Structure and Formation of Gaseous $[C_4H_5O]^{\dagger}$ Ions

III—Ions Derived from Unsaturated Ethers

Johan K. Terlouw, Peter C. Burgers and Henk Hommes

Utrecht University, Laboratory for Analytical Chemistry, Croesestraat 77a, 3522 AD Utrecht, The Netherlands

The abundant $[C_4H_5O]^+$ (m/z 69) ions found in the 70 eV mass spectra of a series of acetylenic, allenylic and unsaturated cyclic ethers are shown to have the following structures: $HC\equiv C-\dot{C}H-OCH_3$ (e), $H_2C=C=\dot{C}-OCH_3$ (f), $\dot{O}-CH=\dot{C}H=\dot{C}H-\dot{C}H_2$ (g) and $H-C\equiv C-CH_2-O\dot{C}H_2$ (h). Of these, the cyclic ion g is the most stable: its ion enthalpy (≤ 165 kcal mol⁻¹) is close to that found for the acyclic $C_3H_5\dot{C}=O$ isomers identified in a previous study. Evidence that these four isomeric $[C_4H_5O]^+$ ions are stable species with lifetimes $\geq 10^{-5}$ s is obtained from their collisional activation spectra, the shape of the metastable peaks and the associated kinetic energy release values for the common loss of CO, thermochemical information and analysis of deuterium and carbon-13 labelled precursor molecules. It is further shown that loss of X' from ethers of the type X-C=C-CH_2OCH_3 involves isomerization into energy rich allenyl type ions $[(X)HC=C=CHOCH_3]^+$. These ions undergo loss of X' by simple bond cleavage, yielding e type product ions, when the C-X bond strength is relatively low (X=I, Br). When X=CI and especially CH₃ or H, X' is only lost after rearrangement yielding the cyclic product ion g. The mechanism for this cyclization reaction is related to that proposed in a previous study for the ester \rightarrow acid isomerization in the molecular ions of the esters of α , β -unsaturated carboxylic acids.

INTRODUCTION

In the first paper of this series¹ it was established that a number of non-interconverting isomeric $[C_4H_5O]^+$ ions exist in the gas phase. Of these, the four $C_{2}H_{4}\dot{C}=0$ $H_2C = C(CH_3)^{\dagger}C = O$ isomers, (a), $H_2C=CH-CH_2-C=O$ (b), $CH_3CH=CH-C=O$ (c) and $\triangleright - \dot{C} = O(d)$ were shown from their characteristic collisional activation (CA) spectra to be stable for $\ge 10^{-5}$ s. It was further concluded from the kinetic energy (KE) release values for the spontaneous loss of CO in the metastable time-frame and thermochemical information, that this loss from a and b type ions yields directly the stable $[C_3H_5]^+$ product ions [2propenyl]⁺ and [allyl]⁺, respectively.

The present communication deals with the structure of the intense $[C_4H_5O]^+$ ions observed in the spectra of unsaturated ethers, i.e. acyclic ethers containing one triple or two double bonds and cyclic ethers having one double bond, a class of compounds whose gas phase ion chemistry has not yet been reported.

The strategy used to identify the structure of the ions generated was to combine the information found in the intensity distributions in the CA spectra with the kinetic energy released in the common decompositions of the metastable ions, thermochemical data and additional evidence from the behaviour of specifically deuterium and ¹³C labelled precursor molecules.

It will be shown that four stable $[C_4H_5O]^+$ ether

type ions exist: HC=C--ČH--OCH₃ (e), H₂C=C= Č--OCH₃ (f) the cyclic ion O--CH=-CH--CH₂ (g) and probably also HC=C--CH₂--OCH₂⁺ (h). Evidence will be presented that the cyclic ion g is also generated from the acyclic ether molecular ions via a mechanism related to that proposed earlier for the ester \rightarrow acid isomerization in the molecular ions of methyl esters of unsaturated carboxylic acids.²

RESULTS AND DISCUSSION

General considerations

The ether type precursor molecules used in this study are given in Table 1. It is seen that the $[C_4H_5O]^+$ (m/z 69) ion is of high intensity in all spectra and that it forms the base peak in the spectra of the acetylenic ethers. Ethers of the type R_1 — $C \equiv C$ — OR_2 ($R_1, R_2 =$ alkyl) which could generate ions of the type CH_3 — $C \equiv C$ — OCH_2^+ and $H_2C \equiv C = C^+$ — OCH_3 have not been included because the m/z 69 ion intensity is very low and these compounds decompose readily in the mass spectrometer inlet system to yield ketenes.³

The precursor molecules studied can be divided (see also Table 4) into compounds of the types

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Table 1. Principal fragment ions in the 70 eV mass spectra of some acetylenic, allenylic and unsaturated cyclic ethers

1 HC=CCH(CH_3)OCH_3 69(100) 83(10) 54(7) 53(20) 2 HC=CCH(SCH_3)OCH_3 69(100) 101(27) 85(25) 53(5) 3 HC=CCH(OCH_3)OCH_3 69(100) 99(6) 53(10) 41(5) 39(20) 29(5) 3 HC=CCH(OCH_3)OCH_3 69(100) 99(6) 53(10) 41(5) 39(14) 38(7) 31(6) 29(12) 69(100) 181(10) 54(23) 5 H_2C=C-C-C(I)OCH_3 69(100) 80(10) 81(10) 54(23) 5 H_2C=C-C-CH_2OCH_3 69(100) 117(68) 41(70) 39(100) 38(60) 37(20) 29(30) 69(100) 75(30) 73(20) 69(100) 7 BrC=C-CH_2OCH_3 69(100) 75(30) 73(90) 61(15) 42(45) 41(45) 39(45) 29(30) 9 CH_3C=C-CH_2OCH_3 69(100) 83(5) 53(45) 42(5) 41(20) 39(55) 29(20) 27(15) 14(20) 39(55) 29(20) 27(15) 14(100) 40(30) 39(55) 29(20) 27(15) 14(16)	Compound	m/z (I)
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 H ₂ C=CC(I)OCH ₃	69(100) 196(20) 181(10) 54(23) 53(12) 39(8) 38(7) 26(25)
$ \begin{array}{ccccc} & \text{G}(80) & 196(90) & 165(35) & 41(50) \\ & 39(100) & 38(60) & 37(20) & 29(30) \\ & 7 & \text{BrC} = C - CH_2 \text{OCH}_3 & 69(100) & 119(65) & 117(68) & 41(70) \\ & & 39(95) & 38(55) & 37(20) & 29(10) \\ & 8 & \text{CIC} = C - CH_2 \text{OCH}_3 & 69(100) & 75(30) & 73(90) & 61(15) \\ & & 42(45) & 41(45) & 39(45) & 29(30) \\ & 9 & \text{CH}_3 \text{C} = C - CH_2 \text{OCH}_3 & 69(100) & 83(5) & 53(45) & 42(5) & 41(20) \\ & & 39(55) & 29(5) & 27(10) \\ & 10 & 2,5 - \text{Dihydrofuran}^a & 69(35) & 70(100) & 42(73) & 41(100) \\ & & 40(30) & 39(95) & 29(20) & 27(15) \\ & 11 & (\text{CH}_3)\text{HC} = C - \text{CHOCH}_3 & 69(100) & 84(40) & 55(15) & 53(23) \\ & & 41(50) & 39(65) & 29(20) & 27(25) \\ & 12 & \text{H}_2 \text{C} = \text{CH} - \text{CH} = \text{CHOCH}_3 & 69(100) & 42(30) & 41(40) & 40(20) \\ & & & 39(90) & 38(15) & 29(20) & 27(15) \\ & 14 & \text{H}_2 \text{C} = \text{C} = \text{CHOCH}_3 & 69(100) & 42(30) & 41(40) & 40(20) \\ & & & 39(90) & 38(15) & 29(20) & 27(15) \\ & 14 & \text{H}_2 \text{C} = \text{C} = \text{CHOCH}_2 \text{I} & 69(100) & 165(6) & 55(5) & 41(17) & 40(6) \\ & & & 39(100) & 38(14) & 29(9) \\ & 16 & \text{HC} = \text{C} - \text{CH}_2 \text{OCH}_2 \text{CH}_3 & 69(100) & 83(10) & 55(40) & 43(20) \\ & & & 41(30) & 39(100) & 29(15) & 27(25) \\ & 17 & \text{H}_2 \text{C} = \text{C} = \text{CHOCH}_2 \text{CH}_3 & 69(100) & 84(24) 83(13) 56(28) 55(100) \\ & & & 41(11) & 39(34) & 27(37) \\ & 18 & \text{H}_2 \text{C} - \text{CH} - \text{CH} = \text{CH}_2 & 69(20) & 42(55) & 41(25) & 40(28) \\ & & & & & & & & & & & & & & & & & & $	5 H ₂ C=CC(CH ₃)OCH ₃	69(10) 84(60) 83(24) 54(20) 53(37) 43(100) 41(37) 39(77)
7 $BrC \equiv C - CH_2OCH_3$ $69(100)$ $119(65)$ $117(68)$ $41(70)$ 8 $CIC \equiv C - CH_2OCH_3$ $69(100)$ $75(30)$ $73(90)$ $61(15)$ 9 $CH_3C \equiv C - CH_2OCH_3$ $69(100)$ $83(5)$ $53(45)$ $42(5)$ $41(45)$ 9 $CH_3C \equiv C - CH_2OCH_3$ $69(100)$ $83(5)$ $53(45)$ $42(5)$ $41(20)$ $39(55)$ $29(5)$ $27(10)$ $29(20)$ $27(15)$ $40(30)$ $39(95)$ $29(20)$ $27(15)$ 10 $2,5$ -Dihydrofuran ^a $69(100)$ $84(40)$ $55(15)$ $53(23)$ $41(50)$ $39(65)$ $29(20)$ $27(25)$ 11 $(CH_3)HC = C = CHOCH_3$ $69(100)$ $84(40)$ $53(15)$ $41(93)$ $40(8)$ $39(85)$ $29(15)$ $27(30)$ 13 $HC \equiv C - CH_2OCH_3$ $69(100)$ $42(30)$ $41(40)$ $40(20)$ $39(90)$ $38(15)$ $29(20)$ $27(15)$ 14 $H_2C = C = CHOCH_3$ $69(37)$ $70(90)$ $42(36)$ $41(32)$ $40(25)$ $39(100)$ $29(50)$ $27(80)$ 15 $HC \equiv C - CH_2OCH_2 CH_3$ $69(40)$ $83(10)$ $55(40)$ $43(20)$ $41(30)$ $39(100)$ $29(15)$ $27(25)$ 17 $H_2C = C = CHOCH_2 CH_3$ $69(10)$ $84(24)$ $83(13)$ $56(28)$ $55(100)$ $41(11)$ $39(34)$ $27(37)$ $27(27)$ $89(100)$ $31(17)$ $29(10)$ $27(11)$ 18 $H_2C - CH - CH = CH_2$ $69(20)$ $42(55)$ $41(25)$ $40(28)$ $39(100)$ <	6 IC=C-CH ₂ OCH ₃	69(80) 196(90) 165(35) 41(50) 39(100) 38(60) 37(20) 29(30)
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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	13 HC≡C—CH₂OCH₃	69(100) $42(30)$ $41(40)$ $40(20)39(90)$ $38(15)$ $29(20)$ $27(15)$
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	0 19 4,5-Dihydro-2- methylfuran	69(3) 84(30) 83(15) 43(100) 41(15) 39(25) 31(30) 27(20)

^a The double bond isomer, 2,3-dihydrofuran yields the same mass spectrum.

$$HC \equiv C - CH(X)OCH_3/H_2C = C = C(X)OCH_3,$$

 $XC \equiv C - CH_2OCH_2/XHC = C = CHOCH_2.$

the two cyclic unsaturated ethers 2,5- and 2,3- dihydrofuran and

$$HC = C - CH_2OCH_2X/H_2C = C - CHOCH_2X$$

in which X represents simple groups (CH₃, OCH₃, SCH₃) or atoms (H, Cl, Br, I) of which the C—X bond dissociation energy varies considerably. This was done to account for a possible effect of the method of ion preparation, in particular the occurrence of isomerization preceding the generation of the $[C_4H_5O]^+$ ions, which will lead to ion structures differing from those expected on the basis of the loss of X by a simple cleavage reaction from the original unrearranged structure. That complex rearrangements play an important role in the fragmentations of these unsaturated ethers already follows from a cursory examination of the spectra in Table 1. For example, the two isomeric ionized precursor molecules $[HC\equiv C CH(CH_3)OCH_3]^+$ and $[H_2C=C=C(CH_3)OCH_3]^+$ lose ${}_{c}C_3H_5$ to yield intense peaks at m/z 43 $(CH_3C=O)$. This must involve a complex rearrangement, which might occur via a cyclic ion, i.e. the molecular ion of 4,5-dihydro-2-methylfuran, in which the m/z 43 ions give rise to the base peak:



Note that it follows from the spectra of $HC \equiv C - CH(CH_3)OCD_3$ and $HC \equiv C - CH(CH_3)O^{13}CH_3$ (Table 2) that the $CH_3C = O$ ion contains the α -methyl group exclusively in agreement with this tentative proposal.

Similarly, the isomers $[HC \equiv C - CH_2OCH_3]^+$, $[H_2C = C = CHOCH_3]^+$ the cyclic isomers [2,5dihydrofuran]^+ (2,5-DHF) and [2,3-dihydrofuran]^+ as well as ionized butadiene monoxide all yield intense ions at m/z 42 ($[C_3H_6]^+$) by loss of CO, a reaction which also requires a complex rearrangement for which isomerization into a common (molecular) ion structure prior to the fragmentation should be considered.

Acetylenic type ions have much lower stability with respect to the allenylic and cyclic isomers, e.g. ΔH_f^+ HC=C--CH₂OCH₃ = 1050 kJ mol⁻¹, whereas ΔH_f^+ H₂C=-C=CHOCH₃ and ΔH_f^+ 2,5-DHF are 874 and 816 kJ mol⁻¹, respectively. [From ΔH_f values for the

Table 2. Principal fragment ions in the 70 eV mass spectra of some ¹³C and deuterium labelled acetylenic and allenylic ethers

Compound	m/z (l)
$HC = C - CH(CH_3)O^{13}CH_3$	70(100) 84(10) 54(6) 53(18) 43(20) 40(8) 39(9) 27(15)
$HC = C - CH(CH_3)OCD_3$	72(100) 86(9) 55(8) 53(15) 43(15) 42(6) 41(6) 27(15)
HC≡C−−CH ₂ O ¹³ CH ₃	70(100) 43(25) 42(40) 41(10) 40(25) 39(80) 38(8) 29(15)
HC≡CCH₂OCD₃	72(90) 71(23) 45(30) 44(30) 43(10) 41(15) 40(15) 39(100)
H ₂ CCHOCD ₃	72(31) 73(100) 45(48) 44(26) 43(16) 41(39) 40(32) 39(32)
$HC \equiv C - CH_2 OCD_2 CD_3$	71(30) 88(10) 60(15) 56(18) 45(19) 44(10) 43(27) 39(100)
$CH_3C \equiv C - CH_2O^{13}CH_3$	70(100) 84(5) 53(50) 43(10) 42(20) 41(13) 40(16) 39(50)
$CH_3C \equiv C - CH_2OCD_3$	72(100) 87(4) 53(45) 45(10) 44(20) 41(20) 40(20) 39(50)

neutral compounds estimated by group additivity⁴ and photoelectron spectroscopy ionization energy values of 10.12 eV for HC=C--CH₂OCH₃, 8.73 eV for H₂C=C--CHOCH₃ and 9.14 eV⁵ for 2,5dihydrofuran.]Therefore isomerization of the acetylenic ether molecular ions into energy rich allenylic or 5-membered ring cyclic structures is especially likely when this rearrangement opens up a fragmentation pathway which leads to the formation of an isomeric product ion of higher stability.

This implies with respect to the generation of the $[C_4H_5O]^+$ ions, that the intense loss of CH₃ from $[HC \equiv C - CH(CH_3)OCH_3]^+$ may well be a simple cleavage reaction from the intact molecular ion yielding product ions having the (initial) structure $HC \equiv C - CH - OCH_3(e)$, because loss of CH_3 from the allenylic $(H_2C=C=CH(CH_3)OCH_3)$ or the cyclic isomer (4,5-dihydro-2-methylfuran) (see above) cannot yield an ion of higher stability directly: loss of methyl from both stable isomers is of minor importance, 10 and 3% of base peak, see Table 1. (The major part of the methyl loss from $H_2C==C=C(CH_3)OCH_3$ is probably that of the methoxy methyl group: the [M- $CH_3]^+$ ion intensity in the spectrum of $H_2C = C = CHOCH_3$ $([M-CD_3]^+)$ in H₂C=C= $CHOCD_3$) is 12% of the base peak.) The fact that loss of X' from $[H_2C=C=C(X)OCH_3]^{+}$ is again the base peak for X = I is possibly due to the weakness of the C-I bond which allows its cleavage to compete with rearrangements leading to more favourable processes. The $[{\rm \check{C}}_4 H_5 O]^+$ ion thus generated would have

the (initial) structure $H_2C = C = C - OCH_3$ (f).

Loss of H' from $[HC \equiv C - CH_2OCH_3]^+$ on the other hand could lead to $HC \equiv C - CH - OCH_3$ (e) and perhaps also $HC \equiv C - - CH_2OCH_2$ (h) type product ions by direct cleavage, but in this case isomerization into the allenylic isomer followed by a 1,4 H shift prior to the hydrogen radical loss can yield the resonance stabilized 5-membered ring product ion (g):



The measured ionic heat of formation of the $[M-H]^+$ ion from 2,5-dihydrofuran, which most probably has the ion structure g ($\Delta H_f^+ \leq 690 \text{ kJ mol}^{-1}$), is indeed considerably lower than that of the methoxy substituted propargyl cation HC=C--CH--OCH₃ (e) or the ion HC=C--CH₂OCH₂ (h) for which ΔH_f^+ values of 774-816 and 837-879 kJ mol⁻¹ are calculated respectively, using the substitution method proposed by Lossing for saturated oxygen containing carbo cations.⁷

Similar arguments apply to compounds of the type $XC \equiv C - CH_2OCH_3$ where the loss of X' is the most important fragmentation pathway. Direct loss of X' from the unrearranged molecular ion is highly improbable: $\Delta H_f = C \equiv C - CH_2OCH_3$ is crudely estimated to be 628 kJ mol⁻¹ higher than that of ion g; moreover, direct cleavage of X' cannot be expected to compete

with other simple cleavage reactions such as the loss of $'OCH_3$ for which the reaction enthalpy is considerably lower.

Isomerization via a 1,3 H shift (or two consecutive 1,2 H shifts) would yield ions of the type $[XHC=C=CHOCH_3]^+$ (an analogous 1,3 H shift may explain the intense loss of CH₃' from $[H_2C=CH-CH=CH-OCH_3]^+$). These ions could lose X' to yield the same product ions e HC=C- $CH=OCH_3 \Leftrightarrow$ HC=C=CHOCH₃ generated upon loss of X' from the $[HC=C-CH(X)OCH_3]^+$ ions but cyclization involving the more stable product ion g is also feasible:



If it plays a role, this mechanism may be expected to become more important when the C-X bond strength becomes higher. A related mechanism involving cyclization was proposed in a previous paper² to explain the intense loss of CH₃' from *trans*-methyl crotonate, $[(CH_3)HC=CH-COOCH_3]^+$.

Finally, compounds of the type $HC\equiv C-CH_2OCH_2X$ and $H_2C=C-CHOCH_2X$ are candidates for the generation of two isomeric $C_3H_3-OCH_2$ product ion structures $HC\equiv C-CH_2OCH_2$ (*h*) and/or $H_2C=C=CH-OCH_2$ (*i*), but the generation of the cyclic product ion (cf. the behaviour of ethyl acrylate²) should also be considered:



Another possibility is that g type ions are generated from the h or i product ions:



Apart from this discussion of the possibility of generating ions of a certain initial structure the question of conversion among the product ions should also be considered. Although the barrier for interconversion among isomeric even electron ions seems to be much higher than in odd electron species, it is often difficult to extract detailed information about this from the ion structure probes used, i.e. metastable ion (MI) and CA spectra. These contain information about the reactions which the reactive species undergo. Unfortunately, these reactions sometimes are of a complex nature, i.e. not directly related to the structure of the

4

generated fr	om unsat	urated	ethers				
Precursor Molecule	Neutral X [°] lost	To =		Precursor Molecule	Neutral X lost	T. 5	
HC≡C–CH(X)OCH₃	CH ₃ , SCH	i₃ 150	515ª	XHC=C=CHOCH ₃	СН₃	60	290
	OC	Н _з		H ₂ C—CH—CH—CHOCH ₃	CH₃	70	270
$H_2C = C = C(X)OCH_3$	l	400	620	HC=C-CH_OCH	н	30	200
XC≡CCH₂OCH₃	l Br	140 105	440° 380°	H ₂ C=C=CHOCH ₃	н	30	230
	CI	80	320	HC==CCH2OCH2X	1	75	350
	CH₃	40	255		СН _з	60	310
CH ₃ CH=CH-CO-X ^{b)}	OCH ₃	32	114	H ₂ C==C=CHOCH ₂ X	CH ₃	50	280
2,5-dihydrofuran	н	40	225	H ₂ C—CH—CH=CH ₂	н	35	210

Table 3. Kinetic energy releases (meV) for the unimolecular loss of CO from $[C_4H_5O]^+$ ions generated from unsaturated ethers

^a These metastable peaks are clearly composite.

^b This metastable peak is of a Gaussian shape, see Ref. 1.

non-reacting ions, like the formation of $[C_3H_3]^+$ ions in the CA spectra of $C_3H_5C=0$ isomers (second largest peak)¹ and the $[C_3H_5]^+$ ions found in the MI and CA spectra of the $[C_4H_5O]^+$ ions investigated in this study, for example.

Metastable ion and collisional activation spectra

All compounds investigated have m/z 41, corresponding with the loss of CO as the base peak in the MI spectrum of their $[C_4H_5O]^+$ ions. Other fragmentations are of no importance except for the loss of CH₂O which is prominent in the spectra of the $[M-X]^+$ ions, $HC\equiv C-CH-OCH_3$ (e), generated from $[HC\equiv C-CH(X)OCH_3]^{++}$ (ratio CO:CH₂O loss $\approx 1:1$) but also for ions formed by loss of X' from $[XC\equiv C-CH_2OCH_3]^{++}$ when X = I and to a lesser extent for X = Br. When X = Cl, CH₃ or H and also for the ion derived by loss of H' from $[H_2C=C=CHOCH_3]^{++}$ loss of CH₂O is a minor process (ratios CO:CH₂O

losses are $\approx 10:1$). No loss of CH₂O was observed in the MI spectra of the $[M-I]^+$ ion generated from $[CH_2=C=CI-OCH_3]^+$ (which suggests that the ion generated is not e), the ion generated upon loss of H' from ionized 2,5-(and 2,3-) dihydrofuran and also not for the $[M-X]^+$ ions derived from the $[C_3H_3OCH_2X]^+$ isomers (although this loss involves a single bond rupture if the structure of the ions is $C_3H_3OCH_2$, h or i).

Loss of CO is the reaction of lowest calculated heat of formation $\Sigma \Delta H_f$, of the products. Using $\Delta H_f(CO) =$ -110 kJ mol⁻¹⁶ and values of 946 and 992 kJ mol⁻¹ for the two stable $[C_3H_5]^+$ isomers known, CH_2 — CH_-CH_2 and CH_3 — $C=CH_2$,⁶ reaction enthalpies of 837 and 883 kJ mol⁻¹ are calculated. For the loss of CH_2O these values are 958 and 1059 kJ mol⁻¹ (from ΔH_f $CH_2O = -117$ kJ mol⁻¹ and $\Delta H_f[C_3H_3]^+$ is 1075 (cyclopropenium ion) or 1176 (propargyl cation) kJ mol⁻¹⁶).

However, contrary to the behaviour of two of the stable $C_3H_5\dot{C}=O$ isomers i.e. $CH_2=C(CH_3)\dot{C}=O(a)$ and $CH_2=CH_-CH_2-\dot{C}=O(b)$, for which the loss of CO - the only reaction of the metastable ions - is a simple cleavage reaction yielding either of the stable $[C_3H_5]^+$ product ions directly, this loss must involve a (complex) rearrangement for the $[C_4H_5O]^+$ ether ion structures envisaged so far.

Depending upon the nature of the rearrangement the energy barrier for loss of CO may become so high that generation of either of the stable $[C_3H_5]^+$ product ions cannot occur at or near the thermochemical threshold. As a result the amount of kinetic energy released in the field free regions will be larger than that found for the loss of CO from a and b type ions $(T_{0.5} = 5 - 10 \text{ meV})$ and the metastable peaks may become of a composite nature. Moreover, when the loss of CO involves a rearrangement with unfavourable energy and entropy factors, reactions with a higher calculated reaction enthalpy (like the loss of CH₂O) may become competitive in the metastable timeframe. The kinetic energy (KE) release values observed for loss of CO from the ether type ions, measured from the width of the metastable peaks at 50 and 10% of the height, are given in Table 3. It is seen that all $[C_4H_5O]^+$ ether type ions are characterized by a much higher energy release than that observed for a and b type ions.

This indeed indicates that the loss of CO from the $[C_4H_5O]^+$ ions examined in this study occurs via mechanisms with energy and entropy requirements which prevent the generation of stable $[C_3H_5]^+$ product ions at or near threshold. The metastable peaks for loss of CO and the associated energy releases (Table 3) can be roughly divided into three groups:

(1) Peaks with rather low $(T_{0.5} = 30-70 \text{ meV})$ half-height KE releases are observed for the loss of CO from the ion generated by loss of H[•] from ion-

ized 2,5-dihydrofuran ($\stackrel{\bullet}{O}$ -CH==CH==CH= $\stackrel{\bullet}{C}$ H₂, g), the [M-H]⁺ ions from [HC=C-CH₂OCH₃]⁺, [H₂C=C=CHOCH₃]⁺ and ionized butadiene monoxide, as well as the [M-CH₃]⁺ ions generated from [CH₃C=C-CH₂OCH₃]⁺,

$$[(CH_3)HC=C=CHOCH_3]^+$$

$$[H_2C=CH-CH=CH-OCH_3]^+$$
,

$$[HC \equiv C - CH_2 OCH_2 CH_3]^+$$

and $[H_2C=C=CHOCH_2CH_3]^{+}$. The $[M-I]^+$ ion from $[HC=C-CH_2OCH_2I]^{+}$ displays a metastable peak for loss of CO which is markedly broader at the base. These peaks all have a non-Gaussian shape as indicated by the relatively large $T_{0.1}$ values $(T_{0.1}/T_{0.5}=3.32)$ for a Gaussian shaped peak) and probably consist of more than one component.



Figure 1. Metastable peaks for the loss of CO from: (a) the $[M-X]^+$ ions from $HC\equiv=C-C(X)OCH_3$ ($X = CH_3$, SCH_3 , OCH_3); (b) the $[M-H]^+$ ions from 2,5-dihydrofuran.

(2) Clearly composite metastable peaks (see Fig. 1) of a similar shape with a much higher KE release are observed for the $[M-X]^+$ (HC=C-CH-OCH₃, e) ions derived from $[HC=C-CH(X)OCH_3]^+$. Ions generated by loss of X' from $[XC \equiv C - CH_2OCH_3]^+$ yield an almost identical metastable peak for X = I; for X = Br and especially for X = Cl the energy release values become lower, whereas for $X = CH_3$ the peak shape is similar to that described above for the g type ion from ionized 2,5-dihydrofuran. These results support the suggestion presented earlier that loss of X' from $[XC \equiv C - CH_2OCH_3]^+$ involves isomerization into $[XHC = C = CHOCH_3]^+$ followed by rupture of the C-X bond—thus yielding e type ions—when this bond is relatively weak (X = I, Br). When the C-X bond strength becomes higher $(X = Br \rightarrow X = Cl \rightarrow X)$ $X = CH_3$) a second $[C_4H_5O]^+$ ion is co-generated in the primary loss of X', probably g via ring closure of $[XHC=C=CHOCH_3]^+$ as proposed above. This process is still of only minor importance for X = Br but it prevails for $X = CH_3$.

Note also that loss of CO from the proposed ion structure e requires a complex rearrangement not inconsistent with the high energy release observed for this loss and also the competition of the loss of CH₂O. This point will be elaborated further when the results of the ¹³C and deuterium labelled ions are discussed.

(3) The $[C_4H_5O]^+$ ion generated upon loss of X' from $[H_2C==C=CXOCH_3]^+$ shows, for $X = I^+$, a very broad metastable peak for loss of CO ($T_{0.5} =$ 400 meV, $T_{0.1} = 620$ meV), whereas no loss of CH₂O is observed. This points to the generation of a unique structure, probably the ion resulting from direct cleavage of the weak C—I bond, CH₂==C==C-OCH₃ (f), although formation of the isomeric methoxy cyclopropenium ion cannot be ruled out.

The CA spectra of the $[C_4H_5O]^+$ ions investigated are shown in Table 4. The spectra were obtained by †Loss of methyl from H₂C=C=C(CH₃)OCH₃ does not seem to yield f type ions: $T_{0.5}$ for loss of CO is only 40 meV. Moreover, the CA spectrum (54(36), 53(20), 41(100), 40(17), 39(58), 38(24), 37(13), 29(6), 26(7) is completely different from that of the $[M-I]^+$ ion from H₂C=C=C(I)OCH₃ and it also differs from the other ion structures identified. Possibly, a considerable fraction of the $[M-CH_3]^+$ ions is generated by loss of the methoxy methyl group, yielding ions having the (initial) structure H₂C=C-C-CH₃.

0

applying an external voltage (see Experimental) across the collision chamber. This has the effect of separating the peaks for metastable ion decompositions (losses of CO/CH_2O) from those due to collision induced dissociations in the cell (Fig. 2). Comparison of the spectra with those reported in our previous study¹ provides further support for the conclusion that none of the precursor molecules described in this paper yields a $[C_4H_5O]^+$ ion of the type $C_3H_5C=O$.

It is further seen from the data in Table 4 that the CA spectra of the $[M-X]^+$ ions generated from compounds of the type HC=C-CH(X)OCH₃ and also those derived from XC=C-CH₂OCH₃ for X = I and Br, are similar, but largely different from the spectra observed for the other ions. The spectra are characterized by intense peaks at m/z 53 (loss of CH₄), m/z 39 (loss of CH₂O), m/z 38 (loss of OCH₃, CH₂O+H⁻), m/z 29 (H⁺C=O) and m/z 15 (CH₃⁺), whereas loss of CO is greatly suppressed.

These observations strongly support the tentative conclusion derived from the MI data that the ions generated upon loss of X' from $[HC \equiv C - CH(X)OCH_3]^+$ and $[XC \equiv C - CH_2OCH_3]^+$ (for X = I, Br) have the common structure $HC \equiv C - CH - OCH_3$ (e). Loss of X' from $[XC \equiv C - CH_2OCH_3]^+$ probably yields a mixture of ions (e and g) when X = Cl, but for X = CH_3 the CA spectrum is close to that of the g type ion derived from ionized 2,5-dihydrofuran. The latter CA spectrum is characterized by an intense



Figure 2. Partial CA spectra of m/z 69 [C₄H₅O]⁺ ions (from compound 3) recorded at a collision gas cell potential of 0 V (a) and -320 V (b). The negative potential on the cell causes a shift to lower energies of all peaks resulting from collision induced dissociations in the cell. The position of peaks (denoted with an asterisk) which (largely) result from unimolecular dissociations outside the cell remains unchanged.

	Neutral							m/z	of dau	ghter ion ^a					_					Struc-
Precursor molecule	X' lost	54	53	52	51	50	49	43	42	41 ^b	40	39 ^b	38	37	29	27	26	25	15	ture
1 HC≡C—CH(X)OCH _a	CH ₃	7	100	6	1.5	1.5	0.5	5	2	15(50)	<6	95(65)	74	32	30	2	9	7	18	е
2	SCH ₂	3	95	5	1	0.5	_	2	<2	10(55)	<5	100(80)	75	31	35	2	11	8	14	е
3	OCH ₃ °	3	100	5	1	1	0.5	3	<2	9(20)	<4	90(35)	75	30	35	2	10	8	13	e
4 $H_2C = C = C(X)OCH_3$	1	100	25	_				3	<5	<5(7)		10	5	4	2		13	3	6	f
6 XC≡CCH₂OCH₃	ł	3	100	6	1	1		2	2	<15(45)	<4	80(50)	72	32	31	2	10	7	11	е
7	Br	3	90	5	1	2		2	2	65(120)	<7	100(35)	72	35	32	3	10	7	10	е
8	CI	1	25	2	1.5	4	1.5	1	5	100(220)	12	75(25)	35	17	18	3	6	2	3	e/g
9	CH₃	1	8	1	з	6	2	_	5	85(85)	18	100(13)	33	16	18	5	6	2	2	g
11 XHC=C=CHOCH ₃	CH ₃	2	8	2	3	5	2	1	6	95(70)	17	100	30	19	18	5	8	2	2	g
12 H ₂ C==CHCH==CHOCH ₃	CH3	2	6	2	3	6	2	2	5	100(160)	20	90	30	16	14	5	6	2	2	g
HC=CH																				
10 H ₂ C CH ₂	Hª	0.5	2		3	5	2	2	7	100(150)	20	90	27	14	14	4	5	1.5	0.5	g
13 HC≡C—CH₂OCH₃	H٩	2	11	1	2	3	2	0.5	4	100(200)	15	80(20)	23	11	12	5	6	2	1	g
14 H ₂ C-C-CHOCH ₃	H°	3	13	1.5	3	4	2	2	5	100(170)	15	90(23)	25	12	14	4	6	2	1	g
18 H ₂ C-CH-CH=CH ₂	н		8	1.5	3	5	2	2	6	100(250)	18	90(25)	26	14	14	5	8	2		q
15 HC≡C—CH₂OCH₂X	le.	0.5	4	_	_		_		1	35(20)	2	100	18	10	9	0.5	2	1		ĥ/g
16	CH®	0.5	3	_	0.5	1	0.5		3	55(75)	6	100	17	9	12	1	3	1		h/a
17 H₂C=CCCHOCH₂X	CH₃	1	4	0.5	3	4	1	1	5	85(140)	16	100	25	11	17	4	5	1		g

Table 4. Collisional activation spectra of $[C_4H_5O]^+$ ions generated from unsaturated ethers

^a Abundances (average of three runs) relative to the base peak = 100%; peaks at m/z 68 have been omitted because interference makes them of little diagnostic value: the MI spectra of several ions have a sharp m/z 68 peak due to MI decompositions in the first field free region.

^b Values in parentheses refer to the intensities of MI decompositions in spectra which were run with a gas cell voltage of -320 V; differences among the ratios are due in part to variations in the amount of collision gas used (which does not affect the intensity distributions in the CA spectrum, see Experimental.) But differences in ion structure also have an effect, see also Ref. 1. ^c Ionization with Iow energy electrons (c. 12 eV) has no effect on the CA spectrum and the peak shape for Ioss of CO in the MI

spectrum. ^d The double bond isomer 2,3-dihydrofuran yields identical MI and CA spectra.

^e These ions also have CA peaks at m/z 44 and 30 (3% of base peak).

collision induced loss of CO. Not unexpectedly, considering the proposed structure, loss of CH₂O (m/z 39) is also important, but other principal peaks in the spectra of *e* type ions are of only minor intensity. This CA spectrum is also close to the spectra of the $[C_4H_5O]^+$ ions generated from compounds **11–18**.

In view of the similar CA and MI spectral characteristics, the high stability of the g type ion and the rationale for its formation by the cyclization mechanisms under 'general considerations', we propose that the major fraction of the ions generated from the abovementioned compounds have the cyclic structure g.

The largest deviation from the CA spectrum of the 2,5-DHF product ion g is observed in the spectra of the $[M-X]^+$ ions from HC=C--CH₂OCH₂X where the loss of CH_2O (not found in the MI spectrum) is much more intense than that of CO'(I(CO))/ $I(CH_2O) = 0.35$ for X = I but higher for X = $CH_3: 0.55$). This may be taken as evidence for the co-generation of $HC \equiv C - CH_2 - OCH_2$ (h) type product ions. Note also that the CA spectra of these ions contain unique peaks at m/z 30 (3%, [CH₂O]⁺⁺) and m/z 44 (2.5%, loss of H—C=C'). (Although the data do not allow a clear distinction to be made between the two isomeric $C_3H_3OCH_2$ ions, this second loss points to the presence of h rather than i type ions.) Finally it is seen from the CA spectrum of the $[M-I]^+$ ion from $[H_2C=C=CIOCH_3]^{+}$ that this ion indeed represents a unique structure. The spectrum is dominated by loss of CH₃, whereas the loss of CO (base peak MI spectrum) is largely suppressed. These observations are consistent with the proposal that the structure of the ion is $H_2C=C=C-OCH_3$ (f).

The metastable ions dissociate via the pathway which is energetically most favourable, i.e. by loss of CO. A plausible mechanism is

$$H_2C = C \stackrel{\frown}{=} H_3C \stackrel{\frown}{=} C \stackrel{$$

At higher internal energies (CA spectrum) entropy factors become more important, thus favouring the simple cleavage loss of CH_3 over the rearrangement

$$H_2C=C=C=O^+ + CH_3 - - - + H_2C=C=O^+ + CH_3$$

Summarizing, we conclude that the unsaturated ethers investigated in this study yield four different $[C_4H_5O]^+$ ions which are stable for $\ge 10^{-5}$ s: HC==C--CH--OCH₃ (e). H₂C==C=C-OCH₃ (f), the cyclic ion O--CH==CH=-CH₂ (g) and HC==C--CH₂--OCH₂ (h). The proposals for the generation of these ions from the various precursor molecules studied are summarized in Scheme 1.

Further evidence for the structure identity of e type ions and the generation of g type ions from the acyclic unsaturated ethers was obtained from the examination of a few selected deuterium and ¹³C labelled precursor molecules (see Table 2). The results will be given in a separate discussion of both ions.



Scheme 1. Proposals for the generation of $[C_4H_5O]^+$ ions from unsaturated ethers.

Reactions of ions e

Four of the most intense peaks in the CA spectrum of the $[M-X]^+$ ion generated by loss of X' from $[HC \cong C - CH(X)OCH_3]^+$, viz. those at m/z 53, 39, 38 and 15, can be related to the proposed ion structure *e* by the following reactions:

 $HC \equiv C - CH_{2} O - CH_{3} \cdots \rightarrow [C_{3}H_{2}]^{+} (m/z \ 38) + CH_{3}O'$ (3)

$$HC \equiv C - CH - O \not\leftarrow CH_3 \cdots \not\leftarrow [CH_3]^+ (m/z \ 15) + C_3H_2O$$
(4)

However, the CA peak of sizeable intensity at m/z 29 (HC==O) as well as the base peak at m/z 41 ([C₃H₅]⁺)

in the MI spectrum cannot simply be explained on the basis of the proposed structure *e*. Moreover, the possibility should be considered that the reactions presented above do not occur from the methoxy substituted propargyl cation *e* but rather from the cyclic isomer, the methoxy cyclopropenium ion. \Rightarrow —OCH₃. (Note that irrespective of the structure of the precursor molecule used, $[C_3H_3]^+$ ions generated at threshold are always cyclopropenium ions⁶.)

Therefore, we have examined the MI and CA spectra of the following deuterium and ¹³C labelled analogues of the precursor molecule $HC \equiv C - CH(CH_3)OCH_3$: $DC \equiv C - CH(CH_3)OCH_3$, $HC \equiv C - CH(CH_3)OCD_3$ and $HC \equiv C - CH(CH_3)O - ^{13}CH_3$ (Tables 7, 6 and 5 respectively). In agreement with the proposal given above [reaction (1)], methane is exclusively eliminated as ¹³CH₄ from the ¹³C labelled ion $HC \equiv C - CH(CH_3) - ^{13}CH_3$ and as CD_3H from the OCD₃ labelled ion $HC \equiv C - CH - OCD_3$. Moreover, the label is not involved in the methane loss from the $[M - CH_3]^+$ ion derived from the acetylenic deuterium

Table 5. Metastable ion and collisional activation spectra of ¹³C labelled m/z 70 $[C_4H_5O]^+$ ions generated from HC=C--CH(CH₃)O¹³CH₃, CH₃C=C--CH₂O¹³CH₃ and HC=C--CH₂O¹³CH₃

Precursor																				
molecule	N	Al spe	ctrum								CA s	pectru	um ^{a,b}							
	m/z 42	41	40	39	54	53	42	41	40	39	38	37	30	29	28	27	26	25	16	15
$HC \equiv C - CH(CH_3)O^{13}CH_3$	100	1	50	75	3	100	7	6	75	30	80	30	7	22	1.5	2	9	7	18	1
CH ₃ C≔C—CH ₂ O ¹³ CH ₃	100	23	8	11	3	12	100	55	100	80	40	15	13	16	5	7	8	2	1	0.5
HC≡C—CH₂O ¹³ CH₃	100	17	6	9	3	16	100	40	60	50	30	10	6	9	3	4	5	1.5	1	0.5

^a Abundances (average of three runs) relative to the base peak = 100%.

^b Peak intensities at m/z 42-39 have been corrected for the contributions of MI decompositions; peaks at m/z 69 and the low intensity peaks at m/z 50–52 have been omitted.

Table 6. Metastable ion and collisional activation spectra of deuterium labelled m/z 72 $[C_4H_2D_3O]^+$ ions generated from $HC \equiv C - CH(CH_3)OCD_3$, $CH_3C \equiv C - CH_2OCD_3$, $HC \equiv C - CH_2OCD_3$ and $H_2C = C = CHOCD_3$ and the m/z 71 ion derived from $HC \equiv C - CH_2OC_2D_5$

Precursor																							
Molecule		MI spe	ctrum											С	A spe	ctrum	a,b						
	m/z 44	42	41	40	54	53	44	43	42	41	40	39	38	37	30	29	28	27	26	25	18	17	16
$HC \equiv C - CH(CH_3)OCD_3$	100	8	21	52	3	100	10	4	20	50	30	15	55	25	7	30	3	3	10	10	18	_	
$CH_3C \equiv C - CH_2OCD_3$	100	2	5.5	9.5	5	15	100	15	35	90	45	25	20	10	15	15	7	7	4	1.5	2	2	1.5
$HC \equiv C - CH_2 OCD_3$	100	1.5	3.5	6.5	3	16	100	10	20	55	35	15	15	7	7	10	4	4	3	2	2	1	0.5
H ₂ C=CCHOCD ₃	100	2	5.5	9	5	20	100	10	20	60	40	20	20	10	9	13	5	5	3	1.5	2	1	0.5
HC≡C—CH ₂ OC ₂ D ₅	100	(m/z	(43)		0.5	5	—	70	6	15	20	100	20	12	10	5	1	1	0.5	—	—	—	

^a Abundances (average of three runs) relative to the base peak = 100%.

^b Peak intensities at m/z 44–40 have been corrected for the contributions of MI decompositions; peaks at m/z 71, 70 and the low intensity peaks at m/z 50–52 have been omitted.

Table 7. Metastable ion and collisional activation spectra of deuterium labelled m/z 70 $[C_4H_4DO]^+$ ions generated from $DC \equiv C - CH(CH_3)OCH_3$, $DC \equiv C - CH_2OCH_3$ and $DC \equiv C - CH_2OCH_2CH_3$

Precursor molecule	м	l spectru	m								c	A spec	trum ^{a,b}					
	m/z 42	40	39	54	53	42	41	40	39	38	37	30	29	28	27	26	16	15
$DC \equiv C - CH(CH_3)OCH_3$	100	100	10	100	5	12	7	75	90	25	15		34		14	10	—	14
$DC \equiv C - CH_2OCH_3$	100	9	2	11	3	100	15	60	45	20	10	2	10	4	6	5	1	2
$DC \equiv C - CH_2OCH_2CH_3$	100	—	—	3		65	5	100	20	15	6	3	10	1	2	1.5		_

^a Abundances (average of three runs) relative to the base peak = 100%.

^b Peak intensities at m/z 42–39 have been corrected for the contributions of MI decompositions; peaks at m/z 69, 68 and the low intensity peaks at m/z 50–52 have been omitted.

labelled ether. This rules out the possibility that the product ions could have the methoxy cyclopropenium ion structure because these cyclic ions are expected to lose CH_4 and CH_3D to the same extent. The CA spectra of the labelled ions are also in agreement with the proposals for the generation of the m/z 38 and m/z 15 ions given above [reactions (3) and (4)].

Loss of formaldehyde, on the other hand, can only be partially rationalized by the pathway reaction(2)—envisaged so far: the *metastable* ¹³C labelled *e* type ions, HC=C-CH-O- $^{13}CH_3$, not only show the expected loss of ¹³CH₂O, but ¹²CH₂O is also lost to an appreciable extent (*c*. 40% of the total formaldehyde loss). Furthermore, the shapes of the metastable peaks and the associated KE release values are different for both losses: for loss of ¹³CH₂O $T_{0.5}$ = 40 meV and $T_{0.1}$ = 160 meV; for the loss of ¹²CH₂O higher values are observed, $T_{0.5}$ = 90 meV and $T_{0.1}$ = 280 meV. These observations strongly suggest that two distinct pathways are involved in the loss of formaldehyde. We propose that the loss of ¹³CH₂O occurs directly from *e* type ions via reaction (2) shown above and that the loss of ¹²CH₂O involves rearrangement of *e* into *e'* type ions followed by a 1,3 H transfer of a methoxy hydrogen to the aldehyde moiety:



The proposed (partial) rearrangement of e into e' type ions also explains the formation of the HC^{+} =O ions found in the CA spectrum (both the ¹³C and the deuterium labelled ions largely retain the label in the formation of HC=O) and predominant loss of CO in the MI spectrum which specifically occurs as ¹²CO. For the loss of CO from e' type ions several mechanisms can be envisaged, one possibility being the generation of the stable $[C_3H_5]^+$ product ion CH₃--C=-CH₂ via



The metastable peak for this process is composite (Fig. 1) which suggests that two pathways are available.

In agreement with the mechanistic proposals for the loss of formaldehyde are the observations that the deuterium labelled metastable ions HC=C-CH-OCD₃ show a high preference for the losses of CHDO and CD₂O over that of CH₂O, whereas the acetylenic deuterium labelled ion, DC=C-ČH-OCH₃ almost exclusively eliminates CH₂O. Moreover, the mutually different shapes of the metastable peaks for the losses of CHDO and CD_2O from $HC \equiv C - CH - OCD_3$ are superimposable on those found for the losses of ${}^{12}CH_2O$ and ${}^{13}CH_2O$ respectively from HC==C-- $\dot{C}H$ —O—¹³CH₃. However, the acetylenic hydrogen does participate in the formaldehyde loss when the average internal energy content of the dissociating ions becomes higher, i.e. for the collision induced dissociations. For example, the CA spectrum of $HC \equiv C - CH - OCD_3$ shows that 20% of the total formaldehyde loss occurs as CH_2O , probably from e'type ions in which the acetylenic hydrogen has extensively exchanged with the methylic hydrogen atoms. (It can be seen from Tables 5 and 6 that the sum of the peak intensities for the losses of CHDO and CD_2O relative to that for the loss of CO from $HC \equiv C - CH(CH_3)OCD_3$, is considerably lower than that found for the losses of ¹²CH₂O and ¹³CH₂O from $HC \equiv C - CH(CH_3)OCH_3$, thus showing that an appreciable deuterium isotope effect is involved.)

Formation and reactions of g type ions generated from $XC \equiv C - CH_2OCH_3$ (X = H, CH₃) and H₂C = C = CHOCH₃

Based on evidence from the MI and CA spectral characteristics of the product ions, it was proposed that loss of X' from precursor molecules of the type $X-C\equiv C-CH_2OCH_3$ only occurs after isomerization into allenyl type ions $[X-HC=C=CHOCH_3]^+$ with a high internal energy content. These ions undergo loss of X' by direct cleavage to yield *e* type ions when X = I or Br. When the C-X bond strength becomes higher, however, this direct loss is replaced by a competitive mechanism, probably that depicted below in which a 1,4 methoxy H transfer initiates loss of X' via a displacement reaction $(gc \rightarrow g)$ yielding the stable cyclic product ion g. A further indication that



the loss of H' from $[HC \equiv C - CH_2OCH_3]^+$ and $[H_2C = C = CHOCH_3]^+$ may well yield the cyclic product ion g is found in the observed $[M-H]^+/[M-D]^+$ intensity ratios for the specifically deuterium labelled analogues presented in Table 8.

It follows that all hydrogen atoms participate in the primary loss of a hydrogen radical. For the labelled methyl propargyl ethers, $HC \equiv C - CH_2OCH_3$, it is inferred from the data in Table 8 that the hydrogen radical loss comprises the methoxy C-1, methylenic C-2 and acetylenic C-3 hydrogen atoms in the ratio 1:3:1. For the methoxy allenes $H_2C==C=CHOCH_3$, the corresponding ratio is 1:1:2. The results for methoxy allene are compatible with reaction (5) given above if it is assumed that the four hydrogens in the C_3H_4 moiety of ion gc have become equivalent. For $[HC = C - CH_2 - OCH_3]^+$ an additional pathway for the generation of g type ions has to be invoked, which accounts for the preferred loss of the methylenic C-2 hydrogen atom (calculated ratio on the basis of reaction (5) is 1:2:1, observed 1:3:1). One possibility is that part (~20%) of the [HC=C--CH₂--OCH₃]⁺ ions does not isomerize into methoxy allene molecular ions, but rather undergoes a competing 1,5 methoxy H shift to the terminal carbon atom concomitant with a 1,2 H shift and (specific) loss of the C-2 hydrogen atom:



Note also that the CA results do not rule out the possibility that a *minor* fraction of the molecular ions undergoes direct cleavage of the C-2—H bond to yield e type product ions.

The most important MI and CA loss of the g type ions is that of CO. This reaction is most simply rationalized by a 1,2 H shift in the ring followed by expulsion of CO yielding the most stable $[C_3H_5]^+$ product ion, $[allyl]^+$. Another important loss in the CA spectra is that of CH₂O for which it is not necessary to invoke a rearrangement. Ion g generated from $[XC \equiv C - CH_2 - O - {}^{13}CH_3]^+$ via loss of X' (X = H, CH₃) is therefore expected to lose ${}^{12}CO$ in the CO and ${}^{13}CH_2O$ in the formaldehyde elimination, unless the height of the energy barriers and the associated rate

Table 8.	[M-	-H] ⁺ /[M-	- D]*	intensit	y ratios
	for	various	deut	erium	labelled
	HC	=CCH ₂	OCH:	and	H,C=
	C==(CHOCH ₃	molec	ular ion	is

	/[M-H	H]'//[M-I) (C
Precursor molecule	Caic. ^a	Calc. ⁵	$Obs.^{c}$
$DC \equiv C - CH_2 OCH_3$	3	4.0	4.5
HC=C-CH2OCD3	3	4.0	3.8
DC=C-CH2OCD3	1	1.5	1.6
HC=C-CD2OCH3	1	0.7	0.8
HC=C-CHDOCH ₃	3	2.3	2.3
DC=C-CHDOCH ₃	1	1.0	1.1
H ₂ C=CCHOCD ₃	3	—	3.3
H ₂ C=CCDOCH ₃	3	—	3.0

^a Assuming only reaction (5), see text.

^b Assuming 80% of the hydrogen loss via reaction (5) and 20% specific loss from the

methylenic position.

° 70 eV mass spectra.

constants for (1, 2) H shifts are such that the isomerization reactions shown below are feasible. Loss of CO in the MI spectrum consists mainly of 12 CO (80–85%) of the total CO loss for X = H, CH_3 ; a slightly lower value is found (\sim 70%) for the collision induced loss), but for the loss of formaldehyde, whose activation energy is considerably higher, only a slight preference is found for the loss of ¹³CH₂O. In the collision induced formaldehyde elimination the two carbon atoms adjacent to the oxygen atom have become equivalent: equal probabilities are found for losing ${}^{12}CH_2O$ and ${}^{13}CH_2O$. (The ratios calculated from the peak intensities in Table 5 are 50:50 for HC=C-CH(CH₃)O¹³CH₃ and 87:80 for CH₃C=C-CH₂O¹³CH₃. The *m*/*z* 41 peak intensity was corrected for the contribution of the loss of ¹³HCO: the total amount (12HCO+13HCO) of HCO loss relative to that of formaldehyde follows from the CA spectrum of the unlabelled ion; the ratio for loss of ¹³HCO' vs ¹²HCO' was assumed to correspond with the [¹³HCO]⁺/[¹²HCO]⁺ peak intensity ratio.)

These observations indicate that isomerization of g_1 into g_1' type ions (via g_2 and g_2' intermediate ions, see below) does occur and that the associated energy barrier is slightly higher than that for loss of ¹²CO from g_1 but markedly lower than that for the loss of



formaldehyde. For the metastable ions which lose 13 CO this isomerization is rate determining. As a consequence the ions g_1' have additional excess energy in the reaction coordinate and will eliminate CO with a relatively high rate in the metastable time-frame. This is reflected in the metastable peak shapes for the

losses of CO: the loss of ¹³CO is accompanied by a noticeably higher KE release than that of ¹²CO $(T_{0.5}(-^{13}\text{CO}) = 55 \text{ meV})$, whereas $T_{0.5}$ $(-^{12}\text{CO}) = 35 \text{ meV}$.)

These proposals also imply complete equilibration of all five hydrogen atoms in ion g prior to the loss of formaldehyde. Indeed, this is borne out in the relative probabilities for the (collision induced) elimination of CH_2O , CHDO and CD_2O from the various $[C_4(H, D)_5O]^+$ ions given in Table 9.

It is seen that the observed intensity ratios are close to those calculated for $(A, B)_5$ (z = 2) scrambling assuming no isotope effects.

EXPERIMENTAL

Mass spectrometric measurements

Measurements were performed on a VG ZAB-2F double focusing mass spectrometer of reversed geometry. A 100 μ A electron beam of ionizing energy 70 eV and an accelerating potential of 7920 V were used; sample reservoir and ion source temperatures were ~150 °C. For MI the magnetic field was set to select the m/z 69 $[C_4H_5O]^+$ ions under investigation; ionic products of their decompositions in the field free region between the magnetic and electrostatic analysers were detected by scanning the electric sector (ES) potential under conditions of good energy resolution (main beam width 0.2 V at an ES voltage of 422.1 V). KE release values were calculated in the usual way without correction for the main beam width. CA spectra were obtained in the same way after introduction of helium as a collision gas in the collision chamber near the β focal point. An external voltage of -320 V was applied on the chamber in order to separate the normal metastable peaks and the CA peaks (see ref. 8 for a detailed explanation of this procedure.) For CA the pressure was $1-3 \times 10^{-7}$ Torr as measured by an ion gauge situated near the diffusion pump located between the magnetic analyser and the gas cell; the actual gas cell pressure was higher by approximately a factor of 10^3 . The data in Table 10 show that the

Table 9. Peak intensities in the CA spectra corresponding with the losses of CH_2O , CHDO and CD_2O from $[C_4H_xD_{(5-x)}O]^+$ g type ions

Precursor molecule	Neutral lost	×	CH₂O	CHDO	CD ₂ O
$DC \equiv C - CH_2 OCD_3$	Н.	1 obs.		47	53
		1 calc. ^b	—	40	60
$CH_3C \equiv C - CH_2OCD_3$	CH3.	2 obs.	21	53	26
$HC \equiv C - CH_2 OCD_3$	Н.	2 obs.	18	50	32
$DC = C - CH_2 OCD_3$	D.	2 obs.	20	53	28
		2 calc.ª	10	60	30
$HC = C - CH_2 OCD_3$	D.	3 obs.	30	50	20
		3 calc. ^a	30	60	10
$DC \equiv C - CH_2 OCH_3$	н.	4 obs.	57	43	
		4 calc. ^b	60	40	

 $^{\rm a}$ Calculated for A_3B_2 (z = 2) scrambling, assuming no isotope effects.

^b Calculated for A_4B (z = 2) scrambling.

Pressure ×10 ⁻⁷ Torr	l (%) main beam	/ (% CApe m/z 5) ak 53	54 5	53	52	51	50	43	42 41		40	CA spect 39	rum m/z 38	of da	ughteri 36	on ^a 29	28	27	26	25	24	15	14	13	12
0.4	100	0.2	_	80	_				_	30(700) ^b		100	(80 0) ^ь	40	10		30	_	_	10	10			_		
1.0	73	34	4	100	5	1	1	2	2	9(53)	4	94	(75)	75	30	3	32	_	2	10	8	1	9		_	_
2.2	40	87	4	100	5	1	1	2	2	7(17)	4	96	(30)	77	34	3	34	_	2	12	10	1	11	1	1	
3.8	23	100	3	100	4	1	1	3	2	6(12)	4	94	(25)	79	37	5	38	2	2	12	11	2	11	1	1	
6.5	7	91	3	100	7	1	1	3	2	6(8)	4	92	(20)	83	48	11	41	3	2	13	14	4	12	1	1	0.5
11.0	1.5	60	2	100	8	1	1	3	2	7(5)	4	91	(16)	87	60	20	50	6	3	14	19	7	14	2	2	2

Table 10. Collisional activation spectra of m/z 69 $[C_4H_5O]^+$ ions (from compound 3, Table 4) as a function of collision gas pressure

^a Abundances relative to the base peak = 100%.

^b Values in parentheses refer to the intensities of MI decompositions in the spectra, which were run with a gas cell voltage of -320 V.

intensity distributions of the CA spectra do not change significantly within this range of pressures.

using the procedure described below for the synthesis of the labelled analogues.

Synthesis of the unlabelled compounds

The purity and where necessary, the structure of the compounds synthesized was checked by NMR spectroscopy.

3-Methoxy-1-butyne $(HC \equiv C - CH(CH_3)OCH_3)$ was prepared from 1-butyne-3-ol using dimethyl-sulphate or methyl iodide (see synthesis of ¹³C labelled analogue) as a methylating agent.⁹

1-Methylthio-1-methoxy propyne (HC=C-CH $(SCH_3)OCH_3)$ was prepared by the method of Hommes and Brandsma.¹⁰

1,1-Dimethoxy propyne $(HC \equiv C - CH(OCH_3)_2)$ was synthesized by the procedure described in Ref. 8 for 1,1-diethoxy propyne employing methyl orthoformate instead of ethyl ortho-formate (b.p. 112 °C/ 760 mm, n_{D}^{20} 1.4138, yield 60%.)

1-Methoxy-1-iodo propadiene $(CH_2 = C = C(I)$ -OCH₃) was a gift from Mr J. Oostveen (Department of Organic Chemistry.)

3-Methoxy-1,2-butadiene $(CH_2 = C = C(CH_3)OCH_3)$. To a solution of ethyl lithium (0.1 mol) in dry ether (80 cm³) was slowly added (nitrogen atmosphere) 0.1 mole methoxy propadiene at -60 °C. After raising the temperature to -30 °C, CH₃I (6.5 cm³) in ether (50 cm³) and hexamethyl phosphoric acid triamide (HMPT, 10 cm³) were slowly added. The mixture was agitated for 1 h and subsequently poured into ice water (100 cm^3) . The aqueous layer was extracted three times with ether (50 cm^3) and the combined organic layers were dried over potassium carbonate. Distillation yielded a colourless liquid (b.p. $26 \,^{\circ}C/138 \,\text{mm}, n_{D}^{20} \,^{1}1.4314$, yield 80%.)

The halogenated methyl propargyl ethers IC=C-**CH₂OCH₃** (b.p. $34 \degree C/0.07 \text{ mm}$, n_D^{20} 1.5163, yield 70%), **BrC=C-CH₂OCH₃** (b.p. 30 °C/15 mm, n_D^{20} 1.4684, yield 80%) and CIC=C-CH₂OCH₃ (b.p. 66 °C/50 mm, n_D^{20} 1.4231, yield 70%) were prepared from $LiC \equiv C - CH_2OCH_3$ following the general procedure described in Ref. 8 for the synthesis of halogenated acetylenes employing iodine, bromine and chlorosulphonic acid as halogen donors.

1-Methoxy-2-butyne⁹ (CH₃C \equiv C–CH₂OCH₃) was prepared from LiC \equiv C–CH₂OCH₃ and CH₃I. The compound was also synthesized from 2-butyn-1-ol

2,5-Dihydrofuran was purchased from Merck. Its

double bond isomer 2,3-dihydrofuran was obtained therefrom by the method reported by Paul et al.¹¹

1-Methoxy-1,2-butadiene ((CH₃)HC=C=CHO-CH₃) was synthesized from 1,1-dimethoxy propyne analogous to the procedure described by Tadema et *al.*¹² (b.p. 77 °C/760 mm, n_D^{20} 1.4308, yield 40%.) **1-Methoxy-1,3-butadiene** (H₂C=CH-CH=CHO-

 $(CH_3)^{13}$ was a gift from Dr R. H. Everhardus. 3-Methoxy propyne $(HC \equiv C - CH_2OCH_3)$, methoxy propadiene (H₂C=C=CHOCH₃), 3-ethoxy propyne $(HC \equiv C - CH_2 OCH_2 CH_3)$ and ethoxy propadiene $(H_2C=C=CHOCH_2CH_3)$ were synthesized as described in Ref.⁹.

1-Iodomethoxy-2-propyne $(HC \equiv C - CH_2OCH_2I)$. A vigorous stream $(2-31 \text{ min}^{-1})$ of gaseous HI was introduced to a solution of paraformaldehyde (15 g) and propargyl alcohol (30 cm³). Introduction of HI and stirring were stopped when copious fumes evolved. The mixture was extracted four times with ether/pentane $(2:5, 10 \text{ cm}^3)$. The combined organic lavers were dried over magnesium sulphate. After removal of the drying agent careful fractional distillation yielded a sample (5 ml, b.p. 32 °C/0.07 mm) containing 80% 1-iodomethoxy-2-propyne and 20% propargyl iodide. This sample was used without further purification. Butadiene monoxide and 4,5dihydro-2-methylfuran were obtained from Aldrich Europe and used without further purification.

Synthesis of the deuterium and ¹³C labelled ethers 3-ethoxy- d_5 , and 3-methoxy-¹³C 3-Methoxy-d₃, labelled ethers

The acetylenic alcohols $R_1C \equiv C - CH(R_2)OH$ (10 mmol; $R_1 = H/R_2 = H$; $R_1 = CH_3/R_2 = H$; $R_1 =$ $H/R_2 = CH_3$) which were a gift from Dr L. Brandsma were added in a nitrogen atmosphere to a mixture (room temperature) of sodium hydride (10 mmol) and dimethylformamide (DMF, 10 cm^3). The mixture was stirred for 2 h at 40 °C. After cooling to 0 °C CD₃I, C₂D₅I (Merck, Sharp and Dohme 99.5 and 99 atom % D respectively or ${}^{13}CH_3I$ (Prochem, 96.8 atom%) (8 mmol) was added. After 1 h of stirring at room temperature the yellow coloured reaction mixture was filtered. Careful distillation at atmospheric pressure yielded pure samples with the expected isotopic contents. (The purity of the compounds was checked by mass spectrometry against samples of the unlabelled compounds prepared in the same way.)

A small sample of **methoxy-d_3 propadiene** was obtained by isomerization⁹ of 3-methoxy- d_3 propyne.

The **D**—**C**==**C**— labelled ethers were prepared by exchange of the acetylenic ethers (25 mmol) (vigorous agitation for 2 h at room temperature) with a solution of NaOD in D_2O (1 M, 25 cm³). After removal of the aqueous layer the procedure was repeated with a fresh sample of the NaOD/ D_2O solution. Subsequent distillation yielded samples with deuterium contents better than 97%. Prolonged storage in the mass spectrometer inlet system was found to result in a noticeable loss of the label.

3-Methoxy propyne-1,3- d_2 (DC=C-CHDOCH₃). To a solution of LiC=C-CH(Li)OCH₃. (0.1 mol, prepared from 3-methoxy propyne (0.1 mol) and ethyl lithium (0.2 mol in 180 cm³ of dry ether) at -15 °C) was added excess D₂O at -5 °C. Distillation yielded a mixture of 90% 3-methoxy propyne-1,3- d_2 and 10% 3-methoxy propyne 1- d_1 .

3-Methoxy propyne-3,3- d_2 (HC=C-CD₂-OCH₃). To a solution of LiAlD₄ (Aldrich Europe 98 atom % D, 10 mmol) in dry ether (10 cm³) was added

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(nitrogen atmosphere) ethyl propiolate (Aldrich Europe, 10 mmol in 10 cm^3 of dry ether). The mixture was refluxed for 1 h. After cooling to 0 °C a small amount of powdered NaOH (40 mg) was added along with CH₃I (10 mmol). The reaction mixture was filtered and carefully distilled. Yield: 60% of the d_2 labelled ether with a deuterium content of 96 atom%.

Methoxy propadiene-1- d_1 (H₂C==C=CDOCH₃). To a solution of H₂C==C=C(Li)OCH₃ (0.1 mol, prepared from methoxy propadiene (0.1 mol) and ethyl lithium (0.1 mol in 90 cm³ of dry ether) at -15 °C) was added excess D₂O at -5 °C. Distillation yielded a pure sample. Yield 90%, deuterium content better than 97%.

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