ANDERSON SERANGOON JUNIOR COLLEGE
H3 CHEMISTRY
BASIC PHYSICAL ORGANIC CHEMISTRY

CONTENT

LEARNING OUTCOMES

Students should be able to understand and apply the following concepts involving kinetic control and thermodynamic control to the study of reaction mechanisms:

(i) the Hammond postulate: relationship between the transition state and the nearest stable species

(ii) the Bell–Evans–Polanyi principle
- relationship between activation energy and enthalpy change of reaction
- quantitative calculations based on $E_A = A + B\Delta H_r$

1 INTRODUCTION

1.1 Reaction Mechanism

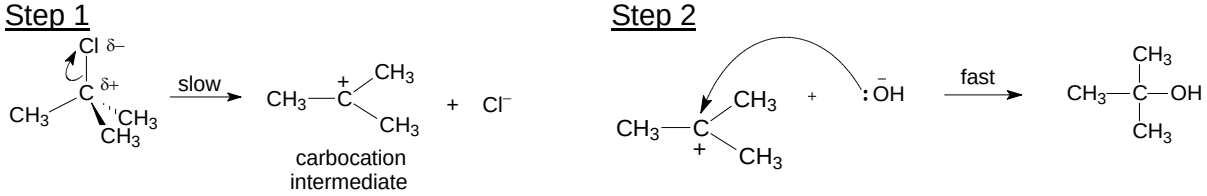
For a chemist involved in synthesis, mechanistic knowledge of a reaction allows intelligent variation of reaction conditions, temperatures and proportions of reagents to maximise yield of pure products.

Reaction mechanism is a sequence of elementary steps that are involved in the pathway from reactants to products.

Elementary step refers to the simplest step which cannot be further broken down into simpler steps.

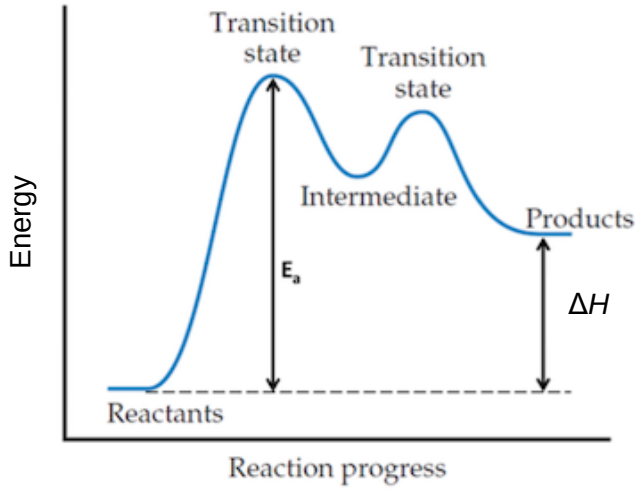
E.g. Overall reaction: $(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3COH + Cl^-$
(Reactants) (Products)

The S_N1 mechanism involves 2 elementary steps:



1.2 Energy Profile Diagram

An energy profile (or reaction profile) diagram is a graph showing how the energy of the reacting system changes as a function of the reaction coordinate.



A reaction intermediate is a species that is formed in one step of a reaction mechanism and consumed in a subsequent step. This species can be a molecule, ion or a free radical.

A transition state (TS) is defined as the state corresponding to the highest energy along the reaction coordinate of an elementary reaction. TS can neither be isolated nor can it be studied by spectroscopic method.

However, TS does have a _____ which allow chemists to investigate how changes in the reagents and solvent influence the difference in energy between reagents and TS. If these influences make the transition state more stable compared with the reagents, the reaction will be faster.

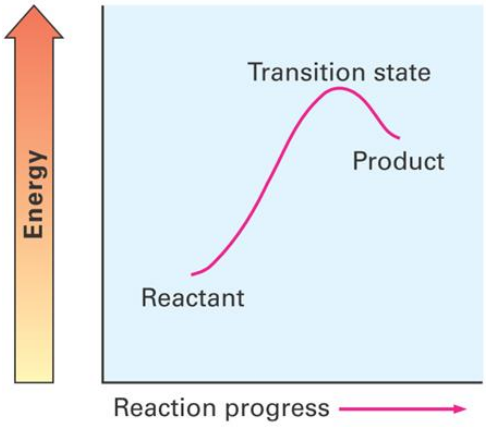
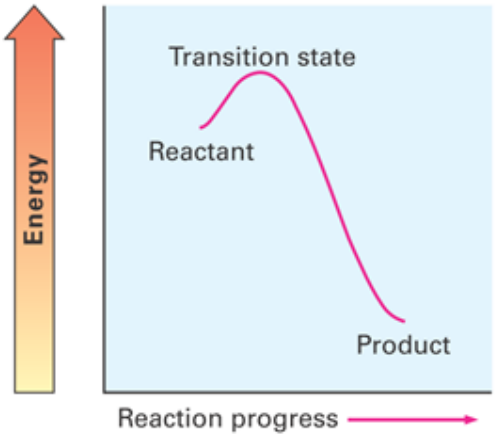
2 HAMMOND POSTULATE

2.1 Definition

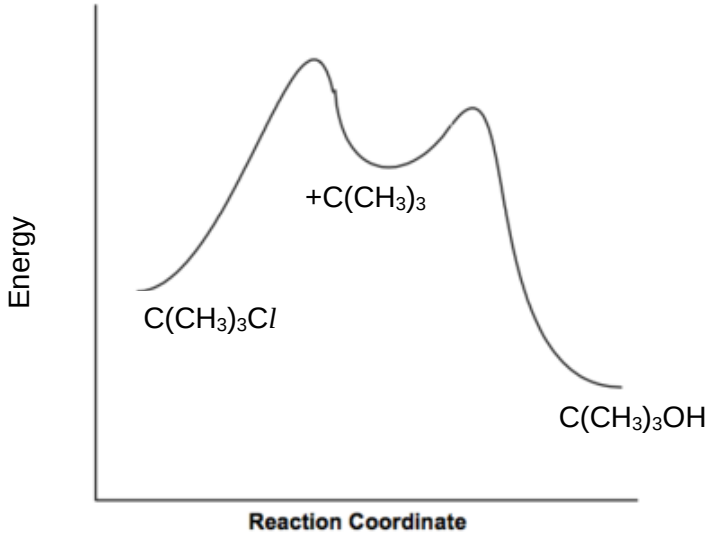
Hammond postulate is helpful to understand the relationship between the rate of reaction and the stability of the products/intermediates formed.

In 1955, George S. Hammond postulated that: If two states, as for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small re-organisation of the molecular structures. This means that the geometrical structure of the transition state resembles the structure of the intermediate species.

Hence, the structure of a transition state resembles the structure of the nearest stable species.

Endothermic reaction	Exothermic reaction
	
transition state • Energy level of the TS is closer to that of the _____. • Structure of the TS resembles the structure of the _____ of that step.	transition state • Energy level of the TS is closer to that of the _____. • Structure of the TS resembles the structure of the _____ of that step

E.g. For a S_N1 reaction for the hydrolysis of $C(CH_3)_3Cl$,



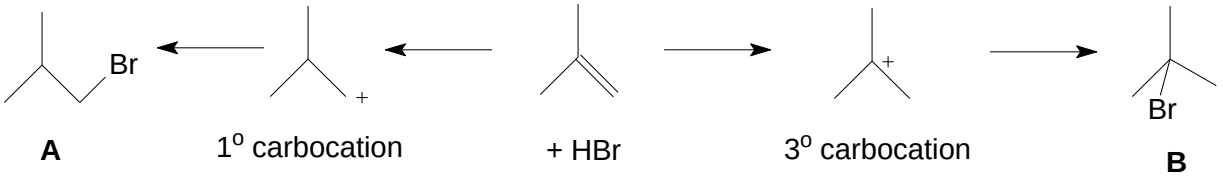
TS of step 1 is _____TS.

TS of step 2 is _____TS.

2.2 Application of Hammond Postulate

The Hammond Postulate suggests that high-energy intermediates and the transition states that lead to their formation are affected by similar substituent effects.

Example
In an electrophilic addition of unsymmetrical alkene, consider the reaction of methylpropene and HBr:

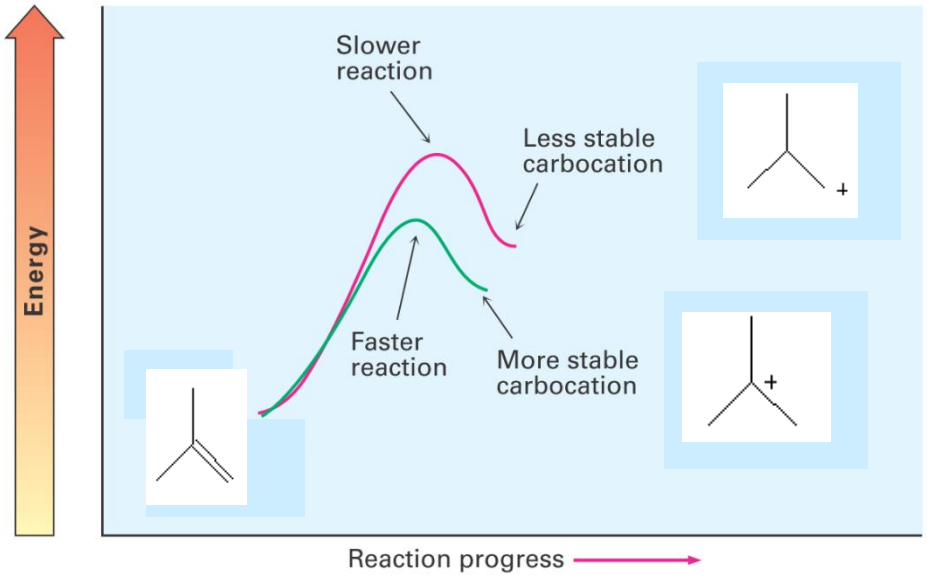


A 1^o carbocation + HBr 3^o carbocation **B**

Why is product **B** formed in a greater proportion as compared to product **A**?

From H2 Chemistry:
3^o carbocation is more stable than 1^o carbocation since it has _____ alkyl groups attached to the C+ which _____ the positive charge on the carbocation to a greater extent. Hence 3^o carbocation is more stable and is formed at a faster rate leading to a greater proportion of product **B** being formed.

Why does a more stable carbocation lead to a faster rate of reaction?
What is the link between stability and rate of reaction?



TS of step 1 is a _____ TS which means that TS is closer in energy to the _____ and its structure resembles that of the _____. Hence any factor that stabilises the _____ will also stabilise the TS.

Since _____ is stabilised by greater number of electron-donating R groups, the 3^o TS is also **stabilised by** _____. Therefore, the more stable 3^o TS has a _____ for its formation leading to a _____ rate of formation.

3. BELL-EVANS-POLANYI (BEP) PRINCIPLE

3.1 Definition

The BEP Principle describes the experimental observation that a linear relationship exists between the activation energy (E_A) and the enthalpy change of reaction (ΔH) for similar reactions.

This relationship can be expressed as: $E_A = A + B\Delta H_r$

where
- E_A is the activation energy of a reaction,
- ΔH_r is the enthalpy change of reaction, and
- A and B are constants

How is the expression ($E_A = A + B\Delta H_r$) derived?

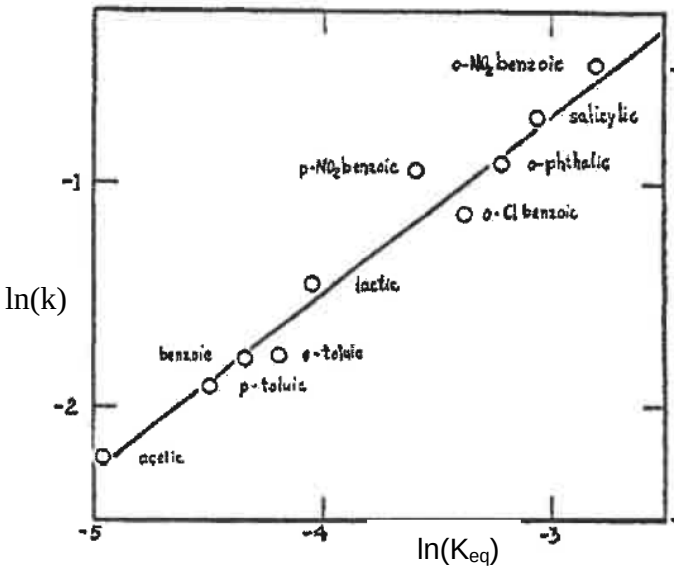
The BEP Principle was derived from the observation that, for certain closely-related reactions, the rate constant (k) and equilibrium constant (K_{eq}) are related by the equation

$$\ln(k) = \ln(\gamma) + \beta\ln(K_{eq})$$

where γ and β are experimentally determined constants.

An example of such reaction is

$$RCOOH + N(CH_3)_3 \rightleftharpoons RCOO^- + N(CH_3)H^+$$



From the graph, a linear relationship is observed between ln(k) and $\ln(K_{eq})$. The gradient of the line will give the value for β while the y-intercept will give the value for $\ln(\gamma)$.

Using the Arrhenius equation ($k = Ae^{\frac{-E_A}{RT}}$) and $\Delta G^o = -RT\ \ln(K_{eq})$,

$\ln(k) = \ln(\gamma) + \beta\ln(K_{eq})$ can be manipulated to

$$\ln A - \frac{E_A}{RT} = \ln\gamma - \beta\frac{\Delta G^\theta}{RT}$$

$$\frac{E_A}{RT} = \ln A - \ln\gamma + \beta\frac{\Delta G^\theta}{RT}$$

$$E_A = RT\ln\frac{A}{\gamma} + \beta(\Delta H^\theta - T\Delta S^\theta)$$

$$E_A = RT\ln\frac{A}{\gamma} - \beta T\Delta S^\theta + \beta\Delta H^\theta$$

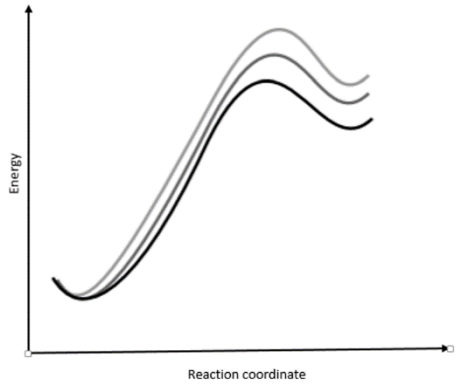
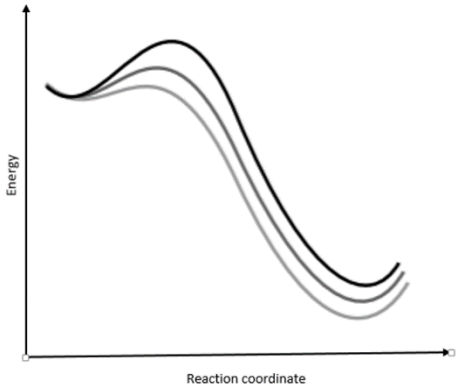
For closely-related reactions, $RT\ln\frac{A}{\gamma} - \beta T\Delta S^\theta$ is constant, hence the equation is simplified to

$$E_A = \alpha + \beta\Delta H^\theta$$

3.2 Application of BEP Principle

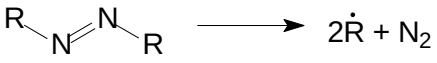
(a) Predicting the rate of reaction

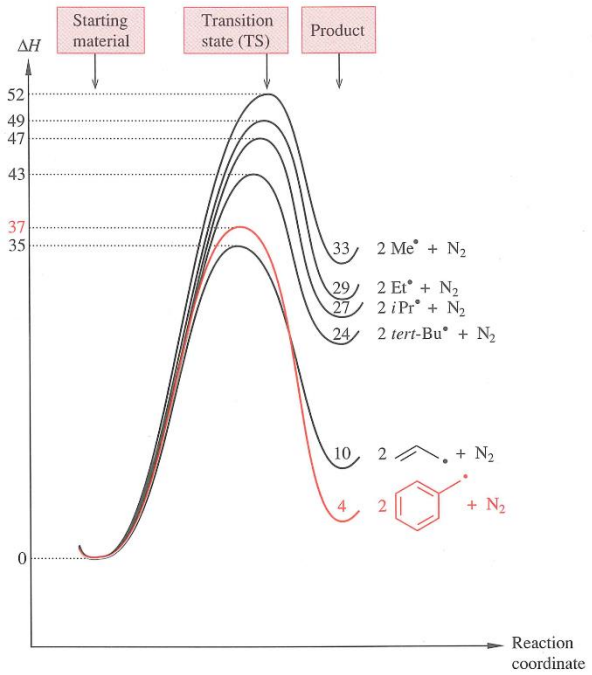
This relationship provides an efficient way to estimate the activation energy of reactions, and hence, reaction rate within the same family.

endothermic reaction	exothermic reaction
An _____ in the positive enthalpy of reaction results in an _____ in the activation energy. This thus _____ the rate of the reaction.	An _____ in the negative enthalpy of reaction results in a _____ in the activation energy. This thus _____ the rate of reaction.
	

Example

In the following reaction:



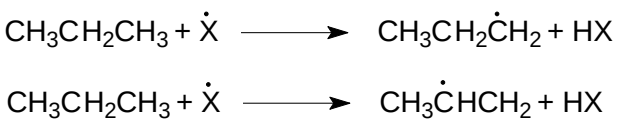


From the diagram, it can be observed that the _____ the reaction, the _____of the reaction. Hence it can be predicted that the rate of reaction involving _____ will be the slowest.

(b) Calculations based on $E_A = A + B\Delta H_r$

Example

In a free-radical substitution of propane with either chlorine or bromine, it is possible for either of the two different hydrogen atoms to be abstracted from propane.



The table shows the results of H-atom abstraction from propane by chlorine and bromine separately.

	Primary H / kJ mol^{-1}		Secondary H / kJ mol^{-1}	
	ΔH_r	E_A	ΔH_r	E_A
Cl_2	–20.9	4.1	–35.5	To be calculated
Br_2	+43.9	To be calculated	+29.3	42.4

The BEP Principle related the activation energies of a series of related reactions to their enthalpy changes.

(i) Calculate the E_A for the secondary H abstraction for the reaction between chlorine and propane given that A = 3.62 and B = –0.0231.

(ii) Calculate the E_A for the primary H abstraction for the reaction between bromine and propane given that A = –257 and B = 7.07.

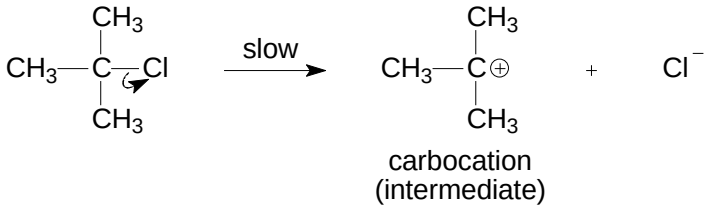
Solution

4. THE RELATIONSHIP BETWEEN HAMMOND POSTULATE AND THE BEP PRINCIPLE

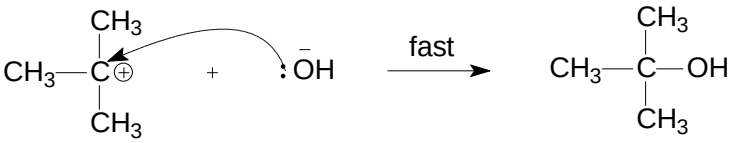
Both the BEP and Hammond Postulate can be used to discuss the kinetics of a given reaction. Generally, the results complement each other.

Example
In a S_N1 reaction for the hydrolysis of $C(CH_3)_3Cl$,

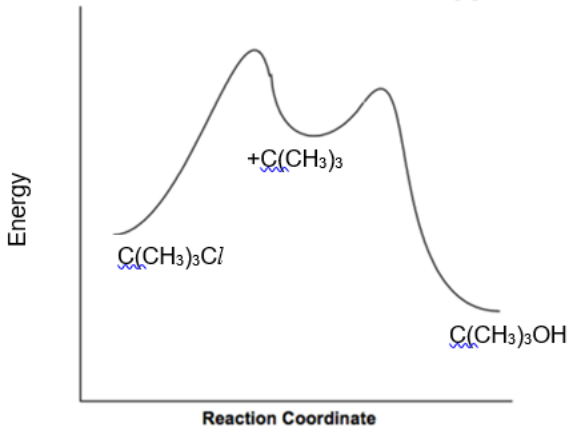
Step 1:



Step 2:



Energy Profile diagram



How do we use Hammond Postulate and BEP principle to explain why S_N1 reaction with tertiary alkyl halides is faster as compared to secondary and primary alkyl halides?

Using Hammond Postulate, TS of the slow step (step 1) is a _____which means that TS is close in energy to the _____ and its structure resembles that of the _____. Hence any factor that stabilises the _____ will also stabilise the TS. Since 3º carbocation is stabilised by greater number of electron-donating R groups, the 3º TS is also _____. Therefore, the 3º TS has a _____ for its formation leading to a _____of formation.

Using BEP, since a 3º carbocation formed is _____ than a 2º carbocation, the ΔH_r for step 1 is _____. As a result, 3º TS has a _____ for its formation leading to a _____ of formation.

-END-