The Collisionally Induced Dissociation of Allyl and 2-Propenyl Cations

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Pure $[CH_2CHCH_2]^+$ and $CH_3\dot{C}==CH_2$ ions are generated only in *metastable* fragmentations of $[CH_2==CHCH_2X]^+$, X = CI, Br, I, and $[CH_3CX==CH_2]^+$, X = Br, I, respectively. For ion source generated $[C_3H_5]^+$ ions there is some structural interconversion. The structure characteristic feature of their collisional activation mass spectra is the ratio m/z 27 ($[C_2H_3]^+$): m/z 26 ($[C_2H_2]^+$). For $CH_3\dot{C}==CH_2$ the ratio is only weakly dependent upon the translational energy of the ion. For $[CH_2CHCH_2]^+$ ions generated by charge reversal of $[CH_2CHCH_2]^-$ show higher ratios, resulting from their lower average internal energy content. It must therefore be emphasized that $[C_3H_5]^+$ ion structure assignments should only be made using reference data which apply to specific experimental conditions. $[C_3H_5]^+$ daughter ion structures for a number of well-known fragmentations have been established. The heat of formation of the 2-propenyl cation was measured to be 969±5 kJ mol⁻¹. Labelling experiments show that at *low* internal energies, allyl cations do not undergo atom randomization in *c*. $1-2 \mu$ s; *high* internal energy ions of longer lifetime (*c*. 8 μ s) show complete atom randomization. H⁺ atom loss from $[^{13}CH_2CHCH_2]^{++}$ has been shown to generate

INTRODUCTION

Experimental observations have shown that two $[C_3H_5]^+$ ion structures exist as stable species in the gas phase: the allyl cation and the 2-propendic ation.¹⁻⁴ Their heats of formation, ΔH_t^0 , have also been measured: $\Delta H_t^0[CH_2CHCH_2]^+) = 945$ kJ mol⁻¹⁵ and $\Delta H_t^0(CH_3C=CH_2) = 962 \text{ kJ mol}^{-1.3}$ The most recent *ab initio* calculations,⁶ which include electron correlation effects, give a difference of 48.5 kJ mol^{-1} for the above enthalpies, in only fair agreement with the experimentally derived 17 kJ mol⁻¹. The same work⁶ shows the 1-propenyl cation to be barely stable with respect to the 2-propenyl cation. The two stable species may be identified by means of their collisional activation (CA) mass spectra but this is an insensitive method because the structure characteristic peak intensity ratio, $m/z \ 27 : m/z \ 26 \ ([C_2H_3]^+ : [C_2H_2]^+),$ changes only from 0.83 ($[allyl]^+$) to 0.46 ([2propenyl]⁺) at 8 kV ion translational energy³ and from 1.0 to 0.4 at 3 kV². However, no convincing data has yet been presented to show that the CA spectra are derived from pure [CH₂CHCH₂]⁺ and CH₃C=CH₂ ions, it having been assumed that simple bond cleavages (e.g. loss of halogen) generate a single species in the ion source. In support of these assignments it has been argued that the high barrier to their interconversion, predicted theoretically⁷ to be c. 142 kJ mol^{-1} above the allyl cation, precludes their interconversion prior to the collision process. However, it should be noted that the fragmentation of lowest energy requirement yielding [cyclopropenium]⁺ + H_2 , lies a further 144 kJ^8 above the calculated barrier to interconversion and so assertions as to the structural 'purity' of ion source generated species should be viewed with caution.

The chief purpose of this paper is to examine in detail the above assumption and to investigate the effect of ion translational energy on the CA characteristics of the allyl and 2-propenyl cations.

RESULTS AND DISCUSSION

It was noted by Bowers *et al.*³ that the m/z 27 : m/z 26 ratio for ion source generated $[C_3H_5]^+$ ions from allyl bromide showed some variation with the energy of the ionizing electrons, but no details were presented. It was proposed that the observations resulted from some cogeneration of CH_3C — CH_2 at high electron energies.

In the present work, we have investigated the CA mass spectra of $[C_3H_5]^+$ ions generated in the ion source and in the first field free region (see Experimental) from a wide variety of precursor molecules.

[CH₂CHCH₂]⁺ ions

The metastable peak for the reaction $[ICH_2CH==CH_2]^+$. $\rightarrow [CH_2CHCH_2]^+ + I'$ is intense and very narrow; the kinetic energy release measured from the peakwidth at half-height $(T_{0.5})$ was $\leq 0.2 \text{ meV}$. The appearance energy (AE) for the metastable peak was $9.9 \pm 0.1 \text{ eV}$. Using $\Delta H_f^0(CH_2==CHCH_2I) =$ $91.5 \text{ kJ mol}^{-1.9}$ and $\Delta H_f^0(I) = 107 \text{ kJ mol}^{-1.10}$ yields $\Delta H_f^0([C_3H_5]^+) = 940 \text{ kJ mol}^{-1}$, the same as for [allyl]⁺,

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within experimental error. Thus, it is highly unlikely that metastably generated $[C_3H_5]^+$ ions, i.e. those of low internal energy, from allyl iodide have other than the $[CH_2CHCH_2]^+$ structure. We therefore propose that the CA mass spectrum of these ions is that for pure $[CH_2CHCH_2]^+$ having 2 kV translational energy. The low translational energy for these metastably generated ions results from the large mass change, m/z 168 $\rightarrow m/z$ 41. The structure-characteristic feature of the CA mass spectrum, m/z 27: m/z 26 was 1.9; $[C_3H_5]^+$ ions generated in the ion source and having 2 kV translational energy displayed a significantly smaller ratio, 1.5. This ratio increased to 1.9 at the lowest ionizing electron energy compatible with an acceptable signal-to-noise ratio, showing, in agreement with Bowers et al.,³ that at higher internal energies another $[C_3H_5]^+$ ion structure is generated.

The metastable fragmentations (1)–(3), wherein the ion acceleration voltage was adjusted so that the $[C_3H_5]^+$ ions again had 2 kV translational energy, all gave a m/z 27: m/z 26 ratio of 1.9, showing that the daughter ion is indeed [allyl]⁺.

$$[CH_2 = CH - CH_2X]^+ \xrightarrow{*} [CH_2CHCH_2]^+ + X^{\cdot}(=CI, Br)$$

$$[CH_2 = C(CH_3)_2]^+ \xrightarrow{*} [CH_2 CHCH_2]^+ + CH_3 \quad (2)$$

$$[CH_{3}CH(Br)CH_{3}]^{+} \xrightarrow{-Br} [C_{3}H_{7}]^{*} \xrightarrow{} [CH_{2}CHCH_{2}]^{+} + H_{2}$$
(3)

CH₃C=CH₂ ions

The metastable peak for the loss of Br from 2bromopropene is also very narrow, $T_{0.5} = 2.2$ meV. Its $AE(10.8\pm0.1 \text{ eV})$ leads to $\Delta H_{\rm f}^{0}([C_{3}H_{5}]^{+}) = 973\pm$ 10 kJ mol⁻¹ using $\Delta H_{\rm f}^0$ (CH₃C(Br)=CH₂) = 43.5 kJ $mol^{-1 \ 11}$ and $\Delta H_f^0(Br') = 112 \text{ kJ mol}^{-1 \ 10}$. Furthermore, the AE of the daughter ion measured using energy selected electrons (see Experimental) was $10.72 \pm 0.05 \text{ eV}$, whence $\Delta H_f^{\circ}([C_3H_5]) =$ 966±5 kJ mol⁻¹ in excellent agreement with the value for $\Delta H_f^0(CH_3C=CH_2)$ reported elsewhere.³ Similarly $AE(m/z \ 41)$ from $CH_2 = C(I)CH_3$ was $10.28 \pm 0.05 \text{ eV}$ $(\Delta H_f^0(CH_3 CI = CH_2) = 88 \text{ kJ mol}^{-1})$,¹³ leading to $\Delta H_f^0(CH_3C=CH_2) = 973 \text{ kJ mol}^{-1}$. For these ions, metastably derived, the m/z 27: m/z 26 ratio in their CA mass spectra was 0.54 at 2 kV translational energy. This ratio is therefore proposed to be characteristic of pure [CH₃C=CH₂] ions having the above translational energy. Similarly, metastable fragmentations (4) and (5) also generated $CH_3\dot{C}=CH_2$ ions (again at 2 kV). These fragmentations of $[C_4H_0]^+$ ions generate a common composite metastable peak⁸ which must reflect two reacting configurations rather than cogeneration of two different daughter ions.

$$[CH_{3}CH_{2}CH_{2}CH_{2}CH_{3}]^{+} \xrightarrow{-CH_{3}^{+}} [C_{4}H_{9}]^{+} \xrightarrow{*} CH_{3} \xrightarrow{+} CH_{2} + CH_{4} \quad (4)$$
$$[(CH_{3})_{3}Br]^{+} \xrightarrow{-Br} [C_{4}H_{9}]^{+} \xrightarrow{*} CH_{3} \xrightarrow{+} CH_{2} + CH_{4} \quad (5)$$

For ion source generated species from the above precursor molecules there is little change in the $m/z \ 27 \ m/z \ 26$ ratio but it is displaced slightly but significantly upwards (from 0.54 to 0.62 at 2 kV and from 0.44 to 0.51 at 8 kV translational energy). By lowering the electron energy near to threshold the lower value may be regained. Presumably some rearrangement to [CH₂CHCH₂]⁺ can take place among high energy ions.

Translational energy effects

It was observed that the m/z 27: m/z 26 abundance ratio for [CH₂CHCH₂]⁺ depended markedly on the translational energy of the ions. For example, allyl cations metastably generated from [CH2==C(CH3)2]+ at 5.8 kV (ion source acceleration voltage, 8 kV) gave a ratio of 1.25 to be compared with 1.9 for 2 kV metastable ions (ion source acceleration voltage, 2.7 kV). The complete results of similar experiments for $[CH_2CHCH_2]^+$ and $CH_3C = CH_2$ ions are shown in Fig. 1. In marked contrast to the behaviour of [allyl]⁺, the $CH_3C = CH_2$ ions show very little dependence on collision energy. These results may be explained most simply as follows. High energy collisions impart on average more internal energy to the ions than do lower energy encounters. For $[CH_2CHCH_2]^+$, a postcollision rearrangement is formally required before CH_3 can be lost. This reaction becomes more competitive with the direct CH2 loss at higher internal energies. For CH3C=CH2, no formal rearrangement is required to produce $[C_2H_3]^+$ or $[C_2H_2]^+$ and so there is no marked translational energy dependence. For [allyl]⁺, at higher translational energies, the observed ion lifetimes become shorter; nevertheless the



Figure 1. m/z 27: m/z 26 abundance ratios as a function of $[C_3H_g]^+$ ion translational energy. \triangle : Metastably generated $CH_3C=CH_2$; \bigcirc : metastably generated $[CH_2CHCH_2]^+$; \bigcirc : $[CH_2CHCH_2]^+$ generated by charge reversal of $[CH_2CHCH_2]^-$; \bigcirc : $[C_3H_g]^+$ ions subjected to a second collision 8 μ s after their generation by charge reversal.

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Figure 2. Partial CA mass spectra of $[C_3H_5]^+$ ions. All have 2 kV translational energy. (a) Metastably generated $[CH_2CHCH_2]^+$ from $CH_2=CHCH_2$; (b) ion source generated $[C_3H_6]^+$ ions from $CH_2=CHCH_2$; (c) (b) ions subjected to collision in the first and second field free regions; (d) metastably generated $CH_3C=CH_2$ from $CH_3C=CH_2$.

rearrangement reaction becomes more competitive with CH_2 loss, indicating that kinetic factors play a lesser role than energetics. This is also supported by the observations on metastable and ion source generated $[CH_2CHCH_2]^+$ ions described above, namely, ratios of 1.9 and 1.5 respectively,

An alternative method of observing the behaviour of high internal energy $[CH_2CHCH_2]^+$ ions is to collisionally activate all the ions in the first field free region, select $[C_3H_5]^+$ ions by their mass: charge ratio with the magnet and analyse the $[C_3H_5]^+$ survivors in the second field free region by means of their CA mass spectra. The results are shown in Fig. 2 where it can be seen that rearrangement of $[CH_2CHCH_2]^+$ into its isomer becomes greater with increase of internal energy, E(a) < E(b) < E(c) (see Fig. 2).

Another method for generating allyl cations is by collisionally induced charge reversal of allyl anions. The latter are readily generated by reacting propene with $OH^{-.14}$ Lehman *et al.*¹⁵ have reported such a charge reversal CA mass spectrum and, apart from the absence of doubly charged ions, concluded that the ions were solely $[CH_2CHCH_2]^+$. We repeated these experiments, again as a function of ion translational energy and found the structure characteristic

m/z 27: m/z 26 ratio, at any given translational energy, to be substantially higher than for the $[CH_2CHCH_2]^+$ ions produced by direct dissociative ionization. This is also shown in Fig. 1. The reason for the observed displacement of the [allyl]⁺ CA curve to higher translational energies may well result from the energy required to strip two electrons from the anion(approx. $11 \pm 1 \text{ eV}$, as measured from the displacement of the charge reversed m/z 41 peak from its calculated position¹⁶); i.e. the charge reversed ions have lower internal energies than their cation counterparts having the same translational energies. A similar effect has been observed with $[C_3H_3]^{\pm}$ ions.¹⁷

The CA mass spectra of $[C_3H_5]^+$ ions generated by protonation with H_3O^+ of the three C_3H_4 isomers were examined, for 8 kV translational energy ions. The m/z 27 : m/z 26 ratios were, for propyne, 0.47, for allene, 0.50 and for cyclopropene, 0.79. The former two values show, in agreement with Bowers *et al.*,³ that the predominant species is CH₃C=CH₂. In marked contrast the cyclic compound produces essentially $[CH_2CHCH_2]^+$ ions, presumably via a cyclopropyl cation of short lifetime.

It seems unlikely that pure $[CH_2CHCH_2]^+$ ions can be generated in an ion source other than at minimal

electron energies. It is worth noting that even the CI CH₄ plasma does *not* produce pure allyl cations; Wesdemiotis *et al.*¹⁸ compared such ions with those produced from CH₂==CHCH₂Br under normal dissociative ionization conditions where, as we have shown above, mixed $[C_3H_5]^+$ ions are formed.

Labelled allyl cations

The unimolecular dissociation, $[C_3H_5]^+ \rightarrow [C_3H_3]^+ + H_2$, of deuterium-labelled $[C_3H_5]^+$ ions produced by dissociative ionization, takes place with virtually complete loss of positional identity of the H/D atoms.¹⁹. However, whether this takes place in the ionized precursor molecule and or among the $[C_3H_5]^+$ ions themselves has not been established.

Reaction of $CD_3CH=CH_2$ with OH^- leads cleanly to $[CD_2CHCH_2]^-$. Charge reversal at 2 kV translational energy yields only two intense C_2 fragment ions at m/z 29 (loss of CH_2) and m/z 27 (loss of CD_2) of equal abundance. Values m/z 28 and m/z 26 are only one third of the abundance of the former, showing that methyl loss is relatively unimportant (see also Fig. 1) and that little or no positional mixing of H and D occurs before fragmentation.

At 8 kV, peaks appear at m/z 28 (CH₃⁻ loss) and m/z 26 (CHD₂⁻ loss); only a small increase is observed in m/z 27 relative to m/z 29, showing that little CH₂D is lost (c. 10% of total methyl loss). This result leads us to suggest that allyl cations indeed rearrange into 2-propenyl cations (and not into [CH₃CH=CH]) prior to the loss of a methyl radical, e.g. reaction (6).

$$\xrightarrow{\rightarrow} [CD_2H \xrightarrow{\dot{C}} CH_2]$$

$$[CD_2CHCH_2]^+ \xrightarrow{} [CH_3 \xrightarrow{\dot{C}} CD_2]$$

$$\xrightarrow{\rightarrow} [CH_2D \xrightarrow{} CH \xrightarrow{} CD]$$

$$(6)$$

Also shown in Fig. 1 are the results of double collision experiments on unlabelled allyl anions (charge reversal in first field free region, CA mass spectra of $[C_3H_5]^+$ ions transmitted to the second field free region). The m/z 27 : m/z 26 ratio for such ions is substantially lower than that for either single collision experiments on $[CH_2CHCH_2]^+$ or $[CH_2CHCH_2]^-$. These observations are interpreted as showing that the non-decomposing charge-reversed ions undergo significant rearrangement into [2-propenyl]⁺ and thus, on average, have even higher internal energies than those produced by dissociative ionization in the ion source. This conclusion is supported by the behaviour of [¹³CH₂CHCH₂]⁻, which, on charge reversal followed by CA, show essentially complete loss of positional identity of carbon atoms (Table 1). Thus at these internal energies and ion lifetimes (approx. 8 µs flight time from first to second field free region compared with c. $1-2 \mu s$ from collision cell to electric sector) the loss of carbon-atom positional identity could proceed via a cyclopropyl cation with concomitant H transfers. Some evidence for the existence of [cyclopropyl]⁺ in a potential well comes from the behaviour of cyclopropane, which yields $[C_3H_5]^-$ ions on dissociative electron capture, which in turn on charge reversal yield a CA mass spectrum with a weak peak at m/z 41

Table 1.	Partial CA mass spectra of $[^{13}CC_2H_5]^+$ ions generated by charge reversal of $[^{13}CH_2CHCH_2]^-$ followed by a second
	field-free region collision. Ion transla- tional energy, 8 kV

Abundances	N CH ₂	eutral species lo ¹³ CH ₂ /CH ₃	¹³ CH ₃
Observed Calculated for random loss	31 30	52 52	17 18 27
specific loss	23	50	27

and a new peak at m/z 28, $[C_2H_4]^{+}$. (Relative abundances, 8 kV translational energy of m/z 28, 27, 26, 25 and 24 were 8, 38, 41, 10 and 3, and respectively, compare $[CH_2CHCH_2]^+$: 0, 41, 43, 13 and 3). The presence of the peak at m/z 41 is not conclusive evidence for the finite existence of [cyclopropyl]⁺ because they may be the ring-opened ion, [allyl]⁺. Ab *initio* calculations have indicated that the energy required for [cyclopropyl]⁺ to convert to [allyl]⁺ via the allowed disrotatory process is only 5–10 kJ mol⁻¹,²⁰ for the negative ions the corresponding barrier is c. 100 kJ mol⁻¹.

Mechanisms for the loss of H' from ionized propene

Bowers *et al.*³ reported that loss of H' from ionized propene in the ion source generated a mixture of 65% $[CH_2CHCH_2]^+$ with 35% $CH_3C=CH_2$. We have measured the CA mass spectrum of $[^{13}CC_2H_5]^+$ ions produced by dissociative ionization of $^{13}CH_3CH=CH_2$ (see Table 2). Comparison is made between these observations and those calculated assuming (a) that only allyl cations are produced but with complete positional loss of identity among carbon atoms and (b) that only allyl cations are produced with complete retention of carbon atom position. Note that the observed loss of 15 daltons is higher than that calculated for either (a) or (b). We propose therefore that 2propenyl cations are generated, $CH_3C=^{13}CH_2$. Now the observations can well be reproduced by a mixture

Table 2. Partial CA mains generated [¹³ CH ₃ CH=CH ₂ 8 kV	ss spec by le] ⁺⁻ in	tra of [¹³ (oss of H the ion so	CC ₂ H ₅] ⁺ from urce at
		Neutral species lost	
Abundances	CH₂	¹³ CH ₂ /CH ₃	1 ³ CH ₃
Observed	18	65	17
Calculated ^a	30	52	18
Calculated ^b	23	50	27
Calculated	19	65	12
$(65\%(a) + 35\%CH_{3}\dot{C} = {}^{13}CH_{2})$			
Calculated	17	65	18
(65%(b)+35% CH ₃ Č= ¹³ CH ₂)		
* Accumer only [13CH CHC	1+	o complete r	andomi

^a Assumes only [¹²CH₂CHCH₂]⁺ with complete randomization of carbon atoms.

^b Assumes only [¹³CH₂CHCH₂]⁺ with retention of structure of 65% allyl cations of type (b) with 35% of $CH_3C = {}^{13}CH_2$. Thus 2-propendl cations would appear to be produced from ionized propene thus:

$$[CH_{3}-CH=CH_{2}]^{+}\rightarrow CH_{2}=CH_{3}+H' \quad (7)$$

Furthermore, propene molecular ions do not undergo any skeletal rearrangement prior to H' loss. Note, however, that for the higher energy fragmentation (reaction 8):

$$[CH_{3}CH = CH_{2}]^{+} \rightarrow CH_{3} + CH_{2}CH \qquad (8)$$

[product energies for the H⁻ loss reaction 1188 kJ mol⁻¹ and 1268 kJ mol⁻¹ for the latter process (ΔH_f^0) $(CH_3) = 142 \text{ kJ mol}^{-1};^{10}$ $\Delta H_{\rm f}^0({\rm CH_2CH}) = 1126 \, {\rm kJ}$ mol⁻¹)¹⁰] Harrison and Dymerski²¹ observed some carbon atom mixing prior to dissociation in the ion source.

In conclusion, we strongly urge that before any unequivocal ion structure assignment is made on the basis of CA mass spectra, ions from selected internal energy ranges should be studied together with an evaluation of translational energy effects.

EXPERIMENTAL

CA mass spectra using He as collision gas were recorded using a VG ZAB-2F mass spectrometer as described elsewhere.²² Metastable peak appearance energies were measured as previously described.²³ Daughter ion AE values were obtained using an apparatus comprising an electrostatic electron monochromator with a quadrupole mass analyser and minicomputer data system.²

The production of negative ions and charge reversal experiments were performed as described elsewhere.17

All compounds were of research grade and obtained commercially with the exception of 2-iodopropene which was prepared by the addition of HI to propyne at room temperature in a sealed tube. CD₃CH=CH₂ was prepared by the reaction at -20 °C of CD₃I with CH2CHLi and ¹³CH3CH=CH2 was prepared similarly using ¹³CH₃I. Labelled starting materials were obtained from Merck, Sharp and Dohme (Canada).

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