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Short communication

# Photolysis of matrix-isolated perfluoroacetyl chloride, $CF_3C(O)Cl$

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#### Abstract

Perfluoroacetyl chloride is decomposed in an argon matrix to produce  $CF_3Cl$  and CO. The compounds are identified when the bands of the initial IR spectra disappear with the concomitant appearance of signals at 1207, 1098, 782 and 562 cm<sup>-1</sup>, and the band 2137 cm<sup>-1</sup> belonging to the CO stretching vibration of the CO molecule.

This result is compared with related studies of similar compounds.

## 1. Introduction

The recently published study on the photolysis of the matrix-isolated acetyl chloride by Kogure et al. [1] together with previous reports on the photolysis of FC(O)SCI [2], FC(O)SBr [3], CH<sub>3</sub>C(O)H [4] and as yet unpublished results on CF<sub>3</sub>C(O)SCI [5] constitute the basis for the study of the matrixphotochemical behaviour of CF<sub>3</sub>C(O)Cl.

Matrix-isolated CH<sub>3</sub>C(O)Cl decomposed on irradiation ( $\lambda > 270$  nm) forming ketene, H<sub>2</sub>C=C=O and HCl. When FC(O)SCl, FC(O)SBr, CH<sub>3</sub>C(O)H and CF<sub>3</sub>C(O)SCl are irradiated with  $\lambda < 300$  nm, SClF, SBrF, CH<sub>4</sub> and CF<sub>3</sub>SCl respectively, are detected together with CO in the matrix-IR spectra.

The randomization taking place when both FC(O)SCl and FC(O)SBr are irradiated is inter-

esting. When FC(O)SCI [6] and FC(O)SBr [3] are still present in the matrix, a trans-cis randomization can be observed, with roughly 50% of each conformer. This process was used in order to calculate the ratio of the trans and cis conformers in the vapour phase. The values agree with those obtained by electron diffraction experiments and in ab initio studies.

Thus, taking into account the above-mentioned facts, we will report in this paper the results of the photolysis of  $CF_3C(O)Cl$ . Moreover, the results will be compared with those reported in the study of the photolysis of the compound in the vapour phase, giving an important term for comparison.

## 2. Experimental

 $CF_3C(O)Cl$  was prepared by reaction of  $CF_3C(O)OH$  with  $PCl_5$ . The product of the reaction was purified by several trap-to-trap distillations. The purity was checked by comparison with reported data from the literature [7].

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Fig. 1. Subtraction IR spectra of  $CF_3C(O)Cl$  after 20 minutes of UV irradiation and  $CF_3C(O)Cl$  without irradiation. The photolysis products ("positive IR spectrum") and the original spectrum ("negative IR spectrum") are thus clearly discriminated.

Infrared spectra between 4000 and  $400 \text{ cm}^{-1}$  were recorded with a FT Bruker IFS 66 spectrometer (resolution  $1 \text{ cm}^{-1}$ ).

Low temperature spectra in Ar (1:100) were obtained in a cryogenic system and the continuous deposition technique was employed. The mixture was deposited for 2 h at a rate of 1mmol h<sup>-1</sup> onto a CsI window maintained at around 15 K.

For the photochemical study, a TQ 150 mercury lamp (Hereaus) was employed. The radiation was filtered with water.

### 3. Result and discussion

In the photolysis of CF<sub>3</sub>C(O)Cl in argon matrices with UV radiation, all the infrared absorptions corresponding to this compound disappear and five new bands clearly appear in the region  $2500-400 \text{ cm}^{-1}$ . In Fig. 1, we present a record resulting from the subtraction of the IR spectrum after 20 minutes of UV irradiation from the original IR spectrum of CF<sub>3</sub>C(O)Cl.

In the "positive" region, bands at 2137, 1207, 1098, 782 and  $562 \text{ cm}^{-1}$  are observed. The absorption in the region of  $2137 \text{ cm}^{-1}$  is undoubtedly caused by the CO stretching vibration of the CO molecule, whereas the remaining bands are

ascribed to fundamental vibrations belonging to the  $CF_3Cl$  molecule [8] (see Table 1).

The formation of  $CF_3Cl$  and CO can be interpreted with the following mechanisms:

$$CF_{3}C(O)Cl \rightarrow \frac{(a) \cdot CF_{3} + \cdot C(O)Cl}{(b) \cdot CF_{3}CO + \cdot Cl} \rightarrow CF_{3}Cl + CO$$

Table 1

Fundamental vibration	ons (cm <sup>-+</sup> ) for	r CF <sub>3</sub> C(O)Cl and	l CF₃Cl
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	CF <sub>3</sub> C(O)Cl			CF₃Cl	
	Matrix IR	<b>Re</b> f. 7		Matrix IR	Ref. 8(a)
$\nu_1(\mathbf{A}')$	1799	1821	$\nu_4(E)$	1207	1212
$\nu_2(\mathbf{A}')$	1281	1284	$\nu_1(A_1)$	1098	1105
$\nu_3(\mathbf{A}')$	1228	1240	$\nu_2(A_1)$	782	781
$\nu_{11}(A'')$	1184	1202	$\nu_5(E)$	562	563
$\nu_4(A')$	939	933	$v_1(A_1)$		470
$\nu_5(\mathbf{A}')$	750	750	$\nu_6(E)$		356
$\nu_6(\mathbf{A}')$	702	703	.,		
$\nu_7(\mathbf{A}')$	583	583			
$\nu_{12}(A'')$	514	517			
$\nu_9(\mathbf{A}')$	512	511			
$\nu_{13}(A'')$		411			
$\nu_8(\mathbf{A}')$		334			
$\nu_{14}(A'')$		234			
$\nu_{10}(\mathbf{A}')$		198			
$\nu_{15}(\mathbf{A}'')$		45			

This result is in accordance with that obtained by UV irradiation (254 and 280 nm) of vapour CF<sub>3</sub>C(O)Cl at room temperature [9]. In this work the decomposition of CF<sub>3</sub>C(O)Cl is assumed to evolve in radical processes such as those indicated above. 80-90% of the reaction evolves through step (b) [9].

It is also worth noting that the photolysis of CF<sub>3</sub>C(O)Cl evolves in a similar way to FC(O)SCl, FC(O)SBr, CH<sub>3</sub>C(O)H and CF<sub>3</sub>C(O)SCl, i.e. with the appearance of the CO molecule, but in a different way to CH<sub>3</sub>C(O)Cl, where HCl and H<sub>2</sub>C=C=O are the main photolysis products. The possibility of the formation of stable products such as CO in some cases and HCl in others should be related to the origin of the phenomena. In a similar way, CF<sub>2</sub>ClSCl and CFCl<sub>2</sub>SCl form SCF<sub>2</sub> and SCClF, respectively, under photolysis ( $\lambda < 300$  nm) and Cl<sub>2</sub> is formed in both cases [10].

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