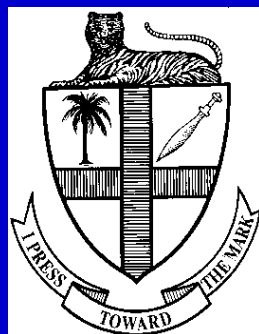


Importance of π -Bonding in the $2p$ – Sublevel: Impact on Molecular Structure and Reactivity



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Elements with Their Oxides and Common Acids

Group	Oxides	Common Acids
14 (IVB)		
C	CO, CO₂, C₃O₂ etc.	H₂CO₃
Si	(SiO₂)_n	H₄SiO₄, H₂SiO₃
Ge	(GeO₂)_n
.....	

Elements with Their Oxides and Common Acids

Group	Oxides	Common Acids
15 (VB)		
N	N_2O , NO , N_2O_3 , NO_2 , N_2O_4 , N_2O_5	HNO_3 (monomeric (oxidizing), HNO_2 (stronger oxidant but weaker reductant)
P	$(\text{P}_2\text{O}_3)_2$, $(\text{P}_2\text{O}_5)_2$	$(\text{HPO}_3)_n$ (non- oxidising), H_3PO_4 , H_3PO_3
As	$(\text{As}_2\text{O}_3)_2$, $(\text{As}_2\text{O}_5)_2$	H_3AsO_4 (oxidizing), $\text{As}(\text{OH})_3$

Elements with Their Oxides and Common Acids

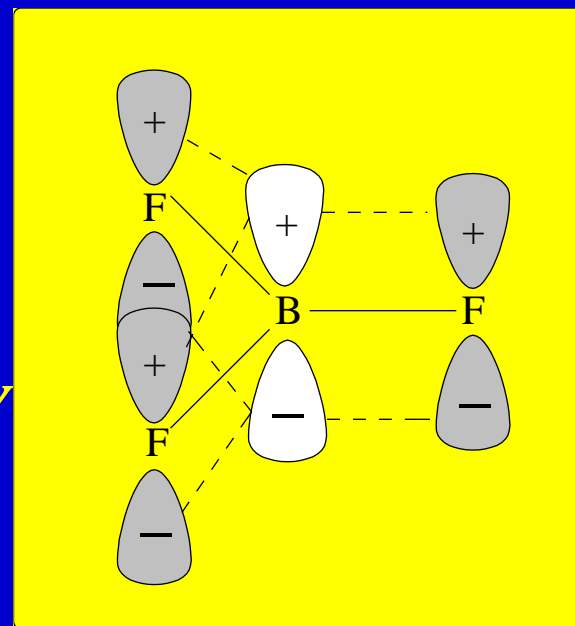
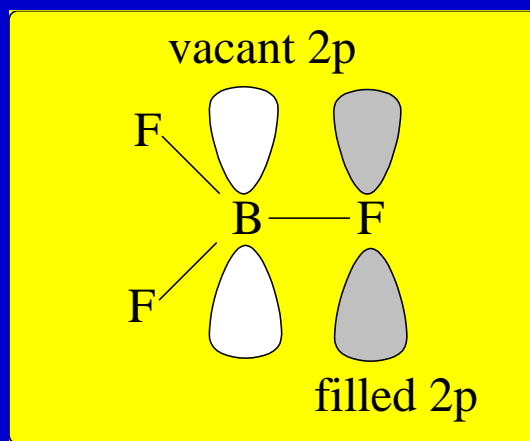
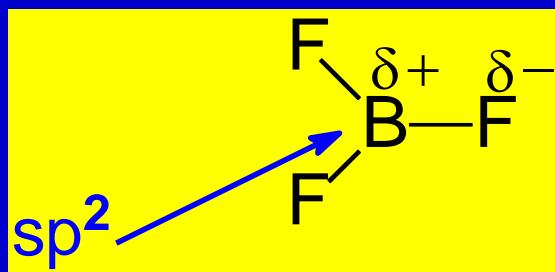
Group	Oxides	Common Acids
16 (VIB)		
O
S	SO₂ (mainly reducing in aqueous solution)	H₂SO₃ (aqueous, reducing), H₂SO₄ (feebly oxidizing)
Se	(SeO₂)_n (oxidizing)	H₂SeO₃ (oxidizing)
Te	(TeO₂)_n	Te(OH)₆

Elements with Their Oxides and Common Acids

Group	Oxides	Common Acids
17 (VIIB)		
F	Practically no tendency to form oxyacids
Cl		HClO₄ (non-oxidizing in aqueous solution but powerful oxidant at elevated temperature)
Br		HBrO₄ (Strong oxidant)
I		H₅IO₆ (moderately strong oxidant but kinetically labile)

2p-Orbital Involvement in Controlling Dimerization and Polymerization Reactions

unlike BX_3 , the halides of other congeners are dimeric:



separation of charge due to EN difference: INSTABILITY

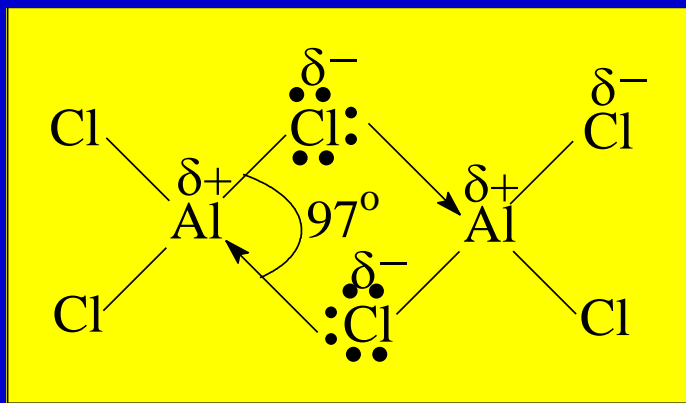
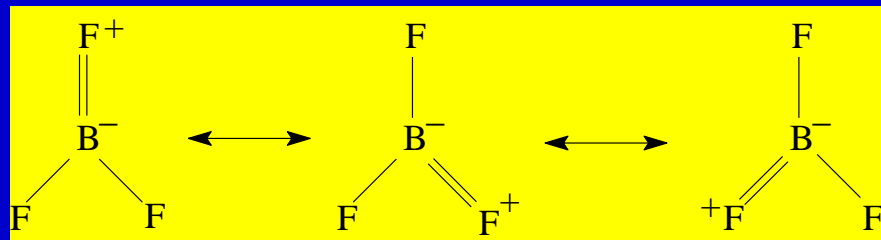
neutralization of charge occurs either by:

(a) suitable π -bond formation

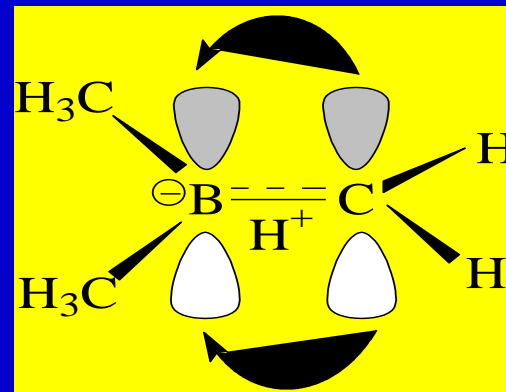
(b) heterocatenation leading to aggregation

2p-Orbital Involvement in Controlling Dimerization and Polymerization Reactions

equivalent resonance structures:



inefficient π bonding due to larger internuclear separation and more diffuse nature of 3p orbitals



$\text{B(CH}_3)_3$: MONOMERIC

BMe_3 fails to dimerize due to:

- (i) loss in hyperconjugational stability*
- (ii) steric congestion around the relatively small B atom by the CH_3 groups*

for $\text{M}_2(\text{CH}_3)_6$ ($\text{M} = \text{Al(III)}, \text{Ga(III)}, \text{In(III)}$) dimers are available owing to lack of hyperconjugational stability and larger atomic volume of central atom to expand coordination number without facing severe steric congestion

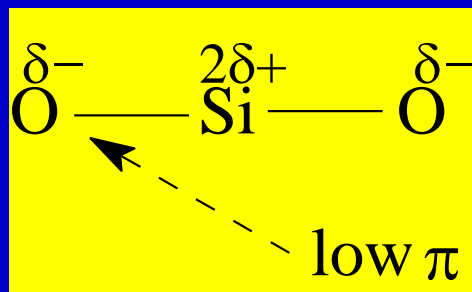
2p-Orbital Involvement in Controlling Dimerization and Polymerization Reactions



high degree of π -nature in C-O linkages

C=O bond energy = 806 kJ mol⁻¹

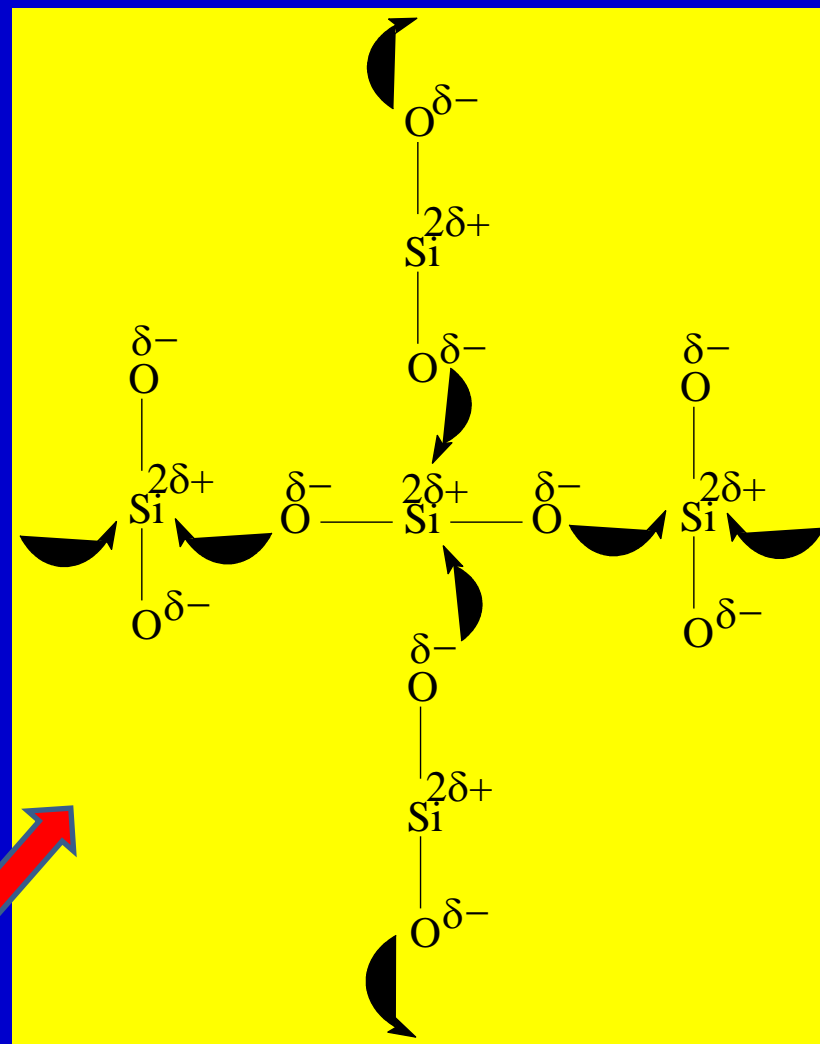
C-O bond energy = 359 kJ mol⁻¹



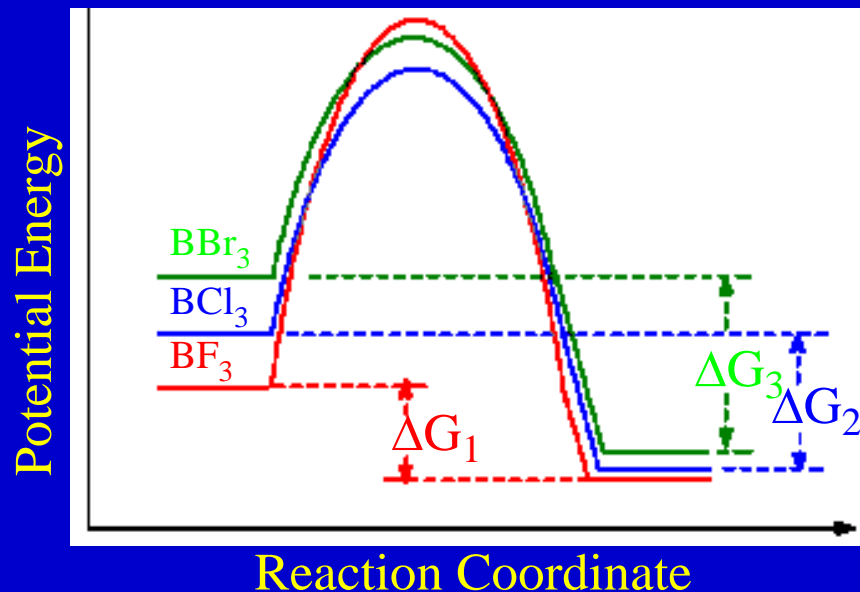
Si-O bond energy 466 kJ mol⁻¹

Si=O bond energy 642 kJ mol⁻¹

polymerization: to satisfy Lewis acidity of Si^{δ+} and Lewis basicity of O^{δ-}



Effect on Lewis Acidity



for BX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) the change of Gibbs free energy follows the order:

$$-\Delta G_1 < -\Delta G_2 < -\Delta G_3$$

$$\Delta G^0 = -RT \ln K_{eq}$$

the trend for Lewis acidity:



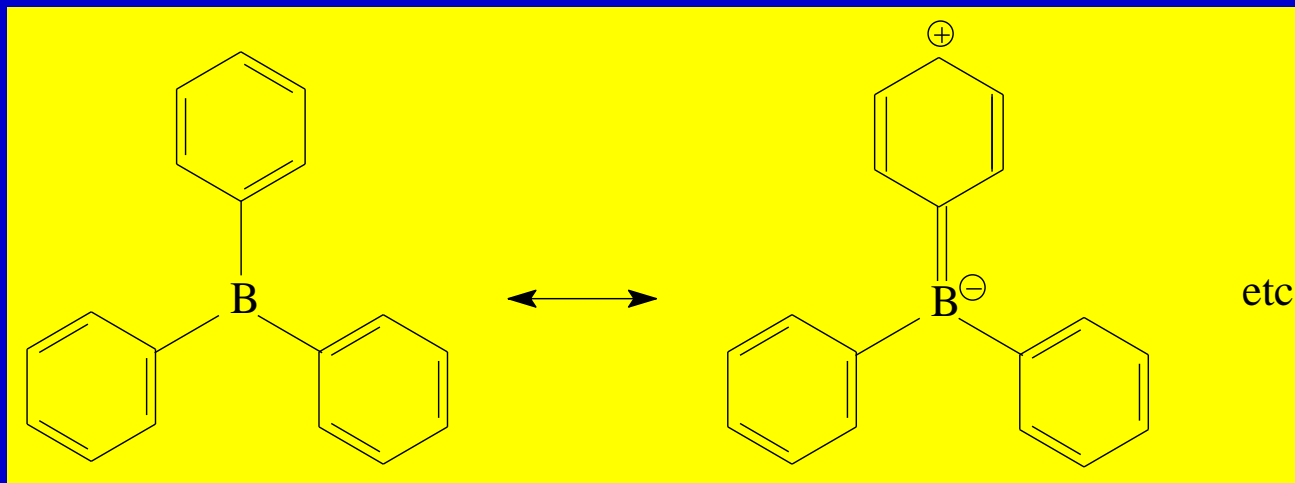
BF_3 being enjoying high degree of π bonding stability, will have the maximum loss of stabilization due to loss of π bonding in course of exhibiting Lewis acidity

reverse order of acidity is found for SiX_4 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$)

p_π - d_π back bonding is feeble and the effect of EN difference between Si and X atoms governs the relative acid strengths, thus: $\text{SiF}_4 > \text{SiCl}_4 > \text{SiBr}_4$

Effect on Lewis Acidity

BPh_3 is a weaker acid than BMe_3

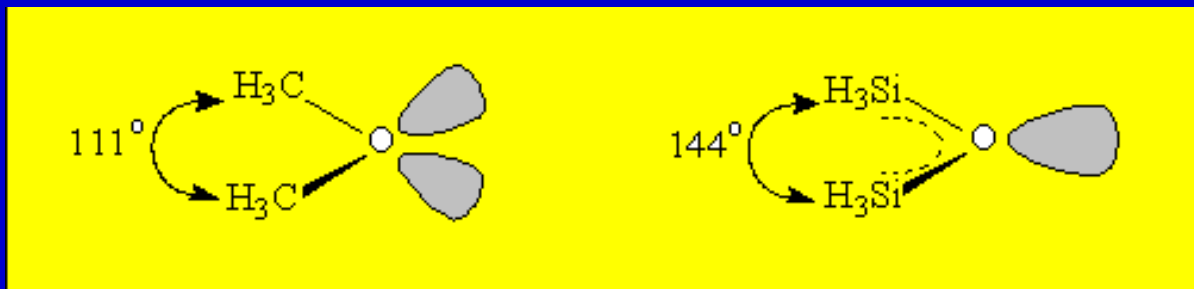


direct conjugation of the boron acceptor orbital into the phenyl aromatic π system in triphenyl boron lowers the acidity of BPh_3 relative to BMe_3 where only hyperconjugation is operative

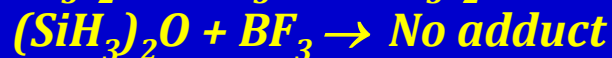
if σ effects were only operative, BPh_3 would have been a stronger acid than BMe_3

Effect on Lewis Basicity

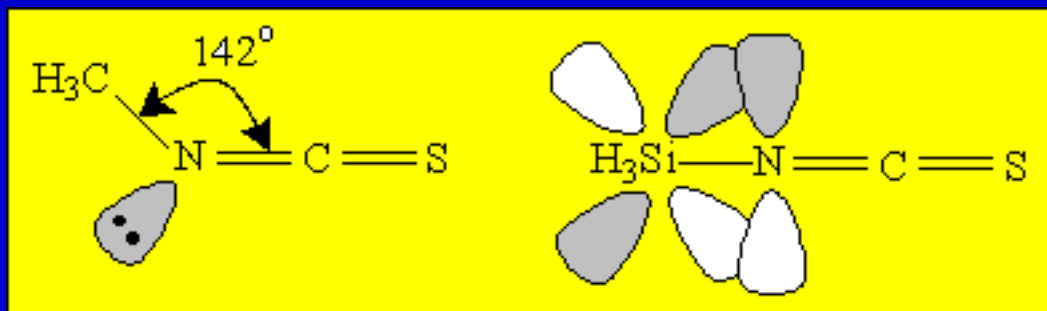
dimethyl ether is a better Lewis base than disiloxane



absence of disiloxane adducts with BF₃ and BCl₃:



H₃CNCS is a better Lewis base than H₃SiNCS



delocalization of the lone pair into a π orbital on the Si atom leads to insignificant Lewis basicity in H₃SiN=C=S

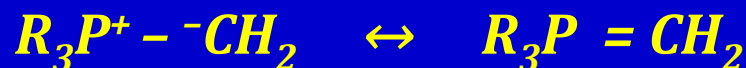
Stability of Ylids and Effect on Dipole Moments



ammonium ylids are more basic and reactive than the phosphorus ylids

commercially available because of stability in air

reason:



both resonating structures contribute towards stability of the phosphorus ylids;

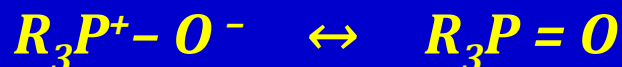
the second resonating structure arises from d orbital conjugation

but



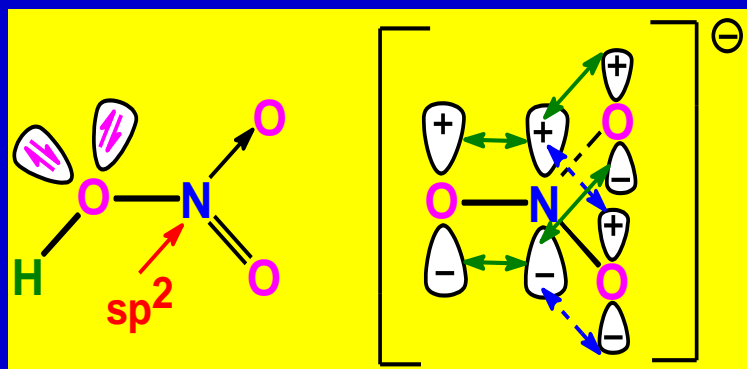
dipole moment of $R_3N \rightarrow O$ (5.02 D) > $R_3P \rightarrow O$ (4.37 D)

the phosphine oxides can have contribution from dative $d\pi$ bonding:

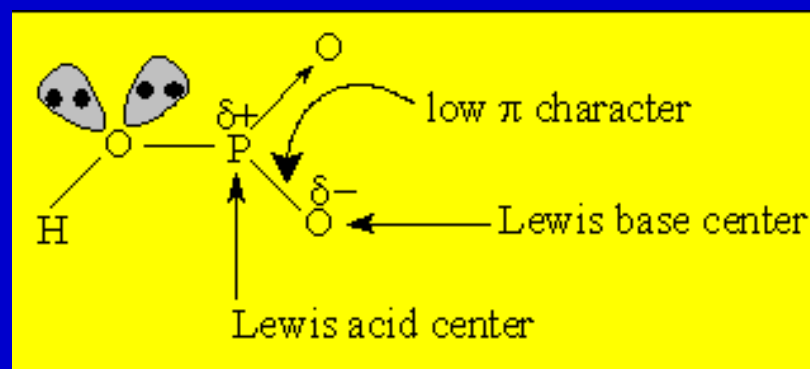


Effect on Structure of Oxyacids & Influence on Redox Properties

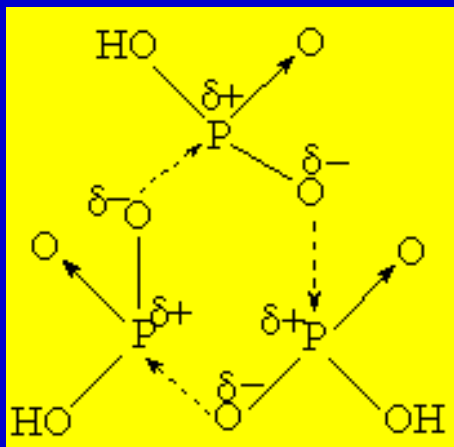
HNO₃ and its analog of phosphorus



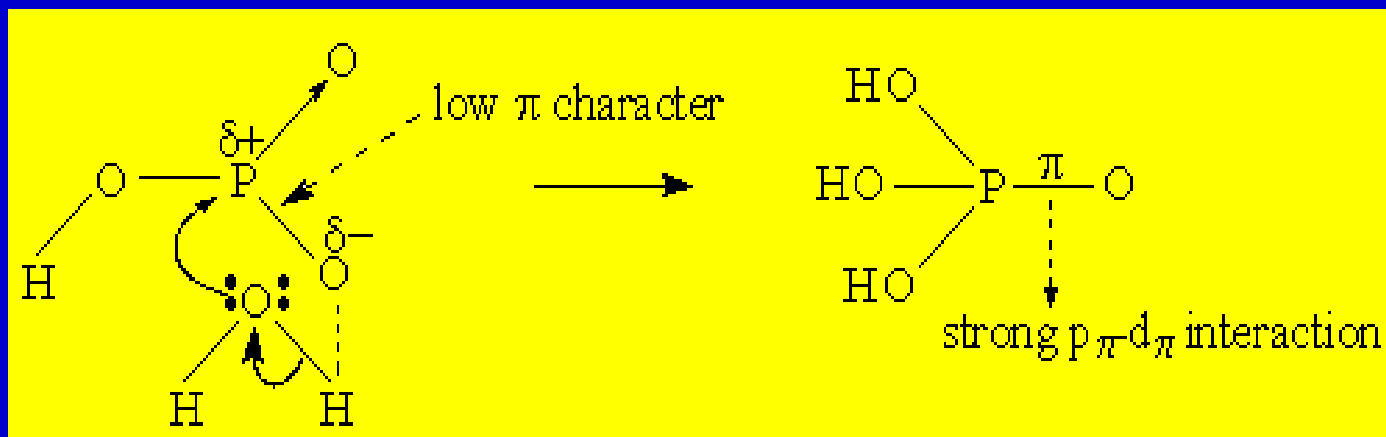
extensive π bonding in NO_3^-



HPO₃ (hypothetical):

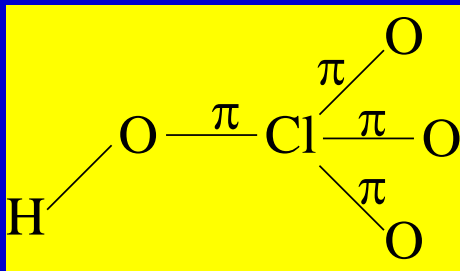


*heterocatenated
P-O-P bond*

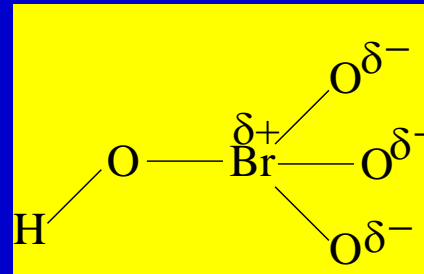


HPO₃ \rightarrow H₃PO₄

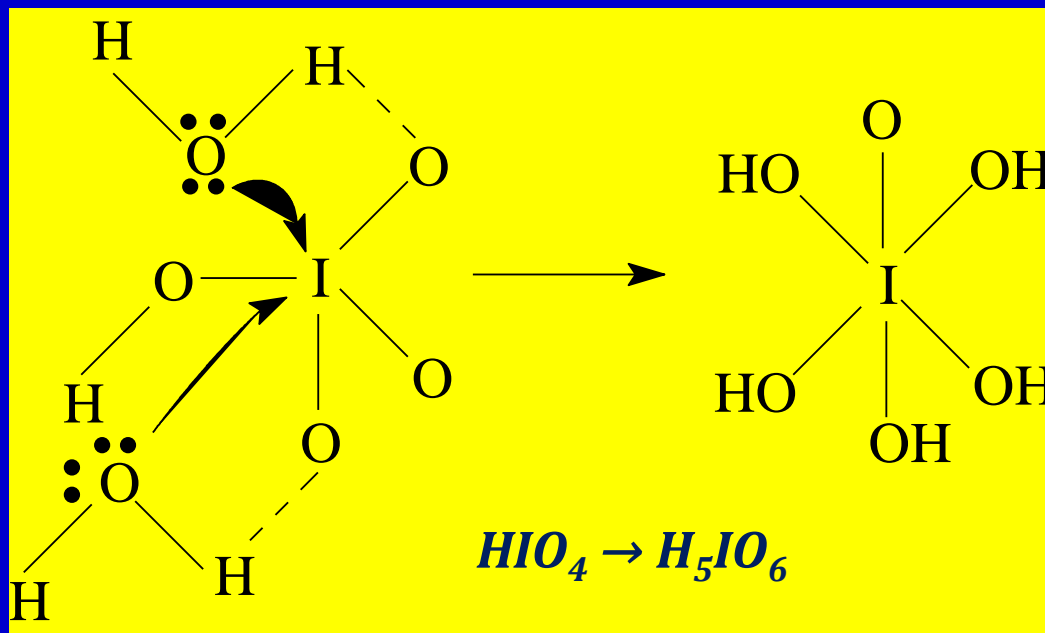
Effect on Structure of Oxyacids & Influence on Redox Properties



neutralization of charge separation through extensive π bonding



lower π character in Br-O linkages



similar behavior is expected for H_2SO_4 , H_2SeO_4 and $Te(OH)_6$

Effect on Structure of Oxyacids & Influence on Redox Properties



BrO_4^- is thermodynamically less stable than either ClO_4^- or IO_4^-

ΔG_f° values :

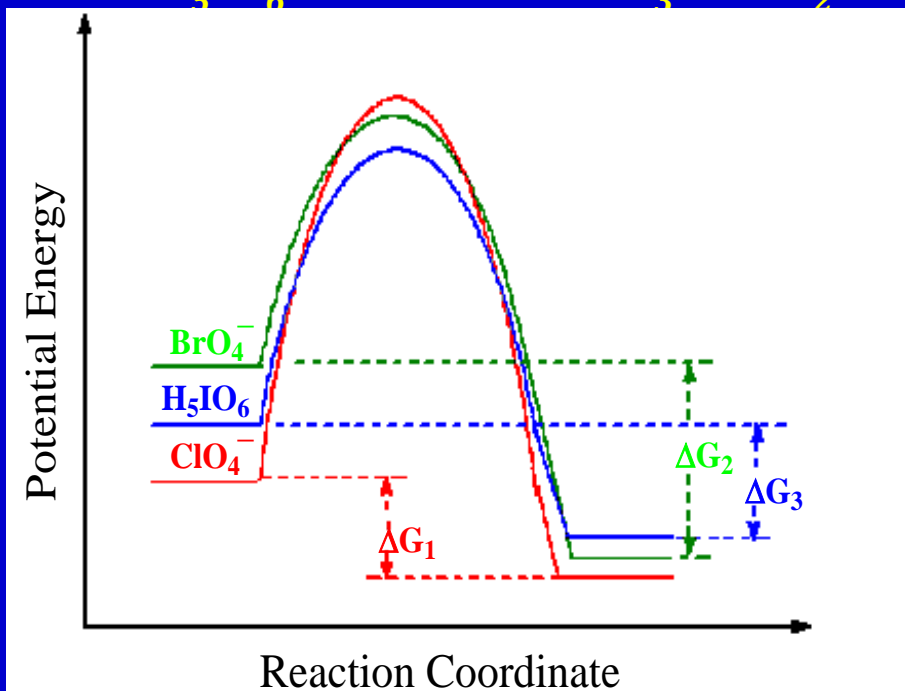
$$\text{KClO}_4: -302 \text{ kJ mol}^{-1}$$

$$\text{KBrO}_4: -174 \text{ kJ mol}^{-1}$$

$$\text{KIO}_4: -349 \text{ kJ mol}^{-1}$$

thus, $-\Delta G_1 < -\Delta G_2 - \Delta G_3$

i.e. trend for oxidizing property:



but, kinetic studies reveal the order of rate of oxidizing capacity:



Effect on Disproportionation Reactions

the initially surprising non-existence of SF₂ is often rationalized in thermodynamic terms by a highly favorable energy for disproportionation reactions :



NOTE:

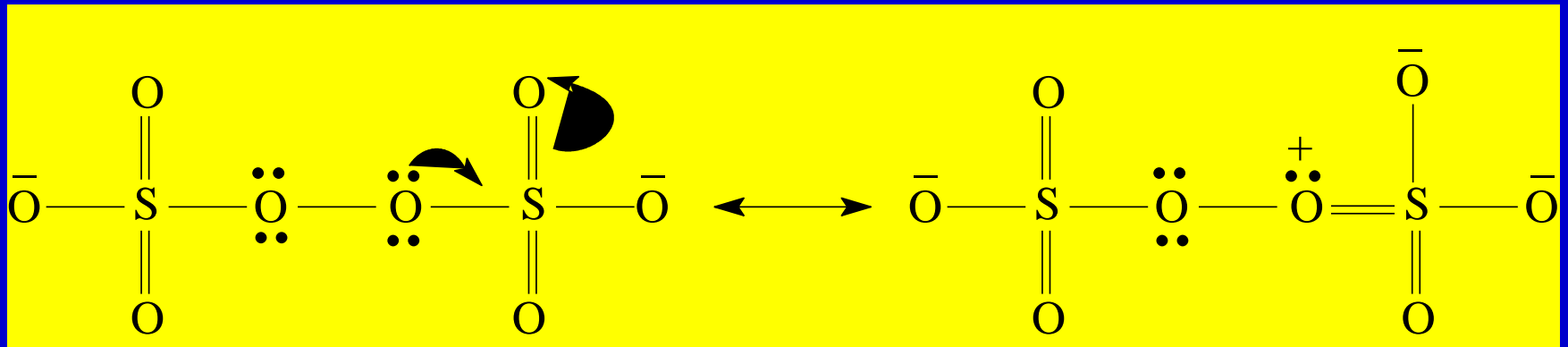
SF₄ does not disproportionate into S and SF₆ though the reaction should be thermodynamically spontaneous

disproportionation possible only at elevated temperatures

reaction is kinetically sluggish due to high potential barrier of the reaction involving S-F bond weakening for high π nature of the S ^{δ^+} -F ^{δ^-} linkage

Stability of Peroxo Compounds with Respect to H_2O_2

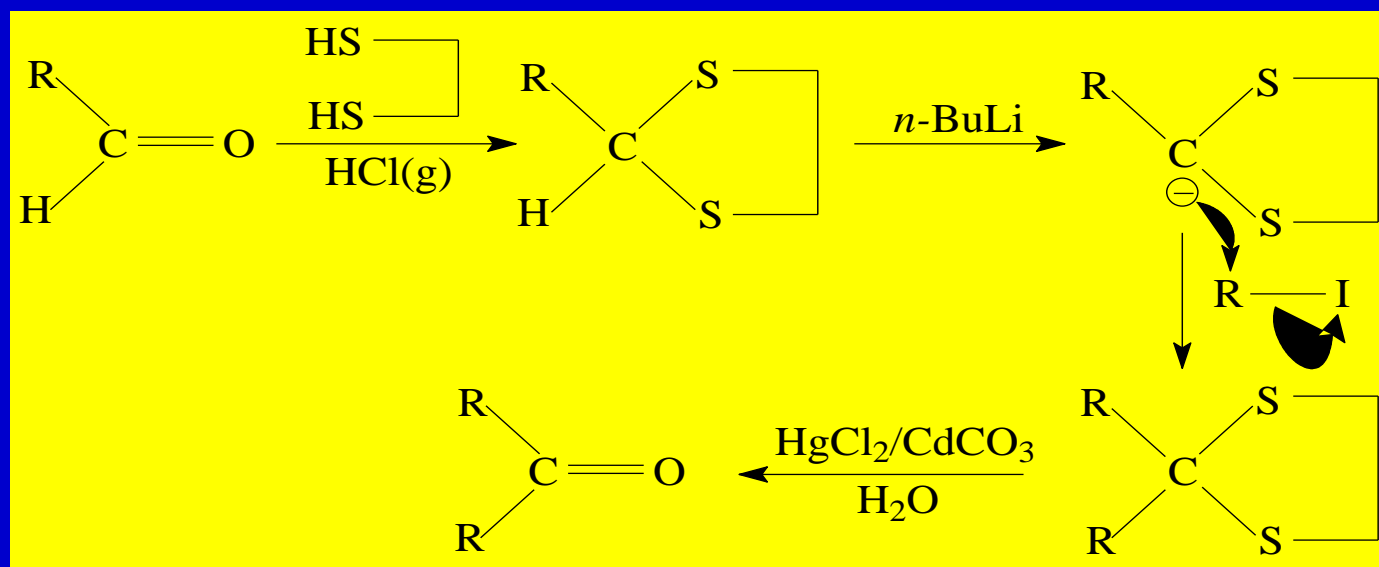
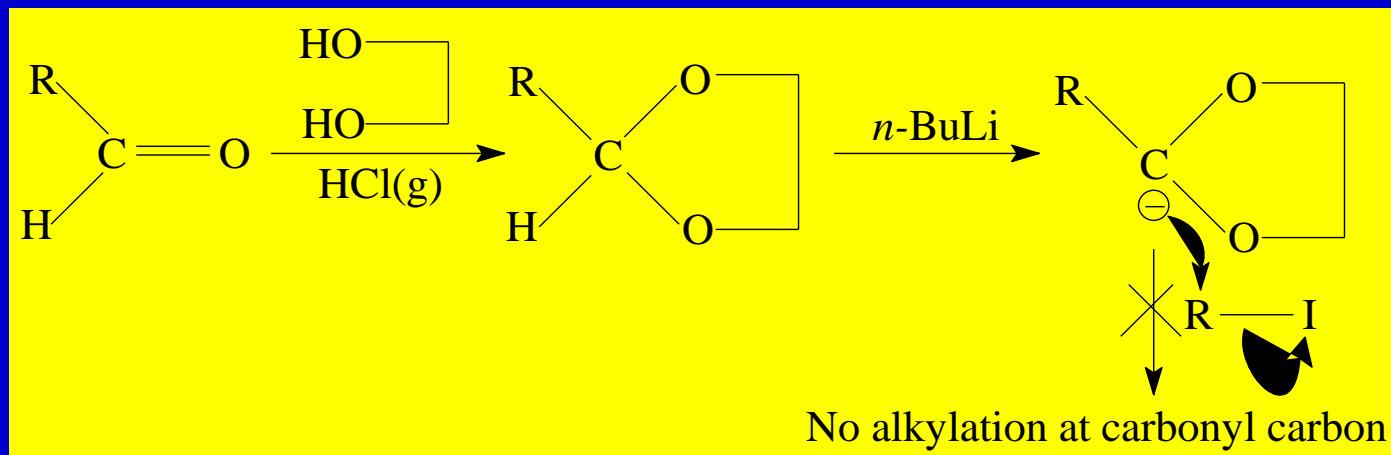
$\text{H}_2\text{S}_2\text{O}_8$ has greater stability than H_2O_2 in spite of higher reduction potential for $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ couple ($E^0 = +2.01 \text{ V}$) its oxidizing action is very slow and can be enhanced in presence of a suitable catalyst like Ag^+



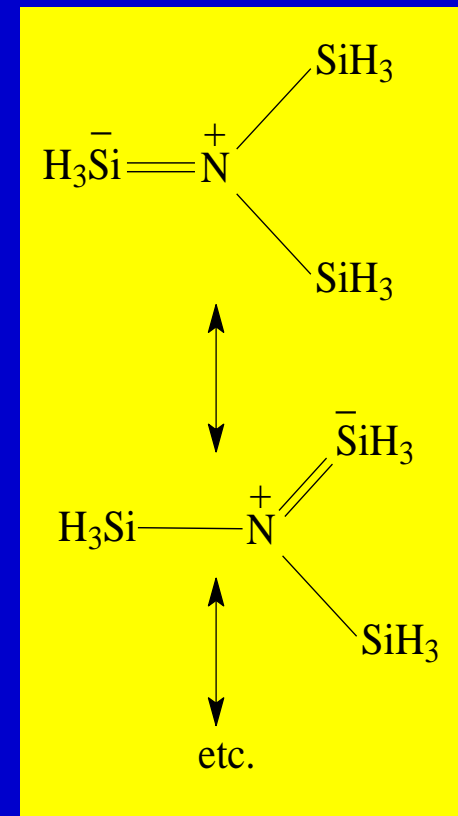
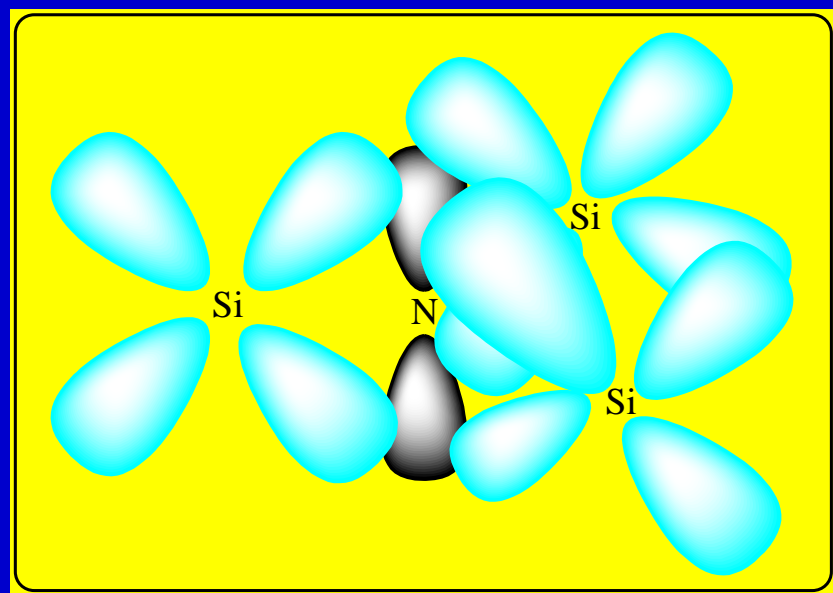
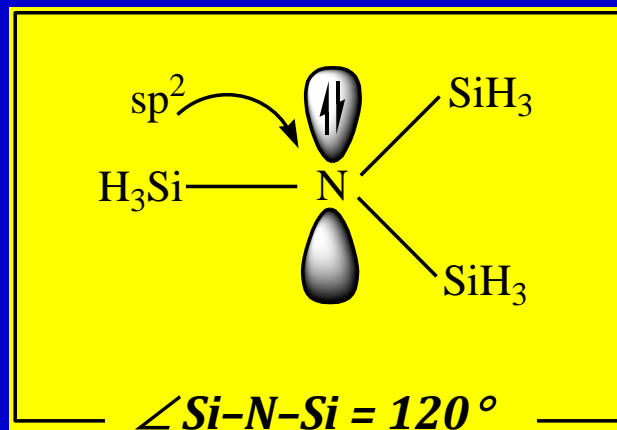
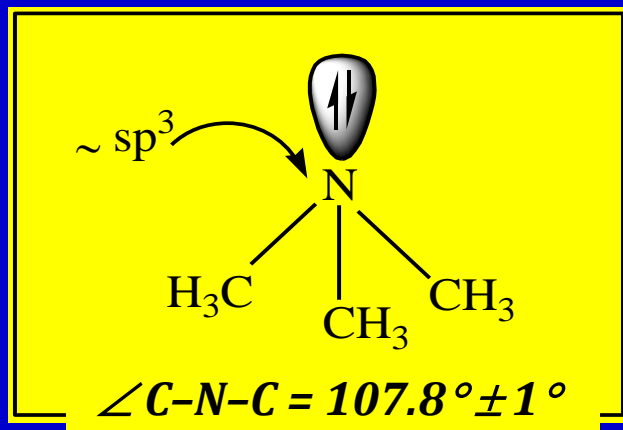
stabilization of the $\text{O}-\text{O}$ linkage by the SO_3^- groups arising from their conjugation with oxygen lone pairs to confer double bond character to the lone pair via $p_\pi-d_\pi$ bonding

Feasibility of Reactions Determined by Stability of Intermediates

feasibility of the conversion of an aldehyde to a ketone via cyclic acetal formation followed by alkylation of the carbanion depends on the stabilization of the latter as a reaction intermediate



Effect of π Bonding on Stereochemical Arrangement: A Controversy



reduced basicity of $N(SiH_3)_3$ is shown by the absence of trisilylammonium salts

instead:

