1. What sort of structural information can you obtain for the compound whose 70 eV electron ionization (EI) mass spectrum is shown below? The more information you provide, the greater grade you will receive.

16 pts TOTAL.

Molecular ion: 170; 170+172: Br; ions m/z 37; m/z 91: benzyl; m/z 65: benzene; no N; No Cl; 6 pts total; benzyl bromide: 10 pts; isomer: 7 pts

2. Explain why collision-activated dissociation (CAD) mass spectra of molecular ions often look very different from the 70 eV EI mass spectra of the same compound. 10 pts.

Because P(E) deposited into the fragmenting ion is very different. 10pts
Different “energy”: 10 pts
1 pt: EI is more reproducible than CAD. 3 pt: CAD goes through lower energy pathways.

3. What type of compounds are likely to produce similar high- (keV) and low-energy (eV) CAD mass spectra? 6 pts. Justify. 6 pts.
Compounds whose ions have low activation energies for fragmentation because they fragment under both conditions.

4. Are the bonds in ions likely to be stronger or weaker than in neutral molecules? 5 pts. Justify. 5 pts.

Weaker; the excess or lack of electron density makes nearby bonds weaker

5. Give at least three problems that may be associated with using multiple activating collisions in CAD experiments. 12 pts; 4 pts each

Lowest energy pathways dominate; isomerization before activation; fragmentation of fragment ions

6. Since proton transfer plays an important role in many ionization methods used in mass spectrometry, it is important that you can differentiate strong gas-phase bases and acids from weak gas-phase bases and acids. Consider the structures shown below. Put them in the order of increasing gas-phase basicity or proton affinity. 14 pts: 2 pt each correct assignment

\[ \text{CH}_4 \quad \text{NH}_3 \quad \text{CH}_2=\text{CH}_2 \quad \text{H}_2 \quad \text{H} \quad \text{O} \quad \text{OH} \]

2 6 3 1 7 5 4

7. Show the main fragmentation reaction of the molecular ion of ethyl amine. 10 pts; any errors: -1 pt each

Unable to draw ethyl amine: -9 pts; the only thing correct is ethyl amine: 1 pt

8. Give typical values for eight (8) of the following items: 16 pts, 2 pt each

a. Resolution of an orbitrap: 250,000
b. Resolution of a linear quadrupole mass spectrometer: unit
c. Mass range of a typical quadrupole mass analyzer: 2000 - 4000
d. A typical bond dissociation energy of an organic molecule: 120 kcal/mol
e. The average amount of internal energy that an ion gains upon 10 eV CAD and 3 keV CAD: 1.5 eV
f. Kinetic energy of an ion in a time-of-flight mass spectrometer: 10 keV

g. Time an ion spends in a quadrupole mass filter: 100 µs

h. The pressure in a quadrupole mass spectrometer: 10^{-5} torr

i. Low detection limit: fM, pg, pg/ml

j. High mass accuracy: 1 ppm

k. Linear dynamic range: 10^5
1. Carbon monoxide (CO) is a very common ligand used in organometallic chemistry. Draw the molecular orbitals for CO (15 points). Point out which electron pair is used for the coordination bond formed between CO and a transition metal M. (5 points)
2. Between C and O in CO, which atom has more control over the electron pair as the direct ligand to the metal center (5 points)? Why (10 points)?

Oxygen.

To find out which atom has a better control over the coordinating e pair, you may draw a Lewis structure and calculate the formal charge on C and O. C carries a -1 charge, and O carries a +1. Such a charge distribution is not totally reasonable as C is less electronegative than O; O likely gains the electron to form a stable compound. However, it does indicate that the lone pair on C has higher energy, making it energetically favorable to form the M-CO bond with a transition metal center.

\[ \begin{align*}
\text{-1} & \quad +1 \\
:\text{C} & \equiv: \\
: & \equiv: \\
\end{align*} \]

The more reasonable explanation comes from the MO orbitals you just draw in problem 1. As indicated by the energy levels of the 2p_x and 2s orbitals on Carbon and the 2p_z orbital on Oxygen, these three orbitals have the right geometries and the right energies to interact to form the \( \pi \) orbital. The resulting \( \sigma \) orbital has significant contributions from two orbitals on carbon and only one on oxygen, leading to a larger lobe on the carbon end. As the consequence, the carbon has a better control over this lone pair when it coordinates to the transition metal M.
3. Among Fe, Fe$^{2+}$ and Fe$^{3+}$, which has the strongest interaction with CO (5 points)? Which is unlikely to support a stable carbonyl complex (5 points)? Why (10 points)?

*Fe has the strongest interaction in a Fe-CO$_2$ complex and Fe$^{3+}$ is unlikely to form a stable carbonyl complex.*

*As shown in problem 2, although carbon has a better control over the lone pair, it is less electronegative than oxygen. Therefore, the electron pair is easily polarized. Thus, the CO is a very soft base. Among the three species, Fe is the softest acid; Fe$^{3+}$ is the hardest, and it is very hard by nature. Therefore, CO has a very strong interaction with Fe, but barely coordinates to Fe$^{3+}$.*

(4) One key feature for a transition metal-CO complex is the distinctive IR stretches from CO. For the dicarbonyl complex below, how many IR bands do you expect from the two CO molecules? Using symmetry operations and appropriate character table to back up your conclusion. (30 points)

![Cis-dicarbonyl complex](image)
The cis-dicarbonyl complex has a square planar geometry, and belongs to the $C_{2v}$ point group.

The reducible representation is reduced to two irreducible representations $A_1$ and $B_1$.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma'_v(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

$A_1$ transforms as the Cartesian coordinate $z$ and $B_1$ transforms as Cartesian coordinate $x$. Therefore, both are IR active and you should expect two IR bands for this cis-dicarbonyl complex.
(5) Free CO has an IR stretch at 2143 cm\(^{-1}\). For the most stable metal-carbonyl complex formed in problem (3), do you expect its IR stretches to be higher or lower than 2143 cm\(^{-1}\)? Why (15 points)?

*Lower.*

There are two types of bonding interactions between a CO ligand and the Fe center it coordinates to: (1) \(\sigma\) bond formed between the HOMO orbital of CO and an Fe atomic orbital, which donates some electron density from CO to the Fe orbital, reducing the electron population on the bonding orbital of CO. (2) The electron back-donation via formation of \(\pi\) bond. Here the electron density from the Fe \(T_{2g}\) orbitals is donated back to the \(\pi^*\) orbitals on CO. As a consequence, the electron population on the CO anti-bonding orbitals is increased. Collectively, the bond order for a CO molecule in the resulting Fe-CO\(_x\) complex must be smaller than 3. Thus, the IR frequency must be lower than 2143 cm\(^{-1}\) found in free CO.
4 ring Si transfer to O acceptable answer from either of these intermediates

up to 35 pts possible for the 25 pt question
[2. 25 points] The last three steps for synthesis of 15 from alcohol 25 are: (d) 6.0 equiv of \( \text{CIC(S)O}_2p\)-tolyl, 6.5 equiv of DMAP, \( \text{CH}_3\text{CN} \), 82°C, 10 h, 50%; followed by (e) 1.5 equiv of (TMS)\(_2\)SiH, 0.2 equiv of AIBN, toluene, 80 °C, 1 h, 91%; and (f) 10 equiv of \( \text{NaOH} \), \( \text{CH}_3\text{OH} \), 23 °C, 4 h, then 3.0 equiv of DCC, 3.0 equiv of \( \text{BnOH} \), 0.15 equiv of DMAP, \( \text{CH}_2\text{Cl}_2 \), 23 °C, 1 h, 72%. Provide a detailed electron-pushing mechanism for the full three-step process. [Hints: DMAP is 4-dimethylaminopyridine, AIBN is \( \text{NCMe}_2\text{C-N=NCMe}_2\text{CN} \), TMS\(_2\)SiH can be replaced with Bu\(_3\)SnH in the same process, and DCC is dicyclohexyl-carbodiimide \( \text{C}_9\text{H}_{11}\text{N}=\text{NC}_8\text{H}_{11} \). Dragovich, et al. *J. Med. Chem.* 1996, 39, 1872-1884.
Scheme 2. Synthesis of dialdehyde cyclization substrate 2.

Tf = trifluoromethanesulfonyl, TBS = tert-butyldimethylsilyl, TMS = trimethylsilyl, DMF = N,N-dimethylformamide, TBAT = tetra-n-butylammonium difluorotriphenylsilicate, DMAP = 4-dimethylaminopyridine,

Bu₄N +5 - Pd - PPh₃
Ph F Si F Ph F
Ph Ph
BF₃ - CF₃SO₃
TMS +5 TMS +5 acyl Pd intermediate

+5 Product 9 + TMSF + Ph₃SiF

+5 ox add
R₂CuMg(X)
redact elim

+5 ox add
CuR₂

+5 ox add
R₂CuMg(X)
redact elim

+5 ox add
CuR₂

G = MgX or Cu
G = H after workup
rac diast'm mix

+5 in situ Pd(PPh₃)₂
Pd (0) to Pd(II)

+5 up to 60 pts possible
for the 50 pt question

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