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# Conformational analysis and photolysis of matrix isolated 3-chloropropanoyl chloride monitored by FTIR spectroscopy

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**Abstract**

Fourier transform infrared spectra of 3-chloropropanoyl chloride **1**, both as a neat liquid and isolated in an argon matrix at 10 K, have been analyzed. These spectra reveal the existence of three conformers, the SA conformer ($\phi_{1(C3C2C1O)} = 0°$ and $\phi_{2(C1C2C3Cl3)} = 180°$) being the most stable. The semi-empirical PM3 and ab initio 6-31G* methods were used to evaluate the relative stability of these conformers, and to calculate the infrared spectra. Irradiation of 3-chloropropanoyl chloride, at $\lambda >$ 230 nm, yields 3-chloro-1,2-propenone **2** and acryloyl chloride **3** as primary photoproducts. Photolysis of these compounds induces the formation of CO, HCl, vinyl chloride and ethyne as final products. The shifts of the $\nu_{HCl}$ stretching mode, below the frequency of monomeric HCl in argon matrix, are indicative of the formation of HCl : CO and HCl : ethyne complexes. The identification of the reaction products is performed by comparison of experimental FTIR spectra and literature data. © 1998 Elsevier Science B.V.

*Keywords:* 3-chloropropanoyl chloride; 3-chloro-1,2-propenone; Cryogenic matrix; Infrared spectroscopy; Photochemistry

## 1. Introduction

The authors' group is actively involved in the synthesis, identification and reactivity of ketene intermediates trapped in rare gas matrices [1,2]. The matrix isolation technique is certainly the most valuable method for the investigation of these reactive unstable species. Previous studies have shown that UV irradiation of acylchloride [3–6] or 3-halopropene [7] leads to cumulenes derivatives by a photodehydrochlorination process. In the case of acryloyl chloride, irradiation at $\lambda \geq 230$ nm yields 3-chloro-1,2-propenone **2** by 1,3-chlorine migration [8]. To confirm **2** identification, the photodehydrochlorination of 3-chloropropanoyl chloride **1** ($CH_2ClCH_2COCl$) seems to be the most convenient method. The purpose of this work is firstly the study of the vibrational spectra of **1**, as a neat liquid and isolated in an argon matrix, in order to identify the main existing conformers, and secondly, the study of the photolysis process. The molecular structures of all the possible conformations were evaluated using the more recent semi-empirical method, MNDO-PM3 [9]. To confirm the validity of our semi-empirical calculations, a comparison with ab initio ones was performed for the main conformers of 3-chloropropanoyl chloride. Ab initio calculations were also undertaken to compare

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the experimental IR spectra with the calculated ones, and thus to proceed to the assignment of observed absorptions of the photoproducts and furthermore to identify the different photolysis pathways.

## 2. Experimental details

3-chloropropanoyl chloride **1** supplied from Aldrich (purity ≈ 98%) was used after purification by vaccuum distillation Teb = 60°C (35 mmHg). Matrix was obtained by spraying a 1 : 450 mixture of 3-chloropropanoyl chloride and argon onto a CsBr window cooled to 20 K. The spectra were obtained on the Nicolet 7000 FTIR spectrometer with a resolution of 0.12 $cm^{-1}$.

Neat liquid infrared spectra were obtained on the Mattson 1000 FTIR spectrometer with a resolution of 2 $cm^{-1}$. All infrared spectra were recorded in the range of 4000–400 $cm^{-1}$.

Broad-band UV irradiation of the species isolated in a cryogenic matrix was performed using an Oriel high-pressure 200 W mercury lamp ($\lambda > 230$ nm). The temperature of the sample during irradiation was 10 K.

The semi-empirical PM3 method implemented through the Ampac program package [10,11] was used. The Gaussian 94 [12] program package using the Møller Plesset second-order (MP2) procedure with 6-31G* basis set [13–15] was used for ab initio calculations.

## 3. Conformational and vibrational analysis of 3-chloropropanoyl chloride

Prior to the photolysis experiments, the experimental spectra of **1**, as neat liquid and isolated in argon matrices were carefully studied in order to distinguish the conformer spectra. In previous work, Som et al. [16] have observed several bands for the $\nu_{C-Cl}$ and $\nu_{C=O}$ stretching vibrations in the Raman and infrared spectra of liquid 3-chloropropanoyl chloride. They concluded that in the liquid state, **1** adopts four stable conformations. To determine the molecular structures of all the possible conformers, and to obtain their theoretical spectra, the initial potential energy surface (PES) map at the MNDO-PM3 [9] level of theory is produced. This economical method is quite sufficient for rough mapping of the conformational space of organic molecules. The minima were reoptimized at the MP2/6-31G* level [13–15].

### *3.1. Calculation results*

In the first step, relative energies for various dihedral angles $\phi_1(C_3C_2C_1O)$ and $\phi_2(C_1C_2C_3Cl_3)$ in respective steps of 10° were calculated leading to the potential energy surface $V(\phi_1, \phi_2)$ (Fig. 1). The (0°, 0°) and (180°, 0°) conformations corresponding to transition states are easily identified. The repulsion and the steric hindrance between the oxygen and chlorine atoms (0°, 0°) or between the two chlorine atoms (180°, 0°) explain the high energy of these conformations.

The potential energy surface shows four local minima, corresponding to four stable conformations. The energy differences between these conformations are weak ($E < 1$ kcal $mol^{-1}$). It appears that the conformer, wich can be described as SA, and possessing the dihedral angles $\phi_1$ and $\phi_2$ of 0° and 180°, respectively, is lower in energy than the three other conformers: SG ($\phi_1 = 0°$, $\phi_2 = 280°$), GA ($\phi_1 = 120°$, $\phi_2 = 180°$), and GG ($\phi_1 = 120°$, $\phi_2 = 280°$) (cf. Fig. 2). The higher stability of the first ones can be explained by a minimal dipole–dipole interaction between the two chlorine atoms. The two equivalent conformers GG* ($\phi_1 = 120°$, $\phi_2 = 80°$ and $\phi_1 = -120°$, $\phi_2 = 280°$) present a syn 1,3 interaction between the two chlorine atoms and are not stable. Indeed, they do not correspond to local minima in the PES (cf. Fig. 1). The optimized geometries and relative energies obtained by ab initio calculations for the four conformers are reported in Table 1. For the two methods of calculation, the SA form is the more stable. All of these results are in good agreement with those of Stolevik et al. [17], who also carried out calculations on this molecule using the morse-potential formulation. The stability order for the three other conformers is different in semi-empirical and ab initio methods, but the difference between their energies is not important enough to conclude about the stability order between the SG, GA and GG conformers.

The vibrational analysis for the four minima is based on analytical Cartesian force constant matrices calculated at the MP2/6-31G* level. The optimized

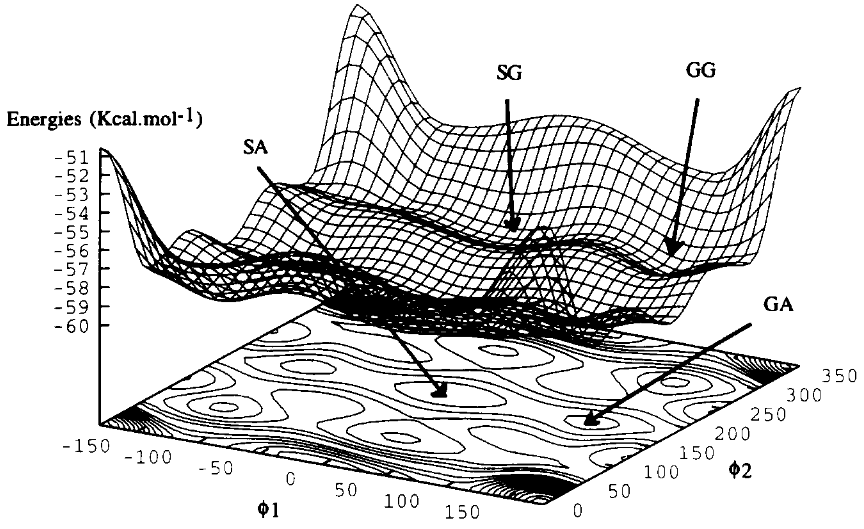
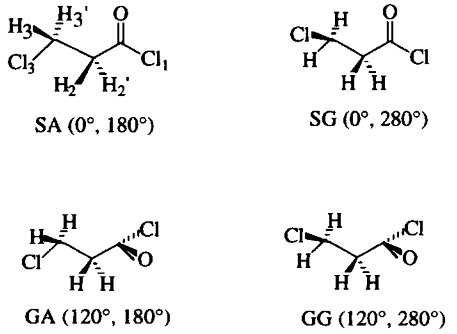


Fig. 1. Potential energy surface and contour plot for the conformation of 3-chloropropanoyl chloride as a function of the $\Phi_1$ and $\Phi_2$ dihedral angles ( $-180° < \Phi_1 < 180°$ and $0° < \Phi_2 < 360°$).

geometries of each conformer, listed in Table 1, were the starting point for the calculation of the second derivatives of the total molecular energy. To allow a comparison with experimental results, the calculated wavenumbers were scaled by a factor of 0.88 for the CH stretching and in-plane deformation vibrations, and by 0.9 for all the other internal coordinates. Unscaled, scaled frequencies and an approximate description of the vibrational modes for each conformers are reported in Table 2.

### 3.2. Experimental results

The infrared spectrum of 3-chloropropanoyl chloride as a neat liquid (Fig. 3) is dominated by the existence of many broad, intense vibration bands. The most interesting spectral features are the large band at 1800 cm$^{-1}$ corresponding to the C=O stretching vibration, and the large number of infrared absorption bands in the 400–800 cm$^{-1}$ range. These evidently arise from the CCl stretching vibration modes and confirm the existence of several conformers.



SA (0°, 180°)

SG (0°, 280°)

GA (120°, 180°)

GG (120°, 280°)

Fig. 2. Four conformers of 3-chloropropanoyl chloride. The numbering system adopted is referred to in the tables.

The infrared spectrum of 3-chloropropanoyl chloride isolated in an argon matrix (Fig. 4) shows some interesting differences when compared with the liquid one. Firstly, the presence of new weak absorption bands which are easily attributed to hydrogen chloride [18–20] and acryloyl chloride [8,21–25] ($CH_2$=CH–COCl). These compounds are induced by the thermal degradation of 3-chloropropanoyl chloride before deposit. Secondly, multiplet structures which are the result of site effects in the matrix are observed in most infrared bands. Finally, the higher resolution enables the identification of three well separated absorption bands for the C=O stretching vibration, one of strong intensity (1800.6 cm$^{-1}$) and two of much weaker intensity (1809.5 and 1812.9 cm$^{-1}$), indicative of the existence of three stereoisomers. Deposition at two different temperatures and annealing of the matrix confirm that these three absorption bands are characteristic of the existence of three conformers. The band positions are very close to those obtained for the

Table 1
Ab initio and semi-empirical optimized geometries and relative energies for the four stable conformations of 3-chloropropanoyl chloride. Bond lengths are in angstroms, and bond angles are in degrees. The relative energies are in kcal mol$^{-1}$

| Parameters | SA | | SG | | GA | | GG | |
|---|---|---|---|---|---|---|---|---|
| | PM3 | 6-31G* | PM3 | 6-31G* | PM3 | 6-31G* | PM3 | 6-31G* |
| C=O | 1.202 | 1.203 | 1.200 | 1.201 | 1.201 | 1.201 | 1.200 | 1.199 |
| $C_1$–$C_2$ | 1.500 | 1.505 | 1.502 | 1.508 | 1.504 | 1.508 | 1.505 | 1.509 |
| $C_2$–$C_3$ | 1.512 | 1.519 | 1.511 | 1.516 | 1.513 | 1.526 | 1.512 | 1.521 |
| $C_1$–$Cl_1$ | 1.777 | 1.790 | 1.781 | 1.791 | 1.775 | 1.798 | 1.779 | 1.799 |
| $C_3$–$Cl_3$ | 1.776 | 1.783 | 1.777 | 1.783 | 1.774 | 1.782 | 1.776 | 1.783 |
| $C_2$–$H_2$ | 1.110 | 1.095 | 1.109 | 1.098 | 1.109 | 1.092 | 1.109 | 1.093 |
| $C_2$–$H_{2'}$ | 1.110 | 1.095 | 1.110 | 1.093 | 1.109 | 1.093 | 1.109 | 1.096 |
| $C_3$–$H_3$ | 1.104 | 1.089 | 1.105 | 1.089 | 1.105 | 1.091 | 1.106 | 1.089 |
| $C_3$–$H_{3'}$ | 1.104 | 1.089 | 1.105 | 1.091 | 1.106 | 1.089 | 1.105 | 1.091 |
| $C_1C_2C_3$ | 113.7 | 110.6 | 114.6 | 112.0 | 111.0 | 111.1 | 112.1 | 113.3 |
| $C_2C_1O$ | 128.5 | 126.4 | 128.9 | 16.6 | 127.1 | 126.7 | 127.4 | 126.7 |
| $C_2C_1Cl_1$ | 111.6 | 112.4 | 111.2 | 112.2 | 112.8 | 112.6 | 112.7 | 112.5 |
| $C_2C_3Cl_3$ | 108.1 | 109.9 | 109.5 | 111.0 | 108.4 | 109.9 | 109.7 | 111.0 |
| $C_3C_2C_1O$ | 0.0 | 0.0 | − 0.3 | − 12.5 | 119.9 | 110.3 | 120.1 | 119.8 |
| $C_1C_2C_3Cl_3$ | 180.0 | 180.0 | 279.9 | 288.0 | 179.7 | 182.2 | 280.1 | 299.7 |
| $\Delta E$ (kcal/mol) | 0.0 | 0.0 | + 0.9 | + 0.6 | + 0.2 | + 1.6 | + 0.8 | + 1.4 |

liquid spectrum and the authors suggest the existence of the same conformers in the two cases.

Each conformer is characterized by calculated frequencies clearly distinct from the other forms (see Table 2). Thanks to these calculated frequencies, it can be established which conformer is present in liquid state or in cryogenic matrix. These specific absorption bands are 404 and 890 cm$^{-1}$, 818 and 1249 cm$^{-1}$, 616 and 789 cm$^{-1}$ and 860 cm$^{-1}$ for the SG, SA, GA and GG conformers, respectively. All these frequencies are observed in the infrared spectra except for the GA conformer. In addition, the experimental absorption bands assigned to the GA conformer in Table 2 can also agree with another form. So, it can be concluded that only three conformers of the 3-chloropropanoyl chloride were present in liquid state or in the argon cryogenic matrix.

## 4. Photolysis experiment

When matrix-isolated 3-chloropropanoyl chloride was subjected to broad band irradiation, with a high pressure Hg lamp ($\lambda > 230$ nm) in its $\pi \rightarrow \pi^*$ electronic absorption band ($\lambda = 243$ nm), the decrease of 3-chloropropanoyl chloride absorption bands and new absorption bands were observed. The photochemical behavior of the 3-chloropropanoyl chloride in the CO stretching region is reported in Fig. 5(a).

Under irradiation, two groups of bands which increase, and then decrease, during irradiation were observed in different areas of the spectra. The first one was observed between 1790 and 1740 cm$^{-1}$ (Fig. 5(a)), and is characteristic of the $\nu_{CO}$ stretching mode of acryloyl chloride **3**. The second, observed between 2130 and 2150 cm$^{-1}$ (Fig. 5(b)), is characteristic of the $\nu_{CCO}$ stretching mode. Other low intensity absorption bands with the same behaviour are observed at 1447.5, 1267.8, 1177.5, 1017.4 and 701 cm$^{-1}$. All these absorption bands are identical with those obtained by irradiation of acryloyl chloride [8] and confirm the identification of **2**.

Acryloyl chloride and 3-chloro-1,2-propenone are trapped with HCl in the same matrix cage. The $\nu_{HCl}$ stretching mode frequencies observed at 2726.4 and 2742 cm$^{-1}$ are lower, by − 143.6 and − 128 cm$^{-1}$, respectively, than the value of the $\nu_{HCl}$ stretching frequency for free HCl trapped in argon matrix [18–20]. The evolution of these absorption bands (Fig. 6(a)) enable us to assign the ones of these intermediate

Table 2

Observed and simulated infrared spectra of the 3-chloropropanoyl chloride. Scaling factors are 0.88 for CH stretchings and in-plane deformations and 0.9 for all other interne coordinates; tors: torsion, oop: out of plane, B: bending, N: stretching

| Assignment | Calculations | | | | | | | | | | | | Experiments | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Calculated frequencies | | | | Scaled frequencies | | | | Relative intensities | | | | Liquid | | | | Argon matrix | | | |
| | SA | SG | GA | GG | SA | SG | GA | GG | SA | SG | GA | GG | SA | SG | GA | GG | SA | SG | GA | GG |
| $\nu$CH | 3243 | 3287 | 3241 | 3239 | 3011 | 3004 | 3008 | 3007 | 1 | < 1 | < 1 | 1 | — | — | — | — | — | — | — | — |
| $\nu$CH | 3180 | 3186 | 3208 | 3198 | 2949 | 2959 | 2975 | 2965 | < 1 | < 1 | < 1 | < 1 | — | — | — | — | — | — | — | — |
| $\nu$CH | 3175 | 3166 | 3165 | 3168 | 2944 | 2936 | 2935 | 2938 | 3 | 5 | 3 | 4 | — | — | — | — | — | — | — | — |
| $\nu$CH | 3128 | 3110 | 3139 | 3120 | 2901 | 2884 | 2911 | 2893 | 2 | 1 | < 1 | < 1 | — | — | — | — | — | — | — | — |
| $\nu$CO | 1842 | 1853 | 1846 | 1855 | 1800 | 1810 | 1804 | 1813 | 100 | 100 | 100 | 100 | | | 1800 | | | 1812.9–1809.5–1800.6 | | |
| $\beta$C$_3$H$_3$H$_{3'}$ | 1550 | 1538 | 1552 | 1545 | 1454 | 1443 | 1456 | 1449 | 1 | 6 | 2 | 4 | 1451 | 1440 | | 1451 | 1457–1455 | 1443–1441 | | 1457–1455 |
| $\beta$C$_2$H$_2$H$_{2'}$ | 1518 | 1505 | 1532 | 1517 | 1424 | 1412 | 1437 | 1424 | 9 | 12 | 3 | 5 | 1407 | 1396 | 1440 | 1407 | 1415–1412 | 1394.5 | 1443–1141 | 1415–1412 |
| $\beta$CCH$_2$ $\beta$CCH$_{2'}$ | 1431 | 1427 | 1412 | 1401 | 1344 | 1341 | 1325 | 1316 | 3 | 13 | 16 | 4 | | 1348 | — | 1299 | | 1347.3–1339.5 | — | 1296–1306 |
| $\beta$CCH | 1343 | 1394 | 1349 | 1397 | 1260 | 1308 | 1266 | 1310 | < 1 | 15 | 2 | 10 | — | 1299 | — | 1299 | — | 1296–1306 | — | 1296–1306 |
| $\beta$HCCl $\beta$CCH$_3$ $\beta$CCH$_{3'}$ | 1331 | 1282 | 1314 | 1271 | 1249 | 1203 | 1233 | 1190 | 9 | 4 | 1 | 5 | 1256 | 1215 | — | 1205 | 1252 | 1208 | — | |
| $\beta$HCCl $\beta$CCH$_2$ $\beta$CCH$_{2'}$ | 1208 | 1228 | 1232 | 1240 | 1132 | 1151 | 1151 | 1163 | < 1 | 2 | 19 | 16 | — | | 1167 | 1178 | | 1150.2 | | 1166.6 |
| $\beta$HCCl $\nu$C$_1$–C$_2$ | | | 1116 | 1108 | | | 1049 | 1053 | | | 45 | 33 | | | | 1044 | | | | 1054.3–1046.7–1041.3 |
| $\nu$C$_2$–C$_3$ | 1115 | 1106 | 1085 | 1085 | 1055 | 1048 | 1028 | 1028 | 17 | 22 | 12 | 17 | | | 1044 | | 1054.3–1046.7–1041.3 | | | 1035.4 |
| HCCl $\beta$CCH$_2$$\beta$CCH$_{2'}$ | 1064 | | | | 996 | | | | < 1 | | | | — | | | | — | | | |
| $\nu$C$_1$–C$_2$ | 1022 | 1027 | 1032 | | 968 | 974 | 976 | | | | | | | 969 | | | | 971.1–963.9 | | |
| $\nu$CC $\beta$CCH$_2$ | | 983 | | | | 935 | | | | 29 | | | | 922 | | | | 938–919 | | |
| oopCl$_1$ $\beta$CCH | | | | 975 | | | | 925 | | | | 5 | | | | 922 | | | | 938–919 |
| $\nu$CCl$_1$ $\beta$CCH $\beta$HCCl | | 948 | | | | 890 | | | | 55 | | | | 896 | | | | 898–893 | | |
| $\nu$C$_1$–C$_2$ $\beta$CCH | | | | 915 | | | | 860 | | | | 47 | | | | 866 | | | | 874–869 |
| $\nu$C$_3$Cl$_3$ $\beta$CCC | 866 | | 834 | | 818 | | 789 | | 8 | | 9 | | 813 | | — | | 821–812 | | — | |
| $\beta$CCH | 801 | 948 | 811 | | 765 | | 771 | | 3 | | 5 | | 761 | | 761 | | 763.6 | | 763.6 | |
| $\nu$CCl$_3$ $\nu$CCl$_1$ | 721 | 734 | 652 | 730 | 682 | 695 | 616 | 692 | 86 | 10 | 49 | 9 | | 687 | — | 687 | 684–682.8 | 686.6–686 | — | 686.6–686 |
| $\nu$CCl$_1$ $\nu$CC $\beta$CCC | | 714 | 605 | | | 673 | 573 | | | 30 | 19 | | | | 572 | | | | 575–573.9 | |
| oopCCl$_1$ $\beta$CCC | | | | 641 | | | | 663 | | | | < 1 | | | | — | | | | |
| torsCC oopCCl$_1$ | 511 | 502 | | | 484 | 476 | | | < 1 | 1 | | | | 497 | | | | | | |
| $\nu$CCl$_1$ | 462 | 461 | 461 | 596 | 436 | 435 | 435 | 563 | 8 | 15 | 8 | 50 | | 439 | | 572 | | | | 575–573.9 |
| $\beta$OCC$_1$ $\beta$CCl$_1$ | | | | 451 | | | | 426 | | | | 6 | | | | 439 | | | | |
| $\beta$CCCl | | 430 | | | | 404 | | | | 15 | | | | | | | | | | |

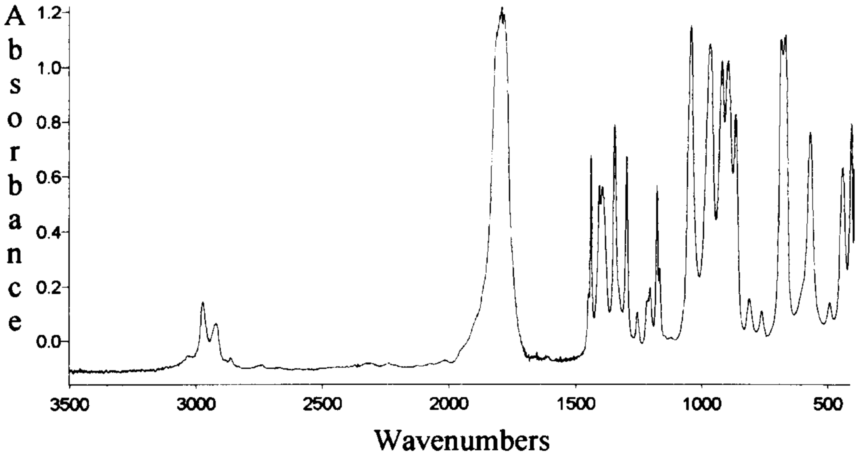


Fig. 3. Infrared spectrum of neat 3-chloropropanoyl chloride in the 3500–400 cm$^{-1}$ range.

products in all the spectral range. The results for 1 : 1 complexes between ketene derivatives and HCl were obtained in earlier work [2,5]. As was observed by Kogure et al. [6], these complexes are characterized by a significant shift of the fundamental vibrational frequency of HCl to a lower frequency. Under irradiation, 2-HCl and 3-HCl 1 : 1 complex is obtained in the matrix. The $\nu_{CO}$ stretching mode (1790–1757 cm$^{-1}$) of acryloyl chloride complexed is shifted by about 10 cm$^{-1}$ with respect to those of pure **3** (1779–1766 cm$^{-1}$), whereas the $\nu_{CCO}$ stretching mode of 3-chloro-1,2-propenone is slighty shifted (1 or 2 cm$^{-1}$).

In the very early stage of the irradiation at $\lambda > 230$ nm, new increasing absorption bands appear in different areas of the infrared spectra. The bands assigned to the $\nu_{HCl}$ stretching mode of CO : HCl

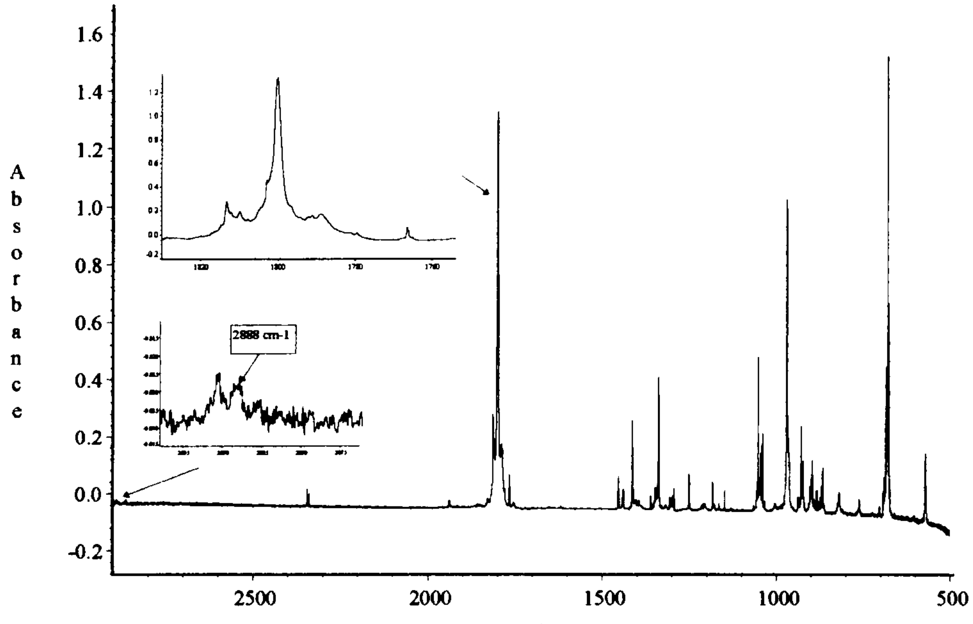


Fig. 4. Infrared spectrum of 3-chloropropanoyl chloride isolated in an argon cryogenic matrix in the 2900–400 cm$^{-1}$ range.

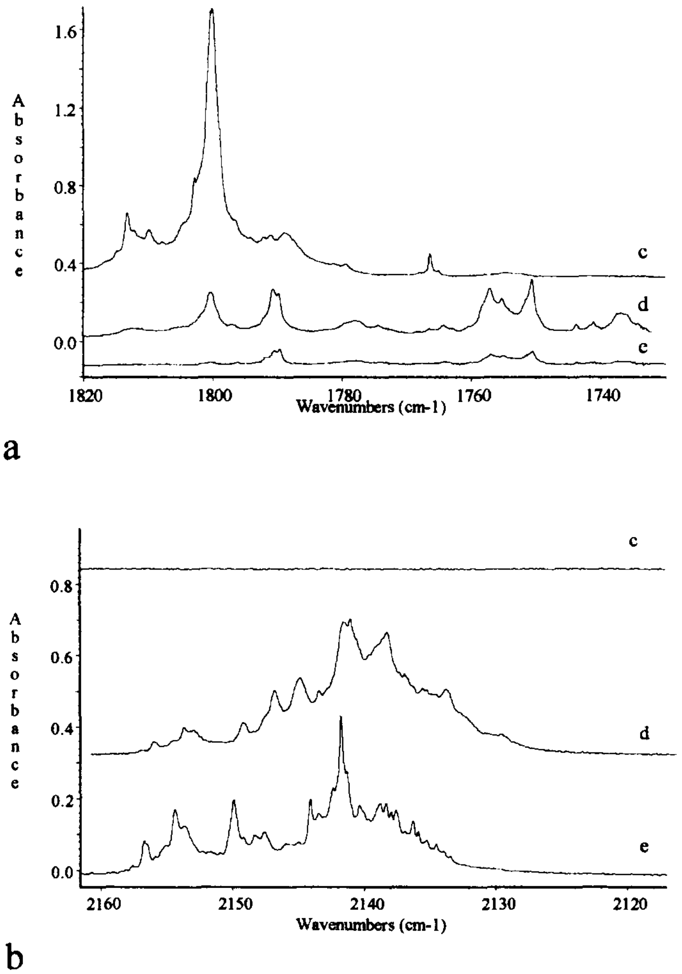


Fig. 5. Evolution of the spectra of **1** isolated in an argon matrix at 10 K during irradiation ($\lambda > 230$ nm) in the $\nu_{CO}$ (a) and $\nu_{CCO}$ (b) ranges. (c) spectrum after deposition; (d) spectrum after 3560 min of irradiation; (e) spectrum after 201 h of irradiation.

(Fig. 6(a)) appear between 2789.4 and 2814.3 cm$^{-1}$ [19,20]. However, in this range, the absorption band can be assigned to the vinyl chloride : HCl complex [26]. A less intense absorption band appears at 2759.4 cm$^{-1}$; this frequency is lower than the value observed for free HCl [18–20] ($\Delta\nu_{HCl} = 110.6$ cm$^{-1}$), and is characteristic of the ethyne : HCl complex [18]. At the same time, in the carbon monoxide stretching frequency range, strong absorption bands appear. The strongest one at 2141.3 cm$^{-1}$ and the less intense one at 2151 cm$^{-1}$ are assigned to CO and CO : HCl [19,20], respectively. Absorption bands at 3282.7, 1971.9 and 1343.6 cm$^{-1}$ and the sharp doublet at 759.9 and 738.7 cm$^{-1}$, are assigned, by comparison with the results of Andrew [18], to ethyne complexed by one molecule of HCl.

Another set of absorption bands (Fig. 6(b)) with similar behaviour is observed at 2704.9 and 2693.6 cm$^{-1}$ ($\nu_{HCl}$) and at 3261 cm$^{-1}$ ($\nu_{CH}$ ethyne) and 1969.9 cm$^{-1}$ ($\nu_{C\equiv C}$) and was assigned to ethyne complexed by two molecules of HCl.

The infrared frequencies of the fundamental vibrational modes of vinyl chloride at 1608.9, 1367.6, 1282.9, 1024.7, 952, 898.9 and 711.8 cm$^{-1}$ were also observed. They are close to those reported in the literature [27–29] for free molecule in liquid state. The experimental frequency values of the reaction products are reported in Table 3. Vinyl chloride is

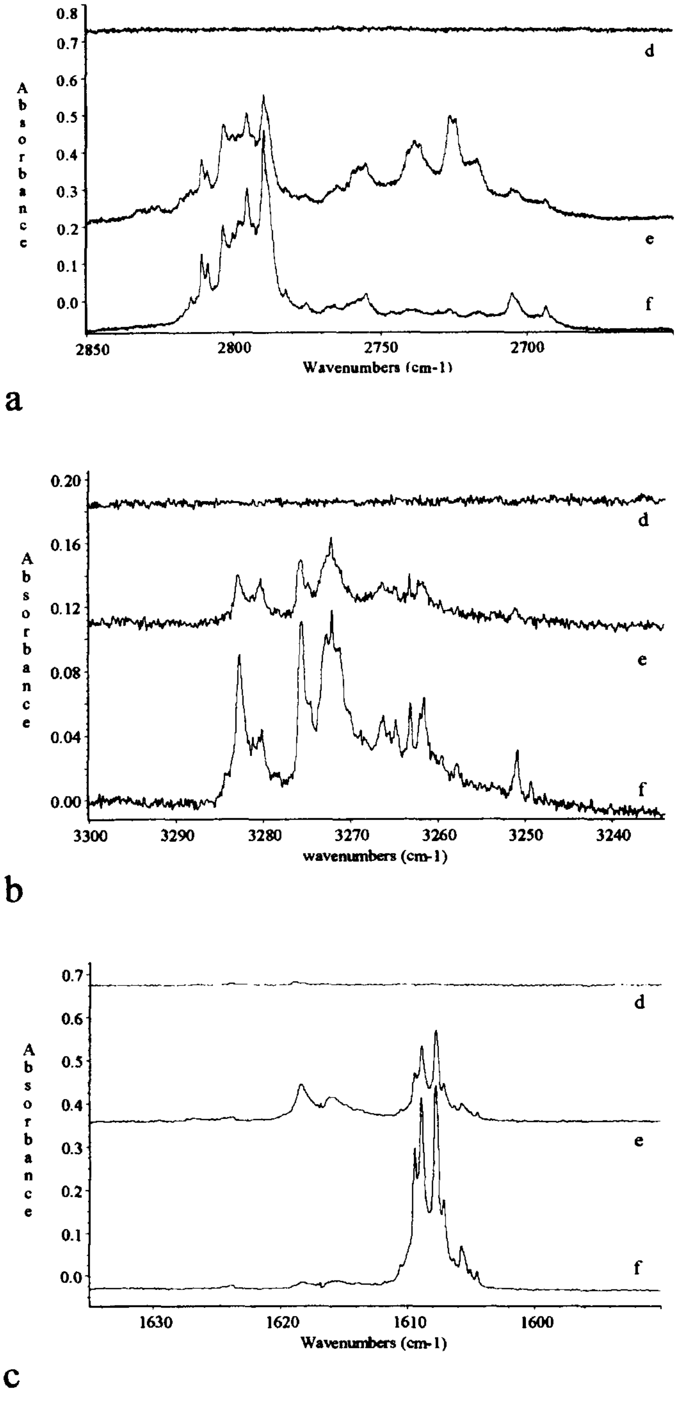


Fig. 6. Evolution of the FTIR spectra of the products of photolysis of 1 during irradiation ($\lambda > 230$ nm). (a) $\nu_{HCl}$ range; (b) $\nu_{CH}$ range; (c) $\nu_{C=C}$ range; (d) spectrum after deposition; (e) spectrum after 3560 min of irradiation; (f) spectrum after 201 h of irradiation.

Table 3
Experimental vibrational frequencies of products obtained from photolysis of the 3-chloropropanoyl chloride

| Observed frequencies (cm$^{-1}$) | | |
|---|---|---|
| Our work | Literature | Assignment |
| 3282.7–3280–3276 | 3282.6[a] | Ethyne : HCl |
| 3272–3261 | — | Ethyne : 2HCl |
| [2789.4–2814.3] | [2782–2815.7][b] | CO : HCl-vinyl chloride : HCl? |
| 2759.4–2754.8 | 2764.4[a] | Ethyne : HCl |
| 2749–2742–2736.9 | — | 3-Chloro-1,2-propenone : HCl |
| 2726.4–2717.6 | — | Acryloyl chloride : HCl |
| 2704.9–2693.6 | — | Ethyne : 2HCl |
| 2145–2139.2 | 2143.6–2138[c] | 3-Chloro-1,2-propenone : HCl |
| [2150–2145] | [2157.2–2140.3][b] | CO : HCl |
| 2141.3 | 2138–2149.4[b] | CO |
| 1971.9 | 1973.1[a] | Ethyne : HCl or/and ethyne : 2HCl |
| 1790 | | Acryloyl chloride : HCl |
| 1777–1774 | 1779[c] | Acryloyl chloride |
| 1766 | 1766[c] | Acryloyl chloride |
| 1750–1757 | | Acryolyl chloride : HCl |
| 1618–1616 | 1626–1619[c] | Acryloyl chloride : HCl |
| 1605.9–1607.8–1608.9–1609.3 | 1608.9[c] | Vinyl chloride |
| 1447.5 | 1448[c] | 3-Chloro-1,2-propenone : HCl |
| 1404–1397 | 1394–1398[c] | Acryloyl chloride : HCl |
| 1367.6 | 1366.8–1350.5[c] | Vinyl chloride |
| 1343.6 | 1343.9[a] | Ethyne : HCl or/and ethyne : 2HCl |
| 1277.2–1282.9 | 1283.7–1282.9[c] | Vinyl chloride |
| 1267.8–1263 | 1268.6–1262[c] | 3-Chloro-1,2-propenone : HCl |
| 1244 | 1288–1284[c] | Acryloyl chloride : HCl |
| 1177.5 | 1183.9[c] | 3-Chloro-1,2-propenone : HCl |
| 1160–1155–1145–1444 | 1150[c] | Acryloyl chloride : HCl |
| 1066–1057 | 1075[c] | Acryloyl chloride : HCl |
| 1024.7 | 1026.7[c] | Vinyl chloride |
| 1017.4 | 1021[c] | 3-Chloro-1,2-propenone : HCl |
| 992 | 999[c] | Acryloyl chloride : HCl |
| 988–985–981 | 986–984[c] | Acryloyl chloride : HCl |
| 966–961 | 979–973[c] | Acryloyl chloride : HCl |
| 952–947–943 | 951[c] | Vinyl chloride |
| 943–912–911–908 | 936[c] | Acryloyl chloride : HCl |
| 902–898.9–896.2 | 896–895[c] | Vinyl chloride |
| 762.3–759.9–748.9 | 751.2[a] | Ethyne : HCl or/and ethyne : 2HCl |
| 741–738.7 | 737.2[a] | Ethyne : Hcl or/and ethyne : 2HCl |
| 720–715–705–698 | 705[c] | Acryloyl chloride : HCl |
| 711.8–704 | 712.3[c] | Vinyl chloride |
| 701 | 701[c] | 3-Chloro-1,2-propenone : HCl |
| 619.9–622.1–624.7 | 629.8[a] | Ethyne : Hcl or/and ethyne : 2HCl |
| 605–604–599 | 605[c] | Acryloyl chloride : HCl |

[a]Refs. [21–25]; [b] Refs. [19,20]; [c] Refs. [3–6].

obtained by the photolysis of **2** which decomposes to CO and 2-chloroethylidene **4**. This last transient collapses to form ground state vinyl chloride by 1,2 hydrogen migration. Formation of ethyne proceeds from irradiation of acryloyl chloride. Under irradiation, this compound is known to yield the vinylidene transient **5** which leaves ethyne by an intramolecular isomerization process [3–6]. The involved compounds and the reaction paths are depicted in Fig. 7.

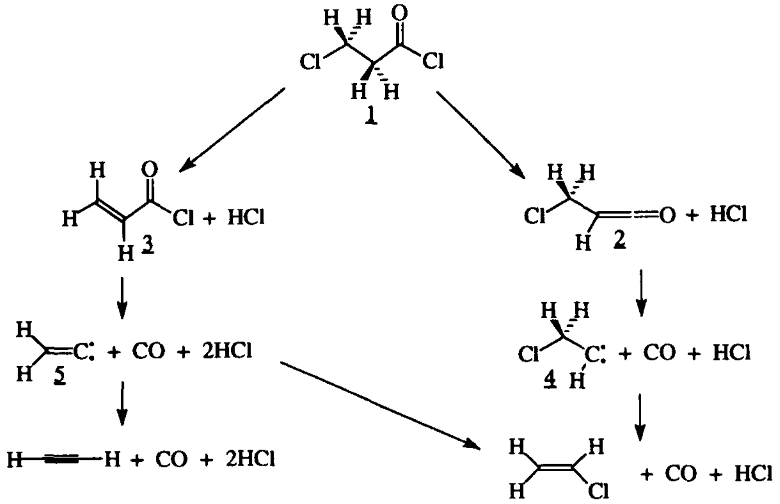


Fig. 7. Reaction paths of the 3-chloropropanoyl chloride photolysis.

## 5. Conclusion

The semi-empirical PM3 and ab initio MP2/6-31G* method predicts, for 3-chloropropanoyl chloride, the existence of four conformers. Only three are observed in liquid state and in argon matrix. The SA conformer ($\phi_1 = 0°$ and $\phi_2 = 180°$) is the most stable. In the argon matrix, the infrared spectra exhibit the predominance of this conformer and allows one to verify the reliability of the calculation, displaying experimental frequencies in good agreement with the calculated ones.

During the photolysis of 3-chloropropanoyl chloride at $\lambda > 230$ nm, the 3 chloro-1,2-propenone **2** and acryloyl chloride **3** are the primary reaction products. HCl, carbon monoxide, ethyne and vinyl chloride are the final reaction products. These last compounds are obtained by intramolecular isomerization of carbene transients.

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