Stereoselective Addition of Tertiary Carbons Radicals

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Chem 250L

Assignment 6.1 Limitations of transition state theory

1. Assuming $k_2 >> 0$, the reaction should not proceed in the reverse direction from the transition state to the product. Therefore, the activated complex is equivalent to the "dividing surface".

2. TST relies on the reactants to $X^\ddagger$ transition to be the rate determinig step so that a quasi-equilibrium is formed. Any reaction in which the intermediate lifetime is short-lived will cause TST to fail. One such reaction is (insert reaction lol)

Assignment 6.2 Eyring equation

1. Derive an expression for k_1 in terms of the change in Gibbs free energy of activation, $\Delta G^\ddagger$, for the quasi-equilibrium reaction in Eq. 6.1.

$$\begin{aligned} \Delta G^\ddagger &= -RTln[K^\ddagger] \\ &= -RTln[\frac{h}{k_B T}k_1] \\ ln[\frac{h}{k_B T}k_1] &= -\frac{\Delta G^\ddagger}{RT} \\ k_1(\frac{h}{k_B T}) &= \text{Exp}[-\frac{\Delta G^\ddagger}{RT}] \\ k_1 &= \frac{k_B T}{h}\text{Exp}[-\frac{\Delta G^\ddagger}{RT}] \end{aligned}$$

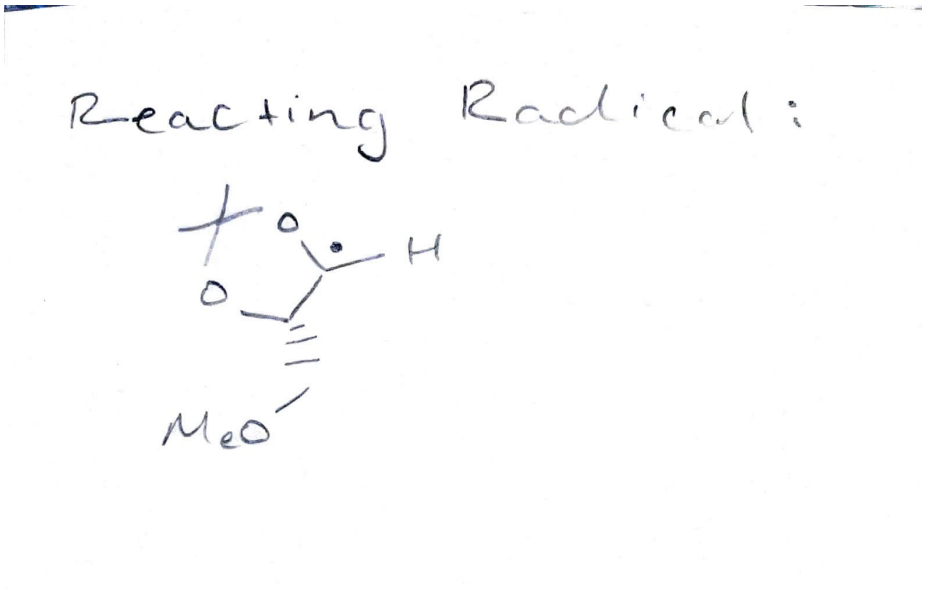
2. Consider two competing reactions of the same passing through two different transition states. Derive an expression for the relative yield of the two resulting products in terms of the difference in Gibbs free energies of activation, sometimes called $\Delta\Delta G^\ddagger$, under the assumption of kinetic

control.

$$\frac{k_1}{k_2} = \frac{\mathrm{Exp}[-\frac{\Delta G_1^\ddagger}{RT}]}{\mathrm{Exp}[-\frac{\Delta G_2^\ddagger}{RT}]}$$
$$= \mathrm{Exp}[\frac{\Delta G_2^\ddagger - \Delta G_1^\ddagger}{RT}]$$
$$= \mathrm{Exp}[\frac{\Delta\Delta G^\ddagger}{RT}]$$

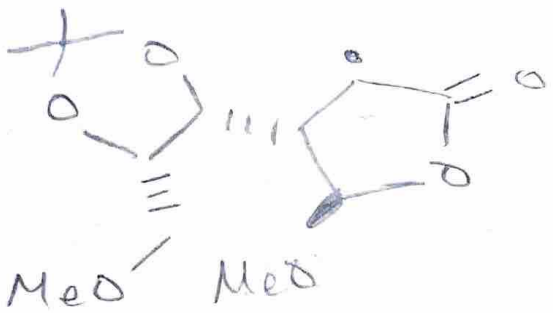
Assignment 6.3 Lewis structures and their limitations

1. Draw the Lewis structure of the reacting radical for the reaction in Fig. 6.2.2.



2. Draw structures for the transition states leading to the syn and the anti products.
3. Why is the syn/anti selectivity difficult to predict without a calculation ?

Syn:



Anti: