

Photolysis of Matrix-Isolated Acryloyl Chloride: 1,3 Chlorine Migration and Further Evolutions

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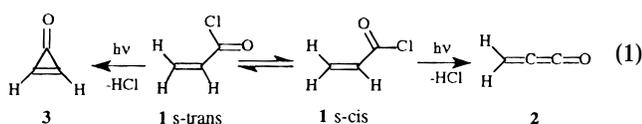
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Photolysis, at $\lambda \geq 310$ nm ($\Delta E < 387$ kJ mol⁻¹), of acryloyl chloride **1** isolated in argon matrixes at 10 K yields 3-chloro-1,2-propenone **4** through 1,3-chlorine migration. There is no evidence of cyclopropenone or propadienone formation. **4** is also synthesized by irradiation of 3-chloropropanoyl chloride ($\lambda \geq 230$ nm) isolated in argon matrix at 10 K. Identification is performed by comparison of experimental FT-IR spectrum with calculated ones (ab initio calculations at the 6-31G** level). Irradiation of **1** at $\lambda \geq 230$ nm induces the photolysis of **4** which breaks into CO and the postulated transient 2-chloroethylidene **5** and/or into propadienone **2** complexed by HCl. The transient **5** collapses to form ground-state vinyl chloride **6** by 1,2 hydrogen migration. In the next step, **2** loses CO to form a new transient assumed to be vinylidene **7** which yields ethyne by intramolecular isomerization process and vinyl chloride by intermolecular reaction with HCl trapped in the same cage. CO, HCl, ethyne, and vinyl chloride are the final reaction products. Modeling of the 1,3 chlorine migration process from **1** using ab initio calculations at the MP2/6-31G* level is performed in the ground state (S_0) and the first singlet excited state (S_1). The reaction energy value for an S_1 (509 kJ/mol) state process is higher than for an S_0 process (207.2 kJ/mol), these theoretical results suggesting the reaction take place in the ground state.

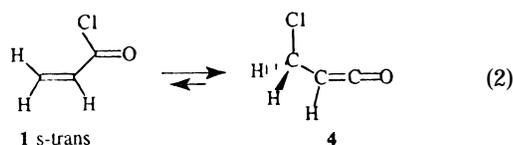
Introduction

Our group is actively involved in the synthesis, identifications, and reactivity of neutral intermediates trapped in rare gas matrixes.^{1–3} The matrix isolation technique is certainly the most appropriate method for investigation of reactive species. In previous works, we showed that aliphatic acyl chlorides isolated in rare gas matrixes lead to ketenes by a syn photodehydrochlorination process when submitted to UV irradiation.⁴ Taking into account such a mechanism, *s-cis* and *s-trans* conformers of acryloyl chloride **1** seem convenient precursors for propadienone **2** and cyclopropenone **3**, respectively (cf. eq 1).



On the other hand, photochemical (1,n) sigmatropic rearrangements are well-known processes and have formed the subject of several reviews.⁵ Further experimental and theoretical investigations on the thermal 1,3

shift in ketene derivatives have been carried out by Wentrup and co-workers.⁶ They have shown that the rate of the 1,3 migration is strongly dependent on the nature of the substituent. In particular, the electron-rich n-donating groups, such as Cl, are found to accelerate this rearrangement. In a recent paper, Koch et al.⁷ have used high level ab initio calculations to examine the 1,3 and 1,5 chlorine migration occurring in ketene derivatives. In the case of chloro oxoketene, they forecast a very low activation barrier for the 1,3 chlorine sigma-tropic migration. Such a rearrangement may occur during acryloyl chloride irradiation and lead to 3-chloro-1,2-propenone **4** (cf. eq 2).



In the present study, we report the first photolysis experiments on **1** isolated in argon matrixes. Experimental data on the photoreactivity of each conformer of acryloyl chloride are expected. Theoretical calculations were undertaken in order to compare the experimental IR spectra with the calculated ones, to assign the observed absorption of photoproducts, and furthermore to identify the different photolysis pathways.

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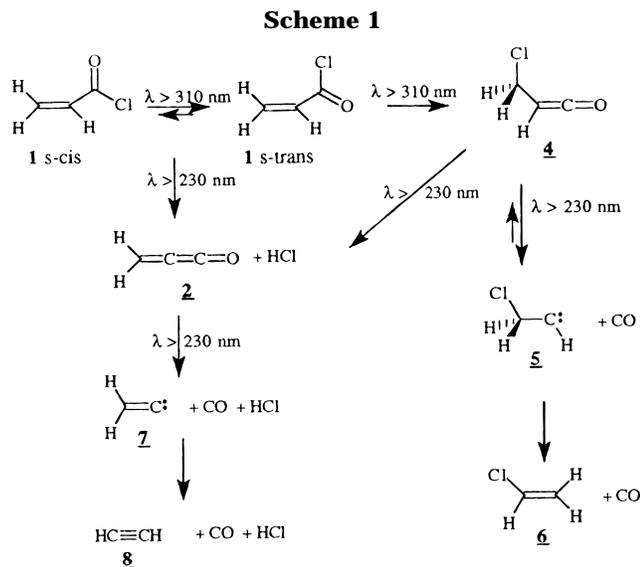
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Acryloyl chloride and 3-chloropropanoyl chloride, supplied from Aldrich, were used after purification by vacuum distillation.

Matrix Isolation Experiments. The apparatus and experimental techniques have been described elsewhere in the literature.⁸ The relative concentration of rare gas to acryloyl chloride, and to 3-chloropropanoyl 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 mixture was heated at 323 K before deposit at 20 K on a CsBr window. The deposition rate of gas mixtures was controlled with an Air Liquide microleak (V.P/RX); it never exceeded 2 mmol/h, a value chosen to avoid, as far as possible, the site splitting of vibrational absorption bands. The thickness of matrices was determined by counting transmission fringes.

FTIR and UV Spectroscopies. The IR spectra were recorded in the 4000–400 cm^{-1} range on a 7199 Nicolet spectrometer equipped with a liquid N_2 cooled MCT detector; the resolution was 0.12 cm^{-1} without apodization. The integrated absorbances A (cm^{-1}) were measured as the area under a simulated peak (giving the best fit with the experimental data) using the FOCAS program of the Nicolet library.

The UV spectra were recorded in the 200–800 nm range on a Unicam UV4 spectrometer.

Irradiation Techniques. Irradiation was carried out using an Osram 200 W high-pressure mercury lamp equipped with a quartz envelope. The broad band was filtered at $\lambda > 310$ nm and $\lambda > 230$ nm. The light intensity is the same in all experiments, and the irradiation area is wider than the surface used to obtain the spectrum. It is assumed that the matrix has no significant absorbance.

Detail of Calculations. The energies of the reaction products as well as the vibrational spectra were determined by ab initio calculations. The Gaussian 94⁹ program package using the Møller–Plesset second-order (MP2) procedure with 6-31G* basis set¹⁰ was used for these calculations. The frozen-core approximation was employed for all correlated calculations.

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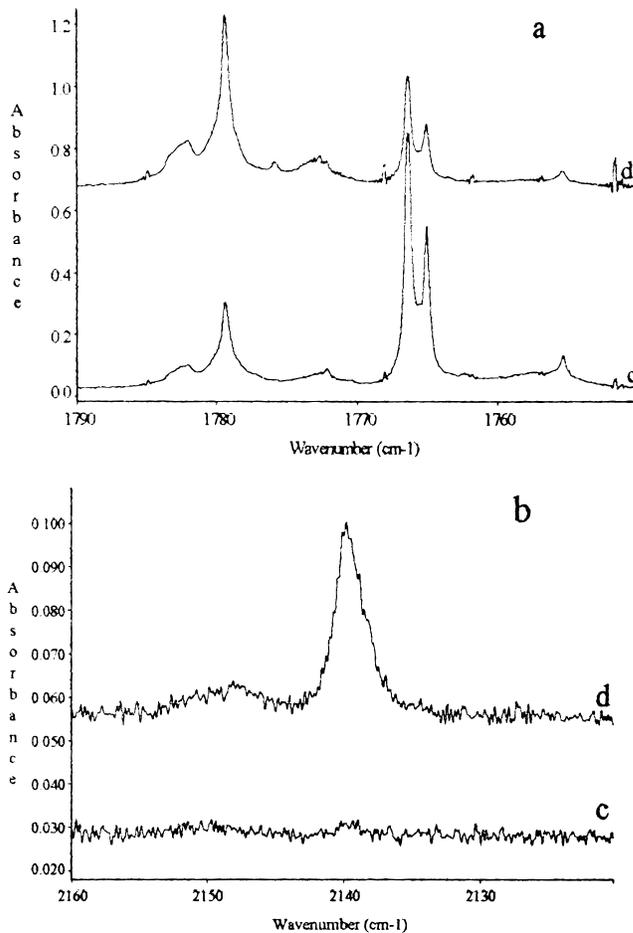


Figure 1. Infrared spectra of ν_{CO} range of the acryloyl chloride **1** (a) and 3-chloro-1,2 propenone **4** (b) isolated in argon matrix: (c) spectrum after deposition; (d) spectrum after 1260 min of irradiation time at $\lambda > 310$ nm.

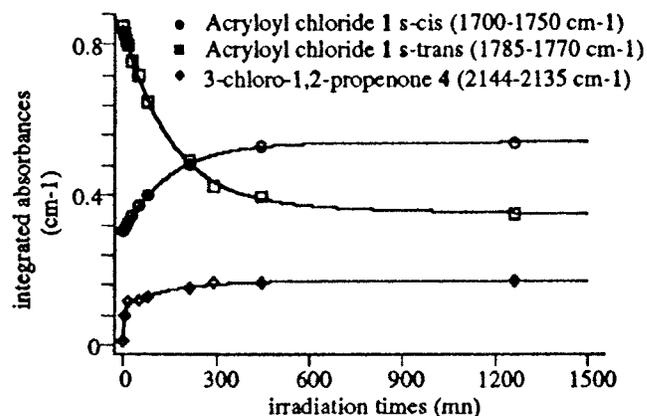


Figure 2. Evolution of integrated absorbances during irradiation of acryloyl chloride **1** at $\lambda > 310$ nm.

tions. The calculated vibrational frequencies were scaled via the standard Pulay procedure.^{11,12} The 1,3 chlorine migration was studied by semiempirical calculations using AMPAC¹³ with intrinsic reaction coordinate (IRC), at the PM3 level.¹⁴ The **1** and **4** ground states and the transition state of the migration reaction are optimized by ab initio calculations. The beryny procedure¹⁵ was used for transition state optimizations.

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The electronic excited-state energies and wave functions were evaluated using the CI-single (CIS) configuration approach which models an excited state as a combination of single excitations from the Hartree–Fock ground state¹⁶ adapted to large systems. A certain portion of CI is actually included, but the computational effort is less formidable. Although CIS was originally developed for organic molecules,^{17a} it has been successfully tested for the computation of electronic absorption spectra of fairly large clusters such as Na₁₈Cl₁₇.^{17b}

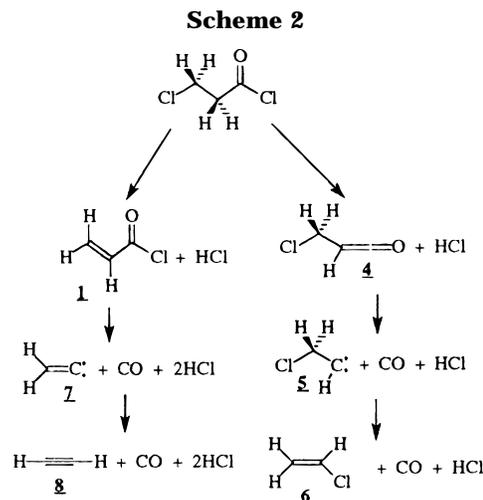
Results and Discussion

The involved compounds and the reaction paths are depicted in Scheme 1. Photolysis experiments were monitored by FT-IR spectroscopy. Reaction compounds were identified by comparison of their experimental IR spectra with literature data. For the 3-chloro-1,2-propenone, the experimental spectra was compared with simulated spectra obtained by ab initio force field calculations using the MP2/6-31G* basis set.

Vibrational Analysis of 1 Isolated in Argon Matrices. Prior to photolysis experiments, the experimental spectrum of **1** was carefully studied in order to distinguish between the conformer spectra. This compound adopts two conformations by rotation around the carbon–carbon single bond: the **1** s-trans and **1** s-cis conformers for which the dihedral angle C=C–C=O is equal to 180° and 0°, respectively.¹⁸ The evolution of the infrared spectrum of **1**, from the liquid to the low-temperature solid at 178 K, shows that the 1-s-trans conformer is more stable.

In our experiments, the infrared spectrum, obtained after deposition at 20 K, features the characteristic absorption bands of the two conformers, with multiplet structure arising from alternative trapping sites. The conformational preference, determined using the two carbon chloride stretching vibration is clearly for the s-cis conformer, and the ratio of the two conformers (*K* (s-cis/s-trans) ≈ 1.4) is similar to those obtained between 276 and 361 K by Katon et al. in the gaseous phase.^{18b}

Our ab initio calculations, at the MP2/6-31G* level, which show that the s-cis conformer is the most stable (ΔE s-cis – s-trans = –0.37 kcal/mol), are in good agreement with the ones obtained by Garcia et al.¹⁹ These authors have performed ab initio calculations at different computational levels in order to study the s-cis/s-trans conformational preference. These results show that the calculated ΔE values are dependent on the computational level (–0.57 and 0.1 kcal/mol using RHF/6-31G* and MP3/6-311++G** levels, respectively). It



can be speculated that the RHF/6-31G* calculations overestimate the steric repulsion between the chloride and the vinyl hydrogen in the s-trans conformation. Nevertheless, there are small differences between the geometries calculated at the different computational levels.

The FT-IR spectra were systematically recorded at different times during the photolysis process. As the integrated intensities of numerous absorption bands were plotted versus time, we were able to detect those having identical behavior, indicating that they belong to the same product. The distinction between **1** s-cis and **1** s-trans infrared spectra was confirmed by observing the opposite behavior of the two sets of absorption bands during the irradiation experiments which reveals the occurrence of a photoisomerization process.

Photolysis Experiments. When matrix-isolated **1** is submitted to a broad band irradiation, with high-pressure Hg lamp, filtered at $\lambda > 310$ nm in its $n \rightarrow \pi^*$ electronic absorption band, we observe the decrease of **1** s-trans IR absorption bands and the increase of **1** s-cis absorption bands. The photochemical behavior of the two conformers of acryloyl chloride in argon matrix is reported in Figure 1 and the evolution of the integrated absorbances versus time in Figure 2.

Under irradiation, new absorption bands appear in different areas of the spectra. In particular, we observe new strong absorption bands growing at 2149 and 2139 cm⁻¹, indicative of the presence of $\nu_{C=C=O}$ stretching mode. The lack of ν_{HCl} absorption bands around 2870 cm⁻¹ and characteristic ν_{CCO} ²⁰ and ν_{CO} ²¹ vibration bands of compounds **2** and **3**, at 2125 and 1835–1870 cm⁻¹, respectively, rule out the occurrence of the deshydrochlorination process. It further suggests that irradiation induces 1,3 migration of the chlorine atom to form **4** as primary photoproduct. This intermediate reaches a photochemical steady state with **1** conformers.

To unambiguously identify **4** as the primary photoproduct, we carried out an other experiment: the irradiation of 3-chloropropanoyl chloride (ClCH₂CH₂COCl) trapped in argon matrix at 10 K (Scheme 2). Broad band filtered irradiation at $\lambda > 230$ nm of 3-chloropropanoyl chloride embedded in argon matrix induces the formation

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Table 1. Observed and Simulated Infrared Spectra of Acryloyl Chloride 1 Conformers

	experiment			calculation					
	no.	obsd ^b	obsd ^a	I ^c	ν_{calcd}	ν^d	I ^c	sym	assignment
1 s-trans	1				3334	3109	1	A'	$\nu\text{CH}_2\text{as}$
	2				3354	3036	<1	A'	νCH
	3				3232	3015	<1	A'	$\nu\text{CH}_2\text{s}$
	4	1761	1766	100	1821	1765	100	A'	$\nu\text{C}=\text{O}$
	5	1617	1626	2	1701	1633	5	A'	$\nu\text{C}=\text{C}$
	6	1393	1394	15	1478	1418	9	A'	βCH_2
	7	1277	1284	2	1336	1282	1	A'	βCH
	8	1143	1150	56	1203	1159	66	A'	$\nu\text{C}-\text{C}$
	9	1001	984	18	1021	995	19	A''	tors C=C
	10	973	979	14	988	974	9	A''	oop CH ₂
	11	932	936	5	976	939	50	A'	$\nu\text{C}-\text{C} + \beta\text{CH}_2$
	12	753	756	5	766	753	8	A''	oop C-Cl
	13	606	605	6	617	597	36	A'	$\nu\text{C}-\text{Cl}$
	14	495	494	3	510	489	11	A'	$\beta\text{C}-\text{C}-\text{Cl} + \beta\text{O}-\text{C}-\text{Cl}$
	15				455	447	<1	A''	oop C-Cl
	16				447	432	7	A'	$\nu\text{C}-\text{Cl}$
	17				263	253	<1	A'	$\beta\text{C}-\text{C}-\text{Cl} + \beta\text{CCO}$
	18				105	101	<1	A''	tors C-C
1 s-cis	1				3328	3105	<1	A'	$\nu\text{CH}_2\text{as}$
	2				3280	3060	<1	A'	νCH
	3				3227	3010	<1	A'	$\nu\text{CH}_2\text{s}$
	4	1772	1779	60	1834	1778	57	A'	$\nu\text{C}=\text{O}$
	5	1608	1619	6	1701	1632	8	A'	$\nu\text{C}=\text{C}$
	6	1393	1398	43	1473	1413	18	A'	βCH_2
	7	1295	1288	<1	1347	1293	<1	A'	βCH
	8	1072	1075	<1	1121	1078	6	A'	$\nu\text{C}-\text{C} + \beta\text{CCH}$
	9	994	999	<1	1023	1000	15	A''	tors C=C
	10	973	986	32	1021	984	7	A'	$\nu\text{C}-\text{C}$
	11	970	973	100	989	969	100	A''	oop CH ₂
	12	737	744	7	747	736	7	A''	oop C-Cl
	13	703	705	58	729	702	30	A'	$\nu\text{C}-\text{Cl} + \beta\text{C}-\text{C}-\text{O}$
	14				783	474	<<1	A''	oop C-Cl
	15	446	446	6	459	443	6	A'	$\nu\text{C}-\text{Cl}$
	16	380			402	386	6	A'	$\nu\text{C}-\text{Cl} + \beta\text{Cl}-\text{C}-\text{O}$
	17				262	252	<1	A'	$\beta\text{C}-\text{C}-\text{Cl} + \beta\text{CCO}$
	18				85	82	<1	A''	tors C-C

^a This work. ^b Liquid state.^{16b} ^c Relative intensities. ^d Scaled frequencies (the scaling factors are as follows: stretching C-C = 0.92; other stretchings = 0.94; bending and torsion = 0.92; deformation = 0.98).

Table 2. Experimental and Calculated Vibrational Frequencies of 3-Chloro-1,2-propenone 4 (cm⁻¹)

no.	experiment		calculation			
	obsd ^a	obsd ^b	ν_{calcd}	ν^c	I ^d	assignment
1			3279	3162	2	νCH
2			3232	3116	<1	$\nu\text{CH}_2\text{as}$
3			3164	3051	2	$\nu\text{CH}_2\text{s}$
4	2143.6–2138	2139.2–2145	2225	2146	100	$\nu\text{C}=\text{C}=\text{O}$
5	1448	1447.5	1540	1445	6	βCH_2
6			1452	1380	<1	$\nu\text{C}-\text{C}$
7	1268.6–1262	1267.8–1263	1362	1277	12	$\beta\text{H}-\text{C}-\text{Cl}$
8	1183.9	1183.5	1253	1182	3	$\beta\text{H}-\text{C}-\text{Cl}$
9			1179	1116	<1	$\beta\text{C}-\text{C}-\text{H}$
10	1021	1017.4	1072	1020	4	$\nu\text{C}-\text{C} + \nu\text{C}=\text{C}=\text{O}$
11			902	854	2	$\nu\text{C}-\text{C} + \beta\text{CH}_2$
12	701	701	746	714	21	$\nu\text{C}-\text{Cl}$
13			635	597	2	oop O5 + $\nu\text{C}=\text{C}-\text{C}$
14			559	523	7	$\beta\text{C}=\text{C}=\text{O} + \text{oopO5}$
15			531	499	<1	$\beta\text{C}=\text{C}=\text{O} + \text{oopO5}$
16			313	294	3	$\beta\text{C}=\text{C}=\text{O} + \beta\text{C}-\text{C}-\text{Cl}$
17			204	192	<1	$\beta\text{C}-\text{C}=\text{C} + \beta\text{C}=\text{C}=\text{O}$
18			69	66	<1	tors C-C

^a Frequencies obtained from photolysis of acryloyl chloride **1** in argon matrix at $\lambda > 310$ nm. ^b Frequencies obtained from photolysis of 3-chloropropionyl chloride ($\text{CH}_2\text{ClCH}_2\text{COCl}$) in argon matrix at $\lambda > 230$ nm. ^c Scaled frequencies. The scaling factors are as follows: 0.93 for stretchings and 0.88 for bendings and deformations. ^d Relative intensities.

of HCl ($\nu_{\text{HCl}} = 2742.5$ cm⁻¹) and of **4**. The frequency shift observed for the ν_{HCl} stretching mode (-127.5 cm⁻¹ lower than the value for free HCl trapped in argon matrix^{3,22}) indicates that HCl and **4** produced by photolysis yield an 1:1 complex. This result is similar to those previously observed in our laboratory^{3,4} and by Kogure et al.²³ The

existence of this complex explains the frequency difference of **4** absorption bands in the two experiments (cf. Table 2).

When the matrix-isolated **1** is submitted to broad band irradiation at $\lambda > 230$ nm in the $\pi \rightarrow \pi^*$ electronic absorption band (277 nm), the IR absorption bands of the

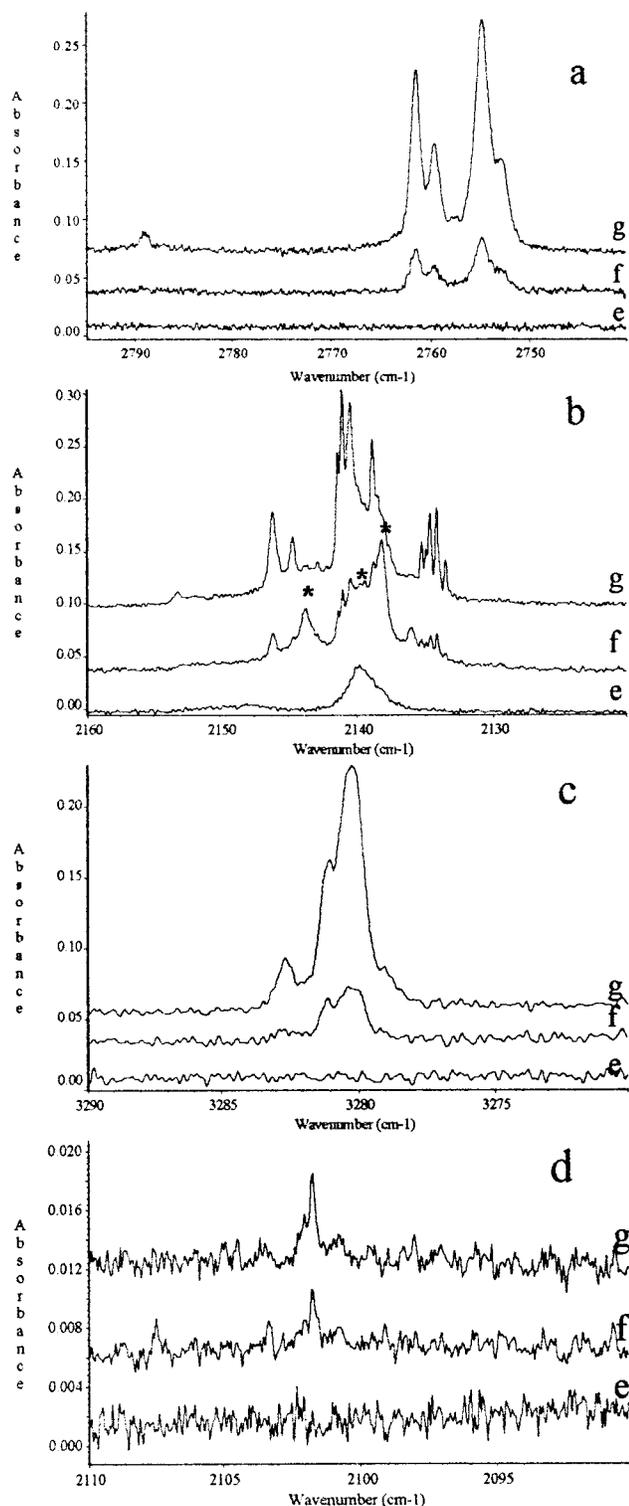


Figure 3. Evolution of the FTIR spectra of acryloyl chloride **1** isolated in an argon matrix at 10 K during irradiation. (a) ν_{HCl} range, (b) ν_{CCO} range; (c) ν_{CH} range, (d) extended part of the ν_{CCO} range: (e) spectrum after 1260 min of irradiation time at $\lambda > 310$ nm; (f) spectrum after 322 min of irradiation at $\lambda > 230$ nm; (g) spectrum after 2460 min of irradiation at $\lambda > 230$ nm. * bands of 3-chloro-1,2-propenone.

two conformers of acryloyl chloride decrease while the absorption bands of 3-chloro-1,2-propenone first increase and then decrease (cf. Figure 4). This last result enables us to assign the absorption bands of this intermediate product in all the spectral range. These experimental

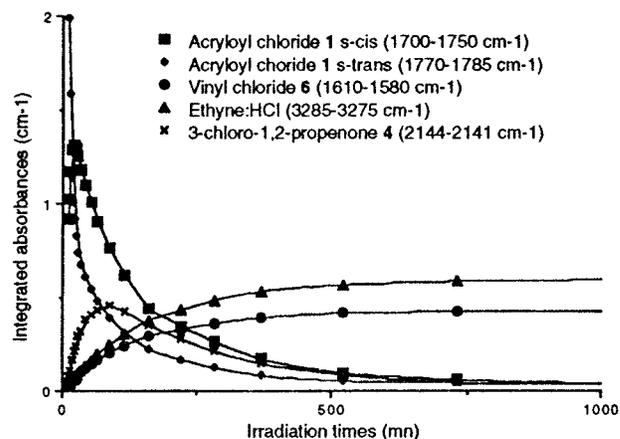


Figure 4. Evolution of integrated absorbance during photolysis of acryloyl chloride **1** at $\lambda > 230$ nm.

Table 3. Experimental Vibrational Frequencies of Products Obtained from Photolysis of the Acryloyl Chloride **1. The Main Peak Frequencies Are Underlined**

observed frequencies (cm^{-1})		
our work	literature	identification
<u>3282.7–3281–3280.8</u>	3282.6 ^a	8 ·HCl
<u>2789–2787</u>		2 ·HCl
<u>2761–2759</u>	2764.4 ^a	8 ·HCl
<u>2754–2752</u>		8 ·HCl
<u>2145.9–2144.5</u>		4
<u>2145–2143.6–2142.7</u>		4
<u>2141.4–2140.9</u>		CO
<u>2138.7</u>		CO
<u>2138.5–2135.9–2134</u>		4
<u>2102</u>		2 ·HCl
<u>1972.2–1971.9</u>	1973.1 ^a	8 ·HCl
<u>1448</u>		4
<u>1608.9</u>	1601–1621 ^b	6
<u>1366.8–1350.5</u>	1360–1381 ^b	6
<u>1344.9</u>	1343.9 ^a	8 ·HCl
<u>1283.7–1282.9</u>	1271–1292 ^b	6
<u>1269–1262.3</u>		4
<u>1183.9</u>		4
<u>1026.4</u>	1021–1038 ^b	6
<u>1021</u>		4
<u>951</u>	941–960 ^b	6
<u>896–895</u>	896 ^b	6
<u>754.3–751.8</u>	751.2 ^a	8 ·HCl
<u>741.5–738.5</u>	737.2 ^a	8 ·HCl
<u>712.3</u>	710–731 ^b	6
<u>701</u>		4
<u>621.6</u>	629.8 ^a	8 ·HCl

^a See ref 24. ^b See ref 25.

vibrational frequencies are reported in Table 2 where they can be compared to theoretical scaled and unscaled frequencies.

In the very early stage of the irradiation at $\lambda > 230$ nm, new absorption bands appear in different areas (cf. Figure 3). A broad absorption band assigned to the ν_{HCl} stretching mode (cf. Figure 3a) appears at 2761 cm^{-1} and a smaller one at 2789 cm^{-1} . These frequencies are lower than the value observed for free HCl²² by $\Delta\nu_{\text{HCl}} = -106$

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Table 4. Relative Energies, Activation Barrier Values, and Geometries (bond lengths in angstroms, valence and dihedral angles in degrees) for Reactant, Transition States, and Products in the Two First Singlet Electronic Levels

parameters	ab initio (MP2/6-31G*)						semiempirical (PM3)					
	S ₀			S ₁			S ₀			S ₁		
	1	TS	4	1	TS	4	1	TS	4	1	TS	4
C2-C3	1.340	1.378	1.487	1.328	1.447	1.491	1.341	1.400	1.485	1.375	1.354	1.463
C3-C4	1.474	1.387	1.326	1.444	1.417	1.394	1.477	1.392	1.321	1.389	1.439	1.426
C4-O5	1.206	1.165	1.179	1.263	1.169	1.178	1.202	1.168	1.176	1.325	1.170	1.174
C4-Cl6	1.796	2.549	3.605	1.737	3.410	4.040	1.781	2.204	3.500	1.657	3.278	4.005
C2-Cl6	3.085	2.449	1.808	3.204	2.221	1.780	3.019	2.214	1.784	3.084	2.221	1.772
C3-H7	1.086	1.085	1.083	1.075	1.080	1.079	1.096	1.092	1.096	1.095	1.097	1.095
C2-H1	1.084	1.076	1.090	1.073	1.073	1.017	1.086	1.092	1.097	1.083	1.119	1.104
C3-C4-O5	124.2	160.5	178.3	123.6	130.6	132.8	126.3	159.5	178.8	119.4	140.8	142.3
C2-C3-C4	125.7	116.7	121.3	126.0	122.4	120.0	123.1	113.8	123.2	121.5	119.3	117.3
H1-C2-H8	117.5	115.9	108.7	117.4	114.8	107.9	114.9	113.7	109.4	116.3	114.7	107.9
Cl6-C4-C3	115.8	86.7	41.6	123.4	63.8	15.0	113.9	87.1	41.1	125.8	65.6	15.6
C2-C3-C4-Cl6	0.0	30.6	99.0	0.0	38.8	179.8	22.1	27.5	46.8	0.0	32.6	179.9
C2-C3-C4-O5	180.0	168.2	0.00	180.0	183.0	180.0	160.0	198.1	157.4	180.0	173.6	180.0
relative energies(*) kJ mol ⁻¹	0	207.2	42.6	457.6	509.0	315.5	0	158.8	29.7	362.1	371.4	268.0

(*) The S₀ state of **1** s-trans is taken as the reference energy.

and -81 cm⁻¹, respectively, and are characteristic of complexed HCl.³

In the range of the ν_{CO} and ν_{CO} stretching frequencies between 2200 and 2100 cm⁻¹, two kinds of absorption bands appear. The strongest ones (2145.9–2140.9–2148.7–2134.5 cm⁻¹) are assigned to CO (trapped in different sites with different surrounding molecules (Figure 3b)). The smaller one (2102 cm⁻¹) can be assigned to **2** complexed with HCl for two reasons: This band has the same kinetic behavior than the ν_{HCl} band at 2789 cm⁻¹, and its shift to low frequency (25 cm⁻¹ in comparison with the value observed by Chapman²⁰) is indicative of a complex (cf. Figure 3d).

Another set of absorption bands at 3280.2, 1971.9, and 1345 cm⁻¹ and the sharp doublet at 781.6 and 738.6 cm⁻¹ with similar behavior must be assigned to ethyne complexed with HCl by comparison with the Andrews results²⁴ (cf. Figure 3c). The infrared frequencies of the fundamental vibrational modes of vinyl chloride at 1608, 1350.5, 1283.7, 1026.4, 954, 754, and 712 cm⁻¹ were also observed. They are close to those reported in the literature²⁵ for free molecules embedded in an argon matrix without a CO molecule as a cage companion. The experimental frequency values are reported in Table 3. The evolution of the integrated absorbances of the different products at different irradiation times are reported in Figure 4.

Theoretical Studies

Absolute energies and calculated geometries by ab initio and semiempirical method are summarized in Table 4. The first calculated singlet excited (S₁) in MP2/6-31G* basis set is 457 kJ mol⁻¹ above the ground state (S₀). The energy available upon photolysis in the range 310–600 nm is not sufficient ($E < 387$ kJ mol⁻¹) to populate the first excited state (S₁). Moreover, in the CIS approximation¹⁶ used in this work, the transition here considered S₀→S₁ ($\sigma \rightarrow \pi^*$) is forbidden. Consequently, the 1,3 chlorine migration has to take place in the ground

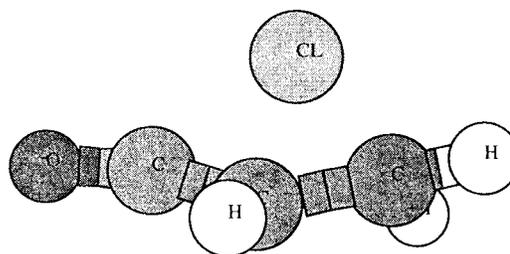


Figure 5. Transition state of the 1,3 chlorine migration calculated in the ground state with MP2/6-31G* basis set.

state ($E_a = 207.2$ kJ mol⁻¹) via an out of plane transition state (Figure 5), probably after relaxation in a high vibrational energy level. These results are similar to those obtained by Kock et al.⁷ for the activation barrier (216 kJ mol⁻¹) and the out of plane transition state of the 1,3 chlorine migration in the 3-chloro-1-propene.

Conclusion

During the photolysis of acryloyl chloride **1** at $\lambda > 310$ nm the initial loss of HCl has been expected to produce **2** and **3** as the first intermediates. Experimentally, 3-chloro-1,2-propenone **4** is the only observed product. There is no evidence for the formation of cyclopropenone **3** and propadienone **2**. A photochemical steady state is reached involving **1** s-trans, **1** s-cis, and **4**. Irradiation at shorter wavelengths speeds up this isomerization process and induces the photolysis of **4** which presents two reaction paths:

(1) splitting into CO and the postulated 2-chloroethylidene transient **5**, the latter isomerizing to vinyl chloride **6**;

(2) elimination of HCl with formation of propadienone **2** complexed by the HCl molecule. Subsequently, the photolysis of **2** gives CO and a new transient assumed to be the vinylidene **7** which isomerizes to ethyne **8**.²⁶

CO, HCl, ethyne, and vinyl chloride are the final reaction output. The 1,3 photoisomerization process

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occurs in the first excited state or in the S_0 ground state after relaxation to a high vibrational energy level which allows isomerization.

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