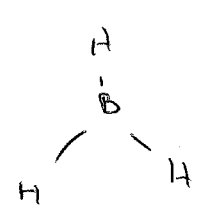


Chem 323 - Problem Set 2

11/4/98

3.24

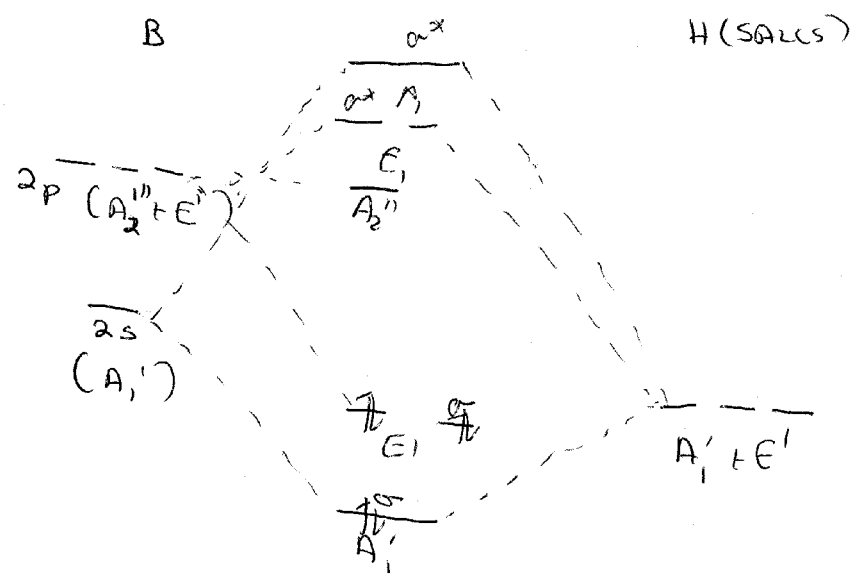


D_{3h}

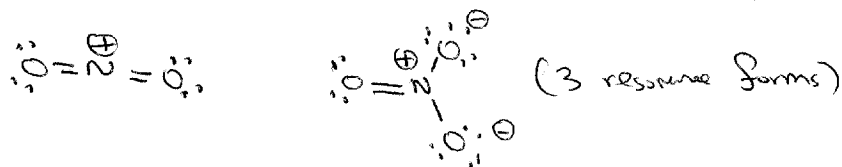
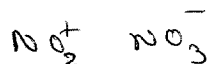
B orbitals) $s \rightarrow A_1'$
 $p_x, p_y \rightarrow E'$
 $p_z \rightarrow A_2''$

for H)

		E	2C ₃	3C ₂	σ_h	2S ₃	3C _v
SALCs	$\rightarrow \Gamma_\sigma =$	3	0	1	3	0	1
		$= A_1' + E'$					

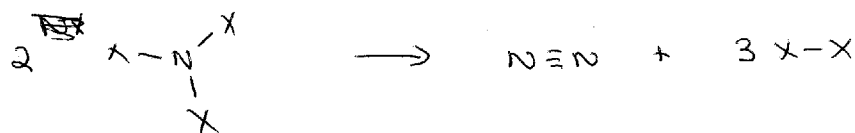


- a) 6 e
 - b) $2p_z \rightarrow$ not correct symmetry for σ bonding to H
 - c) Lewis acid \rightarrow low lying unoccupied orbital on boron
- bond formation is exothermic



4.16) π bonds to heavier group 14 elements are considerable weaker, thus the all σ bonded diamond structure is favored

4.23



$$\Delta H_{\text{rxn}} = 6 E(\text{N}-\text{X}) - E(\text{N}\equiv\text{N}) - 3 E(\text{X}-\text{X})$$

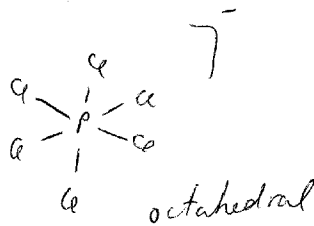
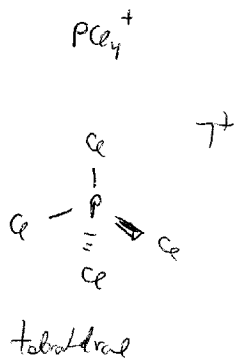
For $\text{X} = \text{F}$

$$\begin{array}{r} 6(278) - 942 - 3(154) \\ 1668 - 942 - 462 \\ \Delta H_{\text{rxn}} = 264 \text{ kJ/mole} \leftarrow \text{endothermic} \end{array}$$

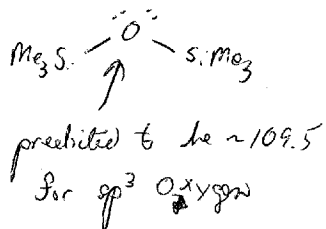
For $\text{X} = \text{Cl}$

$$\begin{array}{r} 6(193) - 942 - 3(240) \\ 1158 - 942 - 720 \\ \Delta H_{\text{rxn}} = -504 \text{ kJ/mole} \leftarrow \text{exothermic} \end{array}$$

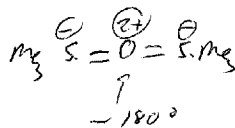
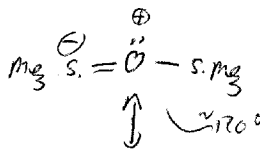
3.5



5.8



wider bond angle is due to partial multiple bonding between O and Si



5.1b

$$\cos \phi = \frac{-C_s}{C_p} = -\frac{C_s}{1-C_s}$$

$$\cos(110.4^\circ) = \frac{-0.3486}{1-C_s} = -\frac{C_s}{1-C_s}$$

$$(-0.3486)(1-C_s) = C_s$$

$$.3486 - .3486 C_s = C_s$$

$$.3486 = 1.3486 C_s$$

$$C_s = \frac{.3486}{1.3486} = \underline{\underline{.2584}}$$

s character of Si-Cl bonds

$$b) \sum_{\substack{\uparrow \\ \text{over all hybrid} \\ \text{orbitals}}} c_s = 1$$

$$2c_s(\text{Si-Cl}) + 2c_s(\text{Si-H}) = 1$$

$$c_s(\text{Si-H}) = \frac{1}{2} - c_s(\text{Si-Cl})$$

$$= 0.5000 - 0.2584 = \underline{\underline{0.2416}}$$

$$c) \cos \theta = \frac{-c_s}{c_p} = \frac{-c_s}{1-c_s} = \frac{-0.2416}{1-0.2416} = -0.31857$$

$$\theta = \cos^{-1}(-0.31857) = 108.6^\circ$$

d) This is not consistent with Bent's rules. The more electronegative Cl substituent should have more p character in its hybrid orbital than H.

Explanation: Partial multiple p bond character in the Si-Cl bond would widen the Cl-Si-Cl angle greater than expected by electronegativity alone.