1. Arrange the compounds in each set in order of decreasing reactivity toward electrophilic aromatic substitution.

- For set A, the reactivity order is: A > B > C, with A being the fastest and C being the slowest.

- For set B, the reactivity order is: A > B > C, with A being the fastest and C being the slowest.

- For set C, the reactivity order is: C > A > B, with C being the fastest and B being the slowest.

+3 pts each
+1 pt bonus only if all 3 parts correct
if the order is wrong, give +1 pt partial credit
if the fastest compound is identified correctly
2. (a) Write a detailed mechanism for the following reaction.

\[
\text{C}_6\text{H}_5\text{Cl} + \text{CH}_3\text{C}=\text{O} \rightarrow \text{C}_6\text{H}_5\text{COCH}_3
\]

\[
\text{H}_3\text{C}=\text{O} \rightarrow \text{C}_6\text{H}_5\text{COCH}_3
\]

\[
\text{AlCl}_3 \quad \text{Cl-AlCl}_3 \quad \text{Cl-AlCl}_3
\]

\[+4\text{pts} \quad \text{correct}\]
\[+2\text{pts} \quad \text{OK, but some mistakes}\]
\[+0\text{pts} \quad \text{totally wrong, or blank}\]

(b) Draw a free energy vs. reaction coordinate diagram for the reaction. Label any transition states or intermediates that may be involved.

\[+6\text{pts} \quad \text{correct answer}\]
\[+4\text{pts} \quad \text{OK, but some mistakes}\]
\[+2\text{pts} \quad \text{problems}\]
\[+0\text{pts} \quad \text{totally wrong or blank}\]
Consider the following electrophilic aromatic substitution reactions:

(i) \[ \text{NO}_2 \xrightarrow{\text{SO}_3 / \text{H}_2\text{SO}_4 / \text{heat}} \text{NO}_2 \]

(ii) \[ \text{SO}_3 / \text{H}_2\text{SO}_4 \xrightarrow{\text{heat}} \text{HO}_3\text{S} \]

Rationalize the fact that reaction (i) gives primarily the meta product, while reaction (ii) gives primarily the para product. (You do not need to write out the entire reaction mechanism for both reactions, but you should draw the structures of key intermediates that form the basis for your explanation.)

In rxn (i), meta attack. \[ \text{NO}_2 \] is "less bad" than ortho or para attack. (System will try to avoid having change on adjacent atoms.)

In rxn (ii), ortho or para attack results in stabilization of the carbocation \( \Rightarrow \) preferred.

alkyl substituent stabilizes positive charge by hyperconjugation (can't happen with meta isomer)