Articles

Vibrational Spectra and Gas-Phase Structure of Pentafluorosulfanyl Hypochlorite[†]

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The preparation of SF_5OCl from ClF and SOF_2 in the presence of CsF is described. The Raman and infrared spectra are discussed, and the 18 fundamental vibrations are assigned. Furthermore, the SF_5OCl has been investigated by gas electron diffraction and by theoretical calculations. The molecule of symmetry C_s has bond lengths of 156.0(2) pm (S−F), 165.7(14) pm (S−O), and 166.7(16) pm (O−Cl) with a S−O−Cl angle of 119.2(6)°.

Introduction

Pentafluorosulfanyl hypochlorite was first prepared by Gould et al. and Schack et al. by the reaction of SF_4O with ClF in the presence of CsF according to eq 1.[2,3]

$$SF_4O + ClF \xrightarrow{CsF} SF_5OCl \qquad (1)$$

The chemistry of SF_5OCl was mainly studied in respect to addition reactions on double bonds.[3−9] SF_5OCl reacts similarly like CF_3OCl under cleavage of the O−Cl bond via an addition mechanism.[3−9] Moreover, the hypochlorite was used for the photochemical synthesis of $(SF_5)_2O$ and the preparation of pentafluorosulfurous acid (eq 2).[10−12]

$$SF_5OCl + HCl \rightarrow SF_5OH + Cl_2 \qquad (2)$$

No structural data have been reported for the SF_5OCl, except for its vibrational and ^{19}F-NMR spectra.[2,3,13] In general, SF_5 compounds can easily be characterized by ^{19}F-NMR spectroscopy due to their typical AB_4 patterns.[14] Investigations by vibrational spectroscopy are considerably more complex, since the symmetry of a SF_5X (X = substituent) molecule affects the number of active fundamental vibrations of the SF_5 group, and the substituting group can cause shifts for SF_5 group vibrations of up to 100 cm^{-1}.[15,16] Therefore, an assignment of the vibrations is difficult even by comparing a series of similar compounds.

In the course of our studies of CsF-catalyzed reactions we chose the formation of SF_5OCl as a model reaction, since it is very sensitive to catalyst conditions.[17,18] Furthermore, the compound was interesting to us for testing the recently developed multichannel Raman matrix isolation spectroscopy for the investigation of unstable compounds.[19] In this paper we report a simplified high-yield preparation of pure SF_5OCl, its vibrational spectra, and the gas-phase structure.

Experimental Section

All synthetic work and sample handling were performed by employing standard Schlenk techniques and a stainless steel vacuum line which was passivated with fluorine. CsF (Ozark) was dried at 400 °C and crushed in a drybox under nitrogen. The ClF was prepared from ClF_3 and $HgCl_2$ by a literature method.[20] The method to obtain highly pure SOF_2 is described elsewhere.[21] (**CAUTION**: *ClF and SF_5OCl can react violently with organic materials!).*

Raman spectra were recorded on a T64000 (ISA) using an argon ion laser (Spectra Physics) at 514.5 nm. The infrared spectra were obtained with a Bruker ifs 113v spectrophotometer using a stainless steel infrared cell equipped with silicon windows.

Preparation of SF_5OCl. A 100 mL stainless steel autoclave was passivated with fluorine and loaded with 2 g of CsF. The CsF catalyst was activated by the addition of 0.5 g of SO_2 (dried over CaH_2) and

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[†] Raman Matrix Isolation Spectroscopy. 5. Part 4: Raman studies of the isotopic effect in solid and matrix-isolated oxygen.[1]

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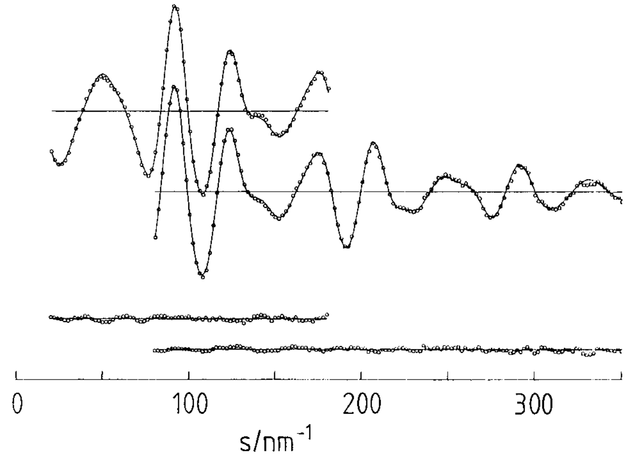

Figure 1. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and differences.

subsequent high vacuum pyrolysis of the formed $CsSO_2F$.[17] The amount of 20 mmol of SOF_2 and 63 mmol of ClF was condensed into the autoclave at −196 °C. The autoclave was warmed up to −40 °C and kept at this temperature for 1 day. The product was isolated by trap-to-trap fractionation (−120 °C; −196 °C). The −120 °C trap contains pure SF_5OCl. The yield of the colorless product was almost quantitative. The SF_5OCl can be stored at −196 °C in stainless steel or Kel-F vessels for a few months. Contact with glass causes decomposition of the compound. The reaction vessel with the CsF catalyst can be used for more than 10 cycles without decreasing the yield of SF_5OCl.

Raman Matrix Spectrum. The apparatus for multichannel Raman matrix spectroscopy has been described elsewhere.[19] The SF_5OCl reservoir was cooled to −115 °C, and the vapor was mixed with a continuous argon stream (4 mmol/h) in front of the cold surface. An estimated M/S (matrix-to-substrate) ratio of *ca.* 300 was achieved using this procedure. The matrix layers had a thickness of 100 μm on average.

Gas-Phase Structure of SF_5OCl. The electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[22] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of ca. 60 kV. The sample reservoir was cooled to −65 °C, and the gas nozzle was at room temperature. The photographic plates (Kodak Electron Image plates 18 × 13 cm) were analyzed with the usual methods.[23] Averaged molecular intensities in the *s* ranges 20−180 and 80−350 nm^{-1} in steps of $\Delta s = 2\ nm^{-1}$ are presented in Figure 1.

Results and Discussion

Formation of SF_5OCl. The common method for the synthesis of SF_5OCl is the reaction of ClF with SF_4O (eq 1). The SF_4O is usually prepared by fluorination of SF_2O with F_2 or BrF_5, respectively. Schack et al. reported an almost quantitative yield.[3] Later DesMarteau et al. encountered considerable difficulties in repeating the method and found somewhat erratic yields, which were attributed to catalyst inhibition due to the formation of $CsClF_4$.[13] During our investigations of the catalytic activity of CsF,[17,18] we found no evidence for the formation of $CsClF_4$, but we found that especially the formation of SF_5OCl requires a highly activated catalyst. Besides the absence of catalyst poisons, such as HF, a sufficient surface is necessary to achieve high yields. Therefore, we produced CsF by the high-vacuum pyrolysis of $CsSO_2F$ in the reaction vessel. Finally, thionyl fluoride was used instead of SF_4O (eq 3). The yield was almost quantitative at temperatures between −60 and −40 °C.

$$SOF_2 + 3ClF \xrightarrow{CsF} SF_5OCl + Cl_2 \qquad (3)$$

Even though this method requires 3 times the amount of ClF, the whole procedure is more efficient, since the SF_4O does not need to be prepared and purified separately. The thionyl fluoride is sensitive toward moisture, but not as much as SF_4O. Furthermore, the SOF_2 can be purified easily by treatment with KF.[21]

Vibrational Spectra of SF_5OCl. As mentioned above, an assignment of the vibrations of SF_5 compounds is difficult. This is largely due to the symmetry of the molecule. The highest symmetry is realized in the octahedral SF_6 molecule with six vibrations ($A_1 + E + 2F_1 + 2F_2$). Substitution of one fluorine atom by other atoms lowers the symmetry to C_{4v} with 11 vibrations ($4A_1 + 2B_1 + B_1 + 4E$), nine of which involve the SF_5 group. Three examples are known (SF_5Cl, SF_5Br, and SF_5O^-) and have been well discussed by Christe et al.[15,16,24] The C_{4v} symmetry is also possible with a linear substituent which is arranged along the 4-fold axis as in SF_5CN, SF_5NC, and SF_5CCH.[25−27] These kinds of molecules also exhibit nine SF_5 group vibrations. A diatomic substituent which is not arranged along the 4-fold axis but divides one of the $F_{eq}-S-F_{eq}$ angles leads to C_s symmetry with 18 fundamentals (11 A′ + 7 A″). In this symmetry group the degeneracies have been lifted and all of the 12 SF_5 group vibrations are active in both the Raman and the IR spectra. The molecules SF_5OH,[11,12] SF_5OF,[28] and SF_5OCl[2,3] are the simplest known SF_5 compounds with this symmetry.

The Raman and infrared spectra of SF_5OCl are shown in Figure 2, and the frequencies are summarized in Table 1. The assignments were made on the basis of C_s symmetry by comparison with calculated frequencies and consideration of the cartesian displacement coordinates. According to C_s symmetry, 18 fundamentals (11A′ + 7 A″) are expected for SF_5OCl. These fundamentals should all be active in both the infrared and the Raman spectra.

Seven stretching modes are expected in the region above 600 cm^{-1}. The infrared spectrum shows a strong band at 923 cm^{-1} and the Raman matrix spectrum a weak broad line at 920 cm^{-1} due to the antisymmetric stretching modes of the SF_4 group, which on the basis of calculation are almost degenerate. The Raman spectrum of the solid shows three lines in this region, probably due to crystal field splittings. The bands at 820 and 880 cm^{-1} belong to vibrational motions of the $F_{ax}-S-O-Cl$ skeleton mainly involving the $S-F_{ax}$ and $S-O$ stretching vibrations. The most intense Raman line at 720 cm^{-1} is the symmetric stretching mode in the SF_4 plane and contains, in part, the O−Cl stretching mode which also appears partly in the line at 820 cm^{-1}. According to the tentative assignment of DesMarteau,[13] none of the observed lines can be ascribed to a separate O−Cl stretching mode, which was found in $ClONO_2$ at 810 cm^{-1} and in CF_3OCl at 780 cm^{-1}.[29,30] The Raman lines at 631 and 646 cm^{-1} were assigned to SF_5 and SF_4 stretching modes, respectively.

Eleven deformation modes are expected for SF_5OCl. Ten were observed in the Raman spectrum, but only three in the

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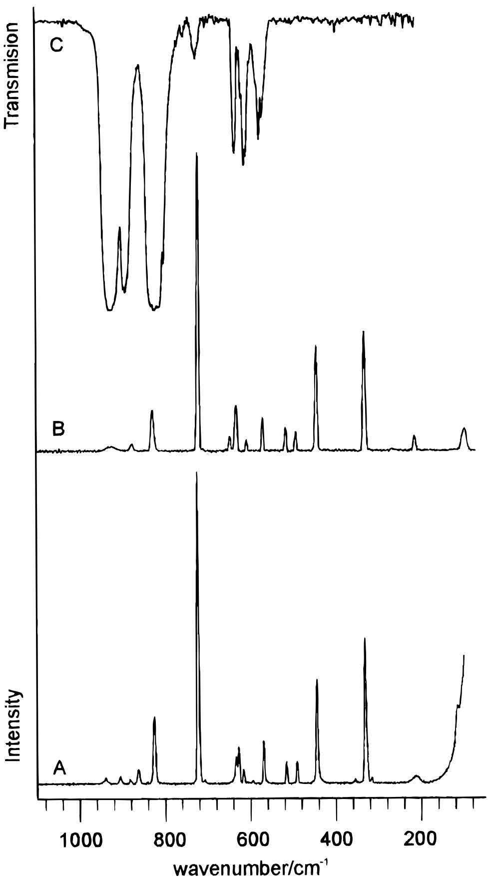

Figure 2. Raman spectrum of solid (trace A) and matrix-isolated (trace B) (M/S = 300) SF_5OCl and infrared gas spectrum (trace C) of gaseous SF_5OCl.

Table 1. Experimental and Calculated Vibrational Frequencies (cm^{-1}) of SF_5OCl

Raman		IR		assignment	
solid	Ar matrix	gas	ab initio[a]		
115 (5)	96 (16)		75 (0.3)	$\tau(SF_5OCl)$	A″
212 (6)	213 (6)		179 (0.2)	$\delta(SOCl)$	A′
317 (1)			310 (0.1)	$\rho(SF_5)$	A″
332 (49)	331 (50)		316 (0.5)	$\rho(SF_5)$	A′
355 (1)			340 (0.0)	$\delta(SF_4)^b$	A″
444 (32)	444 (38)		416 (0.3)	$\delta_s(SF_4)$	A′
491 (6)	491 (5)		470 (0.5)	$\delta(SF_4)^b$	A″
516 (6)	515 (7)		476 (0.0)	$\delta_s(SF_4)$	A′
569 (11)	569 (10)	562 m	534 (4)	$\delta(SF_5O)$	A′
		576 m	556 (10)	$\delta(SF_4)$	A″
603 (1)					
617 (4)	606 (3)	605 m	587 (18)	$\pi(SF_4)$	A′
628 (10)	631 (18)	626 m	621 (8)	$\nu(SF_5)$	A′
634 (6)	646 (4)		685 (0.0)	$\nu(SF_4)$	A″
708 (1)					
723 (100)	720 (100)	720 w	733 (1)	$\nu_s(SF_4, OCl)$	A′
826 (26)	827 (19)	821 vs	850 (6)	$\nu(SF_{ax}, SO)$	A′
863 (5)	876 (3)	888 vs	976 (100)	$\nu(SF_{ax}, SO)$	A′
882 (1)					
906 (2)	920 (5)	923 vs	1013 (66)	$\nu_{as}(SF_4)$	A″
939 (3)			1016 (64)	$\nu_{as}(SF_4)$	A′

[a] HF/3-21G*, frequencies scaled by empirical factor 0.86; relative IR intensities in parentheses. [b] Out of plane.

infrared spectrum. This is in accordance with *ab initio* calculations which yield an extremely low infrared activity for the vibrations in the low-wavenumber region. The band at 605 cm^{-1} was assigned to the $\pi(SF_4)$ mode, which shows a band splitting in the solid SF_5OCl at 617/603 cm^{-1}. Six bending modes are observed in the region between 350 and 600 cm^{-1}, which involve mainly the SF_5 group. The $\delta(SF_4)$ at 355 cm^{-1} and one of the rocking modes at 317 cm^{-1} were not observable in the argon matrix because of their low intensity. The Raman lines at 213 and 96 cm^{-1} were assigned to the SOCl bending mode and the torsional mode, respectively.

Table 2. Results of GED Analysis and Theoretical Calculations

(a) Geometric Parameters

	GED[a]	HF/3-21G*	B3PW91/6-31G*
$S-F_a$	156.0(2)	155.5	160.4
$S-F_e$		155.5	160.7
S−O	165.7(14)	161.7	168.8
O−Cl	166.7(16)	168.5	170.3
F_a-S-Fe	89.6(3)	89.3	89.4
S−O−Cl	119.2(6)	122.7	119.2
tilt[b]	2.9(8)	2.1	3.8

(b) Interatomic Distances and Vibrational Amplitudes

		amplitude	
	distance	GED	ab initio
S−F	156	3.9(2)	3.8
S−O	166	4.4[3][c]	4.3
O−Cl	167		4.4
$F_a\cdots Fe$	220	5.7(4)	5.9
$(F_e\cdots Fe)cis$	221		5.9
$F_e'\cdots O$	224	6.3[3][c]	6.4
$F_e\cdots O$	232		6.2
$F_3\cdots Cl$	279	12.5(16)	13.4
$S\cdots Cl$	287	5.3(7)	5.6
$F_e'\cdots Fe$	312	5.3(14)	4.9
$F_a\cdots O$	321		5.2
$F_e'\cdots Cl$	3.69	9.2(12)	9.7
$F_a\cdots Cl$	4.31	8.8(25)	7.3

[a] r_a values in picomoles and degrees. Error limits are 3σ values and include possible systematic errors (see text). [b] Tilt angle between C_4 axis of SF_5 group and S−O bond direction, away from F_e. [c] Not refined, but varied within the given range.

Structure of SF_5OCl. The molecular structure of SF_5OCl was determined by gas electron diffraction (GED) and by theoretical calculations (HF/3-21G* and B3PW91/6-31G).[31] Cartesian force constants (HF/3-21G*) were scaled by 0.9 and transformed to symmetry force constants. Vibrational amplitudes were calculated with the program ASYM40.[32] The theoretical results are included in Table 2.

The radial distribution function (RDF) which was obtained by Fourier transformation of the experimental electron diffraction intensities is shown in Figure 3. This RDF is reproduced only with a molecular model in which the O−Cl bond staggers the equatorial S−F bonds. The geometric parameters were refined by least squares fitting of the molecular intensities. The SF_5 group was constrained to C_{4v} symmetry, and all S−F bond lengths were assumed to be equal. These assumptions are justified by the theoretical calculations which predict angle and bond length differences of 0.2° and 0.3 pm, respectively, or less. Vibrational amplitudes which caused high correlations were constrained to the theoretical values (see Table 2). With these assumptions six geometric parameters and seven vibrational amplitudes were refined simultaneously. Only one correlation had a value larger than $|0.6|$: SO/OCl = −0.69. The results are listed in Table 2. The experimental uncertainties

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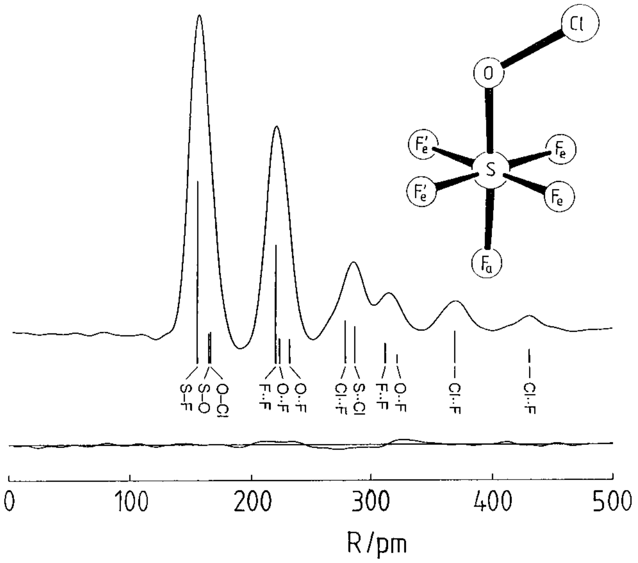

Figure 3. Experimental radial distribution function and difference curve. The positions of interatomic distances are indicated by vertical bars.

are 3σ values and include a possible systematic error due to the assumption for the vibrational amplitudes of the S−O and O−Cl bonds. These amplitudes were varied by ±0.3 pm.

The experimental bond lengths of SF_5OCl are not well reproduced by the two theoretical methods. The HF/3-21G* calculation predicts the S−O bond too short, whereas the B3PW91 method leads to S−F and S−O bond lengths which are too long. The S−F bond lengths in SF_5OCl (156.0(2) pm) are very similar to those in SF_6 (156.23(4) pm)[33] and SF_5OF (155.5(3) pm).[34] The S−O bonds in SF_5OCl (165.7(14) pm), SF_5OF (167.1(7) pm), and SF_5OCN (165.3(3) pm)[35] possess equal lengths within their experimental uncertainties and are considerably longer than those in SF_5OSF_5 (158.6(11) pm).[36] In the four-coordinate S(VI) compounds FO_2SOF (160.6(8) pm)[37] and FO_2SOCl (158.9(10) pm)[37] the S−O bonds are shorter than those in the analogous six-coordinate S(VI) derivatives. The oxygen bond angle increases from 110.89(1)° in ClOCl[38] to 112.9(5)° in CF_3OCl[39] to 115.9(7)° in FO_2SOCl to 119.2-(6)° in SF_5OCl, indicating increasing repulsion from the other substituents. Assuming a 4-fold cosine potential for the internal rotation around the S−O bond, a rotational barrier of 0.57 kcal/mol is estimated from the torsional frequency in the argon matrix (96 cm^{-1}).

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