

Greenwood & Earnshaw

2nd Edition

Chapter 15

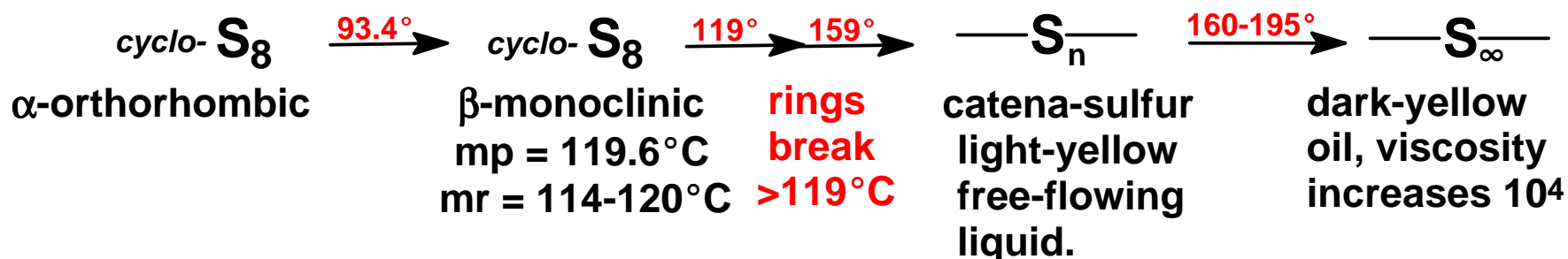
Sulfur

Elemental Sulfur

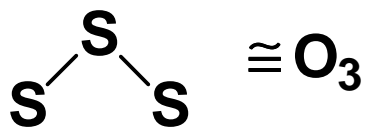
$^{32}_{16}\text{S}$ 95.02 %
 $^{33}_{16}\text{S}$ 0.75 %
 $^{34}_{16}\text{S}$ 4.21 %
 $^{36}_{16}\text{S}$ 0.02 %
 $^{35}_{16}\text{S}$ β emitter
 $t^{1/2} = 87.4 \text{ d}$

Sulfur has many allotropic forms: **cy-S₈** D_{4d} Crown most stable.

Very complex phase relationships exist:



Intensely colored diradicals form in the mixture, cyclic species occur and viscosity decreases.

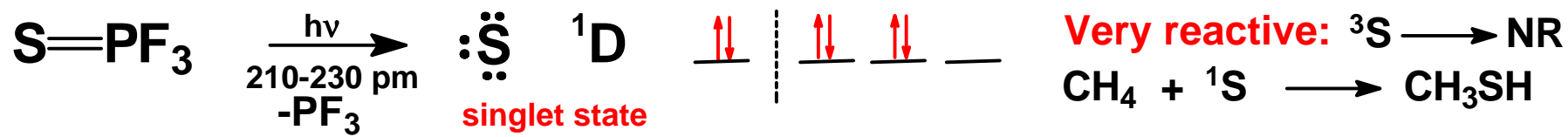
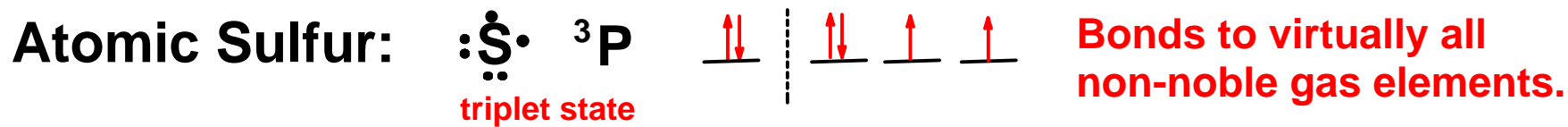


Cherry red color, singlet state.

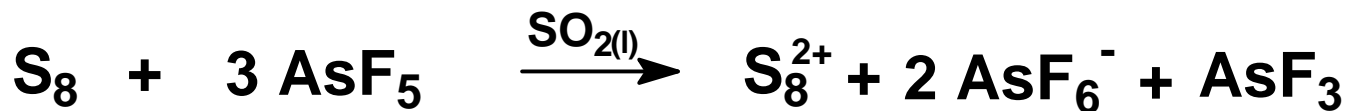
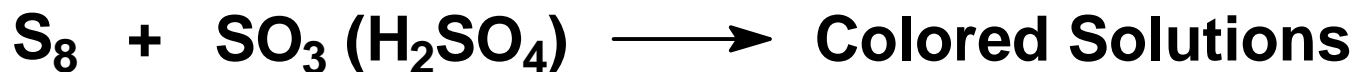
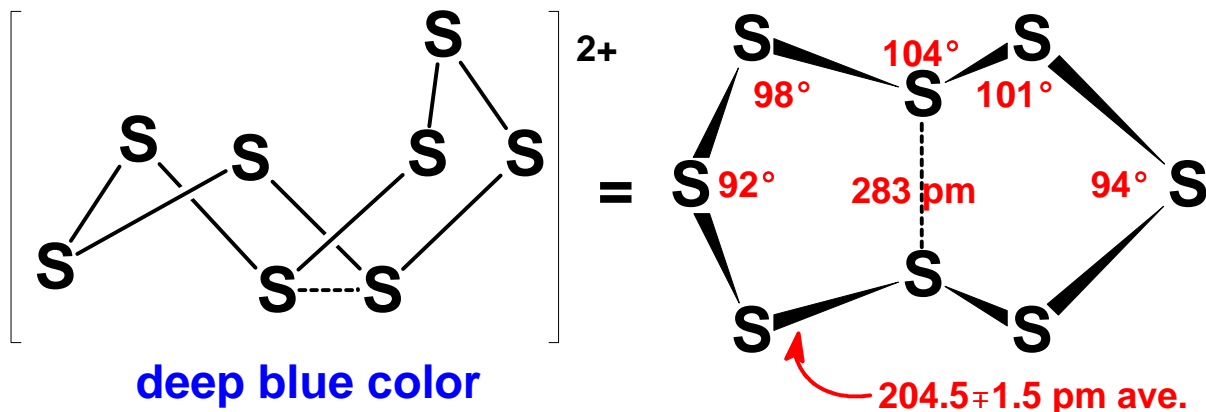
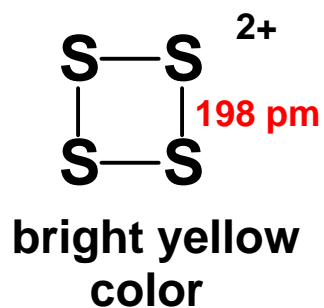


Violet color, diradical, $^3\Sigma_g$ & $^1\Delta$ d_{S-S} 188.7pm, DH_{diss} = 421.3 kJ/mol.

Atomic Sulfur & Sulfur Cations



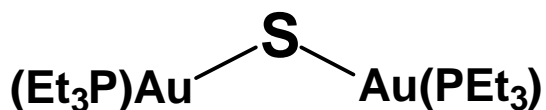
Sulfur Cations:



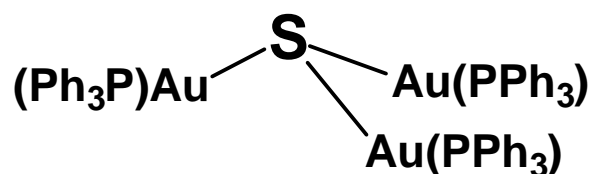
Sulfur as a Ligand

Sulfur is a "Class b" or "soft" donor ligand, cf. Oxygen is a "Class A" or "hard". S and R₂S are known, dπ-bonding (cf. PR₃) is possible. S is usually a 2e⁻ donor but can donate up to 6e⁻ in clusters.

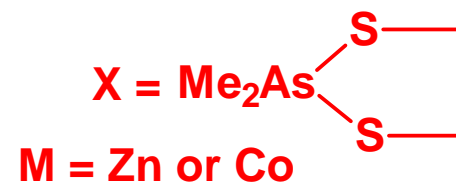
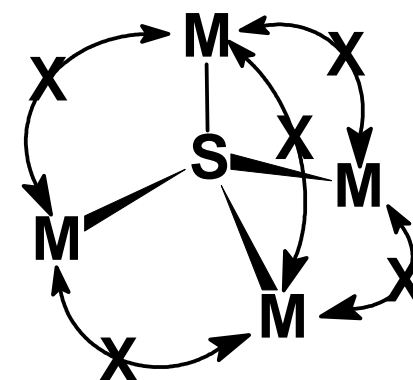
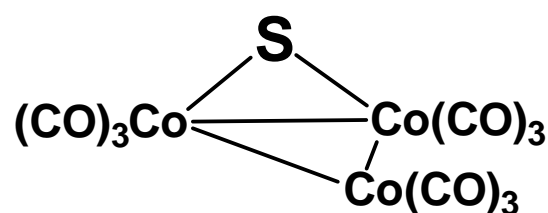
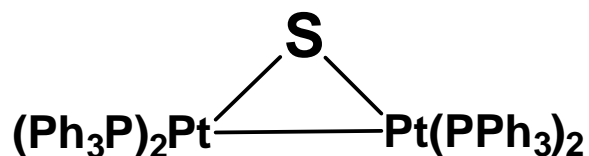
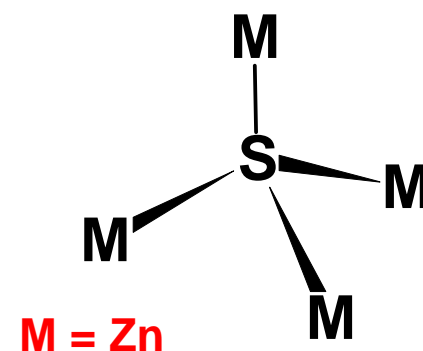
2e



4e

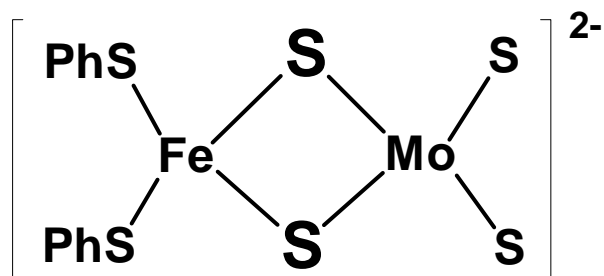


6e

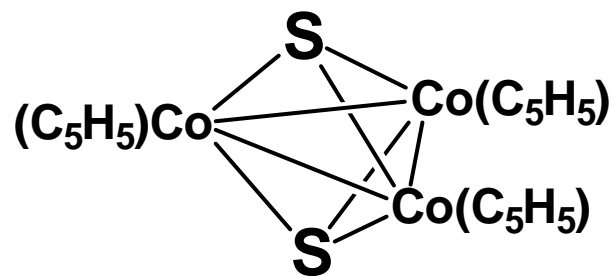


Sulfur as a Ligand

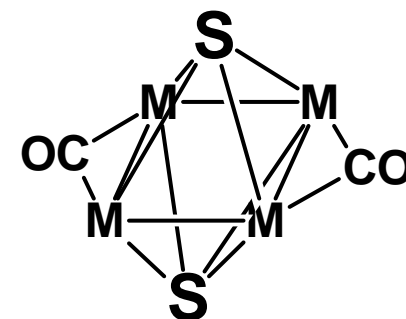
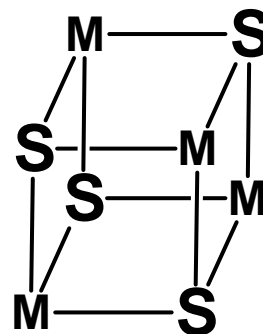
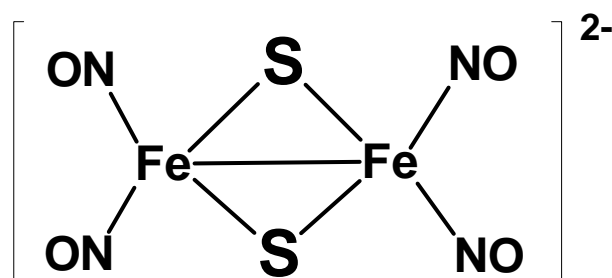
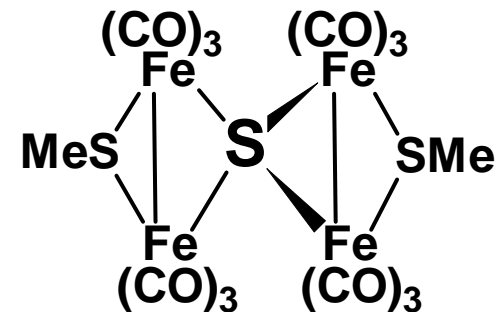
2e



4e



6e

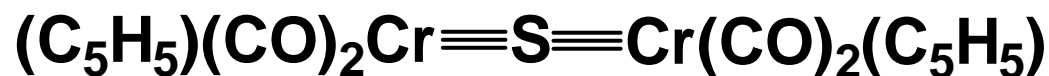


$\text{M} = \{\text{Fe}(\text{NO})\}$ or $\{\text{M}'(\text{C}_5\text{H}_5)\}$

$\text{M}' = \text{Cr}, \text{Mo}, \text{Fe}, \text{Co}$
also ferredoxins

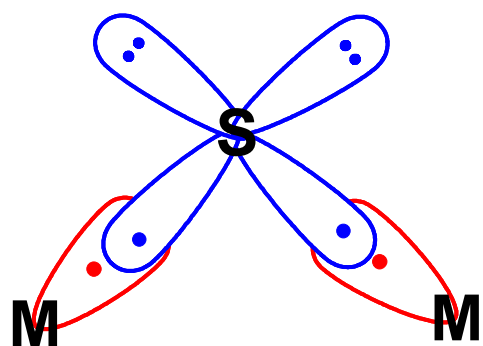
$\text{M} = \{\text{Co}(\text{CO})_2\}$

This linear η^2 complex can also be regarded as a $6e^-$ S donor.

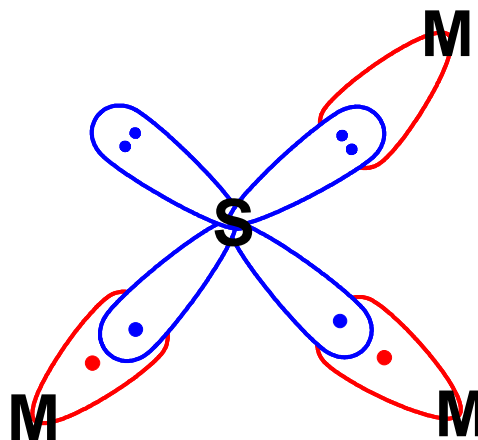


Bonding of Sulfur Ligands

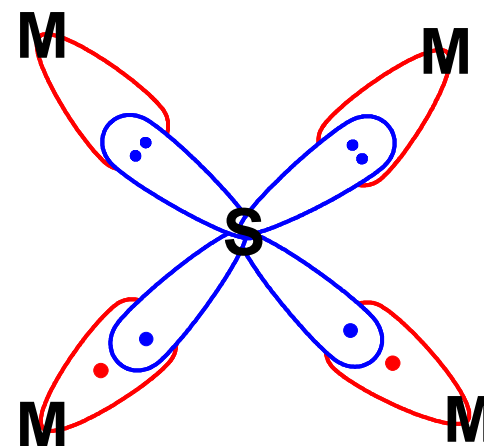
2e⁻



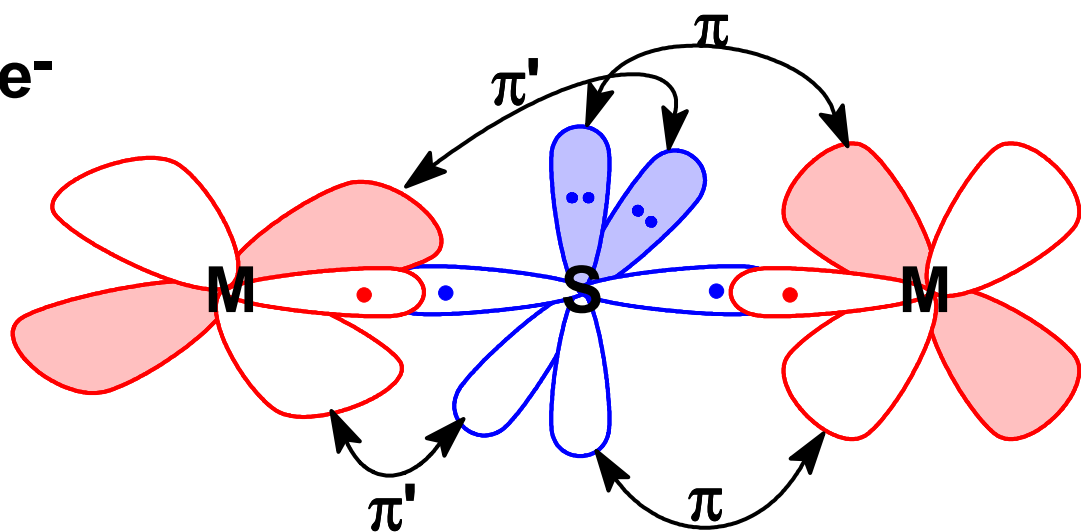
4e⁻



6e⁻



6e⁻



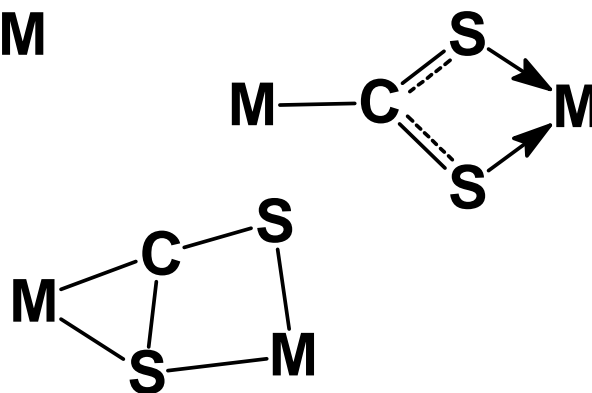
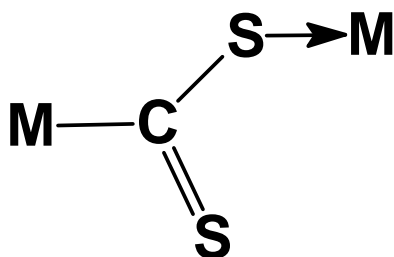
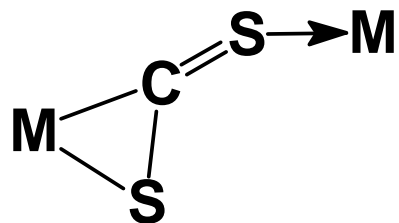
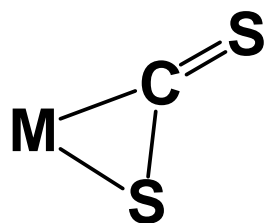
Carbon Disulfide

Synthesis:

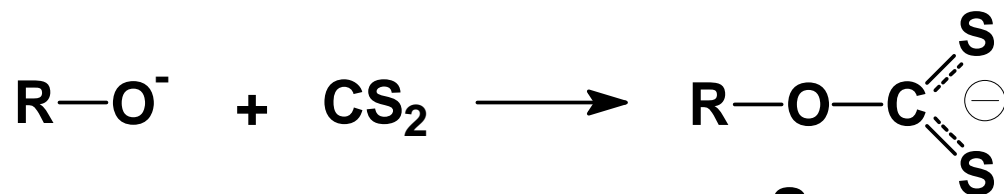


Very important industrial chemical, very toxic, extensive complex chemistry.

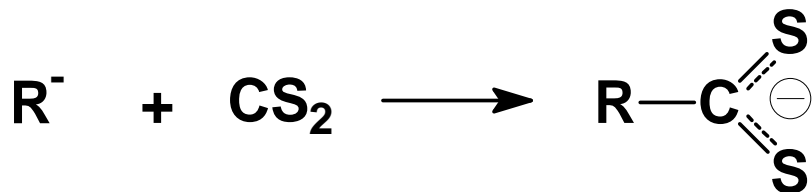
Carbon disulfide as a ligand:



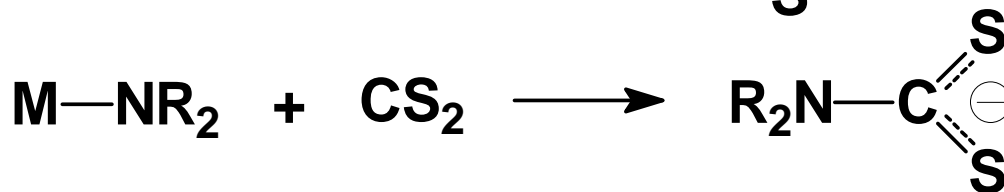
Derivative ligands from carbon disulfide:



Xanthates (dithiocarbonates)
R = Et used to dissolve cotton fiber to make viscose rayon.



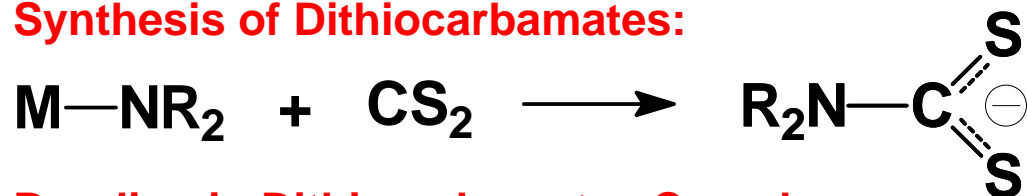
Dithiocarboxylates



Dithiocarbamates, very important agriculturally as fungicides, M = Mn, Zn, Fe

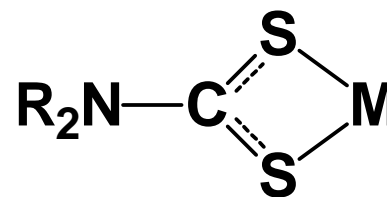
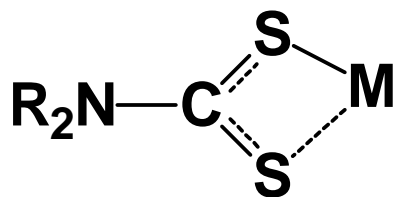
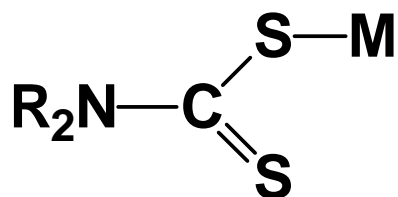
Dithiocarbamates & Other Ligands

Synthesis of Dithiocarbamates:

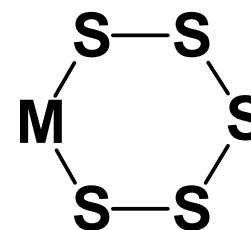
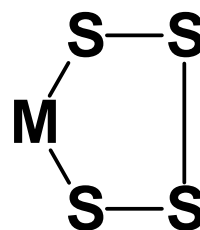
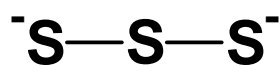


Dithiocarbamates, very important agriculturally as fungicides, $M = Mn, Zn, Fe$

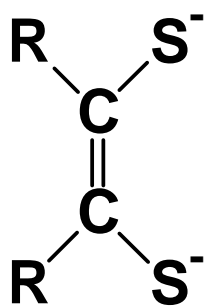
Bonding in Dithiocarbamates Complexes:



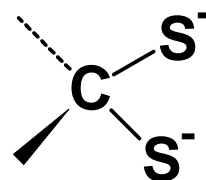
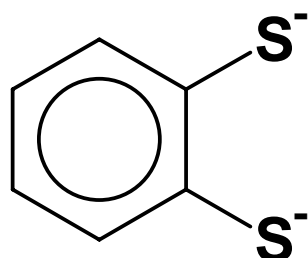
Other sulfur Ligands:



$n = 2, 3$ make chelates

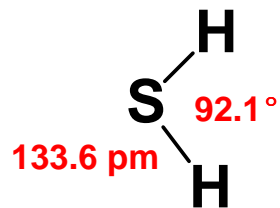


1,2-dithiolato-



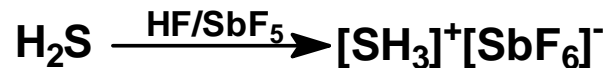
1,1-dithiolato-

Sulfur Hydrides – The Sulfanes



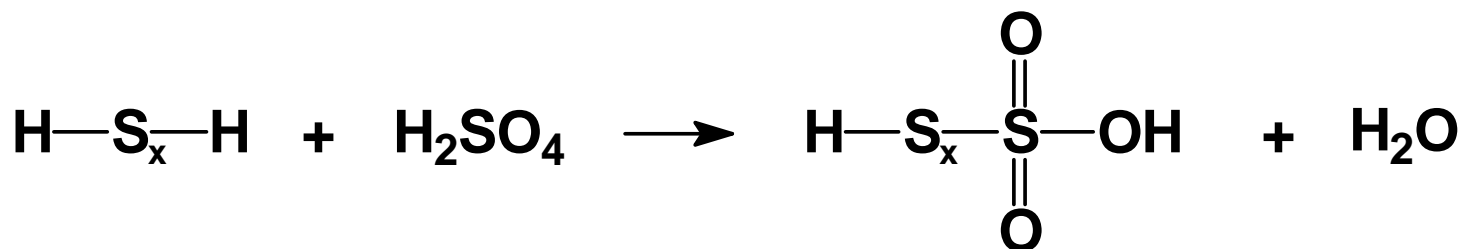
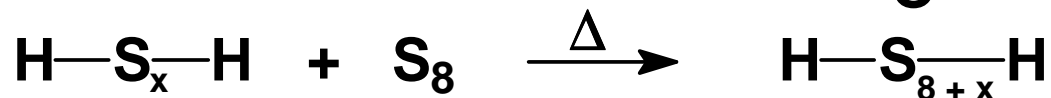
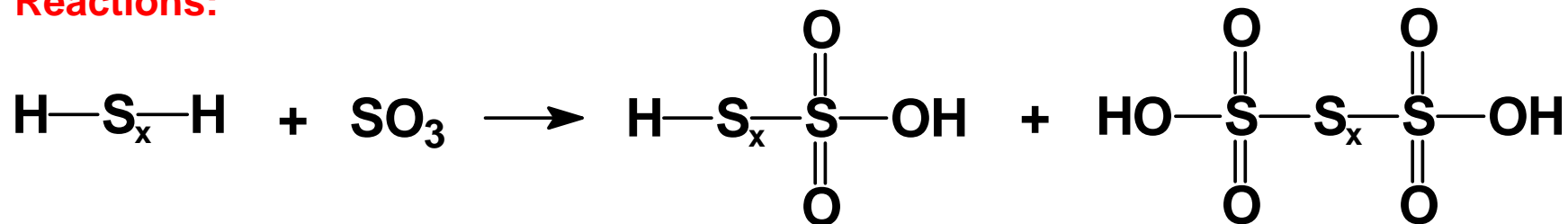
bp -60.3°C
 mp -85.6°C
 $\text{pK}_{\text{a}1} = 6.88$
 $\text{pK}_{\text{a}2} = 14.15$

Hydrogen sulfide is a very toxic gas (~HCN). A weak dibasic acid in water. A base in super acid media:

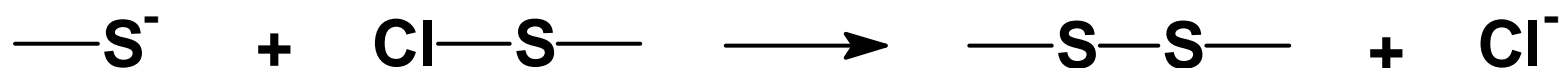
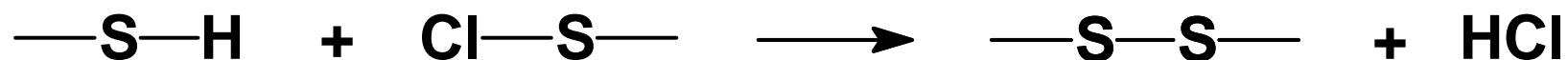


Sulfanes $n = 1-6$ isolated and characterized
 $n = 7 - \infty$ are known as mixtures. All sulfanes are weak acids, all slowly oxidize in air to sulfur.

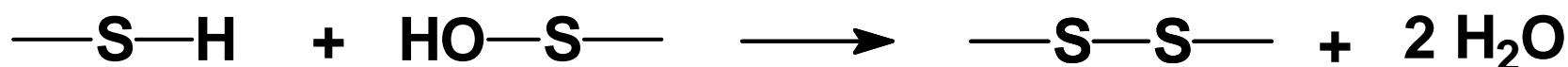
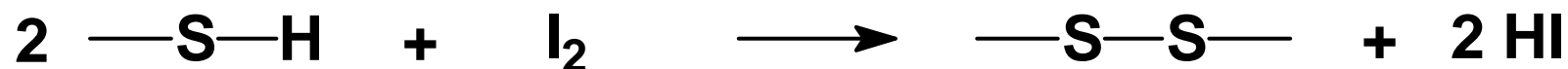
Reactions:



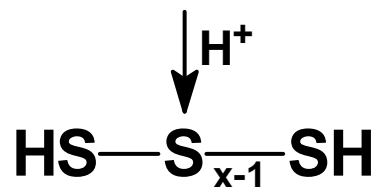
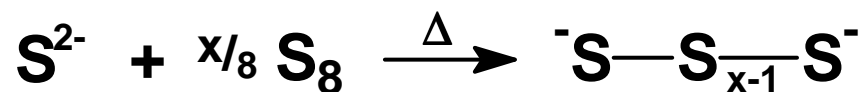
Four General Methods to Make S-S Bonds



This is the reaction in iodometric titrations:



Sulfur Anions - Polysulfides

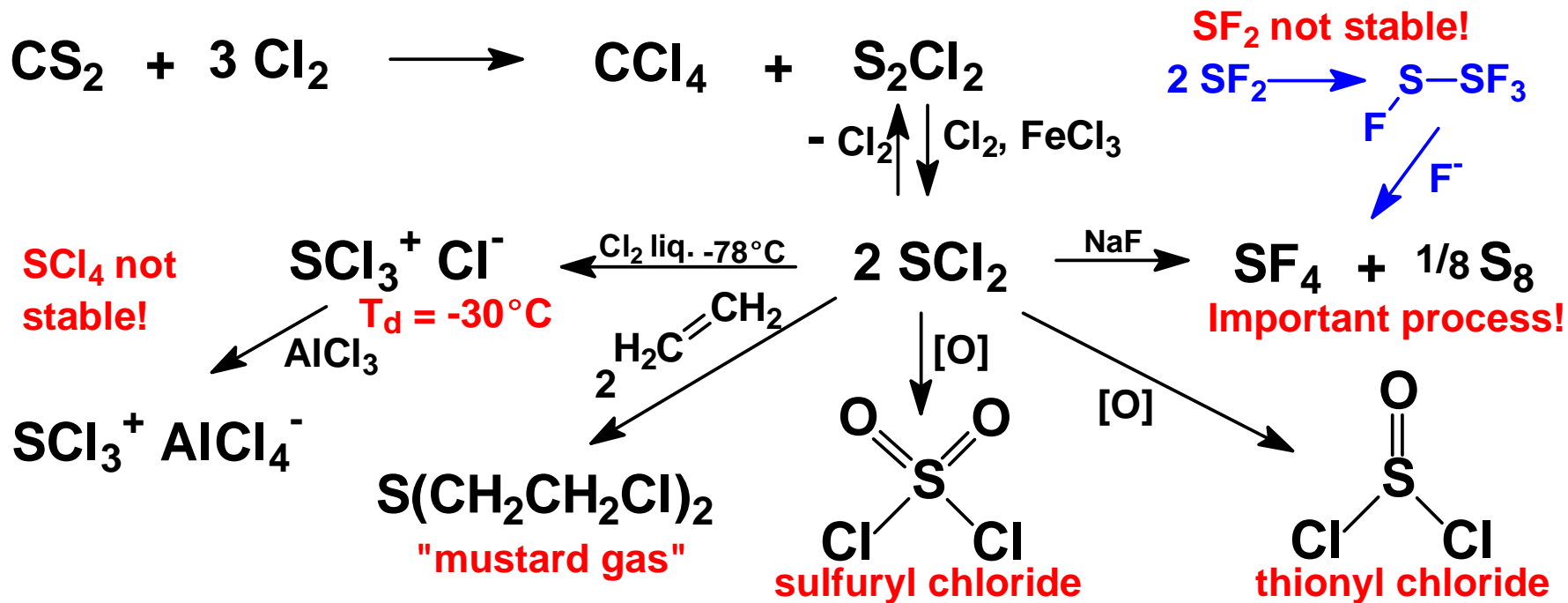
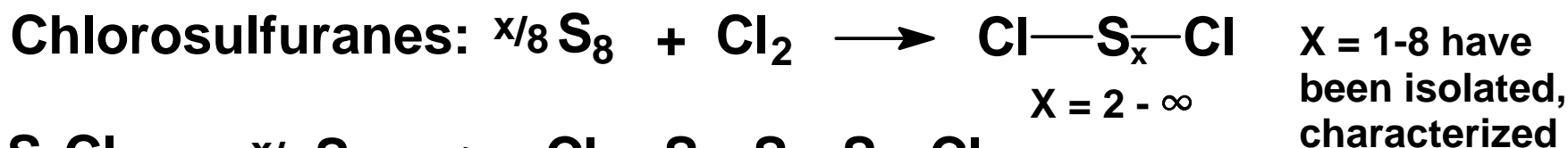


Polysulfides $x = 1-4$ isolated and characterized, $x 1- \infty$ known as mixtures. All are strong bases, hydrolyse in water to hydrogen sulfide. Potent fungicides "lime sulfur" used since antiquity.

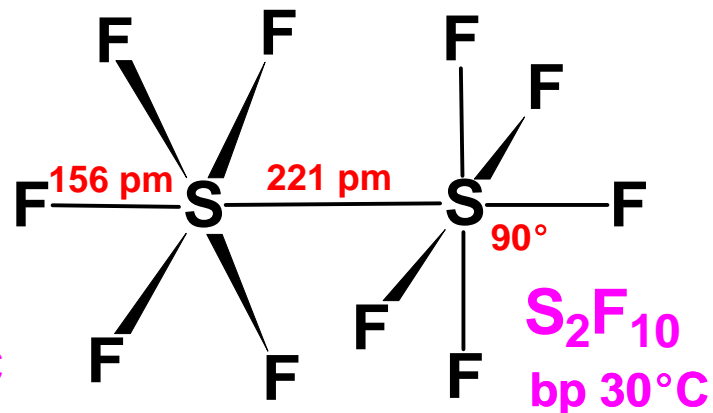
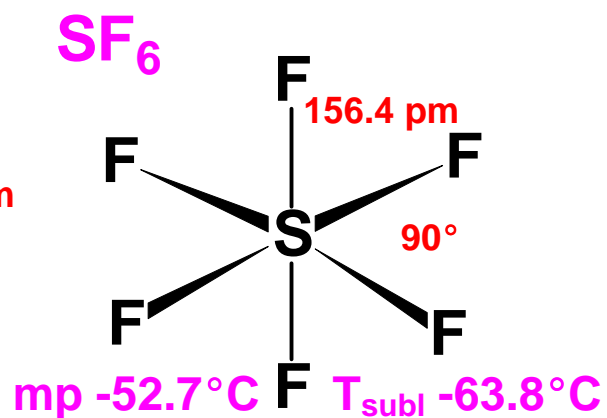
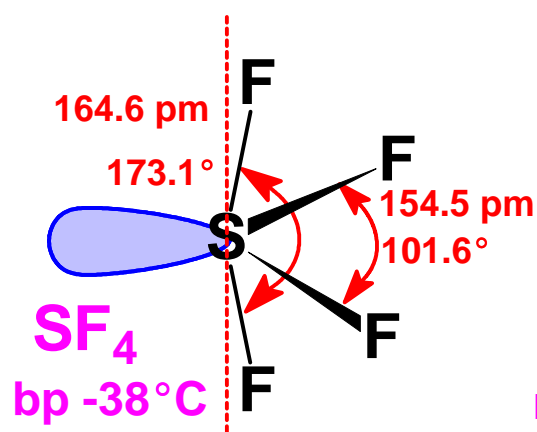
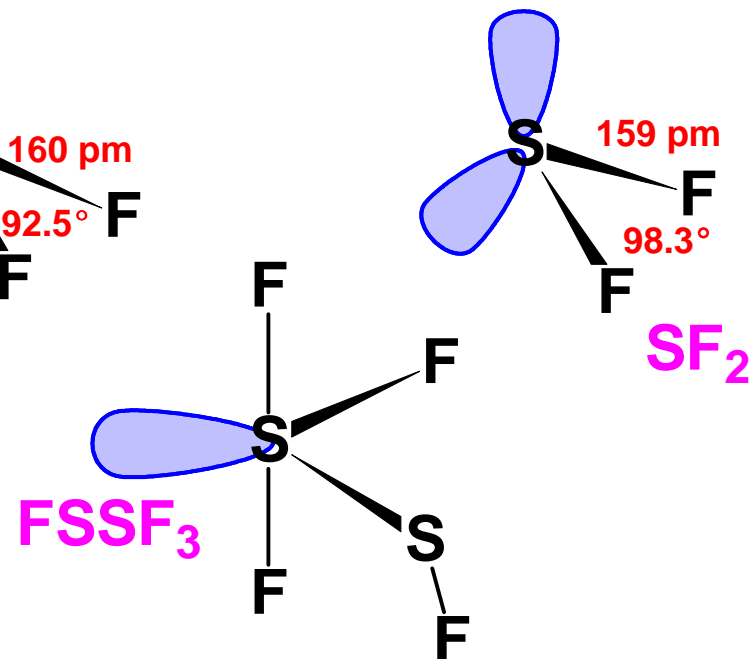
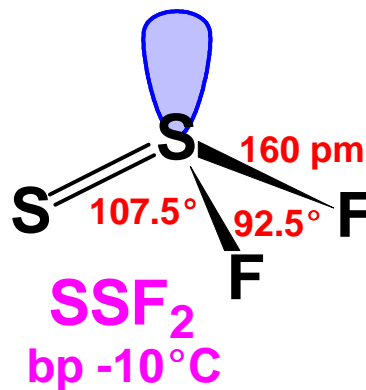
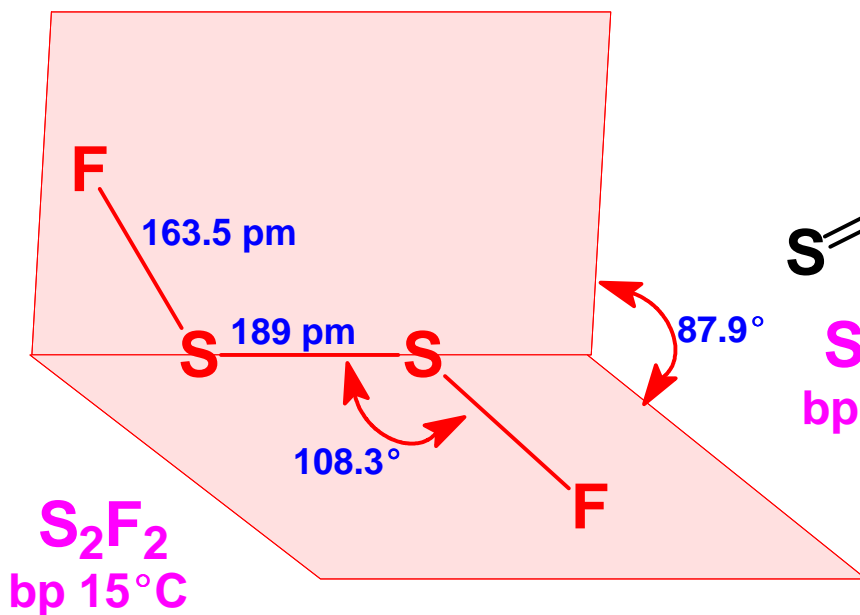
Sulfur Halides

Strengths of Sulfur-Element Bonds:

S—X	X =	F	Cl	Br	I	S	I ₂
ΔH_{diss} kJ/mol		327	271	218	~170	225	150

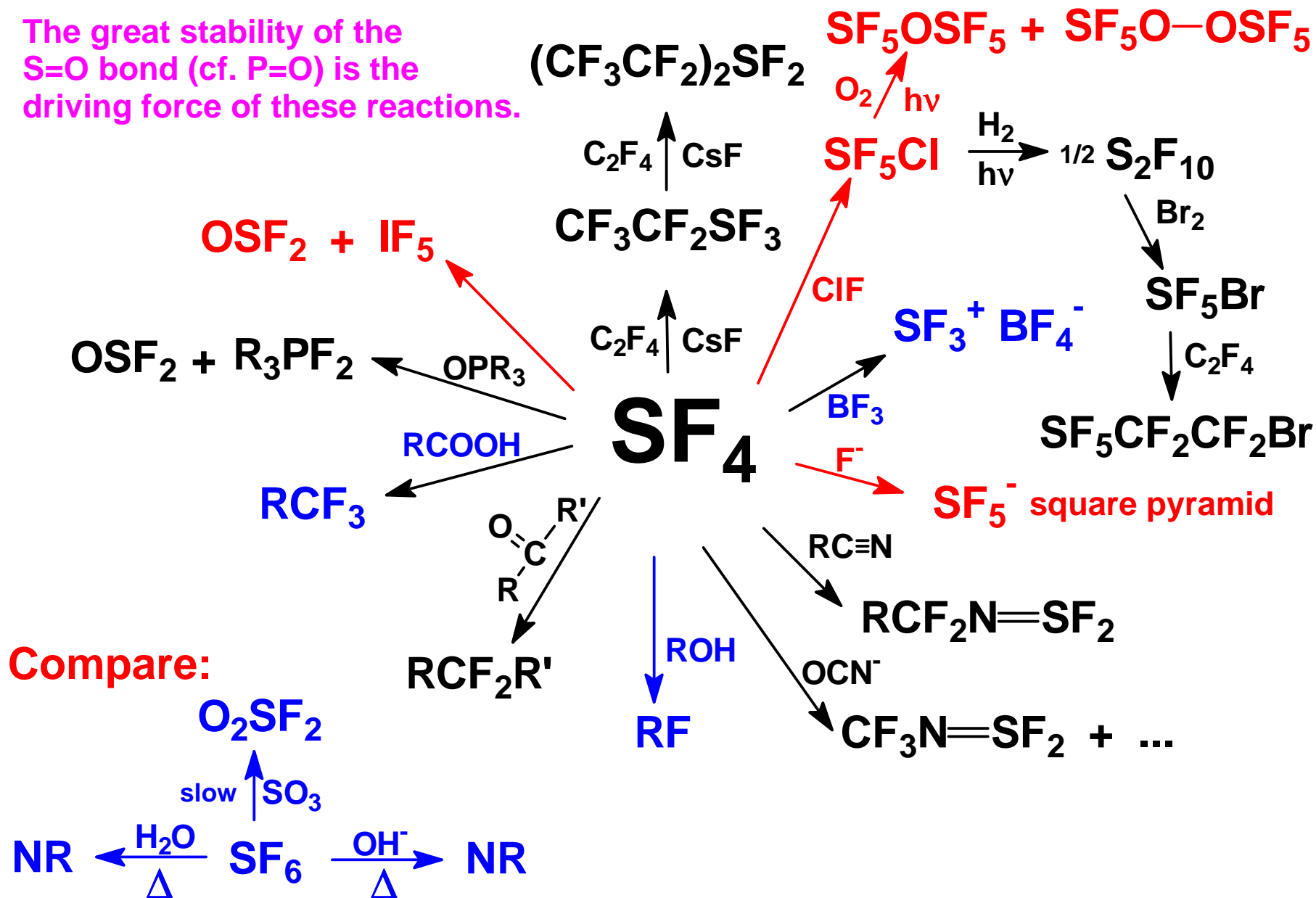


Sulfur Fluorides



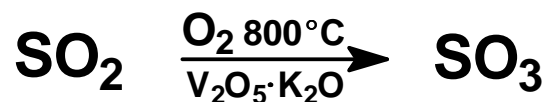
Reactions of Sulfur Tetrafluoride

The great stability of the S=O bond (cf. P=O) is the driving force of these reactions.



Sulfur Dioxide - Reactions

Most sulfur dioxide is used in the manufacture of sulfuric acid. Lesser amounts are used as reducing agents (aqueous), bleaches and as a food sterilant and preservative. Starting point for dithionites, dithionates and thiosulfates. It is an excellent solvent for molecular compounds has a high dipole moment but a low dielectric constant. Sulfur dioxide is a serious air pollutant contributing to acid rain. Has the ability to insert into Metal-Alkyl bonds.

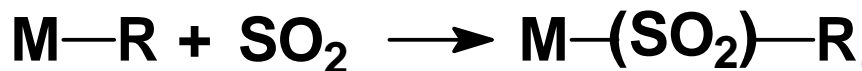


With first row transition metals:

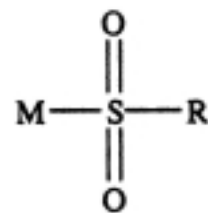


In absence of DMSO metal dithionites are produced. $\text{M(II)} [\text{S}_2\text{O}_4]^{-2}$

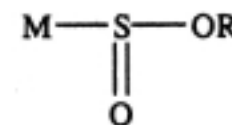
Sulfur dioxide has the ability to insert into a metal alkyl bond.



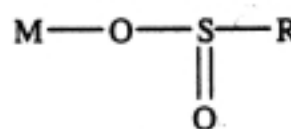
Several different types of products may be formed in this reaction: \longrightarrow



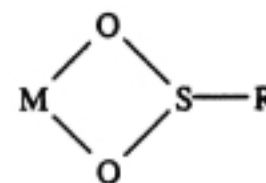
S-sulfinate



O-alkyl-S-sulfoxylate



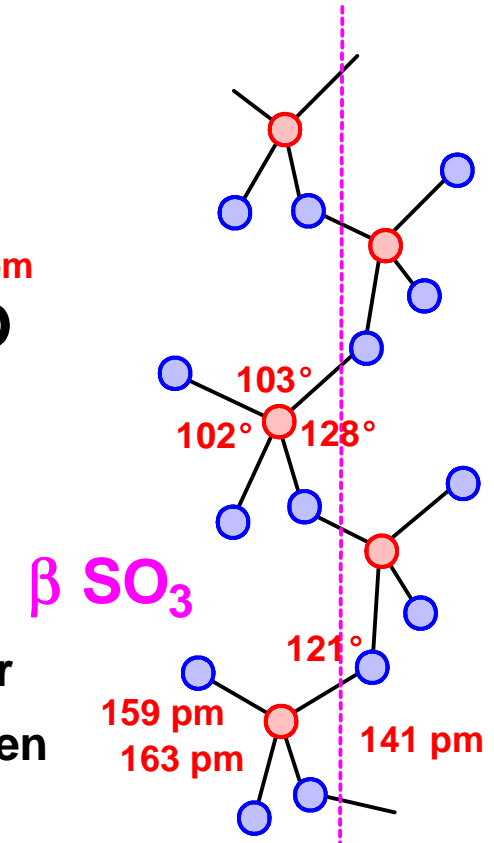
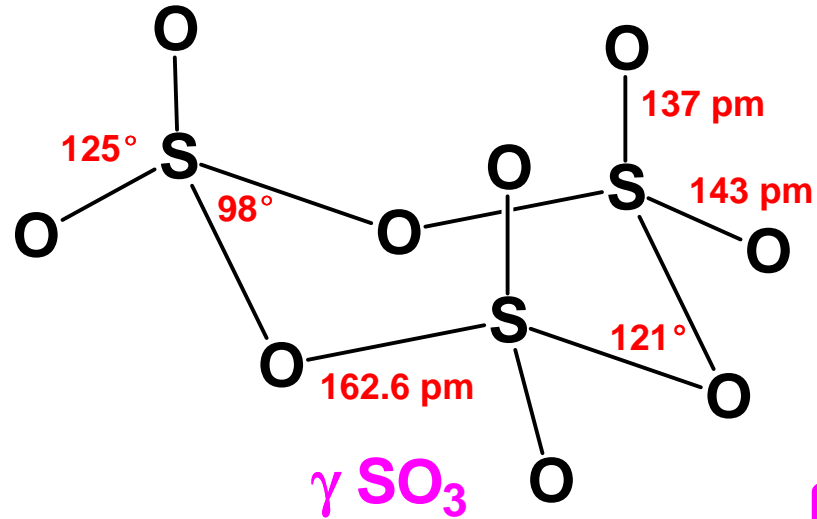
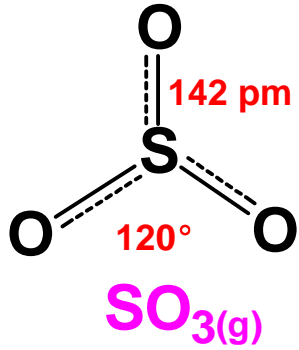
O-sulfinate



O-O'-sulfinate

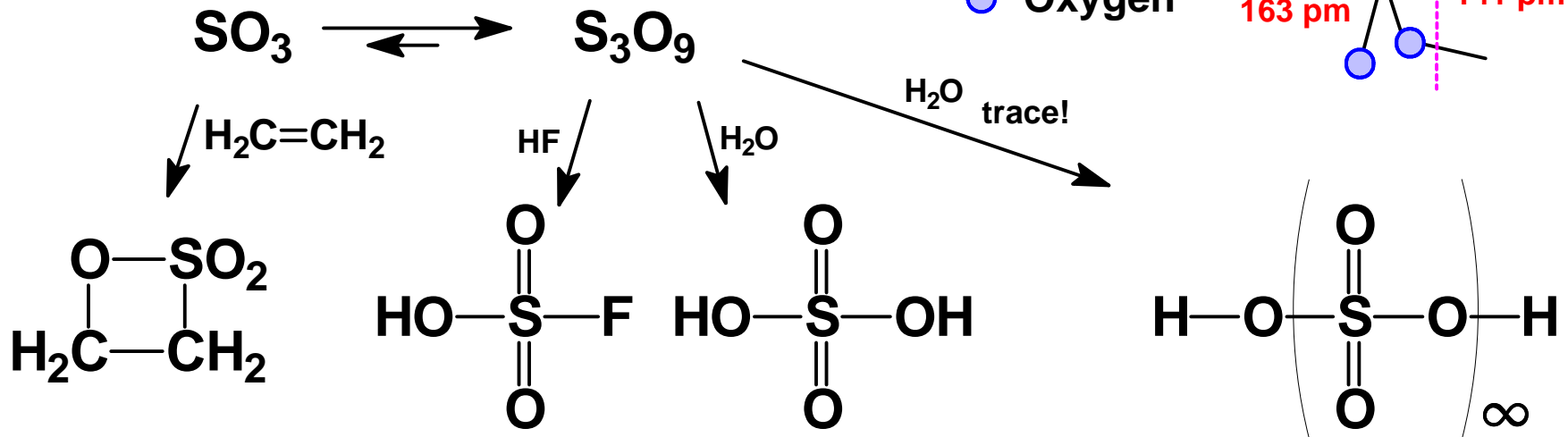
Examples of all except possibly the second mode are known.

Sulfur Trioxide

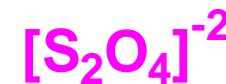
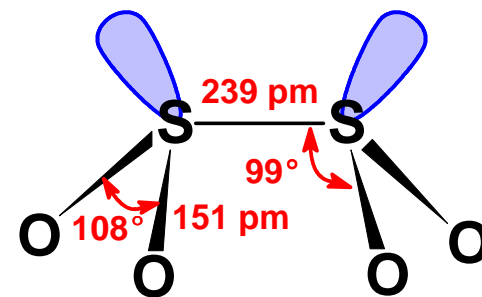
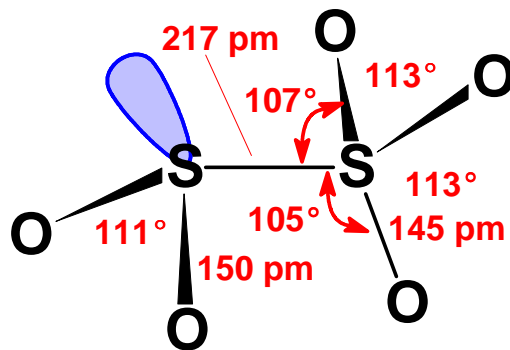
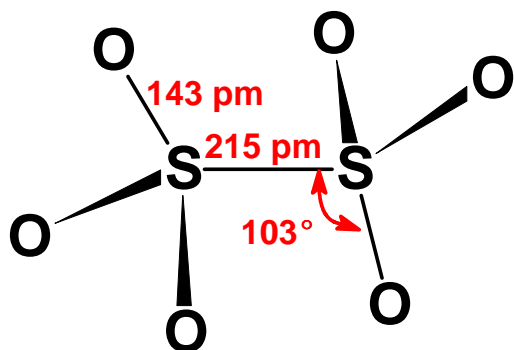


● Sulfur
● Oxygen

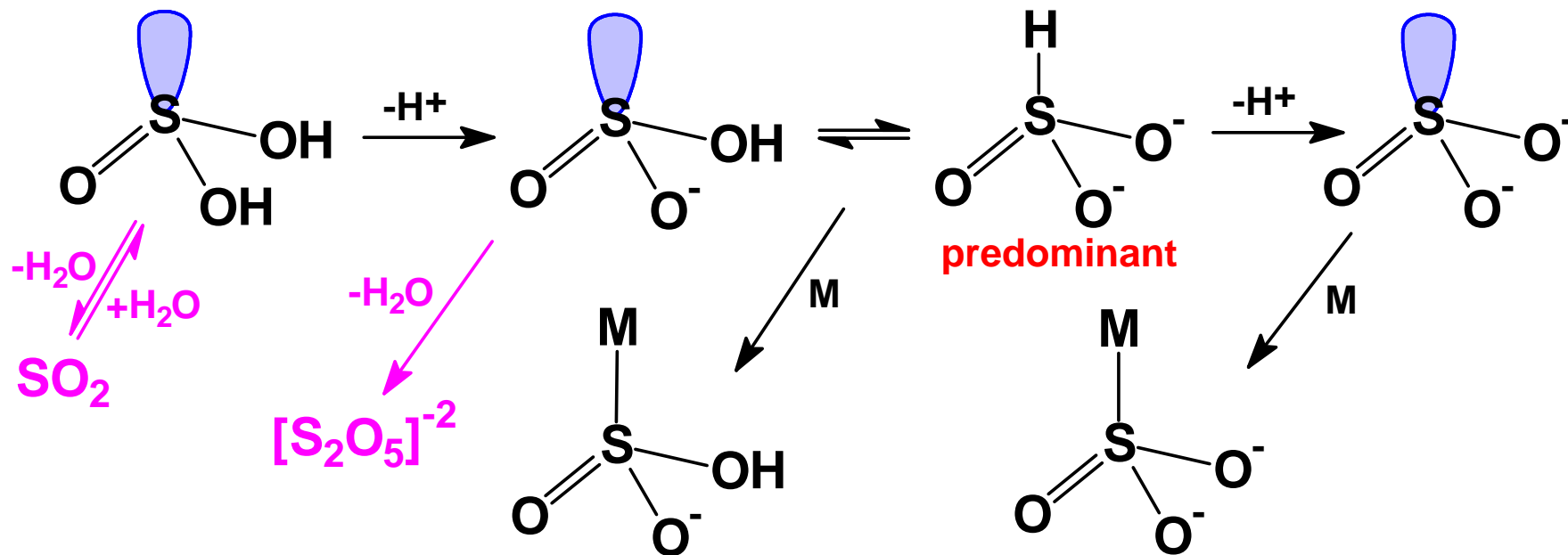
Reactions:



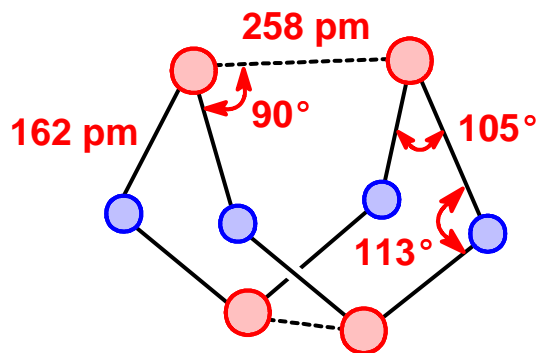
Oxoacids of Sulfur



Some interesting equilibria:



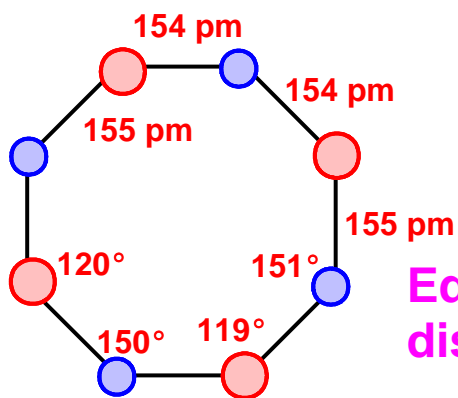
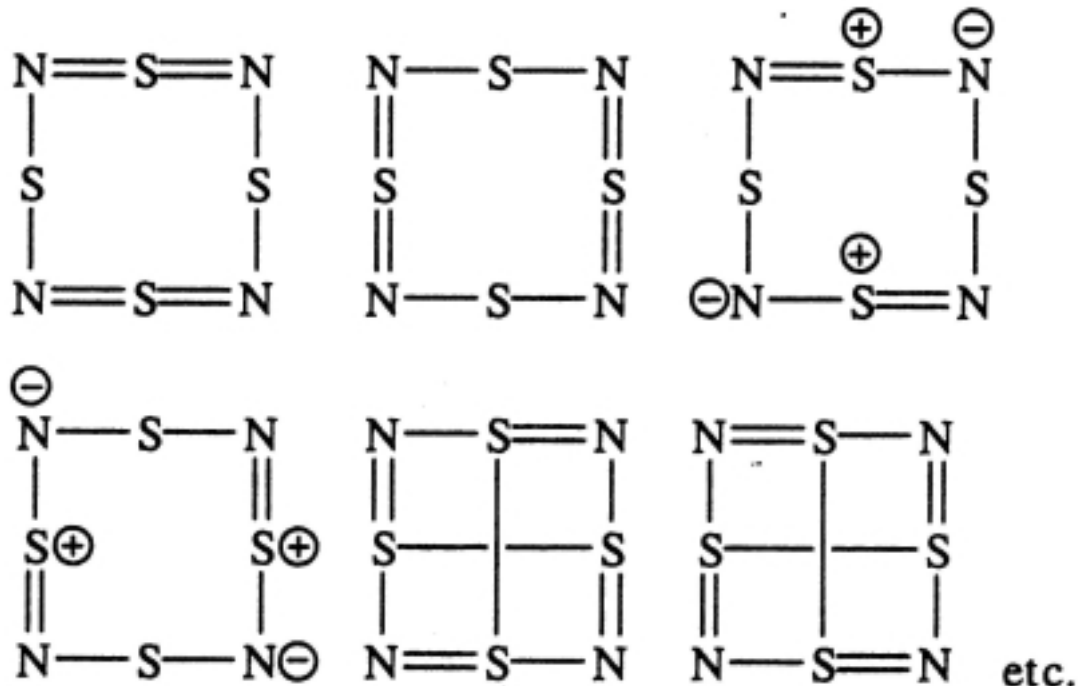
Sulfur Nitrides



● Nitrogen

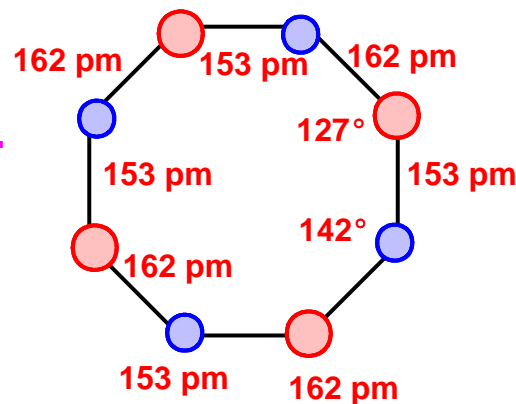
● Sulfur

$-2e^-$



Two different rings occur in the same crystal.

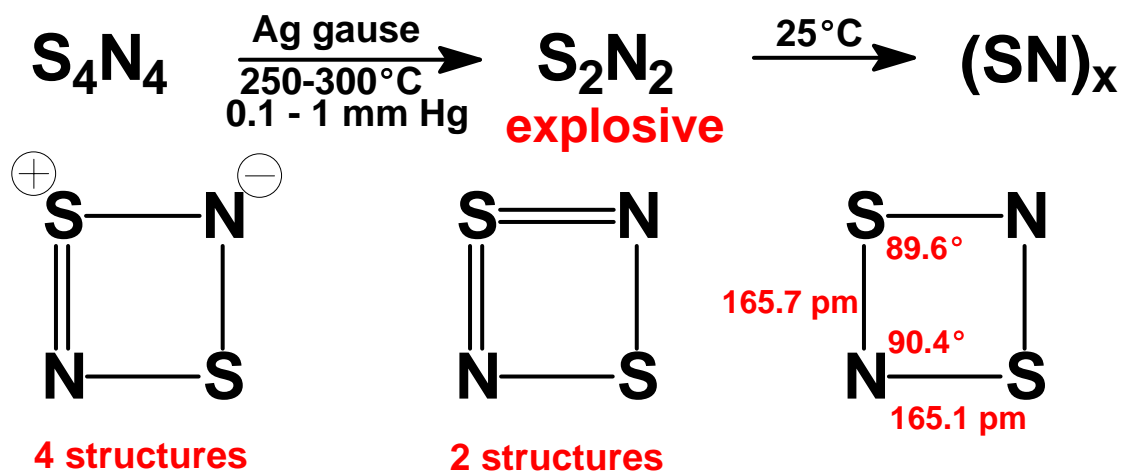
Equal bond distances.



Alternating bond distances.

The $[SbCl_6]^-$ salt has a non-planar boat conformation of the dication.

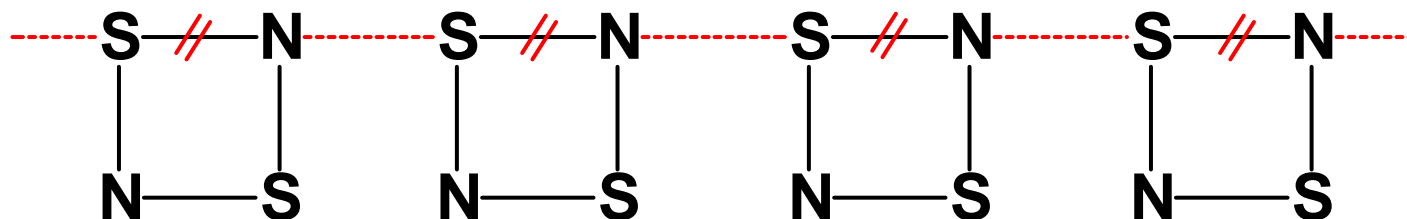
S_4N_4 , S_2N_2 and Polythiazyl



Polythiazyl is a bronze colored, metallic conductor, a super-conductor $T < 0.26 \text{ K}$. Doping with Br_2 , ICl , IBr , I_2 increases conductivity by 10^{16} .

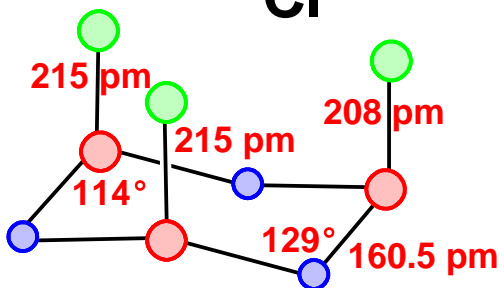
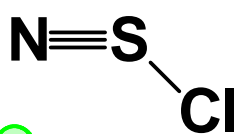
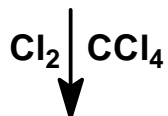
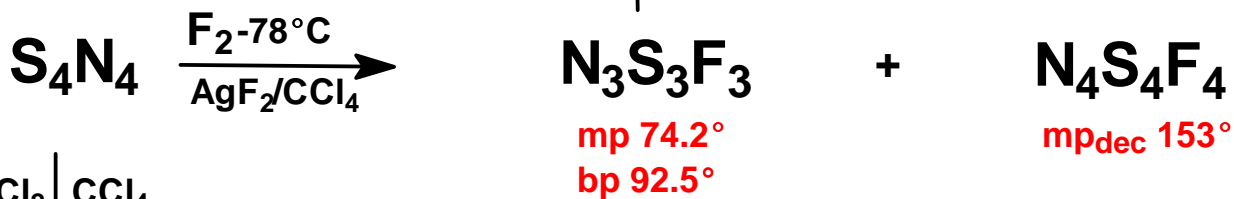
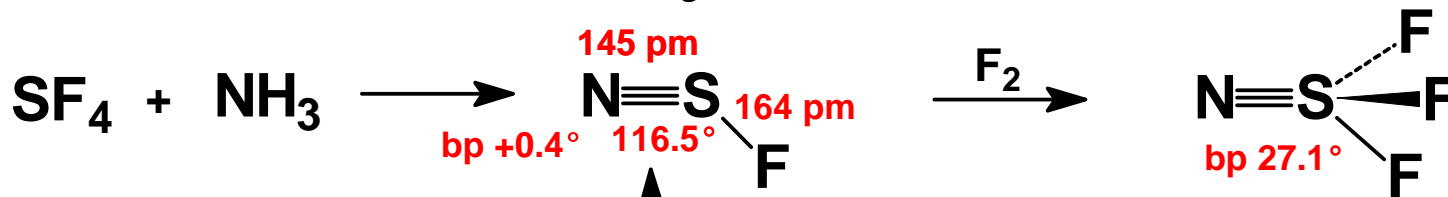
Schematic of the polymerization of S_2N_2 to polythiazyl:

See Fig. 15.36 p 727



Polymer is an almost planar chain of nearly equal, alternating bond distances of 163 and 159 pm. The bond angles centered on sulfur are 106° and on nitrogen are 120° . The polymer is explosive at 240°C but sublimes readily at 135°C in vacuum. The polymer is slowly decomposed by atmospheric moisture.

Thiazyl Halides



- Sulfur
- Nitrogen
- Fluorine
- Chlorine

