Chemistry 125 First Semester

December 19, 2007 Final Exam Answers

Statistics

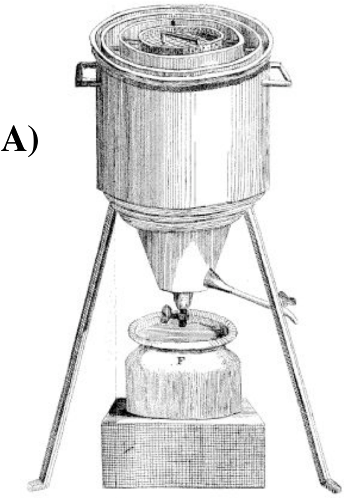
	Final Exam	Semester Total
Average	238	480
Thirds	259 – 234	508 – 460

Grade Borders

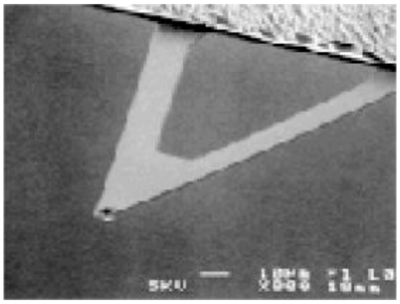
A (521) A- (485) B+ (448) B (415) B- (385) C+

1. (10 min) Explain briefly how each of two **(2 only)** of the following 4 pieces of apparatus are (or were) used and for what purpose.

(A)



(B)



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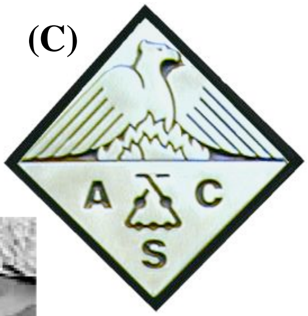
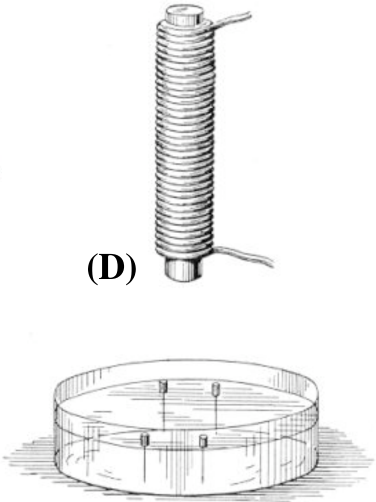


(D)



Questions 1-8 (except Question 2) relate to figures that appeared in the lecture powerpoints and were discussed in the Wiki. It was not expected that the answers would be exhaustive, just that they would cover the key points and be appropriate in length for the time allowed. This Answer Key gives references to the lecture number and date and to the frame number, so that you can consult the relevant original powerpoint and wiki.

A) Lavoisier-Laplace melting-ice calorimeter for measuring heat content of combustible oil. Outer ice layer shields from ambient heat. (Lect 19, 10/19, frame 38)

B) AFM cantilever; laser reflection displaced by sub-Å displacement of 20 nm tip. (Lect 5, 9/14, frame 18)

C) Liebig's kaliapparat on the Am. Chem. Soc. Logo. Efficiently absorbs CO_2 with "self-stirring" for determining weight of C in a sample by combustion. (Lect 22, 10/29, frame 3-4)

D) Thomson's magnetic model for 2D electron shell structure (Lect 4, 9/12, frames 21-23)

2. (9 min) (Write your answer on the Back of this sheet) Choose **any reaction process that involves several steps** and draw a mechanism using curved arrows to show every electron (pair) shift involved (*e.g.* alkene + $Cl_2 \rightarrow$ dichloroalkane; **or** alkane + $Cl_2 \rightarrow$ alkyl chloride + HCl; **or** $NH_3 + Cl_2 \rightarrow NH_2Cl + NH_4Cl$; **or whatever**). No discussion of HOMOs and LUMOs required, but draw the arrows carefully.

alkene + $Cl_2 \rightarrow$ dichloroalkane HOMO-LUMO addition mechanism (Lect 22, 10/29, frame 30)

alkane + $Cl_2 \rightarrow$ alkyl chloride + HCl SOMO radical-chain substitutionmechanism (Lect 22, 10/29, frame 31)

$NH_3 + Cl_2 \rightarrow NH_2Cl + NH_4Cl$ (Lect 17, 10/15, frame 7)

Another good example would have been ammonium cyanate to urea (Lect 21, 10/26, frame 25)

3. (6 min) Explain what two **(2 only)** of the following three formulas are meant to express.

(A)
$$K\, e^{-\rho/2} \qquad \rho \equiv \frac{2Z}{na_o} r$$

(B)
$$\psi_a(r_1,\theta_1,\phi_1) \times \psi_b(r_2,\theta_2,\phi_2)$$

(C)
$$\frac{\geq 1}{2}\,(AO_A{}^2 + AO_B{}^2 - 2\, AO_A\, AO_B)$$

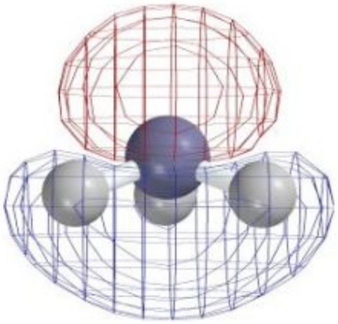
A) *1s* wavefunction for H-like atom; rho scales distance for applicability to different nuclear charges (Lect 9, 9/24, frame 25)

B) Electron density (square) of an antibonding LCAO orbital; overlap term on the right shifts density away from the interatomic bonding region. (Lect 13, 10/5, frame 11)

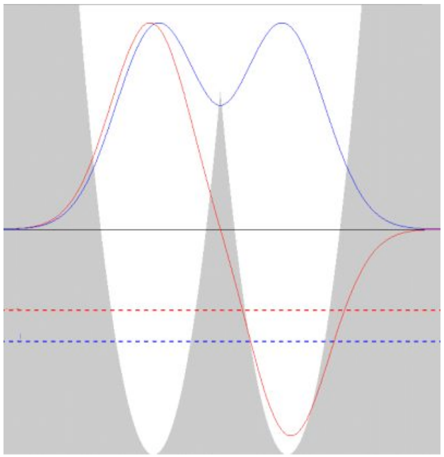
C) Approximation of 2-electron wave function as product of orbitals – impossible because of correlation. (Lect 11, 10/1, frames 4-7)

4. (8 min) Explain the significance of these two figures.

HOMO of NH_3; shape analogous to atomic *2p* orbital; absence of a proton in the upper lobe makes this "lone-pair" orbital higher in energy that the other 2p-like orbitals. (Lect 12, 10/3, frame 19)

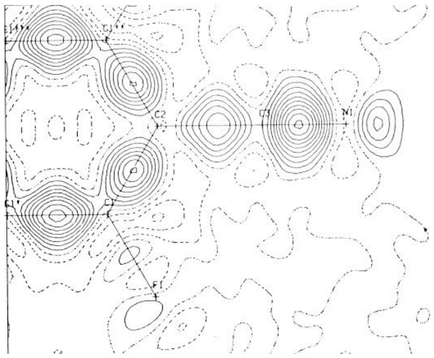


Lowest two quantum levels for a double-minimum potential show tunneling (rate proportional to the energy separation of the two levels) and bonding (lower wave function less curved than single minumum – lower energy; higher wave function more curved – higher energy). (Lect 9, 9/24, frames 4-8)



5. (10 min) Tell a brief story about two **(2 only)** of the following three figures.

(A)



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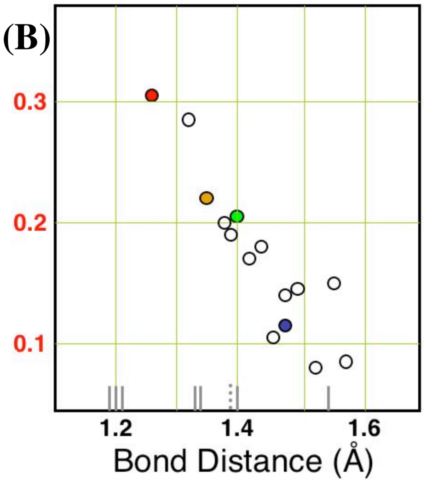

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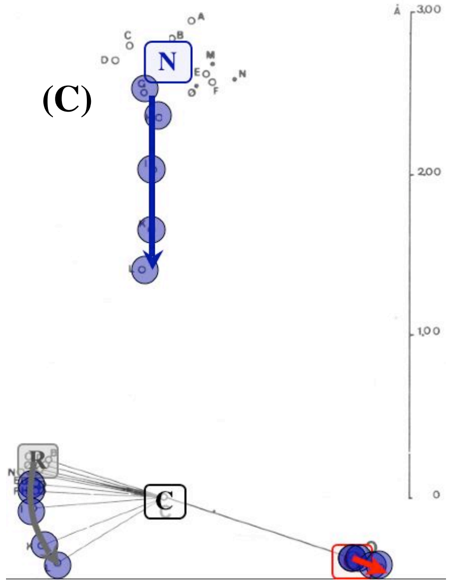
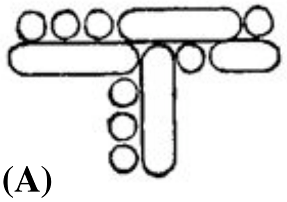


A) Electron deformation density of dicyanotetrafluorobenzene; absent C-F bond from erroneous subtraction; lone pair on N; “resonant” aromatic bonds. (Lect 6, 9/18, frames 30-32)
Cf. cylindrical shape (round cross section) of CN triple bond (Lect 12, 10/3, frame 6)

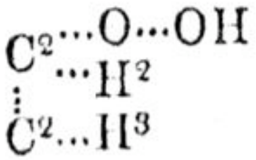
B) Correlation of bond type or bond distance with electron deformation density ~1/20 of a “Lewis” (Lect 6, 19/17, frame 28)

C) X-ray determination of Bürgi-Dunitz angle and reaction trajectory for coordinated motion of N, two R groups, and O during amine
ttack on carbonyl group. (Lect 18, 10/17, frame 3)

6. (15 min) Tell how each of three **(3 only)** of the following five played a role in 19th century organic chemistry.



(A)



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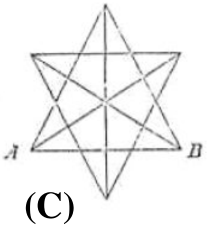

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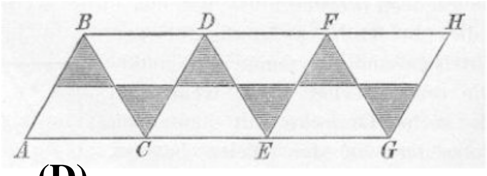
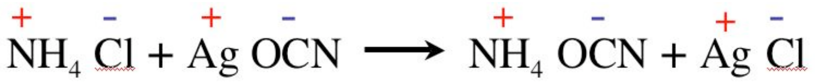


(D)

(E)



$$\overset{+}{NH_4}\,\overset{-}{Cl} + \overset{+}{Ag}\,\overset{-}{OCN} \longrightarrow \overset{+}{NH_4}\,\overset{-}{OCN} + \overset{+}{Ag}\,\overset{-}{Cl}$$

A) Inferior Kekulé sausage constitutional models predict wrong isomer number (Lect 24, 11/2, frame 15)

B) First constitutional formula for ethanol, doubled C,O; tetravalence and self-linking of C (Couper) (Lect 23, 10/31, frame 21)

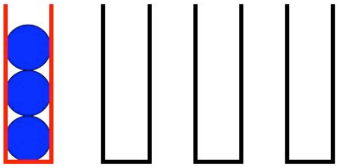
C) 2D star-of-David formula to explain absence of chirality in disubstituted “prism” form of benzene (Ladenburg *vs.* van’t Hoff) (Lect 26, 11/7, frame 8)

D) Fold-up base for mounting C tetrahedra to create chair cyclohexane (Sachse) (Lect 31, 11/28, frame 14)

E) Predicted double decomposition of reagents which actually react to give urea – Wöhler (Lect 21, 10/26, frames 22-23)

7. (10 min) Tell how each of two **(2 only)** of the following four figures relates to thermodynamics or kinetics.

(A)



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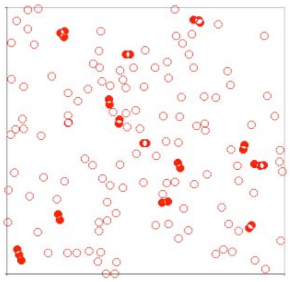
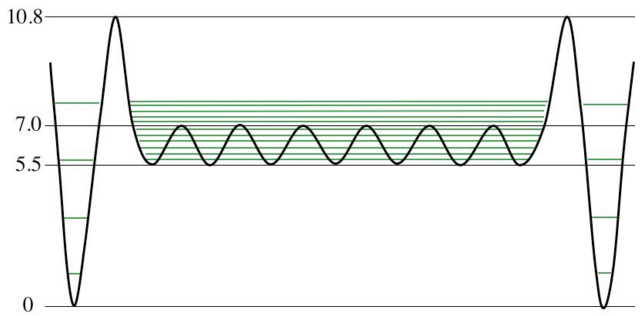
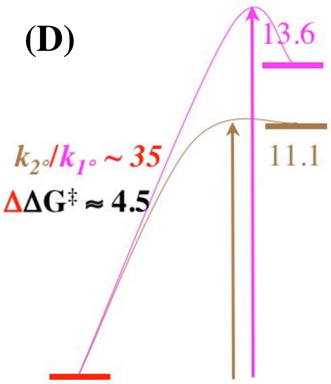




(C)

(D)



A) Counting “complexions” to explain exponential Boltzmann distribution of energy and explain that concentration of energy in a single degree of freedom is unlikely. (Lect 34, 12/5, frames 22-26)

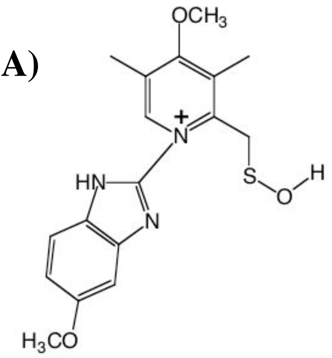
B) Entropy contribution to chair-boat cyclohexane equilibrium. More structures or quantum states for twist boat than for chair. (Lect 34, 12/5, frame 34)

C) Selectivity in bromination greater than predicted by Hammond Postulate. Something special in transition state where energy difference is not intermediate. (Lect 37, 12/12, frames 12-13)

D) Random dimer formation for Law of Mass Action; dimer ∝ monomer^2 (Lect 35, 12/7, frames 6-7)

8. (10 min) Tell how each of two **(2 only)** of the following four figures relates to questions of stereochemistry.

(A)



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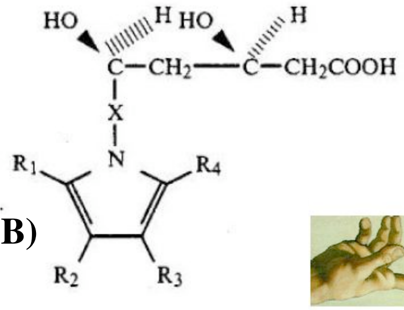

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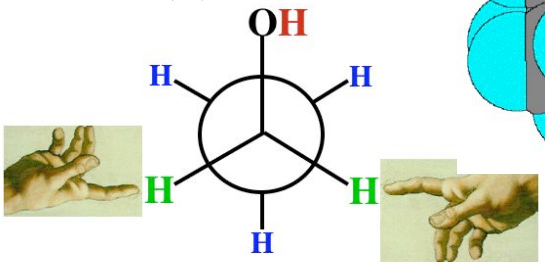

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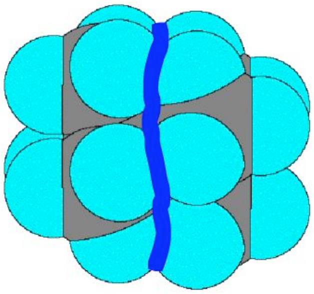


A) Achiral intermediate makes it unlikely that resolution of omeprazole enantiomers would be medically relevant. (Lect 29, 11/16, frame 28)

B) Which isomer is covered by crummy stereochemical diagram in Lipitor patent? Both diastereomers on only enantiomer shown? (Lect 28, 11/12, frame 4)

C) Enantiotopic hydrogens of ethanol have different reactivity with liver alcohol dehydrogenase enzyme. Demonstrated by deuterium removal/addition cycle. (Lect 30, 11/26, frame 46-47)

D) Because of non-1,4-van-der-Waals strain methyl substitution weakens central C-C bond by destabilizing starting material rather than by stabilizing product radicals. (Lect 36, 12/10, frames 23-28)

9. (4 min) Why is HBr the only hydrogen halide that can add to alkenes by a radical-chain mechanism?

For the other halogens one or the other of the two propagation steps is too slow to allow the chain to be favored over termination by radical-radical reaction. For iodine the addition of I atom to the alkene is endothermic and too slow; for fluorine and chlorine the H-X bond is so strong that abstraction of H from HX is too slow. (Lect 37, 12/12, frame 16)

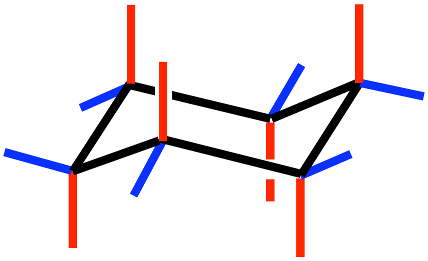
10. (12 min) Describe briefly three different methods that were used to prepare a single-enantiomer samples of omeprazole.

a) chromatography on derivatized chiral cellulose
b) temporary formation and crystallization of diastereomeric mandelate esters
c) oxidation of sulfur catalyzed by a titanium complex with resolved diethyltartrate ligand

(See Lect 30, 11/26, frames 4-7)

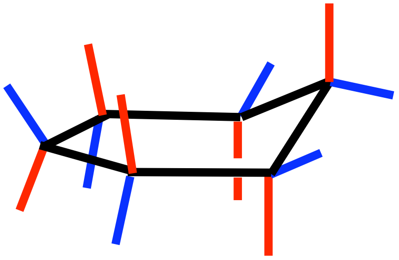
11. (5 min) **Draw** a structure of cyclohexane in the **chair conformation** showing clearly the orientation of the axial and equatorial hydrogen atoms.

Red – axial ; Blue - equatorial
(follow the recipe of
Lecture 32, 11/30, frame 5)



12. (6 min) Suppose that the conversion of your chair to a boat conformation went through a transition state in which one carbon atom becomes **coplanar with the four carbons atoms nearest to it**. **Explain** why you might expect two components of strain energy (as calculated by molecular mechanics) to increase upon this deformation, and why another component might decrease.

Bond angle strain increases as 3 C-C-C angles approach 120°.
Torsional strain increases as 2 C-C-C-C torsions become eclipsed.
Non-1,4-van der Waals repulsion between the red axial H atoms on the bottom of the ring decreases as the leftmost H drifts left.



13. (7 min) If you were in charge of public health, how would you have designed tests for the efficacy of esomeprazole (Nexium) that would be different from those that were actually conducted? Why were such tests not conducted?

"Superiority" of esomeprazole over racemic omeprazole was clinically "demonstrated" only by administering twice as much of the drug (four times as much of the allegedly active enantiomer). It should have been established either that twice as much of the racemate was unsafe, or if not, that such a large dose of the single enantiomer was safe. (Lect 30, 11/26, frames 12-13 or frame 21)

Measures of Bond Strength

One way to measure bond strength is by Average Bond Energy, another is by Bond Dissociation Energy, a third is by the stretching frequency of the bond as observed by Infrared Spectroscopy, a fourth is by Bond Length.

14. Average Bond Energy

(5 min) What is the **purpose** of compiling **Average Bond Energies**, and why do they differ from Bond Dissociation Energies? (an example would help)

Average bond energies are added to approximate the heat of atomization of a molecule, while bond dissociation energies are the energies required to actually break individual bonds. For example four times the average C-H bond energy gives a reasonable approximation of the energy difference between methane and its constituent free atoms, but the actual energies to break the four successive bonds of methane (CH_4 to CH_3 to CH_2 to CH to C) differ from one another by as much as 30 kcal/mole. (Lect 34, 12/5, frame 11).

15. Bond Dissociation Energy

The following table presents recent values of **Bond Dissociation Energies** involving the hydrocarbon radicals named in the first row.

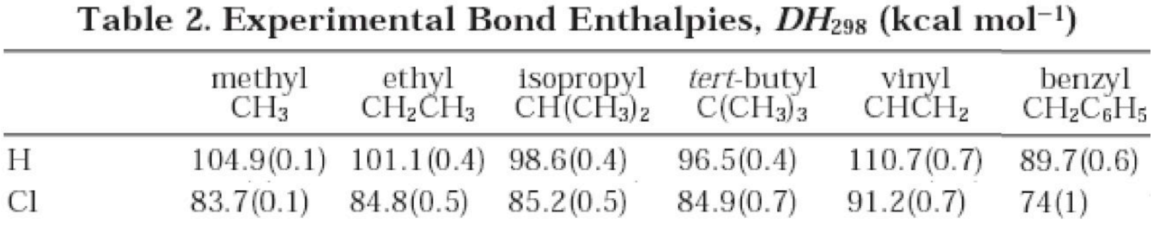


Table 2. Experimental Bond Enthalpies, DH_{298} (kcal mol^{-1})

	methyl CH_3	ethyl CH_2CH_3	isopropyl $CH(CH_3)_2$	*tert*-butyl $C(CH_3)_3$	vinyl $CHCH_2$	benzyl $CH_2C_6H_5$
H	104.9(0.1)	101.1(0.4)	98.6(0.4)	96.5(0.4)	110.7(0.7)	89.7(0.6)
Cl	83.7(0.1)	84.8(0.5)	85.2(0.5)	84.9(0.7)	91.2(0.7)	74(1)

A) (4 min) One of the hydrocarbon radicals is unusually stable. Which radical is it, and why is it stable?

The benzyl radical is unusually stable, because the SOMO 2p orbital of the radical carbon overlaps well with the unusually high HOMO and the unusually low LUMO pi orbitals of the benzene ring. (Lect 35, 12/7, frame 25)

B) (5 min) One of the hydrocarbon radicals forms unusually strong bonds. Which radical is it, and why are its bonds so strong?

The vinyl radical forms unusually strong bond to the H or Cl atom, because for this bond the carbon uses an sp^2 orbital which extends and overlaps better than sp^3. (Lect 35, 12/7, frame 25)

C) (5 min) Despite what many textbooks say, the other radicals do not form a series whose members are increasingly stabilized by substitution. Explain how these data prove that these textbooks are in error.

If the alkyl radicals were increasingly stabilized by substitution, one should see the same trend in both series that generate common radicals. However while there is a dramatic difference (smooth variation from 104.9 to 96.5 kcal/mole) for loss of H atoms, the differences for loss of Cl atoms are modest (83.7 to 85.2 kcal/mole) and irregular.

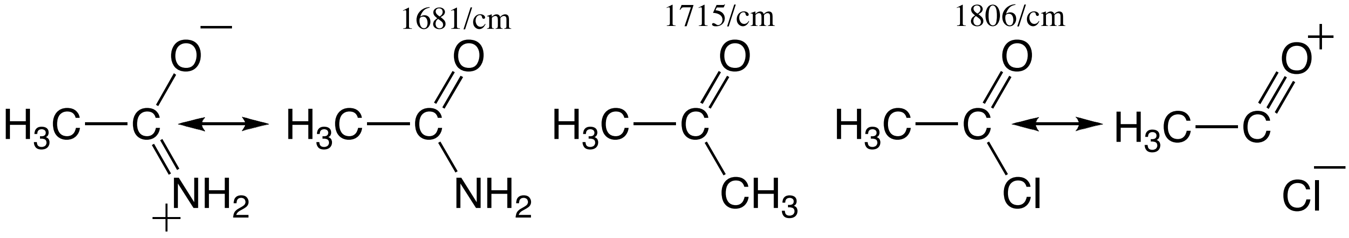
[In fact, after strain correction, there is no trend for H loss and a ***strengthening*** of bond by substitution for Cl. Lect 36, 12/10, frame 30]

D) (5 min) Explain in terms of theory why hyperconjugation could be an explanation for special stability of more highly substituted carbon cations even if the greater stability of radicals is illusory. *i.e.* Why might hyperconjugation be more important for carbon cations that for carbon radicals?

Hyperconjugation involves stabilization through mixing with a sigma CH orbital. Since this orbital is not unusually high in energy (it is in fact the standard energy), a vacant orbital that would mix with it and stabilize its electrons must be superlow. While the SOMO of a radical is not so very low, the LUMO of a cation would be very low because of the + charge and could generate the observed stabilization.

16. IR Spectroscopy

Stronger springs have higher vibration frequency. By this criterion the C=O bond in a ketone (1715/cm) is stronger than the C=O bond in an acetamide (1681/cm) but weaker that the C=O bond in acetyl chloride (1806/cm). It has been suggested that these differences can be explained in terms of ionic resonance structures that give the C=O bond in the amide “single bond character” and the C=O bond in the chloride “triple bond character”.



A) (5 min) Explain **in terms of intramolecular HOMO/LUMO mixing** why the single-bond amide resonance structure is sensible.

The unshared electron pair of the NH_2 group can be stabilized by mixing with the antibonding pi* LUMO of the C=O group. This mixing creates an additional bonding interaction between N and C (shortening the CN distance), but partial occupancy of the antibonding C=O orbital weakens and lengthens this bond.

(Lect 18, 10/17, frame 5)

B) (5 min) Explain **in terms of intramolecular HOMO/LUMO mixing** why the triple-bond chloride resonance structure is sensible.

An unshared sigma (in-plane) electron pair HOMO of the O atom can be stabilized by mixing with the antibonding sigma* LUMO of the C-Cl group. This mixing creates additional bonding between O and C, but partial occupancy of the antibonding sigma* C-Cl orbital weakens and lengthens this bond. The true C-Cl bond should be intermediate between a single bond and no bond at all – as the resonance structures predict. Charge transfer from the unshared pair of O to sigma* accounts for the partial charges.

17. (4 min) **Bond Length**

In the 1987 survey of the Cambridge Structural Database the C=O distance in 551 esters was 1.196Å (±0.01), while the C=O distances in 378 amides was significantly longer, 1.231Å(±0.01). **Explain** this difference in terms of orbital mixing.

The N atom of the amide has a higher-energy unshared pair than does the O atom of the ester. Because of better energy match the HOMO of N mixes more effectively with the antibonding pi* LUMO of the C=O group than the HOMO of O does. This weakens the C=O attraction more in the amide and makes the bond longer than in the ester.