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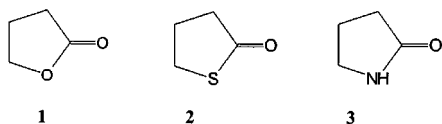
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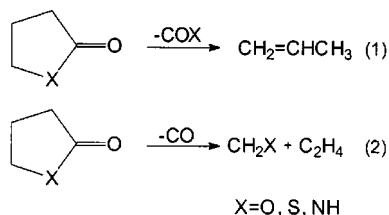
The interconversion and decomposition of furan-2(3*H*)- and -2(5*H*)-one and their methylated derivatives were studied by following the changes in their photoelectron spectra during pyrolysis. Interconversion occurred at 300–400 °C and decomposition at around 600 °C giving CO and acrolein as the only products for the unsubstituted furanones. The experimental results suggest that decarbonylation takes place through the 2(3*H*) form as the common precursor.

Introduction

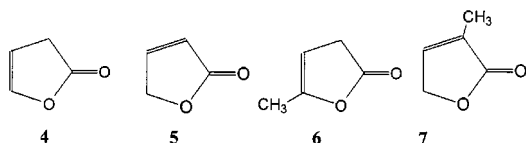
Pyrolysis of esters commonly results in elimination to give an alkene and an acid, through a 1,5-hydrogen shift in a six-membered cyclic transition state.¹ Lactones of ring size larger than six atoms pyrolyze in a similar way to yield an unsaturated ring acid.² In contrast, the relatively unstable four-membered ring β-lactones readily undergo elimination of CO₂ at low temperatures to give an olefin.^{3,4} Recently we studied the pyrolysis of two lactones of intermediate ring size, γ-butyrolactone **1** and γ-thiobutyrolactone **2**,^{5,6} and the related 2-pyrrolidone **3**.⁷



Two modes of reaction were observed for these compounds, *viz.* decarboxylation and decarbonylation [reactions (1) and (2)].



It was found that the importance of reaction (1) relative to reaction (2) was sensitive to the nature of the ring heteroatom, being highest for **1** but lowest for **3** and showing a correlation with the stability of the leaving group (COX) for decarboxylation. In order to investigate the effects of ring unsaturation on the thermal reactivity of medium sized lactones, we have carried out the pyrolysis of furan-2(3*H*)-one **4**, furan-2(5*H*)-one **5** and two methylated derivatives **6**, **7**, and the results are reported here.



There has been no systematic study on the thermolysis of the furanones, apart from the work of Skorianetz *et al.* who reported that heating of **6** resulted in the formation of methyl vinyl ketone.⁸

In the present work the reactions of the furanones were

followed by on-line recording of photoelectron spectra; the various products were readily characterized by their fingerprint bands. The technique also allowed us to differentiate readily the isomeric species of the furanones.

Experimental

Furan-2(3*H*)-one was prepared by the method of Näsman and Pensar,⁹ and purified by distillation; (found: C, 57.17; H, 4.80; calc.: C, 57.14; H, 4.76%). Chemically pure samples of furan-2(5*H*)-one and the two methylated derivatives were obtained commercially and used without further treatment.

Photoelectron (PE) spectra were recorded on a Leybold-Heraeus UPG-200 spectrometer with resolution of about 20 meV, using argon as a calibrant gas.

Pyrolysis was performed in a flow system at low pressures. The pyrolyser consisted of a quartz tube which was 45 cm long and 1.2 cm in inner diameter. Heating was achieved through a tube oven 30 cm in length. In a typical run the vapour of the liquid sample at approximately 1 Torr was passed through the quartz tubing through the pumping action of the spectrometer. Progress of reaction was monitored by on-line recording of photoelectron (PE) spectra of the gaseous product formed.

Results and discussion

Spectral changes and reactions

The PE spectra of **4** and **5** are shown in Fig. 1. Note that the characteristic bands for each compound are those arising from ionization events of the π_{CC}, n_{O(C=O)} orbitals,^{10,11} and they can be located in the energy range below 12 eV, at 9.76 and 10.65 eV for **4**, and 10.57 and 11.54 eV for **5**. Bands at higher energy show extensive overlapping.

The spectral changes during the pyrolysis of **4** are shown in Fig. 2. Heating up to 250 °C produced no noticeable changes. The onset of change occurred at 300 °C with the emergence of a band at 11.54 eV, indicating the formation of **5**. The conversion progressed with increasing temperature and at 550 °C it was about 80% complete. At 600 °C two new peaks appeared at 10.11 and 14.01 eV, characteristic of acrolein and carbon monoxide, respectively.¹² As the temperature was further increased the decomposition was more extensive and the product bands became more prominent. At 800 °C the decomposition was complete as illustrated by the composite spectrum, which consists of only bands of the two products.

When pyrolysis of **4** was carried out using new quartz tubing, the onset of conversion shifted to a higher temperature than that observed for used tubing, and the degree of isomerization

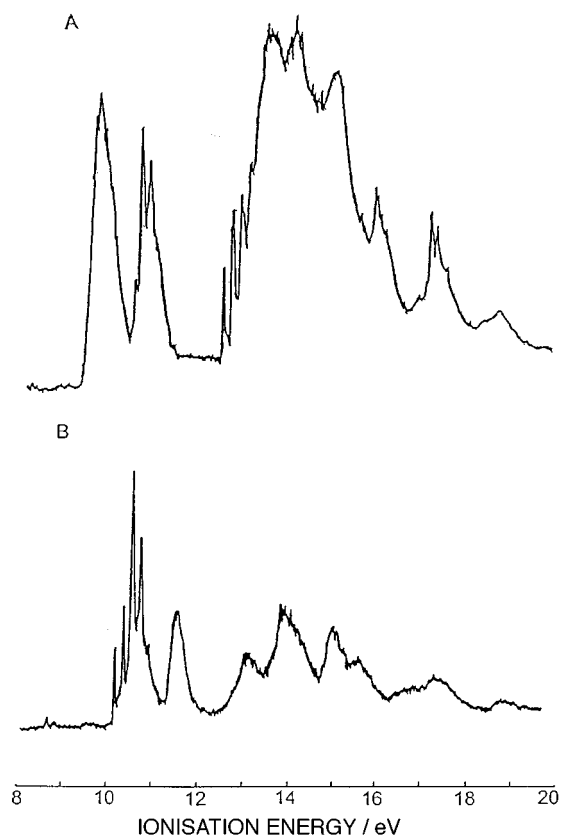
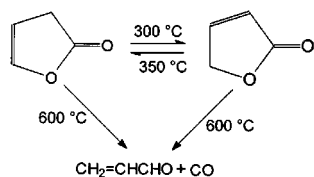


Fig. 1 Spectra of furan-2(3H)-one (A) and furan-2(5H)-one (B).

also became less. However this retardation phenomenon became gradually less pronounced with continual normal use of the tubing and eventually normal results were obtained. On the other hand the progress of decomposition was not affected by the use of new tubing. Thus conditioning of the quartz tubing is important for obtaining reproducible results on isomerization.

The series of spectra shown in Fig. 3 was recorded during pyrolysis of **5**. The spectrum of the reactant remained unchanged upon heating up to 300 °C. At 350 °C a small signal at 9.76 eV appeared and it became more prominent at 400 °C, indicating the conversion to **4**. At 550 °C the composite spectrum was similar to that obtained during pyrolysis of **4** at the same temperature. Thus a stationary state consisting of approximately 20% **4** and 80% **5** was reached at this temperature under the conditions of the flow system. At higher temperatures the spectral variations during pyrolysis of **5** were very similar to those observed for compound **4**, showing that decarbonylation with formation of acrolein was the only mode of decomposition.

The spectral changes thus show that compounds **4** and **5** undergo isomerization at low temperatures and decomposition through decarbonylation at higher temperatures.



The PE spectra of the methylated species **6** and **7** were very similar to those of the respective unsubstituted isomers, but with band positions shifted slightly toward lower ionization energies as expected for the inductive effect of the methyl group. The spectral changes during pyrolysis also followed similar patterns, although isomerization was not as extensive as that

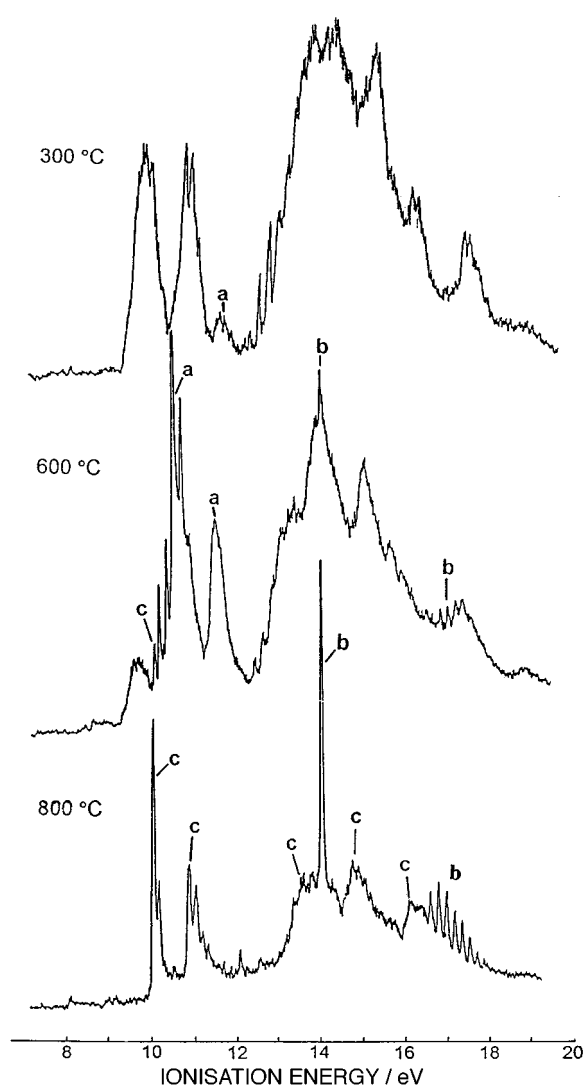


Fig. 2 Spectral changes during pyrolysis of furan-2(3H)-one: (a) furan-2(5H)-one; (b) CO; (c) acrolein.

observed for the unsubstituted compounds. This is illustrated in Fig. 4 which displays a few spectra recorded during pyrolysis of **6**. Isomerization to 5-methylfuran-2(5H)-one occurred around 400 °C with the appearance of a band at 11.5 eV which became prominent at 500 °C. Heating at higher temperatures resulted in decarbonylation with the formation of methyl vinyl ketone which has characteristic sharp bands at 9.69 and 10.67 eV.¹³ The onset of decarbonylation occurred around 520 °C which was 45 °C higher than the reaction temperature reported by Skorianetz *et al.*⁸ who used a static system. Note that there was only one mode of decomposition as was the case for the unsubstituted compounds.

A few spectra recorded during pyrolysis of **7** are shown in Fig. 5. The first sign of change appeared at 450 °C with the emergence of a small signal around 9.4 eV which is indicative of isomerization to 3-methylfuran-2(3H)-one. The signal remained small even at higher temperatures. Decomposition set in at 600 °C with the appearance of the CO band at 14.01 eV and a band at 9.78 eV. These became more prominent as the temperature was raised further; it was also clear that the latter band was associated with another one around 10.3 eV and could be attributed to the formation of crotonaldehyde ($\text{CH}_3\text{CH}=\text{CHCHO}$).¹⁴ At 750 °C or higher temperatures carbon dioxide and methyl vinyl ketone were also detected as minor products through their bands at 13.8 and 18.0 eV,¹² and at 9.69 and 10.67 eV,¹³ respectively. To better identify the products a sample of the reaction mixture was collected in a cold trap at

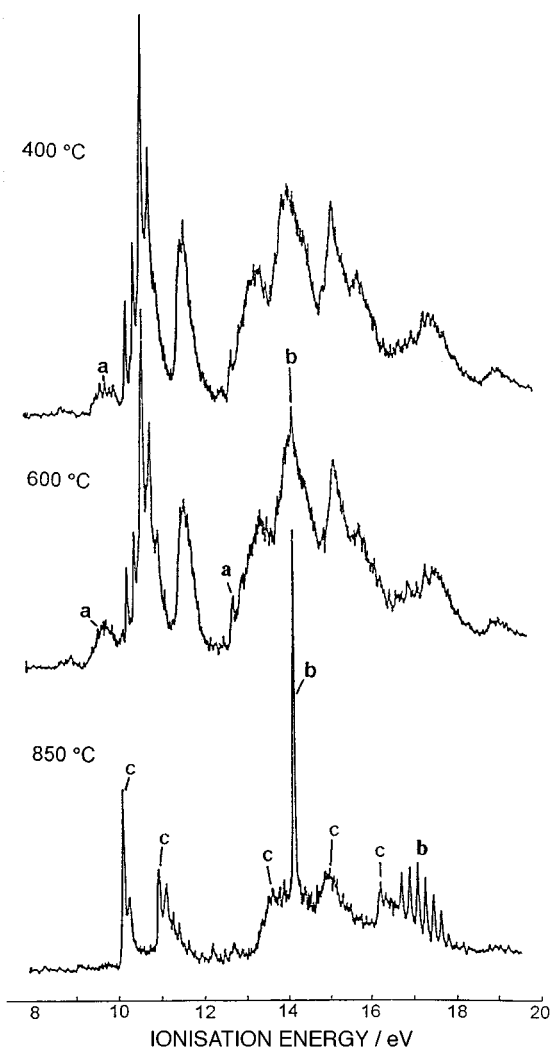


Fig. 3 Spectral changes during pyrolysis of furan-2(5H)-one: (a) furan-2(3H)-one; (b) CO; (c), acrolein.

liquid nitrogen temperature, placed downstream of the heating zone, during pyrolysis of **7** at 780 °C. The components of the trapped mixture were then separated through differential vaporization. The PE spectra of the different fractions indicated crotonaldehyde as a main product and methyl vinyl ketone as a minor product. The other minor products were butadiene and but-2-yne. Thus for compound **7** decarbonylation giving crotonaldehyde was the main reaction, minor processes were decarbonylation giving methyl vinyl ketone and decarboxylation giving butadiene and but-2-yne.

The behavior of the furanones towards decomposition is thus in clear contrast to that of the saturated analogue γ -butyrolactone in two respects, the dominance of the decarbonylation process and the relatively low temperature at which it takes place. For example, the onset of decomposition for the saturated compound was found to occur at 980 °C under the same experimental conditions,⁵ significantly higher than that observed here for the furanones.

Reaction pathways

Isomerization. There has been substantial interest concerning the interconversion of isomeric furanones in the liquid state,^{15–18} but little work has been done for gaseous systems.¹⁹ In the liquid state the reaction is catalysed by acids or bases and is a labile tautomeric process involving proton transfers.^{15,16} In the gas phase such a process is not possible. Under the conditions of a gas flow at relatively low pressures, it is expected that the interconversion would be intramolecular rather than inter-

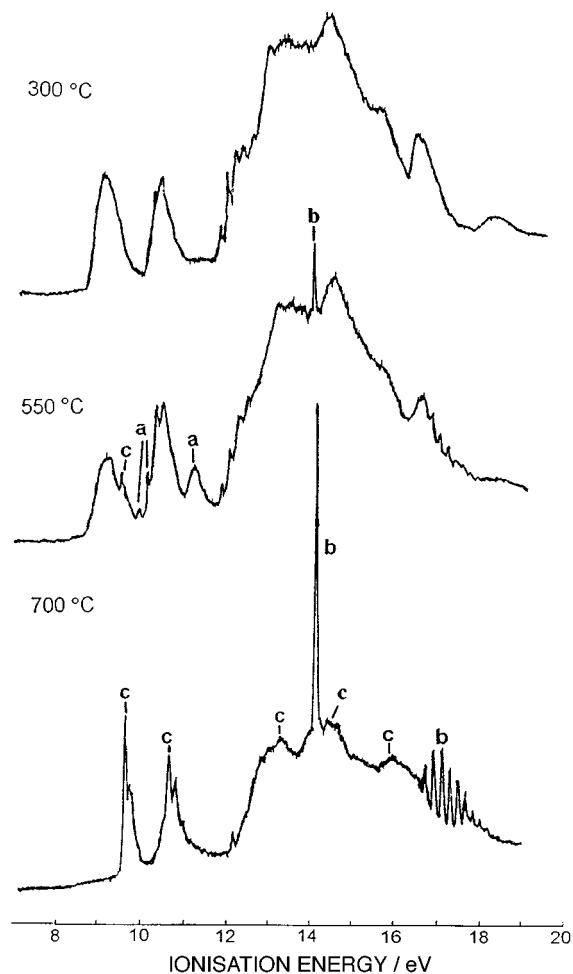
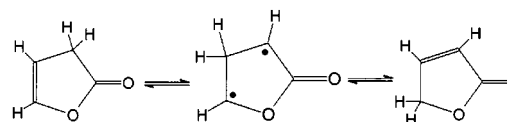


Fig. 4 Spectral changes during pyrolysis of 5-methylfuran-2(3H)-one: (a) 5-methylfuran-2(5H)-one; (b) CO; (c) methyl vinyl ketone.

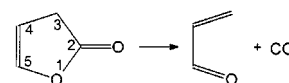
molecular, and would involve the shift of a hydrogen between positions 3 and 5 on the ring. Because of the rigidity of the five-membered cyclic structure, direct 1,3-hydrogen shifts are unlikely to take place, and the interconversion most probably proceeds through consecutive 1,2-hydrogen shifts as depicted in Scheme 1.



Scheme 1

In either direction the first hydrogen shift is expected to be rate determining as the subsequent shift in the biradical intermediate should be labile.

Decomposition of furan-2(3H)-one 4. The decomposition of **4** into acrolein and carbon monoxide is a cycloelimination reaction which involves the fission of two sigma bonds at the same carbon centre.



The mechanism is closely related to the reverse reaction, the [4 + 1] cycloadditions of enones.²⁰ A fundamental issue concerns the asynchronicity of the rupture of the two sigma bonds.²¹ In the case of the decarbonylation of **4**, the extremes

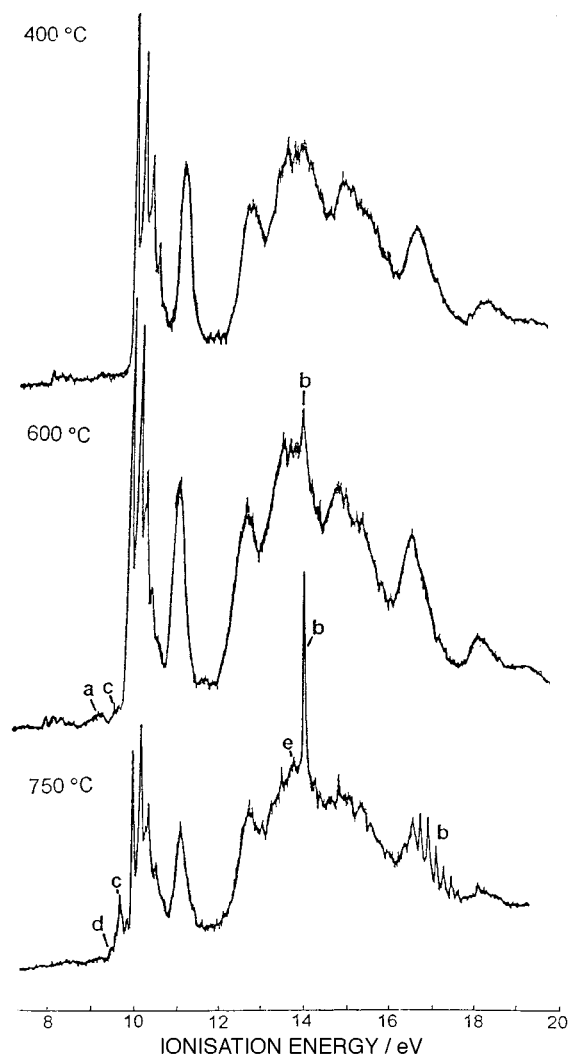
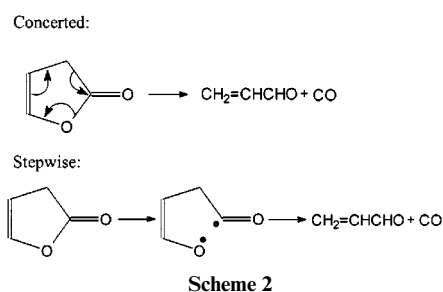


Fig. 5 Spectral changes during pyrolysis of 3-methylfuran-2(5H)-one: (a) 3-methylfuran-2(3H)-one; (b) CO; (c) crotonaldehyde; (d) methyl vinyl ketone; (e) CO₂.

of possibilities, synchronous concerted and asynchronous stepwise pathways, can be depicted as shown in Scheme 2.



It is expected that there would be substantial π -delocalization over the atoms C3–C4–C5–O1 in the transition states in these processes. To date there have been no experimental studies pertaining to the mechanism of the decarbonylation of the furanones. Closely related to the furanone reactions are studies carried out on the thermal decarbonylation reactions of dicyclopentadiene-1,8-dione, cyclopenten-3-one and norbornenone.^{22–24} However experimental data on activation parameters, solvent effects and vibrational energy distribution do not seem to provide an unequivocal decision among mechanistic possibilities.^{22–24}

While the PE spectroscopic data presented here appear to shed little light on the detailed reaction pathways, they show

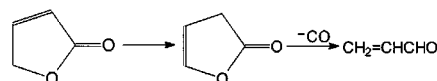
that decomposition was preceded by isomerization which took place at lower temperatures and reached a stationary state. It is expected that the energy barrier for decomposition would be higher than that for isomerization because the former involves complete bond-breaking steps.

As noted above, the furanones decomposed at significantly lower temperatures as compared to the saturated γ -butyrolactone (compound **1**). This can primarily be attributed to the stabilizing effect of π -delocalization in the transition states during decarbonylation of furanones either through the concerted or the stepwise pathway.

Decomposition of furan-2(5H)-one 5. A possible route for the decomposition of **5** is through the formation of the intermediate oxete.



The first step is a decarbonylation reaction and the second step an electrocyclic ring-opening involving four π -electrons. As oxete is expected to be unstable due to ring strain,²⁵ and π -delocalization in the transition state for decarbonylation is not favoured in this case, the energy barrier for the overall process would be high in comparison to the decarbonylation of **4**, and a more likely pathway for decomposition of **5** is through conversion to **4**.



Decomposition of the methylated furanones. The thermal decomposition of the two methylated furanones, namely **6** and **7**, mainly proceeded through decarbonylation leading to the formation of methyl vinyl ketone and crotonaldehyde, respectively. In each case the product species is that predicted if one assumes that dissociation occurs through the corresponding methylated furan-2(3H)-one. Thus the results are in agreement with the hypothesis that the 2(3H) isomer is the precursor for decarbonylation. It is also noted that for compound **7**, methyl vinyl ketone was detected as a minor product; this is consistent with the anticipation that decarbonylation through oxete formation is a relatively high energy pathway.

Concluding remarks

The thermal decomposition of furanones proceeded through decarbonylation as the main channel, and it was only in compound **7** that decarboxylation was observed as a minor reaction. The decarbonylation of the furanones was facile compared to the saturated lactones. Thus the onset of reaction for the furanones occurred at temperatures substantially lower than those of compounds **1–3** under similar conditions.^{5,7} The decarbonylation of furan-2(5H)-one proceeded *via* isomerization to the 2(3H) form. The relative lability of the latter appeared to be enhanced by π -delocalization in the transition state. Such a stabilizing factor was absent in the case of the saturated lactones.

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Paper 8/10028D