

Handin Homework 8: Thermochemistry and Entropy

1. The enthalpy of formation of urea is $-333.0 \text{ kJ mol}^{-1}$ at 298.2 K . Calculate the internal energy of formation at the same temperature. Urea is $\text{CH}_4\text{N}_2\text{O}$.

2. The Haber process is used to manufacture ammonia. However, while the synthesis is done at 500°C , thermodynamic tables list the enthalpy of formation at 25°C . Estimate the enthalpy of formation of ammonia gas at 500°C from $\Delta_f H^\circ(\text{NH}_3, 298.2 \text{ K}) = -46.1 \text{ kJ mol}^{-1}$. Use the estimates for the heat capacities: $C_p(\text{N}_2) = C_p(\text{H}_2) = \frac{7}{2} nR$ and $C_p(\text{NH}_3) = \frac{8}{2} nR$.

3. The dimer of methylvinylketone is shown in Figure 1. For this problem we will study just the axial isomer for the $-\text{CO}-\text{CH}_3$ side chain. Which face of the carbonyl is more susceptible to nucleophilic attack? Nucleophilic attack will be perpendicular to the trigonal plane of the sp^2 hybridized carbon, Figure 1b. According to Cram's rule, the less hindered side is likely to be most susceptible. Make sure that you build the axial isomer. To begin this study we need to know the low energy conformers about the side-chain C-C bond to the ring. What are the low energy conformers? Draw these low energy conformers and note the less hindered side. Space filling models will be helpful in looking at steric influences. Calculate the conformational entropy about the side chain bond and determine the direction of nucleophilic attack.

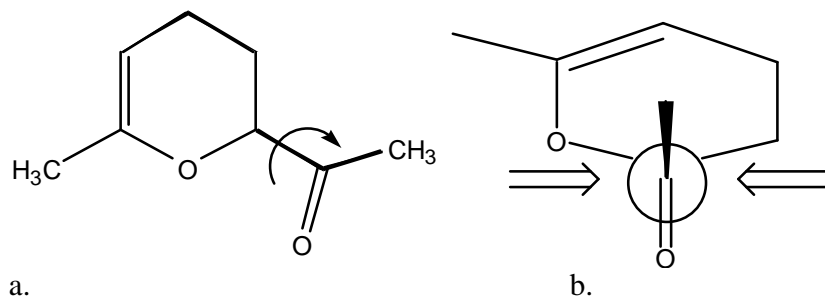


Figure 1 (a). Methylvinylketone dimer. The bond with free rotation is marked. (b) Newman projection. Which side of the carbonyl is attacked by nucleophiles? The favored direction of attack will change with conformation angle. Only one possible conformation is shown here.

4. Calculate the change in entropy for one mole of a diatomic ideal gas ($C_v = \frac{5}{2} nR$) that is heated and compressed from 25.0°C and 10.0 L volume to 100.0°C and 1.00 L volume.