Delocalized Chemical Bonding

Resonance :-

Since bonding of many compds can be adequately described by a single Lewis st, but for many compds, it is not sufficient. Such compds contain one or more bonding orbitals that are not limited to two atoms, but are spread out over 3/more. Such bonding is said → delocalized.

Representation of a real st as a weighted Average of two or more canonical forms is c/a resonance.

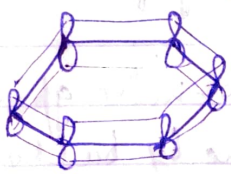
1 (K) 2 (K) 3 (D) 4 (D) 5 (D)

39 % 39 % 7.3 % 7.3 % 7.3 %

of actual mol.

→ Energy of actual mol. is less than that of any one Lewis st. & this difference in energy b/n the actual mol & Lewis st of lowest energy is c/a Resonance energy.

St of benzene



The R.E can never be measured, only estimated. Since we can measure the heat of atomization of the real molecule but can only make an guess at that of the Lewis st. of lowest energy.

* Method used for estimation of R.E → Heat of hydrogenation

Kind

Rules for Resonance :-

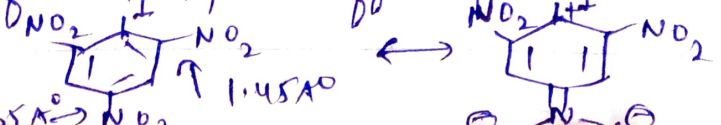
a) R. st. exist only in one's imagination.

b) only e^- movement is allowed. → Nuclei in each of the st. must be in the same relative positions.

c) All resonance st must have the same no. of unpaired e^-.

d) All the atoms taking part in resonance i.e. atoms that are part of delocalized system must lie in a plane or be nearly planar.

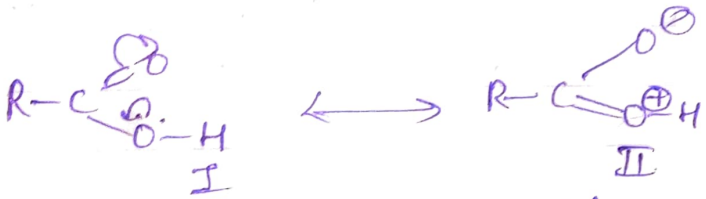
eg. Picryl iodide, B. Length of ortho & para nitro gps are diff.. oxygens of o-nitro gp are not in plane, being pushed out of plane by bulky iodine atom. steric inhibition of reso. explains effect of o-sub. on basic ch. of anilines



e) Energy of actual mol. (Res. hybrid) is lower than the energy that might be estimated from any contributing st.

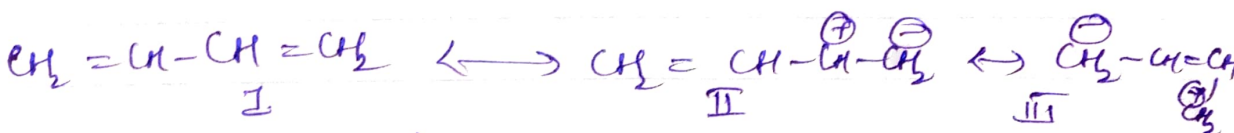
f) All R. st. do not contribute equally to hybrid. Each res. st. contributes in proportion to its stability.

g) In general, non polar str. are more stable than the dipolar unless one atom is electropositive

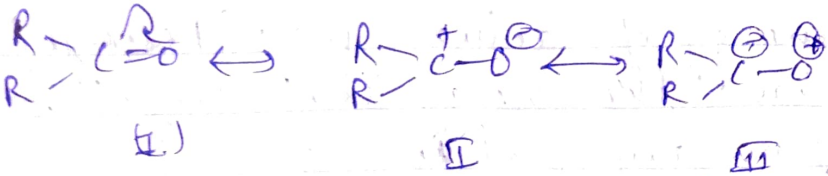


I (less stable)

* Among dipolar st, farther apart the charges are, the less stable is the resonance form.



I (Most stable) II III (least stable)



I) II) III (least stable)

h). st. involving formal charges are the most stable when -ve. & +ve charges resides on the most electro(-ve) & electro(+ve) atoms respectively.

i) st. ∈ like formal charges on adjacent atoms have high energy & are thus unstable.

j) st. ∈ e^- def. +vely charged atoms have very high energy & are thus unstable

k) More the no. of covalent bonds in a resonating st, more will be its stability. Since each C. bond contributes abt 50-100 kCal/mol. of energy, which is to stability of system, while diff. in stability of resonating forms is only a fraction of this amount.

Relative Stabilities of Resonance Str. :-

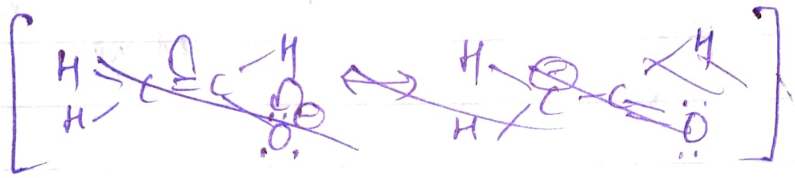
a) St. ē a max. of octets are preferred.

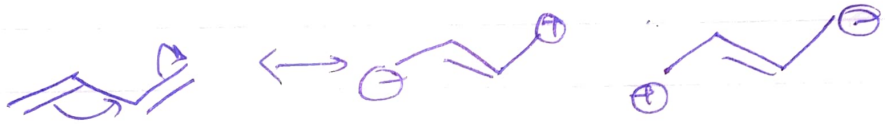
Major

Minor

(St ē max. of octet are most imp.)

b) More covalent bonds, more stable

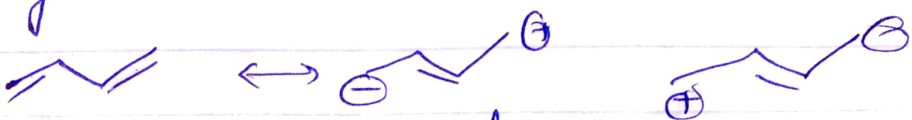




More stable

c). Charge sep. decreases stability

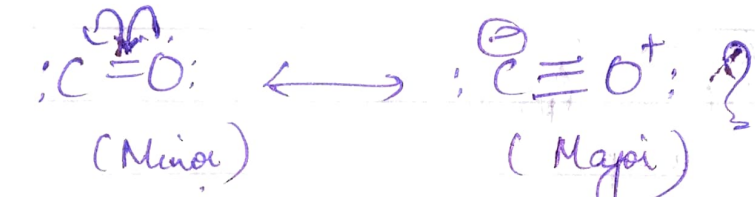
Separating opp. charges require energy, thus res. St. in ⊆ opp. charges are separated, have lower stability.

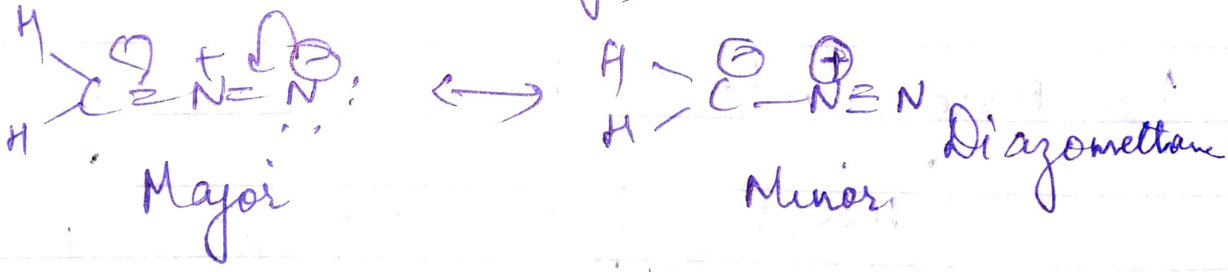


(less contributing) to hybrid

→ Charge separation may be enforced by octet rule

Among charge separated Res. st., most favourable is one in which charge distribution best accomodates the relative electronegativities of component atoms.





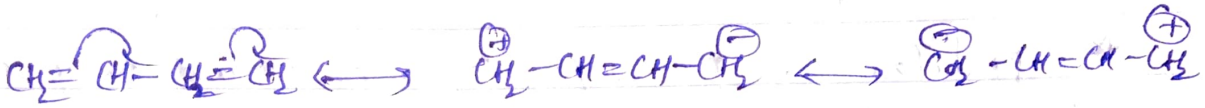
Kinds of Molecules that have delocalized bonds:-

a) = or ≡ bonds in Conjugation

b) = or ≡ " " " with a p orbital on an adjacent atom

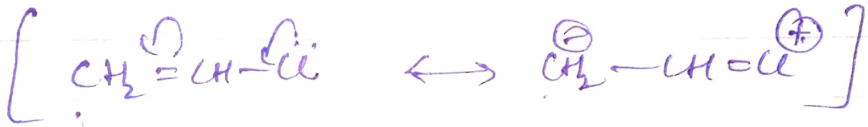
c) Hyperconjugation:-

a)

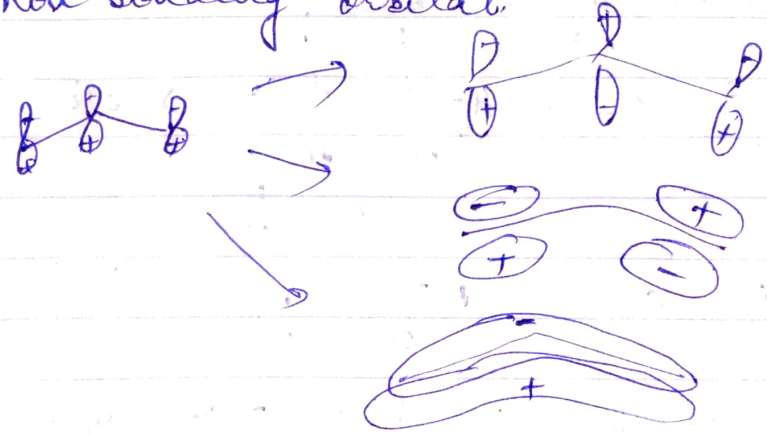


B.L. 1.34 Å for = & 1.48 Å° for single bond. but not 1.53 Å°, giving evidence for resonance, can be explained by hybridization changes.

b)



∴ we know overlap of n atomic orbitals creates n mol. orbitals, so overlap of a p orbital with an adjacent = bond give rise to three new orbitals. Middle orbital is a non bonding orbital of zero bonding energy. Central Carbon atom does not participate in non bonding orbital.



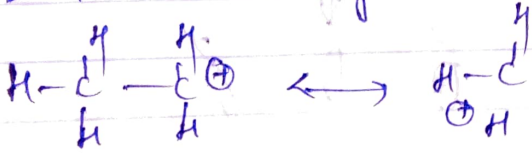
p orbital may contain 0, 1 or 2 e⁻.
thus total no. of e⁻ accomodated by new orbital is 2, 3 or 4.
eg. $CH_2=CH-\ddot{C}l$. Here p orbital of Cl is filled thus on overlapping $\bar{e}$ = bond, 4 e⁻ occupy two M.O. of lowest energies.

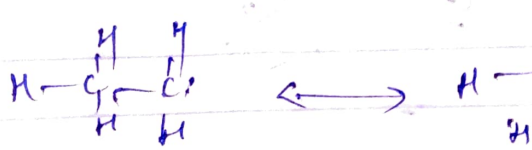
* p orbital cont. 1/0 e⁻, are found only in free radicals & cation.

$$CH_2=CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH_2$$
$$CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$$
$$CH_2=CH-\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH_2$$

Hyperconjugation :- (σ-π overlap as against π-π overlap) It involves σ electrons.
→ When a Carbon attached to at least 1 H is attached to an unsaturated atom or $\bar{e}$ an unshared orbital.

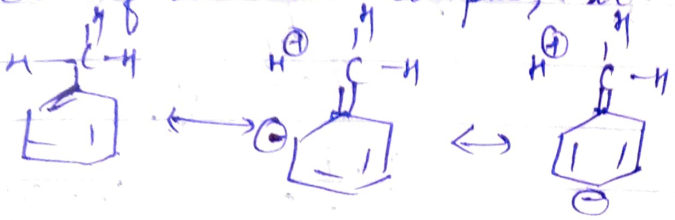
→ It is an overlap of σ orbital of C-H bond & π orbital of C-C bond.





t-butyl > isopropyl > ethyl > methyl
e⁻ release

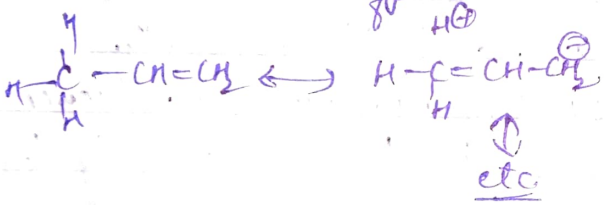
In case of aromatic compds, it was just opposite



Two types

Sacrificial
(in neutral mol.)

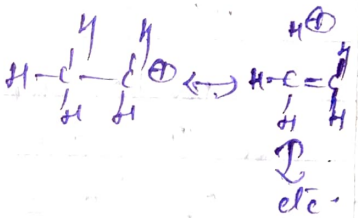
(Here canonical forms involve not only no-bond res. but also a charge separation not possessed by main form.



(Loss of 1 bond)

Isovalent
(In free radicals & Carbocations)

(Here, canonical forms displays no more charge separation than the main form),

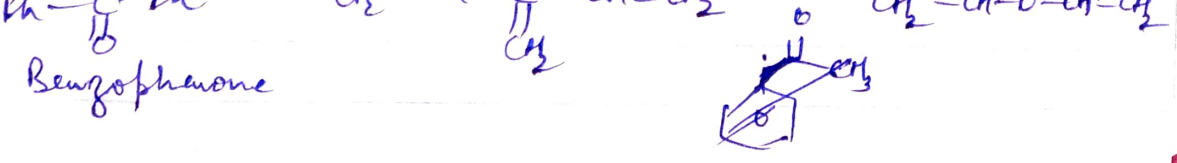


(No loss)

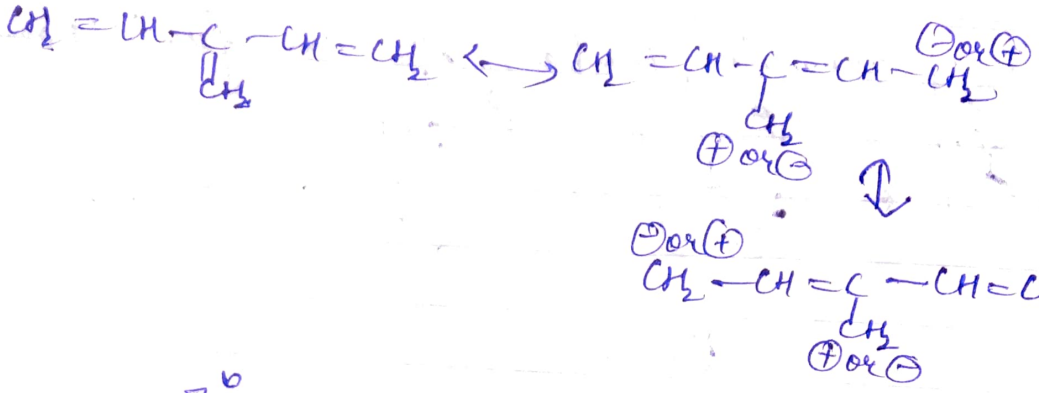
* Special type of conj., when in a set of 3 π bonds, only two π bonds interact each other by conj, third one is excluded from interaction

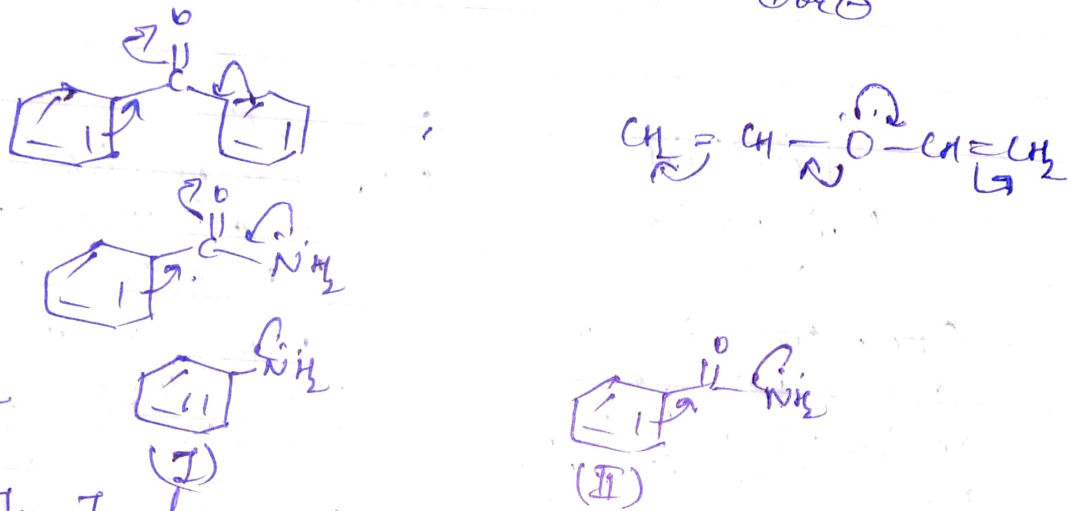
Cross Conjugation :- When conjugation is possible from either end of mol. toward center, it is called as cross conj.

→ Here, three gps are present, two of which are not conjugated with each other, although each is conjugated to third.



Benzophenone





(I) (II)

In I, lone pair on N activates ring & bromination under normal cond. → tribromo aniline

In II, due to cross conjugation, influence of lone pair in activating the ring is less hence bromination leads to only mono sub. acetanilide (p-bromoacetanilide).