Preparation of Cesium Trithionate by the Ultrasonic Reaction of CsF with SO_2

Andreas Kornath* and Frank Neumann

Anorganische Chemie, Fachbereich Chemie, Universität Dortmund, 44221 Dortmund, Germany

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Cesium fluoride reacts with SO_2 under an ultrasonic treatment, with the formation of $Cs_2S_3O_6$ and SO_2F_2 instead of $CsSO_2F$. The trithionate salt crystallizes with one solvent molecule ($Cs_2S_3O_6{\cdot}SO_2$) in the monoclinic space group $P2_1/c$ with $a = 9.702(3)$ Å, $b = 15.315(6)$ Å, $c = 7.558(4)$ Å, $\beta = 97.17(4)°$, and 4 formula units per unit cell. The reaction route for the CsF/SO_2 system is discussed with regard to the activation or reactivation of CsF as catalyst.

Introduction

Cesium fluoride is one of the most important catalysts in fluorine chemistry.[1] It's deactivation by hydrogen fluoride is well-known in the preparation of many fluorine compounds. Sometimes its deactivation or partial modification is desired, and various research groups have developed new catalysts based on CsF. An example is the catalytic reduction of HFC precursors by hydrogen in the presence of a $BaCl_2$/CsF catalyst (eq 1).[2]

$$F_2C{=}CFCl + H_2 \xrightarrow{BaCl_2/CsF} F_2C{=}CHF + HCl \qquad (1)$$

In course of our investigation of sulfur−fluorine compounds we found a significant inhibition of the CsF catalyst by traces of SO_2 due the formation of $CsSO_2F$ (eq 2). To investigate this phenomenon, we carried out more detailed studies on the reaction of alkali metal fluorides with SO_2.

$$CsF + SO_2 \rightarrow CsSO_2F \qquad (2)$$

Fluorosulfites were first reported by Seel and Meier in 1953 in the reaction of “naked” fluoride ($Me_4N^+F^-$) with SO_2.[3] Later, the fluorosulfites of Na, K, Rb, Cs, and NH_4^+ were described and characterized by x-ray powder diffraction and IR spectroscopy.[4−7] Fluorosulfites have been used as mild fluorinating agents and, in case of KSO_2F, for the preparation of activated KF by vacuum pyrolysis.[8,9]

We report here the reaction of CsF with SO_2 under ultrasonic treatment, which yields surprisingly $Cs_2S_3O_6$ instead of $CsSO_2F$.

Experimental Section

All synthetic work and sample handling were performed by employing standard Schlenk techniques and a standard vacuum line. CsF (Ozark) was dried thoroughly several times and crushed in a drybox under nitrogen (average particle size 100 μm). SO_2 (Messer Griesheim) was dried over CaH_2.

Raman spectra were recorded on a T64000 (ISA) using an argon ion laser (Spectra Physics) at 514.5 nm. The SEM was acquired with a Cambridge Instruments S360. Single crystals were placed in Lindemann capillaries in a cooled stream of nitrogen, and an X-ray diffraction study was carried out using a Nicolet R3/mV automated diffractometer.

Preparation of $Cs_2S_3O_6{\cdot}SO_2$. A 500 mg amount of carefully dried CsF was placed in a dried glass tube, and 5 g of SO_2 was condensed into the tube at −196 °C. The frozen mixture was placed in an ultrasonic bath, after sealing of the glass tube. The reaction proceeded on thawing in a few minutes. The colorless crystalline product can be accompanied by $CsSO_2F$ if the efficiency of the ultrasonic bath is not sufficient. The reference reaction of CsF with SO_2 without ultrasound was carried out in the same manner and yielded pure $CsSO_2F$. Raman spectral data for $Cs_2S_3O_6{\cdot}SO_2$ (cm^{-1}): 1244 m, 1229 m, 1209 w, 1152 w, 1053 s, 670 w, 557 w, 525 w, 428 m, 417 m, 323 w, 290 vw, 266 m, 252 s, 141 m, 120 w, 111 m. Raman spectral data for $CsSO_2F$ cm^{-1}): 1183 m, 1168 sh, 1105 s, 1051 w, 595 w, 500 m, 393 m, 378 m, 366 m, 243 vw, 130 w, 111 w.

Results and Discussion

Formation of $Cs_2S_3O_6$. A frozen mixture of CsF and SO_2 reacts on thawing in an ultrasonic bath, forming cesium trithionate and sulfuryl fluoride according to eq 3.

$$2CsF + 4SO_2 \rightarrow Cs_2S_3O_6 + SO_2F_2 \qquad (3)$$

The colorless microcrystalline salt is slightly soluble in SO_2 at room temperature in a sealed glass tube. Single crystals of size suitable for an X-ray diffraction study were obtained by treating the product mixture with ultrasound for 1 day. The crystals contain one solvent molecule of SO_2 and are only stable in an atmosphere of SO_2 or at temperatures below −40 °C for a longer period.

The reaction pathways of the CsF/SO_2 system are summarized in Scheme 1. Usually, cesium fluoride reacts exothermically with SO_2 at room temperature, forming cesium fluorosulfite. The reaction is reversible, if the pressure of SO_2 does not exceed ∼10 hPa.[10] At higher pressures, oxidation of the fluorosulfite by SO_2 is observed (reaction 4). The disproportionation can be completed by addition of SO_2 (eq 5). The decomposition ends with the evolution of sulfuryl fluoride (eq 6).

$$3CsSO_2F \rightarrow 2CsSO_3F + CsF + {}^1/_8S_8 \qquad (4)$$

$$2CsSO_2F + SO_2 \rightarrow 2CsSO_3F + {}^1/_8S_8 \qquad (5)$$

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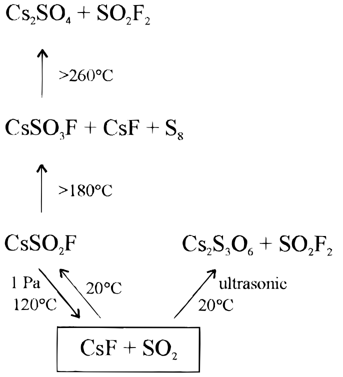
Scheme 1. CsF−SO$_2$ Reaction Pathway



$$2CsSO_3F \rightarrow Cs_2SO_4 + SO_2F_2 \qquad (6)$$

The ultrasonic treatment causes a different reaction. The sulfuryl fluoride is formed at room temperature, and a trithionate salt is formed instead of sulfur and sulfate. To clarify the reaction mechanism and obtain an intermediate, the reaction was carried out at less ultrasonic power and shorter reaction times, but the result was only a smaller yield of the trithionate salt and a larger amount of fluorosulfite. Treatment of the fluorosulfite with ultrasound does not yield the trithionate salt in significant amounts.

The reactions were monitored by Raman spectroscopy.

Raman Spectra. The Raman spectra of CsSO$_2$F and Cs$_2$S$_3$O$_6$·SO$_2$ are shown in Figure 1, and the vibrational wavenumbers are given in the experimental Section. The Raman spectrum of cesium fluorosulfite shows broad lines that are split into parts. The mean value of the vibrational frequencies is in agreement with the IR spectra of Robinson et. al.[11] The fine structure of the lines is probably due to crystal effects and has not been observed in low resolute IR spectra. The Raman spectrum of Cs$_2$S$_3$O$_6$·SO$_2$ exhibits a significantly different pattern. Most typical are the two sharp and intense lines at 1053 cm^{-1} (S−O stretching mode) and 252 cm^{-1} (torsional mode of the ion). The vibrations of the SO$_2$ molecule are of low intensity in comparison with those of the ion, and therefore only the most intense Raman line of SO$_2$ at 1152 cm^{-1} (symmetric S−O stretching) is observable.

Crystal Structure of Cs$_2$S$_3$O$_6$·SO$_2$. The crystal data are summarized in Table 1, and Table 2 contains the atomic coordinates. To ensure that the crystal was representative of the whole sample, its Raman spectrum was recorded and no difference from a scan of the crushed sample was found.

Cesium trithionate crystallizes in the monoclinic space group $P2_1/c$ with 4 formula units per unit cell. For the data reduction, semiempirical correction determined from ψ-scan data, and structure solution and refinement, programs in the SHELXTL PLUS package and PARST were used.[12,13] The cesium layers were found by the Patterson method. All atoms were found in the difference Fourier synthesis, and a final refinement with anisotropic thermal parameters gave a value of $R = 0.061$. The relatively large R(int) value of 0.083 is probably caused by the crystal quality, since the crystals lose SO$_2$ on the surface even at low temperatures during sample preparation.[14]

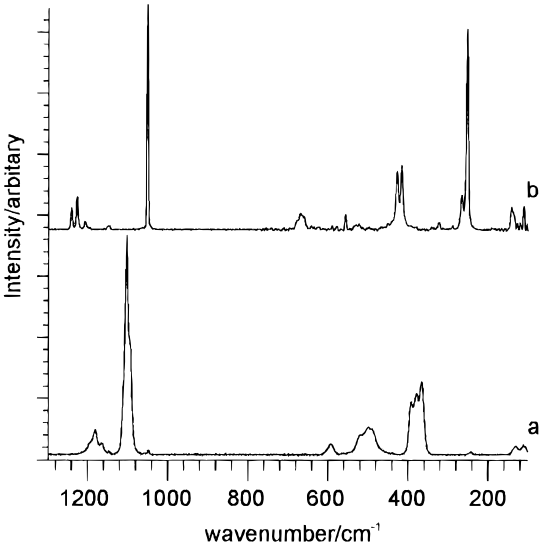


Figure 1. Raman spectra of (a) CsSO$_2$F and (b) Cs$_2$S$_3$O$_6$·SO$_2$.

Table 1. X-ray Diffraction Data of Cs$_2$S$_3$O$_6$·SO$_2$

formula	Cs$_2$S$_4$O$_8$	Z	4
space group	$P2_1/c$ (No. 14)	fw	522.06
a, Å	9.702(3)	μ, cm^{-1}	0.7305
b, Å	15.315(6)	temp, °C	−100(2)
c, Å	7.558(4)	λ, Å	0.710 69
β, deg	97.17(4)	R^a [$I > 2\sigma(I)$]	0.061
V, Å^3	1114.2(8)	R^a (all data)	0.076
ρ_{calcd}, g cm^{-3}	3.112		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. Refinement method: full-matrix least-squares calculations based on F^2.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

	x	y	z	U(eq)[a]
Cs(1)	0.0828(1)	0.0993(1)	0.2134(1)	22(1)
Cs(2)	0.4117(1)	-0.1018(1)	0.6591(1)	23(1)
S(1)	0.0478(2)	-0.1355(1)	0.3403(3)	18(1)
S(2)	0.2145(2)	-0.2027(1)	0.2471(4)	27(1)
S(3)	0.3173(2)	-0.1034(1)	0.1232(3)	23(1)
S(4)	0.3149(2)	0.3273(2)	0.2349(4)	29(1)
O(1)	0.1093(6)	−0.0787(4)	0.4823(9)	22(1)
O(2)	−0.0327(7)	−0.2070(4)	0.4024(11)	33(2)
O(3)	−0.0231(7)	−0.0893(4)	0.1872(10)	28(2)
O(4)	0.3527(7)	−0.0373(4)	0.2580(9)	26(1)
O(5)	0.4348(7)	−0.1519(5)	0.0755(10)	33(2)
O(6)	0.2251(8)	−0.0711(5)	−0.0251(10)	36(2)
O(7)	0.3400(7)	0.2384(4)	0.1996(13)	43(2)
O(8)	0.3308(8)	0.3877(4)	0.0954(13)	40(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U_{ij}}$ tensor.

Bond lengths and selected angles are summarized in Table 3. The lengths of the trithionate S−O bonds and S−S bonds are in good agreement with those of known polythionate salts.[15−17] The S−SO$_3$ ends of the ion have a tetrahedral arrangement. The angle of the triatomic sulfur chain (102.7(1)°) is in the range for such compounds. The sulfur chain and one oxygen atom at the end (O(2)−S(1)−S(2)−S(3)−O(5)) are almost planar. The anion has an approximate point group

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Table 3. Bond Lengths (Å), Selected Angles (deg), and Interionic Distances (pm) for $Cs_2S_3O_6 \cdot SO_2$[a]

S(1)−O(1)	1.450(7)	O(1)−S(1)−O(2)	113.6(4)
S(1)−O(2)	1.454(7)	O(1)−S(1)−O(3)	114.1(4)
S(1)−O(3)	1.457(6)	O(2)−S(1)−O(3)	113.7(4)
S(3)−O(4)	1.447(7)	O(4)−S(3)−O(5)	114.2(4)
S(3)−O(5)	1.443(6)	O(4)−S(3)−O(6)	112.3(4)
S(3)−O(6)	1.432(7)	O(5)−S(3)−O(6)	114.7(5)
S(1)−S(2)	2.112(3)	S(1)−S(2)−S(3)	102.78(12)
S(2)−S(3)	2.101(3)	O(7)−S(4)−O(8)	116.6(6)
S(4)−O(7)	1.414(7)	O(2)−S(1)−S(2)−S(3)	175.7(9)
S(5)−O(8)	1.426(8)	O(5)−S(3)−S(2)−S(1)	172.2(9)

Cs(1)···O(3a)	3.014(8)	Cs(2)···O(1)	3.088(6)
Cs(1)···O(3)	3.064(6)	Cs(2)···O(4d)	3.131(6)
Cs(1)···O(2b)	3.113(6)	Cs(2)···O(4)	3.172(7)
Cs(1)···O(1c)	3.152(7)	Cs(2)···O(6e)	3.205(8)
Cs(1)···O(6a)	3.174(8)		

[a] Symmetry transformations: (a) $1 - x, -y, -z$; (b) $2 - x, y + 0.5, 0.5 - z$; (c) $-x, -y, 1 - z$; (d) $1 - x, -y, 1 - z$; (e) $x, y, z + 1$.

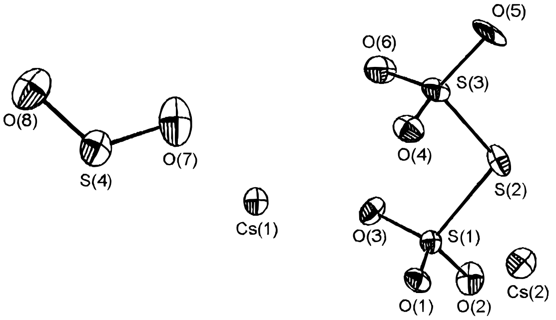

Figure 2. Asymmetric part of the unit cell of $Cs_2S_3O_6 \cdot SO_2$. Thermal ellipsoids are drawn at the 50% probability level.

symmetry of C_2. The SO_2 solvent molecule has regular bond lengths and an angle that are comparable to those of the gas phase structure and therefore are not affected by the crystal lattice.[18]

The anion has distances to the cesium cation smaller than the ionic radius of cesium and the van der Waals radius of oxygen. The cesium atoms are surrounded by four and five oxygen atoms, respectively. Figure 3 shows the different coordinations of the cesium atoms. The crystal packing is shown in Figure 4. The anions and SO_2 molecules are arranged in chains along the *a* axis and are connected with the cesium cations lying between the chains via the interactions shown in Figure 3.

Conclusion

The formation of $Cs_2S_3O_6$ in the CsF/SO_2 system is an example of an ultrasonically stimulated reaction. The regular CsF-SO_2 reaction forming $CsSO_2F$ is reversible if the thermolysis is carried out under vacuum. Therefore CsF catalysts that are poisoned by SO_2 can be reactivated by high-vacuum pyrolysis of the formed $CsSO_2F$.

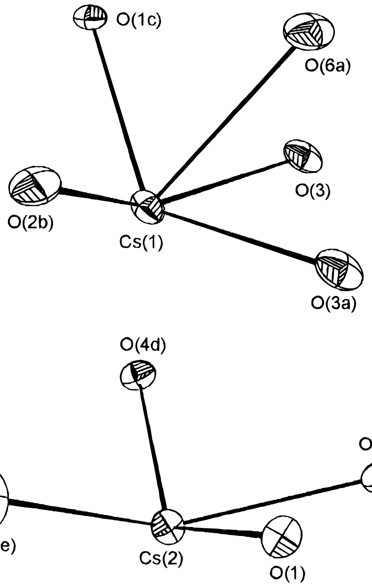

Figure 3. Coordination of the cesium cations. For symmetry operations, see Table 3. Thermal ellipsoids are drawn at the 50% probability level.

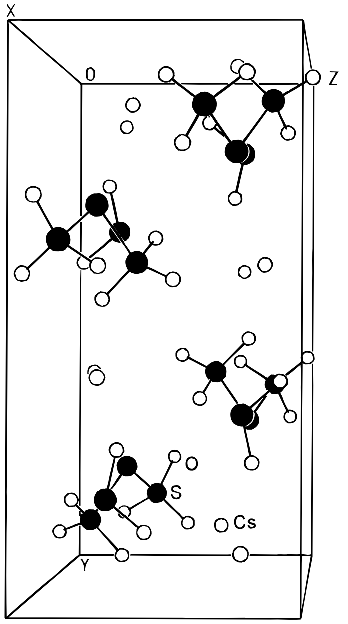

Figure 4. Projection of the structure of $Cs_2S_3O_6 \cdot SO_2$.

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Supporting Information Available: Listings of crystal data and intensity collection parameters, anisotropic thermal parameters, and all bond lengths and angles (8 pages). Ordering information is given on any current masthead page.

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