Semester - I

15.09.2019

CEMGCOR01T

Section B: Organic Chemistry-I

Fundamentals of organic chemistry:

Electronic displacements:

A. **Inductive Effect:** When two atoms of different electronegativities form a covalent bond, the shared pair of electrons is displaced towards the more electronegative atom. As a result, the more electronegative atom gets a small negative charge and the other atom gets eqal amount of positive charge. This type of electron displacement along a covalent bond is known as inductive effect. This is a permanent polarisation and the effect decreases rapidly as the distance from the electronegative atom or group increases. It involves only the σ electron.

e.g. $-\overset{\delta'''+}{C^4}\rightarrow\overset{\delta''+}{C^3}\rightarrow\overset{\delta'+}{C^2}\rightarrow\overset{\delta+}{C^1}\rightarrow Cl^{\delta-}$ Electronegativity order : $Cl > C$

Here, $\delta^+ > \delta'^+ > \delta''^+ > \delta'''^+$

$-\overset{\delta^{-''''}}{C^4}-\overset{\delta^{-'''}}{C^3}-\overset{\delta^{-''}}{C^2}-\overset{\delta^{-'}}{C^1}-\overset{\delta+}{Li}$ " " : $C > Li$

Here, $\delta^{-'} > \delta^{-''} > \delta^{-'''} > \delta^{-''''}$

Types of Inductive Effect:

- **Negative Inductive Effect or Electrom-withdrawing effect: (-I effect)**

  When atom or group of atoms attract shared pair of electrons toward itself.

  eg $NO_2 > CN > COOH > F > Cl > Br > I > OCH_3 > C_6H_5-$

  — The decreasing order of -I effect of some atoms & groups

- **Positive Inductive effect or electron releasing effect (+I effect):**

  Atom or group of atoms push the electrons away from it.

  eg CR_3, CHR_2, CH_2R, CH_3, D

  $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > D$

  — The increasing order of +I effect of groups.

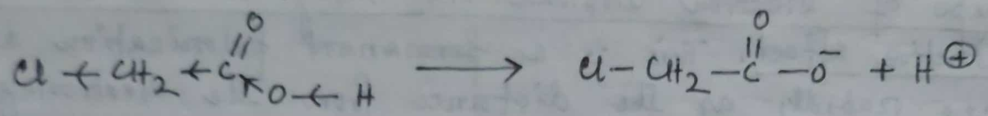
To measure the relative inductive effect (+I or -I), hydrogen atom of the molecule R_3C-H has been taken as standard.

- Group or atoms with -I effect are more electron withdrawing than 'H'.
- " " " +I " " less " " " 'H'.

Problems:

1. How will you explain that chloroacetic acid ($ClCH_2COOH$) is more stronger than acetic acid (CH_3COOH)?

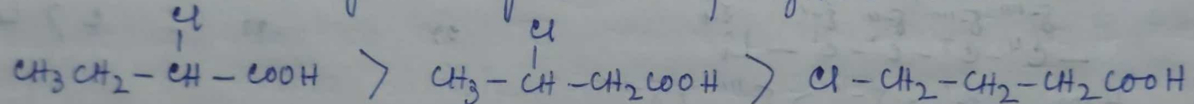
Ans: Chlorine is more electronegative compare to carbon atom, chlorine exerts negative inductive effect (-I effect) and causes displacement of electron from carboxy hydrogen. As a result, the O-H bond dissociates readily to give $H^{\oplus}$ ion in chloro acetic acid. But in acetic acid methyl group ($-CH_3$ group) exerts +I effect and disfavours the release of proton by increasing the electron density on oxygen.



$$Cl \leftarrow CH_2 \leftarrow \overset{O}{\overset{\|}{C}} \nwarrow O \leftarrow H \longrightarrow Cl-CH_2-\overset{O}{\overset{\|}{C}}-\bar{O} + H^{\oplus}$$

2. How will you explain the acidity order of 2-chlorobutanoic acid, 3-chlorobutanoic acid and 4-chlorobutanoic acid?

Ans: The decreasing acidity order of given acids —



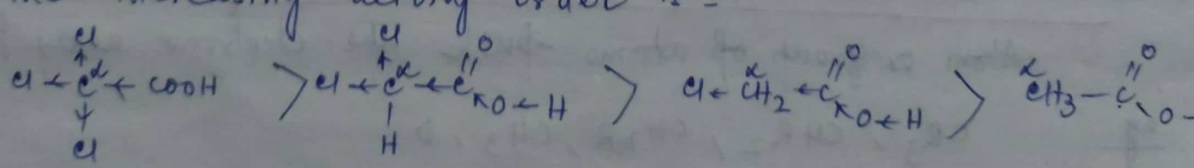
$$CH_3CH_2-\overset{Cl}{\overset{|}{CH}}-COOH > CH_3-\overset{Cl}{\overset{|}{CH}}-CH_2COOH > Cl-CH_2-CH_2-CH_2COOH$$

In 2-, 3-, and 4-chlorobutanoic acids the electron withdrawing Cl atom gradually moves away from the -COOH group. Again, we know that the -I effect decreases rapidly as the distance from the electronegative effect increases. So, the effect of chlorine atom on O-H gr. will decrease and show the given acidity order.

3. Write down the increasing acidity order of the given acid & explain the order.

CH_3COOH, $ClCH_2COOH$, $Cl_2CHCOOH$, Cl_3CCOOH

Ans: The increasing acidity order is -



$$Cl \leftarrow \underset{\underset{Cl}{\downarrow}}{\overset{\overset{Cl}{\uparrow}}{\overset{\alpha}{C}}} \leftarrow COOH > Cl \leftarrow \underset{\underset{H}{|}}{\overset{\overset{Cl}{\uparrow}}{\overset{\alpha}{C}}} \leftarrow \overset{O}{\overset{\|}{C}} \nwarrow O \leftarrow H > Cl \leftarrow \overset{\alpha}{CH_2} \leftarrow \overset{O}{\overset{\|}{C}} \nwarrow O \leftarrow H > \overset{\alpha}{CH_3}-\overset{O}{\overset{\|}{C}} \searrow O-H$$

The insertion of electronegative chlorine atom (-I effect) at α carbon with respect to -COOH gr. will increase the acidity by displacement of electron from carboxy hydrogen (O—H bond). With increasing the number of chlorine atoms on the α-carbon, the strength of -I effect progressively increases and so also the acid strength.

4. Compare the basicity between methylamine & trifluoromethylamine.

Ans: The structure of methyl amine — $CH_3\ddot{N}H_2$ & trifluoro-methylamine — $CF_3\ddot{N}H_2$

The avilability of lone pair of electrons on nitrogen atom determine the basic charecter of nitrogenous compounds. In methyl amine the $-CH_3$ group exerts +I effect and pushes electron towards nitrogen atom. As a result the avilability of lone pair of electron on nitrogen will increase. Whereas in $CF_3\ddot{N}H_2$, due to the presence of electronegative fluorine atoms (-I effect) which pull the electrons from nitrogen atom. For this reason $CF_3\ddot{N}H_2$ is less basic compare to $CH_3\ddot{N}H_2$.

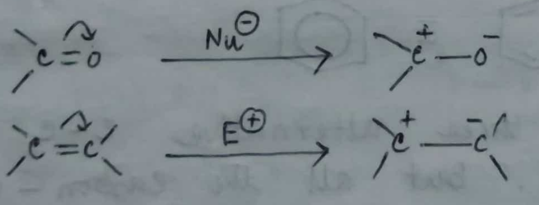
Basicity order: $CH_3\ddot{N}H_2 > CF_3\ddot{N}H_2$

B. Electromeric effect: (E)

It is a temporary effect in which the polarity produced in a multiple bonded compound as it is approached by a reagent. It involves the π electrons.

$$A=B \underset{\text{Reagent removed}}{\overset{\text{Reagent added}}{\rightleftharpoons}} A^+-B^-$$

eg.



C. Mesomeric effect: (M)

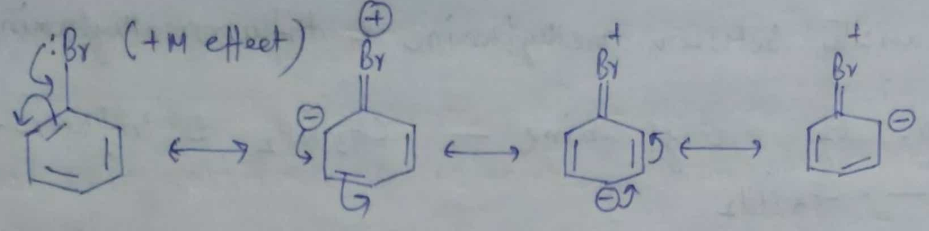
The polarity produced in a molecule as a result of interaction between two π bonds or a π bond and lone pair of electrons. The effect is transmitted along a chain similar to inductive effect. It does not depend upon the presence of a reagent.

e.g. $CH_3-CH=CH-CH=\ddot{O} \longleftrightarrow CH_3-\overset{+}{C}H-CH=CH-\bar{O}$

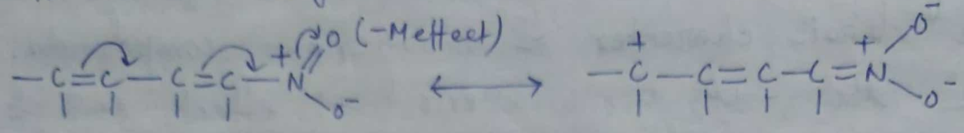
+M effect: Atoms or groups which lose $e^\ominus$ towards a carbon atom
eg Cl, Br, I, NH_2, NR_2, OH, OCH_3

-M effect: Atoms or groups which draw electrons ($e^\ominus$) from carbon atom
eg NO_2, CN, >C=O

eg



- M effect or - NO_2 gr.



D. <u>Resonance</u> :

To explain all the properties of a given compound a single structural formula is not sufficient. For satisfactorily explain the compound is represented by two or more structural formulae which differe only in arrangment of electrons. So resonance can be defined as – A phenomenon in which two or more structures can be written for a compound which involve identical positions of atoms but different arrangment of electrons is called resonance. The actual structure of the molecule is said to be a resonance hybrid of various possible alternative structures. The alternative structures are reffered to as the resonance structures or canonical forms.

eg

In benzene there is three alternative C–C single bond & three C=C double bond. But all the Carbon – Carbon bonds in benzene are identical, bond length 1.40 A° (intermediate single bond 1.54 A° & double bond 1.34 A°).

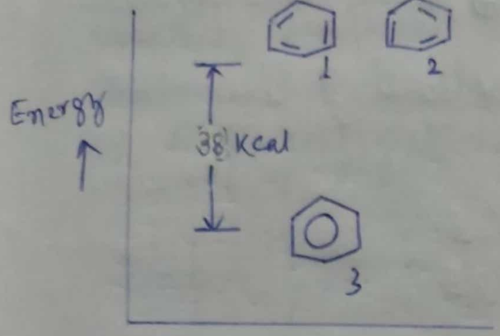
<u>Conditions for resonance</u> :

1. No change in the positions of the nuclei (atom) in each structure.
2. The number of unpaired e⊖ in each structure must be the same
3. Each structure must have the same internal energy.
4. More no. of contributing structures, molechule will be more stable
5. Change separating structure has less contribution towards resonance hybrid.

Resonance Energy:

Resonance hybrid is more stable than the resonance structure. The difference in energy between the hybrid and the most stable resonance structure is known as the resonance energy.

Resonance Energy = (Energy of hybrid) − (Energy of most stable resonance structure)



Resonance energy can be determined by the difference between the calculated & experimental heats of combusion.

In benzene calculated heat of combusion for hypothetical structure ① & ② is 797 Kcal/mol.

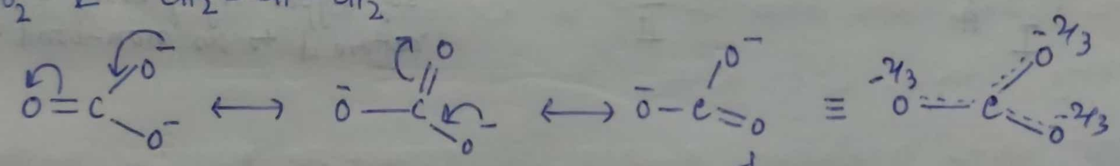
Experimental value for benzene is 759 Kcal/mol.

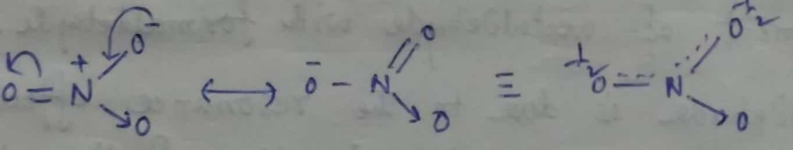
Resonance energy or stabilication energy = 797 − 759
= 38 Kcal/mol

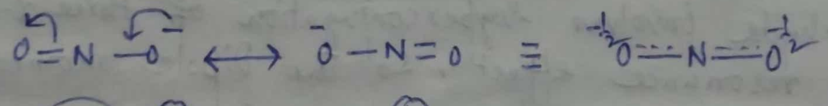
Problems:

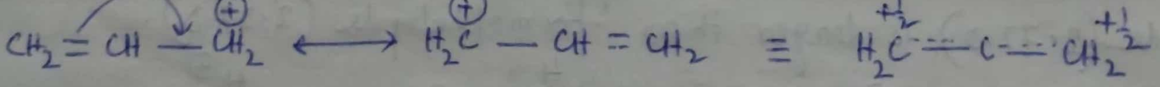
1. Draw the resonating structure for the following CO_3^{2-}, NO_3^-, NO_2^- & $CH_2=CH-\overset{\oplus}{C}H_2$

Ans:



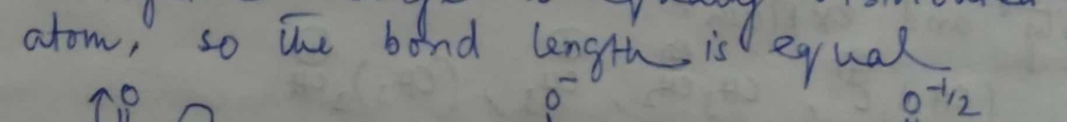






2. How will you account for that the C−O bond in acetate ion are identical?

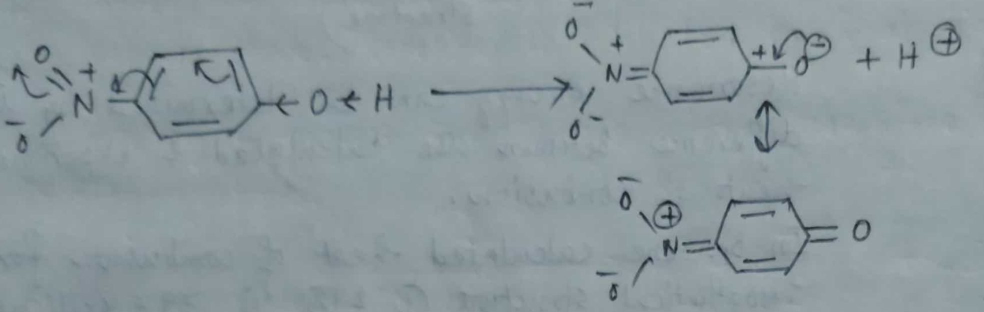
Ans: Acetate ion is a hybrid of two resonating structure and the negative charge is equally distributed over two oxygen atom, so the bond length is equal



The carbon-oxygen bond length is 1.26 A°.

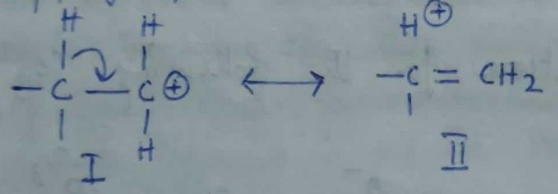
3. p-nitrophenol is more acidic compare to phenol — explain.

Ans: Due to the presence of $-NO_2$ gr. which exerts -R effect, it withdraws electron from benzene ring makes the O-H bond weaker. As a result removal of $H^{\oplus}$ ion from this molecule will be more easier compare to phenol.



E. Hyperconjugation:

It is a special type of resonance which involves the overlapping of σ-orbital with a π-orbital or p-orbital.

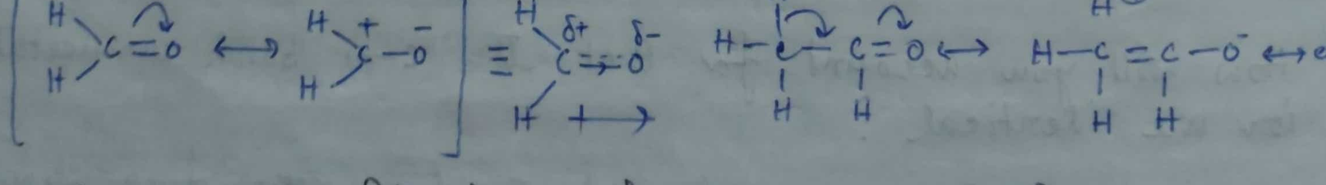


in structure (II) there is no bond between H + & C, so hyperconjugation is also reffered to as non-bond resonance.

Problems:

1. Compare the dipole moment of acetaldehyde with formaldehyde.

Ans: Polarity of formaldehyde is due to the resonance effect. But the polarity of acetaldehyde involves hyperconjugation of three α-hydrogen atoms in addition to resonance effect. So the dipole moment of acetaldehyde (2.72 D) is larger than formaldehyde (2.27 D).



2. Arrange the following carbocations in order of increasing stability and explain.

$(CH_3)_3\overset{\oplus}{C}$, $CH_3\overset{\oplus}{C}H_2$, $\overset{\oplus}{C}H_3$, $(CH_3)_2\overset{\oplus}{C}H$

Ans: The order is,

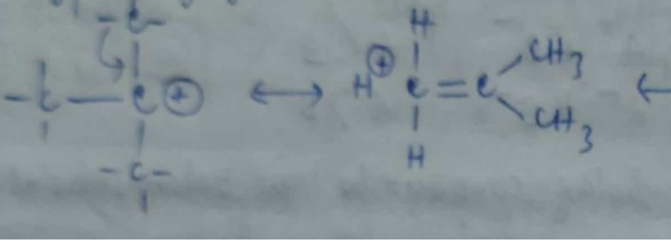
$(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$

IV III II I

The stability order can be explained on the basis of inductive effect & hyperconjugation.

In str. IV there is 3 +I effect, in str. III there is 2 +I effect, in str. II there is 1 +I effect. So, decreacing +I effect stability will decrease.

Again, more number of hyperconjugating structure more stable. In structure IV there is 9 α-H, so 9 hyperconjugative structure. In structure III & II there is 6 & 3 structure progressively. So, stability of hyperconjugation decreases from IV to I.


eight more structure.