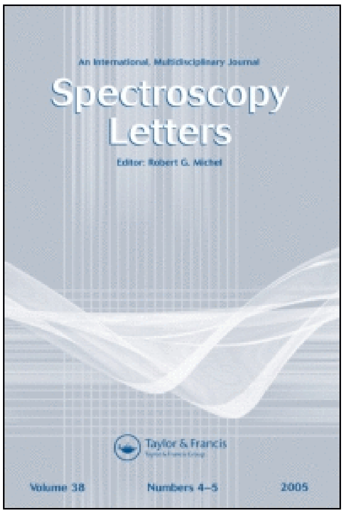

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A KETENE INTERMEDIATE IN 3-CYCLOPENTENONE PHOTOLYSIS : MATRIX-ISOLATION AND GAS PHASE EXPERIMENTS

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ABSTRACT

Photolysis experiments are performed at $\lambda \geq 230$ nm on argon matrix-isolated and on gas phase 3-cyclopentenone (1) ; in both cases, a ketene intermediate (**KE**) is detected (FT-IR spectra : 2121-2126 cm^{-1} in argon matrix ; 2066-2210 cm^{-1} in gas phase). 1,3-butadiene (2) and carbon monoxide are the reaction products. Two first-order consecutive photochemical processes occur $1 \xrightarrow{k1} \mathbf{KE} \xrightarrow{k2} 2 + CO$ with k_1 = 1.7 10-2 s^{-1} and k_2 = 2.4 10-2 s^{-1}.

INTRODUCTION

Previous work on 3-cyclopentenone 1 thermolysis1) and photolysis2) showed that in both cases, 1,3-butadiene 2 and carbon monoxyde are the final reaction products.

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In the gas phase, it has been established that **1** is photolyzed with nearly unit quantum yield, and that the degree of rotational excitation depends on the wavelength of the initial excitation.

Following excitation at $\lambda = 193$ nm, of the $\pi^* \leftarrow \pi$ transition, dissociation process is thought to occur from a highly vibrationally excited ground state, formed by a non radiative decay of the initial electronically excited molecule3). In the hypothesis of a concerted mechanism, the only transition state can be symmetrical or not. Nevertheless, such decarbonylation processes may involve two or several kinetic steps, with one or several reactive intermediates, i.e, species having life time equal to or longer than that of a few vibrations4).

In the present study, we report the photolysis experiments at $\lambda \geq 230$ nm on **1** isolated in argon matrices or in gas phase. The goal of this work was to obtain experimental evidence that would allow a choice between stepwise and concerted mechanisms of the dissociation of **1** following excitation of the $\pi^* \leftarrow n$ transition. Among the different mechanistic proposals, we wish to emphasize that one which involves biradical intermediate **3** resulting from cleavage of one carbon-carbon bond (Norrish I)2b) and subsequently loosing its CO moiety, thermally or photochemically, to give **2**.

$$\underline{\mathbf{3}} : [\overset{\bullet}{\overline{CH_2 - CH - CH}} - CH_2 - \overset{\bullet}{C} = O]$$

EXPERIMENTAL

3-cyclopentene **1** was prepared using the procedure described by Suzuki et al 5).

Matrix isolation experiments have beeen performed as previously described 6). The experimental parameters were: Matrix/solute ratio = 500; deposit temperature =20K; IR-TF spectra are recorded, when the matrix temperature was 10K, on a 7199 Nicolet spectrometer at 0.12 cm^{-1} resolution.

Irradiations were carried out, in matrix or in gas phase, using an Osram 200W hight pressure mercury lamp equipped with a quartz enveloppe.

RESULTS

When irradiated at $\lambda > 300$ nm, argon matrix isolated 3-cyclopentenone looks non reactive (less than 2% is photolyzed after one week) while in the gas photolysis it appears usually reactive (50 % in 2 hours). Performed at shorter wavelengths ($\lambda \geq 230$ nm), the photolysis slowly occurs in the matrix (25% after 66 hours), the gas phase experiments being again faster (30% after 1 hour). Recorded at different times, FT-IR spectra show that CO and **2** are the reaction products. The appearing absorption bands 907 ; 906 ; 905 ; 1015 ; 1020 ; 1024 ; 1380 ; 1596 and 1819 cm^{-1} are similar than those obtained by Squillacote et al7) for the FT-IR spectra of argon matrix isolated **2**. In spite of some spite splittings and frequency shifts ($\delta v \leq \pm 2$ cm^{-1} as a result of the presence of a CO molecule in the same cage), it is obvious that the photolysis exclusively lead to **2** *s-trans* conformer. Among the **2** *s-cis* IR absorption bands8), only the 1602 cm^{-1} one might be mixed up with the close s-trans one (1596 cm^{-1}) ; the intense 996 cm^{-1} absorption band of the **2** *s-cis* conformer is undoubtedly missing in our spectrum.

In the frequency range 2120-2150 cm^{-1} the absorption bands appears clearly separated in two groups as represented in Figure 1. As the separation between the most intense absorption bands in each group is quite large (13 cm^{-1}), all these bands cannot exclusively belong to CO. The broad band observed between 2130-2150 cm^{-1} is attributed to the CO absorption. The FT-IR spectrum obtained after 46 hours of irradiation, when 21% of **1** is photolyzed in Argon matrix, presents absorption bands at 2122.4 ; 2126.5 ; 2132.8 ; 2134.1 ; 2135.6 ; 2136.7 ; 2137.1 ; 2138.7 and 2138.6 cm^{-1}. This splitting of the CO absorption band (last 7 components) results from the presence of different **2** + CO complexes trapped in the same cage. Their population change along irradiation time. After two hours of irradiation, the 2132.8 cm^{-1} component is the strongest one ; after four hours, its intensity became the lowest at the benefit of the 2138.7 cm^{-1} one (cf. Fig. 1).

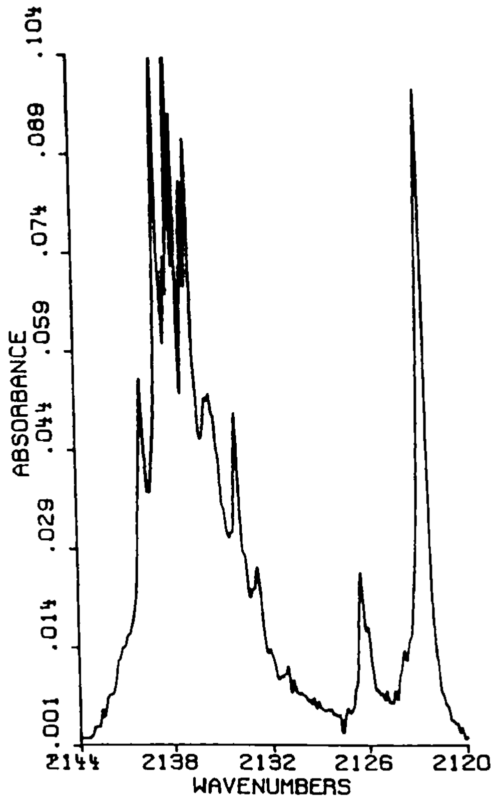

Figure 1 - FT-IR spectrum of photolysis products (CO and KE) after a 66 hours irradiation ($\lambda > 230$ nm) of argon matrix isolated 3-Cyclopentenone

The doublet at 2121-2126 cm^{-1} is clearly that of a ketene[9] KE. 1,4 pentadienone and its 1,3 isomer are logical candidates for the identification. So, for the 1,3-butadienone resulting from furan isomerization, the ν_{CCO} stretching has been observed at 2115 cm^{-1} [9,10]. The lack of the absorption bands of methyl cyclobutenone[11] seems indicative of the formation of the 1,4 pentadienone. But, the very low concentration of the transient, approximatively 1% of the initial concentration of **1**, precludes any other absorption bands to be observed except ν_{CCO} and prevents unambigous identification.

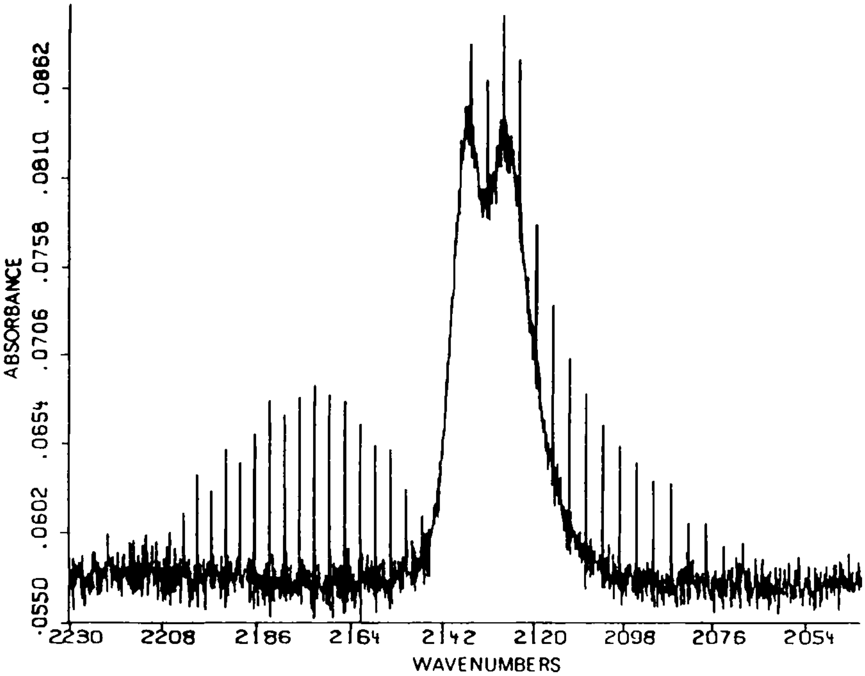

Figure 2 - FT-IR spectrum of photolysis products (CO and KE) in gas phase after a 20 min irradiation (irradiation at $\lambda \geq 230$ nm)

Table 1 - Experimental integrated absorbances (A in cm^{-1}) versus time (min) for 3-cyclopentenone photolysis ($\lambda \geq 230$ nm) in gas phase.

Time	0	6	11	20	40	75	120	300
$\underline{1}^{a)}$	11.30	10.29	9.37	8.04	5.73	3.16	1.47	0.00
$\underline{2}^{b)}$	0.000	0.000	0.003	0.008	0.027	0.061	0.099	0.141
KE$^{c)}$	0.000	0.388	0.371	0.423	0.434	0.380	0.317	0.119

a) $\nu_i - \nu_j$: 1748-1749 cm^{-1} ; ν_i and ν_i being the frequency limits used to measure the integrated absorbances ; b) $\nu_i - \nu_j$: 906-910 cm^{-1} ; c) $\nu_i - \nu_j$: 2100-2160 cm^{-1} ; partial overlap with CO absorption band (40 %).

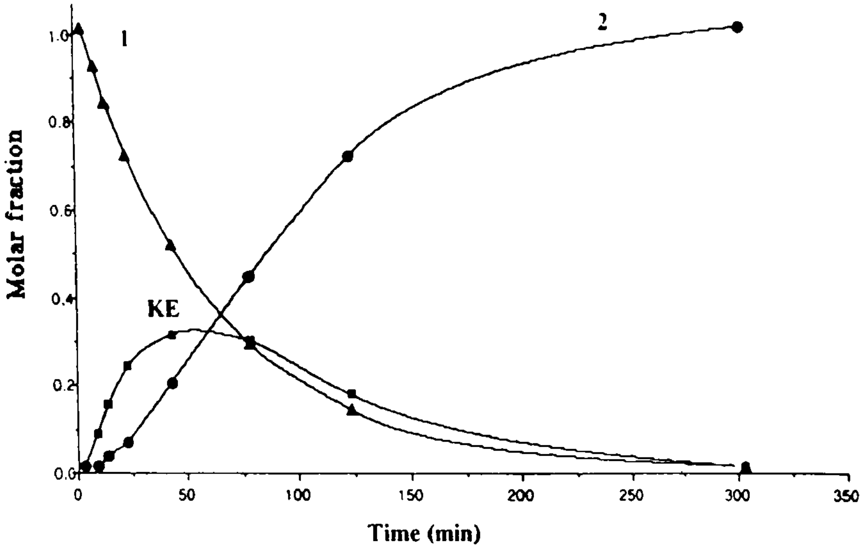

Figure 3 - Kinetics of gas phase **1** photolysis (irradiation at $\lambda \geq 230$ nm)

The photolysis of **1** in the gas phase was also monitored by FT-IR spectrometry and the reaction products **2** and CO are easily identified by comparison with the spectra of pure product. The ν_{CCO} absorption band of the ketene is observed between 2000 and 2160 cm^{-1} (Fig.2).

The evolution of the integrated absorbances versus time (Table 1) show that the ketene is a reactive intermediate (Fig.3). The kinetic behavior suggest a processes involving two consecutive photochemical reactions

$$\mathbf{1} \rightarrow \mathrm{KE} \longrightarrow \mathbf{2} + \mathrm{CO}$$

From the evolution of the integrated absorbance vs time, it is possible to obtain the values of the molar ratio X_i of the different reaction products at different times[12]. At 300 m the KE absorption band has vanished, that justify the hypothesis X(**2**) = 1.00 at 300 m. From least-squares analysis using a computer program[13] we obtain the values of the rate constants $k_1 = 1.70\ 10^{-2} \pm 1.24\ 10^{-3}\ s^{-1}$ and $k_2 = 2.36\ 10^{-2} \pm 7\ 10^{-4}\ s^{-1}$.

The very low reactivity of <u>1</u> embedded in an argon matrix may result from a cage effect that reduces the activation enthalpy of backward step <u>3</u> -> <u>1</u> at the expense of the other ones i.e. biradical would have a more constrained structure in the matrix than in the gas phase which permits reformation of the carbon-carbon bond.

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