The Curie Point Pyrolysis and Electron Impact Induced Decarboxylation of But-3-ynoic Acid and Buta-2,3-dienoic Acid studied by Tandem Mass Spectrometry

Jan W. Dallinga and Nico M. M. Nibbering *
Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands
A. J. Henk Boerboom
FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

It is shown by tandem mass spectrometry that Curie point pyrolysis of but-3-ynoic and buta-2,3-dienoic acid leads to the formation of propyne. This points to a thermodynamically controlled elimination of carbon dioxide which for both acids can be rationalized by a combined 1,4- and 1,2-hydrogen shift of the hydroxylic hydrogen atom. The $C_3H_4^{+\cdot}$ ions, generated upon electron impact induced decarboxylation of the molecular ions of but-3-ynoic and buta-2,3-dienoic acid, have been shown by tandem mass spectrometry to have the allene and propyne structure, respectively. Their formation can be explained by a 1,5-hydrogen shift of the hydroxylic hydrogen atom prior to or during the loss of carbon dioxide from the molecular ions.

Some years ago the flash vacuum pyrolytic decarboxylation of some βγ-acetylenic acids and αβγ-allenic acids was reported.[1,2] The simplest representatives of these groups of compounds, but-3-ynoic acid (I) and buta-2,3-dienoic acid (II), were shown to decarboxylate unimolecularly *via* a 1,5-hydrogen shift of the hydroxylic hydrogen atom to form allene and propyne, respectively. The decarboxylation reactions were suggested to proceed in a concerted fashion.[1,2]

The electron impact (EI) mass spectra of the two compounds (I) and (II) show peaks at *m*/*z* 40 resulting from loss of carbon dioxide from the molecular ions.[3] The mechanism of decarboxylation of the but-3-ynoic acid molecular ion was postulated to involve a six-centre transition state,[3] leading to allene as the product ion and resembling the flash vacuum pyrolysis mechanism.[1] However, neither the structure of this ion nor that of the fragment ion, *m*/*z* 40, generated from ionized buta-2,3-dienoic acid have been established so far. Both ions have now been studied by the collisional activation (CA) method to determine their structures.[4]

Moreover, the availability of a Curie point pyrolysis inlet system on the tandem mass spectrometer used together with a simultaneous ion detection system [5] has enabled us to study by CA the structures of the C_3H_4 species generated upon the short-lasting and low-pressure Curie point pyrolysis of acids (I) and (II).

Results and Discussion

It has recently been shown that the molecular ions of allene and propyne can be distinguished on the basis of their CA spectra.[6] This is confirmed by the CA spectra of these compounds taken with the tandem mass spectrometer used,[5] which have been displayed in Figure 1. As can be seen from Figure 1, the CA spectra of the allene and propyne molecular ions can be distinguished from one another mainly by the difference in intensity of the peak at *m*/*z* 15 which is almost absent in the spectrum of the allene ions. These observations are similar to those reported by Wagner *et al.*[6] Furthermore the doubly charged ions at *m*/*z* 19, 19.5, and 20 show markedly differences for both ions. The CA spectra of the $C_3H_4^{+\cdot}$ ions generated from the molecular ions of but-3-ynoic acid (I) and buta-2,3-dienoic acid (II) by expulsion of carbon dioxide are given in Figure 2. It can be seen that the CA spectrum of the EI induced fragment ion *m*/*z* 40 from (I) clearly matches that of the allene ion, whereas the CA spectrum of the *m*/*z* 40 ion from (II) resembles most that of the propyne ion (*cf.* Figures 1 and 2). Acids (I) and (II) have also been pyrolysed with the Curie point pyrolysis method.[7] The gaseous products formed have then been ionised with low energy electrons (14 eV) to give the so-called pyrolysis mass spectra. These are represented in Figure 3 together with the corresponding 14 eV EI spectra.

$HC{\equiv}CCH_2CO_2H$

(I)

$H_2C{=}C{=}CHCO_2H$

(II)

The intensities of the peaks due to the molecular ions of compounds (I) and (II) in the pyrolysis mass spectra are much lower than those in the EI spectra, showing that the pyrolysis with respect to the evaporation of the acids has been largely successful, though not complete. The ions, *m*/*z* 40, in the pyrolysis mass spectra, predominantly corresponding with the pyrolytically generated C_3H_4 species from acids (I) and (II), have been mass selected and subsequently subjected to CA. The CA spectra obtained are given in Figure 4. These spectra show that both acids yield propyne upon pyrolysis (*cf.* Figures 1 and 4). This result for acid (I) is different from that of the flash vacuum pyrolytic decarboxylation of (I) in the gas phase where allene is obtained exclusively as the product.[1]

Mechanistic Considerations.—(i) *The EI induced* CO_2 *loss from acids* (I) *and* (II). The allene ion formed from ionized (I) and the propyne ion formed from ionized (II) can readily be explained by a 1,5-shift of the hydroxylic hydrogen atom to the terminal carbon atom position with concomitant loss of CO_2 as summarized in Scheme 1. It has been assumed in Scheme 1 that the electron has been removed from the acetylenic and allenic portions of the molecules. This does not seem unreasonable when the ionization energies of a triple bond, a cumulated double bond, and a carboxylic acid group are taken into account (IE of $CH_3C{\equiv}CH$, 10.36; IE of $H_2C{=}C{=}CH_2$, 9.53; IE of CH_3COOH, 10.35 eV [8]). Furthermore, the removal of an electron from the triple and cumulated double bonds will favour the bending of these originally linear groups because of Jahn–Teller distortion. This will enable the

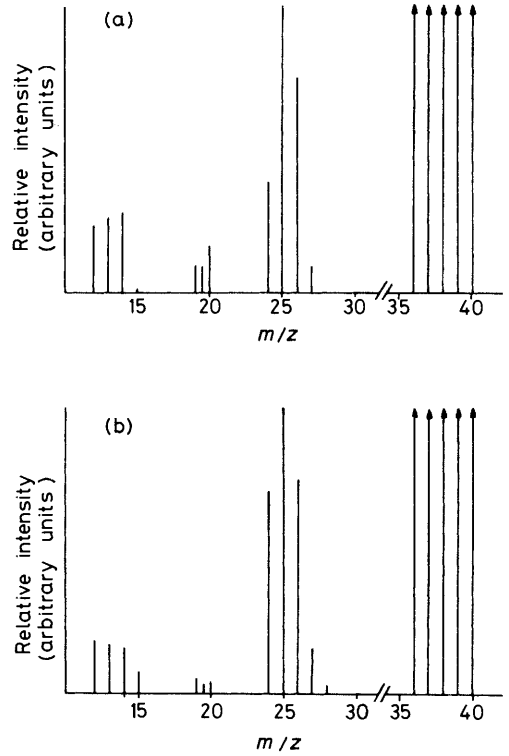


Figure 1. CA spectra of the molecular ions of allene (a) and propyne (b)

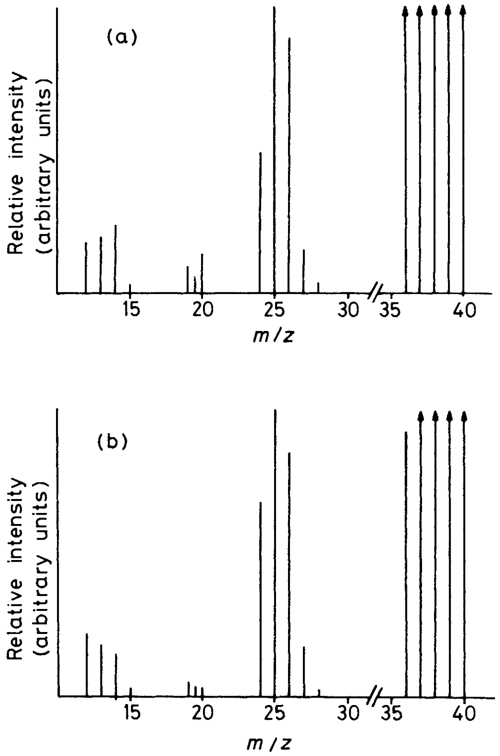


Figure 2. CA spectra of the EI induced fragment ions with *m/z* 40 from but-3-ynoic acid (a) and buta-2,3-dienoic acid (b)

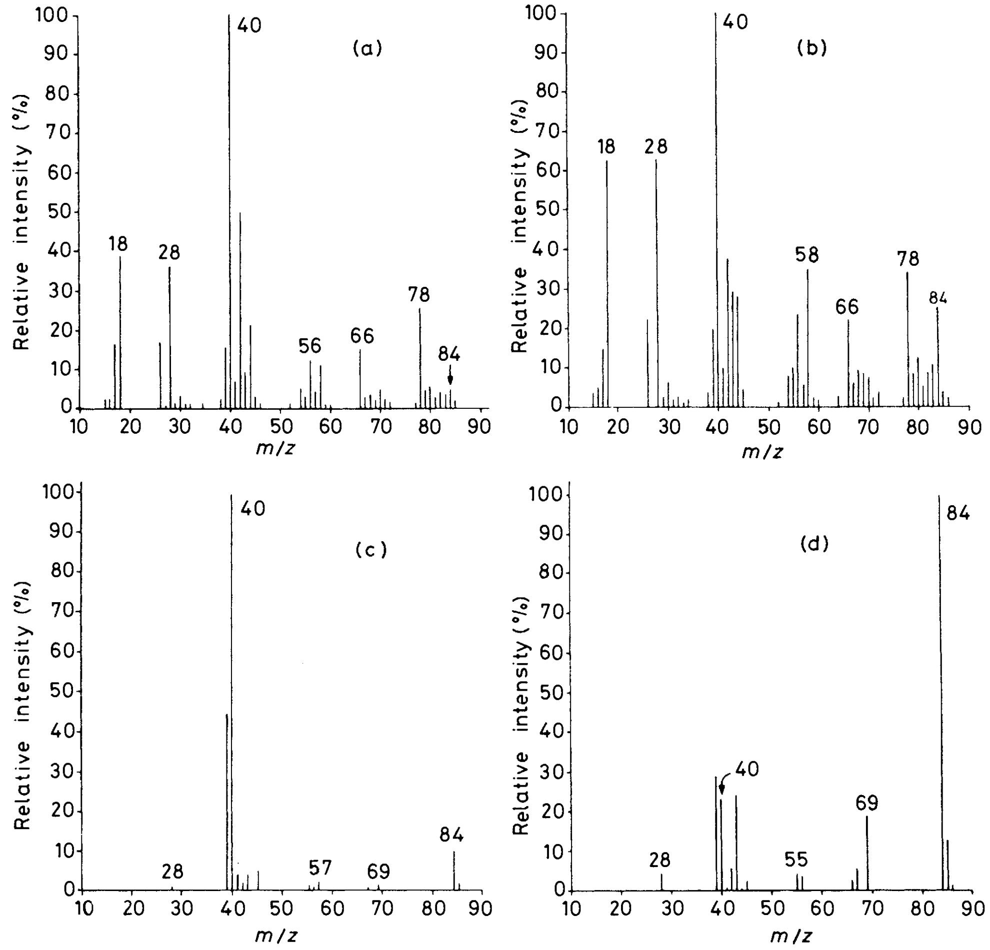


Figure 3. Curie point pyrolysis mass spectra of but-3-ynoic acid (a) and buta-2,3-dienoic acid (b). EI mass spectra (14 eV) of but-3-ynoic acid (c) and buta-2,3-dienoic acid (d)

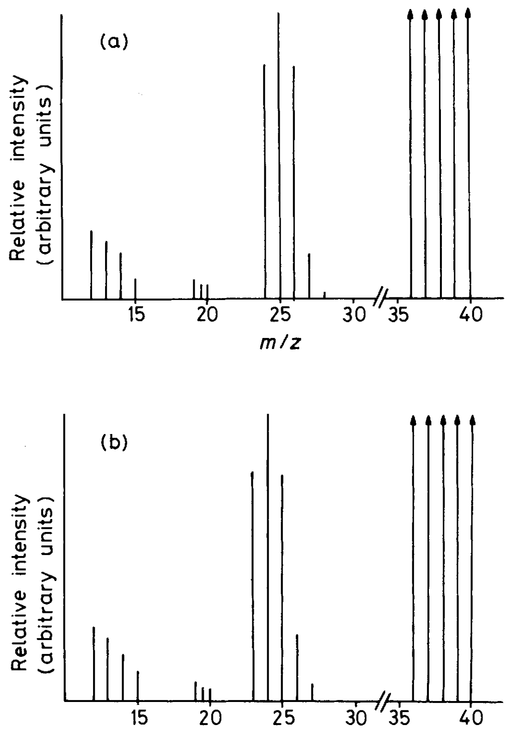
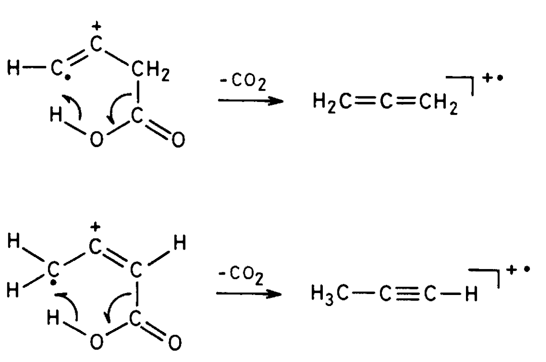
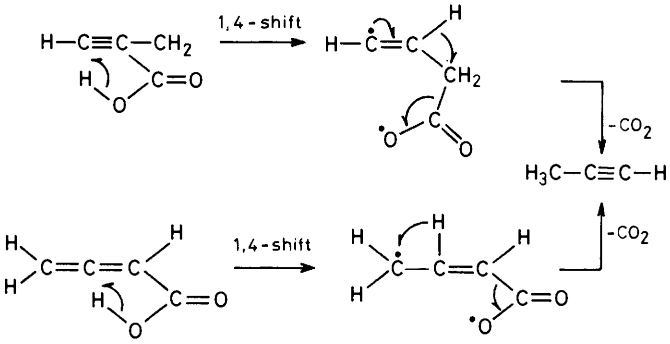


Figure 4. CA spectra of the *m/z* 40 molecular ions from the Curie point pyrolysis mass spectra of but-3-ynoic acid (a) and buta-2,3-dienoic acid (b)



Scheme 1. Rationalization of the CO_2 loss from the molecular ions of acids (I) and (II)



Scheme 2. Rationalization of the Curie point pyrolysis induced CO_2 loss from the acids (I) and (II)

hydroxylic hydrogen atom to come into close proximity of the terminal carbon atom which is required for its 1,5-shift to occur.

(ii) *The pyrolytically induced* CO_2 *loss from acids* (I) *and* (II). As noted in the Introduction, flash vacuum pyrolytic decarboxylation of (I) and (II) in the gas phase yields allene and propyne, respectively.[1,2] Their formation has been proposed to proceed *via* a 1,5-shift of the hydroxylic hydrogen atom with concomitant loss of CO_2.[1,2] This mechanism could also be true for the CO_2 loss from (II) under Curie point pyrolysis conditions to give the observed propyne formation. However, it cannot account for the presently observed propyne formation from (I), where such a mechanism is expected to give allene and not propyne. A possible rearrangement of allene to propyne following the pyrolytically induced decarboxylation is very unlikely as these species have been shown to be distinct stable molecules at relatively high temperatures.[9]

Propyne formation from (I) could be explained by a 1,2-elimination of CO_2 which is known for saturated carboxylic acids,[10] but then it is not clear why such a mechanism is not operative for CO_2 loss from (II).

It should be realized here that the flash vacuum pyrolysis method is based upon a flow system,[1,2] whereas in the Curie point pyrolysis method samples are deposited on a metal surface which is heated in vacuum very fast to pyrolyse the samples.[7] This might explain the difference in results for acid (I) obtained with these methods, notwithstanding the fact that the results for acid (II) are the same for both methods. Incidentally, models of acids (I) and (II) show that the hydroxylic hydrogen atom can come very easily in close proximity of the β-carbon atom, but not the γ-carbon atom because of the linearity of the triple and cumulated double bond system. Taking this into account, the CO_2 loss upon Curie point pyrolysis may occur in two successive steps, transfer of the hydroxylic hydrogen atom (either as a proton or as a hydrogen atom) to the β-carbon atom *via* a 1,4-shift, followed by a thermodynamically controlled 1,2-shift of this hydrogen atom to give propyne which is *ca.* 6.5 kJ mol^{-1} more stable than allene.[8] This mechanism has been summarized in Scheme 2, where the 1,4-shift of the carboxylic hydrogen atom has been assumed to occur *via* a homolytic rather than a heterolytic cleavage of the O–H bond. The latter would eventually result in an energetically unfavourable charge separation.[11]

Conclusions.—The present results show that Curie point pyrolysis, and electron impact induced fragmentations of compounds do not necessarily proceed *via* similar mechanisms nor necessarily lead to species with similar structures, notwithstanding the same elemental composition of some fragments. Similar conclusions have been drawn from a previous Curie point pyrolysis–EI study.[7a]

Experimental

Instruments.—The complete EI mass spectra were obtained with an AEI-MS 902 instrument. Samples were introduced into the ion source (150 °C) *via* the direct insertion probe (25 °C). The complete pyrolysis mass spectra were recorded with a quadrupole mass spectrometer equipped with a Curie point pyrolysis inlet system; details of this instrument and of the Curie point pyrolysis method have been described elswhere.[7] The CA spectra were obtained with a tandem mass spectrometer constructed at the FOM Institute. A detailed description of this instrument has been given by Louter *et al.*[5] Allene and propyne were introduced into the ion source *via* a gas inlet system at room temperature. The carboxylic acids were introduced as concentrated solution in water *via* a septum inlet system (100—120 °C). Ions were generated by electron impact (70 and 14 eV) and accelerated to 6 eV kinetic energy.

The pyrolysis of the acids was performed on line, in high vacuum, by means of a Curie point pyrolysis inlet system to a maximum temperature of 610 °C, reached in 0.1 s.[7] A typical sample amount is 2 μg. The gaseous pyrolysis fragments leaked during 4 s *via* an expansion chamber into the ion source of the tandem instrument. Molecular ions were generated by electron impact (13—14 eV) and accelerated to 6 keV kinetic energy. In the CA experiments the first magnet of the tandem mass spectrometer was set to transmit the ions with m/z 40. Helium was used as the collision gas.

For allene and propyne the helium-pressure in the collision cell was adjusted in such a manner that the total fragment ion current reached a maximum value. This corresponded with a reduction of the precursor ion intensity to *ca.* 20% of its original value. This pressure was used and kept constant during all CA experiments. The post acceleration voltage was set on 15 kV. The mass region, m/z 12—40, was recorded simultaneously and with unit mass resolution.

Materials.—Allene and propyne were commercially available; the acids were prepared using known procedures.[12,13]

Acknowledgement

We thank the Netherlands Organisation for Pure Research (ZWO) for financial support *via* SON and FOM.

References

1 D. B. Bigley and R. H. Weatherhead, *J. Chem. Soc., Perkin Trans. 2*, 1976, 592.

2 D. B. Bigley and R. H. Weatherhead, *J. Chem. Soc., Perkin Trans. 2*, 1976, 704.

3 D. B. Bigley, J. F. J. Todd, and R. H. Weatherhead, *Org. Mass Spectrom.*, 1976, **11**, 352.

4 (*a*) F. W. McLafferty in 'High Performance Mass Spectrometry: Chemical Applications,' ACS Symposium Series, No. 70, ed. M. L. Gross, American Chemical Society, Washington, 1978, p.47; (*b*) R. G. Cooks, 'Collision Spectroscopy,' Plenum Press, New York, 1978; (*c*) K. Levsen and H. Schwarz, *Angew. Chem. Int. Ed. Engl.*, 1976, **15**, 509; (*d*) F. W. McLafferty, A. Hirota, M. P. Barbalas, and R. F. Pegues, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **35**, 299; (*e*) J. W. Dallinga, N. M. M. Nibbering, and G. J. Louter, *Org. Mass Spectrom.*, 1981, **16**, 183.

5 (*a*) G. J. Louter, A. J. H. Boerboom, P. F. M. Stalmeier, H. H. Tuithof, and J. Kistemaker, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **33**, 335; (*b*) G. J. Louter and A. J. H. Boerboom, *Adv. Mass Spectrom.*, 1980, **8B**, 1851; (*c*) H. H. Tuithof, *Int. J. Mass Spectrom. Ion Phys.*, 1977, **23**, 147; (*d*) H. H. Tuithof, A. J. H. Boerboom, P. G. Kistemaker, and H. L. C. Meuzelaar, *Adv. Mass Spectrom.*, 1976, **7B**, 838.

6 W. Wagner, K. Levsen, and C. Lifshitz, *Org. Mass Spectrom.*, 1980, **15**, 271.

7 (*a*) M. A. Posthumus and N. M. M. Nibbering, *Org. Mass Spectrom.*, 1977, **12**, 334; (*b*) J. Haverkamp, W. Eshuis, A. J. H. Boerboom, and P. A. M. Guinée, *Adv. Mass Spectrom.*, 1980, **8A**, 983.

8 H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, 1977, **6**.

9 J. F. Cordes and H. Günzler, *Chem. Ber.*, 1959, **92**, 1055.

10 (*a*) P. G. Blake and K. J. Hole, *J. Chem. Soc. B*, 1966, 577; (*b*) P. G. Blake and G. E. Jackson, *ibid.*, 1968, 1153.

11 F. H. Westheimer and W. A. Jones, *J. Am. Chem. Soc.*, 1941, **63**, 3283.

12 I. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1949, 604.

13 G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 1954, 3197.

Received 8*th June* 1982; *Paper* 2/1025