Resonance and Inductive Effects

1

Resonance Effect

- In chemistry, resonance or mesomerism is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by one single Lewis formula.
- A molecule or ion with such delocalized electrons is represented by several contributing structures
  - Also called resonance structures or canonical forms.

2

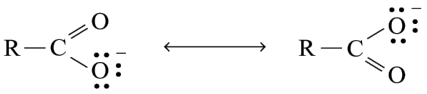
Resonance Effect

- Electron delocalization lowers the potential energy of the substance and thus makes it more stable than any of the contributing structures.
- The difference between the potential energy of the actual structure and that of the contributing structure with the lowest potential energy is called the resonance energy or delocalization energy.

3

Resonance Effect

- **Resonance effect** is an electronic effect involving **π bond electrons** or **electrons present in unhybridized *p* orbitals**.
- The ion become **more stable** when **the charge of the ion can be reduced or dispersed**.



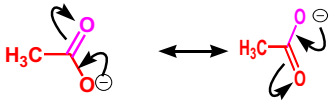
I Resonance structures II

4

Resonance Effect

The Resonance Arrow and its Physical Meaning

- The resonance arrow is not an equilibrium arrow
- The resonance arrow shows only the distribution of electrons.



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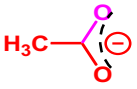
Resonance Effect

The Resonance Arrow and its Physical Meaning

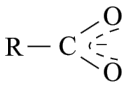
- Thus, for the two degenerate structures, the implication is that there is an even distribution of the two electrons between the two oxygen atoms, at all times.
  - Experimentally it is found that both C-O bonds are the same length and are intermediate in length between the C-O single and double bond, as are the C-C bonds in benzene.



6

Resonance Effect

- The actual structure of carboxylate ion is the **resonance hybrid** of the resonance structures.
- The negative charge of the anion is **dispersed**
- This **resonance stabilization** is responsible for the **high acidity of carboxylic acids**

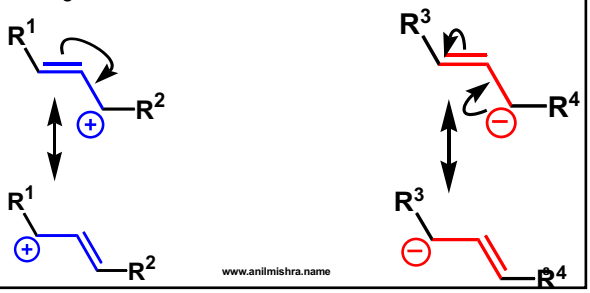


Resonance hybrid of carboxylate ion

7

Resonance Effect

- General Structure that will Display Resonance of Charges and Lone Pairs of Electrons



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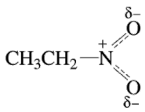
Resonance Structures

resonance contributor resonance contributor



resonance hybrid

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Resonance Contributors

Rules for Drawing Resonance Contributors

- Only electrons moves
- Only π electrons and lone-pair electrons move
- The total number of electrons in the molecule does not change
- The numbers of paired and unpaired electrons do not change

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Resonance Contributors

Rules for Drawing Resonance Contributors

- Move π electrons toward a positive charge or toward a π bond
- Move lone-pair electrons toward a π bond
- Move a single nonbonding electron toward a π bond

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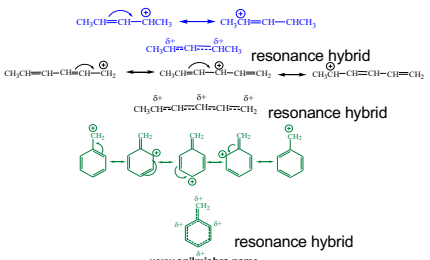
Resonance Contributors

- Moving π electrons toward a positive charge



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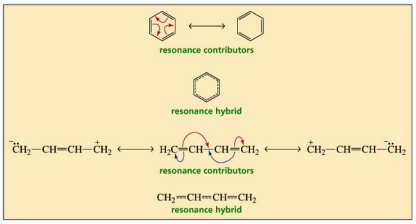
Resonance Contributors

- Moving π electrons toward a π bond



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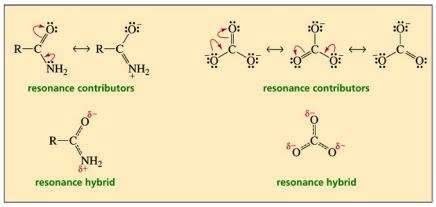
Resonance Contributors

- Moving a nonbonding pair of electrons toward a π bond



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Resonance Contributors

- Electrons move toward an sp^2 carbon but never toward an sp^3 carbon
- Electrons are neither added to nor removed from the molecule when resonance contributors are drawn
- Radicals can also have delocalized electrons if the unpaired electron is on a carbon adjacent to an sp^2 atom

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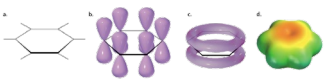
Resonance in Benzene

- A planar molecule
- Has six identical carbon–carbon bonds
- Each p electron is shared by all six carbons
- The p electrons are delocalized



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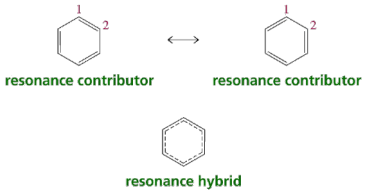
Resonance in Benzene

- Resonance Contributors and the Resonance Hybrid
- Resonance contributors are imaginary, but the resonance hybrid is real



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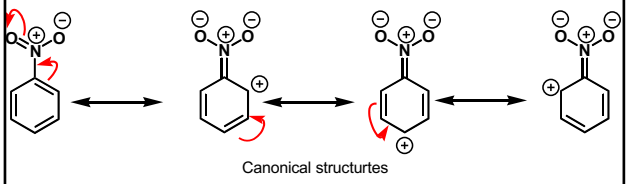
Resonance and Reactivity

Some Important Aromatic Resonance Structures

Nitro Group: An Electron Withdrawing Group



Canonical structurtes

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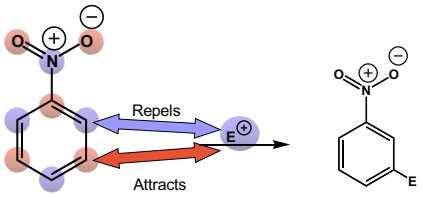
Resonance and Reactivity

Nitro Group: An Electron Withdrawing Group



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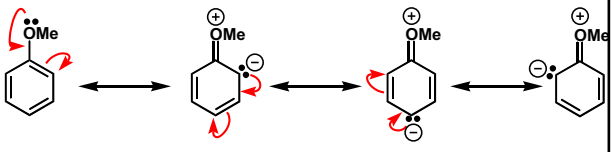
Resonance and Reactivity

Methoxy Group: An Electron Donating Group



Canonical structurtes

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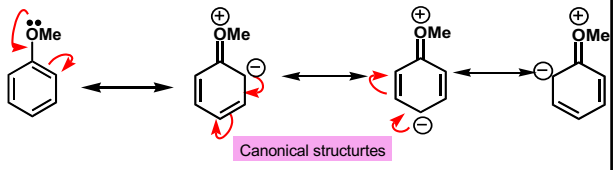
Resonance and Reactivity

- Note in a reaction mechanism we would not show the lone pairs on the carbons carrying the –ve charge…



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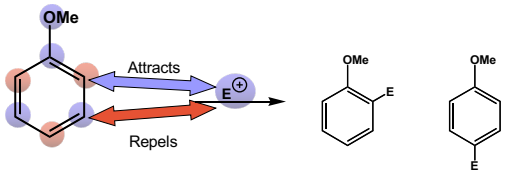
Resonance and Reactivity

These resonance structures allow us to rationalise (and predict) reactivity



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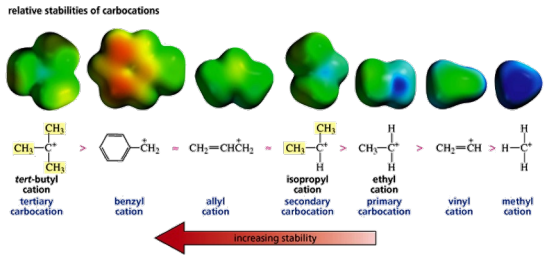
Resonance and Stability



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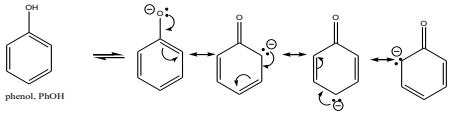
Resonance and Acidity

- Phenol is Acidic



CH_3CH_2OH ethanol, EtOH $\rightleftharpoons$ $CH_3CH_2O^- + H^+$

No resonance structures!!

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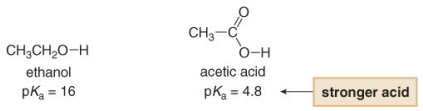
Resonance and Acidity

- When we compare the acidities of ethanol and acetic acid, we note that the latter is more acidic than the former.



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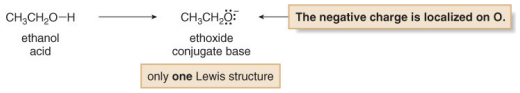
Resonance and Acidity

- When the conjugate bases of the two species are compared, it is evident that the conjugate base of acetic acid enjoys resonance stabilization, whereas that of ethanol does not.



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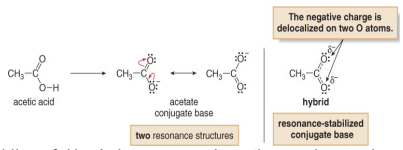
Resonance and Acidity

- Resonance delocalization makes CH_3COO^- more stable than $CH_3CH_2O^-$, so CH_3COOH is a stronger acid than CH_3CH_2OH.



- The acidity of H—A increases when the conjugate base $A:^-$ is resonance stabilized.

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Resonance and Acidity

- Electrostatic potential plots of $CH_3CH_2O^-$ and CH_3COO^- below indicate that the negative charge is concentrated on a single O in $CH_3CH_2O^-$, but delocalized over both of the O atoms in CH_3COO^-.

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Inductive Effect

- Inductive effect is an experimentally observable effect of the transmission of charge through a chain of atoms in a molecule, resulting in a permanent dipole in a bond.

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Inductive Effect

- The electron cloud in a σ-bond between two unlike atoms is not uniform and is slightly displaced towards the more electronegative of the two atoms.
- This causes a permanent state of bond polarization, where the more electronegative atom has a slight negative charge (δ–) and the other atom has a slight positive charge (δ+).

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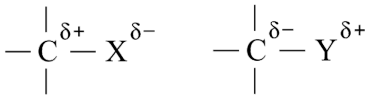
Inductive Effect

- Due to the **difference in electronegativity** between two atoms linked up by σ bonds, **the bonding electrons will displace towards the more electronegative atom**. The atom exhibits a **partial negative charge**.
- The electronic effect of a group that is transmitted by the **polarization of electrons in σ bonds** is called an **inductive effect**.



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Inductive Effect

Electronegativity Values

H 2.1	C 2.5	N 3.0	O 3.5	F 4.0
	Si 1.8	P 2.1	S 2.4	Cl 3.0
				Br 2.8
				I 2.5

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Inductive Effect

- **Inductive effect** is represented by an arrow head in the middle of the covalent bond **pointing in the direction of the displacement of electrons**.

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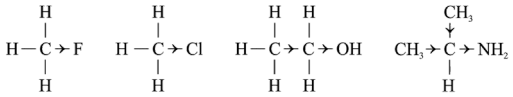
Inductive Effect



Electron-withdrawing group (X) exerts a **negative inductive effect**.

X exerts a negative inductive effect

Electron-donating group (Y) exerts a **positive inductive effect**.

Y exerts a positive inductive effect

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Inductive Effect

- Groups which exert **negative inductive effects**
  - i.e. **electron-withdrawing groups**

$-NO_2 > -F > -COOH > -Cl > -Br > -I$

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Inductive Effect

- Groups which exert **positive inductive effects**
  - i.e. **electron-releasing groups**

e.g.

alkyl groups like $-CH_3$, $-C_2H_5$, $-C_3H_7$

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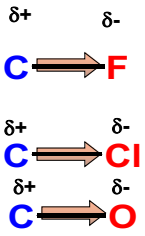
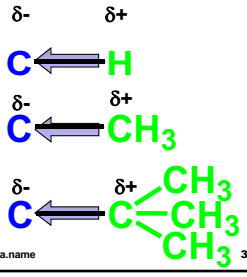
Inductive Effect

Bond Polarisation and Inductive Effects

-I Inductive Effects



+I Inductive Effects



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Inductive Effect

- The strength of inductive effect is also dependent on the distance between the substituent group and the main group that react; the greater the distance, the weaker the effect.

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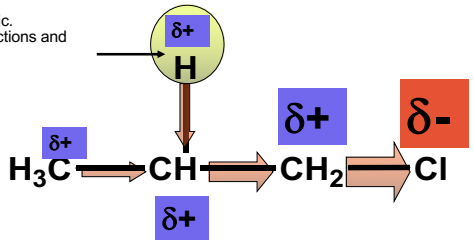
Inductive Effect

This proton is acidic.
eg Elimination reactions and alkene formation.



Inductive Effects are Short Range In Contrast to Resonance Effects

The polarised C-Cl bond transmits further polarisation through the s-bond framework,

But effect drops off quickly

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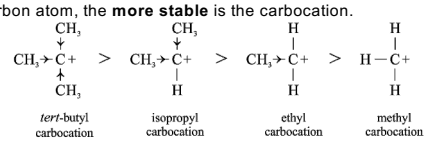
Inductive Effect and Stability

Stability of Carbocations

- *tert*-butyl carbocation is the most stable because **electron-donating groups exert positive inductive effects to reduce the positive charge on the carbon atom**.
- The **greater the number of alkyl groups** attached to the central carbon atom, the **more stable** is the carbocation.



tert-butyl carbocation | isopropyl carbocation | ethyl carbocation | methyl carbocation

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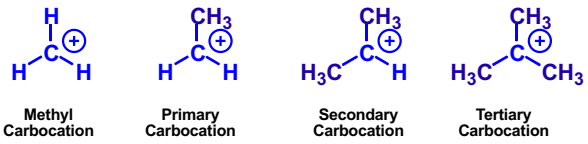
Inductive Effect and Stability

Carbocation Stability

LEAST STABLE → MOST STABLE

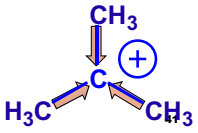


Methyl Carbocation | Primary Carbocation | Secondary Carbocation | Tertiary Carbocation

Carbon atom is electron deficient (only has 6 electrons in its outer valence).

The methyl groups have +I inductive effects.

Thus, extra electron density is 'pushed' onto the carbocation, which stabilises the carbocation.



Inductive Effect and Acidity

- An inductive effect is the pull of electron density through σ bonds caused by electronegativity differ-ences between atoms.
- On comparision of the acidities of ethanol and 2,2,2-trifluoroethanol, we note that the latter is more acidic than the former.

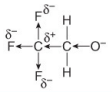
CH_3CH_2O-H	CF_3CH_2O-H
ethanol	2,2,2-trifluoroethanol
$pK_a = 16$	$pK_a = 12.4$ ← stronger acid

Inductive Effect and Acidity

- The reason for the increased acidity of 2,2,2-trifluoroethanol is that the three electronegative fluorine atoms stabilize the negatively charged conjugate base.

$CH_3CH_2O^-$

No additional electronegative atoms stabilize the conjugate base.



CF_3 withdraws electron density, stabilizing the conjugate base.

Inductive Effect and Acidity

- When electron density is pulled away from the negative charge through σ bonds by very electronegative atoms, it is referred to as an electron withdrawing inductive effect.
  - More electronegative atoms stabilize regions of high electron density by an electron withdrawing inductive effect.
  - The more electronegative the atom and the closer it is to the site of the negative charge, the greater the effect.
- The acidity of H—A increases with the presence of electron withdrawing groups in A.

The dark red of the O atom indicates a region of high electron density.

The O atom is yellow, indicating it is less electron rich.

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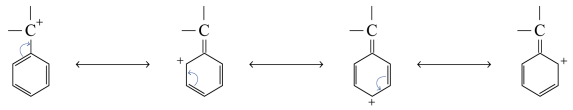
Another example:

Carbocation with the positively charged carbon atom directly bonded to a benzene ring

Its actual structure is represented by four resonance structures shown below:



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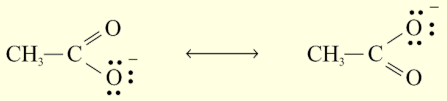
Example 28-1

The following equations represent the ionizations of two organic acids:

$$\underset{\text{Acid 1}}{CH_3CH_2-OH} \rightleftharpoons \underset{\text{Conjugate}}{CH_3CH_2-O^-} + H^+$$

Solution:

(a) ***Conjugate base 2 is more stable***. The anion is ***stabilized by resonance effect and the negative charge of the anion is dispersed over two oxygen atoms***. The two resonance structures of the anion are shown below:



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Example 28-1 (cont'd)

(b) Which conjugate base is less stable? Explain your answer.

(c) Which is a stronger acid?

Solution:

(b) ***Conjugate base 1 is less stable*** because there is no resonance effect stabilizing the anion. Moreover, ***the positive inductive effect of the electron-releasing CH_3CH_2– group further destabilizes the anion***.

$$CH_3 — CH_2 \rightarrow O^-$$

(c) ***Acid 2 is a stronger acid than acid 1***.

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Check Point 28-3

(a) Draw the two resonance structures for propanoate ion ($CH_3CH_2COO^-$).

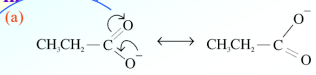
(b) State whether the following species exhibit positive or negative inductive ef

(i) –I

(ii)

(i

(iv)

(a) 

(b) (i) Negative inductive effect

(ii) Negative inductive effect

(iii) Negative inductive effect

(iv) Positive inductive effect

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