CML 738 : The Chemistry of Sulfur

For detailed description and problems and exercises please refer chapter 11 of the book
The three philosophical principles of alchemy: salt, sulfur and mercury

"Bring sulfur, old nurse, that cleanses all pollution, and bring me fire that I may purify the house with sulfur"

Homer's Odyssey

Fumigating power of sulfur mentioned by Homer. Sulfur is also mentioned in the Bible as brimstone.
Sulfuric acid was first prepared by the physician, alchemist and writer from Bagdad, Abu Bekr Mohammad Ibn Zakariya Razi (Rhazes) possibly by roasting green vitriol (FeSO₄).

In 1746 in Birmingham, England, John Roebuck began producing sulfuric acid in lead-lined chambers, which were stronger, less expensive, and could be made much larger than the glass containers which had been used previously.
Sulfur – Historical facts

• Sulfur is known from very ancient times, is mentioned in Bible and Greek mythologies as brimstone and was used by alchemists.

• In the classic literature ‘Odyssey’ written by Homer around 800 BC, Odysseus says “Bring sulfur, old nurse, that cleanses all pollution, and bring me fire, that I may purify the house with sulfur.”

• A Chinese literature in the year AD 808 provides the first method for making gunpowder using saltpeter (KNO₃), carbon and sulfur.

• When the Shakespearian character “Othello” asks for punishment, a suggestion he makes is to ‘roast him in sulfur’.

• Sulfur along with mercury were called philosophical elements (along with the Aristotelian elements air, water, earth and fire) during the time of alchemy and it represented the principle of combustibility.

• [Link to YouTube video] https://www.youtube.com/watch?v=mddfu3TXaRw
Sulfur - unique properties

- Sulfur mostly forms divalent, tetravalent and hexavalent compounds and the latter in its tetracoordinate form is the most stable geometry and oxidation state of sulfur. The common oxidation states -2 (H₂S), 0 (S₈), +1 (S₂Cl₂), +2 (SCl₂), +4 (SF₄), +6 (SF₆)
- Sulfur is stable in its elemental state and was mined directly from the earth for a long time.
- Most industrially important compound of sulfur is sulfuric acid which is used for making sulfate and phosphate based fertilizers. 93% of sulfur produced is used for making sulfuric acid.
- Sulfur forms the maximum number of allotropes (over 30) and many of them are cyclic compounds with ring sizes varying from 6 to 20.
- Sulfur was extracted earlier from sulfur deposits (FRASCH Process), but this method has been obsolete since the late 20th century. Today, almost all of the elemental sulfur (~97%) is produced from natural gas and petroleum as a byproduct from its sulfur-containing contaminants. Another 2% is obtained from coal gasification processes.
• Sulfur is the fourth major plant nutrient after N, P and K. About 12.5 million tons of sulfur was applied as fertilizers worldwide in 2015.

• Sulfur is a component of almost all proteins, present in the amino acids, cysteine (having SH group) and methionine (having S-CH$_3$ group). Disulfide bonds are very important for building the tertiary structure of many proteins and are largely responsible for the mechanical strength and insolubility of proteins such as keratin, found in the hair.

• Sulfur in the organic form is present in the vitamins biotin (B$_7$) and thiamine (B$_1$). Sulfur is also an important part of many enzymes and in antioxidant molecules such as glutathione peroxidase and thioredoxin.

• Sulfonamides which are structural analogues of para amino benzoic acid are a class of bacteriostatic drugs (which stops bacteria multiplication).

• Thionyl chloride is a chlorinating and dehydrating agent while sulfuryl chloride is a chlorinating agent similar in reactivity to Cl$_2$.

• Sulfur tetrafluoride and related compounds are useful as reagents for selective conversion of C=O to CF$_2$ groups.
Sulphur or Sulfur ?

By the 15th century, both full Latin spelling variants *sulfur* and *sulphur* became common in English. The parallel *f~ph* spellings continued in Britain until the 19th century, when the word was standardized as *sulphur*. On the other hand, *sulfur* was the form chosen in the United States, whereas Canada uses both. The IUPAC adopted the spelling *sulfur* in 1990 or 1971, depending on the source cited, as did the Nomenclature Committee of the Royal Society of Chemistry in 1992, restoring the spelling *sulfur* to Britain.

So long sulphur

Why *Nature Chemistry* spells sulfur with an ‘f’.

Many decisions must be made when setting up a new scientific journal. These range from perhaps the more fundamental considerations, such as what subjects will be covered and what article types will be featured, to practical issues of spelling and style. Leading up to the launch of *Nature Chemistry*, a number of these choices had to be made, and the one that raised more than a few eyebrows at the time — and still continues to provoke debate even now — was the decision to spell element 16 down to the fact that it’s not simply a case of Oxford English versus American English when it comes to naming chemical elements.

It is the International Union of Pure and Applied Chemistry (IUPAC) who deal with questions of nomenclature and naming when it comes to chemical elements and compounds. And so when IUPAC decided that element 16 should be spelled as ‘sulfur’ — either in 1971 (ref. 1) or 1990 (ref. 2) depending on the source — there should be no room for disagreement.

A fascinating and detailed account of the history of the name of element 16 can be found elsewhere, but the bottom line is that sulfur is not a Greek loan word and so there is no ‘phi’ that needs to be replaced with ‘ph’. The Greeks called element 16 ‘theion’, which is similar to the prefix ‘thio’ that we commonly encounter when describing sulfur-containing compounds today.

The word ‘sulfur’ can be traced to Latin, where the oldest form seems to be *sulpor*,
In 2015, compressed hydrogen sulfide was found to show superconductivity with the highest $T_c$ observed for any materials so far, 203 K (-70 °C). Drozodov, Eremets and co-workers of the Max Planck institute for chemistry at Mainz, Germany when subjected a tiny sample of hydrogen sulfide to a pressure of 153 GPa, observed Meissner effect and zero electrical resistance at the record high $T_c$ of 203 K.21,22 Interestingly, this temperature actually exists on the earth’s surface at places such as Alaska and Antarctica (-74 to -89 °C).
Superheated water (165 °C, 2.5-3.0 MPa) is introduced into the deposit through the outermost tube. Sulfur (m. p. 115 °C) melts and flows into the middle tube.

The sulphur melts and flows into the middle tube. Water pressure alone is unable to force the sulphur into the surface due to the molten sulphur's greater density, so that the hot compressed air is injected via the innermost tube to froth the sulphur, making it less dense and pushing it to the surface.

Eilhard Mitscherlich discovered sulfur's allotropy: he showed that the crystal shapes of sulfur obtained from cooling molten sulfur (monoclinic) were different from those obtained when the element crystallized from a solution (orthorhombic). It is interesting to note that Berzelius introduced the term allotropy only in 1841 and used monoclinic and rhombic forms of sulfur to explain the concept. However, in the modern definition of allotropy and polymorphism these are classified as polymorphs rather than allotropes.
Naptha, kerosene, diesel and heavier oils contain a range of organic sulfur compounds in varying concentrations. These include thiols, thiophenes, sulfides and disulfides which are basically products of degradation of sulfur containing biological products formed under pressure during formation of fossil fuels such as crude oil.

In the first step of hydrodesulfurization these sulfur based compounds are catalytically converted to H$_2$S and hydrocarbon. The normal catalyst used for this is MOS$_2$ although RuS$_2$ or binary combination of Co and Mo called as cobalt modified MoS$_2$ catalysts have been found to be even more active.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{SH} + \text{H}_2 & \xrightarrow{\text{MoS}_2} \text{C}_2\text{H}_6 + \text{H}_2\text{S} \\
\text{C}_4\text{H}_4\text{S} + 4 \text{H}_2 & \xrightarrow{[\text{CoMo}]} \text{C}_4\text{H}_{10} + \text{H}_2\text{S}
\end{align*}
\]
The gaseous products containing H\textsubscript{2}S called ‘sour gas’ is made to undergo a ‘sweetening process’ where the H\textsubscript{2}S is absorbed in Potassium carbonate or amines mainly aliphatic alkanolamines such as diethanolamine (DEA), monoethanolamine (MEA)

Often it will be a reversible potassium bicarbonate formation or ammonium salt formation. In the absorber, the downflowing potassium carbonate solution absorbs H\textsubscript{2}S and CO\textsubscript{2} from the upflowing sour gas to produce a gas free of hydrogen sulfide and carbon dioxide as a product. The resultant rich amine side product is then routed to a regenerator (a stripper with a reboiler) to produce regenerated amine which is recycled for reuse in the absorber. The stripped overhead gas from the regenerator contains H\textsubscript{2}S and CO\textsubscript{2}. The H\textsubscript{2}S can be separated from CO\textsubscript{2} by distillation (H\textsubscript{2}S B.P \(-60\) °C, CO\textsubscript{2}, Sublim. Point \(-78.5\) °C)

\[
\begin{align*}
K_2CO_3 + CO_2 + H_2O & \rightleftharpoons 2 KHCO_3 \\
K_2CO_3 + H_2S & \rightleftharpoons KHCO_3 + KHS
\end{align*}
\]
Hydrogen sulfide thus produced is converted to elemental sulfur by the Claus process designed by the German chemist Carl Frederich Claus and patented in 1883. The Claus process has two steps: thermal and catalytic.

The first thermal step of the Claus process involves burning one-third of the $H_2S$ with air in a reactor furnace to form sulfur dioxide ($SO_2$) according to the following reaction:

$$2 H_2S + 3O_2 \xrightarrow{980-1540 \, ^\circ C} 2 SO_2 + 2H_2O + \text{heat}$$

In the second catalytic step of the Claus process, the remaining unreacted two-thirds of the hydrogen sulfide undergoes Claus reaction (reacts with $SO_2$) to form elemental sulfur by the self-reduction method as follows:

$$2 H_2S + SO_2 \xrightarrow{\text{Alumina} \, 200-310 \, ^\circ C} 3 S + 2H_2O + \text{heat}$$

In fact, the majority of the 70 million metric tons of sulfur produced worldwide in 2015 was byproduct sulfur from refineries and other hydrocarbon processing plants.
There are about 30 well known allotropes of sulfur. There are 20 crystalline phases, most of them characterized by single crystal X ray structure determination are the follows.

\( S_6; \quad S_7 (4 \text{ phases}); \quad S_8 (3 \text{ phases}); \quad S_9 (2 \text{ phases}); \quad S_{10}; \quad S_6 S_{10}; \quad S_{11}; \quad S_{12}; \quad S_{13}; \quad S_{14}; \quad S_{15}; \quad S_{18} (\text{exo and endo}); \quad S_{20}. \)

A more recent and versatile method involves the use of titanocene pentasulfide which is easily prepared from \( \text{Cp}_2\text{TiCl}_2 \) and aqueous sodium or ammonium polysulfide. The air stable dark red solid \( \text{Cp}_2\text{TiS}_5 \) reacts with many S-Cl containing compounds at 0-20 °C as a sulfur transfer agent and the driving force for this reaction is the formation of \( \text{Cp}_2\text{TiCl}_2 \).

\[
\begin{align*}
S_n + \text{Cl}_2 & \rightarrow \text{Cl-S}_n\text{Cl} & n = 2, 6, 8 \\
\text{Cl-S}_6\text{Cl} + \text{Cl}_2 & \rightarrow \text{Cl-S}_4\text{Cl} + \text{S}_2\text{Cl}_2 \\
2 \text{NH}_3 + \text{H}_2\text{S} + \frac{1}{2} \text{S}_8 & \rightarrow (\text{NH}_4)_2\text{S}_5 \\
(\text{NH}_4)_2\text{S}_5 + \text{Cp}_2\text{TiCl}_2 & \xrightarrow{\text{CHCl}_3} \text{Cp}_2\text{TiS}_5 + \text{NH}_4\text{Cl} \\
& \text{88%} \\
& \text{dark red, air stable solid}
\end{align*}
\]
Synthesis of various allotropes of sulfur by titanocene pentasulfide

\[ \text{CS}_2 \xrightarrow{0^\circ C} \text{S}_{10} (35\%) + \text{Cp}_2\text{TiCl}_2 + \text{SO}_2 \]

\[ \text{SO}_2\text{Cl}_2 \]

\[ \text{S}_{15} (2\%) \quad \text{S}_{15} (8\%) \]

\[ \xrightarrow{25^\circ C} \]

\[ \text{S}_2\text{Cl}_2 \]

\[ \xrightarrow{0^\circ C} \text{S}_7 (23\%) + \text{Cp}_2\text{TiCl}_2 \]

\[ \xrightarrow{25^\circ C} \text{S}_9 (30\%) + \text{Cp}_2\text{TiCl}_2 \]

\[ \xrightarrow{0^\circ C} \text{S}_{11} (7\%) + \text{Cp}_2\text{TiCl}_2 \]

\[ \xrightarrow{25^\circ C} \text{S}_{13} (5\%) + \text{Cp}_2\text{TiCl}_2 \]

\[ \text{SO}_2\text{Cl}_2 \]

\[ \xrightarrow{0^\circ C} \text{S}_6 (87\%) + \text{Cp}_2\text{TiCl}_2 \]

\[ \xrightarrow{25^\circ C} \text{S}_{12} (11\%) + \text{Cp}_2\text{TiCl}_2 \]
The basic reactions of elemental sulfur leading to new reagents

- $\text{Na}_2\text{S} \xrightarrow{16\text{ Na}} \text{Cl}_2$
- $\text{Cl}_2 + \text{CS}_2/\text{CCl}_4 \xrightarrow{0-20 ^\circ\text{C}} 2\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3$
- $\text{NaOH} \xrightarrow{-\text{H}_2\text{O}} \text{S}_2\text{Cl}_2$
- $\text{S}_2\text{Cl}_2 \xrightarrow{} \text{SCl}_2$
- $\text{H}_2\text{S} \xrightarrow{\text{H}^+} \text{FeS} \xrightarrow{\text{Fe}}$
Unlike water, H₂S does not readily form metal complexes. It oxidatively adds to low-valent metal ions as SH and H units. It is slightly soluble in water and acts as a weak acid, giving the ion HS⁻.

Recent studies have demonstrated that hydrogen sulfide (H₂S) protects against multiple cardiovascular disease states in a similar manner as nitric oxide (NO). H₂S therapy also has been shown to augment NO bioavailability and signaling. The cardio-protective role of garlic is possibly related to the conversion of polysulfide group in allicin to H₂S.
Sulfur dioxide is primarily produced for sulfuric acid by contact process. In the United States in 1979, 23.6 million tonnes of sulfur dioxide were used in this way, compared with 150 thousand tonnes used for other purposes. Most sulfur dioxide is produced by the combustion of elemental sulfur. Some sulfur dioxide is also produced by roasting pyrite and other sulfide ores in air.

Sulfur dioxide is sometimes used as a preservative for dried apricots, dried figs, and other dried fruits, owing to its antimicrobial properties and ability to prevent oxidation and is called E220 when used in this way in Europe. As a preservative, it maintains the colorful appearance of the fruit and prevents rotting. It is also added to sulfured molasses.

Sulfur dioxide was first used in winemaking by the Romans, when they discovered that burning sulfur candles inside empty wine vessels keeps them fresh and free from vinegar smell. It is still an important compound in winemaking, and is measured in ppm in wine. It serves as an antibiotic and antioxidant, protecting wine from spoilage by bacteria and oxidation - a phenomenon that leads to the browning of wine and loss of flavor. Wines containing sulfur dioxide are typically labeled with "containing sulphite".
Oxoacids of Sulfur

Sulfoxyllic acid, $\text{H}_2\text{SO}_2$
(+2) (Unstable)
Salt: sulfoxylate

Sulfurous acid, $\text{H}_2\text{SO}_3$
(+4)
Salt: sulfite

Sulfuric acid, $\text{H}_2\text{SO}_4$
(+6)
Salt: sulfate

Peroxosulfuric acid, $\text{H}_2\text{SO}_5$
Caro's acid (+6)
Salt: peroxosulfate

Thiosulfuric acid, $\text{H}_2\text{S}_2\text{O}_3$
Stable as ether adducts at -78 °C
Salt: thiosulfate

Dithionous acid $\text{H}_2\text{S}_2\text{O}_4$
(+3) (Unstable)
Salt: dithionite

Disulfurous acid $\text{H}_2\text{S}_2\text{O}_5$
(Unstable)
Salt: disulfite (metabisulfite)

Dithionic acid $\text{H}_2\text{S}_2\text{O}_6$
(+5) known in solution
Salt: dithionate

Pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$
(Disulfuric acid, Oleum)
(+6)
Salt: disulfate

Peroxodisulfuric acid, $\text{H}_2\text{S}_2\text{O}_8$
(Marshall's acid)
(+6)
Salt: peroxodisulfate
Sulfuric acid

roasting green vitriol (FeSO₄).
940 AD
Abu Bekr Mohammad Ibn Zakariya Razi

destructive distillation of green vitriol
Johann Van Helmont (c.1600)

Justus von Leibig 1843

H₂SO₄ Production - Contact process

1910 80%
1960 15%

We may fairly judge of the commercial prosperity of a country from the amount of sulphuric acid it consumes.
Justus von Liebig

Nitrous Vitrol

GLOVER TOWER

CHAMBER

CHAMBER

CHAMBER

COOLER

Nitrogen Oxide

SO₂

Water

To Stack

H₂SO₄ (60%)  H₂SO₄ (50%)
In the lead chamber process, hot sulfur dioxide gas enters the bottom of a reactor named as the Glover tower where it is washed with nitrous vitriol (sulfuric acid with nitric oxide and nitrogen dioxide dissolved in it). Part of the sulfur dioxide is oxidized to sulfur trioxide and dissolved in the acid wash to form Glover acid. From the Glover tower a mixture of gases gets transferred to a chamber lined with lead blocks where it is reacted with more water. The chamber used to be a large, box-like room. Sulfuric acid formed condenses on the walls and collects on the floor of the lead chamber. Many lead chambers were connected in a series and the gases pass through each in succession. The acid produced, also called fertilizer acid, contains 62-68% H₂SO₄. After the gases have passed through the chambers they are passed into a reactor called the Gay-Lussac tower where they are washed with cooled concentrated acid and the nitrogen oxides and unreacted sulfur dioxide dissolves in the acid to form the nitrous vitriol, which is recirculated back to the Glover tower.
Contact Process for making concentrated sulfuric acid

\[ \text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + 2\text{VO}_2 \]

\[ 2\text{VO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{V}_2\text{O}_5 \]
More of sulfuric acid is made each year than is made of any other industrially produced chemical and more than 200 million tons of it was produced in the world in 2011.

The largest amount of sulfuric acid (more than 60%) is used to make phosphoric acid, used, in turn, to make phosphate fertilizers, calcium dihydrogen phosphate and the ammonium phosphates.

Concentrated sulfuric acid is a very strong dehydrating agent. It is often used as a drying agent and can be used to dehydrate many compounds such as carbohydrates. The acid reacts similarly with plant and animal matter such as skin and cellulose.

It is also used to make ammonium sulfate, which is a particularly important fertilizer in sulfur-deficient soils.

Aluminium sulfate which is used in paper manufacture and water purification is another useful product.

Sulfuric acid is used in processing metals, e.g., in pickling (cleaning) iron and steel before plating them with tin or zinc. It is the electrolyte in lead-acid batteries, commonly used in house hold power inverters and automobiles (often called battery acid, which contains about 33% $\text{H}_2\text{SO}_4$).
Theodore Roosevelt went on a hunting expedition in Brazil in 1913. Standing on the bank of the Amazon River, he watched piranhas attack a cow with shocking ferocity. It was a classic scene: water boiling with frenzied piranhas and blood, and after about a minute or two, a skeleton floating to the suddenly calm surface.

A carefully made mixture of 30% $\text{H}_2\text{O}_2$ and conc. $\text{H}_2\text{SO}_4$ in 1:3 ratio with the pet name ‘Piranha solution’ is used extensively in electronic industry to remove photoresist residues from silicon wafers. This solution is used for oxidatively removing organic residues from electronic surfaces and also to make silicon surfaces hydrophilic by introducing hydroxyl groups. The formation of the strong oxidant per oxy monosulfuric acid (Caro’s acid; $\text{H}_2\text{SO}_5$) ($E^0 = 2.51$ V) and nascent oxygen are two reasons for the very high reactivity of this solution. The vigor with which this reaction eats away organic residues is similar to the way flesh eating Piranha fish do so and so the name. The potassium salt of Caro’s acid is available commercially as a stable triple salt with the trade name Oxone 2K$\text{HSO}_5$.K$\text{HSO}_4$.K$\text{SO}_4$

$$\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_5 + \text{H}_2\text{O}$$

https://www.youtube.com/watch?v=TAYqr-mX000
https://www.youtube.com/watch?v=crtQPZW7vgE
https://www.youtube.com/watch?v=ATZlj7SObrU
Sulfuric acid: The Indigo connection

Marco Polo (13th century) was the first to report on the preparation of indigo in India. Indigo was quite often used in European easel painting since the Middle Ages.

Indigo was soluble in its reduced, yellow form and insoluble in its oxidized, blue form. If clothes were dyed in tropical climates, it was easy to use indigo. During the dying process the leaves of the plant is kept in water and allowed to ferment anaerobically, and clothes are dipped the in the yellow colored dyebath. After exposing the clothes to air, the dye became blue and insoluble in water. Importing indigo to Europe presented a problem. Once the dye was oxidized, it was insoluble in water and could not be used as dye.

In 1744, it was discovered that indigo dissolves in conc. sulfuric acid, forming a water-soluble dye which was named Indigo Carmine.

Indigo carmine. About 20 million kg are produced annually, mainly for blue jeans. On average, a pair of blue jean trousers requires 3–12 g of indigo. It is also used as a food colorant.
Chemistry of thiosulfate

Traditionally it has been used as a primary standard in iodometric titrations as Na$_2$S$_2$O$_3$·5H$_2$O has an excellent shelf life and is not hygroscopic facilitating its easy and accurate weighing. In an iodometric titration it reduces I$_2$ or more specifically its soluble form in water, I$_3^-$ to I$^-$ and gets itself oxidized to tetrathionate.

Thiosulfate is extremely useful for deactivation and safe disposal of halogens and cyanide.

Thiosulfate also has the capability of forming water soluble complexes with AgBr and this property has been utilized in converting undeveloped AgBr grains to soluble silver thiosulfate complexes and removing it from black and white photographic films and X-ray sheets.

It provides a non toxic alternative to the traditional cyanide route in the extraction of gold.
Sulfur based fluorinating agents

SF$_4$, which is a highly reactive gas has the ability to convert carbonyl (C=O) groups to CF$_2$ groups. It also has the unique ability to convert a carboxylic acid group to a CF$_3$ group. Because of the difficulty in handling of SF$_4$ due to its extreme reactivity and instability, a few SF$_3$ and SF$_2$ based reagents have been developed which are liquids or solids and which are easier to store and handle.

\[
\text{(CH}_3\text{OCH}_2\text{CH}_2\text{)}_2\text{N-SF}_3 \quad \xrightarrow{\text{Me}_3\text{SiNR}_2 \text{ (b.p. -38 °C)}} \quad \text{SF}_4 \quad \xrightarrow{\text{Me}_3\text{SiNMe}_2} \quad \text{Et}_2\text{NSF}_3 \quad \xrightarrow{\text{HBF}_4\cdot\text{OEt}_2} \quad \text{[Et}_2\text{NSF}_3]^+\text{BF}_4^- \quad \text{[Et}_2\text{N-SF}_3]^+\text{BF}_4^-
\]

(Deoxofluor) (b.p. 71 °C/ 0.4 mm Hg)
R = CH$_3$OCH$_2$CH$_2$

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<th>Fluorinating agent</th>
<th>SF$_4$</th>
<th>(CH$_3$OCH$_2$CH)$_2$N-SF$_3$</th>
<th>Et$_2$NSF$_3$</th>
<th>[Et$_2$N=SF$_3$]$^+$BF$_4^-$</th>
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<tr>
<td>Substrate</td>
<td>SF$_4$</td>
<td>(CH$_3$OCH$_2$CH)$_2$N-SF$_3$</td>
<td>Et$_2$NSF$_3$</td>
<td>[Et$_2$N=SF$_3$]$^+$BF$_4^-$</td>
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<td>R-OR' or RC(O)OH</td>
<td>R-CF$_3$ (above 85°C)</td>
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<td>With Et$_3$N, HF</td>
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Chemistry of thionyl chloride

Thionyl chloride (B. P 74.6 °C) is especially for conversion of OH groups to Cl groups. It is also an excellent dehydrating agent and is often used for removing water of crystallization/hydration of metal salts. The advantage of this reaction is that the side products of the reaction are highly volatile HCl and SO₂ which can be easily driven out from the reaction flask by an inert gas. Another important reaction is the conversion of amide to nitriles.

Different ways of preparing thionyl chloride

\[
\begin{align*}
\text{SO}_3 + \text{SCl}_2 & \rightarrow \text{SOCl}_2 + \text{SO}_2 \\
\text{SO}_2 + \text{COCl}_2 & \rightarrow \text{SOCl}_2 + \text{CO}_2 \\
\text{SO}_2 + \text{PCl}_5 & \rightarrow \text{SOCl}_2 + \text{POCl}_3
\end{align*}
\]
Sulfuryl chloride (b.p. 69.4 °C) is well known as a very useful chlorinating agent. It brings about almost all reactions which chlorine gas does. Unlike Cl₂ gas, whose reaction in stoichiometric ratio with a substrate is often difficult, SO₂Cl₂ can be used for controlled chlorination, especially when an organic compound has multiple double bonds. Similar to Cl₂, sulfuryl chloride also undergoes substitutive chlorination and oxidative chlorination. Unlike thionyl chloride, sulfuryl chloride when reacted with water results in the formation of sulfuric acid. The advantage of using sulfuryl chloride in oxidative chlorination is that the side product formed is SO₂ gas which can be easily driven out from the system.
Sulfur hexafluoride

Sulfur hexafluoride is a dense gas, first prepared in 1900 by Henri Moissan by the reaction of elemental sulfur and fluorine gas. It is a colourless, tasteless, non-flammable, non-toxic and insoluble gas at room temperature. \( \text{SF}_6 \) is made of octahedral shaped molecules, with a bond length of 1.561 Å (gas phase). It is poorly reactive due to kinetic reasons. The \( \text{SF}_6 \) gas is one of the heaviest and very poorly reactive gases. Density of this gas at 20 °C and 1 atm, is 6.139 kg/m\(^3\) which is approximately 5 times higher than air under the same conditions.

\( \text{SF}_6 \) when heated to 500 °C does not decompose. It does not react with glass, even up to its softening temperature. It does not react with metals such as magnesium and copper, even at red heat. It also does not react with molten sodium, and only with boiling sodium to form \( \text{Na}_2\text{S} \) and \( \text{NaF} \). Phosphorus and arsenic can be distilled in \( \text{SF}_6 \) vapor without decomposition.

\( \text{SF}_6 \) is also one of the most potent greenhouse gases with greenhouse effect 22,000 times that of the reference compound CO\(_2\). It is also having a predicted lifetime in the atmosphere of 3200 years.

Its important uses include as dielectric material for high voltage transformers, as a blanket for molten melt of magnesium and as a filler for multipane windows for noise reduction. It was also used in the soles of ‘Nike Air’ shoes for its flexibility. Due to concern raised on the green house effect, Nike has stopped using \( \text{SF}_6 \) sometime back.
Reactions of Sulfur Hexafluoride

**Room Temperature**

\[
\text{V(C}_5\text{H}_5)_2 + \text{SF}_6 \rightarrow \text{V-F}
\]

\[
\text{Cr(C}_5\text{Me}_5)_2 + \text{SF}_6 + \text{DMAP} \rightarrow \text{Cr-F}
\]

\[
\text{RhH(PEt}_3)_3 + \text{SF}_6, \text{PET}_3, \text{HSiEt}_3 \rightarrow \left[\text{Rh(H)}_2(\text{PET}_3)_4\right]^+ \text{HF}_2^-
\]

\[
\text{R}^1\text{C}═\text{CR}^2 + \text{SF}_6 + \text{Ru(bipy)}_3(\text{PF}_6)_2 \rightarrow \text{R}^1\text{C}═\text{CR}^2 \text{F}
\]

**High Temperature**

\[
\text{SF}_6 + 2 \text{SO}_3 \rightarrow \text{3 SO}_2\text{F}_2
\]

\[
\text{SF}_6 + \text{AlCl}_3 \rightarrow \text{AlF}_3 + \text{Cl}_2 + \text{SCl}_n
\]

\[
\text{SF}_6 + 8\text{Na} \text{ boiling sodium} \rightarrow \text{Na}_2\text{S} + 6\text{NaF}
\]
The first sulfonamide, trade-named as Prontosil, was made by Bayer laboratories was the first medicine ever discovered that could effectively treat a range of gram positive bacterial infections of the body. It had a strong protective action against infections caused by streptococci, including blood infections.

Human beings get their folic acid from food while Bacteria has to make folic acid from the medium and the organic compound it requires is para amino benzoic acid (PABA). Sulfonamides are structural analogues of PABA. Sulfonamides can competitively inhibit the folate synthesis (Bacteriostatic- stopping multiplication).