Photoelectronic Study of the Flash Vacuum Pyrolysis (FVP) of Meldrum's Acid Derivatives: PE Spectra of (Alkoxymethylene)- and ((Alkylthio)methylene)ketenes[1]

F. Chuburu,[†] **S. Lacombe,**[†] **G. Pfister-Guillouzo,***[,†] **A. Ben Cheik,**[‡] **J. Chuche,**[‡] **and J. C. Pommelet**[‡]

Contribution from the Laboratoire de Physico-Chimie Moléculaire, URA CNRS 474, Université de Pau & des Pays de l'Adour, Avenue de l'Université, 64000 PAU, France, and the Laboratoire de Chimie Organique Physique, URA CNRS 459, Université de Reims, Faculté des Sciences, Moulin de la Housse, B.P. 347, 51062 REIMS France. *Received July 26, 1990. Revised Manuscript Received October 29, 1990*

Abstract: The (methoxymethylene)ketenes **6** and **7** and the cyclic alkylthio derivative **9**, generated by flash-vacuum pyrolysis of the corresponding substituted derivatives of Meldrum's acid, were characterized in the gas phase by photoelectron spectroscopy (PES). The experimental IP's arising from the ejection of an electron from the $\pi_{C=C}$ orbitals were determined and were shown to agree with previous results on parent and (alkylmethylene)ketenes. An interesting feature concerns the observation, for the methylmethoxy compound **7**, of different interconverting products at each pyrolysis temperature. The analysis of the PE spectra of these compounds supports Wentrup's mechanism: at 733 K a (carboxyvinyl)ketene **21** would be obtained which is converted at higher temperature (843 K) into the desired (methylmethoxymethylene)ketene (**7**). This latter, on further increase of the temperature (923 K), would give rise to the vinylketene **23**.

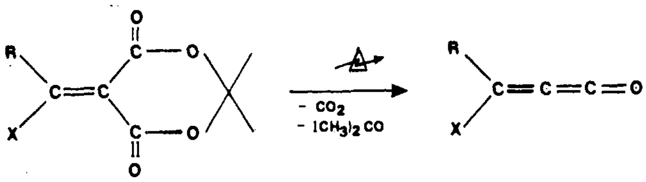
Introduction

The generation and spectroscopic characterization of methyleneketenes has been extensively studied[2-7] not only because of the presumable occurrence of these compounds in interstellar nebula[3] but also because of the peculiar "kinked" structure of propadienone.[4]

Unstable alkylideneketenes are efficiently generated by FVP of alkylidene derivatives of Meldrum's acid,[2] and this reaction has been previously used to record the first microwave spectrum of the parent compound methyleneketene (**1**)[3] (Scheme I). Further high-resolution microwave spectra of **1** were obtained by FVT of acrylic anhydride[4] and definitively established the bent structure of **1**. However different attempts to record the photoelectronic spectrum of **1**[5] and of its methylated derivatives **2** and **3**[6] were impeded by the high instability of these compounds and by the presence of pyrolysis byproducts. Only the first ionization potential of **1** was observed at 9.15 eV,[5] whereas the two first bands attributed to **2** were seen at 8.9 and 10.6 eV in the pyrolyzate of the corresponding Meldrum's acid derivative.[6] By further investigating the pyrolysis mechanism of these compounds, Wentrup and Lorenčak have supplemented the previous photoelectronic results and evidenced a complex pyrolysis pathway with different intermediates such as (carboxyvinyl)ketene, alkylideneketene, vinylethynol, and vinylketene.[7] On the other hand, measurement of the ionization energy of **1**, generated by FVP of a mixed acrylic trifluoroacetic anhydride, by mass spectrometry has led to a value of 9.12 eV, close to the photoelectronic result (9.15 eV).[8] In a similar experiment the ionization energy of **2** has been estimated at 8.68 eV to be compared with Bock's result: 8.9 eV.

In this work, we have investigated by photoelectron spectroscopy the gas-phase pyrolysis of heterosubstituted alkylidene derivatives of Meldrum's acids **4**, **5** and **8**, with the aim of recording the spectra of the corresponding (alkoxymethylene)- and ((alkylthio)methylene)ketenes and of studying the possible intermediates involved in the reaction. As a matter of fact, it has been shown by low-temperature IR spectroscopy that the starting compounds cleanly produce the substituted methyleneketenes.[9a] However, contrary to the alkoxy derivatives, the ((alkylthio)methylene)ketenes **11** and **13** could not be characterized in solution. Instead the substituted thiophen-3(2*H*)-ones were obtained.[9] The gas-phase reactivity of these alkylthio compounds is the subject of a forthcoming paper. As the cyclic alkylthio derivative **9** is not likely to cyclize into the corresponding thiophen-3(2*H*)-one, its gas-phase PE characterization was thus attempted.

Scheme I



	R = X = H	(1)
	R = CH₃, X = H	(2)
	R = X = CH₃	(3)
(4)	X = OCH₃, R = H	(6)
(5)	X = OCH₃, R = CH₃	(7)
(8)	R,X = S(CH₂)₂S	(9)
(10)	R = CH₃, X = SCH₃	(11)
(12)	R = X = SCH₃	(13)

[†] University of Pau.

[‡] University of Reims.

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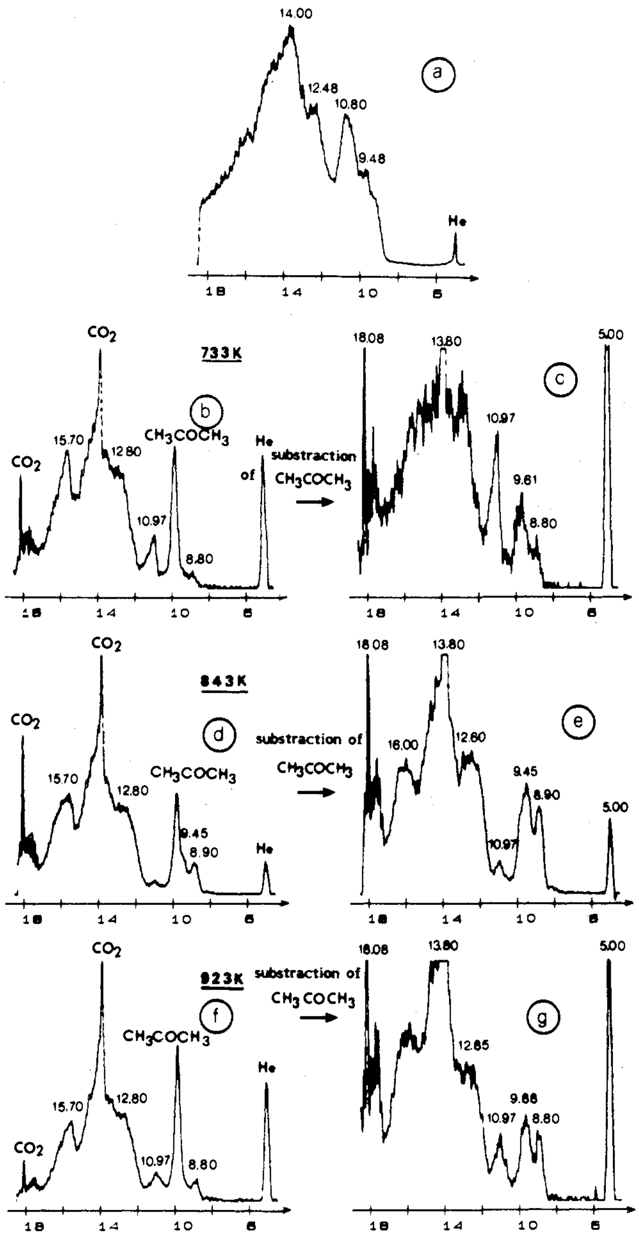
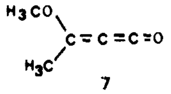


Figure 1. Photoelectron spectrum of (a) isopropylidene 1-methoxyethylidenemalonate (**5**) (b) the pyrolyzate of **5** at 733 K, (d) the pyrolyzate of **5** at 843 K, and (f) the pyrolyzate of **5** at 923 K. Spectra (c), (e), and (g) are the acetone substraction spectra of the pyrolyzate spectra (b), (d), and (f), respectively.

Photoelectron Spectra

Two types of pyrolysis experiments have been performed. With the short-path pyrolysis (SPP) device, the sample is directly pyrolyzed in the vacuum chamber of the spectrometer (distance between the oven outlet and the ionization chamber: 1 cm).[10] In the external pyrolysis (EP) experiment the sample is pyrolyzed in an external oven (12-cm long, 2.5 cm i.d. quartz tube) fitted to a cryogenic trap connected to the spectrometer inlet: the various components of the gaseous pyrolyzate obtained at the oven outlet are selectively vaporized according to the trap temperature. It thus results that pure compounds (and no longer complex pyrolyzate mixtures as in the SPP case) are now directly analyzed in the spectrometer. Due to the longer distance between the oven outlet and the ionization head (60 cm), only "stable" species may be characterized. The differences between the pyrolysis temperatures reported with two devices may be accounted for by



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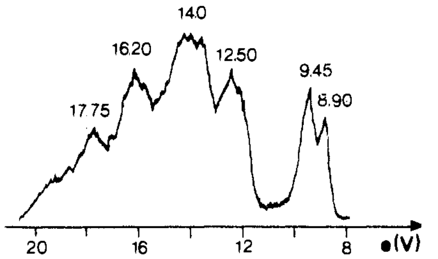

Figure 2. Photoelectron spectrum of (methylmethoxymethylene)ketene (**7**) obtained under EP conditions at 753 K.

different thermocouple locations, vacuum conditions, and oven lengths.

Methylmethoxy Compound 5. For the methylated precursor (**5**) the SP pyrolyzate spectrum at 373 K already displays the characteristic bands of acetone (9.70 eV) and CO_2 (13.78, 17.59, and 18.08 eV), in addition with the bands of the starting compound. Between 433 and 600 K the broad bands of the precursor **5** at 9.48 and 10.80 eV (Figure 1a) are progressively modified with the decrease of the first band and the increase of the third one, while acetone ionization at 9.70 eV becomes stronger. At 733 K no more starting compound is observed; a weak intensity ionization appears at 8.8 eV, and a more intense and sharp one appears at 10.97 eV (Figure 1b). By substracting acetone from this spectrum, another ionization at 9.61 eV is observed (Figure 1c). When the temperature is further raised, the signal at 10.97 eV markedly decreases, while two new ionizations are now observed on the low-energy side of acetone at 8.90 and 9.45 eV (Figure 1d). By substracting acetone from the pyrolyzate spectrum at 843 K, the spectrum displayed in Figure 1e is obtained, which furnishes the evidence for the formation of a new compound(s) with two bands at 8.90 and 9.45 eV in addition to small amounts of the previous product, obtained at 733 K and characterized by its sharp band at 10.97 eV. By further increasing the temperature to 923 K, the smooth shift of the first band from 8.90 to 8.80 eV is observed, while the second one at 9.45 eV disappears, and a third band at 10.97 eV is once again growing in intensity (Figure 1f). In the difference spectrum at 923 K (Figure 1g), three bands are thus obtained at 8.80, 9.68, and 10.97 eV before the broad ionization pattern containing CO_2 bands. Between 973 and 1073 K the pyrolyzate spectrum remains roughly identical, the only difference concerning the apparition of a weak and sharp band at 14 eV corresponding to carbon monoxide evolution.

The EP experiment performed on **5** at 753 K leads to a new product which is stable for trap temperatures between 243 and 283 K and obtained as expected after CO_2 and acetone (respective trap temperatures: 183 and 213 K). This new compound is characterized by the two first bands at 8.90 and 9.45 eV and broader ones at 12.50, 14.00, 16.20, and 17.75 eV (Figure 2). This spectrum is somewhat identical with the difference spectrum obtained from the SPP spectrum at 843 K (Figure 1e) if we except the presence of CO_2 and of small amounts of a compound with an ionization at 10.97 eV in the latter. The ^1H NMR spectrum of this compound (performed by bypassing the SPE inlet and condensing the gaseous flow on a cold finger fitted to a NMR tube) is identical with the reported spectrum of the methylmethoxypropadienone (**7**).[9a] It is thus concluded that the spectrum displayed in Figures 1e and 2 is concerned with the methyleneketene (**7**). However, the results of our SPP experiments obviously indicate that different interconverting products are formed for each pyrolysis temperature. As it has been previously reported that the methyleneketene **7** underwent dimerization to the 2,4-bis(methoxyethylidene)-1,3-cyclobutanedione (**14**),[9a] the PE spectrum of this dimer has also been recorded (Figure 3): in the low IP region three bands are observed at 8.60, 9.30, and 9.70

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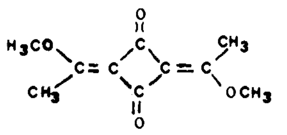

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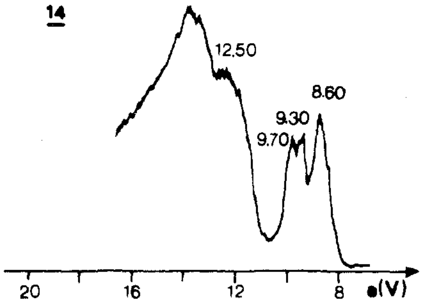

Figure 3. Photoelectron spectrum of 2,4-bis(methoxyethylidene)-1,3-cyclobutanedione (**14**).

eV. From the shape of this spectrum, we may exclude the formation of the dimer **14** in the SP experiment.[11]

Methoxy Compound 4. Under SPP conditions, the unsubstituted derivative **4** begins to react at rather low temperatures (393 K) as deduced from the appearance of the characteristic features of CO_2 and acetone. Between 393 and 793 K, the two first broad bands of the starting compound superimpose with that of acetone and of newly formed products with ionizations at 9.35 and 10.25 eV. The spectra resulting at these temperatures present a broad and varying ionization pattern between 9.35 and 10.85 eV. At 833 K, no more band at 10.85 eV corresponding to the starting compound is observed, while a well-defined band centered at 9.10 eV is obtained just beside the band of acetone at 9.70 eV (Figure 4).

Under EP conditions at 758 K, the precursor **4** splits off CO_2 (trap temperature, 183 K) and acetone (trap temperature, 213 K) indicating that cleavage has occurred. However the detection of the other compound formed during pyrolysis is highly dependent on the evaporation conditions from the cryogenic trap. If the trap is quickly warmed from 213 to 243 K before complete evaporation of acetone, the spectra obtained display a weak band at 9.10 eV beside the band of acetone at 9.70 eV. The low-temperature NMR spectrum of the gaseous flow thus analyzed (obtained by bypassing the SPE inlet and condensing the products on a cold finger fitted to a NMR tube) indicates the formation of the desired methyleneketene **6**[9a] beside large amounts of acetone. However if the trap is slowly warmed to 243 K until complete disappearance of acetone, the previously described PE spectrum is no longer observed. Instead, for a trap temperature of 243 K, spectra with three bands at 9.35, 10.25, and 10.85 eV are obtained with varying relative intensities from one spectrum to the other. It should be mentioned that the same bands may be observed under SP conditions if the sublimation temperature of the sample is not carefully controlled under 373 K. These observations indicate that the methyleneketene **4** is highly unstable and quickly decomposes and/or polymerizes. Nevertheless, its first IP is unambiguously established at 9.10 eV from both SPP and EP experiments.

Alkylthio Compound 8. The cyclic dithioacetal **8**, when submitted to SPP, begins to split off acetone and CO_2 slowly at 473 K. The starting compound disappears completely at 873 K, and the new spectrum presents a broad first band at 8.60 eV with a neat shoulder at 8.70 eV, a sharper one at 9.40 eV, and the band of acetone as expected at 9.70 eV (Figure 5b). Another broad band is clearly distinguished at 11.30 eV just before the usual broad and poorly resolved pattern between 12 and 16 eV where the presence of CO_2 at 13.80 eV is characteristic. Between 473 and 873 K the spectrum evolution may be described as the disappearance of the starting compound and the appearance of the new product. The pyrolyzate spectrum dramatically changes as soon as the temperature is raised. At 893 K, small new bands appear at 10.10, 14, and 14.50 eV. These bands increase as the temperature is raised, and at 1073 K the spectrum contains only the bands of acetone (9.70 eV), CO_2 (13.78 eV) and the ionizations of the newly formed compounds at 10.10 and 14.50 eV (CS_2), 14 eV (CO), and 10.55 eV (C_2H_4). It is thus concluded that the pyrolysis product obtained at 873 K is completely cleaved at 1073 K into CO, CS_2, and C_2H_4. It should be pointed out that the behavior of the pyrolysis compound obtained from **8** at 873 K is strikingly different from those of the pyrolysis products obtained from **10** and **12** which were shown to be quite stable even at high temperatures.[12] As it has been demonstrated that these two latter experiments lead to the cyclic isomers of the methyleneketene,[9a,12] the thiophen-3(2*H*)-ones, it may be concluded that the pyrolysis compound obtained from **8** has a different structure and probably corresponds to the desired methyleneketene **9**.

Discussion

PE Spectra of Methyleneketenes. It has been previously mentioned that the parent alkylideneketene **1** and its methylated derivatives **2** and **3** were highly unstable in the gas phase.[5,6] The (alkoxymethylene)ketenes **6** and **7** have been shown to be more stable as their low-temperature NMR spectra could be recorded up to 253 K for **6** and 301 K for **7**. However, **6** polymerizes within 3 h at 253 K, while **7** is stable between 8 and 10 h at 300 K.[9a] To our knowledge, ((alkylthio)methylene)ketenes have not been characterized neither in the gas phase nor in solution due to the systematic formation of the isomeric thiophen-3(2*H*)-ones.[9]

The orbital description of the parent methyleneketene (**1**) is the following[6] (Table I): the highest occupied orbital is the C=C double bond in the σ plane ($\pi^{\perp}$) in slight antibonding interaction with the n_O orbital. According to the PE results of McNaughton[5] and Bock,[6] the experimental IP arising from the ionization of this $\pi^{\perp}$ orbital is observed at 9.15 eV for **1** and 8.9 eV for **2**, evidencing a slight shift to lower energy upon methylation. The following orbital is the other $\pi_{C=C}$ bond, and its ionization has been experimentally observed by Bock at 10.60 eV for the methylated compound **2**.[6] It is worth noting that for these two examples, the calculated orbital eigenvalues (either in the MNDO or ab initio formalism) are close to the experimental IP's (Table I).

According to this attribution, upon substitution of the methyleneketene skeleton by an alkoxy or alkylthio group, no dramatic change of the $\pi^{\perp}$ orbital is expected, except a slight stabilizing inductive effect. On the other hand, the interaction between the terminal $\pi_{C=C}$ double bond and the OCH_3 or SCH_3 group should lead to the splitting of this orbital into two components, namely a ($\pi_{C=C} - n_{XCH_3}$) and ($n_{XCH_3} + \pi_{C=C}$) orbitals. For the alkoxy derivatives the former one is more heavily located on the double bond and the latter on the oxygen lone pair, while the reverse is expected for the alkylthio compounds: the first component is essentially described as the sulfur lone pair and the second as the $\pi_{C=C}$ double bond.

In the PE spectrum of the (methylmethoxymethylene)ketene (**7**) (Figure 2), the first band is observed at 8.90 eV, and this energetic position is comparable to that of the (methylmethylene)ketene (**2**).[6] It is thus attributed to the ejection of an electron from the ($\pi^{\perp} - n_{OCH_3}$) orbital. The positions of the second and third bands (9.45 and 12.50 eV) are then accounted for by the expected modification induced by the methoxy group on the double bond of **2**. The observed 1.15-eV destabilization of the second band, attributed to the ionization of the ($\pi - n_{OCH_3}$) orbital, is to be compared with the one existing between ethylene and methyl vinyl ether (**15**) (1.40 eV[13]). If the third band at 12.50 eV is associated with the ionization of the ($\pi + n_{OCH_3}$) orbital, the ($\pi - n_O$)/($\pi + n_O$) splitting (3.05 eV) has the same order of magnitude as for the methyl vinyl ether (**15**) (2.99 eV[13]) or the methoxyallene (**16**) (3.61 eV[14]).

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[11] This dimer (*14*) is rather stable under SPP conditions as it is not cleaved before 993 K. At higher temperatures, methanol, carbon dioxide, and carbon monoxide are formed, without any evidence for methyleneketene generation.

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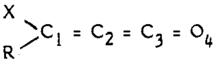
Table I. Experimental IP and MNDO Calculated Orbital Eigenvalues[a] ($-\epsilon_i$) of Parent and (Alkoxymethylene)ketenes


$$\overset{X}{\underset{R}{>}}C_1=C_2=C_3=O_4$$

	1 R = X = H		**2** R = CH$_3$, X = H		**6** R = H, X = OCH$_3$		**7** R = CH$_3$, X = OCH$_3$	
	$-\epsilon_i$	IP	$-\epsilon_i$	IP	$-\epsilon_i$	IP	$-\epsilon_i$	IP
$\pi^{\perp}_{C=C} - n_O$	9.14	9.15	9.07	8.9	9.23	9.10	9.18	8.90
	(9.13)[b]		(9.07)[b]					
$\pi_{C=C} - n_{OCH_3}$	10.72		10.48	10.60	9.86	9.70[c]	9.76	9.45
			(10.82)[b]					
$^nOCH_3 + \pi_{CC}$					13.11		12.82	12.50
n_O, σ_{CH}, σ_{CC}	14.80				13.24		13.10	
					14.70		14.17	
							14.31	14.00
							14.59	
π_{CO}	15.56				15.33		15.28	
								16.20
$\pi^{\perp}_{C=C} + n_O$	16.07				15.46		15.39	16.20

[a] Performed on optimized geometries (bonds in Å, angles in deg). **1**: $C_1C_2 = 1.304 - C_2C_3 = 1.276 - C_3O_4 = 1.185 - C_1H_5 = C_1H_6 = 1.09 - H_5C_1C_2 = H_6C_1C_2 = 123.25 - C_1C_2C_3 = C_2C_3O_4 = 180$. **6**: $C_1C_2 = 1.303 - C_2C_3 = 1.267 - C_3O_4 = 1.186 - C_1H_5 = 1.103 - C_1O_6 = 1.346 - O_6C_7 = 1.406 - C_7H = 1.12 - C_1C_2C_3 = C_2C_3O_4 = 180° - H_5C_1C_2 = 123.02 - O_6C_1C_2 = 126.60 - C_7O_6C_1 = 124.02 - H_8C_7O_6 = 112° - H_9C_7O_6 = 107° - H_8C_7O_6C_1 = 180°$. [b] Ab initio calculations from ref 5. [c] Assumed under the band of acetone.

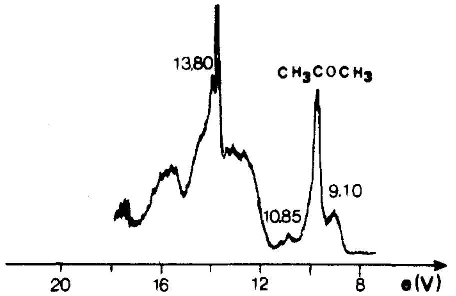


Figure 4. Photoelectron spectrum of the pyrolyzate of **4** performed under SPP conditions at 773 K.

The results of calculations (performed with the NMDO formalism because of the size of the system) support this assignment. The evaluation of the ionization potentials was done within Koopmans' approximation and considered the molecule as linear. As a matter of fact, the MNDO method does not minimize on a bent but on a linear structure for **1**, as expected from an extensive study demonstrating the importance of correlation effects on the description of the molecule.[15] We have checked that whether bent or linear, the orbital localizations were identical and the orbital eigenvalues were close. It may be seen from Table I that the comparison between the experimental IP's and the MNDO orbital eigenvalues is rather satisfactory for the three first ionizations of compound **7**: the calculated eigenvalues, 9.18, 9.76, and 12.82 eV, correspond respectively to experimental values at 8.90, 9.45, and 12.50 eV. The following broad bands in the experimental spectrum at 14.00 and 16.20 eV may thus be assigned to the ionizations of a n_O and σ type orbital for the former, and of two π_{CO} and ($\pi^{\perp}{}_{C=C} + n_O$) orbitals for the latter.

For the parent (alkoxymethylene)ketene (**6**), only the first band at 9.10 eV is available from the PE spectrum (Figure 4). This band probably arises from the ejection of an electron from the ($\pi^{\perp}{}_{C=C} - n_O$) orbital and is found, as for the related derivatives **2** and **7**, at the same energetic level as the unsubstituted methyleneketene (**1**) (Table I). This result indicates that the $\pi^{\perp}$ orbital is somehow insensitive to alkoxy substitution. The second band of **6**, attributable to the ionization of the ($\pi_{C=C} - n_{OCH_3}$) orbital is probably masked by the presence of acetone and should be found at 9.70 eV. However, the important amplitude of the signal of acetone and the superposition of the two ionizations prevent any attempt to obtain the substraction spectrum.

The attribution of the spectrum of the ((dialkylthio)methylene)ketene (**9**) (Figure 5) is better completed by the previous attribution of the spectrum of the starting Meldrum's acid derivative **8** and of its analogues **10** and **12**. For compound **8** bearing two sulfurs in a geminal position of a double bond, two ionizations are observed at 8.64 and 9.23 eV corresponding to the symmetric combination of the sulfur lone pairs in interaction with the double bond for the former and to the antisymmetric combination for the latter[16] (Table II). The third band at 9.71 eV cannot be associated with the ejection of an electron from a sulfur orbital, as its intensity is not reduced on going from HeI (21.21 eV) to HeII (40.81 eV) excitation energy.[17] The possible existence of another gauche conformation is thus excluded.[16] This band is more probably attributable to the ionization of a $n_O(\sigma)$ orbital of the carbonyl groups: the ionization of $n_O(\sigma)$ carbonyl orbitals of various acrylates has been observed between 10.40 and 10.65 eV and between 10.05 and 10.25 eV for the methacrylates.[18] According to the known interactions between the σ carbonyl lone pairs of β-diketonic systems,[19] it is reasonable to assume that the antisymmetric and symmetric combinations of these n_O oxygen lone pairs with the σ bonds of the exocyclic double bond of **8** will give rise, upon ionization, to a first markedly lower IP due to the splitting of these orbitals into two $n_O^-(\sigma)$ and $n_O^+(\sigma)$ components. This attribution is supported by the observation of similar ionization at 9.71 and 9.79 eV, respectively, for the analogous Meldrum's acids **10** and **12**.[12] For the methoxy Meldrum's acids **4** and **5**, this band could be masked by the other one arising from the ionization of the ($\pi - n_{OCH_3}$ orbital) (Figure 1a). The ejection of an electron from the ($\pi + n_s$) orbital of **8** should then correspond to a band in the broad signal around 10.80 eV (energetic position consistent with the experimental IP of vinyl sulfide: 8.45 and 11 eV[20]).

For the ((dialkylthio)methylene)ketene (**9**) three ionizations should be comparable with those of the Meldrum's acid **8**, namely the ones arising from the sulfur lone pairs combinations ($n_s^+ - \pi$) and n_s^- and from the ($\pi + n_s^+$) orbital. Actually the sharp

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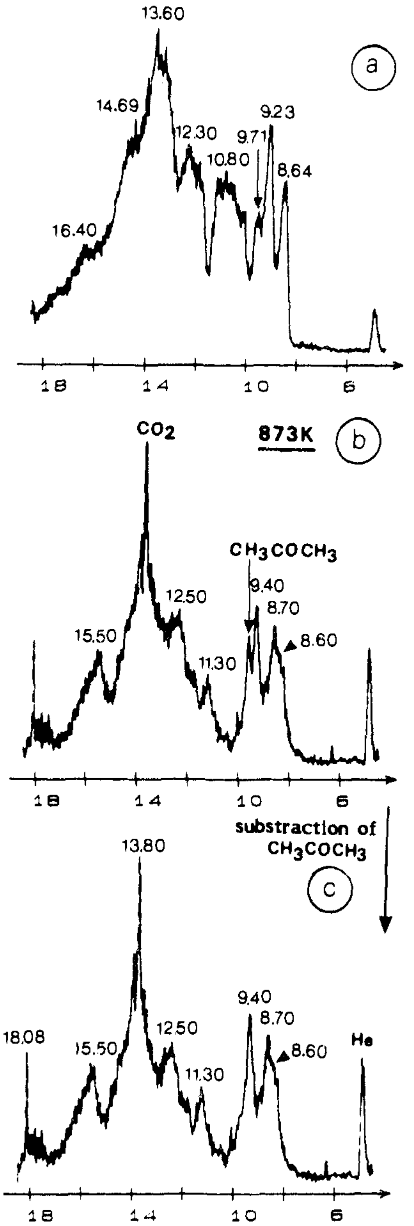
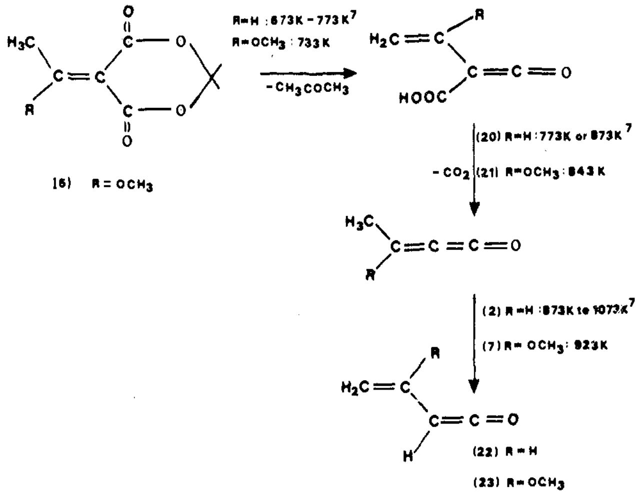


Figure 5. Photoelectron spectra of (a) isopropylidene (1,3-dithiolan-2-ylidene) malonate (**8**), (b) the SPP of **8** at 873 K, and (c) the acetone substraction spectrum of (b).

second and third bands at 8.70 and 9.40 eV (Figure 5c) may be associated with the ionizations of the $(n_s^+ - \pi)$ and n_s^- orbitals, respectively, and are to be compared with the corresponding bands at 8.64 and 9.23 eV of the starting compound **8**. The ejection of an electron from the $(\pi + n_s^+)$ orbital is probably related with the band at 11.30 eV in the spectrum. The comparison between the splitting $(n_s - \pi)/(n_s + \pi)$ orbitals in vinyl sulfide (**17**) (2.55 eV[20]), (methylthio)allene (**18**) (2.61 eV[14]), ((dialkylthio)methylene)ketene (**9**) (2.60 eV), and the Meldrum's acid **8** (2.16 eV) indicates similar interactions for the four systems (Table II). The ejection of an electron from the $(\pi^\perp - n_O)$ orbital of the cumulenone **9** is thus associated with the band at 8.60 eV in the spectrum, partly superimposed with the 8.70-eV band corresponding to the $(n_s^+ - \pi)$ orbital. Accordingly, the $(\pi^\perp - n_O)$ ionization is shifted to lower energy upon substitution of the skeleton by the cyclic dithioacetal system as this band is observed between 8.90 and 9.15 eV for the other studied methyleneketenes ((Table I).

It may be noted that for the parent ((alkylthio)methylene)ketene **19** the MNDO orbital eigenvalues are not so reliable as for the alkoxy derivatives (no d atomic orbitals included for sulfur, more important correlation effects than for oxygen[21]).

Scheme II



Intermediates Involved in the Pyrolysis of 5. As a whole it is concluded that our assigments of the PE spectra of substituted methyleneketenes are consistent with the previous results of McNaughton[5] and Bock.[6] However if the evolution of the pyrolyzate spectra with the temperature for compounds **4** and **8** does not bring forward any convincing evidence for other identified intermediary compounds, then this is no longer the case for the methylated derivative **5**. Our PE results for the pyrolysis of **5** may be analyzed with reference to Wentrup's proposal of a complex mechanism[7] (Scheme II) involving first a (carboxyvinyl)ketene **20** obtained by acetone evolution between 673 and 773 K. The methyleneketene **2** would then be observed either by double pyrolysis[7] of **20** at 773 K or by rapid sublimation of the Meldrum's acid precursor at 973 K. The formation of the vinylketene **22** has then been reported to occur by double pyrolysis above 873 K, and **22** is the sole observed pyrolysis product if the double pyrolysis is performed at 1073 K. According to Wentrup's mechanism, the first pyrolyzate spectrum from the methylmethoxy derivative **5** at 733 K (characterized by three bands in the low IP region at 8.80, 9.61 and a sharper one at 10.97 eV, Figure 1c) could be concerned with a methoxy substituted (carboxyvinyl)ketene **21**. By raising the pyrolysis temperature to 843 K (SP conditions), this (carboxyvinyl)ketene would give rise to the (methylmethoxymethylene)ketene (**7**) isolated in the pure form under EP conditions at 753 K (Figures 1e and 2). By further heating the methyleneketene **7** at 923 K, the (methoxyvinyl)ketene **23** would be obtained and could account for the observed PE spectrum (Figure 1g) with once again three first bands in the low IP region at 8.80, 9.68, and 10.97 eV (Scheme II).

If the formation of the vinylketene **23** is assumed at higher temperatures, its PE spectrum cannot be analyzed by comparison with the parent vinylketene **22** as the latter was considered as being planar.[6] This is no longer the case for the methoxy derivative **23** as several energetically close conformations are found in the MNDO formalism (Figure 6). If ϕ is designed as the dihedral angle between the ketene and the vinyl moieties and Ψ as the dihedral angle between the vinyl moiety and the methoxy group, it is observed that the most stable conformation is a completely planar s-trans one ($\phi = 180°$) with the methoxy group syn to the double bond ($\psi = 0°$). Another minimum (0.31 kJ higher in energy) is obtained for $\phi = 30°$ with a noticeable gauche conformation. However it is clear, according to the weak energetic barrier between the two minima (0.47 kJ), that the free rotation of the system must be considered.

For the planar s-trans system (from $\phi = 100$ to $\phi = 180°$ for which the most stable conformations correspond to $\psi = 0°$), the interactions between the ketene, vinyl, and methoxy oxygen lone pair will give rise to three orbitals described as mixtures of these

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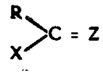
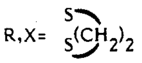
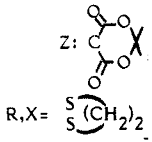
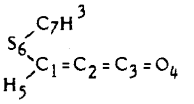
[21] Van Niessen, W.; Cederbaum, L. S. L.; Domcke, W.; Diercksen, G. H. F. *J. Chem. Phys.* **1977**, *66*, 4893.

Table II. Experimental IP and MNDO Calculated Orbital Eigenvalues $(-\epsilon_i)^a$ of Various Vinyl Sulfide Derivatives



	17 Z:CH_2 R = H, X = SCH_3 IP (eV)[20]	**18** Z:C═O R = H, X = SCH_3 IP (eV)[14]	**19** Z:C═C═O R = H, X = SCH_3 $-\epsilon_i^a$ (eV)	**9** Z:C═C═O  IP (eV)	**8**  IP (eV)
$\pi^{\perp} - n_O$			9.26	8.60	
$n_s^+ - \pi$				8.70	8.64
(n_s^-)	8.45	8.24	9.56	9.40	9.23
					$n_o(\sigma)$ 9.71
$\pi + ns$	11.00	10.85	11.94	11.30	10.80

[a] Performed on the optimized geometry (bonds in Å, angles in deg). $C_1C_2 = 1.308 - C_2C_3 = 1.275 - C_3O_4 = 1.185 - C_1H_5 = 1.11 - C_1S_6 = 1.675 - S_6C_7 = 1.726 - C_7H = 1.106 - C_1C_2C_3 = C_2C_3O_4 = 180° - H_5C_1C_2 = 121.46° - S_6C_1C_2 = 128.47° - C_7S_6C_1 = 111.51°$.



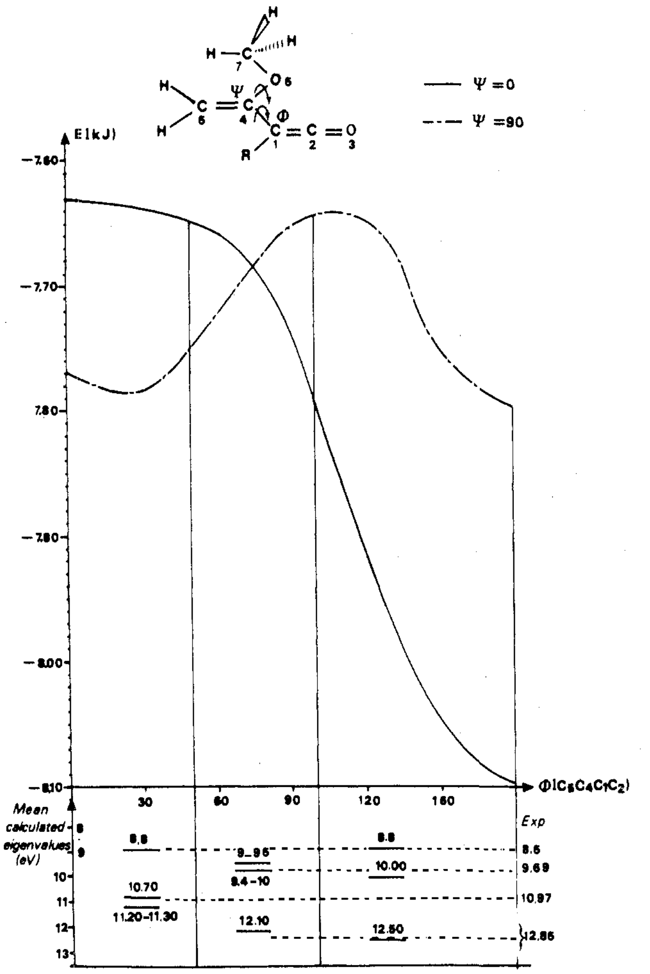


Figure 6. MNDO calculated energies (kJ) of different conformers of the ketene **23** according to the dihedral angle ϕ.

components, the σ methoxy oxygen lone pair remaining unperturbed. The corresponding orbital eigenvalues are 8.8 eV ($\pi_{\text{ket}} - \pi_{\text{vin}} - n_O - n_{OCH_3}$), 10 eV ($\pi_{\text{ket}} + \pi_{\text{vin}} - n_O - n_{OCH_3}$), and 12.70 eV ($\pi_{\text{ket}} + \pi_{\text{vin}} - n_O + n_{OCH_3}$) and 12.50 eV for the unperturbed σ methoxy oxygen lone pair (the orbital eigenvalue of the oxygen lone pair of the methyl vinyl ether (**15**) is 12.55 eV which corresponds to the experimental IP of 12.13 eV[13]).

For planar or quasi-planar ketene/vinyl arrangment arising for ϕ values between 0 and 50°, the gauche conformation of the methoxy group relative to the double bond is now preferred. In such cases the interaction between the ketene and the vinyl group should give rise to ($\pi_{\text{ket}} - \pi_{\text{vin}} - n_O$) and ($\pi_{\text{ket}} + \pi_{\text{vin}} - n_O$) orbitals, the eigenvalues of which are 8.8 and 10.7 eV, whereas the methoxy oxygen lone pair ionization is expected at a much lower IP than in the s-trans syn conformation (12.51 eV) as its eigenvalue is estimated between 11.20 and 11.30 eV.

For intermediate ϕ values between 50 and 100°, the ketene/vinyl arrangment is no more planar, and, when minimized, the ψ angle is found to be deviated from 0° (32°): the result is a completely twisted conformation for which the gap between the two first orbital eigenvalues is still reduced, i.e., 9–9.5 and 9.4–10 eV, respectively, whereas the methoxy oxygen lone pair is slightly destabilized relative to the s-trans syn conformation ($\simeq$12.10 eV).

If the free rotation of the system is assumed, the mixture of these different conformations in the spectrum should give rise to four sets of IP expected around 8.8 eV for the first one, around 10 eV for the second, at 11 eV for the third, and at 12–12.50 for the last band. In the experimental spectrum (Figure 1g) the three first bands are observed at 8.8, 9.68, and 10.97 eV. A fourth one, hidden in the broad following signal, may be deduced at 12.85 eV. The intensity of the band at 10.97 eV, containing, according to the previous analysis, two ionizations of the gauche s-cis conformation (ϕ = 0–50°, ψ = 90°), indicates that significant amounts of the latter are present in the conformers mixture.

If we now consider the formation of the intermediate methoxy substituted (carboxyvinyl)ketene **21** at a lower temperature (Figure 1c), the previously analyzed PE spectrum still holds true. Actually the introduction of the carboxyl group on the ketene skeleton will only bring a new ionization arising from the carbonyl σ oxygen lone pair around 11 eV (the interaction of the ketene double bond with the $\pi_{C=O}$ orbital is expected to be weak due to the high energetic position of the latter). Moreover it is reasonable to assume that the preferred conformation will now be slightly twisted because of the steric hindrance between the difference substituents. Consequently, the first band at 8.8 eV, corresponding to planar systems, should have a weaker intensity than that of **23** (Figure 1c,g). This is indeed observed. The increase of the 10.97-eV band for **21** in comparison with **23** could be associated with the presence of the carbonyl $n_O(\sigma)$ ionization.

The result of our analysis thus indicates that the possible formation of the intermediate vinylketenes **21** and **23** may not be ruled out from our PE experiments. However, if these assumptions were valid, it should be observed that only acetone is split off at 733 K (without carbon dioxide) and that CO_2 is split off at 843 K during the cyclopenten-2-one[22,26] (**21**) → methyleneketene **7** conversion through decarbonylation. The early presence of carbon dioxide (even in the 473 K pyrolyzate spectrum!) indicates that a competitive concerted CO_2 and acetone elimination from **5** probably occurs. It should be pointed out that for the related cyclopentylidene case, CO_2 and the methyleneketene started appearing at 770 K, and this result was accounted for by a similar competitive CO_2 and acetone elimination directly from Meldrum's acid derivative.[25]

Finally it should be mentioned that for (methoxymethylene)-ketenes, no cyclization to the furan-3(2*H*)-one has ever been reported, although it is well-known that ((alkylthio)methylene)-[9] or ((alkylamino)[23,24] methylene)ketenes are quantitatively transformed into thiophen-3(2*H*)-ones and pyrrol-3(2*H*)-ones, respectively. The SPE spectra obtained from **5** do not support the formation of 5-methylfuran-3(2*H*)-one: for this heterocycle the band corresponding to the ionization of the carbonyl oxygen lone pair is expected, as in cyclopenten-2-one[22,26] around 9.35 eV. The interacting double bond and the intracyclic oxygen should give ($\pi - n_O$) and ($\pi + n_O$) orbitals. The IP's arising from the ejection of an electron from these two orbitals are not easily anticipated and could be compared, at first sight, to those of the methyl vinyl ether (**15**) at 9.15 and 12.13 eV.[13] If we exclude the spectrum of the methyleneketene **7** (Figures 1e and 2), the other observed pyrolyzate spectra are not consistent with such a structure.

Conclusion

In conclusion, the assignments of the PE spectra of substituted methyleneketenes are consistent with the previous results of Bock[6] and McNaughton[5] and confirm the formation of these highly unstable methyleneketenes from the pyrolysis of Meldrum's acid derivatives between 700 and 850 K. However when the double bond of the Meldrum's acid derivative is substituted by a methyl group, other intermediary pyrolysis products are observed at lower (730 K) or higher (920 K) temperatures for the methoxy compounds. The assignment of the PE spectra of the obtained products supports the formation of substituted vinylketene, in agreement with Wentrup's mechanism.[7]

However the different behavior of methoxy-substituted alkylidene derivatives of Meldrum's acid from that of alkylthio and alkylamino compounds, which readily cyclize when possible to thiophen-3(2*H*)-one and pyrrol-3(2*H*)-one, respectively, is not yet well understood. Further investigation is being undertaken.

Experimental Section

PE spectra were recorded on an Helectros 0078 spectrometer connected to a microcomputer system supplemented by a digital analogic converter (DAC). The spectrometer is equipped with an internal heating device for the SPP[10] (pressure in the ionization chamber: 10^{-5} mbar without sample). For the EP, the spectrometer is connected to a vacuum device where the pyrolysis is performed (pressure in the oven. 10^{-3} mbar without sample). The spectra are built with 2048 points and are accurate within 0.05 eV. They are calibrated on the known ionizations of xenon (12.13 and 13.43 eV) and argon (15.76 and 15.93 eV).

The starting Meldrum's acid derivatives **4** and **5** were prepared following Polansky's method[27] and the dithiocompound **8** according to Huang's synthesis.[28]

MNDO calculations were performed with the AMPAC program[29] on a VAX computer. All the geometries were fully optimized.

Acknowledgment. We thank Mrs. Maryse Simon for efficient technical assistance.

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Metastable Unimolecular and Collision-Induced Dissociation of Hydrogen-Bonded Clusters: Evidence for Intracluster Molecular Rearrangement and the Structure of Solvated Protonated Complexes

S. Wei, W. B. Tzeng, R. G. Keesee, and A. W. Castleman, Jr.*

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802.

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Abstract: A reflectron time-of-flight mass spectrometer in conjunction with multiphoton ionization was used to study metastable unimolecular and collision-induced dissociation processes of mixed ammonia–pyridine and water–acetone cluster ions. The ion intensity distributions display especially stable pertuberances (magic numbers) at $m = n + 2$ for $(H_2O)_n{\cdot}(C_3H_6O)_mH^+$ and $m = 2(n + 1)$ for $(NH_3)_n{\cdot}(C_5H_5N)_mH^+$, indicating that the core ions are H_3O^+, $H_5O_2^+$, NH_4^+, etc. whenever the cluster size is large enough to form a closed hydrogen-bonded shell structure. Surprisingly, these core ions form even though the proton affinity of water is smaller than that of acetone, and that of ammonia is smaller than that of pyridine. Collision-induced dissociation is studied to probe structure (core ion) changes with cluster size. The structural changes are well-correlated to transitions of the metastable decomposition channels of these mixed cluster ions, and this correlation is successfully applied to other mixed cluster systems including ammonia–trimethylamine and water–dimethyl ether. Metastable decomposition studies show that the mixed cluster ions $H_2O{\cdot}(C_3H_6O)_3H^+$ and $NH_3{\cdot}(C_5H_5N)_3H^+$ lose H_2O and NH_3 molecules, respectively, which results from intracluster molecular rearrangement. This intracluster molecular rearrangement is confirmed by detailed investigations of the dynamics of metastable unimolecular and collision-induced dissociation processes.

Introduction

Clusters offer a means by which to bridge the gap between the gaseous and condensed phase so that the details of solvation as well as condensation and nucleation phenomena can be probed at the molecular level.[1-4] Research into the formation and properties of clusters has been rapidly expanding in recent years.[5-10]

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