Fluorooxy Radicals

DOI: 10.1002/anie.200604346

Side-On versus End-On Bonding of O_2 to the FSO_3 Radical: Matrix Isolation and Ab Initio Study of FSO_5[**]

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Dedicated to Professor Friedhelm Aubke on the occasion of his 75th birthday

Oxy radicals of non-metals such as nitrogen, chlorine, or sulfur play an important part in atmospheric chemistry. They generally form weak complexes with dioxygen. A recent study[1] on the kinetics of formation and the decomposition of the FSO_3/O_2 complex attracted our interest. The intermediate formed by laser flash photolysis ($\lambda = 193$ nm) of FSO_2OF in the presence of O_2 features a strong visible absorption at 450 nm and was claimed to be the chainlike trioxy radical FSO_2OOO.[1] The oxygenated radical was found to dissociate unimolecularly on a millisecond timescale to yield $FSO_3 + O_2$.[1] The short lifetime prevented further spectroscopic investigations. Previously we studied in noble gas matrices O_2 complexes of several oxy radicals such as CF_3O/O_2,[2] SF_5O/O_2,[3] and ClO_4/O_2.[4] However, dioxygen complexes of polyoxy radicals such as FSO_3 have not yet sufficiently been characterized. Herein we report the matrix isolation and a combined UV/Vis/infrared spectroscopic and quantum-chemical characterization of the FSO_3/O_2 complex.

The infrared spectra of the precursor for the synthesis of FSO_3, the peroxide FSO_2OOSO_2F ($S_2O_6F_2$),[5,6] isolated in solid argon at 14 K or in neon at 6 K, revealed no impurities, but did show splitting of the bands owing to the presence of several rotamers. Increasing the temperature of the spray-on nozzle during matrix deposition changed the relative intensities of these splittings, and bands associated with the FSO_3 radical,[7] formed by thermal dissociation of $S_2O_6F_2$ according to Equation (1), appear in the IR matrix spectra.

$$FSO_2OOSO_2F \rightleftharpoons 2\,FSO_3 \qquad (1)$$

$S_2O_6F_2$ is almost completely dissociated at a pyrolysis temperature of 160 °C, as demonstrated in Figure 1 (upper trace). In contrast to previous matrix experiments,[7] much weaker bands of HSO_3F, H_2O, CO_2, HF, and $S_2O_5F_2$ are found in the spectra.

The thermolysis products of $S_2O_6F_2$ were trapped in a Ne matrix containing 10 % of O_2 to investigate the reaction of FSO_3 radicals with molecular oxygen. Part of the IR spectrum of this experiment is displayed in Figure 1 (middle trace). It reveals a strong decrease in intensity of all bands attributed to FSO_3 and the appearance of new broad IR bands of the

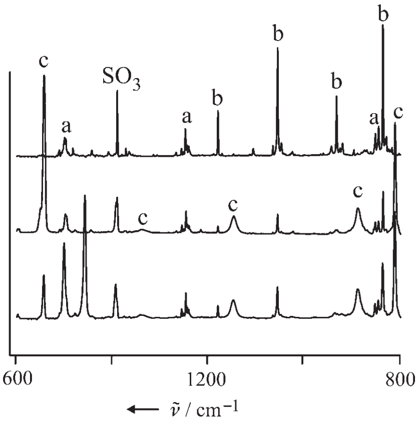

Figure 1. Infrared spectra of the pyrolysis products of FSO_2OOSO_2F at 160 °C isolated in an Ne matrix (upper trace), in an Ne matrix containing 10 % oxygen ($^{16/16}O_2$; middle trace), and in an Ne matrix containing 10 % oxygen ($^{16/18}O_2$; lower trace): bands of a) FSO_2OOSO_2F, b) FSO_3, and c) FSO_3/O_2.

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[**] We acknowledge support from the European Commission through contract No. MRTN-CT-2004-512202 “Quantitative Spectroscopy for Atmospheric and Astrophysical Research” (QUASAAR) and the Deutsche Forschungsgemeinschaft (DFG). G.A.A. thanks the VW Foundation for a grant that allowed the exchange of scientists. C.J.C. thanks the Max Planck Institute for Biophysical Chemistry Göttingen for support through the “Partner Group for Chlorofluorocarbons in the Atmosphere”.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

FSO_3/O_2 complex. The UV/Vis spectrum shows an extremely strong and broad absorption with a maximum at 360 nm. This spectrum revealed about 50 % of unreacted FSO_3 (Figure 2, upper trace). The integrated absorption associated with the FSO_5 radical is much stronger than that of the structured $^2E(2)-\tilde{X}^2A_2$ transition of FSO_3 (Figure 2, lower trace). This observation is in agreement with the absorption cross sections of FSO_5 and FSO_3 reported at 450 nm previously (4.4×10^{-17} [1] and 3.64×10^{-18} $cm^2 molecule^{-1}$,[8] respectively).

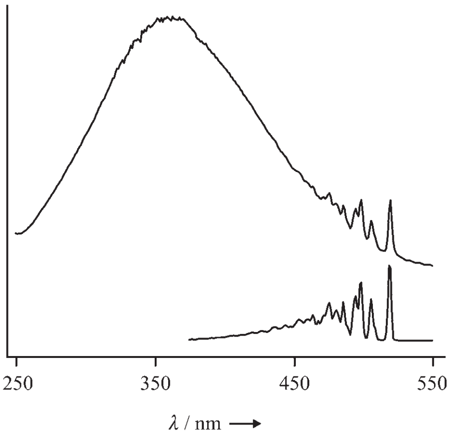

Figure 2. UV/Vis absorption spectra of FSO_3 (lower trace) and FSO_3/O_2 (upper trace) obtained by pyrolysis of FSO_2OOSO_2F and isolated at 6 K in an Ne matrix and in an Ne matrix with 10% oxygen, respectively.

Experimental positions and intensities of the IR bands attributed to the FSO_3/O_2 complex are compared in Table 1 to calculated data obtained at the UB3LYP/6-311 + G(3df) level of theory.[9] In these calculations two isomers of the FSO_3/O_2 complex, shown in Figure 3, were considered: a chainlike trioxy radical FSO_2OOO **I** and a cyclic species **II** with side-on bonding of O_2 to the FSO_3 radical. At the level of theory employed, these isomers were found to have very similar enthalpies of formation (Table S1 in the Supporting Information).

Table 1: Calculated IR data for two isomers of FSO_3/O_2, experimental band positions [cm^{-1}], $^{16}O/^{18}O$ isotopic shifts [cm^{-1}], and a tentative assignment of the observed fundamentals of the matrix-isolated complex.

Observed: $FS^{16}O_3/^{16}O_2$ [a]		$\Delta\nu\,^{18}O/^{16}O$ [b]	Assignment	Calculated:[c]	
Ne/O_2 matrix	Ar/O_2 matrix	Ar/O_2 matrix		Isomer **I**[d]	Isomer **II**[d]
1543.8 (100)	1540.6	0.0	ν(OO)	1623 (567)	1628 (651)
1340 (5)	1335	40.2	$\nu_{as}(SO_2)$	1240 (26)	
1148.6 (23)	1142.2	47.4	$\nu_s(SO_2)$	1105 (77)	1162 (18)
888.9 (38)	893.4	27.0	ν(SO)	927 (64)	1078 (71)
					1012 (1)
811.1 (54)	811.1	12.9	ν(SF)	798 (215)	796 (226)
543.2 (16)	544.3	18.5	SO_2 scissor	534 (28)	537 (26)
392.6 (7)	398.8	17.2	FSO deformation	447 (7)	444 (2)

[a] Most intensive matrix site; relative integrated intensities [%] in parentheses. [b] Isotopic shifts relative to $FS^{16}O_3/^{16}O_2$ for $FS^{18}O_3/^{16}O_2$. [c] UB3LYP/6-311 + G(3df), absolute band intensities [$km\,mol^{-1}$] in parentheses. [d] For assignment, see reference [9].

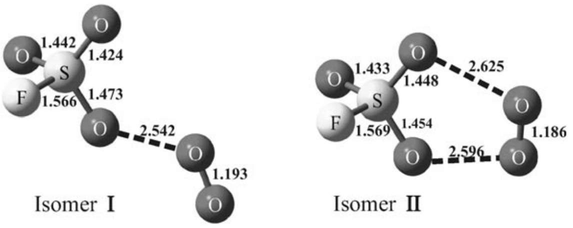

Figure 3. Structures of two isomers of the FSO_3/O_2 complex calculated at the UB3LYP/6-311 + G(3df) level of theory (distances in Å).

The constitution of the FSO_3/O_2 complex was confirmed by photolysis experiments. During photolysis of an Ne matrix containing $FSO_3/FSO_5/O_2$ with visible light, all bands of FSO_5 disappeared simultaneously and new product bands due to SO_3,[10] O_2F,[11] and FSO_3[7] appeared, thus indicating the stoichiometric reactions shown in Equation (2). The two

$$O_2F + SO_3 \xleftarrow{h\nu} FSO_5 \xrightarrow{h\nu} FSO_3 + O_2 \tag{2}$$

different photolysis channels can proceed either simultaneously or stepwise. In the latter case, FSO_5 loses O_2, the resulting FSO_3 dissociates into $SO_3 + F$, and finally the F atoms are scavenged by O_2 to form O_2F.

The strongest band associated with the FSO_3/O_2 complex isolated in an Ne matrix is located at 1543.8 cm^{-1} and is assigned to the O–O stretch, which is IR-activated by complexation. This band is accompanied by a strong overtone at 3063.4 cm^{-1} (not shown). In experiments with equilibrated $^{16/18}O_2$ mixtures, each of these two bands split into three components, located at 1543.8, 1501.5, and 1458.2 cm^{-1} (Figure 1, lower trace), and 3063.4, 2981.6, and 2896.2 cm^{-1}, respectively. At first glance, this $^{16/18}O$ isotopic pattern points to equivalent bound oxygen atoms of the O_2 unit, which is in contrast to the bonding found in the chainlike trioxy radicals XO–OO ($XO = F_3CO$,[2] F_5SO,[3] and ClO_4[4]). However, the observed $^{16/18}O$ isotopic pattern for the OO stretch in FSO_3/O_2 is very similar to that found for F–OO[11] and more recently for the terminal OO stretch in $F_3CO–OO$.[12,13] Although these end-on bound peroxy species should give rise to four different isotopomers ($R–^{16}O^{16}O$, $R–^{16}O^{18}O$, $R–^{18}O^{16}O$, $R–^{18}O^{18}O$), only three O–O stretches are observed in the IR spectrum. The $^{16/18}O$ isotopic pattern for the OO vibration is thus not a conclusive indication for end-on or side-on bonding.

In addition to the O–O vibration of FSO_3/O_2, four new strong IR bands appear in the S–O/F stretching region at 1335, 1142, 893, and 811.1 cm^{-1} which are certainly attributed to stretching fundamentals of the FSO_3 moiety. These bands are very broad; especially the S–O stretching bands display a large half-width (fwhm) of 12 cm^{-1} (Figure 1, middle trace), whereas the fwhm of the S–F band at 811.1 cm^{-1} is only 3.7 cm^{-1}. Furthermore, these bands displayed no shifts in the band positions in experiments with ^{18}O enriched dioxygen.

As neither the calculated energy differences (Table S1 in the Supporting Information) nor a comparison of experimental and predicted fundamental frequencies (Tables 1, as well as Tables S2 and S3 in the Supporting Information)[9] of the two isomers give strong evidence for either the linear or the cyclic isomer, additional matrix-isolation experiments with ^{18}O-enriched $S_2O_6F_2$[13] were carried out. The results of these experiments provide more insight into the bonding mode of the O_2 unit in the FSO_3/O_2 complex. The observed $^{16/18}O$ isotopic shifts by using 95 % ^{18}O-enriched $S_2O_6F_2$[12] are also gathered in Table 1. In experiments with less enriched $S_2{}^{18}O_6F_2$ (64 %), the two bands at 1335 and 1142 cm^{-1} split into three groups of unresolved and partly overlapping bands. This pattern indicates the involvement of two equivalent or nearly equivalent O atoms. Both, their $^{18}O/^{16}O$ isotopic shifts ($\Delta\nu = 40.2$ and 47.7 cm^{-1}) and their band positions are in agreement with two S=O stretches of a SO_2 group. This feature is comparable to that of the bands ν_3 (1351.3 cm^{-1}, $\Delta\nu = 43.5$ cm^{-1}) and ν_1 (1147.2 cm^{-1}, $\Delta\nu = 50.0$ cm^{-1}) of molecular SO_2.[14]

The broad band at 893 cm^{-1} splits only into two unresolved lines separated by approximately 27 cm^{-1}. As the $^{18}O/^{16}O$ wavenumber ratio of this band (866.4/893.4 = 0.970) is slightly greater than the theoretically predicted value for the diatomic SO molecule (0.962), this band is attributed to one S–O bond, and the band position at 893 cm^{-1} is in harmony with a single S–O bond. The very strong band at 811 cm^{-1} displayed a much smaller $^{18}O/^{16}O$ isotopic shift of 12 cm^{-1} and is assigned to the S–F stretch of the FSO_3 moiety. On the basis of the $^{18/16}O$ isotopic pattern of the three S–O stretching bands, we conclude that the chainlike isomer **I** is formed by the reaction of FSO_3 and O_2. For the cyclic isomer **II** one would expect two equivalent S–O bonds and one S=O bond. Although according to DFT calculations both isomers have almost the same energy (Table S1), only **I** is detected experimentally.

The FSO_3 radicals were only partly converted into FSO_5 radicals in Ne gas matrices doped with 10 % O_2 at 6 K (Figure 1), but were formed quantitatively at 14 K in Ar matrices doped with the same content of oxygen, which indicates a low but significant activation energy for the bimolecular reaction between FSO_3 and O_2. The quantitative reaction in O_2-doped Ar matrices accounts for the previously unassigned bands by Nibler and co-workers,[7] who observed weak bands at 1544 and 811 cm^{-1} in the spectra of FSO_3 isolated in solid argon and attributed them to the unknown species "A", which can now be assigned as the FSO_3/O_2 radical formed with traces of air.

The estimated bonding enthalpy of the FSO_3/O_2 complex (42.7 kJ mol^{-1}, Table 2) agrees with the calculated value at the PMP2//MP2/6-311 + G(3df) level (44.4 kJ mol^{-1}) and with the results of recent kinetic measurements.[1] This bonding energy is comparable to those of F–OO ($D^{\circ}_{298} = 53.6$ kJ mol^{-1})[16] and Cl–OO ($D^{\circ}_{298} = 23.2$ kJ mol^{-1}).[17] Despite the small FSO_2O–OO bonding energy, the IR fundamentals of the FSO_3 moiety in the adduct are quite different from those of the free FSO_3 radical, which indicates the formation of a new molecular FSO_5 species rather than a molecular FSO_3/O_2 van der Waals complex.

Table 2: Calculation of the bond enthalpy of the FSO_3/O_2 complex on the basis of isodesmic reactions and experimental activation energies.

Reaction		ΔH_{298} [kJ mol^{-1}]
$FSO_3/O_2 + FSO_2OF \rightarrow FSO_2OOO_2SF + O_2F$	(1)	35.1[a]
$FSO_2OOO_2SF \rightarrow FSO_3 + FSO_3$	(2)	92.4 ± 2.9[8], [b]
$FSO_3 + F \rightarrow FSO_2OF$	(3)	−138.4 ± 3.8[15], [b]
$O_2F \rightarrow F + O_2$	(4)	53.6[c]
$FSO_3/O_2 \rightarrow FSO_3 + O_2$	(5)	42.7[d]

[a] Isodesmic reaction; value calculated at the UB3LYP/6-311 + G(3df) level of theory. [b] Experimental activation energies (high-pressure limits, assuming $E_{a,\infty} \cong \Delta H_{298}$). [c] Calculated from the known enthalpies of formation of F (79.2 ± 0.3 kJ mol^{-1}) and O_2F (25.6 ± 2.1 kJ mol^{-1}).[16] [d] Calculated from the enthalpies of reactions (1)–(4).

The strong UV band of FSO_5 at 360 nm (Figure 2) may be viewed as a charge-transfer transition [Eq. (3)] However, the

$$FSO_5 \xrightarrow{h\nu} O_2{}^+FSO_3{}^- \qquad (3)$$

difference in the electron affinity of FSO_3 (534 kJ mol^{-1})[18] and the ionization energy of O_2 (1170 kJ mol^{-1})[19] suggest that the formation of a charged $O_2{}^+FSO_3{}^-$ complex may not be feasible. Furthermore, the red shift of the O–O stretching mode of FSO_5 with respect to that of matrix-isolated O_2 (1548 cm^{-1}, IR-active in the matrix) rules out a $O_2 \rightarrow FSO_3$ charge transfer.

The first fully characterized dioxygen complex of a polyoxy radical—the title species FSO_5—exhibits very unusual spectroscopic properties and unexpected bonding properties. As oxy radicals of sulfur play an important role in atmospheric chemistry, the FSO_5 radical is of particular importance in this field. Fluorooxy radicals such as FSO_3 may act as molecular models for atmospherically relevant species in which a fluorine atom takes the place of an OH radical (the most important oxidizing species in the atmosphere). Moreover, the unambiguous characterization of side-on or end-on bonding modes of O_2 to polyoxy radicals such as FSO_3 remains a challenge.

Experimental Section

Bis(fluorosulfuryl)peroxide was prepared according to a literature procedure[6] and manipulated in a glass vacuum line.

Preparation of the matrices: Small amounts of pure samples (ca. 0.1 mmol) were transferred into a small U trap held at a temperature of −105 °C. Streams (1–3 mmol h^{-1}) of argon, neon, or noble gas/oxygen mixtures were directed over the cold sample, and the resulting gas mixture was passed through a quartz nozzle heated to approximately 160 °C ($\phi = 4$ mm inner diameter with an end orifice of 1 mm, heated over a length of 20 mm) and quenched on the cold matrix support (14 and 6 K for Ar and Ne matrices, respectively). Photolysis experiments were carried out by using a high-pressure mercury lamp (TQ 150, Heraeus) in combination with a water-cooled quartz lens optic and cut-off filters (Schott). Details of the matrix apparatus have been described elsewhere.[20]

Spectroscopic investigations: Matrix infrared spectra were recorded on a Bruker IFS 66v FT spectrometer in reflectance mode with transfer optics. An MCT detector together with a KBr/Ge beam splitter were used in the region 5000–650 cm^{-1}. For each spectrum, 64 scans were coadded with an apodized resolution of 0.12 cm^{-1}. A Ge-coated 6-μ Mylar beam splitter and a liquid-helium-cooled Si bolometer were used in the region 650–80 cm^{-1}. In this region, 64 scans were coadded for each spectrum with an apodized resolution of 0.5 cm^{-1}. Matrix UV/Vis spectra were recorded in the region 200–600 nm on a Lambda 900 instrument (Perkin–Elmer) in reflectance mode by using two 2-m-long quartz single fibers with a special condenser optic (Hellma). A slit width of 0.5 (or 2) nm, data point separation of 0.1 (or 0.4) nm, and an integration time of 0.52 s were employed for each spectrum.

Computational Calculations: All calculations were carried out with the Gaussian 03 program.[21] Geometry optimization was performed with the spin-unrestricted B3LYP density-functional method.[22,23] The 6-311+G(3df) basis set[24] was used in all calculations. All the stationary points were identified for local minima by vibrational frequency analysis. Comparative DFT studies of the relative enthalpies and the vibrational frequencies of the two isomers were performed with several functionals (B3LYP, B98, mPW1PW91, PBE1PBE, B97-2; see Tables S1–S3 in the Supporting Information). Preliminary coupled cluster calculations at several levels of theory failed because of limited computer resources.

Received: October 24, 2006
Revised: February 7, 2007

Keywords: density functional calculations · matrix isolation · radicals · vibrational spectroscopy

[1] A. E. Croce, C. J. Cobos, E. Castellano, *J. Fluorine Chem.* **1997**, *82*, 91.
[2] G. A. Argüello, H. Willner, *J. Phys. Chem. A* **2001**, *105*, 3466.
[3] M. Kronberg, S. von Ahsen, H. Willner, J. S. Francisco, *Angew. Chem.* **2005**, *117*, 258; *Angew. Chem. Int. Ed.* **2005**, *44*, 253.
[4] R. Kopitzky, H. Grothe, H. Willner, *Chem. Eur. J.* **2002**, *8*, 5601.
[5] F. B. Dudley, G. H. Cady, *J. Am. Chem. Soc.* **1957**, *79*, 513.
[6] D. Zhang, C. Wang, F. Mistry, B. Powell, F. Aubke, *J. Fluorine Chem.* **1996**, *76*, 83.
[7] E. M. Suzuki, J. W. Nibler, K. A. Oakes, D. Eggers, Jr., *J. Mol. Spectrosc.* **1975**, *58*, 201.
[8] C. J. Cobos, A. E. Croce de Cobos, H. Hippler, E. Castellano, *J. Phys. Chem.* **1989**, *93*, 3089.
[9] Comparison of experimental and predicted wavenumbers favors isomer **I** over **II**, as the weak band at 1335 cm^{-1}(Ar matrix) does not fit to any of the computed SO stretching vibrations of **II**, and the predicted intensity of the SO stretch of **II** at 1012 cm^{-1} may be to small to be detected experimentally. However, the assignment given in Table 1 results in a better overall match of computed and observed band positions of **II**, if the weak band observed at 1335 cm^{-1} may be attributed to the combination band $811+544=1355$ cm^{-1}. Improved DFT calculations with last generation functionals appropriate for weak complexes indicate that no significant differences in the vibrational wavenumbers and relative intensities appear in comparison to Table 1 (see Tables S2 and S3 in the Supporting Information).
[10] S.-H. Jou, M.-Y. Shen, C.-H. Yu, Y.-P. Lee, *J. Chem. Phys.* **1996**, *104*, 5745.
[11] M. E. Jacox, *J. Mol. Spectrosc.* **1980**, *84*, 74.
[12] S. von Ahsen, H. Willner, J. S. Francisco, *Angew. Chem.* **2003**, *115*, 4838; *Angew. Chem. Int. Ed.* **2003**, *42*, 4690.
[13] H. Willner, unpublished results.
[14] L. Schriver-Mazzuoli, A. Schriver, M. Wierzejewska-Hnat, *Chem. Phys.* **1995**, *199*, 227.
[15] A. E. Croce de Cobos, C. J. Cobos, E. Castellano, *J. Phys. Chem.* **1989**, *93*, 274.
[16] P. Campuzano-Jost, A. E. Croce, H. Hippler, M. Siefke, J. Troe, *J. Chem. Phys.* **1995**, *102*, 5317.
[17] J. M. Nicovich, K. D. Kreutter, C. J. Shackelford, P. H. Wine, *Chem. Phys. Lett.* **1991**, *179*, 367.
[18] S. T. Arnold, T. M. Miller, A. A. Viggiano, *Int. J. Mass Spectrom.* **2002**, *218*, 207.
[19] T. A. York, J. Comer, *J. Phys. B* **1983**, *16*, 3627.
[20] H. G. Schnöckel, H. Willner in *Infrared and Raman Spectroscopy, Methods and Applications* (Ed.: B. Schrader), VCH, Weinheim, **1994**, p. 297.
[21] Gaussian 03 (Revision B.05): M. J. Frisch et al., see the Supporting Information.
[22] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
[23] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[24] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650.