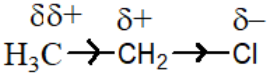
Notes on Electronic displacement

Inductive effect

The permanent dipole induced in a bond due to unequal sharing of bonding electrons, which relayed along a chain of atoms in a molecule is called inductive effect.

- **It is a permanent effect in the ground state of the molecule.**
- **It is supposed to operate through single bond.**
- **The effect is greatest for adjacent bonds, and decreases with increasing distance from the starting dipole.**



$$\overset{\delta\delta+}{H_3C} \rightarrow \overset{\delta+}{CH_2} \rightarrow \overset{\delta-}{Cl}$$

Where δ+ > δδ+

Functional groups can be classified as electron withdrawing (-I) or electron donating (+I) groups relative to H.

- **The atoms or groups of atoms that draw electrons toward themselves i.e. away from the carbon chain are known as electron withdrawing groups and the effect is called electron withdrawing effect, represented by –I effect.**
- **The atoms or groups of atoms that releases electrons toward the carbon chain are known as electron releasing groups and the effect is called electron releasing effect, represented by +I effect.**

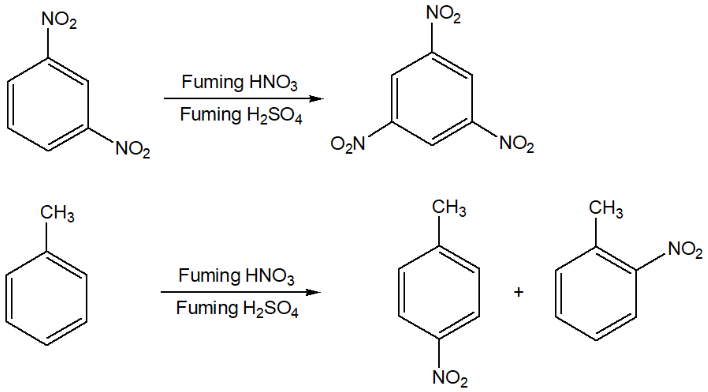
Table 1: Inductive effect of various groups relative to H.

+I	-I		
O^-	NR_3^+	COOH	OR
COO^-	SR_2^+	F	COR
CR_3	NH_3^+	Cl	SH
CHR_2	NO_2	Br	SR
CH_2R	SO_2R	I	OH
CH_3	CN	OAr	$C\equiv CR$
D	SO_2Ar	COOR	Ar
			$C\equiv CR_2$

Application of Inductive effect

1. Dipole moment: Inductive effect is intimately associated with the dipole moment of the molecule. Generally, dipole moment increases with the increase in inductive effect provided this effect due to more than one group do not act in opposition to each other.

2. Chemical reactivity: Inductive effect has a dominant role in chemical reactivity of molecules. Therefore, m-dinitrobenzene when heated with fuming HNO_3 and H_2SO_4 requires five days to completely form the product, trinitrobenzene, while toluene is easily nitrated to form o- and p-nitrotoluene. The –I effect of nitro group makes m-dinitrobenzene less reactive, and +I effect of methyl group makes toluene more reactive towards nitration.



3. In comparing basicity of bases: Organic species containing N or O with donatable lone pair of electrons are considered as bases. If any electron withdrawing group is attached to such N or O atom in a base, it will decrease the electron density on the atom and hence basicity of the base will decrease. On the other hand, if any electron releasing groups is attached to N or O atom in organic base, it will increase the electron density on the atom and hence increase the basicity of the molecule. Therefore,

Methylamine is more basic than ammonia.

Trifluoromethylamine (CF_3NH_2) is less basic than methylamine (CH_3NH_2).

4. In comparing acidity of acids: The ability of donating proton of a chemical entity is called acidity of the chemical specie and the entity is said to be an acid.

If we compare the acidity of formic acid (HCOOH), acetic acid (CH_3COOH) and chloroacetic acid ($ClCH_2COOH$),

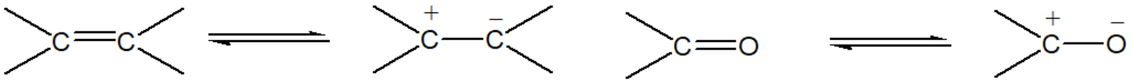
The increasing order of acidity is: $CH_3COOH < HCOOH < ClCH_2COOH$

This is due to the fact that electron releasing group (CH_3-) attached to the carboxyl carbon atom decreases its ability to donate proton. Therefore, acetic acid is less acidic than formic acid. While, electron withdrawing effect of Cl increases the ability of chloroacetic acid to donate proton, thus increases its acidity.

Electromeric effect

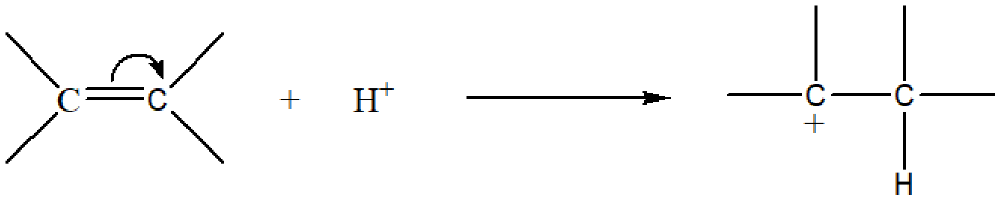
The temporary effect involving the complete transfer of a shared pair of pi electrons to one of the atoms joined by a multiple bond, double or triple, at the requirement of an attacking reagent is known as electromeric effect.

The electromeric effect has no specific direction. Its direction is always that which favours the reaction. If one of the atoms joined to the multiple bond is more electronegative than the other, the transfer of electrons usually occurs towards the more electronegative atom.

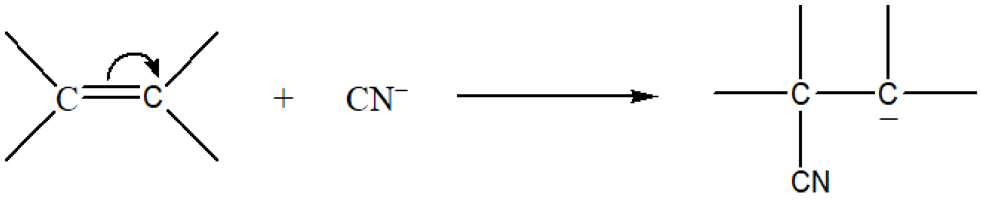


The direction of electromeric effect is the same as that of inductive effect. The effect is denoted by the symbol E.

The +E effect : When the electron pair of pi bond is moved towards the attacking reagent, the effect is known as +E effect.



The -E effect : When the electron pair of pi bond is moved away from the attacking reagent, the effect is known as -E effect.



Application of electromeric effect

The electromeric effect i.e. the close approach of a reagent to a multiple bond enhances the reactivity of the reactant molecule and explains its addition reaction product.

Difference between inductive and electromeric effect

Inductive effect	Electromeric effect
Permanent effect	Temporary effect
It is permanent polarisation of a single bond	It is the polarisability of a multiple bond.
Sigma electrons are involved in this case	Pi electrons are involved in this case
Only electron displacement takes place in the inductive effect	Complete transfer of pi electrons takes place in the electromeric effect
It determines both physical properties and chemical reactivity of the molecules concerned.	It has nothing to do with physical property but it enhances chemical reactivity of the molecules concerned.
Electronegativity of bonded atoms controls the direction of the inductive effect	The E effect has no specific direction. The electronegativity of bonded atoms and inductive effects of the attached groups may determine the direction of the electromeric effect. Its direction is that what favours the reaction.

Mesomeric or conjugative effect or resonance effect

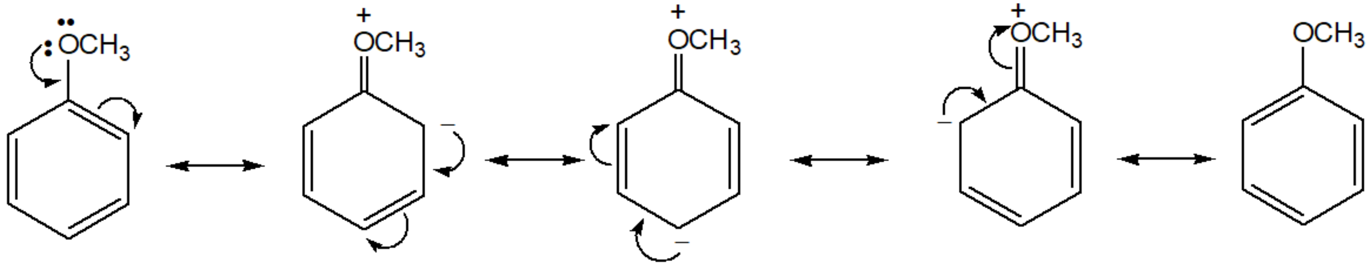
The effect which helps redistribution of electrons with permanent polarisation in the ground state of an entity in unsaturated and chiefly in conjugated systems *via* pi orbitals is called conjugative or resonance effect. Mainly pi-pi or pi-p type of orbital overlap gives rise to conjugation.

Mesomeric effect may be represented by the symbol M or R.

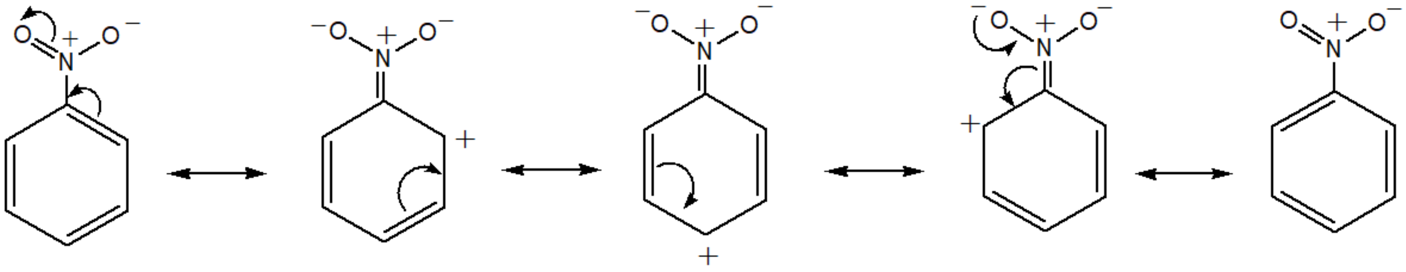
There are two types of resonance effect, viz. positive resonance effect and negative resonance effect.

1. **Positive resonance effect (+M or +R): When the electronic displacement occurs away from the group concerned towards the conjugated system via p orbital overlap, the mesomeric effect is said to be +M effect. For example: NH_2, OH, OR, Cl etc.**
2. **Negative resonance effect (-M or –R): When the electronic displacement takes place towards the group concerned, the mesomeric effect is said to be +M effect. E.g. NO_2, C=O, COOH, CΞN etc.**

Donation of electrons into benzene ring by resonance



Withdrawal of electrons from benzene ring by resonance



Application of mesomeric effect

❖ Resonance is used to explain the stability of molecules

(1) A resonance hybrid possessing a greater number of resonating structures is more stable than resonance hybrid consisting of a fewer number of such structures.

(2) Electron redistribution over a wider range brings greater stability to a system than that over a shorter range.

❖ Resonance can be used to explain relative acidity and basicity of molecules

If the conjugate base of an acid is more stable than the acid itself, then basicity of the conjugate base is lower than the acid strength of the acid. This means: the weaker is the conjugate base, stronger is the acid.

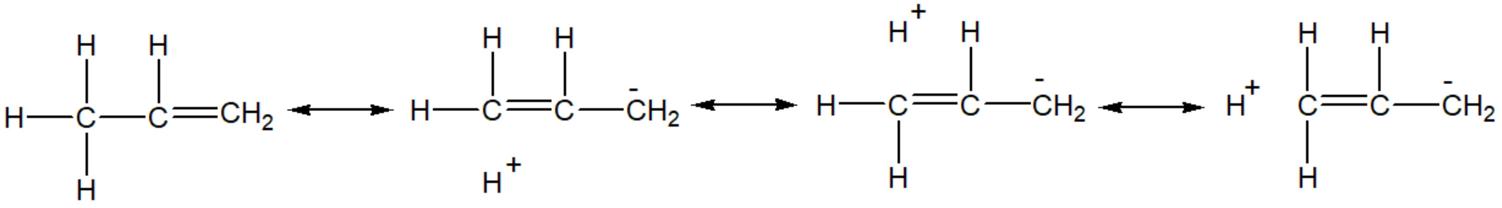
If lone pair of electrons of a base gets delocalised, it is not readily available for donation and hence the compound will be of low basicity.

❖ This effect can be used to explain the relative reactivity of molecules.

Hyperconjugative effect

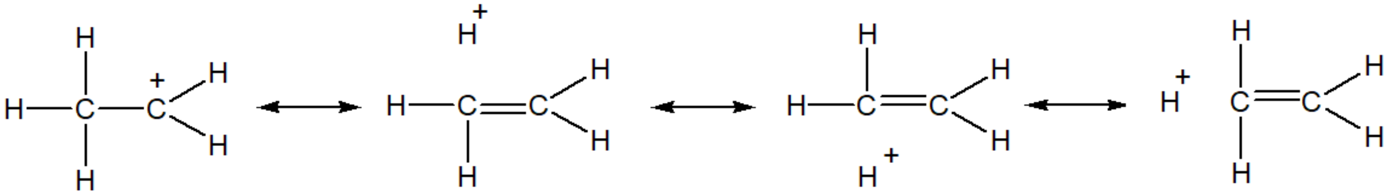
The excessive conjugation involving sigma orbitals, generally of C-H or C-X (X= Cl, F) or C-C bond is called hyperconjugation. σ –π or σ–p (incomplete or vacant) type of orbital overlap gives rise to conjugation.

For example, in propene, delocalisation occurs between C=C π M.O. and C-H σ M.O. of the C atom adjacent to the double bonded C.



Each of these resonating structures is hypothetical and non-existent. This sort of resonance also stabilises the molecule.

Similarly, in ethyl cation ($CH_3CH_2^+$), hyperconjugation is regarded as the overlap of the C-H orbital and vacant p orbital of the positively charged C atom.



Application of hyperconjugative effect

The hyperconjugative effect can be used to explain the stability of free radicals, carbenium ions with adjacent C-H bonds etc.

❑ **Propene is more stable than ethene- explain.**

➢ **Hyperconjugative effect plays its role in bringing stability to propene, that is absent in ethene. For this reason, ethene is less stable than propene.**

❑ **The order of stability is**

a. $(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$

b. $(CH_3)_3C\cdot > (CH_3)_2CH\cdot > CH_3CH_2\cdot > CH_3\cdot$

Explain the stability order in both cases.

➢ **(a) Two effects can be considered in explaining the order-**

(i) Hyperconjugative effect

We know that the more the number of contributing structures of comparable energy in resonance hybrid, the greater is its stability. In tertbutyl cation, there are nine C-H sigma bonds and hence its resonance hybrid consists of ten resonating forms, while in case of isopropyl, ethyl and methyl cation, there are six, three and none resonating forms, respectively. Therefore, the stability of carbenium ions follows the order as in the question.

(ii) Inductive effect

Due to the +I effect of the three methyl groups attached to the positively charged carbon atom of the tertbutyl cation, its charge is neutralised to a greater extent in comparison to isopropyl, ethyl and methyl cation where there are only two, one and none methyl groups attached to the positively charged carbon atom, respectively.

(b) **$(CH_3)_3C\cdot$ has nine resonating forms without odd electron in its resonance hybrid, $(CH_3)_2CH\cdot$ has six such structures, while ethyl radical has three and methyl radical has none such structures. Therefore, stability of the radicals follows the order:** $(CH_3)_3C\cdot > (CH_3)_2CH\cdot > CH_3CH_2\cdot > CH_3\cdot$