



JECRC Foundation



**JAIPUR ENGINEERING COLLEGE
AND RESEARCH CENTRE**

JAIPUR ENGINEERING COLLEGE AND RESEARCH CENTRE

Year & Sem – B.Tech I year I Sem

Subject –Engg.Chemistry

Unit – V

Presented by – Ms.Rekha Vijay

Designation - Asst.Professor

Department - Chemistry

VISION OF INSTITUTE

To become a renowned centre of outcome based learning, and work towards academic, professional, cultural and social enrichment of the lives of individuals and communities.

MISSION OF INSTITUTE

- ❖ Focus on evaluation of learning outcomes and motivate students to inculcate research aptitude by project based learning.
- ❖ Identify, based on informed perception of Indian, regional and global needs, the areas of focus and provide platform to gain knowledge and solutions.
- ❖ Offer opportunities for interaction between academia and industry.
- ❖ Develop human potential to its fullest extent so that intellectually capable and imaginatively gifted leaders may emerge in a range of profession.

Engineering Chemistry: Course Outcomes

Students will be able to:

CO1: Explain the impurities of water (mainly hardness) and boiler troubles.

CO2: Describe processing technologies of fuel with numerical aspects of combustion of fuel.

CO3: Describe the engineering material (cement, glass and lubricant) with respect to their manufacturing, composition, classification & properties.

CO4: Explain corrosion with its controlling measures, organic reaction mechanism and synthesis of drugs (Aspirin & Paracetamol) with their properties and uses.

JECRC
Department of Applied Sciences
Lecture Plan (Session- 2020-2021)

Course Name: Engineering Chemistry

Year/Semester: 1st Year/ Semester- I

Course code: 1FY2-03

No. of Lecture Req. /(Avl.): /(40/44)

Semester starting: 21 Sept. 2020

Semester Ending: 24 Dec. 2020

Unit No./ Total Lect. Req.	Topics	Lect. No.	Date of Delivery	Book Referred	Pg. No.
Unit-I 10	Introduction to syllabus, Common natural impurities, hardness, Degree of hardness,	1			
	Units of hardness, Determination of hardness by complexometric (EDTA method).	2			
	Municipal water supply, Requisite of drinking water, purification of water, Sedimentation,	3			
	Filtration, disinfection, Breakpoint chlorination.	4			
	Boiler troubles: Scale and Sludge formation, Internal treatment Methods	5			
	Priming and Foaming, Boiler corrosion and caustic embrittlement	6			
	Water softening: Lime-Soda process	7			
	Water softening: Zeolite (Permutit) process, Demineralization process.	8			
	Numerical problems based on Hardness, EDTA,	9			
	Numerical problems based on Lime-Soda and Zeolite process.	10			

Unit-II

10

2.Organic Fuels: Solids fuels: Coal, Classification of Coal, Proximate analyses of coal and its significance	11			
Ultimate analyses of coal and its significance,	12			
Gross and Net Calorific value, Determination of Calorific value of coal by Bomb Calorimeter.	13			
Metallurgical coke, Carbonization processes; Otto-Hoffmann byproduct oven method.	14			
Liquid fuels : Advantages of liquid fuels, Mining, Refining and Composition of petroleum, Cracking	15			
Synthetic petrol, Reforming, Knocking, Octane number, Anti-knocking agents, Cetane number	16			
Gaseous fuels; Advantages, manufacturing, composition and Calorific value of coal gas and oil gas	17			
Determination of calorific value of gaseous fuels by Junker's calorimeter, Numerical problems based on Junkers calorimeter	18			
Numerical problems based on determination of calorific value bomb calorimeter, /Dulong's formula, proximate & ultimate Analysis.	19			
Numerical problems based on combustion of fuel.	20			

Unit-III

3

3. Corrosion and its control: Definition and significance of corrosion, Mechanism of chemical (dry) corrosion	21			
Mechanism of electrochemical (wet) corrosion, galvanic corrosion, concentration corrosion and pitting corrosion.	22			
Protection from corrosion; protective coatings-galvanization and tinning, cathodic protection, sacrificial anode and modifications in design.	23			

Unit-IV 10

4.Engineering Materials: Portland Cement; Definition, Manufacturing by Rotary kiln.	24		
Chemistry of setting and hardening of cement. Role of Gypsum.	25		
Glass: Definition, Manufacturing by tank furnace, significance of Annealing	26		
Types and properties of soft glass, hard glass	27		
Borosilicate glass, glass wool, safety glass.	28		
Lubricants: Classification	29		
Lubricants: Mechanism	30		
Properties; Viscosity and viscosity index	31		
Flash and fire point, cloud and pour point.	32		
Emulsification and steam emulsion number.	33		

Unit-V

7

5. Organic reaction mechanism and introduction of drugs: Organic reaction mechanism: Substitution; SN1, SN2.	34			
Electrophilic aromatic substitution in benzene, free radical halogenations of alkanes,	35			
Elimination: elimination in alkyl halides, dehydration of alcohols,	36			
Addition: electrophilic and free radical addition in alkenes, nucleophilic addition in aldehyde and ketones	37			
Rearrangement: Carbocation and free radical rearrangements	38			
Drugs : Introduction, Synthesis, properties and uses of Aspirin	39			
Drugs : Introduction, Synthesis, properties and uses of Paracetamol, Revision	40			

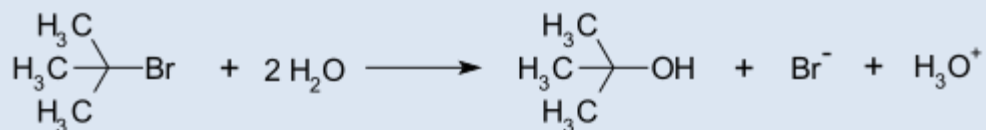
Lecture-34 & 35 (Unit-V)

- Organic reaction mechanism :
Substitution; SN1, SN2.
- Electrophilic aromatic substitution in benzene
- free radical halogenations of alkanes,

S_N1 reaction

The S_N1 reaction is a [substitution reaction](#) in [organic chemistry](#). "S_N" stands for "[nucleophilic substitution](#)", and the "1" says that the [rate-determining step](#) is [unimolecular](#). Thus, the rate equation is often shown as having first-order dependence on [electrophile](#) and zero-order dependence on [nucleophile](#). This relationship holds for situations where the amount of nucleophile is much greater than that of the intermediate. The reaction involves a [carbocation](#) intermediate and is commonly seen in reactions of secondary or tertiary [alkyl halides](#) under strongly basic conditions or, under strongly acidic conditions, with [secondary or tertiary alcohols](#)

An example of a reaction taking place with an S_N1 [reaction mechanism](#) is the [hydrolysis](#) of [tert-butyl bromide](#) forming [tert-butanol](#):



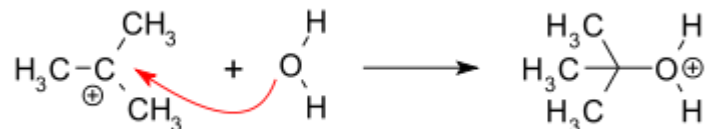
This S_N1 reaction takes place in three steps:

This S_N1 reaction takes place in three steps:

Formation of a tert-butyl carbocation by separation of a leaving group (a bromide anion) from the carbon atom: this step is slow and reversible.



Nucleophilic attack: the carbocation reacts with the nucleophile. If the nucleophile is a neutral molecule (i.e. a solvent) a third step is required to complete the reaction. When the solvent is water, the intermediate is an oxonium ion. This reaction step is fast.



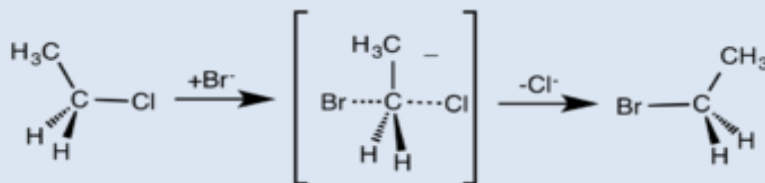
Deprotonation: Removal of a proton on the protonated nucleophile by water acting as a base forming the alcohol and a hydronium ion. This reaction step is fast.



$$\text{Rate} = k[\text{Br}]$$

S_N² reaction

- The **S_N² reaction** is a type of [reaction mechanism](#) that is common in [organic chemistry](#). In this mechanism, one bond is broken and one bond is formed synchronously, i.e., in one step. S_N² is a kind of [nucleophilic substitution](#) reaction mechanism. Since *two* reacting species are involved in the slow ([rate-determining](#)) step, this leads to the term substitution nucleophilic ([bi-molecular](#)) or S_N²;
- In an example of the S_N² reaction, the attack of [Br⁻](#) (the nucleophile) on an [ethyl chloride](#) (the electrophile) results in [ethyl bromide](#), with [chloride](#) ejected as the leaving group.



$$\text{rate} = K [\text{CH}_3\text{Br}] [\text{OH}^-]$$

S_N² attack occurs if the backside route of attack is not [sterically hindered](#) by [substituents](#) on the [substrate](#). Therefore, this [mechanism](#) usually occurs at unhindered [primary and secondary carbon](#) centres. If there is steric crowding on the substrate near the leaving group, such as at a tertiary carbon centre, the substitution will involve an S_N¹ rather than an S_N² mechanism.

S_N1	S_N2	
Steps	Two : (1) $R:XI \rightarrow R^+ + X^-$ (2) $R^+ + Nu^- \rightarrow RNu$	One : $R:X + Nu^- \rightarrow RNu + X^-$
Rate	$=k [RX]$ (1st order)	$=k[RX] [Nu^-]$ (2nd order)
TS of slow step		
Stereochemistry	Inversion and racemization	Inversion (backside attack)
Molecularity	Unimolecular	Bimolecular
Reactivity structure of R Determining Factor Nature of X Solvent effect on rate	$3^\circ > 2^\circ > 1^\circ > CH_3$ Stability of R^+ $RI > RBr > RCl > RF$ Rate increases in polar solvent	$CH_3 > 1^\circ > 2^\circ > 3^\circ$ Steric hindrance in R group $RI > RBr > RCl > RF$ with Nu^- there is a large rate increase in polar aprotic solvents.
Effect of nucleophile	No effect as it does not appear in the rate expression.	Rate depends on nucleophilicity $I^- > Br^- > Cl^-$; $RS^- > RO^-$
Catalysis	Lewis acid, eg. Ag^+ , $AlCl_3$, $ZnCl_2$	None
Competitive reaction	Elimination, rearrangement	Elimination

Electrophilic aromatic substitution in benzene

Arenes are characterised by electrophilic substitution reaction. Common reactions are nitration, sulphonation, halogenation, friedal-crafts alkylation. In this reaction first the electrophile generation takes place then electrophile attack on the substrate to form carbocation. Afterwards proton removes from carbocation intermediate to form substituted benzene.

electrophilic reaction supposed to proceed via the following three steps

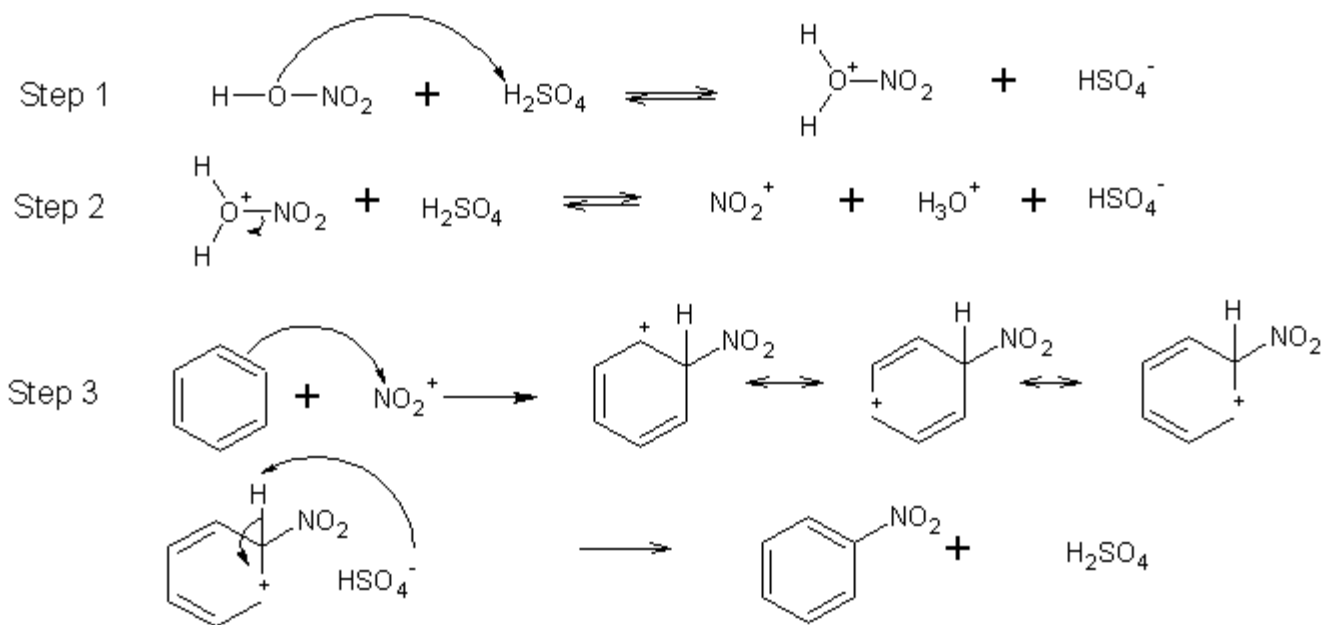
1. Generation of the electrophile.

2. Formation of carbocation intermediate.

3. Removal of proton from the carbocation intermediate to regain aromaticity.

MECHANISM OF NITRATION OF AROMATIC HYDROCARBON

- Step 1: Nitration is a typical example of an aromatic electrophilic substitution reaction in which the nitronium ion (NO_2^+) acts as an electrophile. The function of H_2SO_4 is not that of a dehydrating agent but acts on HNO_3 to form the reactive nitronium ion.
- Step 2: Benzene and other arenes are electron rich molecules. The electron rich benzene molecules (nucleophile) attacks nitronium ion (electrophile) leading to the formation of a carbocation which is stabilized by resonance.
- Step 3: The carbocation formed in step 2 loses a proton to yield nitrobenzene.



Free radical halogenations of alkanes

Free radical halogenation is a reaction that substitutes a chlorine or a bromine for a hydrogen on an alkane. This reaction is a photochemical one. That is, it occurs only when performed in the presence of uv light

Typically, free radical reactions are described in three steps:

- Initiation steps
- Propagation steps
- Termination steps

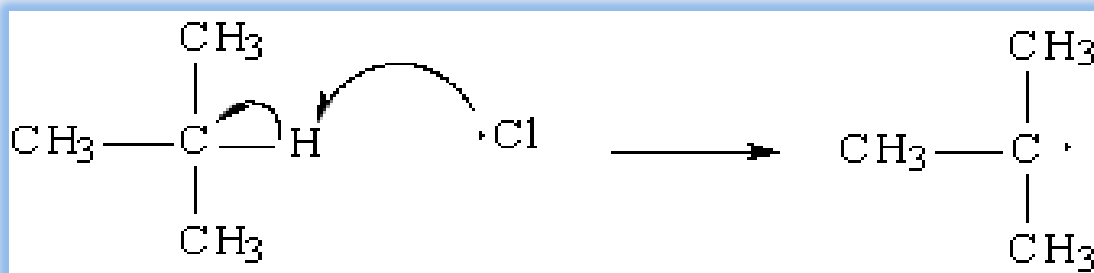
Initiation Step

The reaction begins with an *initiation step*, which is the separation of the halogen (X_2) into two radicals (atoms with a single unpaired electron) by the addition of uv light. This is called the initiation step because it initiates the reaction.

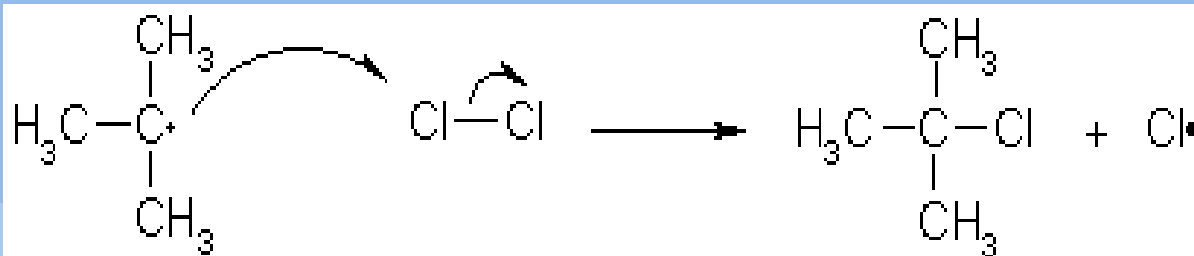


Propagation Steps

The initiation step, or the formation of the chlorine radicals, is immediately followed by the propagation steps--steps directly involved in the formation of the product. As an example, isobutane (C_4H_{10}) will be used in the chlorination reaction. The first step is the abstraction of the hydrogen atom from the tertiary carbon (a tertiary carbon is a carbon that is attached to *three* other carbon atoms) Note that these are not protons (H^+ ions) that are being abstracted, but actual hydrogen atoms since each hydrogen has one electron. This first propagation step forms the tertiary radical.

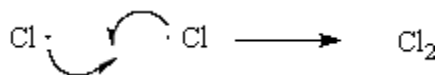
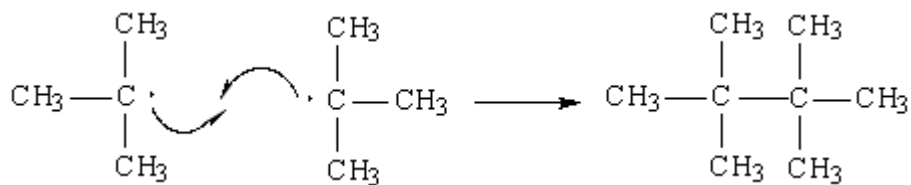
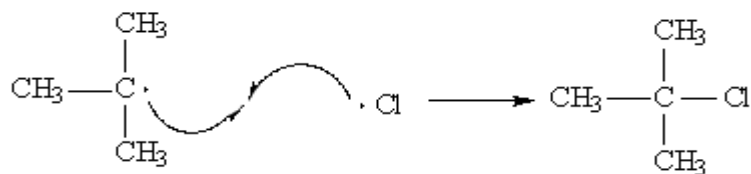


In the last step, the tertiary radical then reacts with another one of the chlorine molecules to form the product. Notice that another chlorine radical is regenerated, so this reaction can, in theory, go on forever as long as there are reagents. This is called a chain reaction



Termination Step

Side reactions that can stop the chain reaction are called termination steps. These termination steps involve the destruction of the free-radical intermediates, typically by two of them coming together.



Suggested links

https://web.iit.edu/sites/web/files/departments/academic-affairs/academic-resource-center/pdfs/SN1_SN2.pdf

<https://www.masterorganicchemistry.com/2017/07/11/electrophilic-aromatic-substitution-introduction>



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*Thank
you!*