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Article

Photoisomerization of Matrix-Isolated Bis(trifluoromethyl) Sulfoxide: Formation of the Sulfenic Ester CF_3SOCF_3

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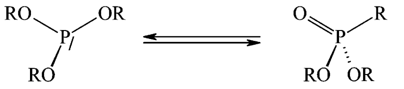
Bis(trifluoromethyl) sulfoxide, $CF_3S(O)CF_3$, isolated in noble gas matrixes at low temperatures, isomerizes upon UV irradiation into the sulfenic ester CF_3SOCF_3. The new species is characterized spectroscopically, and the vibrational assignment is supported by ^{18}O isotopic labeling experiments and by DFT calculations. The calculated structural parameters of CF_3SOCF_3 are compared with the calculated and experimental data of the related compounds CF_3SSCF_3 and CF_3OOCF_3. In addition, the computed enthalpy differences between the sulfoxide $R_2S{=}O$ and sulfenate RSOR structures for R = H, F, CH_3, and CF_3 are included.

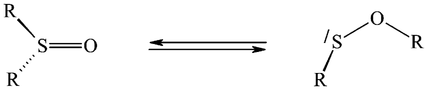
Introduction

An interesting feature of non-metal oxo derivatives is their ability for connectivity isomerization accompanied by a change in the coordination number of the central atom, e.g.:



(1)

A similar connectivity isomerization is observed between sulfoxides, $R_2S{=}O$, and sulfenic esters, RSOR:



(2)

If the R groups differ, chirality is possible, and racemization of chiral organic sulfoxides under acid[1] and thermolytic[2-4] condition has been well studied. The difference in stability between the sulfoxide and sulfenic ester structures depends strongly on the nature of the substituent R. If R is an organic substituent, the sulfoxide structure is more stable. However, many sulfenic esters with bulky substituents have been prepared because they are kinetically stable.[3] Upon heating, the sulfenic esters rearrange to the corresponding sulfoxides.[3]

An opposite behavior is observed for the very few known perfluoroalkyl sulfoxides,[5] e.g. $(iso\text{-}C_3F_7)_2S{=}O$ rearranges upon heating to $iso\text{-}C_3F_7S{-}O{-}iso\text{-}C_3F_7$.[6] For the parent species, the HSOH isomer is more stable than $H_2S{=}O$. Sulfenic acid—also called oxadisulfane—was first detected in a reaction of oxygen atoms with H_2S molecules in a matrix.[7] Recently its rotational spectrum was observed following the low pressure thermolysis of di-*tert*-butyl sulfoxide.[8]

Rearrangement and depletion of organic sulfoxides by photolysis in different solvents are well investigated,[9] but to our knowledge respective matrix isolation studies are missing. Motivated by the clean photoisomerization of matrix-isolated $CF_3S(O)F$ into CF_3OSF,[10] we have now studied the photoisomerization of $(CF_3)_2S{=}O$, the most simple perfluoroalkyl sulfoxide, into CF_3SOCF_3 under matrix

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isolation conditions. The results, presented here, are supported and extended by quantum chemical calculations.

Experimental Section

Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (221 AHS-1000 and 221 AHS-10, MKS Baratron, Burlington, MA), three U-traps, and valves with PTFE stems (Young, London, U.K.). The vacuum line was connected to an IR cell (optical path length 200 mm, Si windows) contained in the sample compartment of the FTIR instrument (Impact 400D, Nicolet, Madison, WI). This allowed us to observe the purification processes and to follow the course of reactions. The samples were stored in flame-sealed glass ampules under liquid nitrogen in a long-term Dewar vessel. The ampules could be opened by the use of an ampule key[11] and resealed.

Synthesis of $CF_3S(O)CF_3$. $CF_3S(O)CF_3$ was prepared according to the literature procedure.[12] $CF_3S(^{18}O)CF_3$ was obtained by the reaction of $CF_3SF_2CF_3$, HCl, and $H_2{}^{18}O$ in a PTFE vessel at room temperature within 48 h. Both compounds were isolated by repeated fractional condensation in vacuo through a series of traps held at −65, −100, and −196 °C. The trap at −100 °C retained pure $CF_3S(O)CF_3$ and $CF_3S(^{18}O)CF_3$, respectively.

Preparation of Matrixes. A small sample of $CF_3S(O)CF_3$ was transferred into a 1 L container of the stainless steel vacuum line and diluted 1:1000 with Ar or Ne. The vacuum line was connected to the spray-on nozzle of the matrix support by a stainless steel capillary. About 0.5−1 mmol of the gas mixture was deposited within 10−20 min on the rhodium-plated copper block with two mirror planes as matrix support held at 16 or 6 K (for Ar or Ne). For the photolysis experiments radiation from a 150 W mercury high-pressure lamp (TQ150, Haereus, Hanau, Germany) with and without a $\lambda < 235$ nm cutoff filter (Schott, Mainz, Germany) was used over a period of 10−60 min. The photolysis process was observed by IR spectroscopy. Details of the matrix apparatus are given elsewhere.[13]

Instrumentation. Vibrational Spectroscopy. Gas-phase infrared spectra were recorded with a resolution of 2 cm^{-1} in the range of 4000−400 cm^{-1} in absorbance mode on the FTIR instrument Bruker IFS 66v (Bruker, Ettlingen, Germany).

Matrix IR spectra were recorded on a IFS 66v/S spectrometer with a resolution of 1 cm^{-1}, in absorption/reflection mode as described in ref 13.

UV Spectroscopy. UV matrix spectra were recorded in the region 200−360 nm with a Lambda 900 spectrometer (Perkin-Elmer, Norwalk, CT) equipped with a deuterium lamp and two quartz fibers of 2 m length with special condensor optics (Hellma, Jena, Germany).

Quantum Chemical Calculations. The calculations were performed using the Gaussian98 software package.[14] Both optimized geometries and frequency analysis used the B3LYP[15−17] density functional method with standard grid and convergence criteria. The presence of a sulfur atom requires larger basis sets. Significant changes result when the level of theory was increased from 3 to 21 G via 6-311G(d,p) to 6-311++(3df,3pd). Only when using the largest basis set did the calculated vibrational frequencies match the experimental values well. With an increasing level of theory the energy difference between $CF_3S(O)CF_3$ and CF_3SOCF_3 decreases—the latter being more stable in all cases.

An MP2[18,19] calculation result in an analytically solved force field suitable as starting point for the force field and PED calculation program ASYM40.[20]

Results and Discussion

The structure of $CF_3S(O)CF_3$ was determined in the gas phase by electron diffraction.[21] C_s symmetry was assumed in light of the analysis of the Raman spectrum.[22] Because the infrared spectra were not completely assigned, IR matrix and gas-phase spectra of the natural and ^{18}O isotopic substituted species are included in this study. However, our main interest is focused on the photoisomerization of matrix-isolated $CF_3S(O)CF_3$.

UV-Photolysis of Matrix-Isolated $CF_3S(O)CF_3$ and $CF_3S(^{18}O)CF_3$. The infrared band positions and relative intensities obtained from gaseous and matrix isolated $CF_3S(O)CF_3$ are listed in Table 1. After 15 min of photolysis with unfiltered light from a high-pressure mercury lamp, about 60% of $CF_3S(O)CF_3$ isolated in an Ar matrix was decomposed. A new set of bands appeared, and the peak position and intensities of the new absorptions are listed in Table 2. A difference spectrum before and after photolysis of $CF_3S(O)CF_3$ is shown in Figure 1; the new bands, assigned to CF_3SOCF_3, point upward while the decreasing absorptions of $CF_3S(O)CF_3$ are represented by negative bands. After 25 min of photolysis two additional sets of bands appeared that had grown simultaneously and were less abundant when a $\lambda < 235$ nm cutoff filter was used during the photolysis experiment. According to literature data, the first additional set of wavenumbers (1936, 1907, 1243, 968, 765, 622 cm^{-1}) is due to CF_2O,[23] while the second set (1192, 1174, 800 cm^{-1}) is due to CF_3SF.[24] Not all CF_3SF absorptions were observed as some bands overlap with the IR absorptions of the new species. Both molecules arise from secondary photolysis of the primary photoproduct. The formation of

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Table 1. Experimental and Calculated Vibrational Wavenumbers and Isotopic Shifts ($\Delta\nu$) of CF$_3$S(O)cf$_3$ and CF$_3$S(^{18}O)CF$_3$

CF$_3$S(O)CF$_3$									CF$_3$S(^{18}O)CF$_3$			
gas phase		Ar matrix		Ne matrix:	calcd ^{b}				gas phase:	Ar matrix		calcd:^{b}
ν (cm^{-1})	σ^c	ν (cm^{-1})	int^d	ν (cm^{-1})	ν (cm^{-1})	int^b	assgmt and approx descriptn^a		ν (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
1243	743	1245.4	100	1250.0	1236.4	450	ν_1 (ν_1)	ν_{as}(CF$_3$ ip)	1243	1244.6	0.8	1.5
		1230.8	76	1234.3	1213.8	391	ν_2 (ν_2)	ν_{as}(CF$_3$ ip)/δ_s(C$_2$SO)		1230.8	0.0	2.6
					1188.7	0.52	ν_3 (ν_{14})	ν_{as}(CF$_3$ op)				0.1
		1188.0	3.1	1191.3	1187.1	20	ν_4 (ν_3)	ν_s(CF$_3$ ip)/ν(S═O)		1174.5	13.5	19.9
1183	386	1179.1	48	1182.2	1160.9	229	ν_5 (ν_{15})	ν_{as}(CF$_3$ op)	1183	1178.9	0.2	0.1
		1121.1	4.1	1125.6			$\nu_8 + \nu_{16}$ ($\nu_5 + \nu_9$)					
1121	271	1114.4	34	1119.8	1110.0	131	ν_6 (ν_4)	ν(S═O)/ν_s(CF$_3$ ip)	1100	1086.3	28.1	19.2
1100	606	1095.7	66	1100.2	1076.4	381	ν_7 (ν_{16})	ν_s(CF$_3$ op)		1095.7	0.0	0.0
755	27	755.0	3.2	756.3	747.3	2.6	ν_8 (ν_5)	ν_s(SC$_2$)/δ_s(CF$_3$ ip)	755	756.6	e	0.1
					746.5	18	ν_9 (ν_{17})	ν_{as}(SC$_2$)/δ_s(CF$_3$ op)		754.7	e	0.1
590	21	590.6	4.5	590.8	584.6	14	ν_{10} (ν_6)	δ_{as}(CF$_3$ ip)/δ_s(C$_2$SO)	589	588.7	1.9	2.0
556	11	559.6	1.2	559.8	552.6	4.8	ν_{11} (ν_{18})	δ_{as}(CF$_3$ op)/δ_a(C$_2$SO)	554	557.7	1.9	0.8
					549.6	0.73	ν_{12} (ν_7)	δ_{as}(CF$_3$ ip)/δ_s(C$_2$SO)				0.6
530	3	528.8	0.2	528.5	522.3	0.63	ν_{13} (ν_{19})	δ_{as}(CF$_3$ op)/δ_a(C$_2$SO)	530	528.8	0.0	0.0
466	86	469.4	9.9	469.6	464.9	22	ν_{14} (ν_8)	δ_{as}(CF$_3$ ip)/δ_s(C$_2$SO)	465	467.9	1.5	1.5
		466.2		467.4	456.6	23	ν_{15} (ν_{20})	ν_a(SC$_2$)/δ_{as}(CF$_3$ op)/δ_a(C$_2$SO)		464.6	1.6	1.6
		(366)^f			365.0	5.2	ν_{16} (ν_9)	ω(CF$_3$ ip)/δ_s(C$_2$SO)				4.0
					273.3	0.14	ν_{17} (ν_{21})	ω(CF$_3$ op)/δ_a(C$_2$SO)				3.0
					262.0	1.0	ν_{18} (ν_{10})	ν_s(SC$_2$)/ρ(CF$_3$ ip)				0.2
					228.4	0.74	ν_{19} (ν_{22})	ν_{as}(SC$_2$)/ρ(CF$_3$ op)				0.7
					192.3	4.8	ν_{20} (ν_{11})	ω(CF$_3$ ip)/δ_s(C$_2$SO)				3.6
					178.9	3.9	ν_{21} (ν_{23})	ω(CF$_3$ op)/δ_a(C$_2$SO)				4.9
					132.2	0.48	ν_{22} (ν_{12})	δ(CSC)				0.4
					71.7	0.49	ν_{23} (ν_{13})	τ(FCSO ip)				0.9
					16.3	0.02	ν_{24} (ν_{24})	τ(FCSO op)				0.1

[a] ν: stretching. δ, ρ, ω: deformation. τ: torsion. s: symmetric. a: antisymmetric. as: asymmetric. ip: in phase. op: off phase. Numbering according to C_1 symmetry (C_s symmetry in parentheses). [b] B3LYP/6-311++G(3df,3pd), intensities in km·mol^{-1}. [c] σ at band maximum in 10^{-20} cm^2. [d] Relative integrated intensities. [e] Overlap in the spectrum of the natural compound; no shifts are given. [f] Estimated from combination mode.

Table 2. Experimental and Calculated Vibrational Wavenumbers and Isotopic Shifts ($\Delta\nu$) of CF$_3$SOCF$_3$ and CF$_3$S^{18}OCF$_3$

CF$_3$SOCF$_3$						CF$_3$S^{18}OCF$_3$		
Ar matrix		Ne matrix:	calcd^b			Ar matrix		calcd:^{b}
ν (cm^{-1})	I^c	ν (cm^{-1})	ν (cm^{-1})	I^b	assgmt^a	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
1273.3	89	1277.5	1245.5	349	ν_{as}(C$'$F$_3$)	1272.1	1.2	0.9
1227.1	88	1232.4	1205.2	587	ν_{as}(C$'$F$_3$)/ν_{as}(CF$_3$ ip)	1227.1	0.0	1.3
1203.2	62	1208.8	1179.6	259	ν_{as}(C$'$F$_3$)/ν (C$'$O)/ν_{as}(CF$_3$)	1200.6	2.6	3.5
1183.4	48	1187.2	1162.2	342	ν_{as} (CF$_3$)/ν_{as}(CF$_3$)/ν(C$'$O)	1182.1	1.3	0.5
1140.0	2.8	1144.9	1147.3	22	ν_s(C$'$F$_3$)/ν_{as} (CF$_3$ op)	1140.0	0.0	1.6
1117.9	100	1124.5	1097.0	545	ν_s(C$'$F$_3$)/ν_s(CF$_3$ op)	1117.3	0.6	0.8
937.5	6.6	937.2	933.3	33	θ(OC$'$F$_3$)	910.5	27.0	27.1
791.6	2.6	793.3	777.8	17	ν(S-O)/δ_s(C$'$F$_3$)	769.2	22.4	20.0
765.0	2.2	765.2	759.9	13	ν(CS)/δ_s(CF$_3$)	765.0	0.0	−0.5
666.4	0.9	666.0	659.4	1.8	δ_s(C$'$F$_3$)/δ(C$'$OS)	653.6	12.8	12.9
621.5	1.9	622.1	614.6	4.0	δ_{as}(C$'$F$_3$)	614.9	6.6	6.7
572.6	0.7	572.8	566.8	4.4	δ_{as}(CF$_3$)/δ(CSO)	571.7	0.9	0.9
547.3	1.2	548.2	539.5	5.5	δ_{as}(C$'$F$_3$)/δ_{as}(CF$_3$)	543.6	3.7	3.5
529.6	0.5	534.9	533.2	1.7	δ_{as}(CF$_3$)	529.6	0.0	0.5
476.7	2.3	478.1	468.9	7.9	ν(CS)/δ(CSO)	464.4	2.3	2.4
439.7	0.8		430.5	3.9	ν(CS)/ω(C$'$F$_3$)	434.4	5.3	4.8
417.9	2.9		412.5	7.3	ω(C$'$F$_3$)/ω(CF$_3$)	416.0	1.9	1.5
			324.0	0.36	ω(CF$_3$)/δ(C$'$OS)			0.0
			294.4	0.17	ρ(C$'$F$_3$)/ρ(CF$_3$)			0.7
			189.8	0.91	δ(SOC$'$)			1.1
			154.3	1.6	δ(CSO)			2.4
			77.4	0.05	τ(CSOC$'$)			0.4
			51.9	0.16	τ(FCOS ip)			0.2
			28.8	0.03	τ(FCOS op)			0.0

[a] ν: stretching. θ breathing mode of OC$'$F$_3$ tetrahedron. δ, ρ, ω: deformation. τ: torsion. ip: in phase. op: off phase. Atom labeling: CF$_3$SOC$'$F$_3$. [b] B3LYP/6-311++G(3df,3pd). IR intensities in km·mol^{-1}.

CF$_2$O and CF$_3$SF can be explained by S−O dissociation and rearrangement of the intermediate radicals CF$_3$O and CF$_3$S in the same matrix cage. Further possible secondary products such as C$_2$F$_6$ and SO[25] could not be detected, and the photochemistry was identical in both Ar and Ne matrixes.

The new compound obtained by photolysis of CF$_3$S(O)CF$_3$ is most likely the isomer CF$_3$SOCF$_3$ for the following reasons: (i) The appearance of a weak band at 791.6 cm^{-1} indicates the presence of an S−O moiety in the molecule as its band position agrees with reported data for S−O-

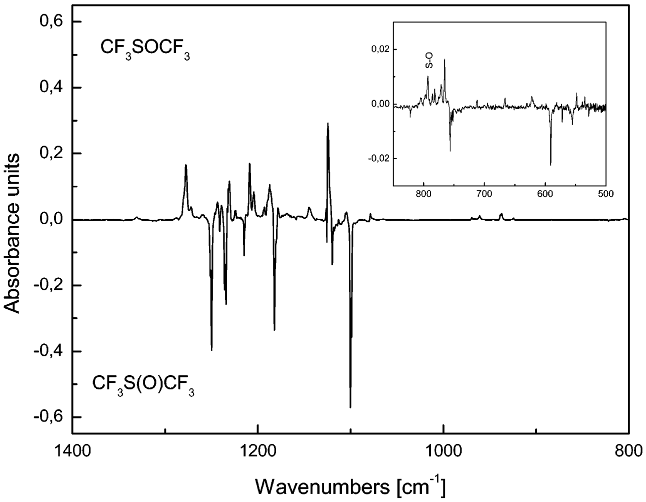

Figure 1. Difference IR spectrum before and after 30 min photolysis of $CF_3S(O)CF_3$ isolated in Ar matrix. The bands of the photoproducts point upward. The spectrum is dominated by the CF_3SOCF_3 absorptions beside minor bands of the byproducts CF_2O and CF_3SF. The disappearing absorptions of $CF_3S(O)CF_3$ are shown as negative bands.

containing compounds.[8,10,26] (ii) A small blue shift of some C−F stretching modes is in accordance with the formation of a OCF_3 unit. In $CF_3S(O)CF_3$, both CF_3 groups are connected to sulfur. (iii) A similar isomerization was reported for the $CF_3S(O)F$ molecule.[10] Upon UV irradiation chainlike CF_3OSF was formed. (iv) Band positions and observed ^{18}O isotopic shifts (after using $CF_3S(^{18}O)CF_3$) of the new compound agree with the calculated data for CF_3SOCF_3 and will be discussed below.

In conclusion, the photolysis of matrix isolated $CF_3S(O)CF_3$ occurs according to

$$CF_3S({=}O)CF_3 \rightarrow [CF_3S{-}O^{\cdot} + {}^{\cdot}CF_3] \rightarrow CF_3SOCF_3 \quad (3)$$

Whether the trifluoromethyl group migrates or intermediate radical formation and subsequent recombination in the matrix cage occurs remains an open question.

The photodecomposition of the sulfenic acid ester probably involves homolytic cleavage of the S−O single bond followed by a fluorine atom transfer:

$$CF_3SOCF_3 \rightarrow [CF_3S^{\cdot} + {}^{\cdot}OCF_3] \rightarrow CF_2O + CF_3SF \quad (4)$$

This process became more pronounced during photolysis with unfiltered UV light.

Vibrational Spectra. $CF_3S(O)CF_3$. In C_1 symmetry 24 fundamental modes are expected for the $CF_3S(O)CF_3$ molecule and all are IR active. Geometry considerations result in 9 stretching, 13 deformation, and 2 torsional modes. A coupling of vibrations within the two CF_3 units is expected leading to in-phase and off-phase modes. The observed data for the natural and ^{18}O isotopic labeled $CF_3S(O)CF_3$ are listed in Table 1 together with the calculated band positions, intensities, isotopic shifts, and approximate descriptions of the modes. The assignments in Table 1 are based on the potential energy distribution, which was derived from the calculated Cartesian force field (MP2/6-31G*) with the program ASYM40[20] and substantially reproduced by the DFT calculations. Because the molecule nearly approaches C_s symmetry in the computations, the assignment is given for both C_1 and C_s symmetries. The gas-phase IR spectrum offers only few strong bands in the CF and S=O stretching region because most fundamentals are not resolved. For isotopically labeled $CF_3S(^{18}O)CF_3$ at first sight no changes appear except that the band at 1121 cm^{-1} (^{16}O compound) vanishes. In contrast, the IR spectrum of matrix-isolated $CF_3S(O)CF_3$ allows the identification of 13 fundamentals out of 15 expected in the region down to 400 cm^{-1}. Most bonds in the molecule are of similar strengths, and all atoms, except for sulfur, have similar masses. Consequently, strong vibrational coupling occurs and the internal vibrational coordinates such as $\nu(S{=}O)$ are "distributed" within several normal modes as presented in Table 1. Nevertheless, ^{18}O isotopic labeling shifts mainly those normal modes which contain most of the $\nu(S{=}O)$ coordinate. Two bands at 1188.0 and 1114.4 cm^{-1} for the natural species isolated in Ar matrix exhibit a large isotopic shift of 13.5 and 28.1 cm^{-1}, respectively. All other bands offer small or no isotopic shift in agreement with the calculations. The "vanishing" of the gas-phase band at 1121 cm^{-1} (that corresponds to the 1114.4 cm^{-1} band for the matrix-isolated molecule) of $CF_3S(O)CF_3$ after ^{18}O isotopic labeling is explained by its shift causing an accidental overlap with the 1100 cm^{-1} band. One interesting absorption is found at 1121.1 cm^{-1} for $CF_3S(O)CF_3$ in Ar matrix. It cannot be attributed to a matrix site effect because it is also found in Ne matrix. On the basis of the calculations, no additional fundamental is expected in this spectral region. A reasonable explanation is the presence of a Fermi resonance with the 1114.4 cm^{-1} fundamental (Ar) that is much less intense in the ^{18}O species as this fundamental is strongly red-shifted. Assuming C_s symmetry, the 1114.4 cm^{-1} fundamental belongs to the A′ modes. A reasonable combination tone with A′ symmetry is given by a combination of the 755.0 cm^{-1} fundamental with a fundamental mode located below 400 cm^{-1}. Hence, this additional fundamental can be identified as the 366 cm^{-1} mode ($1121 = 755 + 366$). This is a nearly perfect match with a calculated mode at 365 cm^{-1}. In addition to the listed absorption bands, overtones and combination modes were observed at 2419, 2284, and 2217 cm^{-1} (gas phase).

CF_3SOCF_3. According to the calculations the new compound possesses C_1 symmetry. A total of 24 fundamental modes are expected to be IR active. From geometry considerations CF_3SOCF_3 possesses 6 C−F, 1 C−O, 1 C−S, and 1 S−O stretches, 5 angle deformation modes in the CF_3O unit, 5 in the CF_3S unit plus 1 deformation of the bond angles C−O−S and O−S−C, and 3 torsions. Due to comparable bond strength and masses of most of the involved atoms, strong vibrational coupling can be expected. The observed and calculated band positions, intensities, and isotopic shifts of the natural and the ^{18}O species together with an assignment of the fundamental modes are presented in Table 2. A characteristic absorption band at 791.6 cm^{-1} is assigned to

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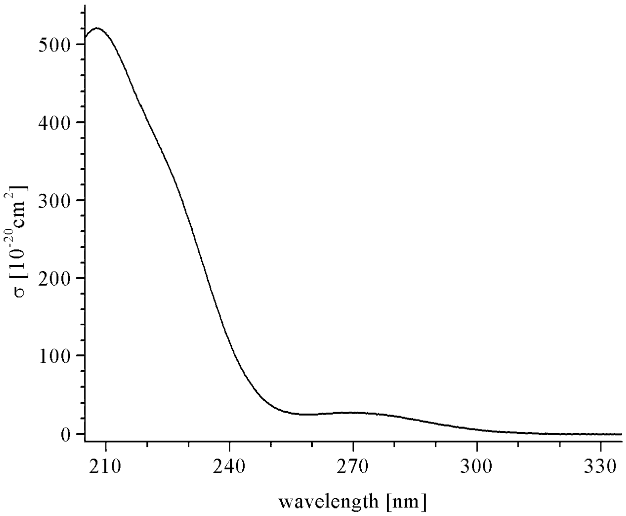

Figure 2. UV spectrum of gaseous $CF_3S(O)CF_3$.

the S−O stretching. This is in good agreement with the theoretically predicted value (778 cm^{-1}) and with known data of the related molecule $CF_3C(O)SOC(O)CF_3$ (783 cm^{-1}, gas phase).[27] In addition, the parent compound HSOH exhibits this band at 763 cm^{-1}.[28]

Compounds containing the CF_3O moiety are known to exhibit a breathing mode (here abbreviated with θ) like CF_4. This vibration as well as the S−O stretch should possess the largest $^{16}O/^{18}O$ isotopic shifts. Upon isotopic substitution of ^{16}O with ^{18}O two strong shifts of absorption bands were observed in the stretching mode frequency range and these absorptions were assigned to $\theta(OCF_3)$, shifted from 937.5 to 910.5 cm^{-1}, and ν(S−O), shifted from 791.6 to 769.2 cm^{-1}, for the matrix-isolated molecule. The observed and the predicted isotopic shifts (27.1/20.0 cm^{-1} calcd and 27.0/22.4 cm^{-1} found) demonstrate that the ^{18}O substitution has an important effect on these modes. Because several other normal modes are also affected by oxygen substitution, vibrational coupling of nearly all deformation modes appears to occur. According to the theoretical calculations and assignments, absorptions at higher wavenumbers exhibit a larger participation of the CF_3O group. The same behavior was observed for the asymmetrical bending and for the rocking modes and also for analogue modes of the related compound $CF_3C(O)SOC(O)CF_3$.[27]

UV Spectra. The UV spectrum of matrix isolated $CF_3S(O)CF_3$ exhibits 3 unstructured bands and an increasing absorption with its maximum below the detection limit of our experimental setup at <210 nm. Very similar is the gas-phase spectrum of $CF_3S(O)CF_3$ as depicted in Figure 2. It exhibits absorption with increasing intensity toward 190 nm and two intense bands at 208 and 227 nm. The last one overlaps with the first one, and it shows up as a shoulder. Moreover, a weak, broad band appears with its maximum at 270 nm.

Dimethyl sulfoxide presents a very similar UV spectrum in the gas phase.[29,30] The absorption at 188 nm was assigned to the $\pi \rightarrow \pi^*$ transition in the S═O group.[31] The band at 205 nm was considered to be due to a n → σ^* transition, and the absorption at about 220 nm was attributed to a n → π^* transition.[31−33]

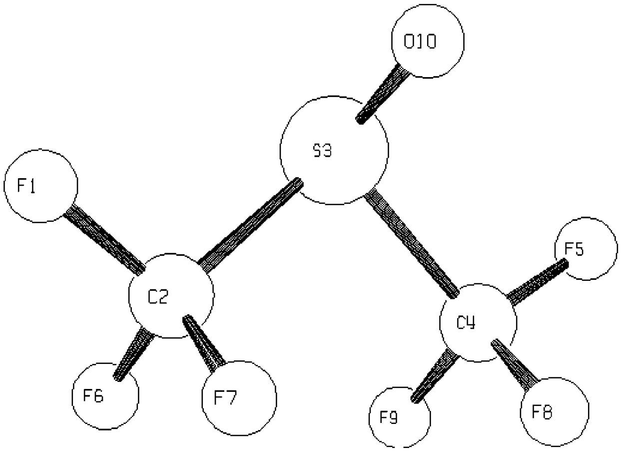

Figure 3. Optimized structure of $CF_3S(O)CF_3$ obtained from B3LYP/6-311++G(3df,3pd).

In comparison to dimethyl sulfoxide the band at 208 nm can be assigned to the n → σ^* transition originated by the S═O chromophore and the shoulder at 227 nm to the n → π^* transition. Because of its weakness the 270 nm transition is probably due to a "forbidden" singlet−triplet excitation. The matrix UV spectrum of $CF_3S(O)CF_3$ is identical with that of the gaseous compound, but there are no cross sections available for the matrix isolated species.

The UV absorptions of CF_3SOCF_3 isolated in a neon matrix are estimated to be 1 order of magnitude weaker than for $CF_3S(O)CF_3$ because in the difference spectrum before and after photolysis of $CF_3S(O)CF_3$ no new absorption could be found. Absorbance around 230 nm may be expected when compared with the following sulfenic esters: *t*-$BuSOC_2H_5$, 266 nm;[34] CCl_3SO-*t*-Bu, 277 nm;[35] $CCl_3SOC_2H_5$, 275 nm;[36] $CF_3SOC_2H_5$, 262 nm.[34]

Structures of $CF_3S(O)CF_3$ and CF_3SOCF_3. For both isomers $CF_3S(O)CF_3$- and CF_3SOCF_3-optimized geometries have been computationally predicted. The sulfur atom of $CF_3S(O)CF_3$ possess a lone pair and is bound to two CF_3 groups and to oxygen with a polar bond that is described by the mesomeric formulas $R_2S{=}O$ and $R_2S^+{-}O^-$. Consequently a pyramidal arrangement of ligands at the sulfur is predicted (and found experimentally[21]), as shown in Figure 3. As the CF_3 units rotate slightly to minimize repulsive interactions, the predicted symmetry of $CF_3S(O)CF_3$ is only C_1. But the deviations from C_s symmetry are small, and the reported experimental structure determination[21] and spec-

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Table 3. Structural Parameters and Properties of $CF_3S(O)CF_3$

param[a]	calcd[b]	expt[c]	param[a]	calcd[b]	expt[c]
R(C−F(av))	1.3285	1.328	α(CSO)	106.61	104.5
R(C−S)	1.9139	1.885	α(C′SO)	106.51	
R(C′−S)	1.9137		α(CSC′)	95.89	94.2
R(S=O)	1.4674	1.469	Σα(S)	309.01	303.2
β(FCSC′)	177.1	(180)	q(C)	+1.10	
β(CSC′F′)	−179.6	(180)	q(C′)	+1.09	
β(FCSO)	67.9		q(S)	+0.30	
			q(O)	−0.38	
μ	1.90		q(F(av))	−0.35	

[a] Bond lengths in Å, angles α and dihedral angles β in deg, charges q in units of e, dipole moment in D, and av means averaged value. [b] B3LYP/6-311++G(3df,3pd). [c] From GED structure determination.[21]

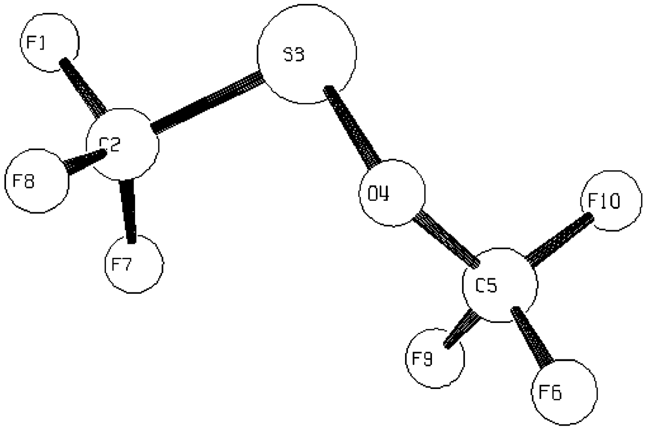

Figure 4. Optimized structure of CF_3SOCF_3 obtained from B3LYP/6-311++G(3df,3pd).

troscopic assignment[22] assume the higher symmetry C_s. Furthermore, a positive partial charge is calculated both for sulfur and the carbon atoms resulting in a long S−C bond. Nevertheless, the lengthening seems to be overestimated; that is, the experimental S−C distance is lower (1.885 Å)[21] than the calculated value (1.914 Å). Other structural parameters are reproduced well by the calculations (see Table 3).

Quantum chemical calculations predict only one conformation for the CF_3SOCF_3 molecule. In agreement with the related compounds CF_3OOCF_3 and CF_3SSCF_3, the CF_3Y (Y = O, S) are orientated with one fluorine atom nearly trans to the central Y−Y′ bond. CF_3SOCF_3 shows a calculated CSOC dihedral angle of 105° well in the range of 126° (calcd for CF_3OOCF_3; found 123.3°[37]) and 96° (calcd for CF_3SSCF_3; found 98°[38]). The optimized calculated structure of CF_3SOCF_3 is depicted in Figure 4.

The optimized theoretical parameters are listed in Table 4, together with calculated structural parameters of related compounds. The agreement between them is rather good. There are no experimental structural parameters for S−O containing compounds available for comparison.

The $S{-}CF_3$ bond lengths increase considerably with increasing sulfur oxidation number (1.819 Å in $(CF_3)_2S$[39] and 1.885 Å in $CF_3S(O)CF_3$[21]). The same behavior is predicted for $CF_3S(O)CF_3$ and CF_3SOCF_3 by quantum chemical calculation (see Tables 3 and 4).

Table 4. Structural Parameters and Properties of CF_3SOCF_3 and Related Compounds

(param[a] X, Y)	CF_3OOCF_3 for X, Y = O		CF_3SOCF_3: calcd[b] for X = S, Y = O	CF_3SSCF_3 for X, Y = S	
	calcd[b]	expt[c]		calcd[b]	expt[d]
R(C−F(av))	1.3257	1.320	1.3327	1.3346	1.330
R(C−X)	1.3886	1.399	1.8296	1.8444	1.825
R(X−Y)	1.4410	1.419	1.6768	2.0413	2.024
R(Y−C′)	1.3886	1.399	1.3758	1.8444	1.825
α(CXY)	107.06	107.2	99.17	102.93	101.15
α(XYC)			117.63		
β(FCXY)	178.5		174.2	174.4	173.4
β(XYC′F′)			177.7		
β(CXYC′)	126.3	123.3	105.0	95.7	98.2
q(C)	+1.83		+1.14	+1.04	
q(C′)			+1.73		
q(S)			+0.04	−0.03	
q(O)	−0.55		−0.61		
q(F(av))	−0.43		−0.38	−0.34	
μ	0.08		0.94	0.90	

[a] Bond lengths in Å, angles α and dihedral angles β in deg, charges q in units of e, dipole moment in D, and av means averaged value. [b] B3LYP/6-311++G(3df,3pd). [c] Reference 37. [d] Reference 38; crystal structure at −160 °C, space group No. 2 (C_i), and averaged values evaluated from original data.

To study the influence of the substituent R on the enthalpy differences between the isomers $R_2S{=}O$ and RSOR the minimum energies on the potential hypersurfaces have been calculated [B3LYP/6-311++G(3df,3pd)] for the symmetrically substituted molecules with R = H, F, CH_3, and CF_3.

In accordance with the observations the enthalpy difference $\Delta H = H(\mathrm{RSOR}) - H(\mathrm{R_2S{=}O})$ at standard conditions predict the sulfenic acid to be more stable (R = H, $\Delta H = -56.5$ kJ·mol^{-1}) than thionyl hydride, while thionyl fluoride $F_2S{=}O$ is more stable than the hypofluorite FSOF (R = F, $\Delta H = +332.2$ kJ·mol^{-1}). For the organosulfur compounds, a higher stability is calculated for dimethyl sulfoxide (R = CH_3, $\Delta H = +18.1$ kJ·mol^{-1}) while bis(trifluoromethyl) sulfenate (R = CF_3, $\Delta H = -88.3$ kJ·mol^{-1}) is predicted to be more stable.

Conclusions

Matrix-isolated bis(trifluoromethyl) sulfoxide has been found to undergo photoisomerization to the sulfenic ester, CF_3SOCF_3, which is the missing link between the well-known peroxide CF_3OOCF_3 and the disulfane CF_3SSCF_3. Additionally, it was possible to measure the UV spectrum of the sulfoxide in the region of 200−360 nm and to record the complete IR spectrum of the new sulfenic ester and of the sulfoxide precursor isolated in inert gas matrix. ^{18}O isotopic labeling experiments and DFT calculations supported the IR band assignment of both compounds.

In accordance with the experiment, quantum chemical calculations predict only one conformation for the CF_3SOCF_3 molecule. The calculated dihedral angle of 105° is between the angles calculated for CF_3OOCF_3 (126°) and for CF_3SSCF_3 (96°).

Additionally, the calculations predict the CF_3SOCF_3 isomer to be more stable than $CF_3S(O)CF_3$, and its synthesis on a preparative scale is the next challenge.

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