Greenwood & Earnshaw

2nd Edition

Chapter 15

Sulfur

Elemental Sulfur

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

Sulfur has many allotropic forms: cy-S_8 D_{4d} Crown most stable.

Very complex phase relationships exist:

cyclo-S_8 $\xrightarrow{93.4°}$ *cyclo*-S_8 $\xrightarrow[159°]{119°}$ —S_n— $\xrightarrow{160\text{-}195°}$ —S_∞—

α-orthorhombic

β-monoclinic mp = 119.6 °C mr = 114-120 °C

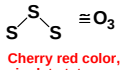
rings break >119 °C

catena-sulfur light-yellow free-flowing liquid.

dark-yellow oil, viscosity increases 10^4

$\xrightarrow{>195°}$ S_3 S_4 S_5 $\xrightarrow[\text{vapor}]{600\text{-}720°C}$ S_6 S_7 > S_8 $\xrightarrow[\text{pressure}]{\text{decreasing}}$ S_4 S_3 S_2

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



≅ O_3

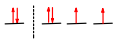
Cherry red color, singlet state.

S=S ≅ O_2

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

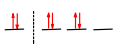
Atomic Sulfur & Sulfur Cations

Atomic Sulfur:  ^3P triplet state



Bonds to virtually all non-noble gas elements.

$S{=}PF_3$ $\xrightarrow[\text{210-230 pm}]{h\nu}$  ^1D singlet state

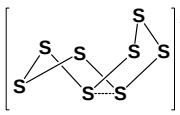


Very reactive: $^3S \longrightarrow$ NR

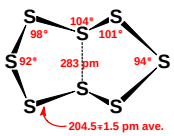
$CH_4 + {}^1S \longrightarrow CH_3SH$

Sulfur Cations:

bright yellow color



deep blue color



204.5±1.5 pm ave.

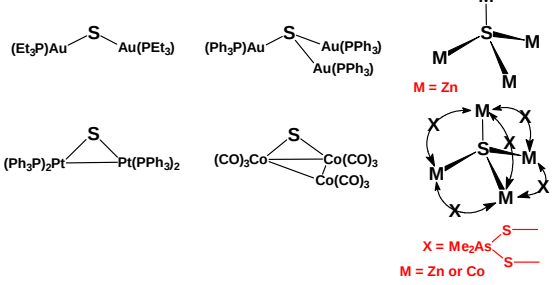
S_8 + SO_3 (H_2SO_4) ⟶ Colored Solutions

S_8 + 3 AsF_5 $\xrightarrow{SO_{2(l)}}$ S_8^{2+} + 2 AsF_6^- + AsF_3

Sulfur as a Ligand

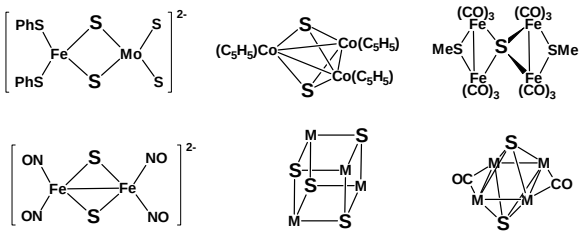
Sulfur is a "Class b" or "soft" donor ligand, cf. Oxygen is a "Class A" or "hard". S and R_2S are know, d_π-bonding (cf. PR_3) is possible. S is usually a $2e^-$ donor but can donate up to $6e^-$ in clusters.

2e 4e 6e



Sulfur as a Ligand

2e 4e 6e

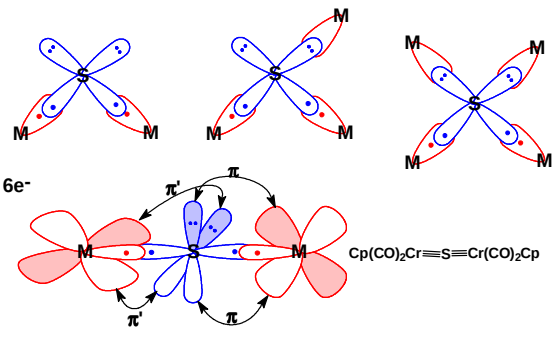


This linear η^2 complex can also be regarded as a $6e^-$ S donor.

$(C_5H_5)(CO)_2Cr{\equiv}S{\equiv}Cr(CO)_2(C_5H_5)$

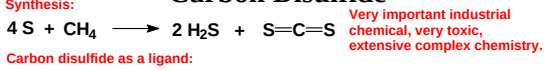
Bonding of Sulfur Ligands

$2e^-$ $4e^-$ $6e^-$



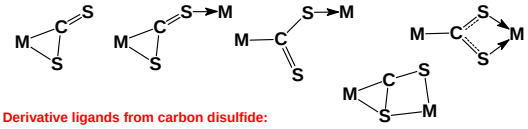
Carbon Disulfide

Synthesis:

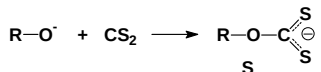


Very important industrial chemical, very toxic, extensive complex chemistry.

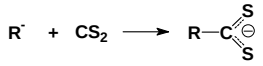
Carbon disulfide as a ligand:



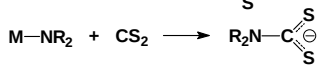
Derivative ligands from carbon disulfide:



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



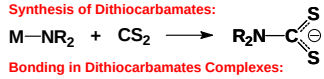
Dithiocarboxylates



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

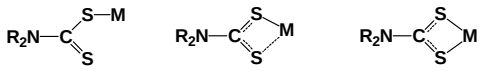
Dithiocarbamates & Other Ligands

Synthesis of Dithiocarbamates:

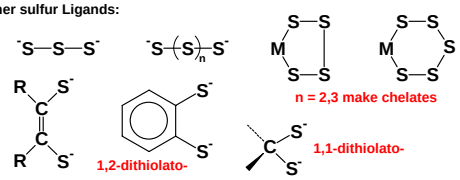


Dithiocarbamates, very important agriculturally as fungicides, M = Mn, Zn, Fe

Bonding in Dithiocarbamates Complexes:



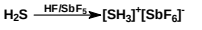
Other sulfur Ligands:

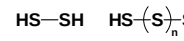


Sulfur Hydrides – The Sulfanes

bp -60.3°C
mp -85.6°C
pK_{a1} = 6.88
pK_{a2} = 14.15

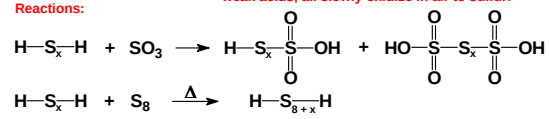
Hydrogen sulfide is a very toxic gas (~HCN). A weak dibasic acid in water. A base in super acid media:

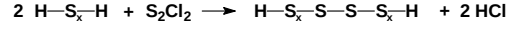


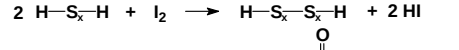


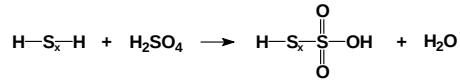
Sulfanes n = 1-6 isolated and characterized n = 7 - ∞ are known as mixtures. All sulfanes are weak acids, all slowly oxidize in air to sulfur.

Reactions:

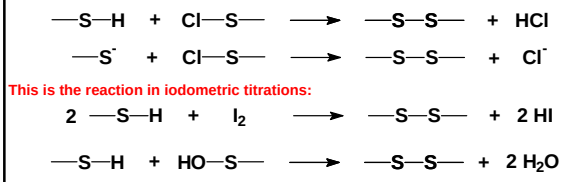






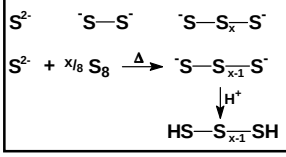


Four General Methods to Make S-S Bonds



This is the reaction in iodometric titrations:

Sulfur Anions - Polysulfides

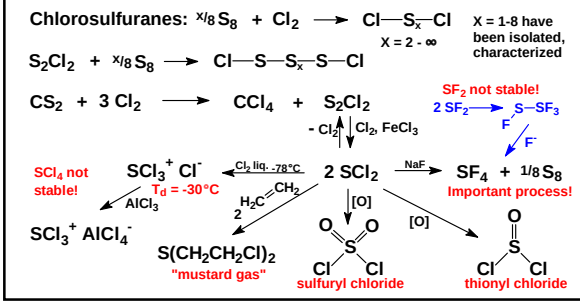


Polysulfides x = 1- 4 isolated and characterized, x 1- ∞ known as mixtures. All are strong bases, hydrolyse in water to hydrogen sulfide. Potent fungicides "lime sulfur" used since antiquity.

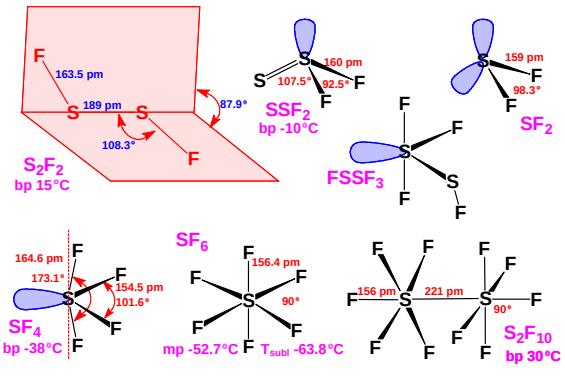
Sulfur Halides

Strengths of Sulfur-Element Bonds:

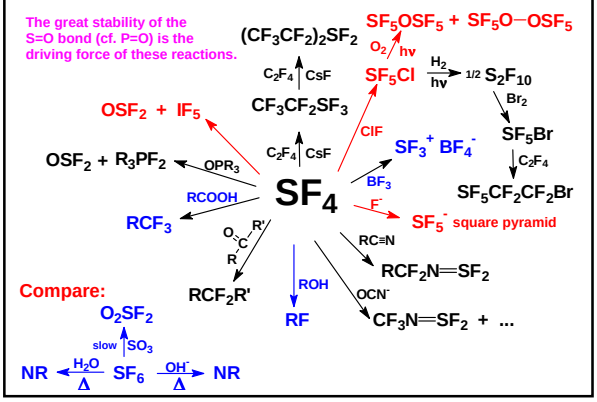
S—X	X =	F	Cl	Br	I	S	I_2
ΔH_{diss} kJ/mol		327	271	218	~170	225	150



Sulfur Fluorides



Reactions of Sulfur Tetrafluoride



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.

$SO_2 \xrightarrow[V_2O_5\text{-}K_2O]{O_2\ 800°C} SO_3$

With first row transition metals:

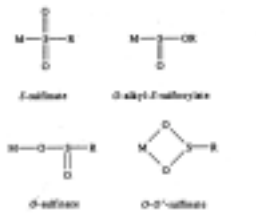
$Ti \xrightarrow[OSMe_2]{SO_2} [Ti(OSMe_2)_6]^{+4}\ [S_2O_7]^{-2}$

In absence of DMSO metal dithionites are produced. M(II) $[S_2O_4]^{-2}$

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

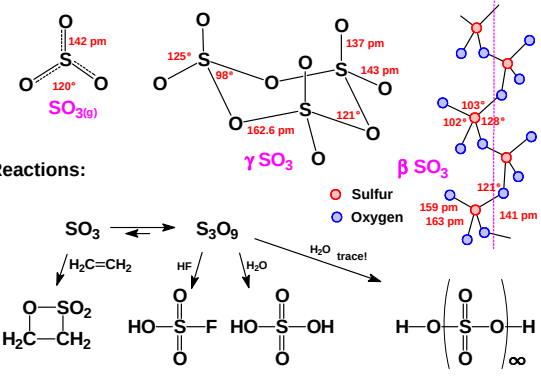
$M{-}R + SO_2 \longrightarrow M{-}(SO_2){-}R$

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



Examples of all except possibly the second mode are known.

Sulfur Trioxide



Reactions:

$SO_3 \rightleftharpoons S_3O_9$

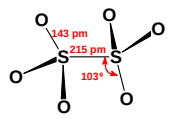
$H_2C{=}CH_2$ → $O{-}SO_2$, $H_2C{-}CH_2$

HF → $HO{-}SO_2{-}F$

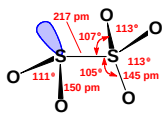
H_2O → $HO{-}SO_2{-}OH$

H_2O trace! → $H{-}O{-}SO_2{-}O{-}H$ (∞)

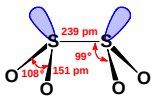
Oxoacids of Sulfur



$[S_2O_6]^{-2}$

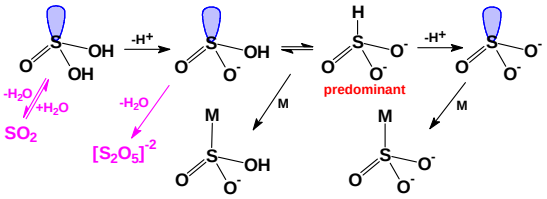


$[S_2O_5]^{-2}$



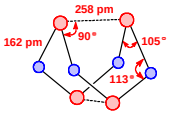
$[S_2O_4]^{-2}$

Some interesting equilibria:



Sulfur Nitrides

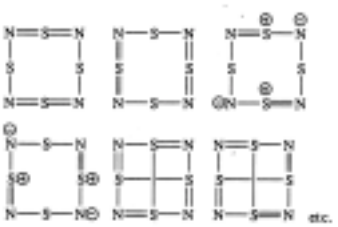
S_4N_4



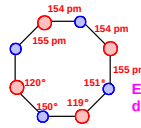
Nitrogen

Sulfur

-2e-

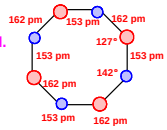


$[S_4N_4]^{+2}[SbF_6]^-[Sb_2F_{11}]^-$



Two different rings occur in the same crystal.

Equal bond distances.



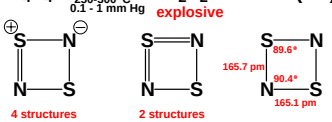
Alternating bond distances.

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

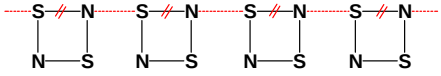
S_4N_4, S_2N_2 and Polythiazyl

$S_4N_4 \xrightarrow[250-300°C,\ 0.1 - 1\ mm\ Hg]{Ag\ gauze} S_2N_2$ explosive $\xrightarrow{25°C} (SN)_x$

Polythiazyl is a bronze colored, metallic conductor, a super-conductor T < 0.26 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