

### ❖ Thermodynamic and Kinetic Requirements

In this section, we will discuss a brief idea of the thermodynamic and kinetic requirements of an organic reaction.

#### ➤ Thermodynamic Requirements for a Reaction

A reaction takes place spontaneously if the magnitude of  $\Delta G$  is negative i.e. the free energy of the reactants must be higher than the free energy of the products and vice-versa. From thermodynamics, we know that

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

$$\Delta G = -RT \ln K \quad (2)$$

Where  $\Delta H = \Sigma H_{products} - \Sigma H_{reactants}$ ,  $\Delta S = \Sigma S_{products} - \Sigma S_{reactants}$  and  $T$  is the temperature. The symbols  $R$  and  $K$  represent the gas constant and equilibrium constant, respectively. Now, as the entropy changes for most of the organic reactions is quite small, the free energy change is primarily governed by the value of  $\Delta H$ . Furthermore, it follows from equation (1) that  $\Delta G$  will become more negative with a more negative value of  $\Delta H$ , which in turn would increase the value of equilibrium constant  $K$ . Hence, more and more product will be formed as the enthalpy of the system decreases.

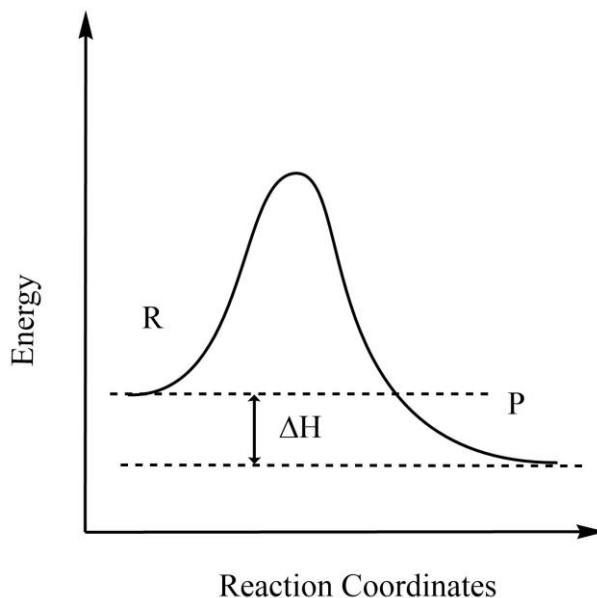


Figure 1. Energy profile diagram for thermodynamics of a typical organic reaction.

Furthermore, it is also very obvious from equation (1) that entropy becomes more important as the temperature of the reaction vessel is raised.

➤ **Kinetic Requirements for a Reaction**

The kinetic requirements of an organic reaction depend upon the activation energy of the same. If the activation energy barrier is low, the reaction will take place at a higher speed. If the activation energy barrier is high, the substance will react slowly and will take a very long time to complete.

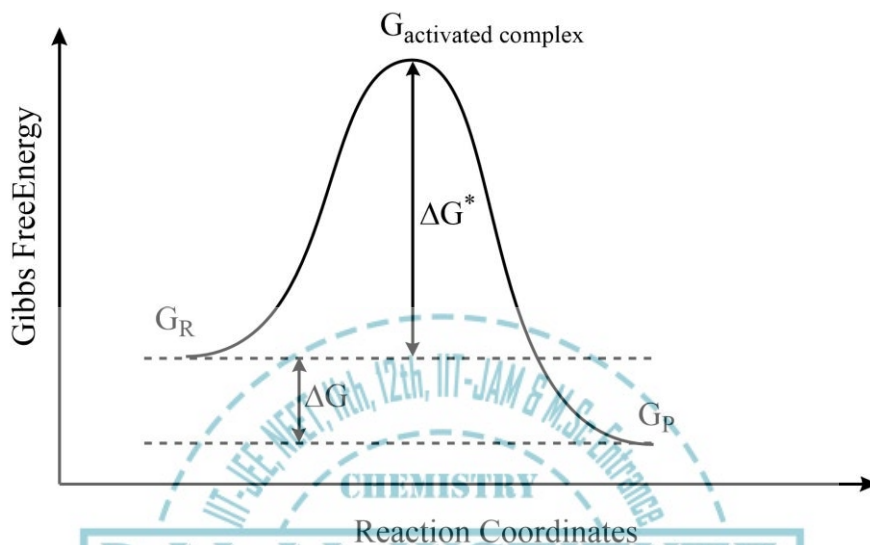


Figure 2. Energy profile diagram for kinetics of a typical organic reaction.

Since the kinetics of organic reactions is generally studied in the framework of “Activated complex Theory”, which states that the rate constant for a typical reaction is

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^*}{RT}} = \frac{RT}{Nh} \times e^{\frac{\Delta S^*}{R}} \times e^{-\frac{\Delta H^*}{RT}} \quad (3)$$

Where  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  are free energy change, enthalpy change, and the entropy change of the activation step, respectively. As far as equation (3) is concerned, it can easily be seen that as the free energy change of the activation step increases, the rate constant would decrease.

However, if we look at the simplified form i.e. equation (3), we find three factors; one is  $RT/Nh$  which is constant if the temperature is kept constant. The second factor involves  $\Delta S^*$ , and therefore, we can conclude that the reaction rate would show an exponential increase if the entropy of activation increases. The third factor includes  $\Delta H^*$ , and therefore, we can conclude that the reaction rate would show an exponential decrease if the enthalpy of activation increases. It is also worthy to note that the first two terms collectively make the frequency factor.

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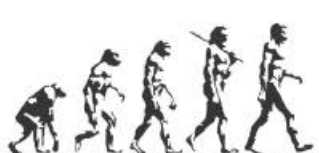
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# A TEXTBOOK OF ORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

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