CHEM 530

Name: KEY

Literature Review – *Inorg. Chem.* **1993**, *32*, 3209-3216

The following questions are intended to reinforce the main points of Cioslowski and Mixon's article. Try to focus on these as you read, and don't allow yourself to be frustrated by the details of the quantum mechanics.

1. What do the authors cite as the main problem with previous computational studies aimed at determining whether or not molecules are hypervalent? They used approximate models incapable of answering the question.

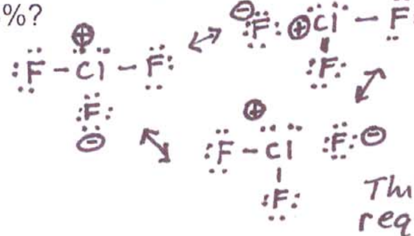
2. What does it mean for a molecule (or polyatomic ion) to be hypervalent? The central atom has >8 electrons around it in the Lewis structure.

3. Consider a two-electron bond between atoms A and B. How many bonding electrons are assigned to each atom if the bond is purely covalent (A-B)? If the bond is purely ionic (A^+B^-)?

equal sharing ("$2e^-$ each")

0 for $A^{\oplus}$, 2 for $B^{\ominus}$

4. Draw the 3 ClF_3 Lewis structures that obey the octet rule (described in the first full paragraph on p. 3211). Calculate the atomic (formal) charges on Cl and F atoms. Why is the minimum ionicity 33%?



Formal Charges: Cl +1 ($\frac{3}{3} = +1$)

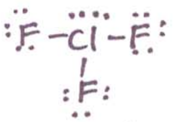
F: −0.333 ($= -\frac{1}{3}$)

(from average of 3 resonance forms)

min. ionicity = $\frac{1 \text{ ionic bond}}{3} = 33.3\%$

This is the minimum amount of ionic character required for the molecule to obey octet rule.

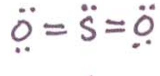
5. Draw a hypervalent Lewis structure for ClF_3 by minimizing formal charges. Explain the authors' assertion that calculated bond ionicities below 33% would indicate hypervalency while values greater than 33% would support a structure that obeys the octet rule.

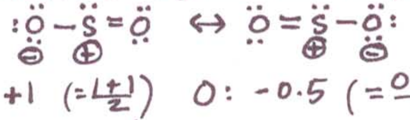


All formal charges = 0

Here, Cl has 10 e^-. There must be one ionic bond in order for Cl to have 8 e^-. Since there are 3 total bonds (and 3 equivalent resonance structures), this corresponds to 33.3% ionicity. A calculated ionicity less than 33.3% would indicate a hypervalent structure with >8 e^- around Cl.

6. For SO_2: (1) Draw a Lewis structure for the hypervalent molecule and (2) Draw Lewis structures that obey the octet rule. (3) Explain the minimum atomic charges (-0.500 for the oxygens and 1.00 for S) and minimum ionicities for the σ and π bonds (0% and 50%, respectively) given in the article. (4) Finally, explain how it is possible for the calculated ionicities to be greater than the predicted minimum values.

① 

② 

③ min. charges: S: +1 ($= \frac{1+1}{2}$) O: −0.5 ($= \frac{0-1}{2}$) min. ionicities: σ: $\frac{2 \text{ cov. bonds}}{2 \text{ S-O pairs}}$ = 100% covalent, 0% ionic

min. ionicities π: $\frac{1 \text{ cov. bond}}{2 \text{ S-O pairs}}$ = 50% covalent; 50% ionic

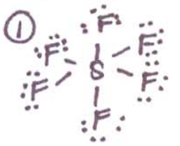
④ Electron sharing in "covalent" bonds may not be equal – if the atoms have different electronegativities and form polar bonds

7. Repeat problem six for (a) PF_5 and (b) SF_6 (using the appropriate minimum charges and ionicities).

PF_5 – See notes

b) SF_6

①



②

+ 14 resonance forms

③ Min. Charges: S: ⊕2

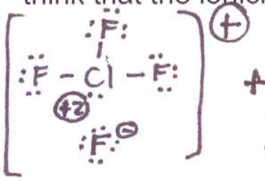
$F = \frac{-2}{6} = -0.333$

Min. ionicity = $\frac{2 \text{ ionic bonds}}{6} \Rightarrow 33.3\%$

8. (a) Draw all Lewis structures required to represent bonding in ClF_4^+, assuming that it obeys the octet rule and predict the minimum atomic charges and bond ionicity that would be required.

(b) As Cioslowski and Mixon point out, PF_4^- and SF_4 have the same sort of Lewis structures, yet calculations show that these two species obey the octet rule while ClF_4^+ may not. Why do you think that the ionicity of the Cl-F bonds is less than those of P-F and S-F bonds?

a)



+ 3 equiv. resonance structures

Min. charges:
Cl: ⊕2 F: −0.25

Min. ionicity
$\frac{1}{4} = 25\%$

b) Cl is more electronegative than P or S, closer to the electroneg. of F. Since there is less of an electronegativity difference between the bonded atoms, Cl-F bonds are less polar: they have more covalent and less ionic character than P-F or S-F bonds.

9. Summarize the main conclusion(s) of this article in one or two sentences.

The authors calculated atomic charges for molecules with central atoms in Period 3 and compared these to minimum charges required to meet the octet rule. Their calculated results show that, in most cases, there is more than the minimum amount of ionic character needed to avoid hypervalency. (According to their work, we should not use "expanded octets" when representing Lewis structures of these molecules.)