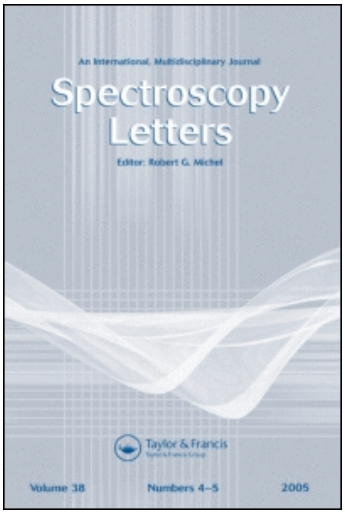

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PHOTOLYSIS OF MATRIX-ISOLATED 1,3,4,6-TETRATHIAPENTALENE-2,5-DIONE

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PHOTOLYSIS OF MATRIX-ISOLATED 1,3,4,6-TETRATHIAPENTALENE-2,5-DIONE

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ABSTRACT

Laser UV irradiation at 300 nm of 1,3,4,6-tetrathiapentalene-2,5-dione **1** isolated in argon matrix at 10K yields CO, CS_2 and SCO by two competitive pathways. The reaction was monitored by FTIR spectroscopy. The reaction products were assigned by comparison of their infrared spectrum with those obtained from literature data and the ab initio RHF/DZP calculated spectrum for **1** was perform. The kinetic data shows similar rate constant for the two processes (about 5 10^{-2} min^{-1}). Irradiation of carbonyl sulfide at 260 nm yields carbon monoxide and S atoms which react with carbon atoms trapped in the same matrix cage to yield CS_2.

Key Words: 1,3,4,6-Tetrathiapentalene-2,5-dione; Photolysis; Cryogenic matrix; Laser UV irradiation; FT-IR spectroscopy; Kinetic.

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INTRODUCTION

Carbon and sulfur are among the most abundant atoms in the universe. Large cumulene compounds containing both carbon and sulfur, with the general formula C_nS_2 have been detected in the interstellar medium (1). The C_2 cumulene, C_2S_2, has been observed in matrix photochemical and flash vacuum pyrolysis studies using bicyclic precursors (2,3). Electron impact ionization (4) of 1,3,4,6-tetrathiapentalene-2,5-dione **1** affords as main important fragments $C_2S_n{\cdot}^+$. The purpose of this work was firstly the determination of the photolysis reaction process of **1** trapped in argon matrix at 10K, using IR spectroscopy to monitor the photolysis and characterize the reaction products, and secondly comparison with the electron impact process.

EXPERIMENTAL DATA

The matrix was obtained by spraying a mixture of **1** and argon onto a golden copper plate cooled at 20K in a closed cycle helium refrigerator. The IR spectra were recorded at 10K by reflection on the Nicolet series II 750 FTIR in the 4000–400 cm^{-1} spectral range with a 0.12 cm^{-1} resolution (100 scans co-added).

The UV spectrum of **1** (solvent CH_2Cl_2), recorded in the 200–800 nm range on a Unicam UV4 spectrometer, shows two electronic transitions at $\lambda_{max} = 227$ nm ($\varepsilon = 5722\ mol^{-1} \cdot l \cdot cm^{-1}$) and 276 nm ($\varepsilon = 6632\ mol^{-1} \cdot l \cdot cm^{-1}$). It is similar to the one reported in the literature (222 and 273 nm in methanol) (5).

UV irradiations were performed using an 5023 DNS 10 Switched Nd:YAG laser equipped with an OPO niobiate and an OPO Vega (option doubling). Compound **1** was irradiated at $\lambda = 300$ nm, the SCO obtained in the matrix after the disapearing of **1** was irradiated at $\lambda = 260$ nm. The temperature of the sample during irradiation was maintained as possible at 10K.

The theoretical vibrational spectrum of **1** was determined by ab initio calculations using Gaussian 94 program package (6). The calculated vibrational frequencies were scaled via the standard Pulay procedure (7).

RESULTS

Vibrational Analysis of 1 Isolated in Argon Matrix

Prior to the photolysis experiments, the experimental spectrum of **1** isolated in argon matrix was carefully studied and compared with the literature data (5). The experimental and the theoretical scaled and unscaled vibrational frequencies of **1** are reported in Table 1 with the attribution of the different vibrational modes (potential energy distribution, PED). The formula of the compound is represented

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Table 1. Observed and Simulated Spectra of **1**. (ν = Stretching, β = Bending, τ = Torsion, OOP = Out of Plane)

	Experiment			RHF/DZP Ab Initio Calculation				
Modes	$\nu_{lit.}$[a]	$\nu_{exp.}$	I	$\nu_{calc.}$[b]	$\nu_{scal.}$[c]	Irel.[d]	$\Delta\nu/\nu$[e]%	P.E.D.[f]
1		1736	f	1869.1	1760.0	0.05	−1.38	100% ν(CO)
2	1727	1725	f	1855.5	1746.8	100	−1.26	100%ν(CO)
3	1678	1685	F	1778.8	1642.1	–	3.39	99% νCC)
4	973	977	f	1115.3	993.8	–	−1.72	71%ν(CS)
5	914	912	m	973.7	898.5	1.09	1.48	100% ν(CS)
6				932.5	834.7	5.88		71% ν(CS) + 23% β(SCO)
7				846.2	770.0	–		76% ν(CS) + 24% β(SCO)
8		739	f	752.5	693.0	5.32	6.22	91% ν(CS)
9				681.2	642.7	–		31% OOP(S) + 61% OOP(C)
10				574.7	542.2	2.06		97% OOP(O)
11				570.4	538.1	–		97% OOP(O)
12				562.3	502.0	–		62% ν(CS) + 33% β(SCS)
13				539.5	488.3	0.68		79% ν(CS) + 12% β(SCS)
14				491.1	451.9	–		87% ν(CS)
15				452.5	406.6	–		69% ν(CS) + 27% β(SCO)
16				451.9	398.5	0.57		72% β(SCO)
17				443.6	393.8	3.15		72% ν(CS) + 22% β(CSC)
18				386.1	341.0	–		29% ν(CS) + 53% β(SCO)
19				337.0	302.2	–		92% ν(CS)
20				317.6	299.6	0.73		33% OOP(O) + 59% OOP(S)
21				218.6	193.1	0.1		76% β(SCS)
22				143.9	135.8	–		54% OOP(S) + 16% OOP(C) +25% Γ(CS)
23				104.7	98.8	–		67% OOP(O) + 19% OOP(C)
24				68.4	64.5	0.25		51% OOP(O) + 22% Γ(CS)

[a]Schumaker, R.R. J. Am. Chem. Soc. **1977**, 5521.
[b]Calculated frequencies.
[c]Scaled frequencies (stretching S–C = 0.86, bending 0.75, other stretchings, torsions and motions out of plane 0.89).
[d]Relative intensity.
[e]$(\nu_{exp.} - \nu_{theor.})/\nu_{exp.}$
[f]Assignments.

in Scheme 1. The experimental vibrational spectrum is characterized by its simplicity, due to the D_{2h} symmetry of the molecule, and by the strong absorption band at 1685 cm^{-1}.

Absorption bands are identified by comparison with the theoretical spectrum (Cf. Table 1) obtained from *ab initio* calculations using DPZ basis. In order

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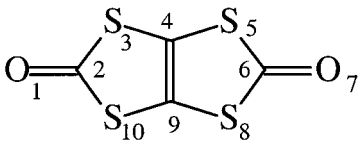

Scheme 1. Structure of tetrathiapentalenedione.

to assign all frequencies we performed a theoretical vibrational analysis for **1**. Its optimised geometry (Cf. Table 2) was the starting point for the calculations of the second derivative of the total molecular energy. To allow a comparison with experimental values, the calculated wavenumbers were scaled by the factors of 0.86, 0.89 and 0.75 for the stretching S−C═, the other ones, out of plane deformations and torsions, and the bending deformations respectively.

Photolysis Experiments

When matrix isolated **1** is submitted to a laser irradiation at $\lambda = 220$ nm in the first absorption band of its electronic spectrum, we do not observe any evolution of the infrared spectrum. However when the matrix is submitted to a laser irradiation at $\lambda = 300$ nm, in its other electronic absorption band, we observe the decrease of **1** infrared absorption bands and new absorption bands appear in different areas of the spectrum.

The photochemical behavior of **1** and of the reaction products embedded in the argon matrix at 10K is shown in Figure 1A where evolution of the spectra is illustrated for three irradiation times. The lower trace shows the spectrum after deposition and before irradiation (time $t = 0$). The middle trace shows the appearance of the spectrum after 17 minutes of irradiation at 300 nm and the upper trace after 60 minutes of irradiation at 300 nm. This later time corresponds to a complete vanishing of **1**.

Table 2. Ab Initio Optimized Geometry of **1**. (Bond Lengths Are in Å, Bond Angles Are in Degrees)

Geometric Parameters Calculated in RHF/DZP					
Length Bonds		Angle Bonds		Diedral Angles	
O_1C_2	1.20	$O_1C_2S_3$	123.3	$O_1C_2S_3C_4$	180.0
C_2S_3	1.84	$S_3C_2C_{10}$	113.4	$C_2S_3C_4C_9$	0.0
S_3C_4	1.80	$S_3C_4S_5$	121.5		
C_4C_9	1.32	$S_3C_4C_9$	119.2		
		$C_2S_3C_4$	94.1		

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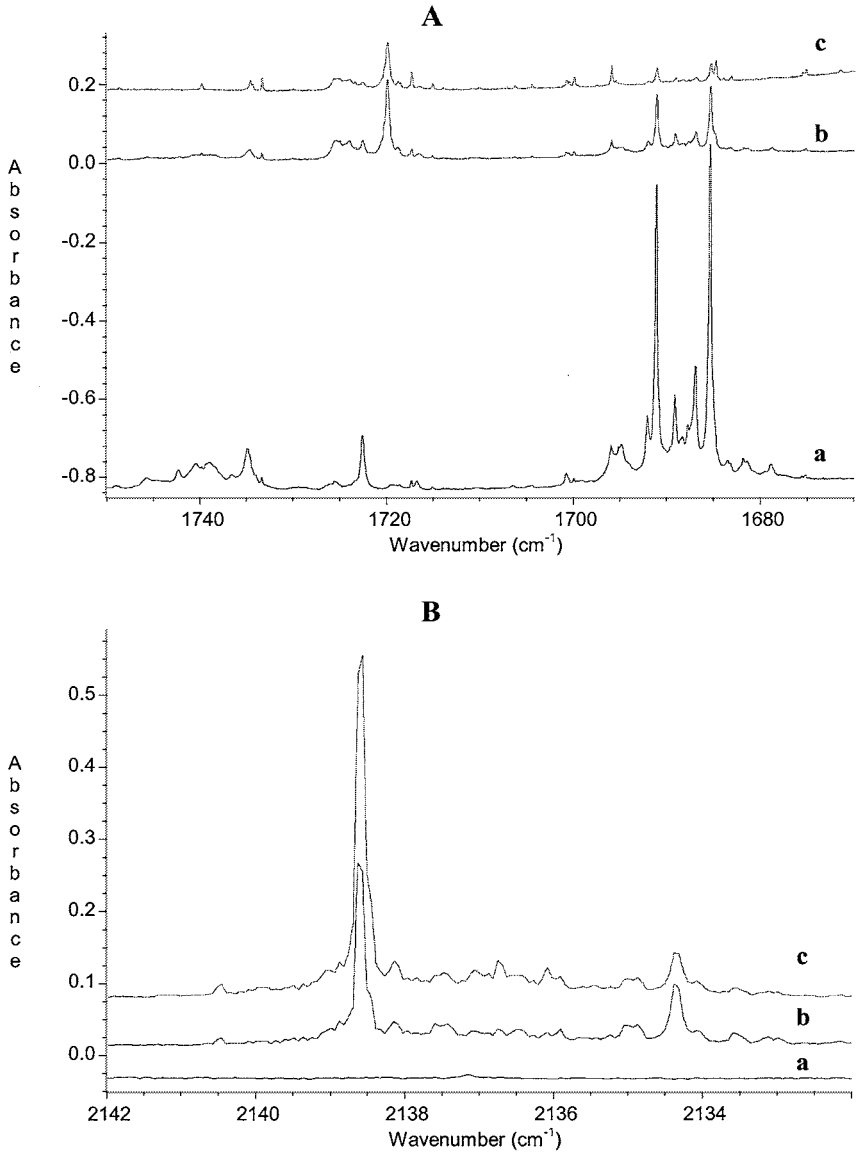

Figure 1. Evolution of the FTIR spectra of **1** and photoproducts isolated in argon matrix at 10K during laser irradiation at $\lambda = 300$ nm. (a) spectrum after deposition, (b) and (c) spectra after 17 and 60 minutes of irradiation respectively.

(*continued*)

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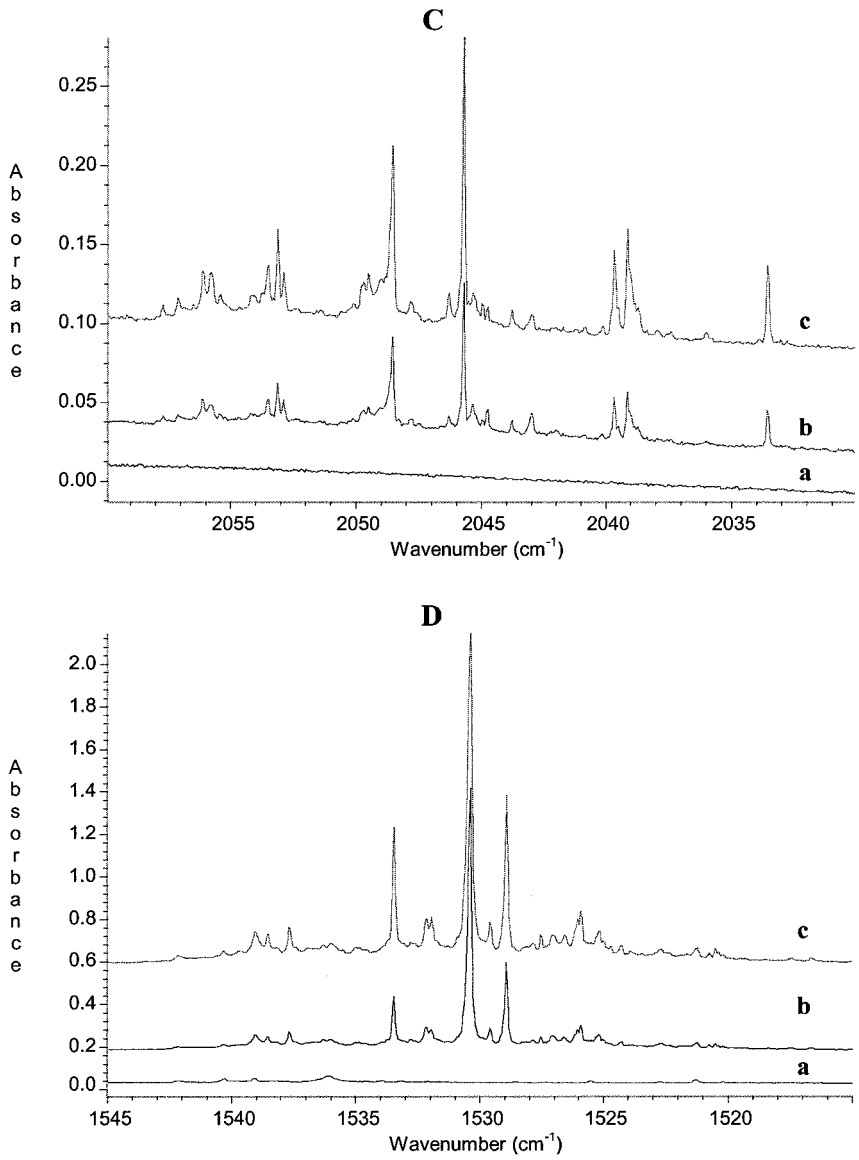

Figure 1. *Continued*

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The new absorption bands were assigned to three different compounds CO, SCO and CS_2. The multiplet structure observed in the infrared spectrum is characteristic of the different photolysis product organisations in the trapping cages.

The characteristic strong absorption band of the ν_{CO} stretching mode appears at 2139 cm^{-1} (Figure 1B).

In the range 2065–2030 cm^{-1} a multiplet of weak absorption bands centered at 2046 cm^{-1} is observed. It is attributed to the characteristic ν_1 mode of carbonyl sulfide trapped in different sites (Figure 1C) (8,9,10).

The multiplet of strong absorption bands centered at 1530 cm^{-1}, which have the same kinetic behaviour as the weak ones observed at 2184 cm^{-1}, can be assigned to carbon disulfide by comparison with literature data (9,11,12).

After complete disappearance of **1**, the matrix was irradiated at 260 nm in the SCO electronic absorption band (13). Under irradiation at this wavelength the carbonyl sulfide is photodecomposed leading to the formation of carbon monoxide and atomic sulfur (9). This evolution is observed in the infrared spectrum (Cf. Figs. 2A–C) by the vanishing of the 2046 cm^{-1} absorption bands. Simultaneously we observe an increase of the ν_{CO} and ν_{CS_2} absorption bands (Cf. Figs 2A–C).

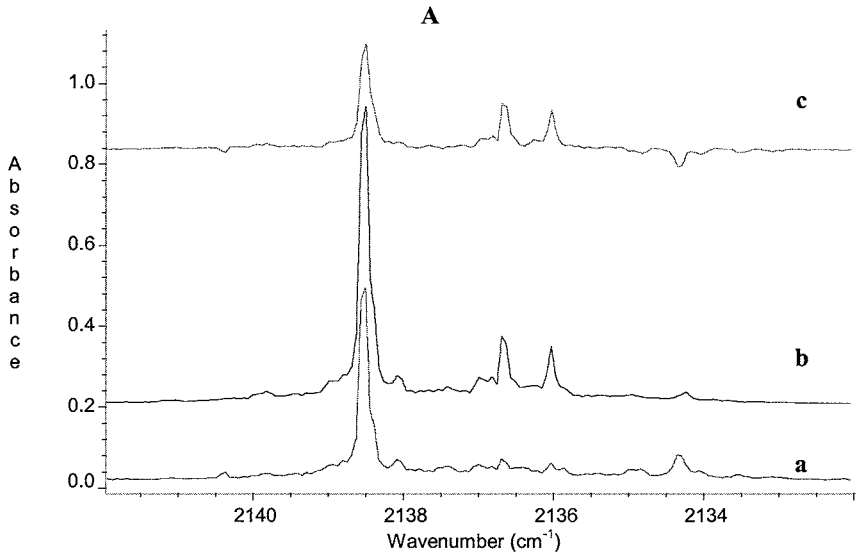

Figure 2. Evolution of the FTIR spectra during irradiation at 260 nm of SCO trapped in argon matrix at 10K. (a) spectrum after 60 minutes of irradiation at 300 nm and before irradiation at 260 nm, (b) spectrum after 16 minutes of irradiation time at 260 nm, (c) spectra differences (b)–(a).

(*continued*)

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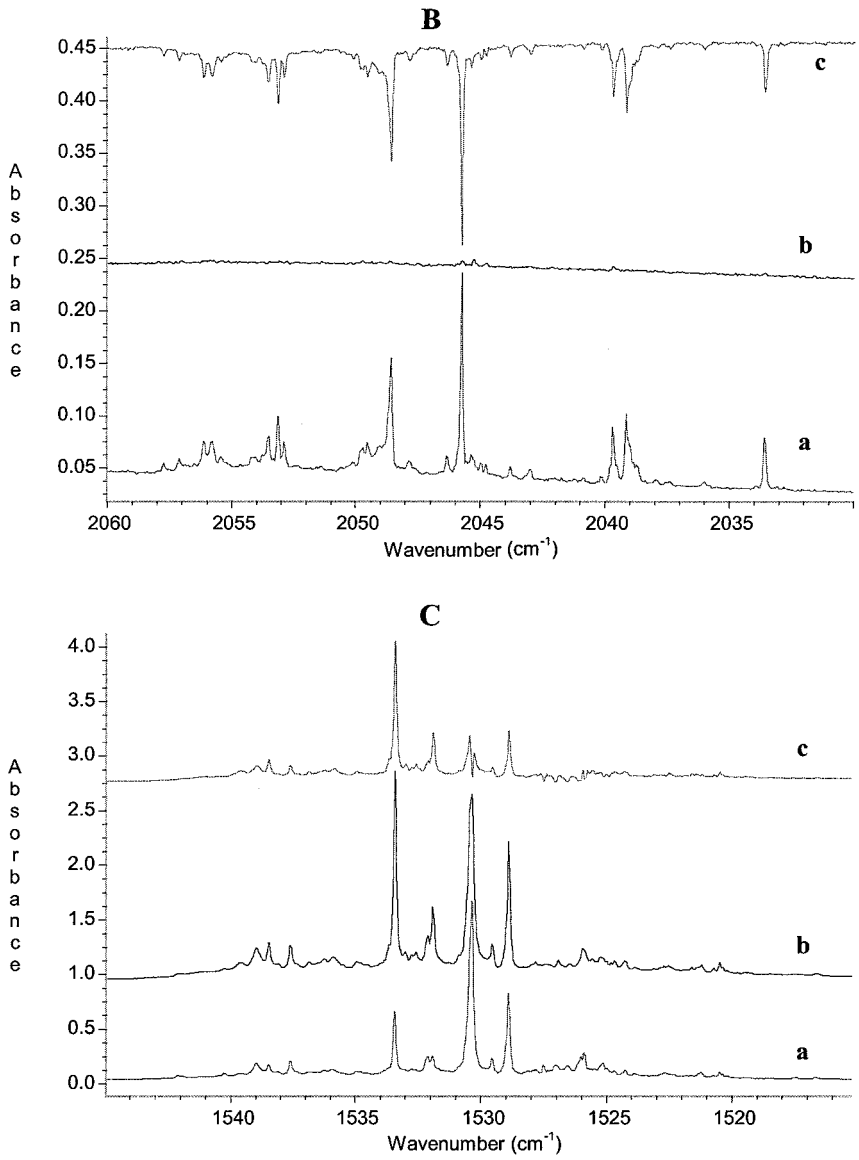

Figure 2. *Continued*

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Table 3. Irradiation of **1**: Evolution of the Molar Ratios of the Reaction Products Versus Time

Time (min)	0	2	4	6	8
1	1	0.690 ± 0.069	0.563 ± 0.056	0.452 ± 0.045	0.374 ± 0.037
SCO	0	0.051 ± 0.005	0.074 ± 0.007	0.109 ± 0.011	0.119 ± 0.012
CO	0	0.046 ± 0.005	0.092 ± 0.009	0.131 ± 0.013	0.172 ± 0.017
CS_2^a	0	0.046 ± 0.005	0.092 ± 0.009	0.131 ± 0.013	0.172 ± 0.017
CS_2^b	0	0.026 ± 0.003	0.037 ± 0.004	0.055 ± 0.006	0.060 ± 0.006
C	0	0.026 ± 0.003	0.037 ± 0.004	0.055 ± 0.006	0.060 ± 0.006
Time (min)	12	17	25	40	60
1	0.261 ± 0.026	0.229 ± 0.023	0.177 ± 0.018	0.129 ± 0.013	0.046 ± 0.005
SCO	0.162 ± 0.016	0.168 ± 0.017	0.202 ± 0.020	0.237 ± 0.024	0.304 ± 0.030
CO	0.245 ± 0.025	0.258 ± 0.026	0.302 ± 0.030	0.353 ± 0.035	0.409 ± 0.041
CS_2^a	0.245 ± 0.025	0.258 ± 0.026	0.302 ± 0.030	0.353 ± 0.035	0.409 ± 0.041
CS_2^b	0.081 ± 0.008	0.084 ± 0.008	0.101 ± 0.010	0.119 ± 0.012	0.152 ± 0.015
C	0.081 ± 0.008	0.084 ± 0.008	0.101 ± 0.010	0.119 ± 0.012	0.152 ± 0.015

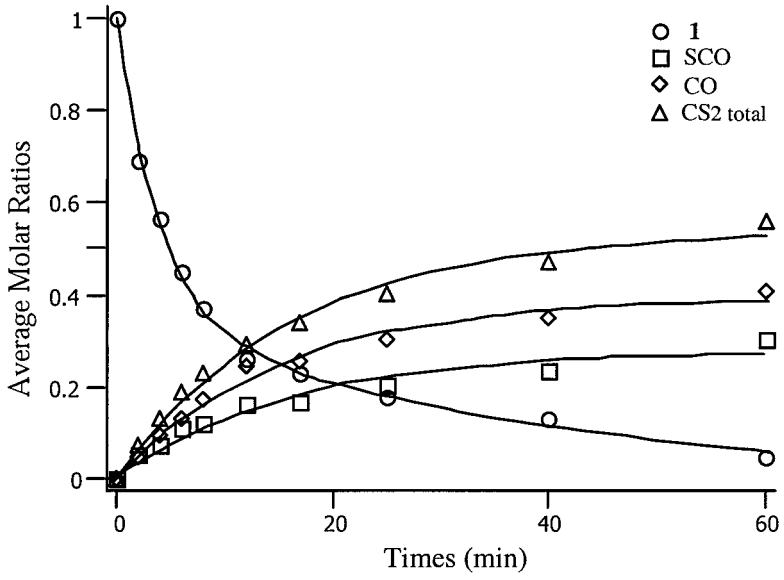

Figure 3. Curve fit of **1**, SCO, CS_2 and CO average molar ratios versus time during the irradiation at $\Lambda = 300$ nm.

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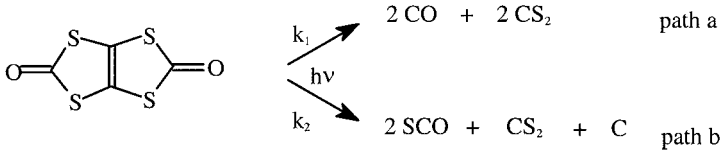

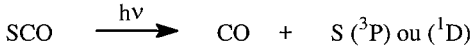

Scheme 2. Photodecomposition mechanism of compound **1**.

KINETIC STUDY

Kinetic analysis was carried out to describe the photochemical processes and explain the increase of carbon disulfide concentration in the matrix (observed in particular at 1533,5 cm^{-1}, Cf. Figs. 2A–C). From the evolution of the integrated absorbances versus time, it is possible to obtain the values of the molar ratios X_i of the different reaction products at different times (14) (Cf. Table 3). The kinetic behaviour of the X_i versus time is reported in Figure 3.

The lack of intermediates in the kinetic evolution of the reaction suggests two competitive pathways for the **1** photolysis. They are reported in Scheme 2. This scheme shows evidence for an unimolecular decomposition process for **1** (first order kinetics) which leads, on the one hand, to the formation of CO and CS_2 (path **a**, $k_1 = (4.84 \pm 0.31)\ 10^{-2}\ min^{-1}$) and on the other hand to the formation of SCO, CS_2 and atomic carbon C (path **b**, $k_2 = (5.90 \pm 0.39)\ 10^{-2}\ min^{-1}$). The C atoms are not observable but their presence is confirmed by the formation of CS_2 during irradiation of SCO at 260 nm. CS_2 formation can occur by recombination of carbon and S atoms trapped in the same matrix cage.

CONCLUSION

Products of **1** photolysis, CO, SCO and CS_2 were isolated in argon matrix at 10K. These compounds are obtained according to two competitive pathways with similar reaction rates. These processes are very different from those observed by Sülzle and Scharwz (4) in electron impact ionization experiments and C_2S_n compounds are not observed.

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