (c) only olefin or alkyne loss is observed.

competition with olefin or alkyne loss which proceed via intermediates of known or easily estimated ΔH_f, useful estimates may be made of the activation energies for H_2 or CH_4 loss from such ions (Fig. 1a). Conversely, when competition does not occur, upper or lower limits respectively may be derived depending on whether exclusive H_2 and CH_4 or olefin and alkyne losses are observed (Figs 1(b) and 1(c)).

For the lower members of the series, $C_3H_3^+$[10,11] and $C_4H_7^+$,[12] H_2 and CH_4 losses are important because olefin and alkyne eliminations must lead to products which are relatively high in energy. For instance, C_2H_4 loss from $C_3H_5^+$ and $C_4H_7^+$ leads to CH^+ and $C_2H_3^+$ respectively; these species are too high in energy to permit significant ethylene loss in slow reactions. However, as the homologous series is ascended, olefin loss becomes favourable because it can now lead to allylic cations. Thus C_2H_4 loss from $C_5H_9^+$ leads to $C_3H_5^+$ and it is this process which dominates the slow reactions.[12] H_2 and CH_4 losses are unfavourable because of the significant reverse activation energies which accompany these dissociations. Therefore once olefin loss proceeding via low energy intermediates can lead to favourable products, H_2 and CH_4 losses should be pre-empted. Experimentally,[12] this is observed to be the case.

Olefin and alkyne loss

Leaving aside the possibility of H_2 and CH_4 losses, it should be possible to explain the observed decomposition, via olefin or alkyne loss, of the ions $C_4H_7^+$, $C_5H_9^+$ and $C_6H_{11}^+$. Some plausible olefin and alkyne losses from these ions are shown in Table 1 together with the sums of the heats of formation of products and plausible reacting configurations ($\Sigma\Delta H_f$ and ΔH_f (RC), respectively).

Consideration of the data given in Table 1 reveals that the most favourable processes which can proceed via simple σ-bond cleavage in accessible reacting configurations of $C_4H_7^+$, $C_5H_9^+$ and $C_6H_{11}^+$ are loss of C_2H_2, C_2H_4 and C_2H_4 respectively. The observed decompositions of these ions are given in Table 2.

These results reveal that the olefin or alkyne fragments eliminated in slow reactions are precisely those expected from the data of Table 1; they are in qualitative agreement with those obtained in our earlier study of these ions.[12] The earlier study also showed similar competition between the various decay channels irrespective of the precursor used to generate the ion,[12] thus indicating complete interconversion of all accessible reactant configurations prior to dissociation.[6] In order to discover if the estimated energy requirements for these reactions are correct we have made appearance potential (AP) measurements. Although there are serious difficulties in determining AP's on conventional mass spectrometers,[17,18] it was felt that approximate values could be obtained. These results, together with ΔH_f (reacting configuration) and $\Sigma\Delta H_f$ (products) for the processes concerned are given in Table 3.

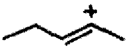
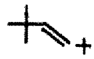
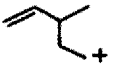
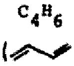
The agreement between the predicted and experimentally measured energy requirements for the observed processes involving σ-cleavage is good. Further evidence in favour of the proposed intermediates may be deduced as follows. For C_2H_2 loss from $C_4H_7^+$ and C_2H_4 loss from $C_5H_9^+$ the energy of the reacting configuration is less than $\Sigma\Delta H_f$ products (Tables 1 and 3). Hence, the dissociation of the reacting configuration is endothermic, and the products are expected to "drift apart" in the course of the reaction. Experimentally, narrow metastable peaks are observed for these processes, the kinetic energy release at half-height being only 0.5 kcal mol^{-1} in each case. In contrast, C_2H_4 loss from $C_6H_{11}^+$ proceeds via a reacting configuration of higher energy than $\Sigma\Delta H_f$ products. Hence the reacting configuration now approximates to the transition state and dissociates exothermically. Some of the energy released may be partitioned as translation, thus resulting in a broadening of the metastable peak (energy release profile) for the process. It is found that C_2H_4 loss from $C_6H_{11}^+$ gives rise to a gaussian but broad metastable peak, a kinetic energy release of 1.6 kcal mol^{-1} being measured from the peak width at half height.

$C_7H_{13}^+$

As no study of this ion was available we have predicted the dissociations which should occur in slow reactions. Relevant data are given in Table 4, where only processes involving σ-bond cleavage of plausible reacting configurations are given. Since H_2 and CH_4 losses are pre-empted by olefin loss for $C_6H_{11}^+$ because of the large reverse activation energies associated with the former, such processes should not occur in slow reactions of $C_7H_{13}^+$.

Consideration of the data of Table 4 reveals that the most favourable decay route is C_3H_6 loss. C_2H_4 loss may lead to products of lower $\Sigma\Delta H_f$, but must proceed via a high energy primary carbonium ion whilst C_3H_6 loss may proceed via a more stable secondary cation. Experimentally, C_3H_6 loss dominates, 94% of the metastable ion current from $C_7H_{13}^+$ being due to this process for decompositions occurring in the first-field free region, the remaining 6% being due to C_2H_4 loss. Furthermore, the measured energy requirement for C_3H_6 loss (AP) is 208 kcal mol^{-1} in good agreement with the value predicted (209 kcal mol^{-1}) on the basis of negligible reverse activation energy.

Table 1. Energy data relevant to loss of olefins and alkynes from $C_4H_7^+$, $C_5H_9^+$ and $C_6H_{11}^+$

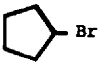
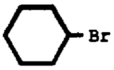
Ion	Neutral lost	Possible Reacting Configuration	ΔH_f(RC) kcal mol^{-1}	Products and $\Sigma\Delta H_f$ (kcal mol^{-1})	
$C_4H_7^+$	C_2H_2		240[b]	$C_2H_5^+$ + C_2H_2 219[13] 54[14]	273
	C_2H_4		231[a]	$C_2H_3^+$ + C_2H_4 266[15] 12[14]	278
	C_3H_4		230[b]	$\overset{+}{C}H_3$ + C_3H_4 261[13] 44[14]	305
$C_5H_9^+$	C_2H_2		235[b]	 + C_2H_2 192[13] 54[14]	246
	C_2H_4		226[a]	 + C_2H_4 226[15] 12	238
	C_3H_4		225[b]	$C_2H_5^+$ + C_3H_4 219[13] 44[14]	263
	C_3H_6		208[a]	$C_2H_3^+$ + C_3H_6 266[15] 5[14]	271
$C_6H_{11}^+$	C_2H_2		230[b]	 + C_2H_2 167[13] 54[14]	221
	C_2H_4		221[a]	 C_2H_4 204[16] 12[14]	216
	C_3H_4		220[b]	 + C_3H_4 192[13] 44[14]	236
	C_3H_6		203[a]	 + C_3H_6 226[15] 5[14]	231
	C_4H_6 (–≡–)		220[b]	$C_2H_5^+$ + C_4H_6 219[13] 35[14]	254
	C_4H_6 		190[c]	$C_2H_5^+$ + C_4H_6 219[13] 26	245
	C_4H_8		187[a]	$C_2H_5^+$ + C_4H_8 266[15] −4[14]	262

a. Value estimated using isodesmic substitution method (ref. 9).
b. Value estimated from known or estimated ΔH_f values of 1- and 2-propenyl cations (D.H.Aue, W.R. Davidson and M.T. Bowers, J. Amer. Chem. Soc., 1976, 98, 6700).
c. Value estimated from ΔH_f 1-methylallyl = 204 kcal mol^{-1} (ref. 16).

H_2 *loss*

It is noteworthy that the relative effectiveness of H_2 loss to compete with other processes increases as the lifetime of the ion becomes longer and therefore the average internal energy of the ions decreases. Thus H_2 loss always competes more effectively in the second than the first-field free region (Table 2). This behaviour was previously noted in a study of $C_3H_6^{+\cdot}$ where H˙ loss dominates the slow reactions although H_2 loss has a lower activation energy by some 6 kcal mol^{-1}.[21] The explanation given is that the rise of k (rate) with E (internal energy above threshold for reaction) is exceptionally slow for H_2 loss. Presumably a similar "entropy" effect is operating in the ions $C_4H_7^+$ and $C_5H_9^+$.

Table 2. Competing metastable transitions for the decomposition of some members of the homologous series of ions $C_nH_{2n-1}^+$

Precursor Compound.	Ion	Neutral lost[a] H_2		CH_4		C_2H_2		C_2H_4	
		1[b]	2[b]	1[b]	2[b]	1[b]	2[b]	1[b]	2[b]
	$C_4H_7^+$	13	59	22	26	65	15		
	$C_5H_9^+$	10	32					90	68
	$C_6H_{11}^+$	c	c					100	100

a. Values normalised to a total metastable ion current of 100 units.
b. 1st and 2nd field-free region respectively.
c. Seen but very weak (< 0.5%).

Table 3. Estimated and measured energy requirements for dissociation of some $C_nH_{2n-1}^+$ ions

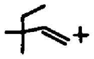
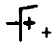
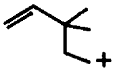
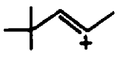
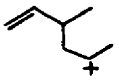
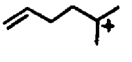
Ion	Neutral lost	ΔH_f (Reacting configuration) (kcal mol^{-1})	$\Sigma\Delta H_f$ products (kcal mol^{-1})	E exp (kcal mol^{-1})[a]
$C_4H_7^+$	H_2			266
	CH_4			268
	C_2H_2	240	273	272
$C_5H_9^+$	H_2			235
	C_2H_4	226	238	238
$C_6H_{11}^+$	C_2H_4	221	216	210

[a] ΔH_f corresponding to the transition state for decomposition of the $C_nH_{2n-1}^+$ ion; determined from appearance potential measurements on the metastable peak for decomposition. The estimated accuracy of these measurements is ± 12 kcal mol^{-1}.

$C_4H_7^+$

As noted above, the observed dissociations of this ion are independent to a first approximation, of the precursor.[12] The estimated potential surface is shown in Fig. 2 from which it is evident that ions which may plausibly be formed at threshold (e.g. 1- and 2-methylallyl) may interconvert at energies lower than those needed to promote dissociation. It is also apparent from Fig. 2 that no radical losses are able to compete at energies appropriate to metastable transitions. This is because the products formed are too high in energy (e.g. ionised butadiene, ΔH_f 235 kcal mol^{-1}[22] and H˙, ΔH_f 52 kcal mol^{-1};[14] $\Sigma\Delta H_f$ 287 kcal mol − 1). It is most significant that no C_2H_4 loss is observed because the estimated energy requirement for this process $\Sigma\Delta H_f(C_2H_3^+ + C_2H_4)$ is 5 kcal mol^{-1} above that needed

Table 4. Energetic data relevant to the dissociation of $C_7H_{11}^+$

Neutral lost	Reacting Configuration	ΔH_f (RC) kcal mol^{-1}	Products	$\Sigma\Delta H_f$ products kcal mol^{-1}
C_2H_2		225[b]	 + C_2H_2 161[19] 54[14]	215
C_2H_4		216[a]	 C_2H_4 184[20] 12[14]	196
C_3H_4		215[b]	 C_3H_4 167[13] 44[14]	211
C_3H_6		199[a]	 C_3H_6 204[16] 5[14]	209
C_4H_6 ()		185[c]	 + C_4H_6 192[19] 26[14]	218
C_4H_8		183[a]	 C_4H_8 226 -4[14]	222

a,b,c. The superscripts have the same significance as in Table 1.

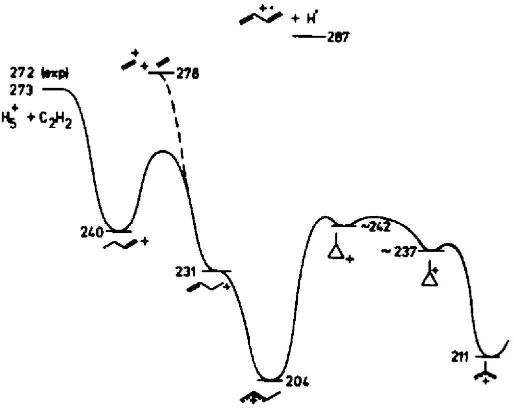
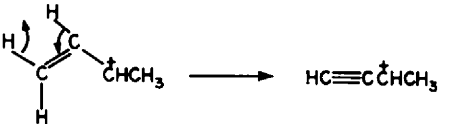


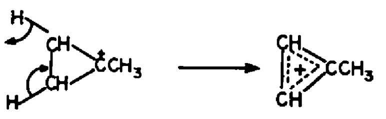
Fig. 2. Potential energy profile for decomposition of $C_4H_7^+$.

to cause C_2H_2 loss. Thus, although C_2H_2 loss is the dominant reaction undergone by $C_4H_7^+$ ions in the first field free region, such ions do not possess the additional 5 kcal mol^{-1} of internal energy needed to promote C_2H_4 loss. This in turn leads to the conclusion that all the observed processes (H_2, CH_4 and C_2H_2 losses) must have transition state energies less than 278 kcal mol^{-1}. Furthermore, since H_2 and CH_4 losses compete with C_2H_2 losses, it is probable that the transition stage energies for these processes are within 5 kcal mol^{-1} of that estimated (273 kcal mol^{-1}) for C_2H_2 loss. The range of energy (268–278 kcal mol^{-1}) for the transition states for H_2 and CH_4 losses from $C_4H_7^+$ derived in this way is consistent with our AP measurements (266 and 268 kcal mol^{-1}, respectively) and are difficult to assess in other ways.

In considering those reactions involving σ-bond formation in the dissociation step (H_2 loss and CH_4 loss) it is difficult to determine the reacting configurations and products formed because several different mechanisms are possible. Thus, for example, H_2 loss can proceed from 1-methylallyl via a 1,2-elimination leading to methylpropargyl (eqn 1) or via 1,2-elimination in 1-methylcyclopropyl leading to methylcyclopropenyl (eqn 2).



(1)



(2)

Both these reactions are symmetry-forbidden[23] and must involve substantial reverse activation energies; furthermore a portion of this energy should be released as translation. It is observed that H_2 loss from $C_4H_7^+$ gives rise to a flat-topped metastable peak and that the measured kinetic energy release is 7 kcal mol^{-1}. In view of the uncertainty concerning the exact nature of products and reacting configuration for H_2 loss we do not discuss this reaction further except to note that it is a *single* process. In contrast, H_2 loss from the lower homologue, $C_3H_5^+$, gives rise to a composite metastable peak,[10,11] thus proving two competing processes (leading to propargyl and cyclopropenyl[11,24,25]) are in operation.

CH_4 loss from $C_4H_7^+$ may also be formulated in several ways: however, it is instructive to note that the metastable peak for this process is gaussian thus suggesting a symmetry-allowed, 1,1-elimination is occurring. Such 1,1-eliminations have previously been postulated in the decomposition of gaseous cations,[11,26] but we feel further speculation on the mechanism of this reaction is unwarranted.

$C_5H_9^+$

Irrespective of the precursor used to generate the ion, $C_5H_9^+$ eliminates mainly C_2H_4 (*ca.* 90%) together with H_2 (*ca.* 10%) in the first field free region.[12] The dominance of C_2H_4 loss for the first time in ascending the homologous series is expected since this reaction can now lead to favourable products (allyl cation, as opposed to vinylium for $C_4H_7^+$) via a low energy reacting configuration. H_2 loss can be formulated as occurring in several ways; a plausible route leading to cyclopentenyl cation (ΔH_f 199 kcal mol^{-1} [27]) is shown in Fig. 3 and Scheme 1, together with C_2H_4 loss.

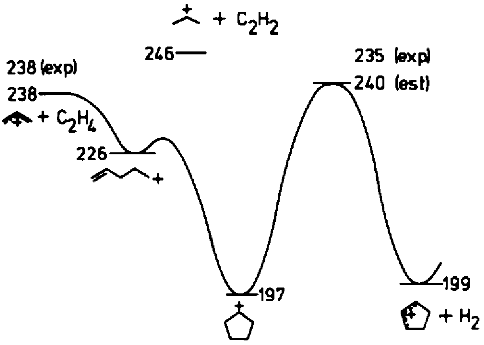
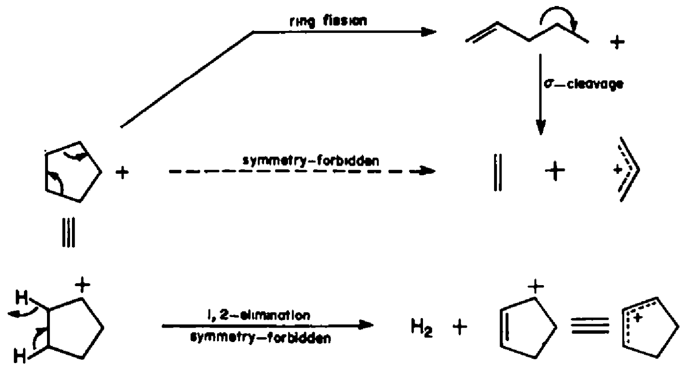


Fig. 3. Potential energy profile for decomposition of $C_5H_9^+$.

It should be noted, that since C_2H_2 loss from $C_5H_9^+$ is not a significant reaction in metastable transitions,[12] ions undergoing slow reactions have insufficient internal energy to form products of $\Sigma\Delta H_f \gg 246$ kcal mol^{-1} although 90% of the ions undergo C_2H_4 loss which requires 238 kcal mol^{-1}. The competition of H_2 loss with C_2H_4 loss allows an estimate (235–245 kcal mol^{-1}) to be made for the transition state energy for H_2 loss. The experimentally determined value (235 kcal mol^{-1}) is in good agreement. Moreover, since the loss of the H_2 is symmetry forbidden, a flat-topped metastable peak is expected for this process. Experimentally, the peak is indeed flat-topped, corresponding to a kinetic energy release of 13 kcal mol^{-1}. Returning to the dominant reaction of $C_5H_9^+$, namely C_2H_4 loss, two possibilities exist which lead to allyl cation from cyclopentyl cation. Either the reaction is stepwise, proceeding via reversible ring fission, or a concerted, symmetry-forbidden dissociation (dotted line in Scheme 1) may occur. It is clear from the results obtained in this study that a stepwise route is operating. This follows since a concerted symmetry-forbidden reaction would involve a significant reverse activation energy which is not observed. Furthermore, if C_2H_4 loss from C_5H_9 proceeded via a symmetry-forbidden route, kinetic energy release accompanying the dissociation would be expected.[26] However, it is found that the metastable peak for C_2H_4 loss is narrow and gaussian, thus precluding the concerted mechanism for the reaction. Conversely, our results



Scheme 1.

indicate that the lowest energy route for addition of ethylene to allyl cation is stepwise rather than concerted.

$C_6H_{11}^+$

One process, C_2H_4 loss, dominates the slow reactions, irrespective of the precursor used to generate $C_6H_{11}^+$. It is significant that H_2 loss is no longer able to compete effectively in slow reactions, and since C_3H_6 loss is also a minor process (<0.5% of metastable ion current from $C_6H_{11}^+$) a lower limit for the transition state energy for H_2 loss may be deduced. From Fig. 4 is is evident that energies of $\geqslant 230\,\text{kcal mol}^{-1}$ are not available to ions decomposing in metastable transitions. Hence it is probable that H_2 loss from $C_6H_{11}^+$ must proceed via a transition state of energy $\geqslant 225\,\text{kcal mol}^{-1}$.

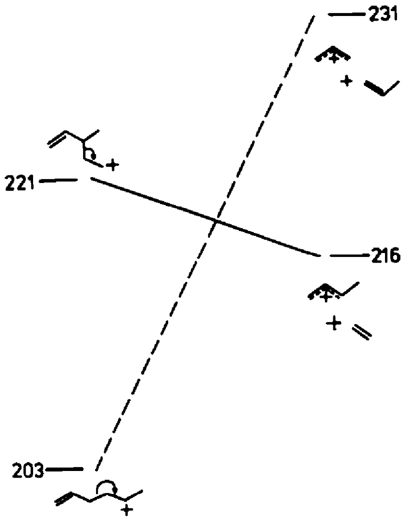


Fig. 4. Energy diagram showing reacting configurations and product combinations for loss of C_2H_4 and C_3H_6 from $C_6H_{11}^+$.

$C_7H_{13}^+$

As discussed above, C_2H_4 loss does not occur to a large extent in slow reactions from this ion because of the unfavourable reacting configuration (primary cation) for this process. Conversely, C_4H_8 loss although it may proceed via a favourable reacting configuration (tertiary cation), does not compete because it leads to relatively unfavourable products. The major reaction (94%) is observed to be C_3H_6 loss, as predicted, the energies of reacting configurations and product combinations being given in Table 4 and Fig. 5. A similar effect is observed for the saturated analogue $C_7H_{15}^+$, which also eliminates predominantly C_3H_6.[1]

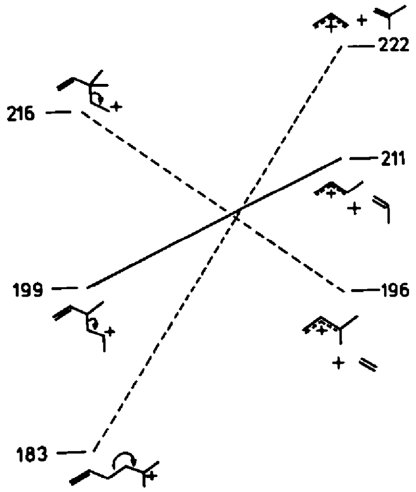


Fig. 5. Energy diagram showing reacting configurations and product combinations for loss of C_2H_4, C_3H_6 and C_4H_8 from $C_7H_{13}^+$.

CONCLUSION

The approach provides a self-consistent explanation of the known reactions of $C_4H_7^+$, $C_5H_9^+$ and $C_6H_{11}^+$. It may be used to predict successfully the reactions of $C_7H_{13}^+$. Furthermore, the model permits values to be estimated for the transition state energies for H_2 losses from $C_4H_7^+$ and $C_5H_9^+$ and may be used to place limits on the transition state energies of hypothetical reactions. The method illustrates the need to consider the energies not only of the possible products but also those of the plausible intermediates which may be involved.

EXPERIMENTAL

All compounds were either available commercially or synthesised via unexceptional methods. The mass spectra were recorded on an AEI MS902 double-focussing mass spectrometer, the samples being introduced using the All Glass Heated Inlet System (AGHIS). The AP's were determined on metastable ions in the first-field free region, the ESA voltage being reduced at constant accelerating voltage and magnetic field strength so as to transmit only ions undergoing the reaction of interest in the first field free region.[28] The results were analysed using the "semi-log plot" method[29] with the molecular ion of 2-chloropropane (AP = 10.8 eV[14]) as internal calibrant.

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REFERENCES

[1] R. D. Bowen and D. H. Williams, *J. Chem. Soc.* Perkin II, 1479 (1976).

[2] D. H. Williams and R. D. Bowen, *J. Am. Chem. Soc.* **99**, 3192 (1977).

[3] R. D. Bowen and D. H. Williams, *Org. Mass Spectrom* **12**, 453 (1977).

[4] R. D. Bowen, J. R. Kalman and D. H. Williams, *J. Am. Chem. Soc.* **99**, 5481 (1977).

[5] R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*. Elsevier, Amsterdam (1973).

[6] H. M. Rosenstock, V. H. Dibeler and F. N. Harllee, *J. Chem. Phys.* **40**, 591 (1964).

[7] L. P. Hills, M. L. Vestal and J. H. Futrell, *Ibid.* **54**, 3834 (1971).

[8] U. Löhle and Ch. Ottinger, *Ibid.* **51**, 3097 (1969).

[9] R. D. Bowen and D. H. Williams, *Org. Mass Spectrom.* **12**, 475 (1977).

[10] P. Goldberg, J. A. Hopkinson, A. Mathias and A. E. Williams, *Ibid.* **3**, 1009 (1970).

[11] G. Hvistendahl and D. H. Williams, *J. Chem. Soc.* Perkin II, 881 (1975).

[12] M. A. Shaw, R. Westwood and D. H. Williams, *Ibid.* (B), 1529 (1970).

[13] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.* **48**, 955 (1970).

[14] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. L. 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).

[15] F. P. Lossing, *Can. J. Chem.* **49**, 357 (1971).

[16] F. P. Lossing, *Ibid.* **50**, 5973 (1972).

[17] J. H. Beynon, R. G. Cooks, K. R. Jennings and A. J. Ferrer-Correia, *Int. J. Mass Spectrom.* **18**, 87 (1975).

[18] H. M. Rosenstock, *Ibid.* **20**, 139 (1976).

[19] F. P. Lossing and A. Maccoll, *Can. J. Chem.* **54**, 990 (1976).

[20] F. P. Lossing and J. C. Traeger, *Int. J. Mass Spectrom. Ion Phys.* **19**, 9 (1976).

[21] J. L. Holmes and J. K. Terlouw, *Org. Mass Spectrom.* **10**, 787 (1975).

[22] K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Radiat. Transfer* **2**, 369 (1962).

[23] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*. Verlag Chemie, Weinheim/Bergstr, Germany (1970).

[24] J. L. Holmes, A. D. Osborne and G. M. Weese, *Org. Mass Spectrom.* **10**, 867 (1975).

[25] D. K. Sen-Sharma, K. R. Jennings and J. H. Beynon, *Ibid.* **11**, 319 (1976).

[26] D. H. Williams and G. Hvistendahl, *J. Am. Chem. Soc.* **96**, 6755 (1974).

[27] F. P. Lossing and J. C. Traeger, *Ibid.* **97**, 1579 (1975).

[28] F. W. McLafferty, J. Okamoto, H. Tsuyama, Y. Nakajima, T. Noda and W. H. Major, *Org. Mass Spectrom.* **2**, 751 (1969).

[29] F. P. Lossing, A. W. Tickner and W. A. Bryce, *J. Chem. Phys.* **19**, 1254 (1951).