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Unsaturated Ketenes: A Study of their Formation and Rearrangement by Tandem Mass Spectrometry and Low-temperature Infrared Spectroscopy

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A combination of collisional activation mass spectrometry and low-temperature infrared spectroscopy has been used to monitor the production and isomerization of vinyl- and methylene-ketenes. Vinyl- and 2-propenyl-ketenes were produced by flash vacuum pyrolysis of β,γ -unsaturated acid chlorides. Vinyl(carboxyl)ketenes, vinylketenes and methyleneketenes were obtained from Meldrum's acid derivatives (5-alkylidene-1,3-dioxane-4,6-diones). The formation of methyleneketenes by pyrolysis of α,β -unsaturated acid chlorides is only indicated in the mass spectrometry experiments. Carbonylcyclopropane was obtained by pyrolysis of cyclopropylcarbonyl chloride or the corresponding Meldrum's acid derivative. The methyleneketenes isomerize to vinylketenes in the gas phase, particularly under conditions involving long contact times. Carbonylcyclopropane thermally decarbonylates to allene, not methylacetylene. Molecular ions of vinylketenes are obtained via pyrolysis of either acid chlorides or Meldrum's acid derivatives. Molecular ions of alkylmethyleneketenes are obtained pure only by electron impact induced fragmentation of Meldrum's acid derivatives.

INTRODUCTION

Ketenes and, in particular, alkylideneketenes are highly reactive compounds which, in many instances, cannot be isolated under 'ordinary' experimental conditions.¹ On the other hand, it was recently concluded that the corresponding radical cations are very stable in the gas phase.² Thus, an analysis of fifteen $[C_4H_4O]^+$ isomers using collisional activation (CA) mass spectrometry and ionic heats of formation indicated a greater stability of the ketene structures compared with isomeric and tautomeric ions.²

The determination of the structures of the ions formed by electron impact (EI) induced fragmentation is not free from complications. For example, citraconic anhydride has been proposed² as a precursor of ionized ethylideneketene, $[CH_3-CH=C=C=O]^+$, but in a more recent paper by the same authors,³ the fragmentation mechanism was found to be more complex and the final ion structure different.

Furthermore, there are ambiguities regarding the production of the neutral methyleneketenes. Thus, although isopropylideneketene, $(CH_3)_2C=C=O$, could be directly observed by infrared (IR) spectroscopy and trapped with aniline, this was not true for ethylideneketene, $CH_3-CH=C=O$, which gave instead a trapping product apparently derived from

vinylketene, $CH_2=CH-CH=C=O$.⁴ The use of photoelectron spectroscopy (PES)⁵ permitted the direct detection of ethylideneketene and its rearranged isomer, vinylketene, but a third ketene expected⁶ in this system, namely vinyl(carboxy)ketene, was not considered. As for carbonylcyclopropane, $CH_2CH_2C=O$, the IR observation of this compound in a thermal system has been reported,⁷ but in a different study using another precursor it was found that only the isomeric vinylketene was produced under thermal conditions.⁸

In order to remove some of these ambiguities we have investigated the direct production of these ketenes by flash vacuum pyrolysis (FVP)⁹ coupled with tandem mass spectrometry¹⁰ and low-temperature IR spectroscopy. The results, reported herein, demonstrate the power of this methodology in elucidating the structures of both neutral and ionized ketenes (for a study of alkylketenes by FVP mass spectrometry see Ref. 11).

RESULTS AND DISCUSSION

Vinylketene (2)

Ketenes were generated by FVP of acid chlorides¹² and Meldrum's acid derivatives.¹ The electron impact (EI) mass spectra, before and after pyrolysis, are

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Table 1. Mass spectra of acid chlorides **1**, **3** and **8** and dioxanes **5** and **9** before and after pyrolysis^a

Compound	T (K)	$m/z = 104 ([M]^{++})$	78	76	69	68	42	41	40	39	38	37	36	35	28	27	26				
1	430	0.8	14	45	48	10	20	<u>100</u>	11	67	23		47								
	930				3	55	6	3	26	54	40		<u>100</u>	9	17						
3	430	0.5	2	6	<u>100</u>		11	64	8	61	12					10	6				
	980				1	1	2	7	<u>100</u>	80	48	21	81	7	66						
8	430	0.9	0.7	2	<u>100</u>			60	8	61	15	9	12	5							
	880				9	8		7	60	59	47	16	<u>100</u>	13	41						
			$m/z = 170 ([M]^{++})$			155	126	113	112	69	68	59	58	44	43	41	40	39	38	37	28
5	430	0		16	4	39		10	67	10			<u>100</u>	8	83	24					
	830								15		38	86	<u>100</u>	5	83	70	24	17	52		
9	430	0	10		31	32		52	11	21	34	<u>100</u>				17	20				
	600					7		27		45	80	<u>100</u>	4	11	31	8	6	8			
	830							15		46	83	<u>100</u>	3	23	29	9	6	17			

^a Relative intensities of the molecular ions ($[M]^{++}$) and the 10 principal fragment peaks are given.

collected in Table 1, and the CA mass spectra in Table 2. Because the most significant spectral differences are found in the region m/z 54–49, two sets of normalization were used for the spectra given in Table 2: (i) normalization with respect to the most intense peak produced by CA and (ii) separate normalization with respect to the most intense peak in the m/z 54–49 region.

The formation of vinylketene (**2**) from 3-butenoyl chloride (**1**) is complete at 930 K as seen from the disappearance of the molecular ion and the appearance of a strong signal at m/z 68 in the normal mass spectrum (Table 1). In the CA spectrum of $[2]^{++}$ (Table 2) the intensity fluctuations in the m/z 54–49 region are less pronounced than for the isomers **4** and **8** to be described below, and the absolute intensities of these peaks are rather low. Apart from some variations in relative intensities, this CA spectrum is very similar to that obtained by Burgers *et al.*² by ionization of the ether $\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{OC}_2\text{H}_5$ followed by decomposition. The assignment of the CA spectrum of the vinylketene radical cation ($[2]^{++}$) as

derived from **1** is corroborated by the previous PES investigation.^{5,13}

Carbonylcyclopropane (**4**)

A second $\text{C}_4\text{H}_4\text{O}$ isomer, carbonylcyclopropane (**4**), is produced by pyrolysis of both the acid chloride **3**¹³ and the dioxane derivative **5**⁶ (Scheme 1). The two CA spectra are very similar in the m/z 54–49 region (see Table 2) and are assigned to the molecular ion $[4]^{++}$. Pyrolysis of the dioxane **5** is complete at 830 K, and since the CA spectrum of m/z 68 is virtually identical with that obtained by direct ionization (i.e. without pyrolysis), it is concluded that **5** gives $[4]^{++}$ both by EI-induced fragmentation and by pyrolysis via ionization of **4** (Scheme 1).

The thermolysis of cyclopropylcarbonyl chloride (**3**) is less facile than that of either **1** or **5**: even at 980 K the occurrence of m/z 69 (1%) signals the presence of the unreacted starting material **3** (Table 1). Furthermore, the low intensity of m/z 68 ($[4]^{++}$) compared to

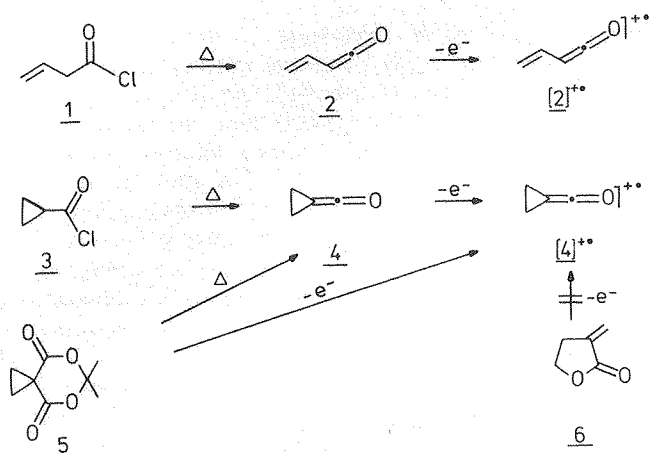
Table 2. Collisional activation (CA) mass spectra of $[\text{C}_4\text{H}_4\text{O}]^{++}$ ions^a

Precursor	Method	$m/z = 54$	53	52	51	50	49	(42)	41	(40)	39	38	37	29	28	27	26	25
1	EIIF ^b	6	6	1	3	6	3	(23)	11	(114)	100	30	16	1	1	4	6	2
		99	96	24	55	100	50											
	FVP, 930 K	6	5	1	3	6	3	(23)	8	(82)	100	28	18	1	1	4	6	2
5	EIIF ^b	100	83	17	54	100	63											
		10	22	2	5	7	3	2	—	(270)	100	35	20	1	3	2	9	3
	FVP, 830 K	45	100	9	22	29	15											
3	EIIF ^b	7	20	2	4	7	3	2	—	(274)	100	32	20	1	3	2	9	3
		42	100	11	22	35	15											
	FVP, 930 K	8	19	2	5	7	3	(22)	4	(261)	100	30	17	1	2	3	8	3
9	EIIF ^b	41	100	13	27	33	19											
		—	100	5	3	6	3	(6)	3	(159)	68	28	20	1	2	2	4	4
	FVP, ° 900 K	—	100	5	3	6	3											
8	EIIF ^b	14	42	4	10	17	10	(24)	9	(115)	100	32	18	1	1	4	6	2
		32	100	8	23	39	23											
	FVP, 930 K	4	61	4	4	7	4	(19)	4	(181)	100	48	19	1	2	4	6	4
		4	100	6	4	8	4											

^a Abundancies are normalized with respect to the most intense peak induced by collision (upper line). Peaks produced by unimolecular processes (non-collisionally) are given in parentheses. The peaks in the region m/z 54–49 are renormalized with respect to the most intense signal in this group (lower line).

^b EIIF = electron impact induced fragmentation.

^c FVP = flash vacuum pyrolysis.



Scheme 1

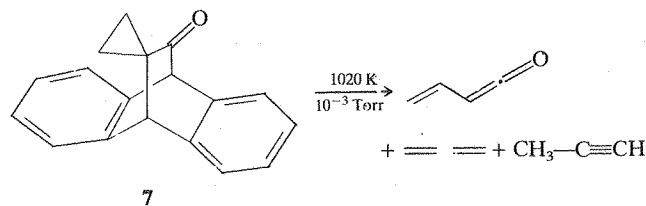
m/z 40 ($[C_3H_4]^+$) indicates that the ketene 4 may undergo decarbonylation to give allene under these reaction conditions. This is confirmed by the IR investigation reported below as well as by the previous PES study.¹³

In view of the high temperature required for the pyrolysis of 3, it might be expected that 4 might also isomerize in part to vinylketene (2).¹³ An indication that this is so when 4 is produced from 3 is seen in the high intensity of m/z 42 in the CA spectrum: this ion is typical of $[2]^+$ (Table 2). The abundances of the other peaks in the m/z 54–49 region are not greatly affected due to the very small contribution of these ions in the CA spectrum of pure vinylketene. However, no evidence for the rearrangement $4 \rightarrow 2$ was observed by IR spectroscopy of the pyrolysate from 5 at 770–1070 K.

The pyrolysis of 5 was further examined using low-temperature IR spectroscopy (see Experimental section).† At pyrolysis temperatures between 770 and 1070 K/ 10^{-4} Torr, two peaks were observed at 2154 and 2135 cm^{-1} in the cold pyrolysis product. In the high-temperature range, an additional peak at 1948 cm^{-1} , ascribed to the formation of allene was observed. These absorptions are undoubtedly due to the same species as reported previously by Brown *et al.*⁷ (2145, 2125, 1940 cm^{-1}), and the frequency shifts may be attributed to the use of different spectrometers. The ratio of the intensities of the 2154 and 2135 cm^{-1} bands remained constant over the temperature range, and the two bands disappeared in concert on warm-up. Therefore, they are both assigned to carbonylcyclopropane (4), which in recent microwave spectroscopic work¹⁴ was definitively identified as a major pyrolysis product of 5. No infrared spectroscopic evidence for an isomerization of 4 to 2 (2118 cm^{-1}) could be found.

At this point it is necessary to enquire whether the 2154 cm^{-1} band could not be due instead to methylacetylene, reported to absorb at 2146–2151 cm^{-1} .¹⁵ This question is all the more important as an alternative generation of 4 by pyrolysis of the

anthracene derivative 7 has been reported to give vinylketene (2, 35%), allene (13%) and methylacetylene (52%).⁸



For this reason, the total pyrolysate from 5 (1070 K) was isolated in a cold trap and the volatile constituents distilled into a second trap from where they were expanded into a gas cell for IR spectroscopy. The IR spectrum of these gases demonstrated the presence of allene (1956 cm^{-1} ; cf. Ref. 16), whereas methylacetylene was undetectable. In an identical experiment, the volatile pyrolysis product was distilled into an NMR tube and the 1H NMR spectrum ($CDCl_3$) demonstrated the exclusive presence of allene and acetone in a 1:1 ratio. Methylacetylene was not detectable. Consequently, the rearrangement reported⁸ for 7 does not occur under our conditions in the pyrolysis of 5, and the ketene 4 remains the sole candidate for the 2154 and 2135 cm^{-1} bands.

The pyrolysis of cyclopropylcarbonyl chloride (3) was similarly examined by IR spectroscopy. At 1070 K allene was obtained quantitatively. Again, methylacetylene was not detectable.†

Ionized carbonylcyclopropane ($[4]^+$) has also been produced by pyrolysis mass spectrometry of the mixed anhydride of cyclopropanecarboxylic and trifluoroacetic acids.¹⁸ Yet another precursor of $[4]^+$, namely α -methylene- γ -butyrolactone (6),² is, however, suspect: the relative intensities of the m/z 54–49 peaks in the CA spectrum of m/z 68 observed by us for 6 were 100, 88, 17, 29, 15 and 24% respectively. These ratios do not correspond to any simple mixture of ionized ketenes.

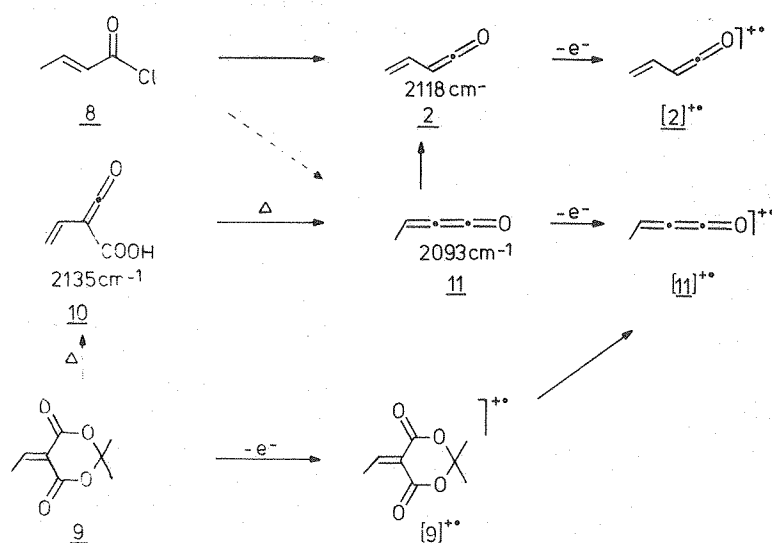
Ethylideneketene (11) and vinyl(carboxy)ketene (10)

The synthesis of a third isomer, ethylideneketene (11), was attempted by FVP of the acid chloride 8 and the dioxane 9 (Scheme 2). The EI-induced fragmentation (without pyrolysis) of $[9]^+$ gave a CA spectrum attributed to ionized ethylideneketene ($[11]^+$). Indeed, the base peak corresponds to the loss of a methyl group, where the loss of a CH_2 group (m/z 54) was not observed, and the ion m/z 42, characteristic of vinylketene (2), was of low abundance (Table 2).

The pyrolysis of 9 appeared to lead to more complex results. At first sight, the CA spectrum of the m/z 68 ions of pyrolysed 9 appears to be a superposition of the spectra of vinylketene and 9 (without pyrolysis): one observes an intense m/z 42 peak characteristic of vinylketene as well as m/z 53 and 52 peaks resembling those obtained from 9 itself. A more thorough IR investigation (see below) led to

† Due to different designs of the pyrolysis reactors, necessitated by the different analytical methods applied, the temperatures used in mass spectrometry and IR investigations need not be identical and should not be directly compared.

† The formation of cyclopropane from 3 was reported in a previous photoelectron spectroscopic study.¹⁷ However, in the full paper,¹³ the compound was correctly identified as allene.



Scheme 2

the observation of a third compound, vinyl(carboxy)ketene(10). Indeed, a careful analysis of the mass spectra given in Table 1 shows, at 600 K, the disappearance of the peaks characteristic of the dioxane 9 (e.g. m/z 155, 113) except the peak at m/z 112 (7%; loss of acetone from 9). The structures of this ion (m/z 112) are clearly different at low and high temperatures as seen in the CA spectra (Fig. 1). Decarbonylation predominates at low temperatures, whereas losses of methyl (m/z 97) and carboxyl (m/z 67) become important fragmentation pathways at high temperature.

The identification of the m/z 112 peak as the molecular ion of vinyl(carboxy)ketene(10) was

achieved using low-temperature IR spectroscopy. On pyrolysis of 9 at 570–770 K acetone was formed (1705 cm^{-1}) together with a ketene absorbing at 2135 cm^{-1} and displaying a strong, broad band at $2500\text{--}3400\text{ cm}^{-1}$, typical of carboxylic acids, as well as new carbonyl and C=C double-bond absorptions at 1660 and 1620 cm^{-1} . No CO_2 (2336 cm^{-1}) was formed under these conditions. On the basis of our previous work with cyclopentylidene-Meldrum's acid,⁶ this ketene is identified as 10. Furthermore, 10 has been trapped with methanol to give methyl vinylmalonate.¹⁹

Vinyl(carboxy)ketene (10) could be observed by IR at pyrolysis temperatures up to 970 K. However, already at 870 K two additional ketenes, absorbing at

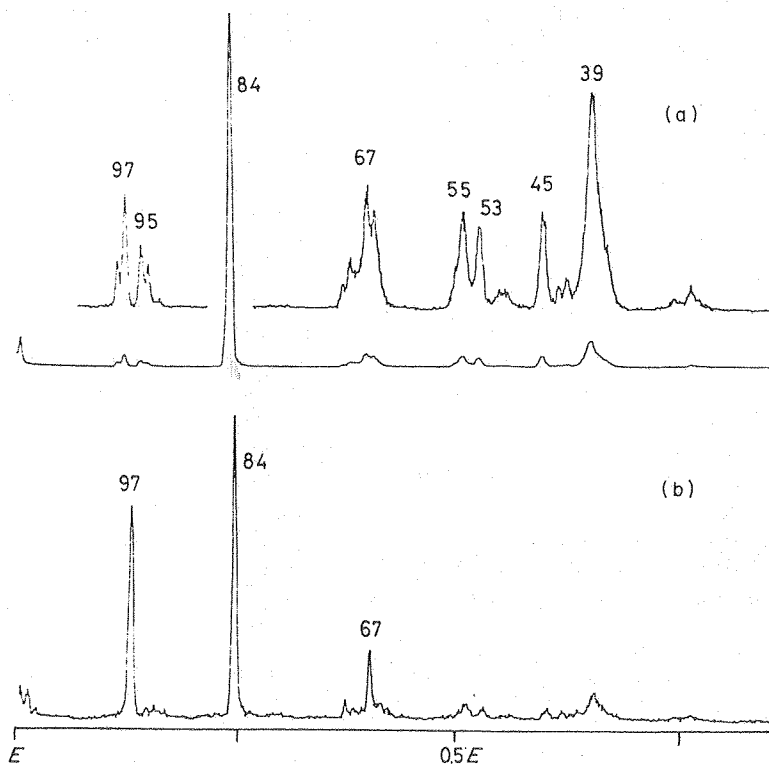


Figure 1. CA MIKE spectra of the m/z 112 ions from the dioxane 9 at (a) 430 K and (b) 680 K.

2093 and 2118 cm^{-1} , appeared. According to our experience with other systems,⁶ these are assigned to **11** and **2**, respectively (Scheme 2). This assignment is supported by the fact that pyrolysis at more severe conditions (double pyrolysis, first at 870, then at 1070 K) gave only **2**.

Ethylideneketene (**11**) has not previously been observed by IR spectroscopy, and attempted trapping with aniline vapour gave the anilide derived from vinylketene (**2**) only.⁴ Nevertheless, we have successfully trapped **11** with aniline vapour in the pyrolysis of **9**.¹⁹

In the previous photoelectron spectroscopic investigation of the pyrolysis of **9**, the observation of **11** and its facile isomerization to **2** was reported.⁵ The facts that, in our hands, the carboxyketene **10** is virtually cleanly formed at 770 K, and that ethylideneketene (**11**) is quite long-lived, surviving double pyrolysis at 870 and 970 K, indicate however that **10** should also have been observable by photoelectron spectroscopy. It seems likely that the bands previously assigned⁵ to **11** were in fact due to **10**, and that those belonging to **11** went undetected. Indeed, the published photoelectron spectra⁵ do exhibit unassigned bands. This complicated system (Scheme 2) is a good example of the necessity of using at least two different methods in identifying unusual and short-lived molecules.

In one attempt to synthesize ethylideneketene by pyrolysis of *E*-2-butenoyl chloride (**8**), we clearly observed the formation of $[\mathbf{11}]^{+\bullet}$ in a mixture with $[\mathbf{2}]^{+\bullet}$ (intense peak at m/z 42; Table 2). However, the formation of **11** from **8** was observed neither in the PES study⁶ nor by IR, where the 2118 cm^{-1} band was the only ketene absorption found in the temperature range 770–970 K. While the origin of the presumed

$[\mathbf{11}]^{+\bullet}$ in the pyrolysis mass spectrum of **8** is uncertain, one possible explanation would be a high efficiency of fragmentation of the $[\mathbf{11}]^{+\bullet}$ ions, thus allowing their detection by mass spectrometry even if their concentration is very low.

The above results allow us to assign the CA spectra of the three isomeric ketenes, **2**, **4** and **11**. The three spectra are shown in Fig. 2.

2-Propenylketene (**15**) and 2-propylideneketene (**16**)

The isomeric acid chlorides **12** and **13** and the dioxane **14** were used as precursors for 2-propenylketene (**15**) and 2-propylideneketene (**16**) (Scheme 3). The extents of pyrolysis at various temperatures can be measured by the ion intensity ratios $[\text{C}_5\text{H}_6\text{O}]^{+\bullet}/[\text{M} - \text{Cl}]^+$ for **12** and **13** and $[\text{M} - \text{acetone}]^{+\bullet}/[\text{C}_5\text{H}_6\text{O}]^{+\bullet}$ for **14**. These data, as well as mass-analysed ion kinetic energy (MIKE) and CA spectra of the $[\text{C}_5\text{H}_6\text{O}]^{+\bullet}$ ions (m/z 82) are collected in Table 3.

On the basis of the results obtained with **9** (*vide supra*), it is plausible that $[\mathbf{16}]^{+\bullet}$ is formed by EI-induced fragmentation (without pyrolysis) of **14**. The MIKE spectrum of the $[\text{C}_5\text{H}_6\text{O}]^{+\bullet}$ ions of **14** is characterized by two intense fragmentations, corresponding to loss of CH_3 and CO , the former predominating. At 830 K **14** undergoes pyrolysis, and the intensity ratio for these two peaks is inverted. At still higher temperatures, the loss of CH_3 decreases and becomes negligible; the spectrum is now similar to that produced from **12**, and it is reasonable to postulate the sequence of events $\mathbf{14} \rightarrow \mathbf{16} \rightarrow \mathbf{15}$ at 1180 K. The changes observed in the CA spectrum as a function of temperature confirm this postulate. The behaviour of the acid chloride **13** is identical with that

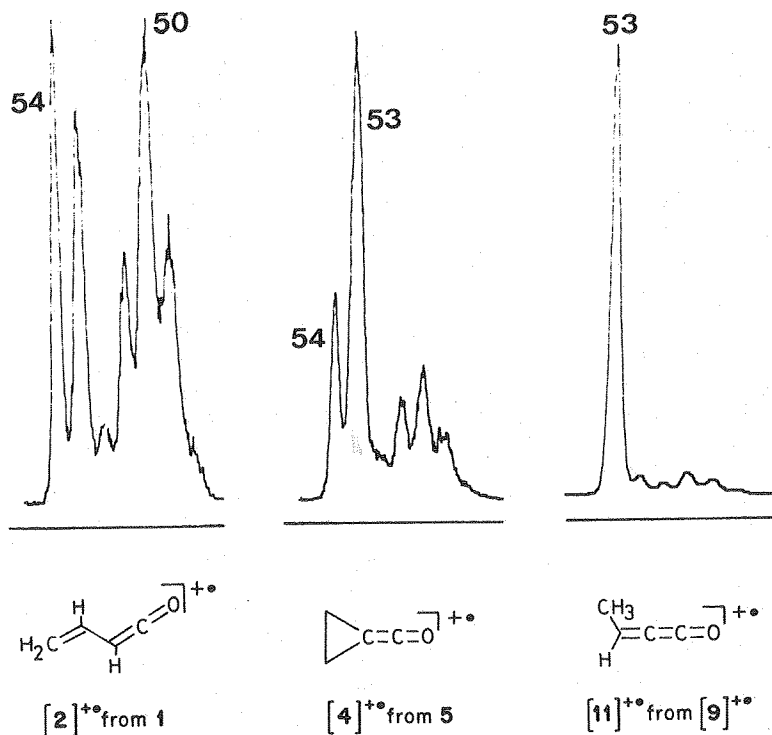
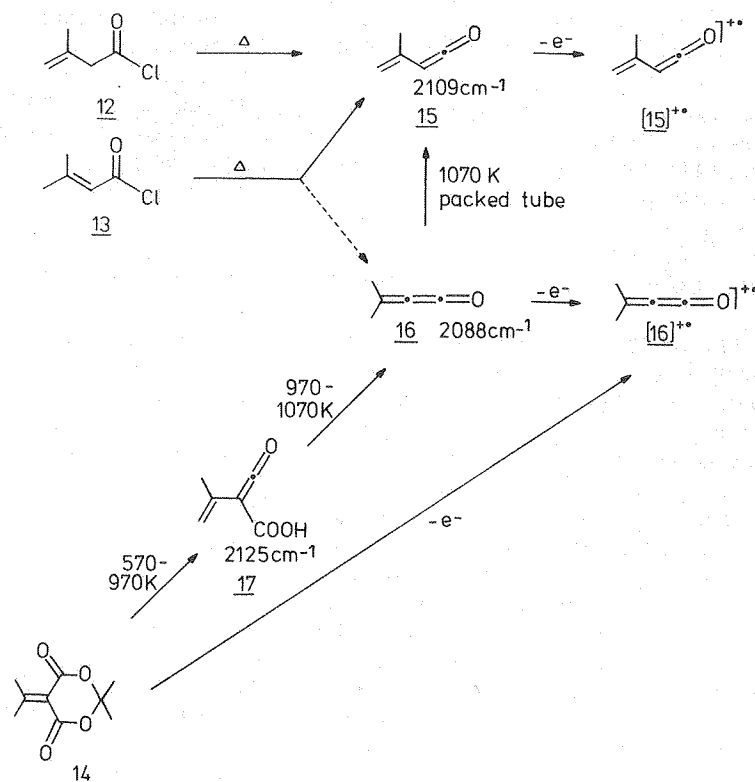


Figure 2. Characteristic parts of the CA mass spectra of the $[\text{C}_4\text{H}_4\text{O}]^{+\bullet}$ ions $[\mathbf{2}]^{+\bullet}$, $[\mathbf{4}]^{+\bullet}$ and $[\mathbf{11}]^{+\bullet}$.



Scheme 3

of the dioxane **14** with the sole exception that no ketene is produced without pyrolysis (430 K).

The mass spectral data may be summarized as follows: 2-propenylketene radical cation ($[15]^{\bullet+}$) is produced by pyrolysis of **12** followed by ionization; 2-propylideneketene radical cation ($[16]^{\bullet+}$) is produced by EI-induced fragmentation of **14** and by pyrolysis/ionization of either **13** or **14**; **16** isomerizes to **15** above c. 980 K.

Further information was obtained using low-temperature IR spectroscopy. At the lowest pyrolysis temperature (570–670 K) only one ketene (2125, 2600–3400, 1690, 1590 cm^{-1}) was observed in

the pyrolysis of **14**. On the basis of the IR spectrum and trapping with methanol,¹⁹ this is identified as **17** (Scheme 3).

At 970 K the main pyrolysis product was a ketene absorbing at 2088 cm^{-1} and assigned as **16**. It was almost the sole product at 1070 K.

In order to observe the rearranged vinylketene (**15**), more severe conditions had to be used. The pyrolysis tube was filled with a few pieces of quartz to prolong the contact times. At 870 K all three ketenes could be seen at approximately equal intensity. At 1070 K, the peak attributed to **17** had only half the intensity of the other two, and the same situation was observed at

Table 3. Mass spectral characteristics of the ions $[\text{C}_5\text{H}_6\text{O}]^{\bullet+}$ produced from **12**, **13** and **14**

Precursor	T(K)	MIKE ^a															CA ^b										Intensity ratio ^c	
		<i>m/z</i> = 67	54	68	(67)	65	54	53	51	50	42	41	39	38	37	28	27	26										
12	430	4	100	5	(48)	10	(375)	76	19	25	15	12	<u>100</u>	23	11	15	25	6		<i>m/z</i> 82/ <i>m/z</i> 83								
	880	3	100	6	(38)	8	(290)	69	15	24	12	9	<u>100</u>	23	9	14	25	6		0.14								
	980	<1	100	6	(27)	8	(267)	75	19	25	14	9	<u>100</u>	23	8	14	24	6		13								
																				13								
13	430	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		<i>m/z</i> 82/ <i>m/z</i> 83								
	880	21	100	5	(156)	10	(293)	69	27	25	10	8	<u>100</u>	23	11	13	24	6		0.06								
	980	5	100	5	(53)	8	(333)	75	27	24	11	9	<u>100</u>	22	10	13	24	4		3.3								
	1140	<1	100	5	(23)	7	(323)	70	26	24	12	9	<u>100</u>	19	9	13	26	6		4.3								
14	430	100	60	—	(1115)	37	(236)	64	35	33	11	8	<u>100</u>	36	19	10	26	7		<i>m/z</i> 82/ <i>m/z</i> 126								
	830	88	100	—	(642)	26	(315)	76	37	35	14	12	<u>100</u>	31	17	14	32	8		0.8								
	980	16	100	4	(109)	11	(284)	78	25	25	11	8	<u>100</u>	24	10	14	25	5		200								
	1180	6	100	4	(38)	5	(253)	64	25	23	10	7	<u>100</u>	20	8	13	23	6		>200								

^a Unimolecular fragmentations.

^b Collisionally induced fragmentations.

^c Intensity ratios from normal mass spectrum (see text).

870 K using a fully packed tube. The pyrolysis at 1070 K in a fully packed tube gave only one ketene, **15**, absorbing at 2109 cm^{-1} .

16 has been reported previously by Brown *et al.*,⁴ where the frequency was given as 2100 cm^{-1} . Trapping with aniline vapour gave products derived from both **16** and **15**.⁴

CONCLUSION

Molecular ions of alkylideneketenes are best obtained by EI-induced fragmentation of Meldrum's acid derivatives. Vinyl(carboxy)ketenes are obtained by flash vacuum pyrolysis of Meldrum's acid derivatives under mild conditions. The vinyl(carboxy)ketenes decarboxylate to alkylideneketenes and/or vinylketenes.⁶ Alkylideneketenes possessing tautomerizable C—H bonds tend to isomerize to the thermodynamically more stable vinylketenes under more drastic conditions involving prolonged contact times. The complementary use of CA mass spectrometry and low-temperature IR spectroscopy is well suited for the investigation of flash vacuum pyrolysis reactions. This study also demonstrates the mandatory use of *at least two different methods* in the elucidation of reaction pathways involving short-lived molecules.

EXPERIMENTAL

Mass spectra were recorded on a triple sector (*E/B/E*) mass spectrometer²⁰ using an accelerating potential of 8 kV and an ionizing energy of 70 eV (100–500 μA). The CA spectra pertain to collisionally

induced dissociations occurring in the third field-free region. Helium was used as the collision gas at a pressure of c. 10^{-4} Torr. Most pyrolysis experiments were carried out using a furnace connected with the ion source through the glass inlet system as previously described.¹¹ For pyrolyses requiring very short contact times the furnace consisted of an electrically heated quartz tube (4 cm long, i.d. 0.4 cm) situated within 2 cm of the ion source.

IR spectra were recorded on a Perkin–Elmer 281 instrument. The pyrolysis unit used here consisted of a 10 cm quartz tube (i.d. 0.8 cm) divided into two heating sections, the first (5 cm) serving to sublime solid starting materials, the second (5 cm) being the actual pyrolysis reactor.^{6,21} The pyrolysis products were condensed on BaF_2 windows conductively cooled to -196°C for IR observation and situated within 2 cm of the exit of the pyrolysis tube. Due to the different dimensions of the reactors used for mass spectrometric and IR measurements, the temperatures required to obtain a particular reaction may differ in the two sets of experiments.

The starting materials were synthesized according to literature procedures,^{12,22,23} and purified by recrystallization or distillation. The purity of the samples was ascertained by thin-layer chromatography, and their identity by ^1H NMR spectroscopy.

Acknowledgements

The financial support of the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the University of Queensland is gratefully acknowledged. We thank Dr J. K. Terlouw (Utrecht) for communicating the contents of Refs 3 and 18 prior to publication and for numerous discussions. An initial sample of compound **13** was kindly put at our disposal by Dr J. Hanuise (Bruxelles).

REFERENCES

1. R. F. C. Brown and F. W. Eastwood, *The Chemistry of Ketenes and Allenes*, ed. by S. Patai, p. 757, Wiley, New York (1980).
2. P. C. Burgers, J. L. Holmes, F. P. Lossing, A. A. Mommers, F. R. Povel and J. K. Terlouw, *Can. J. Chem.* **60**, 2246 (1982).
3. J. K. Terlouw, J. L. Holmes and F. P. Lossing, *Can. J. Chem.* **61**, 1722 (1983).
4. R. F. C. Brown, F. W. Eastwood and K. J. Harrington, *Aust. J. Chem.* **27**, 2373 (1974).
5. S. Mohmand, T. Hirabayashi and H. Bock, *Chem. Ber.* **114**, 2609 (1981).
6. C. Wentrup, G. Gross, H.-M. Berstermann and P. Lorenčák, *J. Org. Chem.* **50**, 2877 (1985).
7. G. J. Baxter, R. F. C. Brown, F. W. Eastwood and K. J. Harrington, *Tetrahedron Lett.* 4283 (1975).
8. J. L. Ripoll, *Tetrahedron* **33**, 389 (1977).
9. R. F. C. Brown, *Pyrolytic Methods in Organic Chemistry*, Academic Press, New York (1980).
10. F. W. McLafferty (Ed.), *Tandem Mass Spectrometry*, Wiley, New York (1983).
11. A. Maquestiau, R. Flammang and P. Pauwels, *Org. Mass Spectrom.* **18**, 547 (1983).
12. D. Borrmann, in *Houben-Weyl: Methoden der Organischen Chemie*, ed. by E. Müller, Vol. 7, Part 4, p. 52, Georg Thieme Verlag, Stuttgart (1968).
13. H. Bock, T. Hirabayashi and S. Mohmand, *Chem. Ber.* **114**, 2595 (1981).
14. R. D. Brown, P. D. Godfrey, B. Kleibömer, R. Champion and P. S. Elmes, *J. Am. Chem. Soc.* **106**, 7715 (1984).
15. P. N. Daykin, S. Sundaram and F. F. Cleveland, *J. Chem. Phys.* **37**, 1087 (1962).
16. J. Blanc, C. Brechner and R. S. Halford, *J. Chem. Phys.* **36**, 2654 (1962).
17. H. Bock, T. Hirabayashi, S. Modmand and B. Solouki, *Angew. Chem.* **89**, 106 (1977); *Angew. Chem. Int. Ed. Engl.* **16**, 105 (1977).
18. J. K. Terlouw, private communication.
19. C. Wentrup and P. Lorenčák, to be published.
20. A. Maquestiau, Y. Van Haverbeke, R. Flammang, M. Abrassart and D. Finet, *Bull. Soc. Chim. Belges* **87**, 765 (1978).
21. H.-W. Winter, Dissertation, Marburg (1980).
22. G. Swoboda, J. Swoboda and F. Wersely, *Monatsh. Chem.* **95**, 1283 (1964).
23. R. B. Wagner, *J. Am. Chem. Soc.* **71**, 3214 (1949).