NEW SYLLABUS

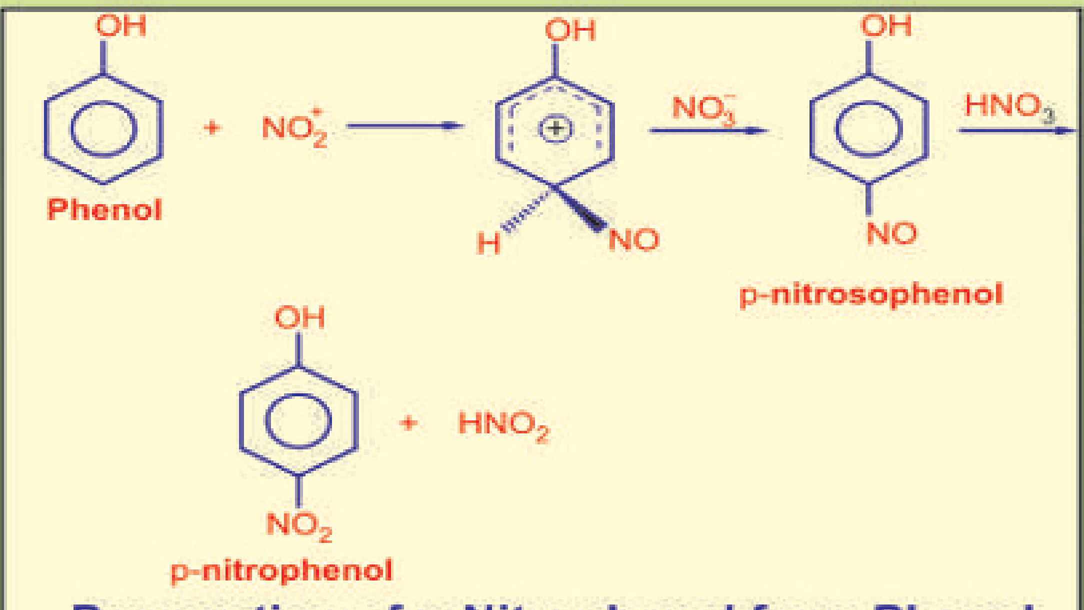
NMU

North Maharashtra University, Jalgaon

T. Y. B. Sc. • SEMESTER-V

ORGANIC CHEMISTRY

Dr. B. R. CHAUDHARI
Dr. S. I. RAJPUT



Preparation of p-Nitrophenol from Phenol

NIRALI PRAKASHAN
ADVANCEMENT OF KNOWLEDGE

A TEXT BOOK OF

ORGANIC CHEMISTRY

For

T. Y. B. Sc. (CH - 353)

Semester - V

According to New Revised Syllabus of
North Maharashtra University, Jalgaon, w.e.f. June 2017

Dr. B. R. CHAUDHARI
M.Sc., Ph. D.
Vice Principal & Associate Prof. in Chemistry,
JET's Z. B. Patil College, Dhule

Dr. S. I. RAJPUT
M.Sc., Ph.D., L.L.B.
Ex-Principal,
B.P. Art's, S.M.A. Science &
K.K.C. Commerce College,
Chalisgaon

Price ₹ 55.00

NIRALI®
PRAKASHAN
ADVANCEMENT OF KNOWLEDGE

N0703

T.Y.B.Sc. Organic Chemistry (Sem.-V) (NMU) **ISBN 978-93-86700-90-2**

First Edition : August 2017

Published By:
NIRALI PRAKASHAN
Abhyudaya Pragati, 1312, Shivaji Nagar
Off J.M. Road, PUNE – 411005
Tel - (020) 25512336/37/39, Fax - (020) 25511379
Email : niralipune@pragationline.com

Printed By:
STAR COPIERS PVT. LTD.
Kumthekar Road, Sadashiv Peth
Pune - 411 030
Tel - (020) 24479201

DISTRIBUTION CENTRES

PUNE

Nirali Prakashan : 119, Budhwar Peth, Jogeshwari Mandir Lane,
Pune 411002, Maharashtra. Tel : (020) 2445 2044, 66022708,
Fax : (020) 2445 1538, Email: bookorder@pragationline.com,
niralilocal@pragationline.com

Nirali Prakashan : S. No. 28/27, Dhyari, Near Pari Company, Pune 411041
Tel : (020) 24690204 Fax : (020) 24690316
Email : dhyari@pragationline.com,
bookorder@pragationline.com

MUMBAI

Nirali Prakashan : 385, S.V.P. Road, Rasdhara Co-op. Hsg. Society Ltd.,
Girgaum, Mumbai 400004, Maharashtra
Tel : (022) 2385 6339 / 2386 9976, Fax : (022) 2386 9976
Email : niralimumbai@pragationline.com

DISTRIBUTION BRANCHES

JALGAON

Nirali Prakashan : 34, V. V. Golani Market, Navi Peth, Jalgaon 425001,
Maharashtra, Tel : (0257) 222 0395, Mob : 94234 91860

KOLHAPUR

Nirali Prakashan : New Mahadvar Road, Kedar Plaza, 1st Floor Opp. IDBI Bank
Kolhapur 416 012, Maharashtra. Mob : 9850046155

NAGPUR

Pratibha Book Distributors : Above Maratha Mandir, Shop No. 3, First Floor,
Rani Jhanshi Square, Sitabuldi,
Nagpur 440012, Maharashtra Tel : (0712) 254 7129

DELHI

Nirali Prakashan : 4593/21, Basement, Aggarwal Lane 15, Ansari Road,
Daryaganj, Near Times of India Building, New Delhi 110002
Mob : 08505972553

BENGALURU

Pragati Book House : House No. 1, Sanjeevappa Lane, Avenue Road Cross,
Opp. Rice Church, Bengaluru – 560002.
Tel : (080) 64513344, 64513355,Mob : 9880582331,
9845021552, Email:bharatsavla@yahoo.com

CHENNAI

Pragati Books : 9/1, Montieth Road, Behind Taas Mahal, Egmore,
Chennai 600008 Tamil Nadu, Tel : (044) 6518 3535,
Mob : 94440 01782 / 98450 21552 / 98805 82331,

niralipune@pragationline.com | www.pragationline.com
Also find us on www.facebook.com/niralibooks

PREFACE

We have a great pleasure in presenting this book of **'Organic Chemistry'.** This book is written strictly according to the revised syllabus and the guidelines prepared by the Board of Studies in Chemistry of North Maharashtra University, Jalgaon for T.Y.B.Sc. to be implemented from June 2017.

The aim of this book is to provide a concise information of each topic in a simple language. More emphasis is given to different mechanistic approaches with supporting evidences and stereochemical aspects which will serve the needs of students in enhancing the comprehension of reaction mechanism. The unique feature of this book is simplified treatment of important topics such as structural effects, substitution reactions, electrophilic and nucleophilic addition reactions, aromatic substitution reactions, rearrangement reactions etc. At the end of each chapter, question sets with problems are given.

We are sure that the book will be useful not only to students but also for the teachers. The authors will appreciate suggestions and useful criticism from friends and teachers for the improvement of this book.

Our special thanks to the publishers Shri. Dineshbhai Furia, Shri Jignesh Furia and entire staff of Nirali Prakashan Pune especially, Mr. Kiran Velankar, Mr. Ilyas Shaikh, Ms. Shilpa Zede and Ms. Chaitali Takle for keen interest and constant encouragement to make this book an ideal one. Mr. P. M. More has also made a thorough follow up of the manuscript.

AUTHORS

SYLLABUS

1. STRUCTURAL EFFECTS (10 L, 10 M)

Inductive effect, Resonance effect, Steric effect, Hyperconjugation, Applications of all these effects in deciding the strength of acids and bases.

2. NUCLEOPHILIC SUBSTITUTION AT SATURATED CARBON (10 L, 10 M)

Introduction, Relation between kinetics and mechanism. The S_N1, S_N2 and S_Ni mechanisms. Stereochemical implications of mechanism. S_N2 mechanism - Inversion of configuration. S_N1 mechanism - Racemisation. S_Ni mechanism - Retention of configuration. Effect of structure, nucleophile, leaving group and solvent on S_N1 and S_N2 mechanism.

3. ELECTROPHILIC ADDITION TO $>C = C<$ BOND (10 L, 10 M)

Introduction, Addition of halogens, Addition of HX and orientation of addition, Other addition reactions (with mechanism) - Hydration, Hydroxylation, Hydrogenation, Ozonolysis.

4. NUCLEOPHILIC ADDITION TO $>C = O$ GROUP (10 L, 10 M)

Structure and reactivity, Addition of Water, Alcohol, Thiol, Hydride ion, Derivatives of ammonia semicarbazide. Carbon nucleophilic addition - Aldol condensation, Cannizzaro reaction, Perkin reaction, Claisen ester condensation.

5. AROMATIC SUBSTITUTION (12 L, 12 M)

Electrophilic Aromatic Substitution - Introduction, General mechanism, Orientation of substitution in monosubstituted benzene.

Mechanism of Nitration, Sulphonation, Halogenation, Friedel Craft alkylation and its limitations, Friedel Craft acylation, Diazocoupling reactions.

Nucleophilic Aromatic Substitution - Introduction

Mechanisms : Addition - Elimination mechanism, Elimination - Addition mechanism (Benzyne intermediate)

6. REARRANGEMENT REACTIONS (08 L, 08 M)

Introduction, Classification: (1) Migration to carbon: Pinacol-Pinacolone rearrangement, (2) Migration to nitrogen: Beckmann rearrangement, (3) Migration to oxygen: Baeyer Villiger rearrangement.

✍✍✍

CONTENTS

✍✍✍

Chapter 1

STRUCTURAL EFFECTS

1.1 INTRODUCTION

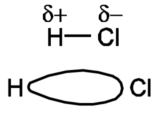
We have already studied a number of basic organic reactions. We have noticed that functional groups are major factors controlling the reactivity of organic compounds. In fact, the reactivity of an organic compound depends on its structure. Two compounds having the same functional group undergo the same set of reactions but their rates are different. The reaction at the functional group is influenced by the rest of the molecule. Inductive effect, resonance, steric effect etc. control the rate of a reaction, the mechanistic features of a reaction and also strength of acids and bases. The main object of this chapter is to study the factors controlling the rate of a reaction.

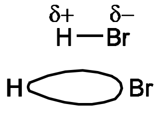
1.2 INDUCTIVE EFFECT

Consider the covalent bond between *homonuclear diatomic molecules* such as H_2, Cl_2, F_2, O_2 etc. In these molecules, the *bonding electron pair* is equally shared between the two atomic nuclei.

$$H : H , \quad Cl : Cl$$

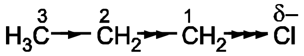
In *heteronuclear diatomic molecules* such as HCl, HBr, HF the bonding electron pair is not equally shared because these atoms possess different electronegativities.





In HCl molecule, chlorine is more electronegative as compared to hydrogen, hence *electron pair is attracted slightly towards* the chlorine atom. Due to this electron density around hydrogen decreases and that around chlorine increases. This develops partial positive charge (δ+) on hydrogen and partial negative charge (δ–) on chlorine. *Thus, HCl molecule gets polarised. The withdrawal of electrons by chlorine is represented by showing an arrow towards chlorine*. All the heteroatomic molecules which show such polarisation are said to be polar molecules.

Consider the molecule



$$H_3\overset{3}{C} \rightarrow \overset{2}{C}H_2 \rightarrow\rightarrow \overset{1}{C}H_2 \rightarrow\rightarrow\rightarrow \overset{\delta-}{Cl}$$

Propyl chloride

The C_1 – Cl bond gets polarised due to more electronegativity of chlorine and C_1 becomes partially electron deficient acquire δ+ charge. In order to overcome the electron deficiency of C_1, *it tries to pull* the sharing electron pair between C_1 and C_2. *This induces some positive charge on C_2*. This positively charged C_2 now pulls the C_2 – C_3 bonding electron pair towards C_2 and some positive charge induces further on C_3. *Thus inductive effect is transmitted from C_3 through C_2 to C_1*. Thus, the polarisation in the C_1 – Cl bond induces polarities in the adjacent carbon bonds.

Definition of Inductive Effect :

The polarisation induced in the adjacent bonds due to polarisation in one bond is called as inductive effect.

Features of Inductive Effect :

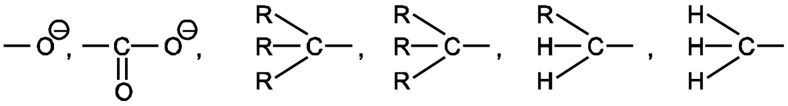
1. It is permanent effect and develops due to polarisation of bond.
2. The magnitude of inductive effect is very small.
3. It operates in straight chain.
4. It is associated with σ bonds connected by two dissimilar atoms or groups.
5. It operates in the ground state of the molecule.
6. The magnitude of inductive effect decreases as distance increases from polar bond and practically diminishes after C_3.

Types of Inductive Effect :

Depending upon the *direction of pulling of electrons,* inductive effects are classified into two types :

(i) Electron donating inductive effect (+ I effect) :

e.g. Following groups show +I effect in decreasing order.



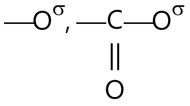
(ii) Electron withdrawing inductive effect (– I effect) :

e.g. Following groups show – I effect in decreasing order.

$-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{N}H_3$, $-NO_2$, $-SO_3H$, –F, –Cl, –Br, I, $-C \equiv N$, $-C \equiv C-R$, $-HC = CR_2$

General trends of inductive effect :

1. Negatively charged groups or atoms exert maximum + I effect.

   e.g.
   
   $-O^{\sigma}, -\underset{\underset{O}{\|}}{C}-O^{\sigma}$ etc.

2. Alkyl groups exert +I effect. Magnitude of +I effect increases with increasing number of alkyl groups.
3. Positively charged groups or atoms exert maximum – I effect.

   e.g. $-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{N}H_3$ etc.

4. *Groups having more number of electronegative atoms* will have more –I effect than groups having less number of electronegative atoms.
5. As the % *of s character* of carbon atom increases, –I effect also increases.
6. *Inductive effects create permanent polarisation in the ground state of a molecule, hence they change the physical properties such as dipole moments*.

1.3 RESONANCE EFFECT (Mesomeric Effect)

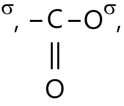
Definition :

Electronic redistribution operating in unsaturated (especially in conjugated) systems via 'π' bond is known as mesomeric or resonance effect.

Many times properties of a molecule cannot be explained by a *single classical structure*. This can be explained by two or more individual structures, *which are generally interconvertible*. These individual structures are known as *resonating, contributing or canonical structures.*

Canonical structures possess nearly same energy. These canonical structures differ only in the arrangements of electrons, but not in the relative positions of atomic nuclei. *Canonical forms are shown by putting a double headed arrow between them*.

+R effect or +M effect : The atoms or groups (*transmitting or) donating electrons by resonance* are said to have electron donating resonance effect (+R effect) or positive mesomeric effect (+M effect).



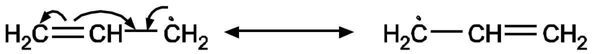
e.g. $-O^{\sigma}$, $-\underset{\underset{O}{\|}}{C}-O^{\sigma}$, –F, –Cl, –Br, –I, $-NR_2$, –H, –SH, –SR etc.

–R effect or –M effect : The atoms or groups *withdrawing electrons by resonance* are said to have electron withdrawing resonance effect (–R effect) or negative mesomeric effect (–M effect).

e.g. $-NO_2$, $-SO_2R$, $-C=O$, $-C\equiv N$ etc.

Conditions for Resonance :

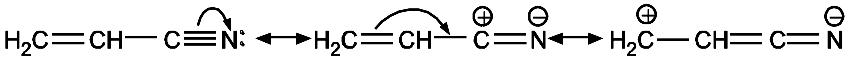
1. The *position of the atomic nuclei in all the contributing* (resonating or canonical) *structures must be same.*
2. The resonance structures must have the *same number of paired or unpaired electrons.*



3. *Each contributing structure should have nearly same internal energy i.e. they should have nearly the same stability*.

Rules for Writing Resonating Structures : (Oct. 14)

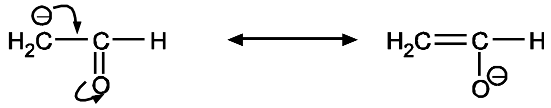
1. *The resonance structures are interconvertible and are represented by a double headed arrow (↔).*
2. *While writing resonance structures, only movement* of electrons is shown. *Atoms remain in the same relative position in each structure*.



Acrylonitrile (Propene nitrile)

3. *All the atoms involved in resonance should be coplanar*. If coplanarity is lost then electron delocalisation will not take place.
4. *The actual molecule is the resonance hybrid* of all the contributing structures. This *resonance hybrid has less energy* and more stability as compared to each of the contributing structures.

5. *More the number of resonance structures, more is the stability of the resonance hybrid.*
6. *The resonance structure in which the negative charge is present on the more electronegative atom is more stable.*

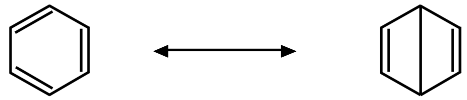


(I) (II)

(Anion of acetaldehyde)

Structure (II) is more stable as the negative charge is on oxygen atom.

7. The *structures which contain different bond angles and bond lengths are less stable.*

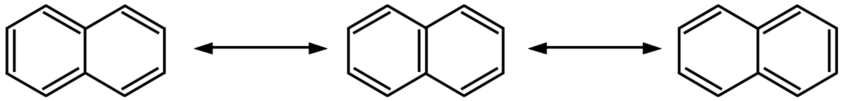


Kekule's structure of benzene (More stable)

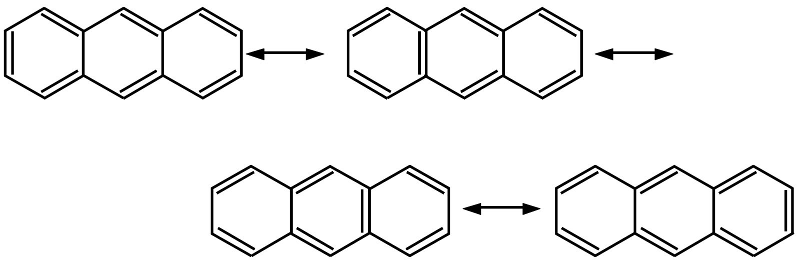
Dewar's structure of benzene (Less stable)

Resonance Structures of some Compounds :

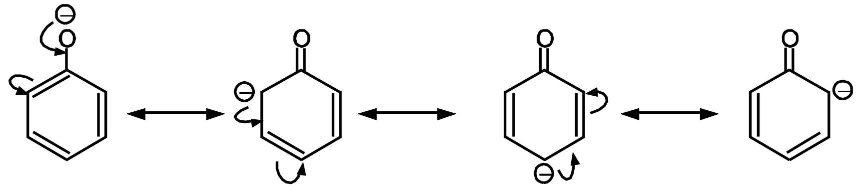
1. Naphthalene



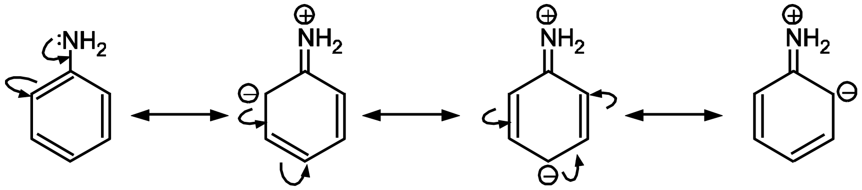
2. Anthracene



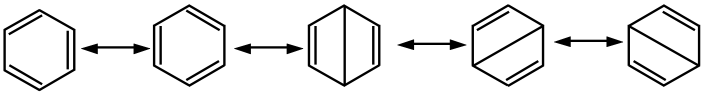
3. Phenoxide ion



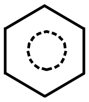
4. Aniline **(Oct. 15)**



Resonance hybrid concept : Resonance hybrid is a combination of two or more canonical structures of a molecule, ion or radical. It represents a true structure of a molecule. e.g. Benzene can be represented by a number of resonating structures as shown.



It was observed that *none of the above structures* can satisfactorily explain all the properties of benzene i.e. none of the above structures is a true structure of benzene. Hence, the combination of all above five structures or a resonance hybrid is a true structure of benzene.



Resonance hybrid

The resonance hybrid *accounts for* the identical C – C and C – H bond lengths and bond energies observed in benzene. Thus, the resonance forms *are fictional or hypothetical.*

Difference between Inductive and Resonance Effects :

Inductive effect	Resonance effect
1. Operates both in saturated and unsaturated compounds.	1. Operates only in unsaturated compounds especially in conjugated compounds.
2. Involves σ electrons in bonds.	2. Involves π electrons in bonds and orbitals.
3. *Transmitted over a short distance* and decreases as distance increases.	3. *Transmitted from one end to other end* of quite large molecule provided the conjugation is present.
4. Less powerful.	4. More powerful.
5. Operates in straight chain only and no planarity is required.	5. Operates only when all the atoms are in the same plane i.e. it requires planarity.
6. It is permanent.	6. It is temporary.

1.4 APPLICATION OF INDUCTIVE AND RESONANCE EFFECT IN DECIDING STRENGTH OF ACIDS AND BASES

Inductive effect and resonance effect are useful in deciding strength of acids and bases as follows :

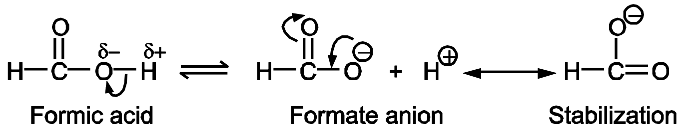
Inductive Effect and Strength of Acids : (Oct. 15)

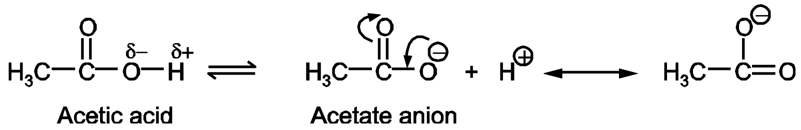
Strength of acids depends on :

1. Inductive effect.
2. Strength of electron withdrawing groups.
3. Number of electron withdrawing groups.
4. Stabilization of conjugate base.
5. pK_a value.

Simple Aliphatic Acids :

Example : Formic acid (pK_a = 3.77) is stronger than acetic acid (pK_a = 4.76).





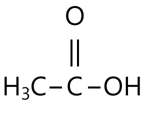
In acetic acid, the +I effect of methyl group decreases the polarity of O−H bond and therefore liberation of proton becomes difficult.

Similarly, the conjugate base (acetate anion) formed is destabilized by the +I effect. In formic acid, +I effect is absent. Hence formate ion is more stable than acetate anion. Due to this, formic acid is stronger than acetic acid.

Substituted Aliphatic Acids :

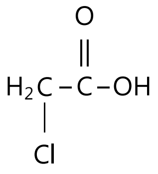
The effect of introducing electron withdrawing substituents into simple aliphatic acid is **more remarkable.**

[A] Consider the following acids with their pK_a values :



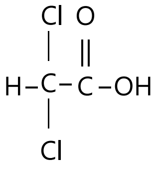
$H_3C-\overset{\overset{O}{\|}}{C}-OH$

Acetic acid
pK_a = 4.76



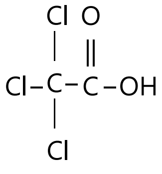
$\underset{\underset{Cl}{|}}{H_2C}-\overset{\overset{O}{\|}}{C}-OH$

Monochloroacetic
acid 2.86



$H-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH$

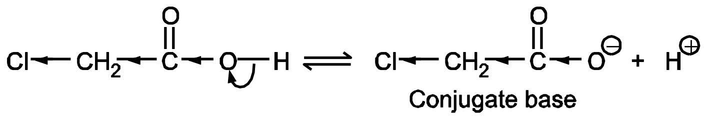
Dichloroacetic
acid 1.25



$Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH$

Trichloroacetic
acid 0.65

Halogens exert −I effect. Therefore, replacement of H atom by Cl atom changes +I effect into −I effect. Thus, acid strength of substituted acid increases.



$$Cl \leftarrow CH_2 \leftarrow \overset{O}{\overset{\|}{C}} \leftarrow O-H \rightleftharpoons Cl \leftarrow CH_2 \leftarrow \overset{O}{\overset{\|}{C}} \leftarrow O^{\ominus} + H^{\oplus}$$

The −I effect helps to dissociate −OH bond and also stabilizes the conjugate base formed. Due to this monochloroacetic acid is stronger than acetic acid.

With increase in the number of chlorine atoms, −I effect increases and therefore acid strength also increases. Thus, trichloroacetic acid is very strong organic acid.

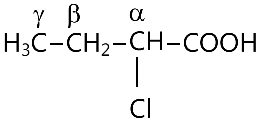
[B] As the electronegativity of the substituent increases, −I effect increases and therefore acidity increases.

e.g.	$F-CH_2 \cdot COOH$	$Cl-CH_2COOH$	$Br-CH_2COOH$	$I-CH_2COOH$
pK_a =	2.37	2.86	2.90	3.16

Electronegativity decreases in the order F > Cl > Br > I and −I effect also decreases in the same order. **Fluorine being the most electronegative** (electron withdrawing), hence **acid strength** of fluoroacetic acid **increases 100 times as compared to acetic acid.**

[C] The introduction of halogen atom further away from the carboxyl group than the adjacent α-position has less effect i.e. more the distance from the $-\underset{O}{\underset{\|}{C}}-OH$ (carboxyl) group, weaker is the acid because inductive effect decreases with increasing distance.

$H_3C-CH_2-CH_2-COOH$



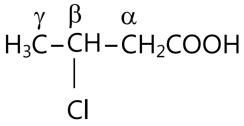
$$\overset{\gamma}{H_3C}-\overset{\beta}{CH_2}-\underset{Cl}{\underset{|}{\overset{\alpha}{CH}}}-COOH$$

Butanoic acid

pK_a = 4.82

α-Chlorobutanoic acid

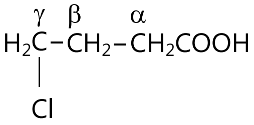
2.84



$$\overset{\gamma}{H_3C}-\underset{Cl}{\underset{|}{\overset{\beta}{CH}}}-\overset{\alpha}{CH_2}COOH$$

β-Chlorobutanoic acid

4.06



$$\underset{Cl}{\underset{|}{\overset{\gamma}{H_2C}}}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}COOH$$

γ-Chlorobutanoic acid

4.52

[D] Other electron withdrawing groups :

e.g. $R_3N^{\oplus}$, $-C \equiv N$, $-\underset{\underset{O}{\downarrow}}{N} = O$, SO_2R, $-\underset{\underset{O}{\|}}{C}-$, $-\underset{\underset{O}{\|}}{C}-OR$ increase the strength of simple aliphatic acids.

$O_2N \leftarrow CH_2COOH$ $\quad$ $Me_3N^{\oplus} \leftarrow CH_2 \leftarrow COOH$

pK_a 1.68 $\quad$ 1.83

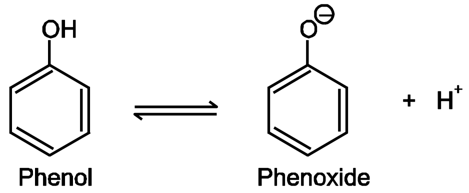
$N \equiv C \leftarrow CH_2 \leftarrow COOH$ $\quad$ $HO \leftarrow CH_2-\underset{\underset{O}{\|}}{C}-OH$

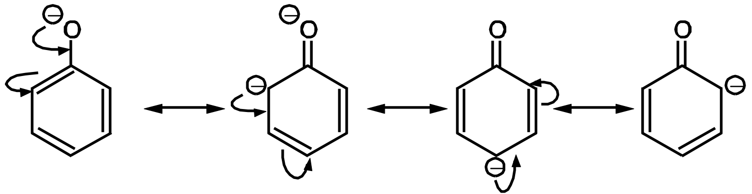
2.47 $\quad$ 3.83

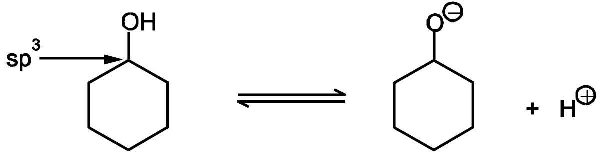
Acidity of Phenols :

Phenol (pK_a = 9.95) is acidic but **cyclohexanol** (pK_a = 16) is neutral even though both possess the −OH group.

In phenol the −OH group is attached to sp^2 carbon. Hence, it exerts −I effect which helps in dissociation of $H^{\oplus}$ ions. After dissociation, the conjugate base of phenol (i.e. phenoxide ion) is stabilized by resonance. Thus, phenol shows acidic properties.



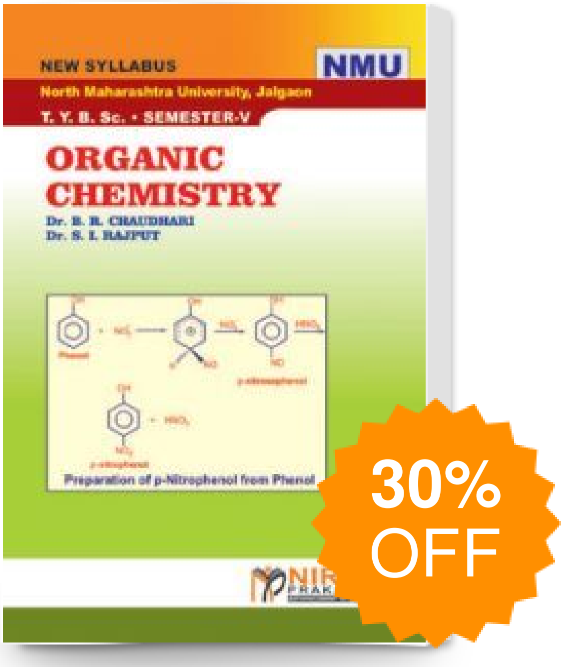




Cyclohexanol $\quad$ Cyclohexyl oxide ion

In cyclohexanol, −OH group is attached to sp^3 carbon which exerts +I effect. On dissociation it gives $H^{\oplus}$ and negatively charged conjugate base (cyclohexyl oxide) which cannot be stabilized by resonance like phenoxide ion.

Organic Chemistry



NEW SYLLABUS

NMU

North Maharashtra University, Jalgaon

T. Y. B. Sc. • SEMESTER-V

ORGANIC CHEMISTRY

Dr. B. R. CHAUDHARI
Dr. S. I. RAJPUT

Preparation of p-Nitrophenol from Phenol

Publisher : Nirali Prakashan

ISBN : 9789386700902

Author : Dr. B. R. Chaudhari, Dr. S. I. Rajput