Inorg. Chem. **1993**, *32*, 948–950

A Matrix Photochemistry Study on FC(O)SBr: The Precursor of SBrF[‡]

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Received June 22, 1992

The compound SBrF was obtained by UV photolysis of FC(O)SBr in a rare gas matrix. The formation of the radicals •FCO and •SBr during that process is proposed. Shorter irradiation times produce a randomization of the conformers of FC(O)SBr in the matrix. Ab initio methods at the Hartree–Fock level of sophistication predict the following geometric parameters for SBrF: S–F = 1.608 Å, S–Br = 2.151 Å, Br–S–F = 101° (HF/3-21G*); S–F = 1.577 Å, S–Br = 2.156 Å, Br–S–F = 101.1° (HF/3-21G* + d(F); additional polarization functions on F, α_d = 0.8). The calculated dipole moments are 1.30 and 0.73 D, respectively. For the sake of comparison, ab initio calculations were also performed for the parent molecule SClF.

Introduction

Some useful criteria to identify conformers through the vibrational spectra are provided by band contour analysis (if the molecule is relatively small) and by polarization measurements in the Raman spectrum of the liquid (if the conformers possess different symmetries). The correctness of the assignment can be verified by the application of the sum and product rules to the conformers. More elegant is the determination of the temperature dependence of the relative integrated absorbances and intensities of selected infrared and Raman bands for each conformer. Thus, the enthalpy differences between stable conformers and the barrier height, in case complementary data are available (for example the torsional frequencies of each conformer), can be determined. The most elegant method for evaluating conformational compositions is, perhaps, through the photolytic interconversion of conformers in an inert-gas matrix. The disadvantages 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. This is intriguing, since the very small molecules are always the targets of the chemist. In particular, attempts to prepare compounds containing sulfur have a long history. Davy, in 1813, reacted HgF_2 with fused S_8, obtaining several sulfur fluorides. These compounds are thermodynamically unstable. They disproportionate into S_8 and SF_6. Only SF_4 and S_2F_{10} are kinetically stable.[1] Simple fluorinated derivatives of sulfur are SF_2, FSSF, SSF_2, S_xF_2, SF_4, SF_6, S_2F_{10},[1] and SClF[2] as well as the radicals SF, SF_3, and SF_5.[1] Known brominated compounds of sulfur are SBr_2, S_2Br_2, S_2BrCl, and S_xBr_2. SBr_4 and SBr_6 have not been isolated. SF_5Br, however, can be synthesized and is, as yet, the the only molecule in which sulfur merely is bonded to fluorine and bromine.

In this context, the isolation of SBrF, which recently was mentioned by us in the literature,[3] and the study of the photochemical behavior of FC(O)SBr in rare gas and CO matrices are of high interest. The aim of this work is the discussion of these results together with the proposition of the molecular parameters for this novel molecule using theoretical calculations.

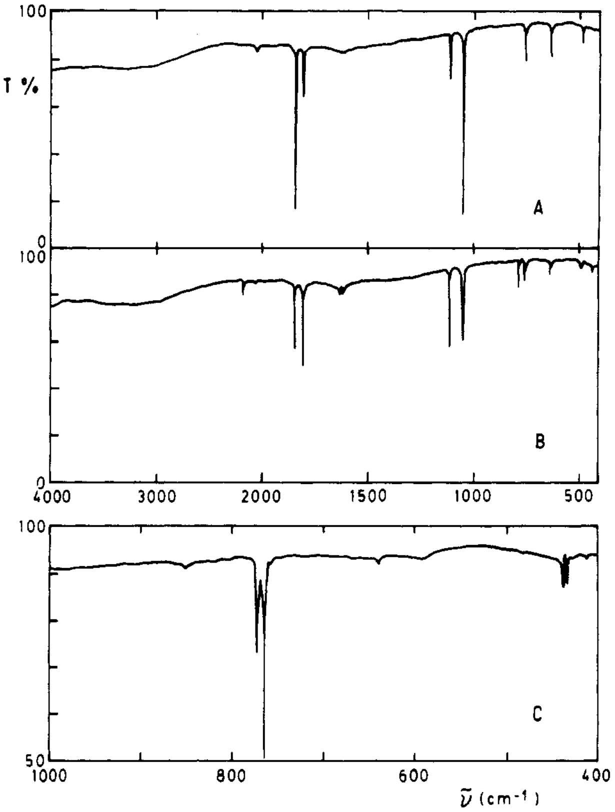

Figure 1. IR spectra of FC(O)SBr in an Ar matrix (Ar:FC(O)SBr ratio = 1500; 2.6 mmol matrix) (A) without UV irradiation, (B) after 5 min of UV irradiation, and (C) after 15 min of UV irradiation. Clearly SBrF is formed under these conditions.

Experimental Section

(Fluorocarbonyl)sulfenyl bromide, FC(O)SBr, was prepared by reaction of FC(O)SCl and $(CH_3)_3SiBr$ at −10 °C and subsequently purified by trap to trap distillation.[3]

Infrared spectra between 4000 and 200 cm^{-1} were recorded with a FT Bruker IFS 66 spectrometer (resolution of 1 cm^{-1}). Low-temperature

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[‡] Dedicated to Professor P. J. Aymonino on the occasion of his 65th birthday, July 20, 1993.

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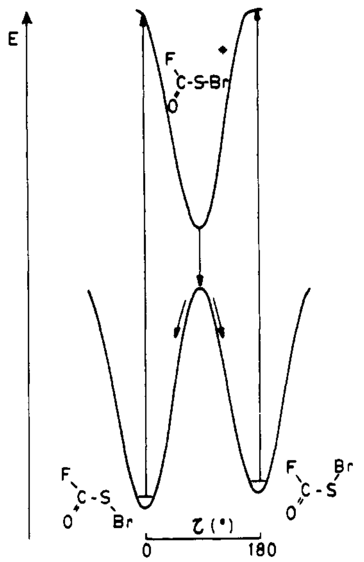

Figure 2. Energy profile describing the randomization of the conformers of FC(O)SBr during UV irradiation.

Table I. Force Constants of SBrF and Related Molecules and Radicals in mdyn Å^{-1}

	f_{SF}	f_{SBr}	ref
SF_2	4.72		7
ClSF	4.30		2
$SF^{\bullet}$	4.50		8
CF_3SBr		2.14	6
S_2Br_2		1.75	9
SBrF	4.11	2.53	this work

matrix spectra in Ar and CO were obtained in a cryogenic system described previously.[4] The continuous deposition technique was employed.

Results and Discussion

Photoisomerization of FC(O)SBr. (Fluorocarbonyl)sulfenyl bromide, FC(O)SBr, is a very interesting molecule. It shows conformational equilibrium at two planar and stable forms. The most stable conformer possesses a syn structure with respect of the position of the C=O double bond relative to the S–Br single bond.[5] These two rotamers are unequivocally observed when FC(O)SBr, isolated in an Ar matrix at low temperature, is irradiated with UV light. Figure 1 depicts this behavior. Two bands are found in the carbonyl and in the C–F stretching regions at approximately 1850 and 1050 cm^{-1}, respectively. If the matrix is irradiated for 5 min with UV light of $\lambda < 300$ nm, a drastic change occurs in these spectral regions due to photolytic interconversion of the two conformers (see Figure 1B). Longer irradiation leads to formation of SBrF and CO (see Figure 1C), but the intensity ratios of the two C=O and the two C–F bands remain constant during this decomposition. This behavior can be rationalized on the basis of Figure 2. In order to produce a randomization of the two forms of FC(O)SBr in the matrix, the minimum in the potential curve of the excited molecule and the maximum in the ground state should correspond to the same torsional angle τ. After UV excitation, the molecule falls into a common minimum of the excited state. The transition to the ground state allows the molecule to reach—with roughly equal probabilities—the potential minima of the two planar conformers. Assuming that equal amounts of syn and anti rotamers are formed, a ratio of the absorption coefficients syn:anti of 0.61 is obtained from spectrum 1b. If this ratio is applied to spectrum 1a, a composition of the mixture of 91% syn and 9% trans forms is derived. This corresponds to a difference in free energy $\Delta G = G_{anti} - G_{syn} = 1.4$ kcal/mol.

Formation of SBrF. Longer irradiation of FC(O)SBr in an Ar matrix leads to formation of SBrF and CO. The bands corresponding to FC(O)SBr disappear in the IR spectrum, and new bands appear at 2150, 765, 434, and 432 cm^{-1}. The first band unambiguously can be assigned to the stretching vibration of the CO molecule. The band at 765 cm^{-1} is assigned to the S–F stretching mode of SBrF, in comparison with relevant data reported in the literature (ν_{SF}(SClF) = 780 cm^{-1} [2]). The bands at 434 and 432 cm^{-1} can be assigned to the ^{79}Br–S and ^{81}Br–S stretching vibrations, respectively, in comparison with the corresponding vibration in CF_3SBr (455 cm^{-1} [6]). The remaining mode, the BrSF deformation, was not observed in the IR spectrum. This vibration could possibly occur below 200 cm^{-1}. Using the two atom approximation, force constants of 4.11 and 2.53 mdyn Å^{-1} can be calculated for the SF and SBr bonds. With this approximation a value of f_{SF} = 4.27 mdyn Å^{-1} was obtained for SClF, in very good agreement with the value derived from a general valence force field (f_{SF} = 4.30 Å^{-1} [2]). Table I compares the stretching force constants of SBrF, as determined in this study, to those reported for related molecules.

The formation of SBrF through the photolysis of FC(O)SBr in an Ar matrix possibly occurs involving several steps, because during irradiation of FC(O)SBr in the gas phase no SBrF was observed, and in a CO matrix C(O)BrF and COS are obtained. The photolytic steps can be interpreted as follows:

$$\begin{array}{l} syn\text{-FC(O)SBr (91\%)} \\ anti\text{-FC(O)SBr (9\%)} \end{array} \xrightarrow{h\nu} \begin{array}{l} syn\text{-FC(O)SBr (50\%)} \\ anti\text{-FC(O)SBr (50\%)} \end{array} \xrightarrow{h\nu}$$

$$^{\bullet}\text{FCO} + {}^{\bullet}\text{SBr} \begin{array}{l} \text{Ar matrix} \rightarrow \text{SBrF} + \text{CO} \\ \text{CO matrix} \rightarrow \text{C(O)BrF} + \text{COS} \end{array}$$

These results are in agreement with results reported for the photoisomerization of FC(O)SCl[10] and subsequent formation of SClF.[2]

Table II. Molecular Parameters (Å and deg), Energies (hartree), and Dipole Moments (D) for SClF and SBrF Using HF/3-21G* and HF/3-21G* + d(F) Basis Sets

	HF/3-21G*		HF/3-21G* + d(F)	
	SClF	SBrF	SClF	SBrF
S–F	1.604	1.608	1.573	1.577
S–X	2.002	2.151	2.008	2.156
FXS	100.2	101.0	100.3	101.1
E	–951.924 840 1	–3054.803 323 2	–951.967 441 5	–3054.845 451 3
μ	1.384	1.294	1.106	0.773

Table III. Molecular Parameters (Å and deg), Energies (hartree), and Dipole Moments (D) for SClF Using the Following Basis Sets and Levels of Theory: HF/6-31G*, HF/D95*, MP2/6-31G*, MP2/D95*, and ClSD/6-31G*

	HF/6-31G*	HF/D95*	MP2/6-31G*	MP2/D95*	ClSD/6-31G*
S–F	1.589	1.601	1.633	1.651	1.620
S–Cl	2.005	2.017	2.018	2.023	2.014
ClSF	99.8	99.8	100.7	100.4	99.9
E	–956.371 568 9	–956.394 743 9	–956.817 973 1	–956.989 140 5	–956.790 929 4
μ			1.396	1.557	

Ab Initio Calculations. The calculations were performed with the programs GAMESS[11] and GAUSSIAN 86[12] on a Convex C220 computer (ZDV, University of Tübingen, FRG). The geometry of SBrF was optimized at the HF/3-21G* and at the HF/3-21G* + d(F) (additional polarization functions on F) levels of theory using standard gradient techniques.[13] For the sake of comparison, structure optimizations for SClF were carried out by applying different basis sets (3-21G*, 6-31G*, D95*) and various theoretical approximations (HF, MP2, CISD). The results are summarized in Tables II and III. The theoretical results obtained for SBrF are quite reasonable compared not only to SClF but also to the experimental data for SF_2, SCl_2, and SBr_2. In Table IV geometrical parameters for SX_2 (X = F, Cl, Br), SClF, and SBrF are listed.

Table IV. Geometrical Parameters (Å and deg) for SX_2 Molecules (with X = Halogen), for SClF and SBrF

	S–F	S–Cl	S–Br	XSY	ref
SF_2 (MW)	1.587 45(12)			98.048(13)	14
SCl_2 (MW)		2.014(5)		102.8 (2)	15
SBr_2 (est[a])			2.16	100	1
SClF (HF/3-21G*)	1.604	2.002		100.2	this work
SBrF (HF/3-21G*)	1.608		2.151	101.0	this work

[a] Estimated from the corresponding molecular parameters of SCl_2, S_2Cl_2, and $S_2Br_2 \cdot \nu_i$ = 180, 415, and 435 cm^{-1} were also estimated for SBr_2 to calculate the corresponding thermodynamical functions. MW = microwave studies.

Acknowledgment. C.O.D.V. thanks Prof. Dr. mult. Dr. h. c. Alois Haas (University of Bochum, Bochum, FRG) for his stimulating contributions and his furtherance of this work. He also thanks CONICET (República Argentina) for the receipt of a Postdoctoral Fellowship and for permission (with stipend)—from the Faculty of Exact Sciences (National University of La Plata) and from CONICET—to work in Germany. He gratefully acknowledges the Fundación Antorchas (República Argentina) and DAAD (FRG) for financial support. H.-G.M. thanks the Deutsche Forschungsgemeinschaft (FRG) for generous financial support.

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