# Potential Energy Profiles for Unimolecular Reactions of Organic Ions: $[C_3H_8N]^+$ and $[C_3H_7O]^+$

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The unimolecular decompositions of two isomers of  $[C_3H_8N]^+$ ,  $CH_3CH_2CH=NH_2$  and  $CH_3CH_2NH=CH_2$ , are discussed in terms of the potential energy profile over which reaction may be considered to occur. The energy needed to promote slow (metastable) dissociations of either ion is found to be less than that required to cause isomerization to the other structure. This finding is supported by the observation of different decomposition pathways, different metastable peak shapes for  $C_2H_4$  loss, the results of <sup>2</sup>H labelling studies, and energy measurements on the two ions. The corresponding potential energy profile for decomposition of the oxygen analogues,  $CH_3CH_2CH=OH$  and  $CH_3CH_2O=CH_2$ , is compared and contrasted with that proposed for the  $[C_3H_6N]^+$  isomers. This analysis indicates that for the oxygen analogues, the energy needed to decompose either ion is very similar to that required to cause isomerization to the other structure. Consequently, dissociation of either ion is finely balanced with rearrangement to the other and similar reactions are observed. Detailed mechanisms are proposed for loss of  $H_2O$  and  $C_2H_4$  from each ion and it is shown that these mechanisms are consistent with <sup>2</sup>H and <sup>13</sup>C labelling studies, the kinetic energy release associated with each decomposition channel, the relative competition between  $H_2O$  and  $C_2H_4$  loss and energy measurements.

# **INTRODUCTION**

In recent work,<sup>1-4</sup> we have emphasized how the slow unimolecular reactions of organic ions may be studied by generating the ion in question in a mass spectrometer and examining the dissociations which occur in metastable transitions. The excess energy present in the transition states when such slow dissociations occur is usually small<sup>5,6</sup> and primary isotope effects are frequently encountered.<sup>7-9</sup> Moreover, it is often possible to understand the observed reactions by constructing a suitable potential energy profile over which the ion may be considered to decompose.<sup>1-4,10</sup>

In this paper, the slow dissociations of two isomers of  $[C_3H_8N]^+$  are considered using this approach and the corresponding oxygen analogues,  $[C_3H_7O]^+$  are also examined. For both the  $[C_3H_8N]^+$  and  $[C_3H_7O]^+$ isomeric ion pairs, hypothetical reaction pathways connecting the isomeric pairs are constructed on the basis of energetic and mechanistic arguments. It is found that the replacement of NH by O results in drastic changes in the relative heights of the energy barriers for decomposition and isomerization of the isomers considered.

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### **RESULTS AND DISCUSSION**

The slow unimolecular reactions of the five 'onium' isomers of  $[C_3H_8N]^+$ , in which the charge may be considered to reside mainly on nitrogen have already been documented.<sup>11,12</sup> The data relevant in the present context are given in Table 1.

It is clear from the results given in Table 1 that a and b do not interconvert prior to slow dissociations. Not only does b undergo exclusively  $C_2H_4$  loss (whereas a also loses NH<sub>3</sub>) but the metastable peaks for  $C_2H_4$  loss from a and b are different in shape, thus proving that these ions decompose over separate potential energy profiles.<sup>13</sup>

The most plausible mechanisms whereby a and b may interconvert and dissociate are given in Scheme 1.

Starting from a, the most likely route for  $C_2H_4$ elimination is via two consecutive 1,2-hydride shifts followed by  $\sigma$ -bond cleavage of the resultant primary carbonium ion d. An alternative decay route is available for the secondary carbonium ion c, namely hydrogen transfer from carbon to nitrogen, thus forming **Table 1. Slow unimolecular dissociations of some isomers of** 

Ion structure C <sub>2</sub> H <sub>4</sub>	NH3	for C <sub>2</sub> H <sub>4</sub> loss
$CH_3CH_2CH==\vec{N}H_2$ (a) 29	71	Flat-topped
$CH_3CH_2\dot{N}H=CH_2$ (b) 100	0	Gaussian

<sup>a</sup> Abundances measured by peak areas in the first field free region (1st FFR) and normalized to a total metastable ion current of 100 units from m/e 58.<sup>13</sup>

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protonated allylamine e. Simple  $\sigma$ -cleavage in e may then lead to loss of NH<sub>3</sub>.

Starting from b, the complex g may be formed via f; break up of g may then result in elimination of  $C_2H_4$ . The only plausible route for NH<sub>3</sub> loss, starting from b, is via rearrangement of g to the open chain carbonium ion d, followed by formation of e via c;  $\sigma$ -cleavage in e then results in NH<sub>3</sub> loss. The critical step in this mechanism is  $g \rightarrow d$ , bearing in mind that combinations of  $C_2H_4$  and  $CH_2=NH_2$  need not dissociate if the internal energy available is insufficient to overcome the attractive ion induced dipole interaction between these species; clearly, if dissociation of g to  $CH_2=NH_2$  and  $C_2H_4$  is energetically more favourable than the isomerization  $g \rightarrow d$ , then this isomerization will be pre-empted by  $C_2H_4$  loss. Since b is found to eliminate only  $C_2H_4$  in slow reactions, it would appear that this situation prevails.

Using known heats of formation for neutral species,<sup>14</sup> CH<sub>2</sub>= $\overset{+}{N}$ H<sub>2</sub>,<sup>14</sup> [C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>,<sup>15</sup> [C<sub>3</sub>H<sub>5</sub>]<sup>+</sup>,<sup>16</sup> and estimated values for open chain carbonium ions<sup>17</sup> and



Figure 1. Potential energy profile for isomerization and dissociation of a and b.

heats of formation of a and b were obtained from the appearance potentials of m/e 58 in the mass spectra of suitable precursors. These appearance potentials were determined using a mass spectrometer equipped with an energy resolved electron beam. Although some of the energy levels for species in Fig. 1 are known only approximately, it is immediately apparent that dissociation of the complex g is greatly favoured over rearrangement to d. This is in accord with the experimental fact that b does not isomerize to a prior to dissociation, and also explains why NH3 loss does not occur in slow reactions of b. In Fig. 1, the rate-determining step in  $C_2H_4$  loss from b is depicted as being isomerization to g via f. There are three pieces of experimental evidence in favour of this postulate: (i) The metastable peak for this process is Gaussian and broad, an average<sup>19</sup> kinetic energy release of 6.5 kcal mol<sup>-1</sup> being deduced from the width of the peak at halfheight. The broadening of the peak arises because excess energy is present in the transition state for the dissociation step,  $g \rightarrow$  products, and part of this excess energy is partitioned as kinetic energy release accom-panying the reaction.<sup>20</sup> (ii) The results of <sup>2</sup>H labelling studies<sup>11</sup> reveal a high specificity in the origin of the hydrogen atom which is transferred from carbon to nitrogen in the course of C<sub>2</sub>H<sub>4</sub> loss from b. For example, CH<sub>3</sub>CD<sub>2</sub>NH=CH<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>NH=CD<sub>2</sub>, generated in approximately equal abundance by ionization and fragmentation of CH<sub>3</sub>CD<sub>2</sub>NHCH<sub>2</sub>CH<sub>3</sub>, are observed to lose CH<sub>2</sub>CD<sub>2</sub> (from CH<sub>3</sub>CD<sub>2</sub>NH=CH<sub>2</sub>) and  $CH_2CH_2$  (from  $CH_3CH_2\dot{N}H=CD_2$ ) but no CH<sub>2</sub>CHD.<sup>11</sup> These data suggest that the transfer of hydrogen from carbon to nitrogen is irreversible and involves specifically the hydrogen atoms of the methyl group in b. This is supported by the observation that CH<sub>3</sub>CH<sub>2</sub>ND=CH<sub>2</sub> eliminates only C<sub>2</sub>H<sub>4</sub> in slow dissociations,<sup>11</sup> thus proving that the reverse process  $(g \rightarrow f \rightarrow b)$  does not occur since this reaction would result in loss of identity of the hydrogen atom originally bound to nitrogen. (iii) Appearance potential measurements yield an approximate transition state energy of 218 kcal  $mol^{-1}$ , which is significantly above the thermochemical threshold  $(190 \text{ kcal mol}^{-1})$  for the reaction.

 $e^{18}$  leads to the potential energy profile of Fig. 1. The

It should be noted that, apart from isomerization to g via f, followed by  $C_2H_4$  loss, no plausible decay routes exist for b. Thus, for instance,  $\sigma$ -cleavage to form  $[C_2H_5]^+$  and  $CH_2$ =NH requires roughly 235 kcal mol<sup>-1</sup>; production of  $CH_2$ = $\overset{+}{N}H_2$  and  $C_2H_4$  is more favourable by some 45 kcal mol<sup>-1</sup>. This preference for olefin loss arises mainly because the potential  $CH_2$ =NH molecule is very much more basic than the incipient olefin  $CH_2$ = $CH_2$ . In fact, we have yet to observe loss of a neutral imine from b or homologous ions even when the potential olefin has a relatively high proton affinity. This is because the basicity ranges of imines and olefins do not overlap greatly, in general olefins having much lower proton affinities.

Considering now the portion of the potential energy profile appropriate to the dissociation of a, it is evident that decomposition of the primary carbonium ion

d into  $CH_2 = NH_2$  and  $C_2H_4$  is exothermic. This conclusion is inescapable even allowing for the inherent inaccuracies in the estimated heat of formation  $(217 \text{ kcal mol}^{-1})$  of *d*. The exothermic nature of the dissociation step is confirmed by experiment: (i) the metastable peak for this process is flat-topped, corresponding to the release of approximately 9 kcal mol<sup>-1</sup> of kinetic energy.<sup>11</sup> (ii) The measured transition state energy is  $224^{11}$  kcal mol<sup>-1</sup> which is greatly above the thermochemical threshold (190 kcal mol<sup>-1</sup>) for  $C_2H_4$ loss. (iii) The major slow reaction of a is  $NH_3$  loss which gives rise to products having a total heat of formation of 215 kcal mol<sup>-1</sup>; since C<sub>2</sub>H<sub>4</sub> elimination is the minor decay route (Table 1) it probably must proceed via a transition state of energy greater than 215 kcal mol<sup>-1</sup>. Bearing in mind this overwhelming evidence that  $d \rightarrow$  products is exothermic, it is easy to understand why a does not isomerize to g. Clearly, dissociation occurs over a repulsive energy profile; therefore the incipient ethylene molecule is unable to move round to 'solvate' the hydrogen atoms bound to

nitrogen in the nascent CH<sub>2</sub>=NH<sub>2</sub> ion.

Further experimental evidence may be cited in favour of the energy levels shown in Fig. 1. For example, the rate-determining step in  $NH_3$  loss from a must be the isomerization  $c \rightarrow e$ . There are three pieces of experimental evidence in favour of this view. (i) The metastable peak for the process is Gaussian and broad, corresponding to an average<sup>19</sup> kinetic energy release of  $3.0 \text{ kcal mol}^{-1}$ . This indicates that excess energy is present in the transition state for the dissociation step<sup>20</sup> and suggests that the ratedetermining step in  $NH_3$  loss from a is rearrangement to another structure of  $[C_3H_8N]^+$ . (ii) The results of <sup>2</sup>H labelling studies establish that the hydrogen atoms originally bound to nitrogen in a are retained exclusively in the expelled NH<sub>3</sub> molecule.<sup>11</sup> This precludes any reversible interconversion of c and e because such a process would lead to loss of identity of the hydrogen atoms attached to nitrogen. (iii) A distinct preference for transfer of H, rather than D, in completing the ammonia molecule is observed. The data are consistent with random selection of any one of the hydrogen atoms originally bound to carbon, together with an isotope effect of approximately 5:1, favouring H (rather than D) transfer to nitrogen.<sup>11</sup> This is good evidence that the rate-determining step in NH<sub>3</sub> loss from a involves the breaking of a C-H bond and suggests that isomerization of  $c \rightarrow e$  proceeds via a transition state with higher energy than  $215 \text{ kcal mol}^{-1}$ (i.e. the total heat of formation of  $[C_3H_5]^+$  and NH<sub>3</sub>). The measured transition state energy is found to be 221 kcal mol<sup>-1</sup> and therefore corresponds to an activa-tion energy of 15 kcal mol<sup>-1</sup> associated with the rearrangement of  $c \rightarrow e$ .

The above case is clear-cut, dissociation of a and b being preferable to rearrangement to the other isomer. In the case of the analogous oxonium ions, h and i, a delicate balance exists between interconversion and dissociation, as will be evident from the following

$$CH_3CH_2CH = OH CH_3CH_2O = CH_2$$
  
h i

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Scheme 2

discussion. The discussion extends previous experimental work on  $[C_3H_7O]^+$  ions.<sup>1,2,20-25</sup>

The most plausible mechanisms whereby h and imay interconvert and dissociate are given in Scheme 2; this scheme is analogous to that (Scheme 1) considered earlier for the nitrogen analogues a and b. A potential energy profile corresponding to Scheme 2 may be constructed using known heats of formation for neutral species,<sup>14</sup> CH<sub>2</sub>=OH and CH<sub>3</sub>CH<sub>2</sub>CH=OH,<sup>18</sup>  $[C_2H_5]^+$ , <sup>15</sup>  $[C_3H_5]^+$  <sup>16</sup> and  $CH_3CH_2O^+$  CH<sub>2</sub>, <sup>26</sup> together with estimated values for open-chain carbonium ions<sup>17</sup> and  $CH_2$ =CHCH<sub>2</sub>OH<sub>2</sub>. The value for CH2=CHCH2OH2 was obtained by estimating the proton affinity of CH<sub>2</sub>=CH-CH<sub>2</sub>OH as 190 kcal mol<sup>-1</sup> (the proton affinity of the saturated analogue,  $CH_3CH_2CH_2OH$  is  $189^{20}$  kcal mol<sup>-1</sup>). In this energy profile (Fig. 2), 1,2-hydride shifts are assumed to occur essentially without activation energies apart from those associated with the reaction endo-thermicities.



**Figure 2.** Potential energy profile for isomerization and dissociation of h and i.

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Other assumptions inherent in Fig. 2 are that the complex k is lower in energy than  $C_2H_4$ , together with

 $CH_2 = OH$  and that the rearrangement of  $n \rightarrow o$  requires an internal energy of 10-15 kcal mol<sup>-1</sup>. The activation energy for  $n \rightarrow o$  is consistent with four pieces of experimental evidence. (i) The metastable peak for  $H_2O$  loss from *n* is relatively broad and Gaussian, corresponding to an average<sup>19</sup> kinetic energy release of  $2.6 \text{ kcal mol}^{-1}$ . This indicates that the rate-determining step in  $H_2O$  loss from h is isomerization to another structure of [C<sub>3</sub>H<sub>7</sub>O]<sup>+</sup>;<sup>20</sup> dissociation then occurs with excess energy in the transition state for the final step. (ii) The results of <sup>2</sup>H labelling studies show that the hydrogen atom originally bound to oxygen in h is predominantly retained in the expelled H<sub>2</sub>O molecule. This is further evidence in favour of  $n \rightarrow o$  being irreversible. (iii) More detailed analysis (see below) of these labelling data reveals a definite preference for H (rather than D) transfer from carbon to oxygen. This isotope effect provides more evidence that  $n \rightarrow o$  is the rate-determining step in  $H_2O$  loss from h. (iv) Appearance potential measurements give an approximate transition state energy of 176 kcal mol<sup>-1</sup> for H<sub>2</sub>O loss from h; this value is significantly above the calculated thermochemical threshold  $(168 \text{ kcal mol}^{-1})$  for the reaction.

A comparison of Figs. 1 and 2 reveals that, in contrast to the  $[C_3H_8N]^+$  isomers, which are clearly not able to interconvert prior to slow dissociations, the analogous oxonium ions, h and i may be able to isomerize before decomposition occurs. The critical

difference is that 
$$CH_2CH_2CH_2NH_2 \rightarrow CH_2 = CH_2 +$$

 $CH_2$ =NH<sub>2</sub> is exothermic and therefore results in dissociation into these two fragments. The conversion of potential energy into relative translational energy of these two fragments ensures that they do not orbit each other while still weakly coupled; thus, their recombination as the complex g is avoided. However,

 $CH_2CH_2CH_2OH \rightarrow CH_2 = CH_2 + CH_2 = OH$  is endothermic; these fragments may be produced in a weakly coupled and orbiting combination as well as in the form of completely separated fragments. The orbiting combination *m* (total energy just less than 176 kcal mol<sup>-1</sup>; Fig. 2) can then form the complex *k*. Thus, the loss of  $C_2H_4$  from *h* and *i* may be in delicate competition with a pathway for their interconversion.

In the discussion which follows the results of extensive <sup>2</sup>H and <sup>13</sup>C labelling studies are presented, and it is shown that these data demand that isomerization and dissociation of h and i are indeed very finely balanced.

Complete equilibration of h and i at energies appropriate to metastable transitions is precluded by the results of <sup>2</sup>H labelling studies which reveal a considerable degree of retention of the hydroxylic hydrogen atom of h in the expelled H<sub>2</sub>O molecule (Table 2). Thus, for example, CH<sub>3</sub>CH<sub>2</sub>CH= $\stackrel{+}{O}D$  loses 26% H<sub>2</sub>O and 74% HOD, whereas the isomeric ion CH<sub>3</sub>CH<sub>2</sub>CD= $\stackrel{+}{O}H$  eliminates 87% H<sub>2</sub>O and 13% HOD in the water loss reaction. Were the interconversion of h and i to be rapid and reversible, such

Table 2. Expected and observed water losses from  ${}^{2}H$  labelled ions of nominal structure h

			Neutral l	ost		
lon		Expected	•		Observed <sup>b</sup>	
structure	H₂O	HOD	D <sub>2</sub> O	H₂O	HOD	D <sub>2</sub> O
CH₃CH₂CH≕ÔD CH₂—CH₂ │ │	24	76	0	26	74	0
ĊH <sub>2</sub> —ÒD	24	76	0	30	70	0
CH <sub>3</sub> CH <sub>2</sub> CD <u></u> →ÕH	87	13	0	87	13	0
CH <sub>3</sub> CH <sub>2</sub> CD=ÖD	21	72	7	19	76	5
CH <sub>3</sub> CD <sub>2</sub> CH=-ŎH CH <sub>2</sub> CH <sub>2</sub>	73	26	1	75	25	C
ĆD₂—ÓH	73	26	1	77	23	c
$CH_{3}CD_{2}^{+}CH=OD$ $CH_{2}CH_{2}$	12	71	17	14	78	8
ĊD₂ÒD	12	71	17	14	73	13
CD <sub>3</sub> CH <sub>2</sub> CH=OH	66	31	3	64	34	2
CH <sub>3</sub> CD <sub>2</sub> CD—ÒH	66	31	3	61	36	3
CD <sub>3</sub> CH <sub>2</sub> CH=OD	7	73	20	4 <sup>d</sup>	88 <sup>d</sup>	8 <sup>d</sup>
CH <sub>3</sub> CD <sub>2</sub> CD <del></del> →ÖD	7	73	20	7	73	20

<sup>a</sup> For model see text.

<sup>b</sup> Abundances measured by peak area and normalized to a total metastable ion current (1st FFR) of 100 units due to water loss. <sup>c</sup> Peak seen but of lower abundance than 0.5%.

<sup>d</sup> Values less reliable owing to difficulty in producing this ion in high isotopic purity.

isomerizations would lead to loss of identity of the hydroxylic hydrogen atom of h, and statistical selection of the hydrogen atoms would be expected, together with a possible isotope effect. In view of these <sup>2</sup>H labelling results, it seems probable that h and iundergo only partial interconversion prior to H<sub>2</sub>O loss in metastable transitions. Table 2 also gives the percentage losses of H<sub>2</sub>O, HOD and D<sub>2</sub>O expected from partly deuterated analogues of h on the basis of a model in which a minor fraction (one-third) of ions generated as h rearrange to i before water loss occurs. The assumptions involved in this model are: (i) 1,2hydride shifts lead to statistical distribution of all carbon-bound hydrogen atoms prior to loss of H<sub>2</sub>O. (ii) Two-thirds of the ions undergo irreversible rearrangement to o via n without any prior isomerization to  $CH_3CH_2O = CH_2$ . The remaining one-third undergo a single rearrangement to CH<sub>3</sub>CH<sub>2</sub>O=CH<sub>2</sub> and then return to CH<sub>3</sub>CH<sub>2</sub>CH=OH before losing H<sub>2</sub>O. The CH<sub>3</sub>CH<sub>2</sub>O=CH<sub>2</sub> ion thus formed undergoes reversible isomerization with k; hence, this process results in the equilibration of the hydroxylic hydrogen atom with any four others. (iii) The hydrogen atom bound to oxygen in the CH<sub>3</sub>CHCH<sub>2</sub>OH ion which rearranges to CH2==CHCH2OH2 is retained in the eliminated H<sub>2</sub>O molecule; the second hydrogen atom is selected at random but an isotope effect of 2:1 operates in favour of H, rather than D, transfer. (iv) The  $CH_2$ =CHCH<sub>2</sub>OH<sub>2</sub> ion, once formed, dissociates in preference to isomerizing to CH<sub>2</sub>CHCH<sub>2</sub>OH.

The agreement between the observed losses of  $H_2O$ , HOD and  $D_2O$  and those expected on the basis of the model is good. All the assumptions involved in the model are reasonable in view of the experimental data given in Table 2. For instance, statistical distribution of all carbon-bound hydrogen atoms is strongly supported by the very similar behaviour of  $CH_3CD_2CD=OH$  and  $CD_3CH_2CH=OH$ . Moreover, since both these ions lose mainly  $H_2O$ , despite the fact that they contain equal numbers of H and D atoms bound to carbon, there must be an isotope effect favouring H (rather than D) transfer to oxygen.

We next consider the possible mechanisms whereby h may eliminate  $C_2H_4$ . In previous work<sup>1,2</sup> we have postulated that this reaction proceeds via simple  $\sigma$ cleavage in the primary carbonium ion l (see Scheme 2). This mechanism accounts for the results of  $^{13}C$ labelling studies on h which reveal that the  $\beta$ -carbon atom is always eliminated in the ethylene and that the  $\alpha$ - and  $\gamma$ -carbon atoms participate equivalently.<sup>2</sup> These data preclude *reversible* isomerization of h to kvia l because such an interconversion would lead to loss of identity of the  $\beta$ -carbon atom. Nevertheless, it is possible that some (or all) of the ions generated as hwhich eventually lose  $C_2H_4$ , may undergo irreversible rearrangement to i via k and l. Reversible isomerization of i, k and j could then lead to equilibration of the hydroxylic hydrogen atom with any four others, but  $C_2H_4$  loss would involve only the components of the  $C_2H_5$  group in *i*. Since the carbon atoms of this  $C_2H_5$  group originate from the end two carbon atoms of l (i.e. those which would be contained in the ethylene molecule if l were to undergo direct decomposition), the <sup>13</sup>C labelling data may be accommodated. For example, p may lose  $C^{13}CH_4$  via  $\sigma$ -bond cleavage of the open chain carbonium ion q and, irrespective of whether ring closure to r-may occur, the original  $\beta$ -carbon atom of p is always eliminated because r can open only to q (Scheme 3). Alternatively, q may rearrange to s, and subsequently t and u but, since the ethylene expelled originates exclusively from the C<sub>2</sub>H<sub>5</sub> group of s, t or u, only C<sup>13</sup>CH<sub>4</sub> will be lost.

Thus, <sup>13</sup>C labelling studies cannot establish whether l rearranges irreversibly to k prior to  $C_2H_4$  loss. However, such a rearrangement should have other consequences. Since the rate-determining step in  $C_2H_4$  loss from some ions generated as h would be isomerization to i, the metastable peak for  $C_2H_4$  loss from h should be broader than that starting from i.<sup>20</sup> Indeed, the average kinetic energy releases associated with  $C_2H_4$  loss from h and i are 1.7 and 1.0 kcal mol<sup>-1</sup>, respectively. Additionally, for the fraction of ions generated as h which undergo the isomerization to k, rearrangement of  $k \rightleftharpoons j \rightleftharpoons i$  equilibrates the hydroxyl hydrogen atom with any four others originally bound to carbon. Therefore, the occurrence of any such rearrangement should be detectable by <sup>2</sup>H labelling. Table 3 gives data for elimination of <sup>2</sup>H labelled ethylene from <sup>2</sup>H labelled analogues of h and

 $\dot{C}H_2CH_2CH_2\dot{O}H$ . Also given in Table 3 are the calculated decomposition ratios corresponding to a model in which: (i) 1,2-hydride shifts  $(h \rightleftharpoons n \rightleftharpoons l)$  result in statistical distribution of all carbon-bound hydrogen atoms prior to  $C_2H_4$  loss. (ii) Two-thirds of the ions generated as h dissociate directly from structure l; thus, for this fraction of the initial population of ions, the hydrogen atom bound to oxygen is retained exclu-

sively in the CH<sub>2</sub>=OH fragment ion. (iii) The remaining one-third undergo a rate-determining isomerization to k; if interconversion of k, j and i then occurs, leading to equilibration of the hydroxylic hydrogen atom with any four of those originally bound to carbon, loss of C<sub>2</sub>H<sub>4</sub> will involve random selection of any four of the five hydrogen atoms in the C<sub>2</sub>H<sub>5</sub> group of i, j and k. Since one of these hydrogen atoms was attached originally to oxygen, the fraction of ions undergoing this isomerization will show a preference (relative to a statistical selection) for eliminating the original hydroxylic hydrogen atom of h in C<sub>2</sub>H<sub>4</sub> loss.

The data of Table 3 are in good agreement with those expected from the model outlined above. Hence, the results of kinetic energy release and <sup>2</sup>H labelling are consistent with a minor fraction of ions generated as h undergoing a rate-determining isomerization to k prior to C<sub>2</sub>H<sub>4</sub> loss.

It should be noted that the postulate of reversible isomerization of a fraction of ions generated as h with k, j and i prior to H<sub>2</sub>O loss is not inconsistent with the hypothesis that some ions formed as h undergo an irreversible rearrangement to k before losing C<sub>2</sub>H<sub>4</sub>. This is because the ions that lose C<sub>2</sub>H<sub>4</sub> comprise mainly those with the highest internal energies which decompose in metastable transitions. Thus, the ions that are able to undergo reversible isomerization with k, j and i possess insufficient internal energy to undergo C<sub>2</sub>H<sub>4</sub> loss; consequently they undergo only H<sub>2</sub>O loss.

The results of <sup>2</sup>H labelling studies on *i* reveal that isomerization of *i* to *h* is not rapid and reversible prior to  $H_2O$  loss (Table 4). Thus, for example,

 $CH_2 = OCD_2CD_3$  and  $CD_2 = OCH_2CH_3$  lose 70%  $D_2O$  and 79%  $H_2O$ , respectively, in the water loss reaction. These data show there is a relatively high



Scheme 3

			<b>-</b> a		Neutral lost			Observed <sup>b</sup>		
lon structure	C₂H₄	C₂H₃D	C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	C₂HD₃	C₂D₄	C₂H₄	C₂H₃D	C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	$C_2HD_3$	C₂D₄
CH <sub>3</sub> CH <sub>2</sub> CH==OD <sup>+</sup>	73	27				65	35			
CH <sub>2</sub> —CH <sub>2</sub>										
ĊH <sub>2</sub> ÒĐ	73	27				68	32			
CH <sub>3</sub> CH <sub>2</sub> CD==OH	33	67				40	60			
CH <sub>3</sub> CH <sub>2</sub> CD==ÕD	25	62	13			21	63	16		
CH <sub>3</sub> CD <sub>2</sub> CH=-OH	10	55	35			12	60	28		
CH <sub>2</sub> CH <sub>2</sub>										
ĊD₂ÒĤ	10	55	35			12	56	32		
CH <sub>3</sub> CD <sub>2</sub> CH <del>=</del> =ÕD	5	44	46	5		4	38	50	8	
CH <sub>2</sub> CH <sub>2</sub>										
ĊD <sub>2</sub> —OD	5	44	46	5		4	39	50	7	
CD <sub>3</sub> CH <sub>2</sub> CH==OH	1	27	56	16		2°	47°	31°	20°	
CH <sub>3</sub> CD <sub>2</sub> CD=OH	1	27	56	16		2	28	56	15	
CD <sub>3</sub> CH <sub>2</sub> CH=OD		16	56	27	1		15	56	28	1
CH <sub>3</sub> CD <sub>2</sub> CD=OD		16	56	27	1		15	55	30	2

Table	3.	Expected	and	observed	ethylene	losses	from	<sup>2</sup> H	labelled	ions	of	nominal	structure	h
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<sup>a</sup> For model see text.

<sup>b</sup> Abundances measured by peak area and normalized to a total metastable ion current (1st FFR) of 100 units due to ethylene loss.

<sup>c</sup>Less reliable values owing to low abundance.

degree of specificity involved in H<sub>2</sub>O loss; the hydrogen atoms originate mainly from the C<sub>2</sub>H<sub>5</sub> group of i. If the formation of k from i via j requires more energy than rearrangement of k to l (and subsequently to *n* and *o*, thus leading to  $H_2O$  loss), then transfer of a methyl group hydrogen of i to oxygen will be favoured. On the other hand, if rearrangement of k to l requires more energy than  $i \rightleftharpoons j \rightleftharpoons k$ , then the hydrogen atoms of the ethyl chain may become equivalent prior to isomerization to l. In either case, it is possible that once l has been formed it can collapse to n (and later o) by hydride shifts. Were H<sub>2</sub>O loss to require marginally more internal energy than rearrangement back to l, the second hydrogen atom in the expelled water molecule would originate mainly from those bound to the  $\beta$ - and  $\gamma$ -carbon atoms in the ion formed as structure l by rearrangement of i. Thus, both hydrogen atoms of the eliminated water molecule could originate mainly from the  $C_2H_5$  group of *i*. Table 4 gives the calculated abundance data for a model in which it is assumed that two-thirds of the ions formed as l, by rearrangement of k, undergo sufficient 1,2hydride shifts and ring closures to permit statistical distribution of all carbon-bound hydrogens of l prior to  $H_2O$  loss. For the remaining one-third, l is assumed to collapse irreversibly to n, which then undergoes interconversion with h prior to rearrangement to o

 
 Table 4. Expected and observed water losses from <sup>2</sup>H labelled ions of structure i

			Neutral Id	ost		
lon		Model <sup>*</sup>			Observed <sup>t</sup>	•
structure	H₂O	HOD	D20	H₂O	HOD	$D_2O$
CD <sub>2</sub> =OCH <sub>2</sub> CH <sub>3</sub>	87	13	0	7 <del>9</del>	21	0
CH <sub>2</sub> =0CD <sub>2</sub> CH <sub>3</sub>	60	38	2	61	37	2
CH <sub>2</sub> =OCD <sub>2</sub> CD <sub>3</sub>	0	33	67	1	29	70

<sup>a</sup> See text for model.

<sup>b</sup> Abundances measured by peak area and normalized to a total metastable ion current (1st FFR) of 100 units due to water loss.

and loss of H<sub>2</sub>O. An isotope effect of 2:1 is assumed to operate in the transfer of hydrogen from carbon to oxygen in  $n \rightarrow o$ . It is also assumed that equal contributions arise due to specific  $\beta$ -hydrogen transfer to oxygen  $(i \rightarrow j \rightarrow k \rightarrow l)$  occurring irreversibly) and nonspecific  $\beta$ -hydrogen transfer to oxygen  $(i \rightleftharpoons j \rightleftharpoons k)$  prior to  $k \rightarrow l$ ). The data are well accommodated by this model (Table 4). We conclude that the rearrangement processes  $i \rightleftharpoons k$  and  $k \rightleftharpoons l$  are indeed very finely balanced with each other.

Several mechanisms are possible for the remaining reaction,  $C_2H_4$  loss from *i*. As in the case of *h*, it is clear that at very low internal energies (ions of long average lifetimes) few ions have sufficient internal energy to undergo  $C_2H_4$  elimination. Instead, most rearrange to *h*, as postulated above, and eventually decompose via loss of  $H_2O$ . In earlier work<sup>20</sup> we have shown that when  $C_2H_4$  is eliminated from <sup>2</sup>H labelled analogues of *i*, the four hydrogen atoms are selected almost statistically from the seven available (Table 5).

In particular, CH<sub>2</sub>=OCD<sub>2</sub>CH<sub>3</sub> and CD<sub>2</sub>=OCH<sub>2</sub>CH<sub>3</sub> undergo loss of partially deuterated ethylenes in very similar ratios, thus precluding specific elimination of  $C_2H_4$  from the ethyl group of *i*. Hence, it would appear that i undergoes rearrangement to l, via j and k, prior to  $C_2H_4$  loss. Equilibration of i, j and k before this rearrangement and possible equilibration of l, n and h after rearrangement can lead to almost statistical elimination of C<sub>2</sub>H<sub>4</sub>. Careful consideration of this mechanism leads to the calculated decomposition ratios given under 'model' in Table 5; these values are close to the experimental data. The assumptions involved in this model are as follows: (i) Rapid interconversion of i, j and k prior to  $k \rightarrow l$  results in random transfer of any of the five hydrogens in the ethyl group of i to oxygen. (ii) The rearrangement  $k \rightarrow l$  occurs for all the ions and is of only marginally lower activation energy than  $C_2H_4$ loss. One-third of the ions thus produced collapse to n

Table 5. Expected and observed entriene tosses nominal tabened tons of subclure	<b>able 5.</b> ]	Expected and	observed	ethylene	losses from	<sup>2</sup> H label	led ions of	f structure
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					Neutral lo	st				
lon			Model <sup>a</sup>					Observed <sup>b</sup>		
structure	C₂H₄	C <sub>2</sub> H <sub>3</sub> D	$C_2H_2D_2$	$C_2HD_3$	C <sub>2</sub> D <sub>4</sub>	C₂H₄	C₂H₃D	$C_2H_2D_2$	$C_2HD_3$	$C_2D_4$
$CD_2 = OCH_2CH_3$	16	58	26			14	58	26		
CH <sub>2</sub> =OCD <sub>2</sub> CH <sub>3</sub>	18	53	29			16	56	28		
$CH_2 = \dot{O}CD_2CD_3$			26	58	16			19	67	14

\* See text for model.

<sup>b</sup> Abundances measured by peak area and normalized to a total metastable ion current (1st FFR) of 100 units due to ethylene loss.

and then undergo reversible isomerization with h before attaining l again. These ions then dissociate via  $\sigma$ -cleavage of l without any further rearrangement. The remaining two-thirds undergo ring closures and 1,2-hydride shifts to an extent sufficient to produce statistical distribution of all carbon-bound hydrogen atoms prior to C<sub>2</sub>H<sub>4</sub> loss. These ions therefore eliminate ethylene in which the hydrogen atoms are selected statistically from any four of those of the original ethyl group of i and the two of the isolated methylene group. At first sight, the assumption that the rearrangement  $k \rightarrow l$  occurs for all the ions may appear inconsistent with the earlier conclusion that one-third of the ions generated as h isomerize to kprior to  $C_2H_4$  loss, and that this fraction of the ions do not revert to l. However, it is plausible that the transition state for isomerization of k and l is not rigidly defined and that a range of geometries (and hence heats of formation) are possible. This situation would permit a lower transition state energy for decomposing ions of structure k to isomerize to l than that for isomerization of decomposing ions of structure l to k. The reason for such behaviour could be that  $C_2H_4$  loss and isomerization pathways are in competition with H<sub>2</sub>O loss, which has a lower activation energy for ions such as h or l. In contrast, ions i and kmust undergo rearrangement to l, n or related structures, before H<sub>2</sub>O loss can occur. Therefore, starting from *i*, competition occurs initially between  $C_2H_4$  loss from structure k and rearrangement;  $C_2H_4$  loss via this mechanism does not occur to a great extent, as evidenced by <sup>2</sup>H labelling. Hence, isomerization of kto l is favoured for energetic reasons; once rearrangement has taken place, decomposition may then occur faster than reversion to k. On the other hand, starting from h, H<sub>2</sub>O loss competes with C<sub>2</sub>H<sub>4</sub> loss and rearrangement to k, via l; since  $H_2O$  loss is the process with the lowest activation energy, only the higher energy ions will undergo rearrangement to k or l, or eliminate C<sub>2</sub>H<sub>4</sub>. Of those ions which eventually undergo  $C_2H_4$  loss after rearrangement, reversion from k to l is now less probable than dissociation. Therefore, these ions decompose via  $C_2H_4$  loss from structure k because, unlike the ions originally generated as i, they all have enough energy to eliminate  $C_2H_4$ . It is particularly significant that the above proposal is in accord with the slightly larger kinetic energy release associated with  $C_2H_4$  loss starting from h compared with that starting from i (see above).

It is noteworthy that the above model demands a preference for elimination of the carbon atoms of the original ethyl group of *i*. The calculated and observed decompositions of a  $^{13}$ C labelled analogue of *i* are

Table 6. Calculated and observed ethylene losses from a  ${}^{13}C$ labelled ion of structure i

		Neutral lo	ist	
lon	M	odelª	Obs	erved <sup>b</sup>
structure	C₂H₄	C <sup>13</sup> CH₄	C₂H₄	C <sup>13</sup> CH₄
¹³CH₂ <del></del> <sup></sup> ÓCH₂CH₃	67	33	74	26

<sup>a</sup> For model see text.

<sup>b</sup> Abundances measured by metastable peak area and normalized to a total metastable ion current (1st FFR) of 100 units due to loss of ethylene.

given in Table 6 and are in accord with the requirement of the model.

Our overall conclusion is that dissociation of either h or i is very finely balanced with isomerization to the other structure (or related structures accessible to the other isomer). The reason for this balance may be seen from Fig. 2; addition of ethylene to protonated formaldehyde is exothermic to form either the open chain carbonium ion l or the complex k. Hence, for ions with almost enough energy to form CH2=OH and  $CH_2 = CH_2$ , interconversion of k to l may occur by allowing the CH<sub>2</sub>=OH and CH<sub>2</sub>=CH<sub>2</sub> fragments to separate partially and then recombine in the other arrangement. This is in contrast to the situation which prevails for the corresponding nitrogen analogues, where rearrangement of the complex g to the open chain carbonium ion d is energetically less favourable than dissociation to  $CH_2 = NH_2$  and  $CH_2 = CH_2$ . Consequently, a and b decompose over separate potential

# EXPERIMENTAL

energy profiles.

All mass spectra were obtained using either an AEI MS 902 or MS 9 double focusing mass spectrometer operating at a source pressure of c.  $10^{-6}$  Torr with a nominal electron beam energy of 70 eV and an accelerating voltage of 8 kV. The samples were introduced into the instruments through the heated inlet systems. The kinetic energy release values were derived from 2nd FFR metastable peaks; no correction was applied for the width of the main beam. The appearance potentials were determined on ions undergoing the reaction of interest in the 1st FFR. These ions were observed by reducing the electric sector voltage at constant accelerating voltage and magnetic field strength.<sup>27</sup> The internal calibrant employed was either argon or isopropyl chloride and the results were evaluated using the semi-log plot method.<sup>28</sup>

The ions of interest were generated by ionization and fragmentation of suitable alcohols, ethers and acetals. Decompositions occurring in the 1st FFR were observed by reducing the electric sector voltage at constant accelerating voltage and magnetic field strength.29

All unlabelled compounds were commercially available; specifically labelled compounds were synthesized by the routes given below:

 $(CH_{3}CH_{2})_{2}C=O \xrightarrow{D_{2}O} (CH_{3}CD_{2})_{2}C=O \xrightarrow{LiAlH_{4}} (CH_{3}CD_{2})_{2}CHOH$  $(CH_{3}CH_{2})_{2}C=O \xrightarrow{\text{LiAlD}_{4}} (CH_{3}CH_{2})_{2}CDOH$  $(CH_3CD_2)_2C=O \xrightarrow{\text{LiAID}_4} (CH_3CD_2)_2CDOH$  $CD_{3}OH \xrightarrow{I_{2}, Red} CD_{3}I \xrightarrow{(i) Mg} CD_{3}CH_{2}CH_{2}OH$  $ClCH_2CH_2CO_2Et \xrightarrow{LiAlD_4} ClCH_2CH_2CD_2OH \xrightarrow{1^-aq} ICH_2CH_2CD_2OH$  $Ba^{13}CO_3 \xrightarrow{H^+} {}^{13}CO_2 \xrightarrow{CH_3CH_2MgBr} CH_3CH_2{}^{13}CO_2H \xrightarrow{(i)} RCO_2H \xrightarrow{(i)} RCO_2H CH_3CH_2{}^{13}CH_2OH$  $CH_3CH_2^{13}CH_2OH \xrightarrow{NaH} CH_3CH_2^{13}CH_2OCH_2CH_3$  $\begin{array}{c} \mathrm{CH_3^{13}CO_2^{-Na}}^+_{a} \xrightarrow[(ii)]{(iii)} \mathrm{RCOCI}\\_{(iii)} \mathrm{LiAIH_4}\end{array} \xrightarrow[(iii)]{(iii)} \mathrm{CH_3^{13}CH_2OH} \xrightarrow[(iii)]{(ii)} \mathrm{PBr_3}\\_{(iii)} \mathrm{Mg}\\_{(iii)} \mathrm{CH_3^{13}CH_2CH(CH_3)OH}\end{array}$ 

All O-deuterated compounds were prepared in situ by exchange of the corresponding O-H compound in the all glass heated inlet system.

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