

# Photochemistry of six- and five-membered-ring $\alpha,\beta$ -unsaturated lactones in cryogenic matrices

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The photochemistry of representative six and five-membered  $\alpha,\beta$ -unsaturated lactones [ $\alpha$ -pyrone and some of its derivatives, including coumarin and 3-acetamidocoumarin, 2(5*H*)-furanone] isolated in cryogenic inert matrices has been investigated by infrared spectroscopy and quantum chemical calculations. In these types of molecules, two main competitive photochemical reaction pathways could be identified: ring opening, leading to formation of the isomeric aldehyde-ketenes, and ring contraction to the corresponding Dewar isomers. For  $\alpha$ -pyrone and 2(5*H*)-furanone, the ring-opening process dominates over the ring-contraction reaction, the same occurring for derivatives of these compounds bearing a voluminous substituent at position 3. In 2(5*H*)-furanone, the ring-opening reaction requires the simultaneous occurrence of a [1,2]-hydrogen atom migration. Nevertheless, it was found to be an easy process upon excitation at  $\lambda > 235$  nm. The ring-opening reaction was also found to occur much easily in  $\alpha$ -pyrone than in coumarin, and factors explaining this observation were discussed. In turn, the Dewar forms of the studied compounds resulting from the ring-contraction photoreaction were found to undergo subsequent photo-elimination of CO<sub>2</sub>, with formation of the corresponding cycloalkenes. In the matrices, CO<sub>2</sub> and the simultaneously formed cycloalkenes were found to exist as associated forms, in which the CO<sub>2</sub> molecule is preferentially placed over the cycloalkene ring in a stacked-type geometry. For coumarin, a third photoreaction channel was observed, leading to the formation of benzofurane and CO. This additional reaction channel corresponds to the photoreaction previously observed for the compound in the gaseous phase. Copyright © 2008 John Wiley & Sons, Ltd.

**Keywords:** matrix-isolation; infrared spectroscopy; photochemistry;  $\alpha,\beta$ -unsaturated lactones;  $\alpha$ -pyrone; coumarin; 2(5*H*)-furanone; aldehyde-ketene; Dewar isomer; ring-opening; ring-contraction

## INTRODUCTION

$\alpha,\beta$ -Unsaturated lactones receive important uses in organic synthesis besides being important biologically active compounds. Their weak toxicity and easy synthesis have made these compounds the subject of great interest and extensive investigation. Coumarins (benzo- $\alpha$ -pyrones), for example, are potent photosensitizers,<sup>[1–6]</sup> also exhibiting anti-coagulant, anti-HIV, anti-tumor, anti-hypertension, anti-arrhythmia, and anti-osteoporosis activities.<sup>[7–11]</sup> Many  $\alpha,\beta$ -unsaturated lactones also exhibit efficient light emission properties, which make them useful for potential applications in molecular electronic devices.<sup>[12–14]</sup>

Since long ago,  $\alpha,\beta$ -unsaturated lactones have been shown to possess an interesting photochemistry. As early as in 1960, Mayo<sup>[15]</sup> observed an open-ring ester photoproduct generated from 4,6-dimethyl- $\alpha$ -pyrone dissolved in methanol. A conjugated aldehyde-ketene was presumed to be the primary product of the photoreaction, although this intermediate species could not have been directly observed. The photochemistry of  $\alpha$ -pyrone was later studied using the matrix isolation technique.<sup>[16–18]</sup> In these studies, the open-ring aldehyde-ketene was observed as the main product, being rapidly produced upon UV irradiation ( $\lambda = 313$  nm) of the matrix. The IR bands assigned to the aldehyde-ketene were interpreted on the basis of coexistence in the matrix of several isomers of the molecule, all exhibiting the *Z* orientation at the double C=C bond. The second photoproduct, the Dewar isomer

of  $\alpha$ -pyrone (2-oxa-3-oxobicyclo[2.2.0]hex-5-ene), was found to be generated very slowly under these experimental conditions. Upon UV irradiation through quartz, the matrix-isolated Dewar  $\alpha$ -pyrone was found to decompose, with evolution of carbon dioxide and creation of antiaromatic cyclobutadiene.<sup>[16–19]</sup> However, the precise structural characterization of the aldehyde-ketene conformers could not be determined nor the structure of the CO<sub>2</sub>-cyclobutadiene complex that is expected to be formed under the matrix cage-confined conditions could be obtained.

On the other hand, somewhat surprisingly, the photochemistry of coumarin (benzo- $\alpha$ -pyrone) in the gas phase appeared to be distinct from that of the parent compound  $\alpha$ -pyrone, with the identified reaction taking place upon photolysis being decarbonylation, with production of CO and benzofurane.<sup>[20]</sup>

The apparent different photochemistry reported for these two analogous molecules stimulated our interest for this problem. Hence, recently, we have started a research program dealing with the photochemistry of  $\alpha,\beta$ -unsaturated lactones, specifically

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$\alpha$ -pyrone and several of its derivatives, including coumarin and 3-acetamidocoumarin, and analogous five-membered compounds. As result of our systematic studies on these compounds, an integrated vision of the photochemistry of this kind of compounds has been emerging. In this paper, we present a general overview of these studies, including novel data recently obtained for 2(5*H*)-furanone and 3-acetamidocoumarin.

## MATERIALS AND METHODS

### Experimental details

All compounds were obtained commercially and are of spectroscopic grade. The infrared spectra were obtained using a Mattson (Infinity 60AR Series) Fourier transform infrared spectrometer, equipped with a deuterated triglycine sulfate (DTGS) detector and a KBr beamsplitter, with  $0.5\text{ cm}^{-1}$  spectral resolution. Necessary modifications of the sample compartment of the spectrometer were done in order to accommodate the cryostat head and allow purging of the instrument by a stream of dry nitrogen to remove water vapors and  $\text{CO}_2$ . For deposition of the matrices, the compounds were placed in a specially designed Knudsen cell with shut-off possibility, whose main component is a NUPRO SS-4BMRG needle valve<sup>[21]</sup> and codeposited together with large excess of the host matrix gas (argon N60, xenon N48, from Air Liquide) onto a cold CsI window ( $T \sim 10\text{ K}$ ) mounted on the tip of the cryostat. All experiments were done on the basis of an APD Cryogenics close-cycle helium refrigeration system with a DE-202A expander. The matrices were irradiated using a series of long-pass optical filters, through the outer quartz or KBr external windows of the cryostat, using either a 200 W output power of the 500 W Hg(Xe) lamp (Oriol, Newport) or a 150 W xenon arc lamp (Osram XBO 150W/CR OFR).

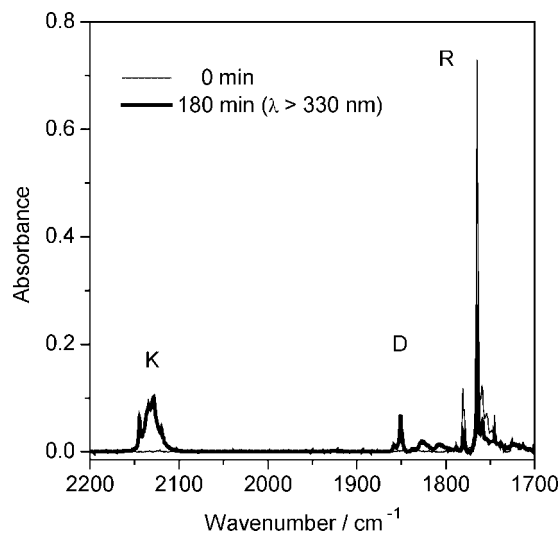
### Computational methodology

The equilibrium geometries for the studied compounds and their photoproducts were fully optimized at the DFT or MP2 levels of theory using basis sets of different sizes, with the 6-311++G(d,p) split valence triple- $\zeta$  basis set as reference basis. The DFT calculations were carried out with the three-parameter B3LYP density functional, which includes Becke's gradient exchange correction<sup>[22]</sup> and the Lee, Yang, Parr correlation functional.<sup>[23]</sup> Vibrational spectra were calculated at the same levels of theory used to optimize geometries, the calculated frequencies being later on scaled down using appropriate scale factors, in order to correct for vibrational anharmonicity, basis set truncation and the neglected part of electron correlation. All calculations were carried out using the GAUSSIAN 98 or GAUSSIAN 03 programs.<sup>[24,25]</sup>

## RESULTS AND DISCUSSION

### $\alpha$ -Pyrone

In agreement with the first reported studies on the photochemistry of  $\alpha$ -pyrone,<sup>[16–19]</sup> both the ring-opening reaction leading to conjugated ketene photoproducts and ring-contracting valence isomerization to the Dewar  $\alpha$ -pyrone form were observed upon photolysis of matrix-isolated  $\alpha$ -pyrone (Fig. 1). However, the new experimental studies<sup>[26]</sup> could be supported by extensive high-level theoretical calculations. This advantage permitted us



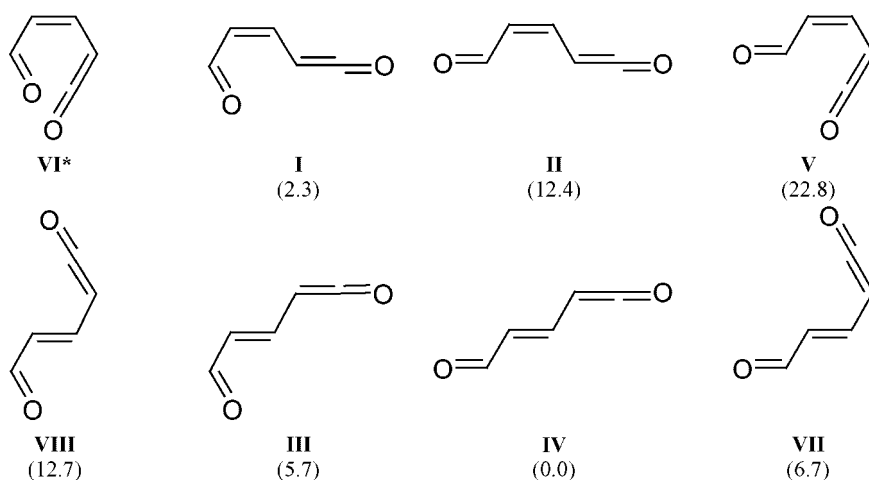
**Figure 1.** Spectral region ( $2200\text{--}1700\text{ cm}^{-1}$ ) show the evolution of the spectrum along the irradiation time. Regular trace, spectrum of  $\alpha$ -pyrone (as-deposited argon matrix; irradiation time = 0); bold trace, spectra obtained after 180 min of irradiation using a xenon arc lamp with a  $\lambda > 330\text{ nm}$  cut-off filter. R, D, and K indicate  $\alpha$ -pyrone, Dewar isomer of  $\alpha$ -pyrone, and aldehyde-ketene bands

to reveal some new facets in the photochemistry of the compound. For example, photoproduction of the *Z* as well as *E* forms of the conjugated ketene was spectroscopically proven for the first time (Figs 2 and 3).

Figure 3A shows the growing of the characteristic ketene antisymmetric stretching absorption along irradiation ( $\lambda > 285\text{ nm}$ ) of  $\alpha$ -pyrone in xenon matrix. At the first stages of irradiation, several component bands (labeled in the Fig. as Z1–Z5) grew rapidly. As detailed below, these bands can be assigned to the conjugated ketene in the *Z* configuration at the central  $\text{C}=\text{C}$  bond, which is first formed from  $\alpha$ -pyrone. After several minutes of irradiation, however, these bands stopped growing, while the two sharp bands at  $2127$  and  $2122\text{ cm}^{-1}$  (E1 and E2, which increased visibly faster only after the population of the initially formed photoproduct was not growing any more) continued to grow at all stages of irradiation. These features were given rise by ketene in the *E* configuration, which formed at the expense of the initially photoproducted *Z* form.

Very interestingly, subsequent irradiation at longer wavelength ( $\lambda > 337\text{ nm}$ ) resulted in partial recovery of  $\alpha$ -pyrone at the expense of the *Z* ketene (Fig. 3B), while the population of the *E* ketene did not change. After 55 min of irradiation with  $\lambda > 337\text{ nm}$ , the bands ascribed to the *Z* ketene practically vanished, while those due to the *E* isomer remained unchanged.

The identification of the different photoproducts manifesting themselves by the bands appearing at  $2140\text{--}2100\text{ cm}^{-1}$  cannot be done using only this spectral region. Indeed, both the photoproducted geometrical isomers of the ketene can exist in several conformational forms (Fig. 2), but theoretical calculations predicted that in the IR spectra of all of them a strong band due to antisymmetric stretching vibration of the ketene group should appear at nearly the same frequency.<sup>[26]</sup> Moreover, matrix site-splitting effects can also introduce some complexity to the analysis of this spectral region. Then, in order to shed light on the structures of the different observed conformers, besides the  $2140\text{--}2100\text{ cm}^{-1}$  region other spectral ranges had to be analyzed,



**Figure 2.** B3LYP/6-311++G(d,p) calculated zero-point energy corrected relative energies ( $\text{kJ mol}^{-1}$ ) for the aldehyde-ketene conformers. Top row, *Z* forms; bottom row, *E* forms. (\*) VI is not a minimum. (Adapted from Reference <sup>[26]</sup>, reproduced by permission of the PCCP Owner Societies)

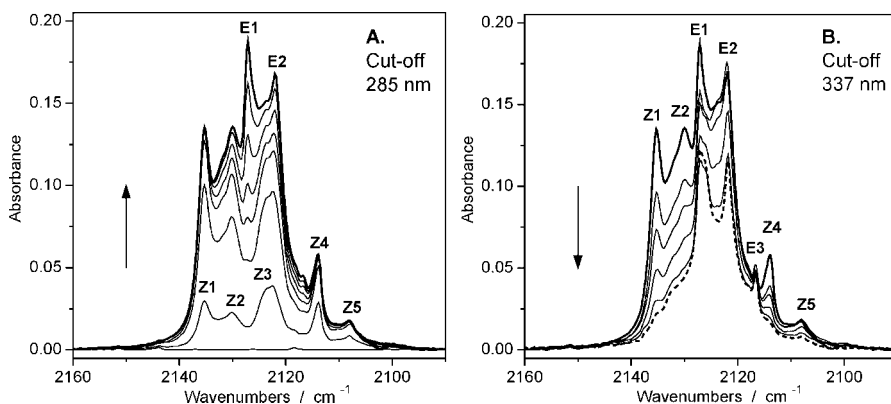
in particular, the  $1800\text{--}1500\text{ cm}^{-1}$  spectral region where the relatively intense bands due to the aldehyde  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  stretching vibrations of the ketene conformers can be expected to absorb.<sup>[26]</sup> From the detailed analysis of the whole spectra and taking into account the two types of behavior upon UV ( $\lambda > 285\text{ nm}$  and  $\lambda > 337\text{ nm}$ ) irradiation observed for the bands of the photoproducts as well as the results of theoretical calculations, the precise characterization of the ketene conformers contributing to the observed spectra was attained.<sup>[26]</sup> This analysis led to the conclusion that in the photolysed matrix four ketene conformers exist (I–IV; as in Fig. 2). These isomers correspond to the two most stable *E* forms and to the two most stable *Z* forms. The *Z* forms are directly obtained from  $\alpha$ -pyrone, while the *E* forms result from *Z* species by internal rotation around the central  $\text{C}=\text{C}$  bond in the excited state: III is produced directly from I and IV from II.

Another new conclusion resulting from our studies resulted from the fact that no evidence could be found of accumulation in the irradiated samples of the aldehyde-ketene conformers V, VII, and VIII. This could be explained considering that these forms have adequate geometries to undergo fast ring-closing reaction

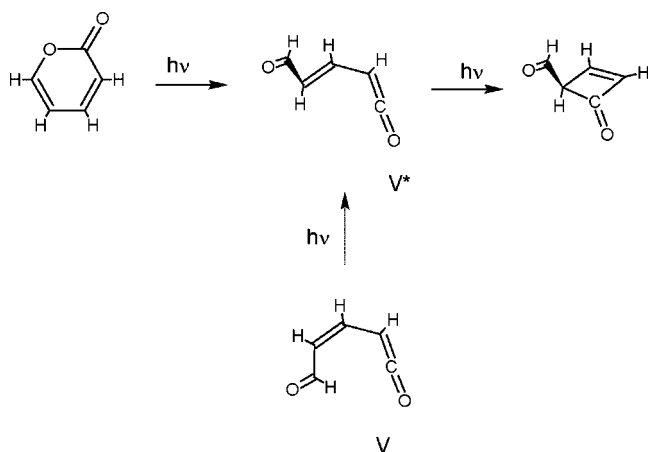
to 4-formyl-2-cyclobutene-1-one (Fig. 4), since in the excited state the aldehyde-ketene shall adopt preferentially conformations where the  $\text{C}-\text{C}=\text{C}-\text{C}$  dihedral angle is *ca.*  $90^\circ$ , as it is usually the case for  $\alpha,\beta$ -unsaturated carbonyl compounds. In consonance with the theoretical predictions of its vibrational spectrum, this compound was found to give rise to the bands observed in the  $1800\text{--}1830\text{ cm}^{-1}$  spectral range in the spectra of the irradiated matrix.

The photoproducted Dewar  $\alpha$ -pyrone gives rise to the very characteristic  $\nu\text{C}=\text{O}$  band at *ca.*  $1846\text{ cm}^{-1}$  (Fig. 1), as well as to other new bands appearing in other spectral regions. Irradiation of the matrix-isolated Dewar  $\alpha$ -pyrone with shorter wavelength UV light ( $\lambda > 235\text{ nm}$ ) leads to evolution of  $\text{CO}_2$  and to creation of antiaromatic cyclobutadiene.

Since after photolysis, the photoproducted  $\text{CO}_2$  and cyclobutadiene must be confined in the same matrix cavity, they form an associate. We have undertaken systematic calculations to identify the structure of this associate. Potential scans for the  $\text{CO}_2$ -cyclobutadiene complex assuming two different orientations within the  $\text{C}_2$  symmetry framework were performed, one with the  $\text{CO}_2$  molecule exhibiting the axial orientation and



**Figure 3.** Ketene antisymmetric stretching infrared spectral region. *E* and *Z* indicate bands assigned to *E* and *Z* ketene isomers, respectively: (A) progress of UV ( $\lambda > 285\text{ nm}$ ) irradiation of  $\alpha$ -pyrone isolated in Xe matrix ( $T = 25\text{ K}$ ). The traces correspond to spectra recorded after 0, 1, 6, 11, 17, 32, 42, and 62 min of irradiation. The arrow indicates general direction of changes. (B) The initial state is equal to the last spectrum of frame A. The subsequent UV irradiations were done with  $\lambda > 337\text{ nm}$ . Spectra recorded after 5, 10, 20, 30, and 55 min of irradiation. (Adapted from Reference <sup>[26]</sup>, reproduced by permission of the PCCP Owner Societies)



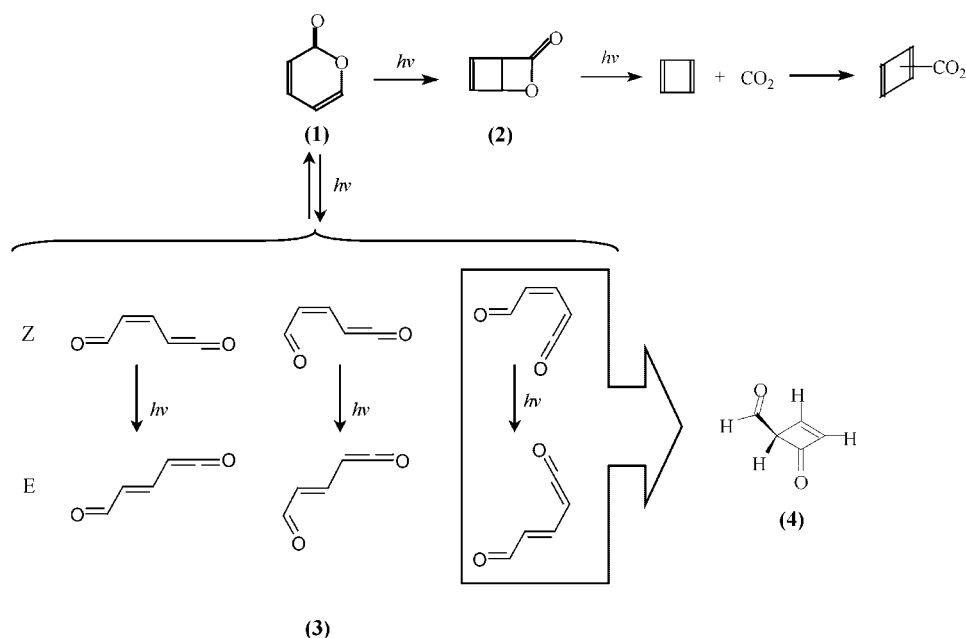
**Figure 4.** Photochemical generation of excited state ketene form  $V^*$  from  $\alpha$ -pyrone and subsequent photoisomerization of this species to 4-formyl-2-cyclobutene-1-one (schematic diagram). Analogous processes can be described for ketene conformers **VII** and **VIII**, all of them having the ketene group and the central C=C bond in the *s-cis* geometry

the other with this molecule exhibiting the parallel orientation to the cyclobutadiene plane. The first scan (axial) revealed a repulsive potential of interaction between  $\text{CO}_2$  and cyclobutadiene. On the other hand, the second one (parallel) showed a binding profile with an equilibrium minimum energy distance between the two molecules of *ca.* 3.45 Å and a stabilization energy of the complex equal to 3.45 kJ mol<sup>-1</sup>. In agreement with the theoretical predictions, the calculated spectra for the stacked  $\text{CO}_2$ -cyclobutadiene complex was shown to fit very nicely the experimentally observed bands ascribable to this species.<sup>[26]</sup>

According to our investigations, the UV-induced photo-transformations of  $\alpha$ -pyrone can then be summarized as shown in Fig. 5.

### Substituted $\alpha$ -pyrones

Following the study on  $\alpha$ -pyrone itself, several substituted  $\alpha$ -pyrones were investigated in our laboratory.<sup>[27–30]</sup> Comparing the photoreactions observed for  $\alpha$ -pyrone with those of 4,6-dimethyl- $\alpha$ -pyrone, 4-methoxy-6-methyl- $\alpha$ -pyrone, and 4-hydroxy-6-methyl- $\alpha$ -pyrone,<sup>[27,28]</sup> for example, it could be concluded that the Dewar isomer formation is much more effective in the case of the substituted derivatives, while the ring-opening photoreaction, leading to the aldehyde-ketene, proceeds easier for unsubstituted  $\alpha$ -pyrone. The ring-opening reaction leading to the ketene species is believed<sup>[31,32]</sup> to originate from excited states with  $n\pi^*$  character, whereas the process leading to the formation of the Dewar isomers should start from  $\pi\pi^*$  states. In  $\alpha$ -pyrones, the lowest excited singlet state has  $n\pi^*$  character.<sup>[14]</sup> Hence, the  $n\pi^*$ -type photochemistry is favored for such compounds when they are free of any substituents. On the other hand, conjugative-type substitution with groups such as —OH, —CH<sub>3</sub>, or —OCH<sub>3</sub>, blue-shifts the  $S_1 \leftarrow S_0$  ( $n\pi^*$ ) transition and red-shifts the  $S_2 \leftarrow S_0$  ( $\pi\pi^*$ ) transition,<sup>[14,33]</sup> reducing the gap between the  $S_1$  and  $S_2$  states and favoring the process leading to the Dewar formation. Note that the ring-opening reaction in  $S_1$  is not a barrierless process<sup>[34,35]</sup> and some excess of excitation energy is needed to promote the  $\alpha$ -bond cleavage. Hence, this process does not necessarily need to dominate, even though the lowest of the excited states is of  $n\pi^*$  character. If the energy gap between the  $n\pi^*$  and  $\pi\pi^*$  states is not too large, the processes typical for  $\pi\pi^*$  photochemistry can compete with the  $\alpha$ -bond cleavage or even dominate. Isomerizations to the Dewar forms, observed as



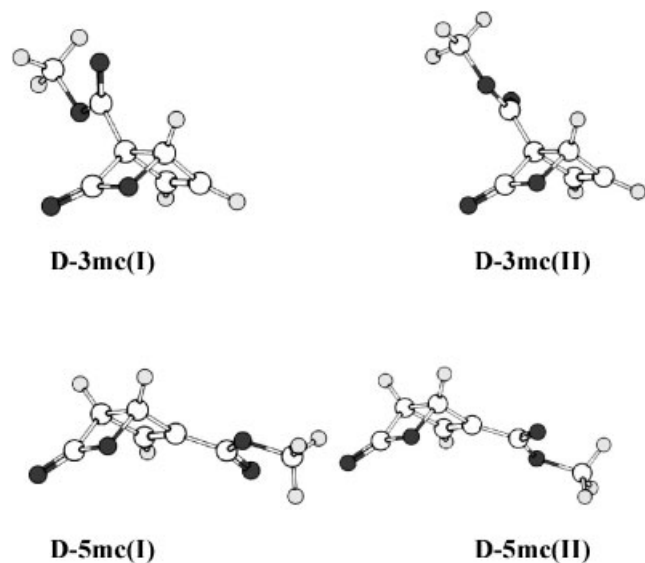
**Figure 5.** Summary of the observed  $\alpha$ -pyrone (1) photochemical reaction pathways: fast photoequilibration with the conjugated aldehyde-ketene (3) and slow ring-closure to the Dewar isomer (2). In the first process, several conformers are produced, with some of them further reacting to yield 4-formyl-2-cyclobutene-1-one (4). The Dewar isomer of  $\alpha$ -pyrone subsequently expels  $\text{CO}_2$ , to produce cyclobutadiene. The two latter species are confined in the matrix in the same cage and form a complex adopting a stacked structure with intermolecular distance of *ca.* 3.45 Å

dominating processes for 4,6-dimethyl- $\alpha$ -pyrone, 4-hydroxy- and 4-methoxy-6-methyl- $\alpha$ -pyrones, are good examples of such behavior.

Very interestingly, when the substituent is a volumous group at the position 3 of the  $\alpha$ -pyrone ring, for the matrix-isolated compounds the ring-contraction reaction becomes less easy and at least in some cases it does not occur at all. This has been recently observed for matrix-isolated 3-methyl coumalate, where only the ring-opening reaction was observed.<sup>[29,30]</sup> On the other hand, the 5-substituted analogue (5-methyl coumalate) shows the expected dominance of the Dewar-isomerization process over the ring-opening reaction, as found for the other substituted  $\alpha$ -pyrones already studied.

The possible reason which could preclude transformation of the 3-substituted compound into its Dewar form may be related with the steric properties of this latter molecule. In its most stable geometry, 3-methyl coumalate has a planar heavy atom backbone, which can fit easily between layers of a closely packed argon crystal, substituting a few argon atoms. This situation is very likely to occur during the deposition of a matrix sample. Once a matrix is deposited and cooled to 10 K, the solid argon becomes rigid and keeps the planar geometry of the matrix cage corresponding to the shape of the studied molecule. The optimized geometry of the Dewar isomer of 3-methyl coumalate, however, is strongly non-planar (Fig. 6). Then, a substantial rearrangement of the matrix cage would be required to accommodate the newly formed species. In practice, this energetically demanding process hinders the transformation of 3-methyl coumalate into its Dewar isomer. On the other hand, as far as ring opening (the alternative reaction pathway) is concerned, the photoproducted aldehyde-ketene does also have a planar structure (Fig. 6), its shape resembling very closely that of the starting compound. Then, the ring-opening reaction requires only a minor readjustment of the rigid argon environment, which is in agreement with its experimental observation.

Note that, according to the given interpretation, this suppression of the ring-contraction reaction channel should in



**Figure 6.** Three-dimensional views of Dewar isomers of 5-methyl-coumalate (D-5mc) and 3-methyl-coumalate (D-3mc) optimized at the DFT(B3LYP)/6-311++G(d,p) level of theory in vacuum (both molecules may exist in two different conformers, I and II). Note the same orientation of the Dewar fragment for all structures

general take place for  $\alpha$ -pyrone ring-containing compounds bearing a volumous substituent. Indeed, this seems to be the case, for example, for 3-acetamidocoumarin, where this process could not also be observed, the ring-opening reaction being the sole observed opened photochemical reaction channel for the matrix-isolated molecule.

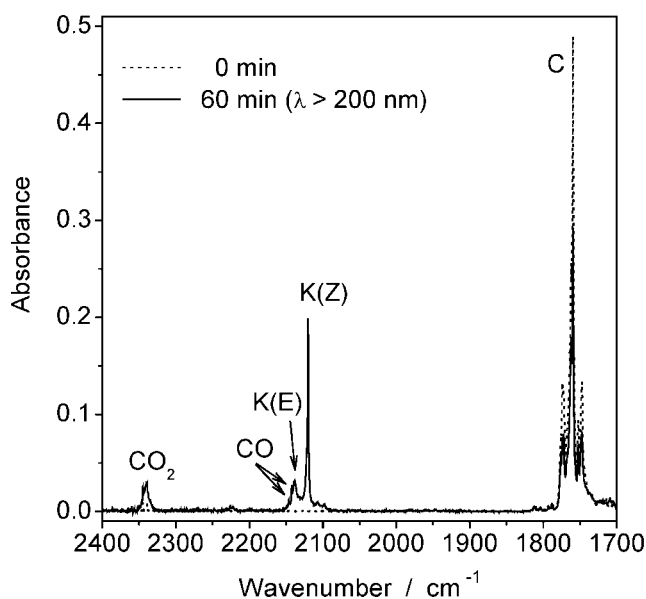
## Coumarin

In the gaseous phase, coumarin was found to decarbonylate, with benzofuran corresponding to the second photoproduct.<sup>[20]</sup> This corresponds to a different photochemical behavior compared to the data obtained for  $\alpha$ -pyrone and many other  $\alpha$ -pyrone derivatives, as described in the previous sections of this paper. Coumarin was then isolated in cryogenic rare gas matrices and its photochemical behavior studied in a similar way as in our previous studies on  $\alpha$ -pyrones.<sup>[36]</sup> Following the general experimental procedure adopted in our laboratory, the matrix-isolated coumarin was subjected to a series of irradiations where the incident light was filtered by different long-pass filters. Somewhat surprisingly, contrarily to what was observed for  $\alpha$ -pyrone, no changes in the spectra were observed when consecutive irradiations were carried out with filters transmitting light with  $\lambda > 337$ , 315, 285 nm, and finally  $\lambda > 235$  nm. The photoreactions started to occur, slowly, only when the sample was irradiated with  $\lambda > 200$  nm through the outer quartz window of the cryostat.

Close examination of the spectra of the irradiated matrices and comparison of the newly formed bands with those calculated for different putative photoproducts revealed that for coumarin three reaction channels are active (Fig. 7). Two of them correspond to those observed for  $\alpha$ -pyrone and simple  $\alpha$ -pyrone derivatives, that is, (a) ring contraction to the Dewar coumarin, followed by decarboxylation, and formation of benzocyclobutadiene and  $\text{CO}_2$ , which in the matrix exist predominantly as a stacked-type complex; (b) ring-opening leading to the formation of the isomeric conjugated ketene, which is first produced as Z isomers that subsequently convert to E forms. The third channel is similar to the UV-induced photochemistry of coumarin in the gaseous phase: decarbonylation, leading to the formation of a [benzofuran + CO] complex. On the other hand, the time evolution of the bands ascribed to the photoproducts resulting from the different observed reaction paths revealed that all products appear concomitantly, with approximately equal probabilities, and grow in parallel at all stages of irradiation.

The striking difference between the photochemistry shown by coumarin and  $\alpha$ -pyrone is that the ring-opening reaction in coumarin occurs only upon excitation with  $\lambda > 200$  nm, while in  $\alpha$ -pyrone it starts readily upon irradiation with  $\lambda > 337$  nm. This difference cannot be explained in terms of different energy gaps between the electronic ground states and the lowest excited states in two compounds. Indeed, in coumarin the two lowest singlet states were found to have energies of 29 100 ( $n, \pi^*$ )  $\text{cm}^{-1}$  and 32 800 ( $\pi, \pi^*$ )  $\text{cm}^{-1}$ ,<sup>[37]</sup> while in  $\alpha$ -pyrone the corresponding energies were comparable or slightly higher: 30 200 ( $n, \pi^*$ )  $\text{cm}^{-1}$  and 35 000 ( $\pi, \pi^*$ )  $\text{cm}^{-1}$ .<sup>[14]</sup> On the other hand, since to initiate the photochemical reaction an energy in the range  $235 > \lambda > 200$  nm was found to be necessary, it can be concluded that the target electronic excitation corresponds to the band at ca. 210 nm (ca. 47 600  $\text{cm}^{-1}$ ) observed in the UV absorption spectrum of coumarin (in ethanol) at room temperature.<sup>[38]</sup> According to calculations in Reference<sup>[37]</sup>, this band relates to  $S_5$ , that is, four

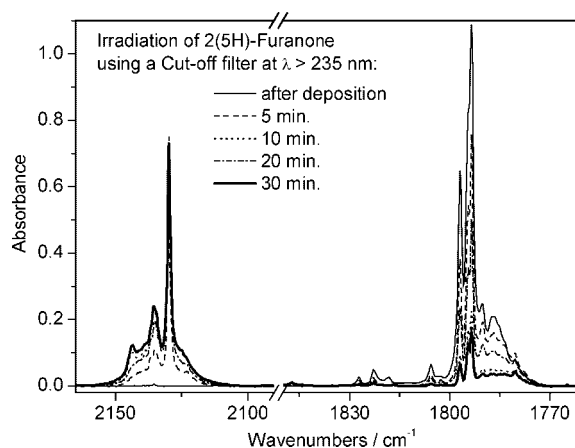




**Figure 7.** IR spectra (2400–1700  $\text{cm}^{-1}$  spectral range) of coumarin isolated in argon matrix ( $T = 10\text{ K}$ ): dotted trace, non-irradiated matrix (the weak doublet at 2345/2339  $\text{cm}^{-1}$  is due to residual impurity of matrix-isolated  $\text{CO}_2$  monomers); regular trace, UV-irradiated ( $\lambda > 200\text{ nm}$ , during 60 min.) matrix, showing bands due to photoproducts. Abbreviations: K(Z), K(E) and C refer to open-ring ketene (in the Z and E configuration) and coumarin, respectively

singlet states and five triplet states are situated below this level! The following main factors can justify the more difficult  $\alpha$ -cleavage in coumarin when compared to  $\alpha$ -pyrone:

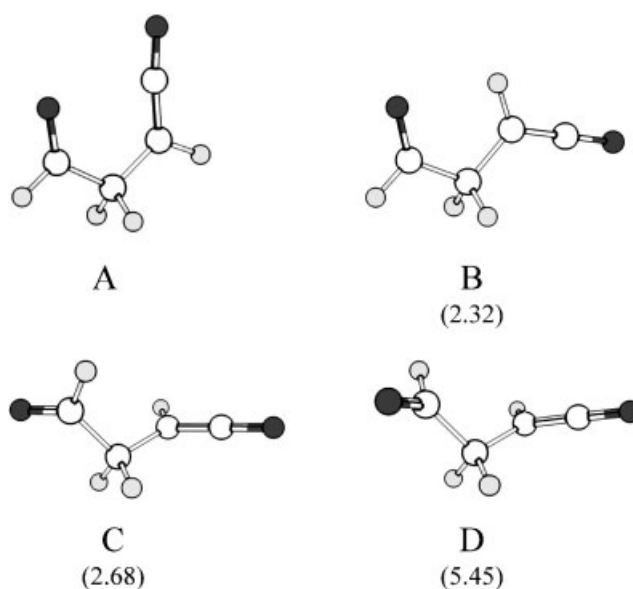
- (i) In coumarin, the presence of the additional phenyl ring results in an increased density of states in the vicinity of  $S_1$  and  $S_2$ . In this molecule,  $S_1$  ( $n,\pi^*$ ) and  $T_3$  ( $n,\pi^*$ ) are almost isoenergetic:  $29\,100 \pm 500\text{ cm}^{-1}$  and  $28\,000 \pm 300\text{ cm}^{-1}$ , respectively.<sup>[37]</sup> This can result in a very effective intersystem crossing and subsequent quenching, via  $T_2$ , to  $T_1$  ( $22\,000 \pm 300\text{ cm}^{-1}$ ). The lowest triplet state is probably too low in energy to induce the ring cleavage.
- (ii) The larger number of atoms in coumarin results in the increase of the vibrational degrees of freedom that can serve as intermediate states for the intramolecular processes of non-radiative dissipation of energy.
- (iii) In  $\alpha$ -pyrone, the ring-opening reaction results in the increase of the number of double bonds, which is a stabilizing factor in terms of the electronic  $\pi$ -system. On the other hand, in coumarin the opening of the pyrone ring reduces the aromaticity of the neighboring phenyl ring (the relative energies of the open-ring molecules relatively to the closed-ring counterparts are equal to ca.  $75\text{ kJ mol}^{-1}$  in  $\alpha$ -pyrone<sup>[26]</sup> and ca.  $140\text{ kJ mol}^{-1}$  in coumarin<sup>[36]</sup>).
- (iv) Competitive photolysis processes are more important in coumarin. Indeed, the present experimental data indicate that, along with the ring-opening reaction, the decarboxylation (through the Dewar isomerization) and decarbonylation reactions do also occur. In  $\alpha$ -pyrone, because the ring-opening reaction occurs at lower excitation energies than the isomerization to the Dewar form, these competing mechanisms are not operative (or not efficient enough).



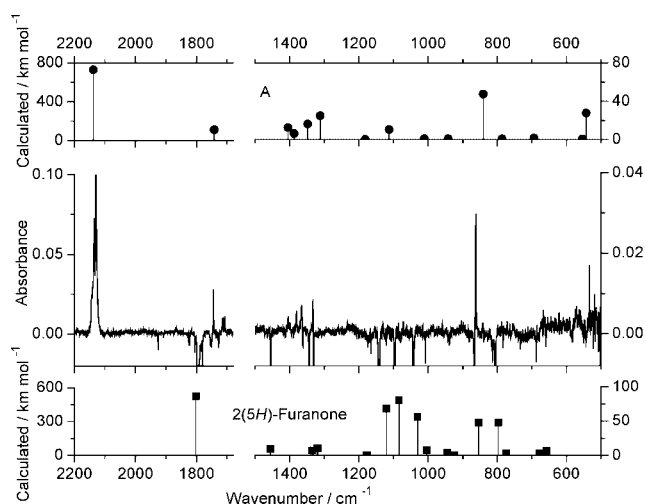
**Figure 8.** Observed infrared spectrum of 2(5H)-furanone isolated in argon matrix (10 K), after deposition and upon 5, 10, 20, and 30 min of irradiation ( $\lambda > 235\text{ nm}$ )

### 2(5H)-Furanone

In the case of 2(5H)-furanone, occurrence of the ring-opening reaction analogous to those observed for  $\alpha$ -pyrone, coumarin, and their derivatives must be accompanied by an H-atom migration from C3 to C4. Nevertheless, matrix-isolated 2(5H)-furanone rapidly reacts to give the corresponding isomeric aldehyde-ketene (Fig. 8). The potential energy surface of the aldehyde-ketene was investigated theoretically (Fig. 9) and the infrared spectra of the different conformers found were calculated. Very interestingly, these were easily distinguishable to each other. Comparison of these theoretical spectra with the spectra of the photolysed matrices (Fig. 10) unequivocally showed that the aldehyde-ketene was produced in a single conformer (form A in Fig. 9). This is also in agreement with the fact that the growing of the bands appearing upon irradiation of the matrices is uniform, revealing the formation of a single species.



**Figure 9.** B3LYP/6-311++G(d,p) calculated structures for the minimum energy conformations of 2(5H)-furanone and their relative energies ( $\text{kJ mol}^{-1}$ )



**Figure 10.** Lower frame, calculated spectra of 2(5H)-furanone. Mid frame, observed difference spectrum (spectrum obtained after 10 min of irradiation ( $\lambda > 235$  nm) followed by 7 min of irradiation ( $\lambda > 215$  nm) minus spectrum of the freshly deposited matrix). Upper frame, calculated spectra of the photoproducted aldehyde-ketene (conformer A)

Together with the generation of the ketene, a band at *ca.*  $2340\text{ cm}^{-1}$  also appears, indicating the formation of  $\text{CO}_2$  in a less probable reaction channel. Observation of  $\text{CO}_2$  in the photolysed matrix seems to point to the initial formation of the Dewar isomer of the furanone, which later expels  $\text{CO}_2$  in a similar way to the photochemical reactions of matrix-isolated  $\alpha$ -pyrone and coumarin. Together with  $\text{CO}_2$ , a second photoproduct must be formed, with formula  $\text{C}_3\text{H}_4$ . By analogy with the reactions of  $\alpha$ -pyrone and coumarin, cyclopropene is the best candidate for this species. Other possibilities are propyne and allene. However, all these compounds give rise only to low intensity bands and, then, the precise nature of the second photoproduct could not yet be determined hitherto.

## CONCLUSION

The results summarized in this paper on the photochemistry of a set of representative matrix-isolated six and five-membered  $\alpha,\beta$ -unsaturated lactones [ $\alpha$ -pyrone and some of its derivatives including coumarin and 3-acetamidocoumarin, 2(5H)-furanone] reveal that these types of molecules possess two main competitive photochemical reaction channels: (i) ring opening, leading to the formation of the isomeric aldehyde-ketenes, and (ii) ring contraction to the corresponding Dewar isomers. For  $\alpha$ -pyrone and 2(5H)-furanone, the ring-opening process dominates over the ring-contraction reaction, the same occurring for the studied derivatives of these compounds bearing a volumous substituent at C3. In 2(5H)-furanone, the ring-opening reaction requires the simultaneous occurrence of a [1,2]-hydrogen atom migration, but it was still found to be an easy process upon excitation at  $\lambda > 235$  nm. The ring-opening reaction was also found to be easier in  $\alpha$ -pyrone than in coumarin, and factors explaining this observation were presented. The Dewar forms of the studied compounds resulting from the ring-contraction photoreaction were found to undergo subsequent photoelimination of  $\text{CO}_2$ , with the formation of the corresponding cycloalkenes. In the matrices,  $\text{CO}_2$  and the simultaneously formed

cycloalkenes were found to exist as associated forms, in which the  $\text{CO}_2$  molecule is preferentially placed over the cycloalkene ring in a stacked-type geometry. For coumarin, a third photoreaction channel exists, leading to the formation of benzofuranone and CO. This additional reaction channel corresponds to the photoreaction previously reported to take place in the gas-phase.

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