ELSEVIER

Journal of Molecular Structure 407 (1997) 171–175

Journal of
MOLECULAR
STRUCTURE

Photolysis of matrix-isolated $CF_3C(O)SH$ and $CF_3C(O)SCl$[1]

S.E. Ulic[2a,b], K.I. Gobbato[3a], C.O. Della Védova[4a,c,*]

[a] *CEQUINOR (UNLP-CONICET)47.115, C.C.962, 1900 La Plata, Argentina,*
[b] *Departamento de Ciencias Básicas, Universidad Nacional de Luján, Luján, Argentina*
[c] *Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP-CIC-CONICET), Departamento de Química, 47 esq. 115, C.C. 962, 1900 La Plata, Argentina*

Received 2 September 1996; revised 6 October 1996; accepted 14 October 1996

Abstract

Perfluoroacetylthiol, $CF_3C(O)SH$, and perfluoroacetylsulphenyl chloride, $CF_3C(O)SCl$, were irradiated in an inert gas matrix to produce CF_3SH and CO, and CF_3SCl, CF_3Cl, CO and SCO, respectively. The compounds are identified by evaluating the apparition of new bands in the FTIR spectrum of the matrix-isolated substance. The results are compared with related studies of similar compounds taking into account both the irradiation and the stability of the formed products. © 1997 Elsevier Science B.V.

Keywords: Photolysis; Matrix-isolated species; FTIR

1. Introduction

A useful method for evaluating conformational composition is through the photolytic interconversion of conformers in an inert gas matrix. The consequence of this procedure is the possible decomposition of the molecule during irradiation. This decomposition, however, can be used as a method for preparing smaller compounds.

We used the interconversion of conformers in order to evaluate the rotational isomerism of FC(O)SCl, FC(O)SSC(O)F, FC(O)SBr, FC(O)SNSO and FC(O)OOC(O)F [1].

In the same cases, smaller unknown species, such as SClF and SBrF, were isolated when the FC(O)SCl [2] and FC(O)SBr [3] matrices, respectively, were irradiated.

Other relevant examples found in the literature are the photolysis of matrix-isolated $CH_3C(O)H$ [4] and $CF_3C(O)Cl$ [5]. The two compounds, when they are irradiated, segregate CO forming also CH_4 and CF_3Cl, respectively.

In all cases we used UV-radiation with $\lambda < 300$ nm, i.e. falling in the carbonylic chromophore absorption region.

At this point, the results reported for $CH_3C(O)Cl$ become interesting. In this case, when the matrix-isolated compound is irradiated with UV-radiation

---

* Corresponding author.

[1] Dedicated to Prof. Dr Alois Haas on the occasion of his 65th birthday.

[2] Member of the Carrera del Investigador Científico del Consejo de Investigaciones Científicas y Técnicas, República Argentina (CONICET), and Dpto. de Cs. Básicas, UNLu, rutas 5 y 7, Luján, Argentina.

[3] Current address: Institut für Physikalische und Theoretische Chemie, Tübingen University, Auf der Morgenstelle 8, (72076) Tübingen, Germany, with DAAD and CONICET Scholarship.

[4] Member of the Carrera del Investigador Científico del Consejo de Investigaciones Científicas y Técnicas, Argentina (CONICET).

PII S0022-2860(96)09639-1

of λ > 270 nm, ketene ($H_2C{=}C{=}O$) and HCl are formed [6]. The conditions of the irradiation may lead to different results in this case.

We have selected $CF_3C(O)SH$ and $CF_3C(O)SCl$ for the present work in order to evaluate whether the irradiation conditions are the only variables to take into account in anticipating the photolysis products of matrix-isolated irradiated substances. The influence of the stability of the formed products will be analysed.

2. Experimental

1. $CF_3C(O)SH$ was prepared by reaction of $CF_3C(O)Cl$ with H_2S. The product of the reaction was purified by trap to trap distillations. The purity was checked by comparison with reported data from the literature [7].
2. $CF_3C(O)SCl$ was prepared by the reaction between $CF_3C(O)SH$ and Cl_2. The presence of the -SH groups allows one to prepare sulphenyl halides that contain a highly reactive trifluoroacetyl group. Purification of $CF_3C(O)SCl$ was performed by trap to trap distillations and the IR data were compared with those reported [7].

The matrix infrared spectra of $CF_3C(O)SH$ were measured with a IFS 66v (resolution 1 cm^{-1}) FTIR spectrometer (Bruker) operating in reflection mode in the range 4000–400 cm^{-1}. They were obtained by running an Ar flow through the cooled sample at – 111°C, and were deposited onto a matrix support (a highly reflecting aluminium-covered, nickel-plated copper block) cooled with the aid of a liquid helium continuous flow cryostat.

Low-temperture spectra of $CF_3C(O)SCl$ in Ar (1:1000) were obtained in a cryogenic system and the continuous deposition technique was employed. The mixture was deposited for 2 h at a rate of 1 mmol h^{-1} 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. Results and discussion

In the photolysis of $CF_3C(O)SH$ in Ar matrices with UV radiation the intensity of infrared absorptions due to this compound decrease and new bands appear clearly in the region 2500–400 cm^{-1}. Fig. 1 shows a record resulting from the subtraction of the IR

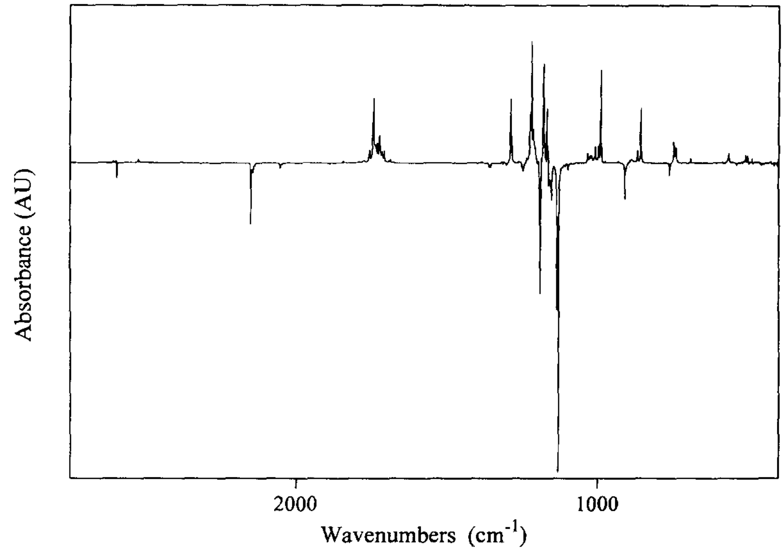

Fig. 1. Substraction IR spectra of $CF_3C(O)SH$ after 5 min UV irradiation and of $CF_3C(O)SH$ without irradiation. The photolysis products (bottom) and the original spectrum (top) are thus clearly discriminated.

Table 1
Fundamental vibrations (cm^{-1}) for $CF_3C(O)SH$ and CF_3SH

$CF_3C(O)SH$		CF_3SH		
Matrix IR	Ref. [1] (gas)		Matrix IR	Ref. [8] (gas)
1743	1758	$\nu_1(a')$	2594	2612
1289	1285	$\nu_2(a')$	1189	1190[a]
1219	1215	$\nu_9(a'')$	1152	1154[a]
1180	1189	$\nu_3(a')$	1134	1130[a]
1033	1040	$\nu_4(a')$	909	903
989	992	$\nu_5(a')$	762	762
857	858	$\nu_6\ (a')\nu_{10}(a'')$		539
741	745	$\nu_7(a')$		457
692		$\nu_8(a')\nu_{11}(a'')$		305
566		$\nu_{12}(a'')$		175
510				
503				
488				

[a] From matrix spectra [8].

spectrum after the UV radiation from the original IR spectrum of $CF_3C(O)SH$.

The new bands located at 2594, 2150, 1189, 1152, 1129, 909 and 762 cm^{-1} are identified as CO stretching of the CO molecule (2150 cm^{-1}) and fundamental vibrations of the CF_3SH molecule (see Table 1).

The proposed mechanism is

$$CF_3C(O)SH \rightarrow \left\{ \begin{array}{l} {}^{\bullet}CF_3 + {}^{\bullet}C(O)SH \\ {}^{\bullet}CF_3C(O) + {}^{\bullet}SH \end{array} \right. \rightarrow CF_3SH + CO\,.$$

In the photolysis of $CF_3C(O)SCl$ in Ar matrices with

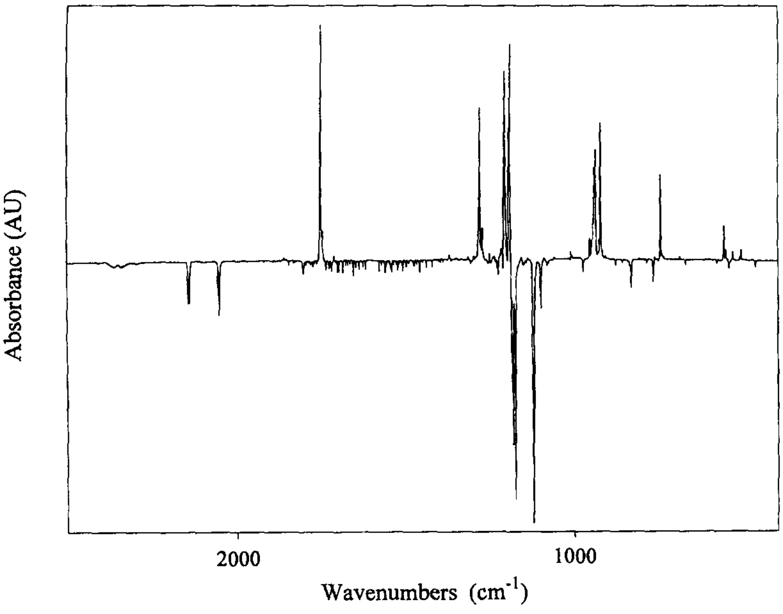

Fig. 2. Substraction IR spectra of $CF_3C(O)SCl$ after 5 min UV irradiation and of $CF_3C(O)SCl$ without irradiation. The photolysis products (bottom) and the original spectrum (top) are thus clearly discriminated.

Table 2
Fundamental vibrations (cm^{-1}) for $CF_3C(O)SCl$, CF_3SCl and CF_3Cl

$CF_3C(O)SCl$		CF_3SCl			CF_3Cl		
Matrix IR	Ref. [1] (gas)		Matrix IR	Ref. [9]		Matrix IR	Ref. [5]
1749	1761	$\nu_1(a')$	1177	1183	$\nu_4(e)$	1209	1207
1278	1279	$\nu_9(a'')$	1172	1175	$\nu_1(a_1)$	1097	1098
1189	1199	$\nu_2(a')$	1121	1120	$\nu_2(a_1)$	782	781
935	933	$\nu_3(a')$	764	762.5	$\nu_5(e)$		562
741	740	$\nu_4(a')$	575	575	$\nu_3(a_1)$		
		$\nu_5(a')$	541	541	$\nu_6(e)$		
		$\nu_6(a')$	462	462			

UV radiation, all infrared absorptions corresponding to this compound disappear and nine new bands appear in the region 2500–400 cm^{-1}.

In Fig. 2 we show the result of the substraction of the IR spectrum after the UV radiation from the original IR spectrum of $CF_3C(O)SCl$.

Bands at 2140, 2051, 1177, 1172, 1209, 1121, 1097, 855, 782, 764, 575, 541 and 462 cm^{-1} are observed.

The band at 2140 is due to the CO stretching of the CO molecule and the bands at 2051 and 855 cm^{-1} are assigned to the CO and SC stretching of the SCO molecule. The remaining bands are assigned to fundamental vibrations belonging to CF_3SCl and CF_3Cl (see Table 2). The formation mechanisms of CF_3SCl and CF_3Cl can be interpreted as follows:

$$CF_3C(O)SCl \rightarrow \begin{cases} {}^{\bullet}CF_3 + {}^{\bullet}C(O)SCl \\ {}^{\bullet}CF_3C(O) + {}^{\bullet}SCl \end{cases} \rightarrow CF_3SCl + CO\,,$$

$$CF_3C(O)SCl \rightarrow \begin{cases} {}^{\bullet}CF_3 + {}^{\bullet}C(O)SCl \\ {}^{\bullet}CF_3C(O)S + {}^{\bullet}Cl \end{cases} \rightarrow CF_3Cl + SCO\,.$$

The decomposition of $CF_3C(O)SH$ and $CF_3C(O)SCl$ is assumed to evolve in radical processes such as those indicated above.

$CF_3C(O)SCl$ shows two decomposition steps, the products being CF_3SCl and CF_3Cl. However, $CF_3C(O)SH$ decomposes producing only CF_3SH. The difference may be due to the photolysis products' stability. CF_3Cl is more stable than CF_3H, and for that reason the photolysis of $CF_3C(O)SH$ evolves in one step, the production of CF_3SH and CO.

The photolysis of $CF_3C(O)SH$ and $CF_3C(O)SCl$ shows similar behaviour to that of FC(O)SCl [2], FC(O)SBr [3] and $CF_3C(O)H$ [4] with the appearance of the CO molecule. The possibility of the formation of stable products, such as CO in some cases and HCl [6] in others, should be related to this phenomenon. In a similar way, SCF_2 and SCClF result from the irradiation of CF_2ClSCl and $CFCl_2SCl$ ($\lambda < 300$ nm), respectively, and Cl_2 is formed in both cases [10].

Acknowledgements

CODV thanks Alois Haas for his helpful advice and for work facilities. SEU thanks Helge Willner for work facilities. The authors thank the Fundación Antorchas and DAAD (Deutscher Akademischer Austauschdienst, Germany) for financial support and for the DAAD–Antorchas Award to the German–Argentine cooperation. They also thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), República Argentina, for financial support. They are indebted to LANAIS-EFO (CONICET) for the spectroscopic measurements and to the Facultad de Ciencias Exactas, Universidad Nacional de La Plata, República Argentina, for financial support. They thank the Fundación Antorchas for a National Award to the Argentine cooperation.

References

[1] C.O. Della Védova, Dissertation, Ruhr-University of Bochum, 1990.
[2] H. Willner, Z. Anorg. Allg. Chemie, 481 (1981) 117.
[3] C.O. Della Védova and H.-G. Mack, Inorg. Chem., 32 (1993) 948.

[4] C.O. Della Védova and O. Sala, J. Raman Spectrosc., 22 (1991) 505.

[5] C.O. Della Védova and R.E. Rubio, J. Mol. Struct., 321 (1994) 279.

[6] N. Kogure, T. Ono, E. Suzuki and F. Watari, J. Mol. Struct., 296 (1993) 1.

[7] W.V. Rochat and G.L. Gard, J. Org. Chem., 34 (1969) 4173.

[8] J. Borrajo, E.L. Varetti and P.J. Aymonino, J. Mol. Struct., 29 (1975) 163.

[9] D. Bielefeldt and H. Willner, Spectrochim. Acta, 36A (1980) 989.

[10] C.O. Della Védova, S.E. Ulic, H-G. Mack and E.H. Cutín, J. Mol. Struct., 301 (1993) 65.