# **Metastable Ion Studies**

## XII—Molecular and Fragment Ion Structures for Isomeric $C_4H_6O_2$ Acids

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Metastable peak characteristics, ionization and appearance energy data and isotopic labelling experiments have been applied to a study of the fragmentation behaviour of the molecular ions of the isomeric  $C_4H_6O_2$ acids, *cis* and *trans*-crotonic acids, methacrylic acid, butenoic acid and cyclopropane carboxylic acid. Prior to the losses of H<sub>2</sub>O and CH<sub>3</sub>, all the metastable molecular ions rearrange to [*cis*-crotonic acid]<sup>++</sup> ions. Loss of H<sub>2</sub>O, which generates a composite metastable peak, is proposed to yield vinylketene and/or cyclobutenone molecular ions. Detailed mechanisms are presented for the isomerizations of the various molecular ions and for the above fragmentations. Ionized 3-butenoic and cyclopropane carboxylic acids display a major loss of CO from their metastable ions, a minor process in the other isomers. The metastable peaks consist of two components and these are ascribed to the formation of propen-1-ol and allyl alcohol as daughter ions. Some comparative data are presented for the isomeric C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> acids, tiglic acid, angelic acid and senecioic acid.

### INTRODUCTION

It has long been known that fragmentations of many simple ionized olefins are preceded by rearrangements sufficiently extensive to lead to the random statistical loss of labelled and unlabelled groups of carbon and hydrogen atoms, and it has been widely concluded that the molecular ions decompose via a single structure or a mixture of common ions.<sup>1</sup> The more complex isomeric 1,1-di- and tri-alkyl substituted ethylenes have closely similar mass spectra, but in these larger molecules it is believed that the unrearranged molecular ions fragment over different potential surfaces to yield a common daughter ion from which all further reactions proceed.<sup>2,3</sup>

In general (although not invariably) the effect of introducing a heteroatom into such molecules is to reduce the interconvertibility of their molecular ions, thus rendering more certain the identification of ion structures. Mass spectral studies of ethylenes having a single carboxyl substituent are few, although some dibasic ethylenic acids have received detailed attention.<sup>4</sup> The higher homologues of some  $\beta$ , $\gamma$ -unsaturated acids have been investigated<sup>5</sup> as have the methyl esters of some hexenoic acids.<sup>6</sup>

Our interest in the simple unsaturated carboxylic acids was aroused by a brief survey of their normal mass spectra and the complex shapes of the metastable peaks associated with their primary fragmentations. In this paper we report observations on metastable peaks accompanying the losses of  $H_2O$ ,  $CH_3$  and CO from all acids of formula  $C_4H_6O_2$  and we discuss the isomerizations of the molecular ions which precede these fragmentations. The analogous reactions of the corresponding methyl and ethyl esters are discussed elsewhere.<sup>7</sup>

### **RESULTS AND DISCUSSION**

# Normal mass spectra and heats of formation of the molecular ions

The 70 eV mass spectra of cis-crotonic acid (1), transcrotonic acid (2), methacrylic acid (3), 3-butenoic acid (4) and cyclopropane-carboxylic acid (5) are shown in Fig. 1. Compounds 1, 2 and 3 have peaks in common, with similar abundances, except for the high mass component  $[C_2H_5O]^+$  of the m/z 45 doublet, which is absent in 3. (The  $[C_2H_5O]^+$  ion is 27% of m/z 45 intensity in 1, 13% in 2. The ion probably originates from hydroxyl transfer to the carbenium ion centre followed by  $\alpha$ -cleavage. A similar mechanism has been proposed by Cooks et  $al.^{8}$ ) It is possible that these three acids rearrange to a common intermediate prior to fragmentation. 3-Butenoic acid (4) displays an appreciably different spectrum; loss of CO assumes greater importance and losses of H<sub>2</sub>O, OH' and CH<sub>3</sub>' are relatively much less than in acids 1-3. The cyclic isomer (5) produces a characteristic intense  $[M-H]^+$ peak, but the presence of prominent ions at m/z 71, 69, 68 and 58 show that this acid has features in common with its four isomers. As with the crotonic acids, m/z 45 is a doublet, [COOH]<sup>+</sup> and [C<sub>2</sub>H<sub>5</sub>O]<sup>+</sup>.

The ionization energies (I(M)) of the five acids were obtained from their photoelectron (PE) spectra; these



**Figure 1.** The 70 eV mass spectra of (a) *cis*-crotonic acid (1); (b) *trans*-crotonic acid (2); (c) methacrylic acid (3); (d) 3-butenoic acid (4); (e) cyclopropanecarboxylic acid (5).

ionization energies, combined with the estimated heats of formation of the neutral species, are presented in Table 1, where it can be seen that the derived  $\Delta H_f([C_4H_6O_2]^{+\cdot})$  values for 1-4 are closely similar. Thus, no strong thermochemical argument can be presented to support isomerizations between [1]<sup>+-</sup> and [4]<sup>+-</sup>, i.e. because of the absence of any clearly most stable molecular ion.

### Survey of metastable peaks

The relative abundances and shapes of metastable peaks were examined under conditions of good energy

resolution. All such measurements (unless otherwise stated) refer to observations made on fragmentations taking place in the 1st field free region (FFR) of an AEI-GEC MS 902S mass spectrometer.

Metastable peak intensities are shown in Table 2. Note that the ratio  $m^*[M-H_2O]^{++}: m^*[M-CH_3^{-+}]^{++}$  is almost constant for all acids and we suggest that for these fragmentations a common molecular ion structure is involved. Figure 2 shows the (possibly composite) metastable peak for CH<sub>3</sub><sup>-</sup> loss from all isomers, while Fig. 3(a) shows those for loss of H<sub>2</sub>O. The latter are all clearly composite and the derived energy release distribution curves<sup>10</sup> [Fig. 3(b)] indicate that a pair of common components in differing proportions may well be responsible for the observed peak shapes. It should be emphasized that the generation of similar *Gaussian* metastable peaks by a series of fragmenting isomers is not conclusive evidence for the participation of common ion structures.

Loss of H' produces a metastable peak of appreciable intensity in all acids. However, although these peaks have comparable shapes ( $T_{0.5}$  values for 2-5, 260, 235, 200 and 220 meV, respectively) they are sufficiently dissimilar to have little diagnostic value. Metastable peaks for CO<sub>2</sub> loss all were composite, with a weak Gaussian component upon a flat-topped peak ( $T_{0.5}$ (overall)~210 meV).

The metastable peaks for CO loss, especially prominent in 3-butenoic acid (where it is also the fragmentation pathway of lowest energy), were all composite (Fig. 4) but sufficiently different to be characteristic of precursor molecular ion structure.

From the foregoing, it appeared that further examination of three of the primary fragmentations should provide information concerning the isomerization of the molecular ions. Therefore, these three reactions are discussed in detail below.

#### Loss of H<sub>2</sub>O

**Metastable peak shapes.** Figure 3(a) shows the metastable peaks for loss of water from the molecular ions of the acids **1**, **2**, **3** and **5**. The peaks are clearly composite and Fig. 3(b) shows the derived kinetic energy release distributions.<sup>10</sup> We propose that for these processes a common pair of metastable peaks is involved but with different proportions of each component generating the observed signals. In the 2nd FFR, the metastable peaks for the crotonic acids become indistinguishable (Table 3); note that the *trans*and cyclic isomers behave identically. [3-Butenoic acid]<sup>+-</sup> produces a metastable peak similar to that of **2** but in the 2nd FFR its shape is close to that of **3**.

The differences in intensity of the two components can be attributed to internal energy differences among the decomposing precursor ions. This may result from the kinetics of their isomerization reactions rather than from different energy acquisition by the neutral molecules (see below).

It is proposed therefore that all these  $[C_4H_6O_2]^+$ isomers rearrange to *cis*-crotonic acid type molecular ions prior to loss of H<sub>2</sub>O (and CH<sub>3</sub><sup>-</sup>). For methacrylic and 3-butenoic acids the rearrangement is a rate controlling step.



Table 1. Ionization energies ( $eV \pm 0.05$  derived from the He(I) PE spectra) and ionic heats of formation (kcal mol<sup>-1</sup>) of isomeric C<sub>4</sub>H<sub>6</sub>O<sub>2</sub> and C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> carboxylic acids<sup>a</sup>

<sup>a</sup>  $\Delta H_{\rm f}$  neutral isomers was estimated by group additivity (Ref. 9).

Table 2. Metastable peak abundances<sup>4</sup> (% of sum) for the losses of H', H<sub>2</sub>O, CH<sub>3</sub>', CO(*n*) narrow component of the composite metastable peak, CO(b) broad component, and CO<sub>2</sub> from the isomeric  $C_4H_6O_2$  acids

	Daughter ion					
	[M-H] <sup>+</sup>	[M-H <sub>2</sub> O] <sup>++</sup>	[M-CH <sub>3</sub> ] <sup>+</sup>	[MCO] <sub>n</sub> +-	[M-CO] <sub>B</sub> +··	[M-CO <sub>2</sub> ]+'
trans-Crotonic acid	14.5	62	20	3.3	0.0	0.3
Methacrylic acid	41	34	11	9.8	2.3	2.0
3-Butenoic acid	46	1.8	0.6	9.3	41	1.9
Cyclopropane carboxylic acid	63	4.0	1.2	24	7	1.8

<sup>a</sup> The data refer to measurements of peak *heights* at 4000 V accelerating voltage and a main beam width of 4 V.





Figure 2. Metastable peak shape for loss of  $CH_3$  from the  $[C_4H_6O_2]^{+}$  isomers.

CH=CO]<sup>+-</sup> is a plausible mechanism. A 1,4 elimination has been shown to occur in aliphatic alcohols<sup>11</sup> and for CH<sub>3</sub>OH loss from *cis*- and *trans*-methylcrotonate.<sup>12</sup> Loss of water from crotylalcohol and ammonia from crotylamide probably occur analogously. The metastable peaks for the last four reactions are all of Gaussian shape with small kinetic energy releases ( $T_{0.5}$  are 27, 27, 30 and 31 meV, respectively). Thus, these are similar to the *narrow* component for the loss of H<sub>2</sub>O from the acids. We suggest that the reaction shown below (Scheme 1), in which methyl hydrogen is





Figure 3(a). Metastable peak shapes for loss of  $H_2O$  from the molecular ions of (a) *cis*-crotonic acid, (b) *trans*-crotonic acid and (c) methacrylic acid.



Figure 3(b). Distributions of released energies from the met-, astable peaks shown in Fig. 3(a).



Figure 4. Metastable peak shapes for the loss of  $CH_3^{-}$  from the molecular ions of (a) senecioic acid and (b) tiglic acid.

transferred to hydroxyl oxygen, generates the Gaussian shaped component of the composite metastable peak.

# Energetic considerations and the structure of the $[C_4H_4O]^+$ daughter ion

The appearance energy  $A([F]^+)$  of the  $[C_4H_4O]^{+\cdot}$  ion derived from *trans*-methylcrotonate could not be determined accurately (the ionization efficiency curve for  $[C_4H_4O]^{+\cdot}$  became asymptotic to the eV axis about 0.2 V above the ionization energy of the ester) and so only an *upper limit* of 208 kcal mol<sup>-1</sup> can be placed on its heat of formation. Loss of  $C_2H_4$  from the molecular ion of 2-cyclohexen-1-one yields an intense peak at m/z 68  $[C_4H_4O]^{+\cdot}$ . These ions may well have the vinylketene structure, i.e. on the reasonable assumption that the retro Diels-Alder reaction predominates (Scheme 2).



The thermochemistry for the above process is as follows: I(M), 2-cyclohexen-1-one =  $9.23 \pm 0.05 \text{ eV}$ (PE spectrum);  $I(M) - A([F]^+)$ ,  $[C_4H_4O]^+ = 0.80 \pm$ 0.05 eV (energy selected electrons);  $\Delta H_f(C_6H_8O) =$  $-24.5 \pm 1 \text{ kcal mol}^{-1}$  (estimated from  $\Delta H_{\rm f}$  (cyclohexane) =  $-29.4 \text{ kcal mol}^{-1}$ ;  $\Delta H_{\rm f}$  (cyclohexene) =  $-0.84 \text{ kcal mol}^{-1}$ and  $\Delta H_{\rm f}({\rm cyclohexanone}) =$ -53.1 kcal mol<sup>-1</sup>);<sup>13</sup> alternatively from group additivities<sup>9</sup> and using a 'ring-correction' term of +4.8 kcal mol<sup>-1</sup>,  $\Delta H_f$  (2-cyclohexen-1-one) = -25.1 kcal mol<sup>-1</sup>. From these data  $\Delta H_f([CH_2CHCHCO]^+) =$  $194 \pm 2 \text{ kcal mol}^{-1}$ . (This value is close to that obtained from the direct ionization of thermally generated vinylketene,<sup>14</sup> 192 kcal mol<sup>-1</sup>.) However,  $\Delta H_{f}([C_{4}H_{4}O]^{+})$  ions generated from trans-crotonic acid is significantly higher, 219 kcal mol<sup>-1</sup>. [I(M) =10.08 eV (PE spectrum;  $\Delta H_f$  (trans-crotonic acid) = -87 kcal mol<sup>-1</sup>;  $I(M) - A([F]^+)$  (energy selected electrons = 0.7 eV (10.78 - 10.08 eV)].

It does not follow that ketene-type ions are not being generated at the observed threshold for  $[C_4H_4O]^+$  from *trans*-crotonic acid. If the reaction shown in Scheme 1 produces the narrow (Gaussian) component of the metastable peak (as proposed above) then the *majority* of the ions detected at low internal energies, near to threshold, will be associated with the *broad* component (see Fig. 3).

Loss of  $H_2O$  from [cis-crotonic acid]<sup>++</sup> ions; mechanism 2. It is now necessary to consider the reaction giving rise to the broad component. Two mechanistic possibilities may be envisaged, apart from a 1,2 elimination which can be discounted; 3-butenoic acid isomerizes prior to water loss—which in any case is a minor fragmentation pathway (see Tables 2 and 3). One involves the transfer of a methyl hydrogen atom to carbonyl oxygen yielding a stable intermediate, b',



Scheme 3

(cf. the recent observations of Benoit *et al.*<sup>15</sup>). Note that interconversion of *b* and b' via a 1,3(hydroxyl $\rightarrow$  carbonyl) hydrogen shift is considered an unfavourable process—as has been shown clearly in studies of the molecular ion of benzoic acid.<sup>16,17</sup> A second possibility is a 1,3 elimination of water from a *trans* molecular ion, i.e.



This latter seems unlikely, however, because: (1) 3,3-dimethylacrylic acid (in which both  $\beta$ -vinylic hydrogen atoms have been substituted by a methyl group) still shows a clearly composite metastable peak for the abundant loss of H<sub>2</sub>O, as do all other isomeric C<sub>5</sub> acids in which a 1,4 elimination is feasible, i.e. acids 6, 7, 8, 11, 13 (see Table 1). In marked contrast noncomposite narrow Gaussian metastable peaks are observed for the remaining  $C_5$  acids (9, 10, 12, Table 1). (2) a 1,3-elimination in crotonic acid type ions is most easily envisaged as being followed by ring closure to yield the molecular ion of methyl cyclopropenone (Scheme 4). Energetic and kinetic considerations invalidate this mechanism. From the PE ionization energy = 9.15  $\pm$  0.05 eV, (see also Ref. 18) and  $\Delta H_{\rm f}$ neutral (estimated with the group additivity data of Ref. 9)  $\approx$  29 kcal mol<sup>-1</sup>. [Methyl cyclopropenone]<sup>+-</sup> has an estimated heat of formation of 240 kcal, i.e.  $\sim 0.9 \,\mathrm{eV}$  higher than the observed threshold for generation of  $[C_4H_4O]^+$  ions from the acids. The threshold for this 1,3 elimination must be even higher than 11.7 eV since an appreciable reverse activation energy is involved. Since the 1,3 elimination undoubtedly (also) has a less favourable entropy of activation than the 1,4 elimination shown in Scheme 1, we suggest that [methyl cyclopropenone]<sup>+</sup> ions are not generated in the metastable time frame.

With regard to the species b', shown in Scheme 3—in which methyl hydrogen was shown as being transferred to *carbonyl* oxygen (cf. b, Scheme 1)—it is now necessary to consider daughter ion structures derived therefrom.

Ionized furan,  $\Delta H_f = 197 \text{ kcal mol}^{-1}$ ,<sup>13</sup> although one of the most stable [C<sub>4</sub>H<sub>4</sub>O]<sup>+.</sup> ions, is considered an

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Table 3. Kinetic energy releases (meV) for loss of  $H_2O$  and  $CH_3$  from  $[C_4H_6O_2]^+$  ions

	Loss of H <sub>2</sub> O		Loss of CH3	
	T <sub>Q.5</sub> <sup>a</sup>	T <sub>0.2</sub> ª	T <sub>0.5</sub> ª	T <sub>0.2</sub> *
cis-Crotonic acid	100 (145) <sup>ь</sup>	370 (395)	100 (100)	215
trans-Crotonic acid	125 (145)	385 (395)	100 (100)	215
Methacrylic acid	240 (195)	480 (475)	110 (95)	230
3-Butenoic acid	135 (215)	430 (490)	105 (c)	215
Cyclopropane carboxylic acid	135 (145)	400 (395)	105 (c)	225

<sup>a</sup> Kinetic energy releases calculated from the half and 20% height widths of the metastable peaks (see Experimental). <sup>b</sup> Values in parenthesis refer to metastable peaks measured in

the normal mass spectrum.

° Interference from the intense ions at m/z 58.

unlikely product for the following reasons: (1) Generation of  $[furan]^{+\cdot}$  requires a complex rearrangement with an entropy of activation higher than that for  $[viny]ketene]^{+\cdot}$  formation via Scheme 1. This should lead to a *smaller* contribution (relative to *cis*-crotonic acid) of the broad component in the composite metastable peak for loss of H<sub>2</sub>O from methacrylic and 3-butenoic acids, where an initial isomerization is rate controlling. However, the opposite effect is observed (see Table 3). (2) The mass analysed ion kinetic energy and collisional activation spectra of the  $[C_4H_4O]^{+\cdot}$  ions derived from all the acids are quite different from those produced from furan molecular ions. These results are discussed in detail elsewhere.

An explanation which satisfies the energetic data and metastable peak observations and which is consistent with deuterium and <sup>18</sup>O labelling experiments, requires the formation of the molecular ion of either vinylketene, or cyclobutenone from ion b', as shown below (Scheme 5). The first step in this mechanism involves a 1,5-hydrogen transfer to the carbonyl oxygen atom, yielding the highly resonance stabilized intermediate ion b', which is probably more stable than a. If this is followed by ring closure, the reactive gem-diol intermediate c' could lose H<sub>2</sub>O to generate [cyclobutenone]<sup>++</sup>, d'. The large kinetic energy release could then be associated with the transition  $c' \rightarrow d'$ .



It is also feasible that the loss of  $H_2O$  from c' is accompanied by ring opening yielding ion d which is that produced via Scheme 1. Loss of  $H_2O$  from metastable molecular ions will preferentially occur via Scheme 5 provided that the  $a \rightleftharpoons b'$  equilibrium lies largely to the right. The relative abundances of the narrow and broad components in the composite metastable peaks for water loss from the various ionized acids (cis-crotonic acid < trans-crotonic acid = cyclopropane carboxylic acid<3-butenoic acid<methacrylic acid) can then be explained by assuming that the preceding isomerizations of the molecular ions of the acids into ionized cis-crotonic acid (from which structure both H<sub>2</sub>O loss mechanisms are proposed to occur) is slow compared with the rate of decomposition.<sup>19,20</sup> This then, results in a preference for the process associated with the higher frequency factor and activation energy, viz. the broad component of the composite metastable peaks associated with Scheme 5. A higher apparent 'overall' frequency factor can indeed be associated with this rather complicated pathway (Scheme 5) again provided that the equilibrium between a and b' lies largely to the right for ions fragmenting in the metastable time frame. At higher internal energies the ratio a/b' will depend more strongly on the frequency factors for the forward and reverse reaction; this can shift the equilibrium to the left and thus favour pathway I by increasing the fraction of crotonic acid molecular ions.

### Labelling experiments

Loss of water from the [OD] labelled acids was examined. They were produced by  $D_2O$  exchange in the mass spectrometer inlet system. The results are presented in Table 4. It is seen that the reaction is accompanied by appreciable hydrogen exchange which increases at long ion lifetimes. No further change was observed in going from the 1st to the 2nd FFR.

A detailed interpretation of these results is not possible because acids specifically labelled at other positions were not studied. Furthermore, the results for methacrylic acid indicate that an isotope effect possibly cannot be neglected. However, it seems plausible that the hydrogen exchange accompanying the metastable loss of water from both crotonic acids and cyclopropane carboxylic acid occurs predominantly by exchange of the hydroxylic deuterium atom with the methyl hydrogen atoms in molecular ions having the cis-crotonic acid structure. This is because a small isotope effect for loss of H<sub>2</sub>O (as observed in methacrylic acid) will reduce the observed ratio for loss of  $H_2O$  vs HDO to  $\sim 1$  and also because the metastable peak abundance ratio for loss of  $CH_3'/CH_2D'(0.38\pm0.02)$  (for which an appreciable isotope effect is unlikely) is in excellent agreement

Table 4. Loss of  $H_2O/HDO$  from OD labelled  $[C_4H_6O_2]^+$  acid ions<sup>4</sup>

	/[M-H <sub>2</sub> O] <sup>+-</sup> //[M-HDO] <sup>+-</sup>			
	Normal mass spectrum <sup>5</sup>	Metastable peaks		
cis-Crotonic acid	0.55	1.55		
trans-Crotonic acid	0.9	1.5		
Cyclopropane carboxylic	acid 0.95	1.5		
3-Butenoic acid	2.5			
Methacrylic acid	2.0	2.5		

<sup>a</sup> Statistical ratios calculated for complete hydrogen scrambling are:  $H_5D=2.0$ ;  $H_4D=1.5$ ;  $H_3D=1.0$ ;  $H_2D=0.5$ .

<sup>b</sup> Assuming that no isotope effect is involved in the loss of OH vs OD.

with the calculated value for equilibration among four atoms (0.33 for 3H, 1D). Another important observation is that no differences could be observed in the relative proportion of the two components in the composite metastable peaks for loss of  $H_2O$  and HDO. This agrees with the proposal that a *methyl* hydrogen atom participates in both water loss mechanisms.

Considering the role of the oxygen atoms in the proposed mechanisms it is expected that the two oxygen atoms will become equivalent in Scheme 5 which is responsible for the major fraction of the metastably fragmenting ions. Indeed, complete equilibration of the oxygen atoms appears to occur prior to the loss of water. This was inferred from the metastable peak characteristics of [ethyl crotonate]<sup>+</sup> and [ethyl methacrylate]<sup>+</sup> fully labelled with deuterium in the ethyl group and having <sup>18</sup>O in the carbonyl group. Both esters showed exclusive loss of C<sub>2</sub>D<sub>4</sub>, yielding ions having the structure of the corresponding parent acids. This is shown by the characteristic metastable peak shapes for their loss of water. By analogy with the arguments<sup>16,17</sup> for the similarly labelled ethyl ester of benzoic acid, it can be argued that these acid type ions have the deuterium atom attached to the original carbonyl <sup>18</sup>O, i.e.



Measurement of the heights of the metastable peaks corresponding to the loss of  $H_2^{16}O$ ,  $HD^{16}O$ ,  $H_2^{18}O$  and  $HD^{18}O$  from methacrylic acid type ions yielded the ratio

$$\frac{I[\text{H}_2^{16}\text{O}] + I[\text{HD}^{16}\text{O}]}{I[\text{H}_2^{18}\text{O}] + I[\text{HD}^{18}\text{O}]} = 1.2 \pm 0.1$$

This value is close to that calculated for complete oxygen equilibration (1.08, assuming triangular shapes for the metastable peaks with normal effects of the various isotopic masses on peak widths). Moreover, no change in the relative proportion of the two components could be detected in the composite metastable peaks associated with the above four losses. The data for crotonic acid type ions generated from the labelled ethyl ester lead to the same conclusion.

Additional supporting evidence for the origins and structures of the  $[C_4H_4O]^+$  ions discussed above has come from a detailed study of isomeric  $[C_4H_4O]^+$  ions which is described elsewhere.<sup>14</sup>

### Loss of CH<sub>3</sub>

The metastable peak abundance ratios (Table 2) for the various acids indicate that the losses of  $H_2O$  and  $CH_3$  occur via a common ion structure. The mechanisms for water loss described above involved crotonic acid ions as intermediates and we propose that methyl loss involves the same species. However, this fragmentation also generates a composite metastable peak (Fig. 2) and so two mechanisms are again required. Both pathways may involve ring closures via attack at the  $\beta$ -carbon atom by (i) the hydroxyl group and (ii) the carbonyl group. (i) can be associated with the narrow component of the metastable peak by analogy with the behaviour of but-2-ene-1-ol; loss of CH<sub>3</sub><sup>•</sup> from this compound produces an intense Gaussian metastable peak,  $T_{0.5} = 30 \text{ meV}$ . (ii) may then be associated with a resonance stabilized product ion and the *broad* component of the metastable peak, as illustrated below (Scheme 6). In this context it is useful to



consider the effect of methyl substitution at doubly bonded carbon from the behaviour of the two isomeric  $C_5$  acids, both of which display an intense metastable peak for loss of CH<sub>3</sub><sup>•</sup> (see Fig. 4) and also for H<sub>2</sub>O loss (not illustrated). The methyl loss metastable peaks



are significantly different and very probably involve the production of different daughter ions (viz.  $[M-CH_3]^+$  from senecioic acid generates a strong metastable peak for loss of C<sub>2</sub>H<sub>2</sub>O; tiglic acid has none, but instead specifically shows a metastable peak for loss of CO). Further, the geometric isomer of tiglic acid, angelic acid, has the same mass spectral characteristics as tiglic acid. The larger kinetic energy release for  $[M-CH_3]^+$  ion formation for senecioic acid can be rationalized by the carbonyl attack mechanism described above for the C<sub>4</sub> acids. For senecioic acid the



activated complex (s) would be less stable than that for tiglic acid (t), whereas the difference in product ion stabilities would be much smaller. (Evidence that the *terminal* CH<sub>3</sub>' group exclusively is lost from tiglic acid has been described.<sup>7</sup>)

Note that in tiglic acid a methyl migration (prior to metastable loss of methyl) analogous to that proposed for methacrylic acid *cannot* be taking place.



Figure 5. Metastable peak shapes for the loss of CO from the molecular ions of (a) methacrylic acid, (b) 3-butenoic acid and (c) cyclopropane-carboxylic acid, (broken line).

#### Loss of CO

The metastable peak shapes for loss of CO are presented in Fig. 5 and the energy release values calculated for the broad and the narrow components in the composite peaks are given in Table 5. It appears that 3-butenoic acid and cyclopropane carboxylic acid have two common components, albeit with strongly differing abundances. On the other hand, *trans*-crotonic acid and methacrylic acid possibly share a different narrow component. The loss of CO from methacrylic acid shows a unique broad component not present in the other acids. This yields evidence that the larger part of the metastable loss of CO from methacrylic acid occurs from the unrearranged molecular ion, i.e. *without* the methyl migration proposed to precede the losses of CH<sub>3</sub><sup>-</sup> and H<sub>2</sub>O.

The  $[C_3H_6O]^+$  product ions generated by loss of CO from the  $[3]^+$ ,  $[4]^+$  and  $[5]^+$  which further fragment by loss of H' may only have the structure of either ionized allyl alcohol  $[CH_2=:CH-CH_2-OH]^+$  or its isomer propen-1-ol  $[CH_3-CH=:CH-OH]^+$ . (The transition m/z [58]<sup>+</sup>  $\rightarrow m/z$  [57]<sup>+</sup> +H' in transcrotonic acid (2) is accompanied by a metastable peak of very low intensity.) This was concluded from the energy released in the metastable loss of H' from the  $[C_3H_6O]^+$  product ions. Distinction can be made between some of the isomeric  $[C_3H_6O]^+$  ions by means of this probe reaction.<sup>21</sup>

However, in agreement with a recent collisional activation study,<sup>22</sup> it is not possible to distinguish between allyl alcohol and propen-1-ol ions. The heat of formation of allyl alcohol molecular ions

Table 5. Kinetic energy release values for loss of CO from  $[C_4H_6O_2]^{+-}$  acid ions

	T <sub>0.5</sub> (meV)		
	Narrow component	Broad component	
trans-Crotonic acid	35	_	
Methacrylic acid	25–35	530	
3-Butenoic acid	10–15	155-170	
Cyclopropane carboxylic acid	13	170	

 $(191 \text{ kcal mol}^{-1})^{13}$  is considerably higher than that estimated for propen-1-ol (159 kcal mol}^{-1}). (From Refs. 13 and 23:

 $\Delta H_{\rm f}([\rm C_2H_4]^{+\cdot}) - \Delta H_{\rm f}([\rm CH_2CHOH]^{+\cdot}) = 70 \text{ kcal mol}^{-1};$ 

$$\Delta H_{f}([CH_{3}CHCHOH]^{+}) \simeq \Delta H_{f}([CH_{3}CHCH_{2}]^{+}) - 70$$
  
= 159 kcal mol<sup>-1</sup>.

Alternatively,

 $\Delta H_{\rm f}([{\rm CH}_{3}{\rm CHCHCH}_{3}]^{+}) = 208 \, \rm kcal \, mol^{-1};$ 

 $\Delta H_{\rm f}([CH_3CHCHOH])^{+-}$ 

$$\simeq \Delta H_{\rm f}([\rm CH_2CHOH]^{+}) - \{\Delta H_{\rm f}([\rm CH_3CHCH_2]^{+})$$

$$\Delta H_{\rm f}([C_4H_8]^{+\cdot}) = 159 \text{ kcal mol}^{-1}.)$$

The upper limit for  $\Delta H_f([C_3H_6O]^{+\cdot})$  from 3-butenoic acid can be estimated to be 185 kcal (from  $\Delta H_f([CH=:CH-CH_2-COOH]^{+\cdot}) = 146.5$  kcal mol<sup>-1</sup>  $\Delta H_f(CO^2) = -26.4$  kcal mol<sup>-1</sup>, and an  $I(M) - A([F]^+)$ difference of  $0.5 \pm 0.05$  eV). Thus propen-1-ol type ions but *not* allylalcohol ions could be generated at threshold if it is assumed that the process of lowest energy is associated with the broad component of the composite metastable peak. The peak shape does not change at low electron energies. Since the generation of other  $[C_3H_6O]^{+\cdot}$  ions<sup>13</sup> which have stabilities comparable with that of ionized propen-1-ol is quite unlikely on mechanistic grounds, it is proposed that the mechanism associated with the broad component for the loss of CO from 3-butenoic acid is as follows (Scheme 7):



The mechanism associated with the (unique) broad component in methacrylic acid may yield propen-1-ol as product ion via a 1,3-hydroxyl transfer and a 1,2hydrogen shift. The common components in the metastable peaks for loss of CO from the molecular ions of 3-butenoic acid and cyclopropane carboxylic acid point to the isomerization of the latter prior to this reaction. The appreciably different intensity ratios of the two components can readily be explained, because the isomerization of  $[5]^+$  into  $[6]^+$  is expected to be slow compared with the rate of decomposition. This is indicated by the fact that the threshold for loss of CO from  $[4]^{+}$  is even lower than the ionic heat of formation of cyclopropane carboxylic acid (see Table 1). This slow isomerization will favour the process associated with a higher frequency factor for which the following mechanism, characterized by the narrow component of the composite metastable peak, is proposed (Scheme 8):



The preceding isomerization  $([5]^+ \rightarrow [4]^+)$  may be expected to reduce the metastable loss of H<sub>2</sub>O and CH<sub>3</sub><sup>·</sup> via  $[4]^+$ . Thus the relatively intense metastable peaks detected for these processes in this compound largely originate from *cis*-crotonic acid type ions which have been generated directly from the molecular ion of 5.

### CONCLUSIONS

In summary it can be stated that the structural integrities of the molecular ions of isomeric  $C_4H_6O_2$  acids are partially retained prior to or during the principal fragmentation routes of low activation energy.

The low energy losses of both  $H_2O$  and  $CH_3^{-}$  occur from ions having the structure of *cis*-crotonic acid. Loss of water generates a composite metastable peak having a narrow (Gaussian) and broad (dished) component. Two mechanisms are proposed. The first, which is associated with the narrow component, involves transfer of methyl hydrogen to hydroxyl oxygen and upon loss of  $H_2O$  produces [vinylketene]<sup>++</sup>. The second, which is deemed responsible for the broad component, involves transfer of methyl hydrogen to carbonyl oxygen yielding a resonance stabilized intermediate ion. Following ring closure, this ion eliminates water to yield either [cyclobutenone]<sup>++</sup> or [vinylketene]<sup>++</sup>.

Loss of CH<sub>3</sub><sup> $\cdot$ </sup> is proposed to occur via attack at the  $\beta$ -carbon atom by the hydroxyl or carbonyl group yielding two different product ions each having a 4-membered ring.

The molecular ion isomerizations in the  $C_4$  acids which produce crotonic acid type ions are proposed to occur as follows: Methacrylic acid—a 1,2 methyl migration together with a 2,1 hydrogen shift. This step is rate controlling with respect to the subsequent metastable loss of H<sub>2</sub>O which involves the larger energy release. 3-Butenoic acid—a 1,3 hydrogen shift or alternatively two consecutive 1,2 hydrogen shifts. This process is, however, of minor importance.

Cyclopropane carboxylic acid-ring opening by  $\alpha$ - $\beta$  bond cleavage, followed by a 1,2 hydrogen shift to the terminal C atom prior to the loss of water and a 1,2 hydrogen shift to the  $\alpha$ -carbon atom prior to the loss of CO.  $\beta$ - $\gamma$  ring cleavage would lead to methacrylic acid type ions but no evidence could be found for this process.

Loss of CO is the most 'prominent' fragmentation at low internal energies for 3-butenoic acid molecular ions; the broad component of the composite metastable peak for this reaction has been ascribed to a mechanism yielding propen-1-ol molecular ions, whereas the generation of ionized allyl alcohol is proposed to be responsible for the narrow component. Loss of CO is unimportant in the ionized crotonic acids at all internal energies, again indicating the difficulty of interconversion with [3-butenoic acid]<sup>+</sup>. The substantial loss of CO from ionized methacrylic acid (which generates a unique metastable peak), clearly indicates that the molecular ions of this acid retain their structural identity in this reaction. The

prominent loss of CO from ionized cyclopropane carboxylic acid is accompanied by a composite metastable peak whose components are the same as those for 3-butenoic acid. The higher intensity of the narrow component from the cyclic isomer is attributed to a slow isomerization into 3-butenoic acid ions in the metastable time frame.

### **EXPERIMENTAL**

The mass spectra were recorded on a GEC-AEI MS 902 S instrument. Samples were introduced via the all-glass heated inlet system (T = 80-110 °C) at an ion source temperature of 80-120 °C. Operating conditions were: ion accelerating voltage 8 kV; trap current 100  $\mu$ A; ionizing energy 60 eV; source pressure  $\sim 1 \times 10^{-6}$  Torr; analyser pressure  $\sim 5 \times 10^{-8}$  Torr. Metastable peaks were recorded on the same instrument by the accelerating voltage scan technique using a narrow energy resolving  $\beta$ -slit (main beam width 2.5 V). Energy release (T) values were calculated in the usual way from the metastable peak width without corrections for the main beam width.

The appearance energies used in this work were measured by Dr F. P. Lossing (National Research Council of Canada, Ottawa) using an electron impact apparatus, comprising an electrostatic electron monochromator, together with a quadrupole mass spectrometer and minicomputer data system. The PE spectra were recorded on a Vacuum Generator instrument model ESCA-2 using 21.22 eV photons and argon as a calibration gas.

The acids 2-7 and 13 (see Table 1) were obtained commercially and used without further purification; cis-crotonic acid (1) (containing 5-10% of the trans isomer) and angelic acid were a gift;  $\alpha$ -ethyl acrylic acid (8) was isolated by careful fractional distillation (spinning band column) under reduced pressure from the mixture of unsaturated acids obtained from thermal decomposition of  $\alpha$ -hydroxy- $\alpha$ -methylbutyric <sup>4</sup> 3-methyl-3-butenoic acid (9) was obtained by acid;<sup>2</sup> carbonation of methallyl Grignard reagent as described by Wagner;<sup>25</sup> 2- and 3-pentenoic acid (10 and 11, trans isomers) were synthesized by the methods of Linstead et al.<sup>26</sup>—the acids were purified by careful fractional distillation (spinning band column) under reduced pressure; 4-pentenoic acid was obtained by decarboxylation of commercially available allylmalonic acid.<sup>27</sup> The purity of all compounds was checked by NMR spectroscopy and analysis in a JEOL-07 GCMS system. The <sup>18</sup>O labelled esters were synthesized on a microscale by converting the purified acid chlorides to <sup>18</sup>O labelled acids with  $H_2^{18}O$  (Prochem, the 90 atom % <sup>18</sup>O) in a small Pyrex tube at room temperature and subsequently adding C2D5OD (Merck Sharp and Dohme, 99.5 atom % D). The esters were isolated from the reaction mixture by preparative GC.

### Acknowledgements

The authors wish to thank Dr F. P. Lossing (National Research Council of Ottawa) for the measurement of the appearance energies in this work and Dr P. C. Burgers for obtaining the photoelectron spectra. They are also indebted to Dr A. F. Thomas (Research Laboratory, Firmenish SA, Geneva) for a gift of angelic acid and to Dr R. J. J. A. Lousberg for a gift of cis-crotonic acid.

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Received 28 June 1978; accepted 24 November 1978

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