Photolysis of Matrix-Isolated Cyclopropylidene Ketene: Kinetic and Theoretical Studies of the Cyclopropylidene Formation

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Cyclopropylidene ketene **2** is generated by ultraviolet irradiation ($\lambda \geq 230$ nm) of cyclopropanecarbonyl chloride isolated in argon matrices at 15 K. FT-IR spectra of the primary photolysis products (**2** and HCl) trapped in the same cage show the formation of molecular complexes. The HCl stretching mode observed at 2793.5, 2739 cm^{-1} is shifted to 61 cm^{-1} below the frequency of monomeric HCl (2888.0, 2863.5 cm^{-1}) in argon matrix. Irradiation of **2** at $\lambda \geq 230$ nm induces reversible formation of CO and of a new transient assumed to be cyclopropylidene **3**. This carbene reacts with HCl trapped in the same cage or gives 1,2-propadiene by intramolecular rearrangement. The kinetic data show that the rate constant of 1,2-propadiene formation is twice as large as that of cyclopropyl chloride formation. To account for the results of matrix isolation experiments the photodissociation of the cyclopropylidene ketene was modeled by *ab initio* calculation using 6.31G* and "mini" Huzinaga basis sets.

Introduction

The matrix isolation technique is certainly the most valuable method for the investigation of reactives species.[1,2] Our interest in the synthesis, identification, and chemical reactivities of neutral intermediates[3,4] had led us to carry out an experimental and theoretical study of the cyclopropylidene ketene **2** isolated in argon matrices at 15 K. The choice of this ketene for our study provides an interesting comparison with extensive theoretical work of this system by Fukui and co-workers.[5]

Carbon suboxide, C_3O_2, is effectively known to undergo a photochemical reaction with olefins.[6,7] With ethylene, the major products of reaction are 1,2-propanediene **5** and carbon monoxide. It was proved that the newly inserted carbon atom derives from the center position of C_3O_2 and is found predominantly in the 2 position of propadiene.[8] Theoretical investigations by Minato et al.[5] suggest that the reactive intermediate, the carbonyl carbene C_2O, adds to ethylene to produce cyclopropylidene ketene **2** as previously postulated by Willis and Bayes;[6c] subsequently **2** is decomposed into CO and cyclopropylidene **3**. This transient collapses to form ground-state propadiene **5** as was observed experimentally from cyclopropylidene derivatives obtained by insertion of carbon atoms in double bonds.[9] Theoretical calculations by Minato,[5] Dewar,[10] Pasto,[11] and recently Ruedenberg et al.[12] confirm this experimental sequence. Still, some discrepancies exist between calculated values for the **3** → **5** transition state energy (between 18[11] and 40[12] kcal·mol^{-1}) and experiment (**3** gives **5** spontaneously at temperatures as low as 77 K[13]).

In the present study, we report the first photolysis experiments on **2** isolated in argon matrices. Cyclopropylidene ketene **2** and HCl are the primary products obtained by UV photolysis of cyclopropanecarbonyl chloride **1** and trapped in the same inert gas cage.[14,15] The goal of this work was to obtain experimental evidence that would allow a choice between stepwise and concerted mechanisms of the photolysis of **2**. The theoretical studies of the reaction were essentially limited to the rate-determining step **2** → **3**.[5] Moreover, the geometries and the energies of the two conformers of **1** were calculated. The amounts of the reaction products were carefully examined, and kinetic data were obtained by FT-IR monitoring.

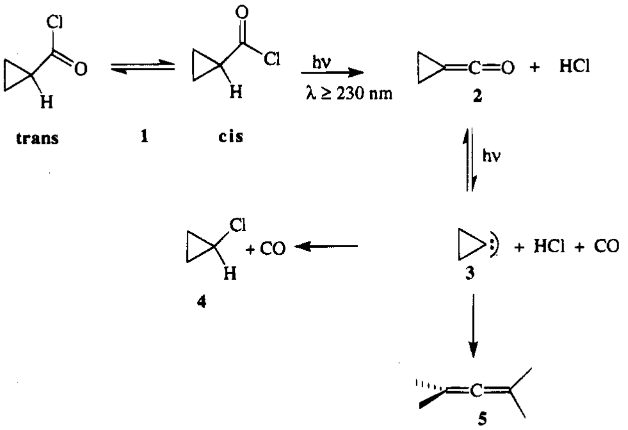

Figure 1. Compound formulas and reaction paths for cyclopropanecarbonyl chloride photolysis.

Experimental Section

Matrix Isolation Experiments. The apparatus and experimental techniques were described previously.[14,16] Commercial cyclopropanecarbonyl chloride (Aldrich) was purified by distillation before use. The relative concentrations of rare gas to cyclopropanecarbonyl chloride at room temperature (M/S ratio) was adjusted by pressure measurements; reproducible solute partial pressures required the use of a Datametrics (Barocel, Series 600) capacitance manometer. The deposition temperature (20 K) and the deposition rate of gas mixtures was controlled with an Air Liquide microleak (V.P/RX); it never exceeded 2 mmol/h and it was chosen to avoid, as far as possible, a site splitting of the vibrational absorption bands.

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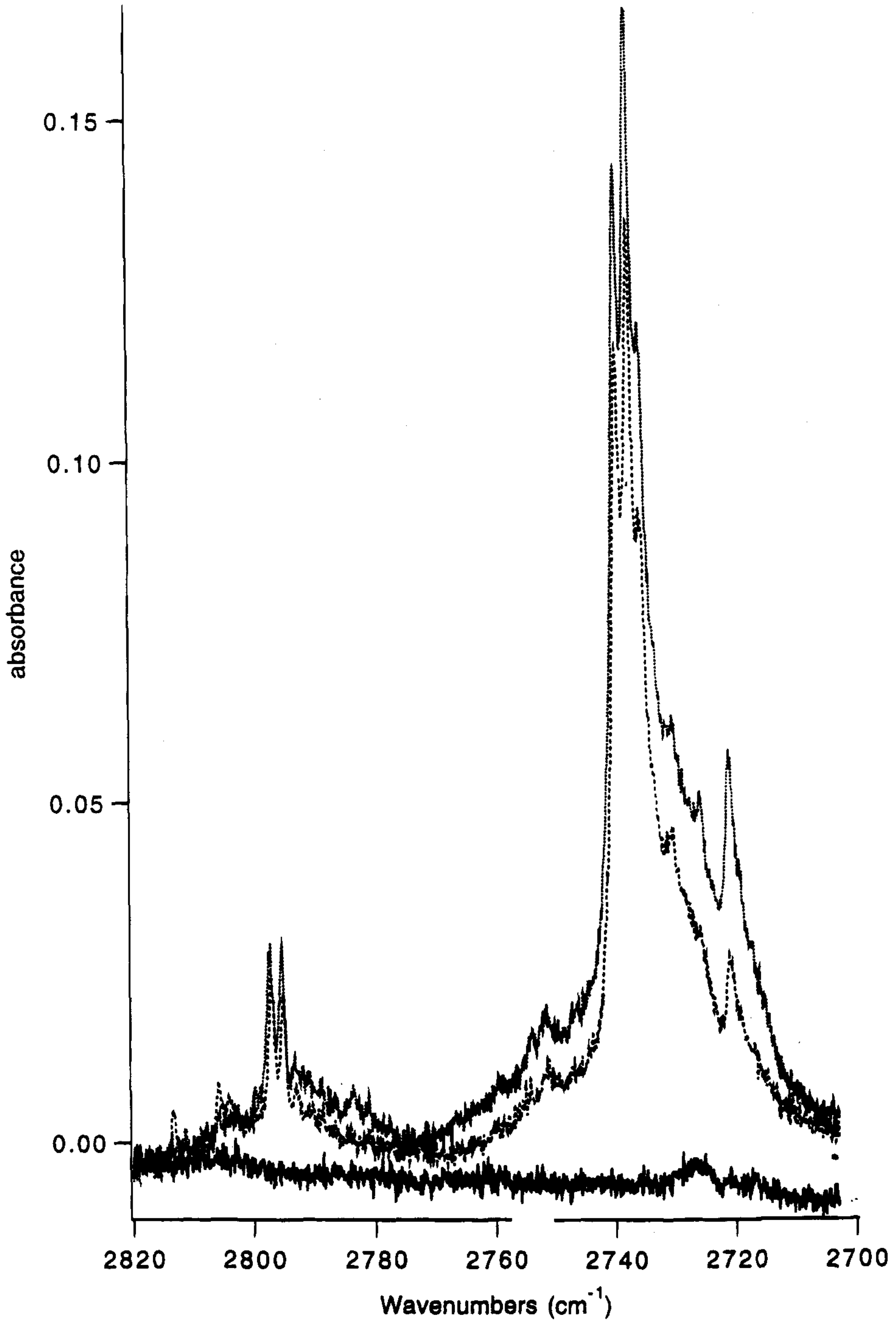

Figure 2. IR spectra of the reaction mixture from the photolysis of cyclopropanecarbonyl chloride: —, $t = 0$; ···, $t = 410$ min; - - - -, $t = 1410$ min. ν(HCl) range.

FT-IR Spectroscopy. The IR spectra were recorded on a 7199 Nicolet Spectrometer equipped with a liquid N_2 cooled MCT detector; the resolution was 0.12 cm^{-1} without apodization. Owing to multiscan procedure, signal/noise ratios were at least larger than 50 even in the worst cases. The integrated absorbances A (cm^{-1}) were measured as the area under a simulated peak (giving the best fit with the experimental data) by use of the FOCAS program of the Nicolet library.

Irradiation Techniques. The broad band (230–900 nm) irradiations were carried out using an Osram 200 W high-pressure mercury lamp equipped with a quartz envelope. The cryostat KBr windows filtered the beam at $\lambda > 230$ nm. The spectrometer used a globar source.

Details of Calculations. All calculations were performed within the framework of the *ab initio* approximation using the GAMESS package of computer codes.[17] The standard split-valence basis sets of the type 6-31G*[18,19] and the "mini" Huzinaga's basis set[20] were used.

Results and Discussion

The formulas of the compounds and the reaction paths are depicted in Figure 1. Photolysis experiments were monitored by FT-IR spectroscopy. **4** and **5** were identified by comparison of the IR experimental spectra with literature data. For **2**, the experimental spectra were compared with simulated spectra obtained by calculations of the *ab initio* force field using the 6-31G* basis set.

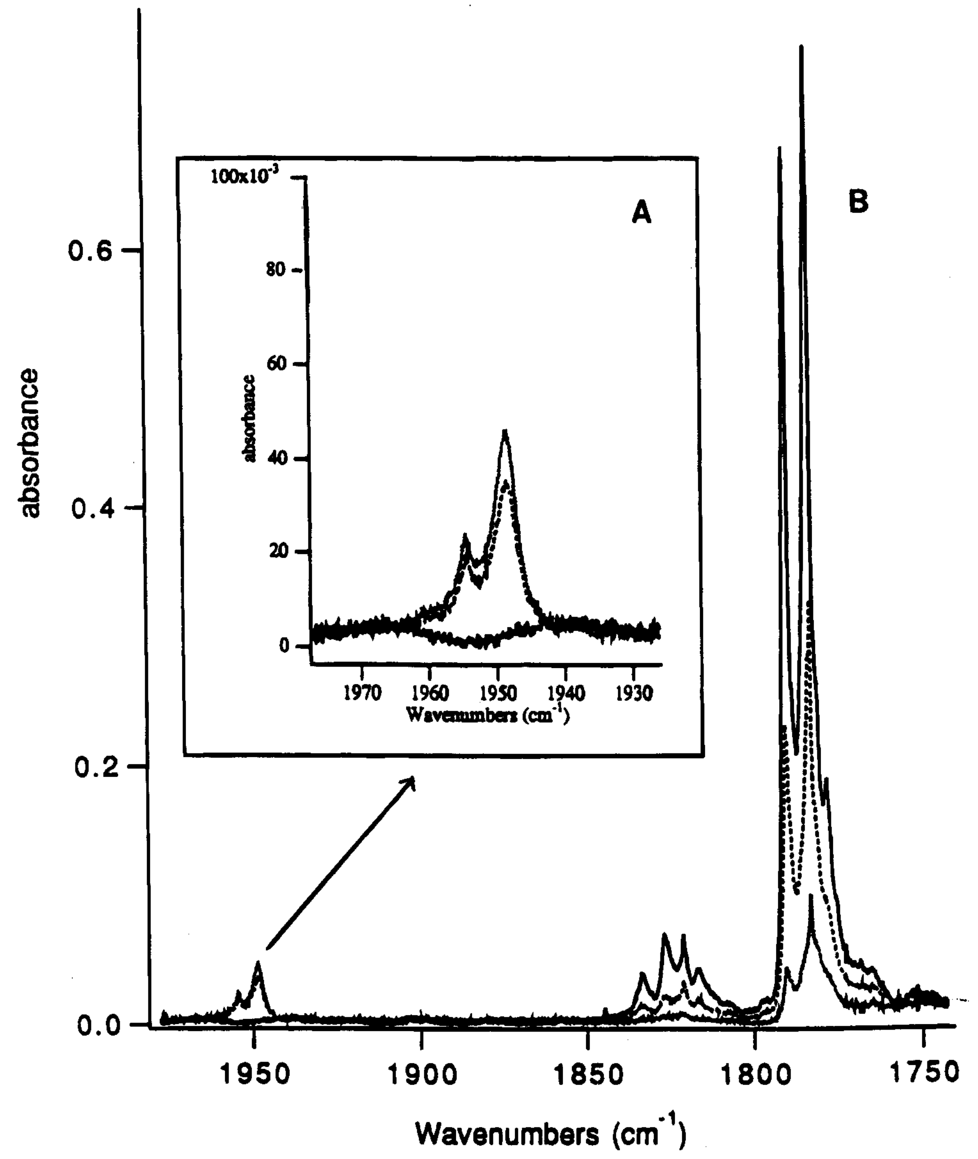

Figure 3. IR spectra of the reaction mixture from the photolysis of cyclopropanecarbonyl chloride: —, $t = 0$; ···, $t = 410$ min; - - - -, $t = 1410$ min. (**A**) 1,2-propadiene $\nu_{C=C=C}$ stretching; (**B**) cyclopropanecarbonyl chloride $\nu_{C=O}$ stretching.

Vibrational Analysis of Cyclopropanecarbonyl Chloride Isolated in Argon Matrices. Prior to the photolysis experiments, the experimental spectra of cyclopropanecarbonyl chloride isolated at 15 K in argon matrices were carefully studied in order to distinguish the conformer spectra. As previously observed by Katon[21] and Durig,[22] cyclopropanecarbonyl chloride adopts two conformations by rotation around the exocyclic carbon–carbon single bond: the *cis*-**1** and the *trans*-**1** conformers for which the dihedral angle ClC_1C_2H is equal to 0° and 180°, respectively (cf. Figure 1).

The spectrum obtained after deposition at 15 K (cf. Table 1) presents the characteristic absorption bands of the two conformers, with multiplet structure arising from alternative trapping sites. The ratio of the two conformers ($K(cis/trans) \approx 1$) is similar to those observed by Durig and Katon in the gas phase.

The results of geometry optimization of *cis*- and *trans*-cyclopropanecarbonyl chloride using the 6-31G* split valence basis set are shown Table 2.

Total molecular energies are −688.702 763 hartrees for the *cis* form and −688.700 556 hartrees for the *trans* conformer. This very small energy difference at the HF level is in rather good agreement with the experimental values. The structural parameters for the two conformers are very similar except for the angle $C_2C_1C_4$ which is larger for *trans* isomer. Together with the dihedral angles, this indicates a larger repulsion between the chlorine atom and the three membered ring.

Photolysis Experiment. When matrix-isolated **1** was subjected to broad band irradiation (filtered high-pressure Hg lamp; $\lambda \geq 230$ nm), it decomposed slowly (96% in 1000 min) and new absorption bands were observed. The photochemical behavior of the precursor **1** and of the reaction products, embedded in an argon matrix at 15 K, is reported in Figures 2–5, where the evolution of the system is illustrated for three different irradiation times. The lower trace presents the spectrum after deposition and before irradiation (time $t = 0$ min). The middle trace shows the appearance of the spectrum after 410 min of irradiation and the upper trace after 1410 min of irradiation.

Strong absorptions around 2735 cm^{-1} are characteristic of the ν_{HCl} stretching mode (cf. Figure 2). These frequencies are lower by 61 cm^{-1} than the value for the stretching frequency of free HCl trapped in argon matrix[23] and thus indicate that HCl and **2** produced by photolysis form a 1:1 complex. This result is similar to those observed by Watari and co-workers during the photolysis of matrix-isolated acetyl chloride.[24] Other

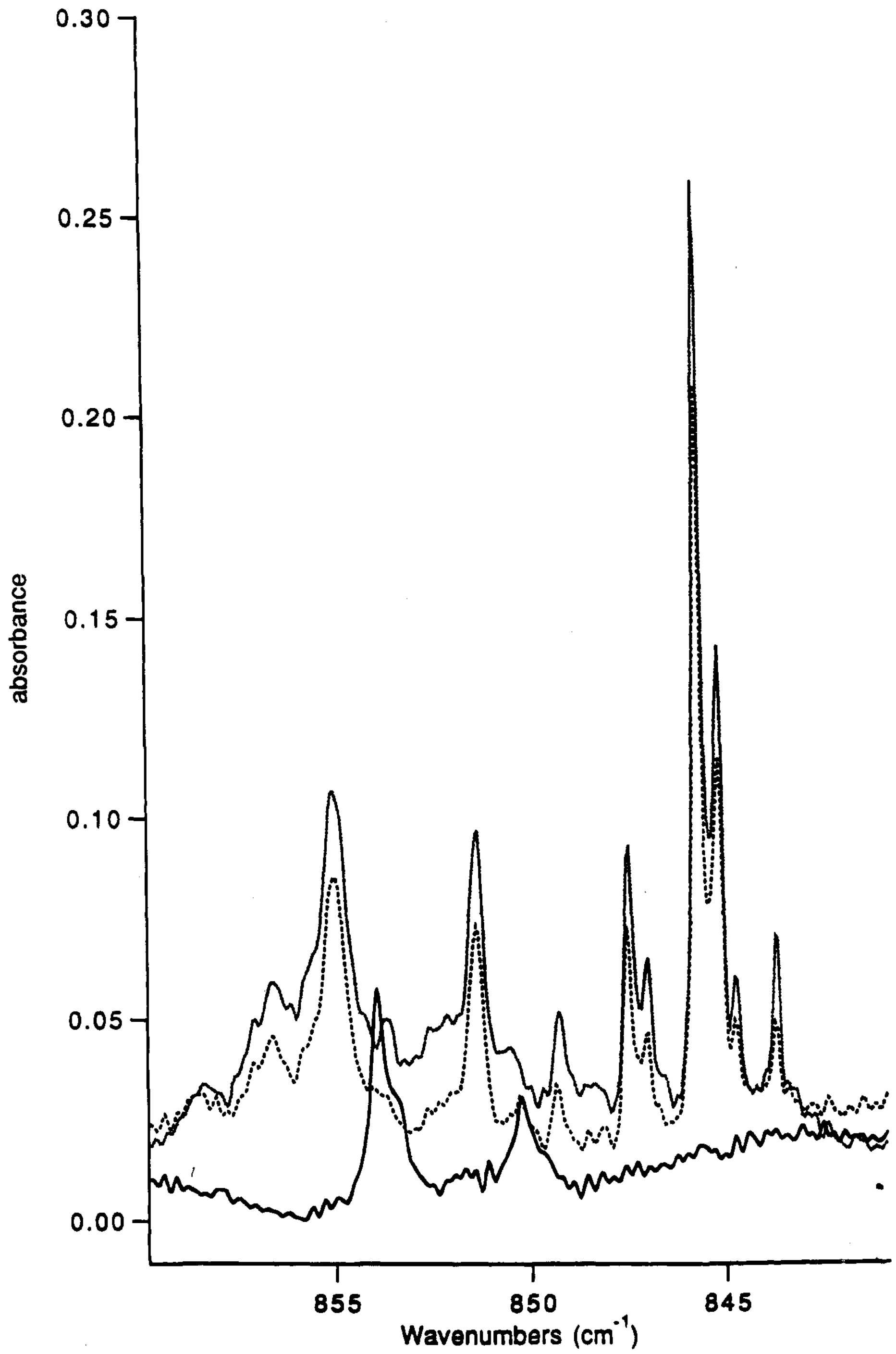

Figure 4. IR spectra of the reaction mixture from the photolysis of cyclopropanecarbonyl chloride: —, $t = 0$; ···, $t = 410$ min; - - - -, $t = 1410$ min. Cyclopropyl chloride.

experiments are currently in progress in order to determine the structure of this complex.

After a 1000 min irradiation, we observed an evolution of the structure of the absorption band pattern between 2145 and 2125 cm^{-1} and the appearance of new absorption bands in different frequency ranges of the spectra. The FT-IR spectra were systematically recorded at different times during the photolysis process. As the integrated intensities of numerous absorption bands were plotted against time, we were able to detect those having identical behavior indicating that they belong to the same product and hence to detect reaction products that showed different kinetic behavior.

Thus the infrared frequencies of the fundamental vibrational modes of 1,2-propadiene **5** were observed (Table 3). They are quite similar to those measured for **5** isolated in argon matrix.[25] Moreover, some experimental data were indicative of formation of a complex with other photoproducts. Particularly, we observed an additional absorption band at 1948 cm^{-1}. This can be attributed to the $\nu_{C=C=C}$ asymmetric stretching mode of complexes **5** (lowered by 10 cm^{-1} from $\nu_{C=C=C}$ of **5** isolated in argon matrix.[25]

A second set of absorption bands with similar behavior must be assigned to chlorocyclopropane **4** by comparison with the spectra of the pure product.[26] Evolution of the $\nu_{C=C=O}$ frequency range between 2145 and 2125 cm^{-1} shows a decrease of the absorption band of **2** and an increase of the carbon monoxide absorption band.

Kinetic Analysis. In order to fit the experimental integrated intensities at different times to monoexponential rates (decay of **1**, or increase of HCl + **2**, HCl + **5**, **5**, CO + **2**, and **4**),

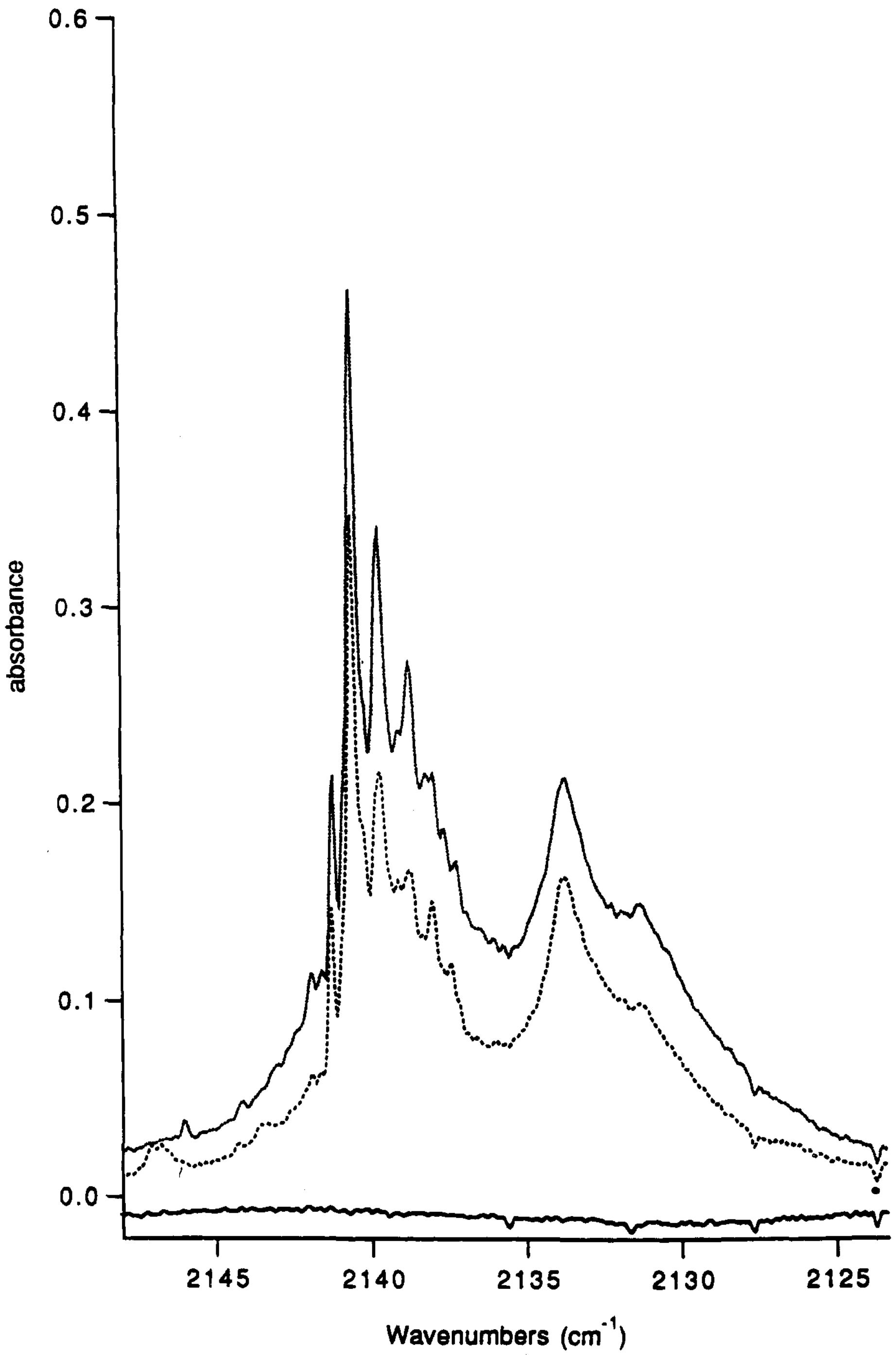

Figure 5. IR spectra of the reaction mixture from the photolysis of cyclopropanecarbonyl chloride: (—, $t = 0$; ···, $t = 410$ min; - - - -, $t = 1410$ min. Ketene $\nu_{C=C=O}$ and carbon monoxide $\nu_{C\equiv O}$ stretching range.

least-squares analyses were performed using a computer program[6] that provides the first-order rate constants and the integrated absorbances at zero and infinite times and their standard deviations. The photolysis reaction was studied as a sum of elementary steps:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

whose evolution was governed by the equation $A_\infty + (A_0 - A_\infty)\exp(-kt)$ with $k = k_1 + k_2$. If the reaction is not reversible, A_0 or A_∞ equals zero for increasing or decreasing products, respectively. In this case, $k_2 = 0$ and $k = k_1$ is the apparent rate constant. Experimental results demonstrate that in argon matrices, CO reacts with the carbene intermediate.[1,2,4] For this reason the reaction **2** → **3** was modeled as a fast-to-equilibrium step. Integrated absorbances are collected in Table 4 and kinetic parameter fits in Table 5. Figures 6 and 7 show a good agreement between theoretical curves and experimental data.

Ab Initio MCSCF Study of the Dissociation of the Singlet Cyclopropylidene Ketene 2

The photodissociation of cyclopropylidene ketene **2** has been theoretically studied by Minato et al.[5] for the triplet state.

The singlet ground state of **2** is C_{2v}, but if the reaction coordinate $d = d_{1-2}$ increases, the molecule adopts the C_s symmetry and the more stable structure is the bent in-plane type where σ_h is defined by atoms $C_1C_4C_7$ (Figure 8a), while the C'_s structure (σ_h normal to $C_1C_4C_7$) is higher in energy. In the

TABLE 1: Frequencies (cm^{-1}) and Assignments for Cyclopropanecarbonyl Chloride

this work		Durig[a]		
cis	trans	cis	trans	assignments[a]
		3114	3112	ν_{17}, CH_2 asym str A″
3087	3092	3092	3099	ν_1, CH_2 asym str A′
		3062	–	ν_2, CH sym str A′
3030	3028	3038	3033	ν_{18}, CH_2 sym str A″
3026	3026	3029	3021	ν_3, CH_2 sym str A′
1790.2	1783.3	1796	1768	ν_4, CO str A′
1789.6	1782.8			
		1458	1451	ν_5, CH_2 sym def A′
1426.2	1425.7	1431	1426	ν_{19}, CH_2 asym str A″
1362.2	1358.1	1364	1351	ν_6, CH bend A′
1205	1205	1202	1201	ν_7, ring breathing A′
1199.7	1199.7	1190	1189	ν_{20}, CH_2 twist A″
1165.3	1114.3	1167	1108	ν_8, CH_2 twist A′
1164.3	1113.3			
	1109.9 (?)			
1071.6	1097	1070	1089 (1099)	ν_{21}, CH_2 wag A″
1070.1				
1049.7	1043.9	1047	1045	ν_9, CH_2 wag A′
1045.8	1041.4			
973	971.7	982	982	ν_{22}, CH_2 bend A″
968.0	946.5	978	955	ν_{10}, CC str A′
876.7	870.8	878	878	ν_{23}, ring def A″
853.7	850.0	856	850	ν_{11}, ring def A′
821.3	816.2	828	813	ν_{24}, CH_2 rock A″
780.8	794.5	781	799	ν_{12}, CH_2 rock A′
543.3	701.9	544	692 (699)	ν_{13}, C-Cl str A′
542.4	697.6			
540.9				
		476	436	ν_{14}, CClO def A′
		415	431	ν_{25}, CClO wag A″
		359	334	ν_{15}, CClO rock A′
		287	261	ν_{26}, ring−CClO bend A″
		224	239	ν_{16}, ring−CClO bend A′
		72	(50)	ν_{27}, asym torsion A″

[a] Reference 22.

TABLE 2: Geometric Parameters of *cis*- and *trans*-Cyclopropanecarbonyl Chloride

cis				trans			
C_1C_2	1.5113	C_4Cl	1.7823	C_1C_2	1.5086	C_4Cl	1.7895
C_2C_3	1.4796	$C_2C_1C_3$	58.5°	C_2C_3	1.4819	$C_2C_1C_3$	58.8°
C_1C_3	1.5166	$C_2C_1C_4$	117.5°	C_1C_3	1.5110	$C_2C_1C_4$	122.8°
C_1C_4	1.4802	OCCl	120.0°	C_1C_4	1.4828	OCCl	119.1°
C_4O	1.1712	HCCCl	8.5°	C_4O	1.1693	HCCO	8.5°

TABLE 3: Frequencies (cm^{-1}) and Assignments for 1,2-Propadiene[a]

vibrational mode[a]	sym species[a]	gas[a]	matrix[a]	this work
ν_1, CH_2 sym str	A_1	3015 (R)[d]	n.o.[b]	n.o.
ν_2, CH_2 def	A_1	1443 (R)	n.o.	n.o.
ν_3, C=C=C sym str	A_1	1073 (R)	n.o.	n.o.
ν_4, CH_2 torsion	B_1	865	864.7	855.4; 854.7[c]
ν_5, CH_2 sym str	B_2	3007	3000.1	n.o.
ν_6, C=C=C asym str	B_2	1957	1955.4	1953.9; 1944.7 [c]
ν_7, CH_2 def	B_2	1398	1388.7	1392.4; 1390.4 [c]
ν_8, CH_2 asym str	E	3086	3091.8	n.o.
ν_9, CH_2 rock	E	999	996.4	998.04
ν_{10}, CH_2 wag	E	841	837.5	851.1
ν_{11}, C=C=C def	E	355	n.o.	n.o.

[a] Reference 17. [b] n.o. = not observed. [c] Splitting due to the site effect. [d] (R) = Raman active mode.

following, we proceed with the C_s structure, discarding the C'_s as less stable.

TABLE 4: Evolution of the Integrated Absorbances (cm^{-1}) during the Cyclopropanecarbonyl Chloride Photolysis

	integration range (cm^{-1}) $\nu_j - \nu_i$					
time (min)	2825–2773[a]	1972–1930[b]	2773–2770[c]	2175–2090[d]	1308–1288[e]	1800–1760[f]
0	0	0.0	0.0	0.0	0	2.995
6	0.0031	0.0134	0.0187	0.3643	0.0004	2.817
12	0.0136	0.0118	0.0582	0.4377	0.0050	2.715
22	0.0193	0.0211	0.1059	0.6477	0.0032	2.557
40	0.0476	0.0365	0.2038	0.8602	0.0103	2.307
50	0.0649	0.0465	0.2611	0.8485	0.0114	2.188
70	0.0816	0.0556	0.3418	0.9276	0.0179	1.961
100	0.1112	0.0737	0.4434	1.0155	0.0215	1.689
160	0.1460	0.0909	0.5593	1.1345	0.0325	1.296
223	0.1884	0.1094	0.6403	1.2195	0.0373	1.015
343	0.2002	0.1253	0.7017	1.3135	0.0452	0.6625
463	0.2119	0.1253	0.7146	1.3755	0.0476	0.464
996	0.2227	0.1290	0.6907	1.6234	0.0591	0.1207

Frequency domain: [a] ν_{HCl} complexed with 1,2-propanediene, [b] 1,2-propanediene $\nu_{C=C=C}$ asym str; [c] ν_{HCl} complexed with cyclopropylidene ketene, [d] CO (ν_{CO}) + cyclopropylidine ketene ($\nu_{C=C=O}$), [e] cyclopropyl chloride, [f] *cis* + *trans*-cyclopropanecarbonyl chloride ($\nu_{C=O}$).

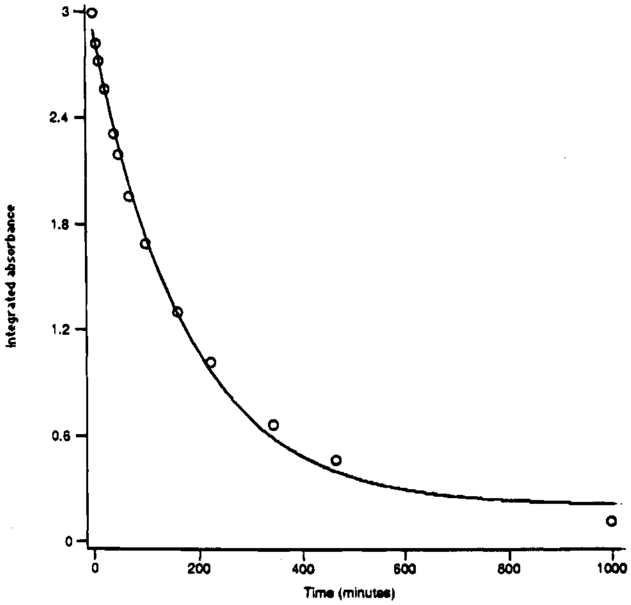

Figure 6. Curve fit of cyclopropanecarbonyl chloride decreasing during the photolysis. (O) Experimental data.

Owing to the great number of calculations, it is not possible to use an extended basis set such as 6-31G*. We therefore used the mini Huzinaga basis set[20] which gives much lower energies than does the standard STO-3G.

The ground state is $^1A''$ and the first excited electronic state is $^1A''$. The four highest occupied and the four lowest unoccupied energy levels used to span the MCSCF configuration space including all the single and double excitations along the reaction path are displayed in Figure 9.

At every point of the reaction coordinate d, the molecular geometry is fully optimized for the $^1A'$ and $^1A''$ states, and the MCSCF lowest roots give the first electronic excited states. The $^1A'$ and $^1A''$ electronic states are represented in Figure 10.

The $^1A'$ state grows continuously in energy and cannot be responsible for the molecular dissociation. The energy levels crossing between $d = 1.3$ and $d = 2.1$ shown in Figure 9 gives rise to the $^1A'$−$^1A''$ crossing in Figure 10.

Concerning the $^1A'$ state, within the bracket formalism and expliciting only the four higher and the follower molecular levels the MCSCF ground state is mainly |22220000> up to $d = 2.1$ Å. From $d = 2.1$ to 2.4 Å, the MCSCF state is a strong mixing

TABLE 5: Kinetic Parameter Fits for Monoexponential Function: $A_\infty + (A_0 - A_\infty)\exp(-kt)$; $k = k_1 + k_2$ (See Text)

	$\nu_j - \nu_i$ (cm^{-1})					
	2825–2773[a]	1972–1930[b]	2773–2700[c]	2175–2090[d,g]	1308–1288[e]	1800–1760[f]
A_∞	$0.225 \pm 4 \times 10^{-4}$	$0.129 \pm 2. \times 10^{-3}$	$0.719 \pm 1 \times 10^{-2}$	$1.31 \pm 7 \times 10^{-2}$	$5.8 \times 10^{-2} \pm 1.7 \times 10^{-3}$	0.0
A_0	0.0	0.0	0.0	0.0	0.0	$2.85 \pm 4.4 \times 10^{-2}$
k	$6.7 \times 10^{-3} \pm 3.5 \times 10^{-4}$	$8.3 \times 10^{-3} \pm 3.3 \times 10^{-4}$	$9.2 \times 10^{-3} \pm 3.8 \times 10^{-4}$	$2.3 \times 10^{-2} \pm 3.4 \times 10^{-3}$	$4.7 \times 10^{-3} \pm 3.2 \times 10^{-4}$	$5.6 \times 10^{-3} \pm 2.3 \times 10^{-4}$

[a] ν_{HCl} complexed with 1,2-propadiene. [b] 1,2-Propadiene $\nu_{C=C=C}$ asym str. [c] ν_{HCl} complexed with cyclopropylidine ketene. [d] CO (ν_{CO}) + cyclopropylidine ketene ($\nu_{C=C=O}$). [e] Cyclopropyl chloride. [f] *cis* + *trans*-cyclopropanecarbonyl chloride ($\nu_{C=O}$). [g] Bad agreement for this domain due to overlapping of νCO and νC=C=O frequencies, and the two products do not have the same rate constant.

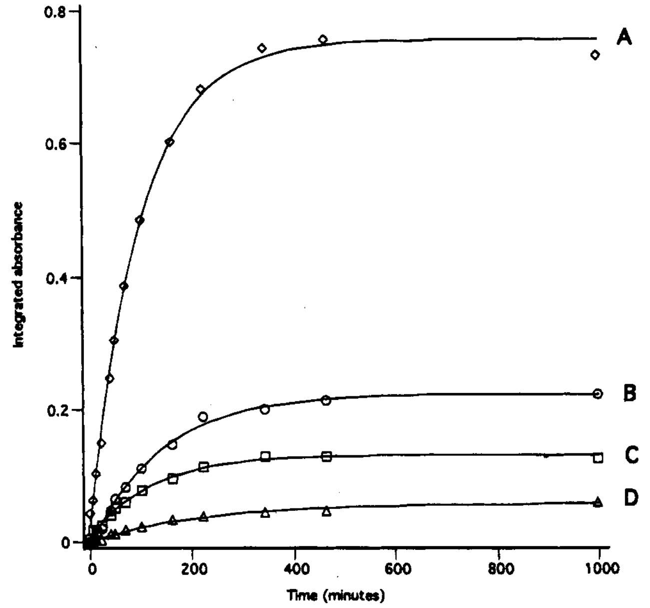

Figure 7. Curve fit of increasing absorption bands: (A) HCl complexed with ketene; (B) HCl complexed with 1,2 propadiene; (C) 1,2-propadiene; (D) cyclopropyl chloride. Marked points are experimental data.

TABLE 6: Mulliken Population of the MCSCF Natural Orbitals of the Transition State

	S	S	P_x	P_y	P_z
C_1	1.99	1.57	1.05	0.98	0.23
C_2	2.00	1.65	0.55	0.98	0.56
C_3	2.00	1.85	1.57	1.52	1.44
C_4	1.98	1.15	1.11	0.96	1.13
C_7	1.99	1.15	1.10	0.99	1.13

of the microstate obtained by promoting electrons from the lower molecular levels to the virtual eigenstates. Among these microstates the doubly excited |22202000> state is highly predominant.

In Figure 10, light dashed lines represent the |22220000> and |22202000> SCF molecular energy. This shows that a simple SCF calculation as in the Minato[5] calculation would produce an activation energy twice the MCSCF activation energy, which is about 124 kcal/mol.

In Figure 8b is displayed the transition state configuration d = 2.1 Å. The Mulliken population of the MCSCF natural orbital (Table 6) shows the biradical character of the C_3H_4 group as postulated by Minato et al.[5] Thus the dissociation of cyclopropylidene ketene **2** in its singlet state can be described by a scheme analogous to that for triplet state.

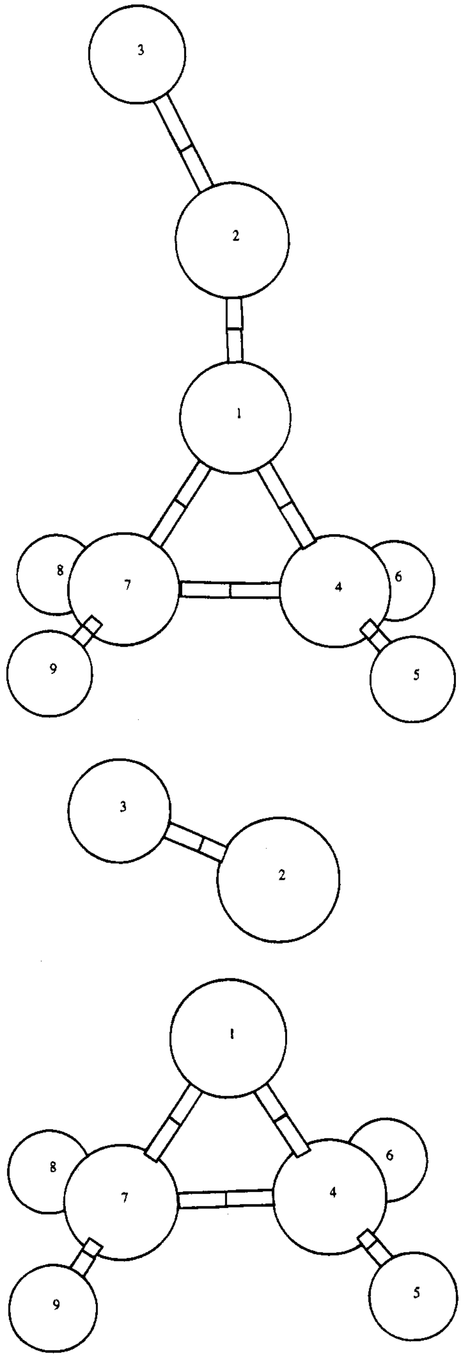

Figure 8. (a, top) Bent in-plane structure of cyclopropylidene ketene (C_s). (b, bottom) Transition-state configuration.

Conclusion

In this work, experimental and theoretical data for the photochemical reaction of **2** trapped at 15 K in argon matrices were obtained. The products of ketene photolysis, CO and cyclopropylidene **3**, are identified: CO by its stretching absorption band at 2138.3 cm^{-1}, and **3** by its intermolecular and intramolecular evolution which give **4**, CO, and **5**, respectively. The formation of cyclopropyl chloride is an experimental proof for a nonconcerted reaction path in agreement with theoretical

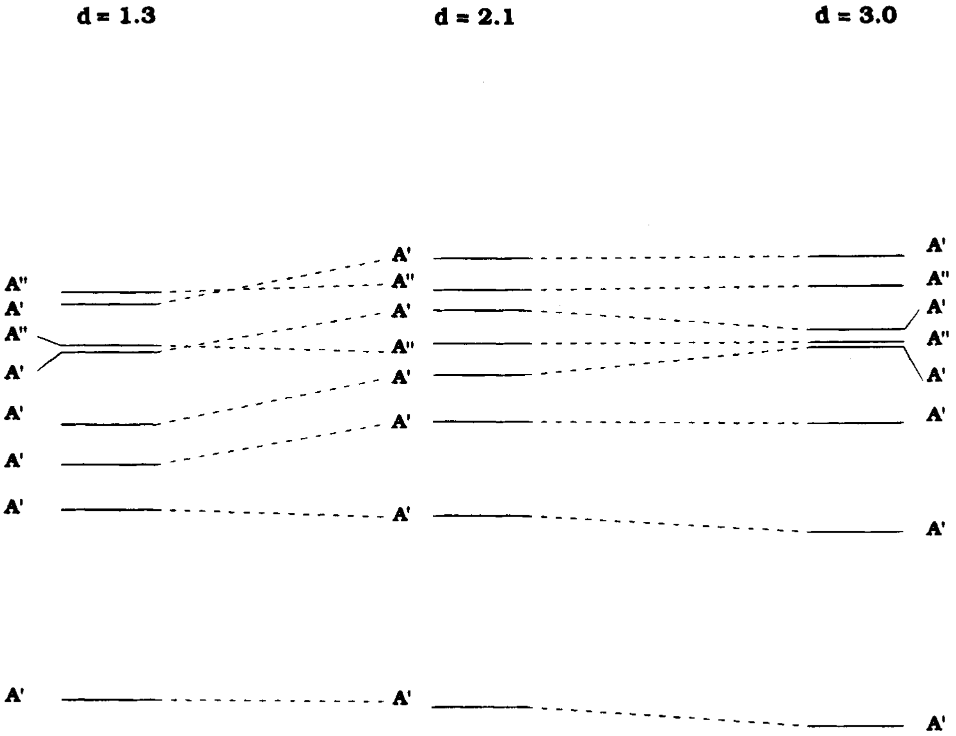

Figure 9. Higher occupied and lower unoccupied energy levels involved in MCSCF calculation vs the reaction path coordinate.

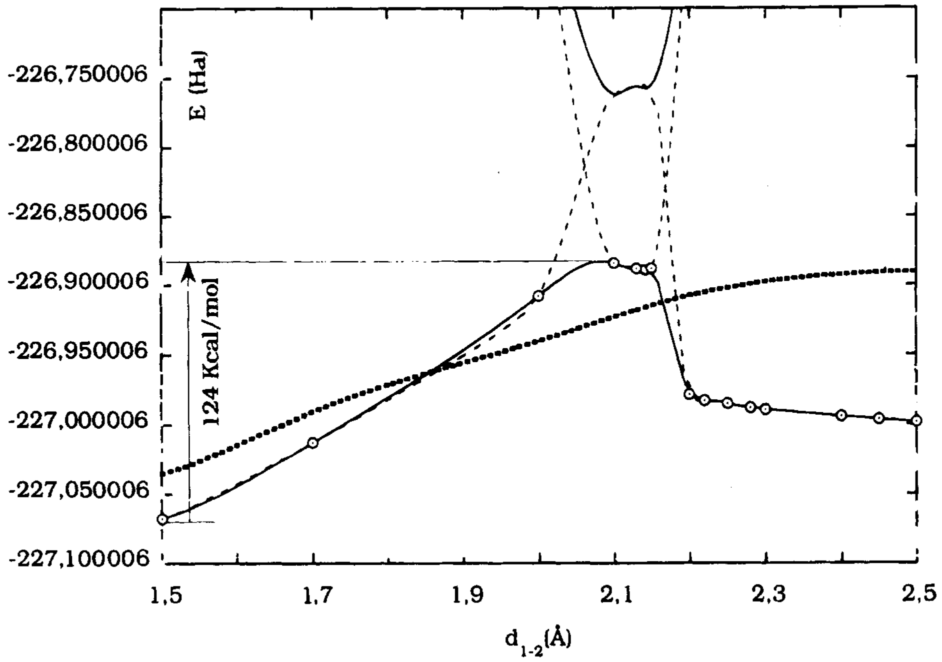

Figure 10. MCSCF potential energy profile for cyclopropylidene ketene (C_s) dissociation: solid line, 1A′ electronic states; bold dotted line, 1A″ electronic state; broken lines, |22220000> and |22202000> predominant MCSCF states.

simulation. Since the transition state energy is calculated with a small basis set, the value obtained is qualitative. Moreover, a significant displacement of the HCl stretching frequency is indicative of the formation of complexes with other photoproducts.

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