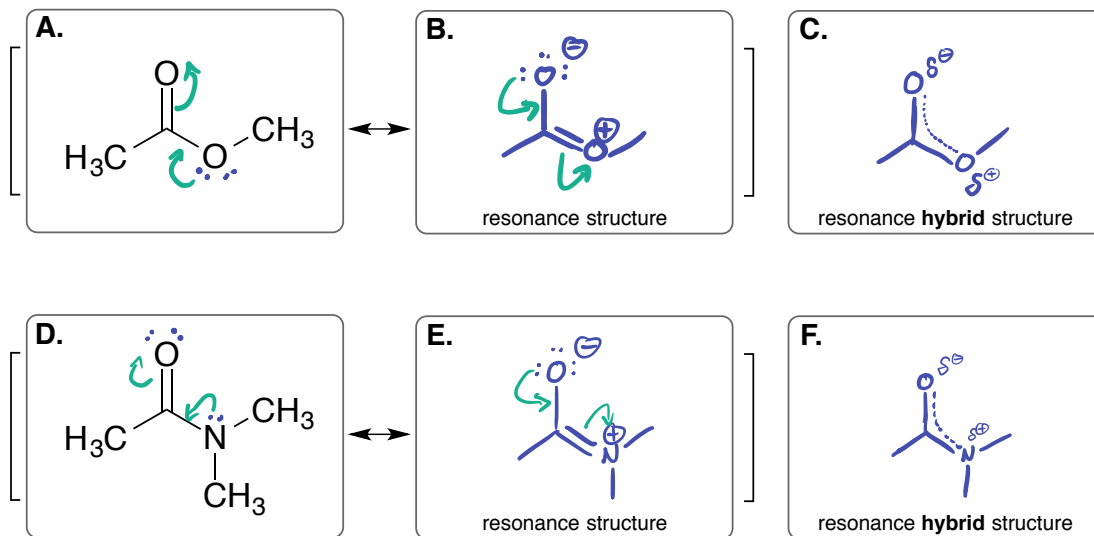


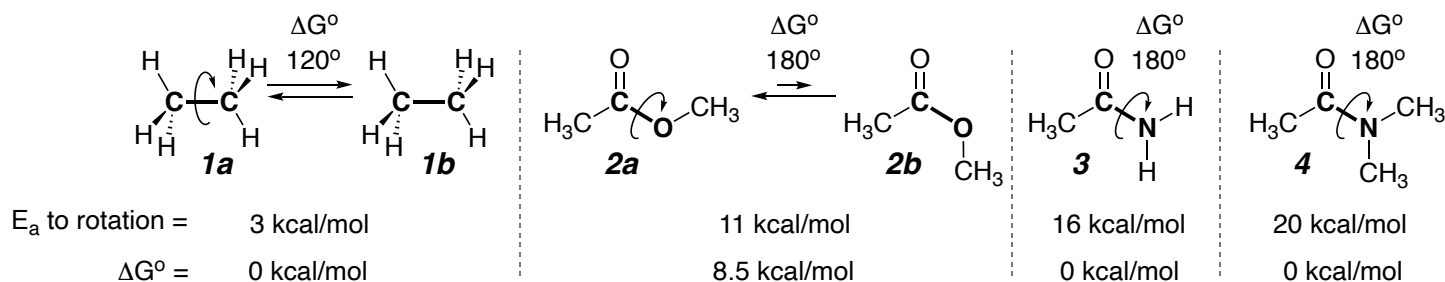
A-F. 6 pts. Consider the molecules drawn in boxes **A** and **D** below. Add the lone pairs where necessary. In boxes **B** and **E**, draw the best resonance structure (make sure that all octets are filled, don't forget to add the lone pairs and charges).

Draw the curly arrows that show the movement of electrons between *both* structures in **A – B** and **D – E**.

In boxes **C** and **F**, draw the single resonance structure that represents both **A – B** and **D – E**. Include symbols for “slightly positive” (δ^+) and “slightly negative” (δ^-) on the appropriate atoms, if any.



The C-X single-bond in **bold** (where X = C, O, or N) shows the 120° rotation for ethane (from **1a** to **1b**), and the 180° rotation for compounds **2**, **3** and **4**, and the corresponding activation energies (E_a) and ΔG° . In compounds **1**, **3**, and **4**, the process of bond rotation is thermoneutral ($\Delta G^\circ = 0$ kcal/mol), but it is endothermic from **2a** to **2b**.

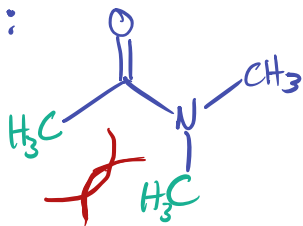


G. 4 pts. Comparing molecules **1** and **3**, briefly explain why the activation energy (E_a) to rotate the **C-N bond** is higher in energy than the process to rotate the **C-C bond** in compound **1**. Use chemical structures in your answer.

The barrier to rotation in ethane is small because it is a C-C single bond without steric hindrance (only H-H eclipse). The E_a is much higher in **3** because the resonance structure in Box E shows double-bond character between C and N, which keeps it from rotating freely. The hybrid resonance structure also shows this partial double-bond character.

H. 2 pts. Comparing molecules **3** and **4**, briefly explain why the activation energy (E_a) to rotate the **C-N bond** is higher in energy in **4** than in **3**. Draw structures to aid your answer.

Compound **4** contains two methyl groups that add steric hindrance, as shown here:



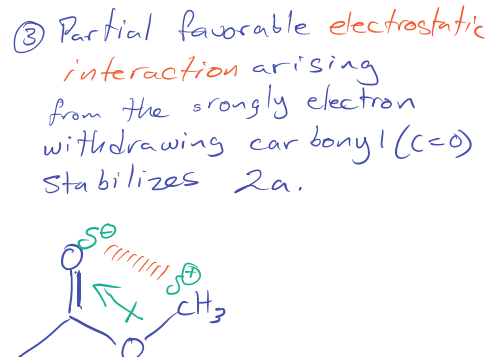
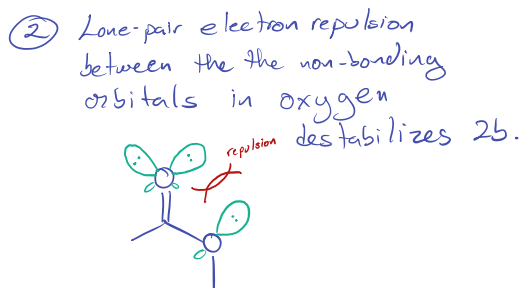
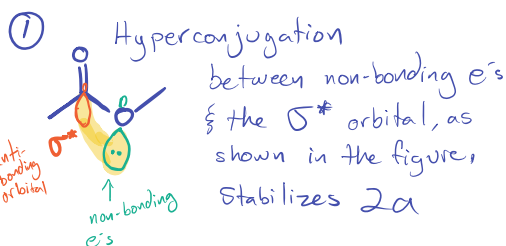
Therefore, the rotational energy barrier is much higher.

I. 3 pts. Comparing molecules **2** and **3**, briefly explain why the activation energy (E_a) to rotate the **C-N bond** is higher in energy in **3** than rotating the **C-O bond** in **2**. Draw structures to aid your answer.

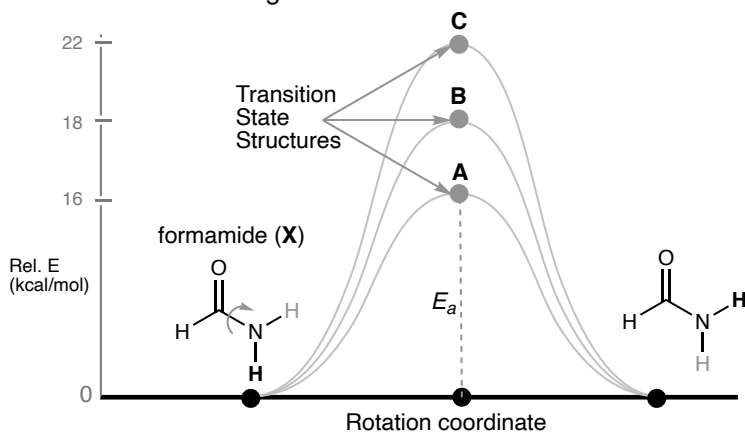
The resonance structures in boxes **B** & **E** show that there is a positive charge \oplus on Oxygen & Nitrogen. Since N can stabilize the charge better than O, the resonance structure of **3** has greater double-bond character. This raises the rotational energy barrier more than in the resonance structure of **2**.

J. 3 pts. Now look at the ΔG° values to go from **2a** to **2b**. Briefly explain why equilibrium favors **2a** than the **2b** conformer. (Hint: both molecules are flat). Draw structures to aid your answer.

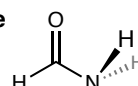
Three reasons



K. 2 pts. As the C-N bond in formamide (compound **X**) rotates, the nitrogen *rehybridizes at the transition state* to access the lowest energy path for rotation. There are three possible modes for the rotation of the C-N bond, with relative activation energies (E_a) in the order of: **A** = 16 kcal/mol, **B** = 18.5 kcal/mol, and **C** = 22 kcal/mol. The three possible drawings that can represent the structure of the transition state for each possible path in the C-N bond rotation are shown on the right of the free-energy diagram. Match the label (**A**, **B**, **C**) from the free energy diagram to the representative transition state structure on the right.

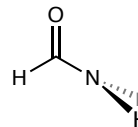


Representative Transition State Structures:

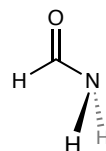


Label

A



C



B