9.9: Sulfur Halides

Sulfur hexafluoride

Sulfur hexafluoride (SF_6) is a gas at standard temperature and pressure (25 °C, 1 atm). The most common synthesis involves the direct reaction of sulfur with fluorine yields SF_6.

$$S + 3F_2 \rightarrow SF_6 \tag{9.9.1}$$

It should be noted that while SF_6 is highly stable, SCl_6 is not formed. The explanation of this difference may be explained by a consideration of the Born-Haber cycle shown in Figure 9.9.1. A similar cycle may be calculated for SCl_6; however, a combination of a higher dissociation energy for Cl_2 and a lower S-Cl bond energy (Table 9.9.1) provide the rational for why SCl_6 is not formed.

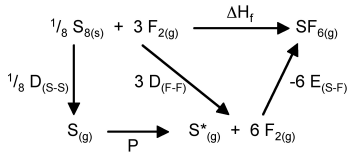

Figure 9.9.1: Born-Haber cycle for the formation (ΔH_f) of SF_6: where $D_{(X-Y)}$ = dissociation energy for X-Y bond, $E_{(S-F)}$ = S-F bond energy, and S* indicates 6 coordinate sulfur.

Table 9.9.1: Comparison of diatomic bond dissociation and S-X bond energy for the fluorine and chlorine analogs.

Bond dissociation energy	**kJ/mol**	**Bond energy**	**kJ/mol**
$D_{(F-F)}$	158	$E_{(S-F)}$	362
$D_{(Cl-Cl)}$	262	$E_{(S-Cl)}$	235

The S-F bond length (1.56 Å) is very short and consistent with π-bonding in addition to σ-bonding. Like SiF_6^{2-}, SF_6 is an example of a hypervalent molecule (Figure 9.9.2).

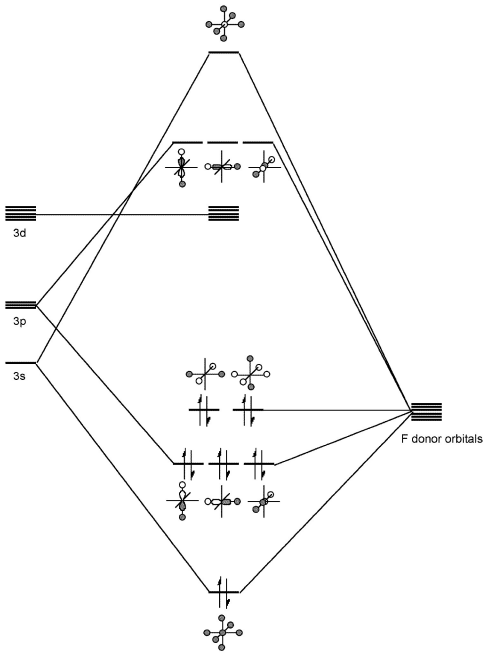

Figure 9.9.2: Molecular orbital bonding in SF_6.

Sulfur hexafluoride is an unreactive, non toxic compound. Its inert nature provides one of its applications, as a spark suppressor. The hexafluoride is generally resistant to chemical attack, e.g., no reaction is observed with potassium hydroxide (KOH) at 500 °C. The low reactivity is due to SF_6 being kinetically inert due to:

- Coordination saturation precluding associative reactions with nucleophiles.

- Strong S-F bond (360 kJ/mol) limiting dissociative reactions.

Thermodynamically SF_6 should react with water (ΔH = -460 kJ/mol), but the rate factors are too great. Sulfur hexafluoride can be reduced with sodium in liquid ammonia, (9.9.2), or with $LiAlH_4$. In each of these reactions the mechanism involves the formation of a radical, (9.9.3). The reaction with sulfur trioxide yields SO_2F_2, (9.9.4), however, the reactions with carbon or CS_2 only occur at elevated temperatures (500 °C) and pressure (4000 atm).

$$SF_6 + 8Na \rightarrow Na_2S + 6NaF \tag{9.9.2}$$

$$SF_6 + e^- \rightarrow SF_6^- \tag{9.9.3}$$

$$SF_6 + 2SO_3 \xrightarrow{250\ ^\circ C} 3SO_2F_2 \tag{9.9.4}$$

Sulfur monochloride pentafluoride

Although the hexachloride is unknown, it is possible to isolate the monochloride derivative (SF_5Cl) by the oxidative addition of Cl-F across SF_4.

$$SF_4 + ClF \rightarrow SF_5Cl \tag{9.9.5}$$

Sulfur monochloride pentafluoride is a gas (Bp = -21 °C), but unlike SF_6 it is fairly reactive due to the polarization of the S-Cl bond (Figure 9.9.3), and as a consequence it reacts with water, (9.9.6).

$$SF_5Cl + 3H_2 \rightarrow SO_3 + 5HF + HCl \tag{9.9.6}$$

Figure 9.9.3: Polarization of the S-Cl bond in SF_5Cl.

Sulfur pentafluoride

Although SF_5 does not exist as a stable molecule, the gaseous dimmer S_2F_{10} (Bp = 29 °C) may be isolated from the photochemical hydrogen reduction of SF_5Cl, (9.9.7).

$$2SF_5Cl + H_2 \xrightarrow{h\nu} S_2F_{10} + 2HCl \tag{9.9.7}$$

While the sulfur is octahedral in S_2F_{10} (Figure 9.9.4a) the S-S bond is weak and long (2.21 Å versus an expected 2.08 Å for a single S-S bond). Despite the apparently weak S-S bond, S_2F_{10} shows almost no reactivity at room temperature; however, the S-S bond undergoes homoleptic cleavage at high temperatures. The resultant $SF_5\cdot$ radicals disproportionate to give highly reactive fluoride radicals, (9.9.8), which is the source of the highly oxidative properties of S_2F_{10}.

$$2SF_5 \rightarrow 2SF_4 + 2F\cdot \tag{9.9.8}$$

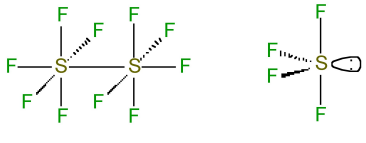

Figure 9.9.4: Structures of (a) S_2F_{10} and (b) SF_4.

The $SF_5\cdot$ fragment is stabilized by the addition of an alkyl radical, and thus, there are a large number of RSF_5 derivatives known. Unlike, the chloride analog, these are very stable.

Sulfur tetrafluoride

Sulfur tetrafluoride (SF_4) is prepared from sulfur dichloride and sodium fluoride in acetonitrile solution at 70 - 80 °C.

$$3SCl_2 + 4NaF \rightarrow SF_4 + S_2Cl_2 + 4NaCl \tag{9.9.9}$$

The structure of SF_4 (and its substituted derivatives RSF_3) is based upon a trigonal bipyramidal structure with one of the equatorial sites being occupied by a lone pair (Figure 9.9.4b). Unlike the hexafluoride, sulfur tetrachloride is a highly reactive compound. It hydrolyzes readily, (9.9.10), and is a useful fluorinating agent (Figure 9.9.5).

$$SF_4 + 2H_2O \rightarrow SO_2 + 4HF \tag{9.9.10}$$

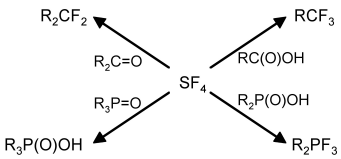

Figure 9.9.5: Examples of the use of SF_4 as a fluorinating agent.

Sulfur chlorides

The chlorination of molten sulfur yields the fowl smelling disulfur dichloride (S_2Cl_2). If the reaction is carried out with a catalyst such as $FeCl_3$, SnI_4 or I_2, an equilibrium mixture containing sulfur dichloride (SCl_2) is formed. However, the dichloride dissociates readily, (9.9.11), although it can be isolated as a dark red liquid if it distilled in the presence of PCl_5. The reaction of chlorine at -80 °C with SCl_2 or S_2Cl_2 allows for the formation of SCl_4 as a yellow crystalline compound which dissociates above -31 °C. Sulfur chlorides are readily hydrolyzed. Sulfur chlorides are used to dissolve sulfur (giving species up to $S_{100}Cl_2$) for the vulcanization of rubber.

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2 \tag{9.9.11}$$

In the vapor phase S_2Cl_2 has C_2 symmetry (Figure 9.9.6a) while that of SCl_2 has C_{2v} symmetry (Figure 9.9.6b).

(a) (b)

Figure 9.9.6: Structures of (a) S_2Cl_2 and (b) SCl_2.