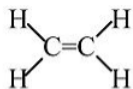


2.7: Periodic Trends in π Bonding

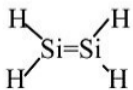
As we noted in Section 2.3, *p π -bonding almost always involves a second-row element*.

We encounter π -bonding from the sideways overlap of p-orbitals in the MO diagrams of second-row diatomics ($B_2 \dots O_2$). It is important to remember that π -bonds are weaker than σ bonds made from the same AOs, and are especially weak if they involve elements beyond the second row.

Example:



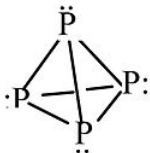
Ethylene: Stable molecule, doesn't polymerize without a catalyst.



Silylene: Never isolated, spontaneously polymerizes. Calculations indicate 117 kJ/mol stability in the gas phase relative to singly-bonded (triplet) $H_2Si-SiH_2$.

The large Ne core of Si atoms inhibits sideways overlap of 3p orbitals \rightarrow weak π -bond.

Other examples: P_4 vs. N_2



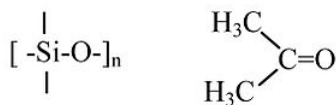
P cannot make π -bonds with itself, so it forms a tetrahedral molecule with substantial ring strain. This allotrope of P undergoes spontaneous combustion in air. Solid white phosphorus very slowly converts to red phosphorus, a more stable allotrope that contains sheets of pyramidal P atoms, each with bonds to three neighboring atoms and one lone pair.



White phosphorus (P_4) is a soft, waxy solid that ignites spontaneously in air, burning with a bright flame and generating copious white P_4O_{10} smoke. The sample shown here is photographed under water to prevent the oxidation reaction

N can make π -bonds, so N_2 has a very strong triple bond and is a relatively inert diatomic gas.

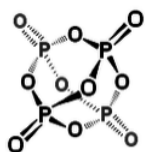
$(CH_3)_2SiO$ vs. $(CH_3)_2CO$



"RTV" silicone polymer (4 single bonds to Si) vs. acetone ($C=O$ double bond). Silicones are soft, flexible polymers that can be heated to high temperatures ($>300^\circ\text{C}$) without decomposing. Acetone is a flammable molecular liquid that boils at 56°C .



Silicone polymers $(R_2SiO)_n$ are used in non-stick cookware like these muffin cups, in Silly Putty, soft robotics, and many other applications.



Exceptions:

2nd row elements can form reasonably strong π -bonds with the *smallest* of the 3rd row elements, P, S, and Cl. Thus we find S=N bonds in sulfur-nitrogen compounds such as S_2N_2 and $S_3N_3^-$; P=O bonds in phosphoric acid and P_4O_{10} (shown above), and a delocalized π -molecular orbital in SO_2 (as in ozone).

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