Sulfur hexafluoride

Sulfur hexafluoride (SF₆) 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 SF₆.

\[
\text{rm S + 3 F}_2 \rightarrow \text{SF}_6
\]

It should be noted that while SF₆ is highly stable, SCl₆ is not formed. The explanation of this difference may be explained by a consideration of the Born-Haber cycle shown in Figure 1. A similar cycle may be calculated for SCl₆; however, a combination of a higher dissociation energy for Cl₂ and a lower S-Cl bond energy (Table 1) provide the rational for why SCl₆ is not formed.

![Born-Haber cycle for the formation (ΔH_f) of SF₆: where D(X-Y) = dissociation energy for X-Y bond, E_(S-F) = S-F bond energy, and S* indicates 6 coordinate sulfur.](image)

Table 1: Comparison of diatomic bond dissociation and S-X bond energy for the fluorine and chlorine analogs.

<table>
<thead>
<tr>
<th>Bond dissociation energy</th>
<th>kJ/mol</th>
<th>Bond energy</th>
<th>kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(F-F)</td>
<td>158</td>
<td>E_(S-F)</td>
<td>362</td>
</tr>
<tr>
<td>D(Cl-Cl)</td>
<td>262</td>
<td>E_(S-Cl)</td>
<td>235</td>
</tr>
</tbody>
</table>

The S-F bond length (1.56 Å) is very short and consistent with π-bonding in addition to σ-bonding. Like SiF₆²⁺, SF₆ is an example of a hypervalent molecule (Figure 2).
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 ($\Delta H = -460$ 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$_2$F$_2$, (9.9.4), however, the reactions with carbon or CS$_2$ only occur at elevated temperatures (500 °C) and pressure (4000 atm).

\[ \text{SF}_6 + 8 \text{Na} \rightarrow \text{Na}_2\text{S} + 6 \text{NaF} \]

\[ \text{SF}_6 + e^- \rightarrow \text{SF}_6^-\]

\[ \text{SF}_6 + 2 \text{SO}_3 \xrightarrow{\text{250 °C}} 3 \text{SO}_2\text{F}_2 \]
Sulfur monochloride pentafluoride

Although the hexachloride is unknown, it is possible to isolate the monochloride derivative (SF$_5$Cl) by the oxidative addition of Cl-F across SF$_4$.

\[
\text{SF}_4 + \text{ClF} \rightarrow \text{SF}_5\text{Cl}
\]

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 \(\PageIndex{3}\)), and as a consequence it reacts with water, (9.9.6).

\[
\text{SF}_5\text{Cl} + 3 \text{H}_2 \rightarrow \text{SO}_3 + 5 \text{HF} + \text{HCl}
\]

Figure \(\PageIndex{3}\): Polarization of the S-Cl bond in SF$_5$Cl.

Sulfur pentafluoride

Although SF$_5$ does not exist as a stable molecule, the gaseous dimmer S$_2$F$_{10}$ (Bp = 29 °C) may be isolated from the photochemical hydrogen reduction of SF$_5$Cl, (9.9.7).

\[
2\text{SF}_5\text{Cl} + \text{H}_2 \xrightarrow{h\nu} \text{S}_2\text{F}_{10} + 2\text{HCl}
\]

While the sulfur is octahedral in S$_2$F$_{10}$ (Figure \(\PageIndex{4}\)) a) 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$_2$F$_{10}$ shows almost no reactivity at room temperature; however, the S-S bond undergoes homoleptic cleavage at high temperatures. The resultant SF$_5^-$ radicals disproportionate to give highly reactive fluoride radicals, (9.9.8), which is the source of the highly oxidative properties of S$_2$F$_{10}$.

\[
2\text{SF}_5 \rightarrow 2\text{SF}_4 + 2\text{F}^-
\]

Figure \(\PageIndex{4}\): Structures of (a) S$_2$F$_{10}$ and (b) SF$_4$.

The SF$_5^-$ 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.

\[
3 \text{SCl}_2 + 4 \text{NaF} \rightarrow \text{SF}_4 + \text{S}_2\text{Cl}_2 + 4 \text{NaCl}
\]

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 \(\PageIndex{4}\)b). Unlike the hexafluoride, sulfur tetrachloride is a highly reactive compound. It hydrolyzes readily, (9.9.10), and is a useful fluorinating agent (Figure \(\PageIndex{5}\)).

\[
\text{SF}_4 + 2 \text{H}_2\text{O} \rightarrow \text{SO}_2 + 4 \text{HF}
\]

**Sulfur chlorides**

The chlorination of molten sulfur yields the fowl smelling disulfur dichloride (S\(_2\)Cl\(_2\)). 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\(_2\)Cl\(_2\) 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.

\[
2 \text{SCl}_2 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{Cl}_2
\]

In the vapor phase S\(_2\)Cl\(_2\) has C\(_2\) symmetry (Figure \(\PageIndex{6}\)a) while that of SCl\(_2\) has C\(_{2v}\) symmetry (Figure \(\PageIndex{6}\)b).

Figure \(\PageIndex{5}\): Examples of the use of SF\(_4\) as a fluorinating agent.

Figure \(\PageIndex{6}\): Structures of (a) S\(_2\)Cl\(_2\) and (b) SCl\(_2\).