

CHEMISTRY 412/512

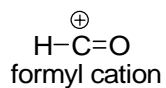
MIDTERM # 1

February 14, 2007

Name

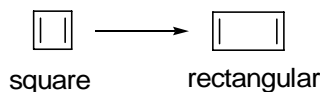
The total number of points in this midterm is 45. The total exam time is 90 min (1.5 h).

1. (8 pts) Acyl cations ($\text{R}-\overset{\oplus}{\text{C}}=\text{O}$) are key intermediates in *Friedel – Crafts* acylation reactions. They are stabilized by the presence of oxygen and this can be demonstrated through either resonance or MO analysis.
- a. Consider the formyl cation, shown below. Show how it is stabilized, using appropriate resonance structures.

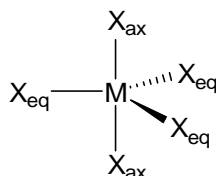


- b. Construct the orbital mixing diagram for the formyl cation, starting with group orbitals for CH and O-atom. Consider only first order mixing. Place the appropriate number of valence electrons and demonstrate how QMOT explains the stabilization of the cation.

2. (6 pts) Antiaromatic molecules avoid antiaromaticity by structural distortion. For example, cyclobutadiene is not square (and antiaromatic) but rectangular. Show, using π -group orbital analysis, that such distortion would indeed be stabilizing.

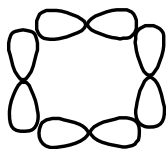


3. (6 pts) **This problem treats 3-center-4-electron bonds:** Species with formula MX_5 exist in trigonal bipyramidal geometry, as shown below. To explain bonding in such molecules, especially in introductory courses, participation of d -orbitals is invoked. A number of studies have shown, however, that for main group elements (such as C, P, S, Cl, etc.) d -orbitals are much higher in energy compared to s - and p -orbitals, and cannot effectively mix with them, in order to form sp^3d hybrid orbitals and the necessary number of bonds. A more comprehensive view is based on the 3-center-4-electron bond. The central atom is envisioned in sp^2 -hybridization state, using the sp^2 -hybrid orbitals to form the three equatorial bonds to X_{eq} . Bonding to the axial groups is realized by the use of the single, unhybridized p -orbital of M, which combines with appropriately oriented p -orbitals of the X_{ax} groups, to form what is actually a 3-center-4-electron bond.



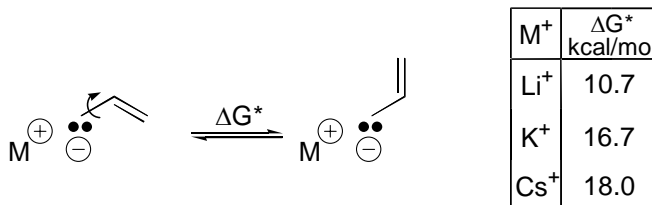
- Consider the fragment $\text{X}_{\text{ax}} - \text{M} - \text{X}_{\text{ax}}$. Use a p -orbital at each of the centers to construct the mixing diagram for the 3-center-4-electron bond.
- Consider the particular case of CX_5^- . It is a good approximation to the transition state for S_N2 reactions. Fill the mixing diagram with the appropriate number of electrons.
- It is well known that in trigonal bipyramids the most electronegative substituents always tend to be axial. Account for it based on your mixing diagram analysis.

4. (6 pts) **This problem is about σ -aromaticity:** We are inclined, almost instinctively, to associate aromaticity with cyclic conjugated π -systems. The fact of the matter is, however, that aromaticity is a broader phenomenon that can occur in any type of system, as long as we have a cyclic array of orbitals. If they overlap in a σ -bonding fashion, then this could give rise to a σ -aromatic or antiaromatic system. Consider the cyclic array of four p -orbitals, shown below. Construct the group orbitals for this system and fill in the appropriate number of electrons (starting with one electron per p -orbital). Show that the resultant system is σ -antiaromatic.

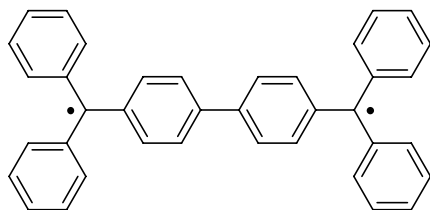


5. (8 pts) The following questions deal with stability and structure of particular carbanions. Offer a structural rationalization for each one.
- According to calculations the BH_2 group is almost as stabilizing to carbanions as a CN or a CF_3 group, even though boron is less electronegative than carbon.

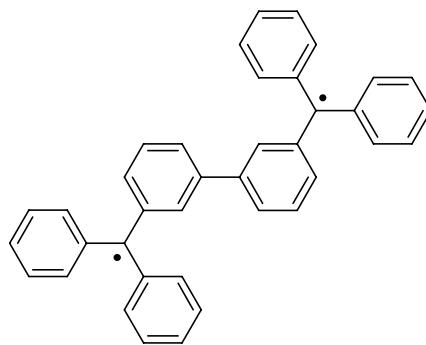
- The rotational barrier in the allyl anion shows an obvious dependence on the counter ion (See results below!).



6. (5 pts) The two diradicals, **A** and **B**, shown below, exhibit very different properties. Diradical **A** is a singlet species (except for very high temperatures) while **B** is a triplet at all temperatures. Use resonance analysis to rationalize this difference.



A



B

7. (6 pts) The following reaction has been used to predict the standard heat of formation (ΔH_f^0) of *p*-benzyne, an important intermediate in the Bergman cyclization, which is a key step in the biological activity of the *enediynes antibiotics*. Use the *Benson* additivity tables to evaluate ΔH_f^0 of *p*-benzyne.

