Hyperconjugation

Hyperconjugation (Beker Nathan effect) :→

It is defined as the interaction between an empty p-orbital with the adjacent (C-H) σ bond i.e the interaction between the π system and the adjacent σ-bonds of the substituent group. The partial overlap between an empty p-orbital and sp^3-s of a (C-H) σ bond may be shown as under in case of ethyl Carbonium ion.

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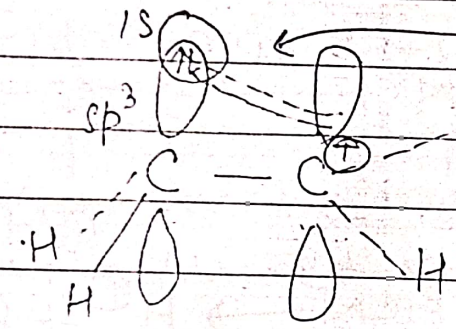
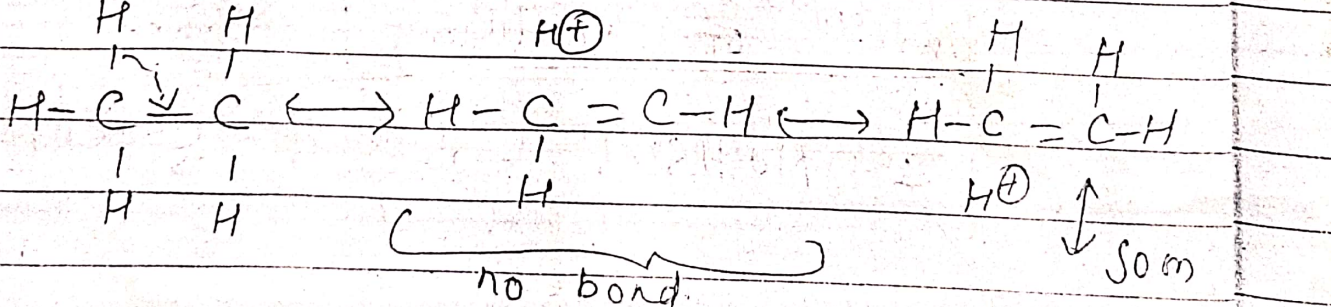


(Ethyl Carbonium ion)

Due to such conjugation the +ve charge of the C-atom gets dispated and no bond structure arise as shown below:—



In no-bond structures proton CH^+/O is not separated rather it is present in the vicinity of the molecule and entrapped into the π-system.

Applications :→

(1). By hyperconjugation the stability of the Carbonium ion can be explained.

$\therefore 3°C^{\oplus} > 2°C^{\oplus} > 1°C^{\oplus} > CH_3^{\oplus}$

e.g. $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C^{\oplus}}}}} > CH_3-\underset{H}{\overset{CH_3}{\underset{|}{\overset{|}{C^{\oplus}}}}} > CH_3-CH_2^{\oplus} > CH_3^{\oplus}$

(tert. butyl C^+ ion) (iso-propyl C^+ ion) (ethyl C^+ ion)

Explanation:→

In case of $3°C^{\oplus}$ ion, the +ve charge of C-atom gets dissipated to 9-α-hydrogen atoms, i.e. 9-no bond resonating structures may be obtained.

$$H_3C-\underset{CH_3}{\overset{H_1-CH_2}{\underset{|}{\overset{\rightarrow\!\!|}{C^{\oplus}}}}} \longleftrightarrow H_3C-\underset{CH_3}{\overset{H^{\oplus}\quad CH_2}{\underset{|}{\overset{\|}{C}}}} \longleftrightarrow \text{So on.}$$

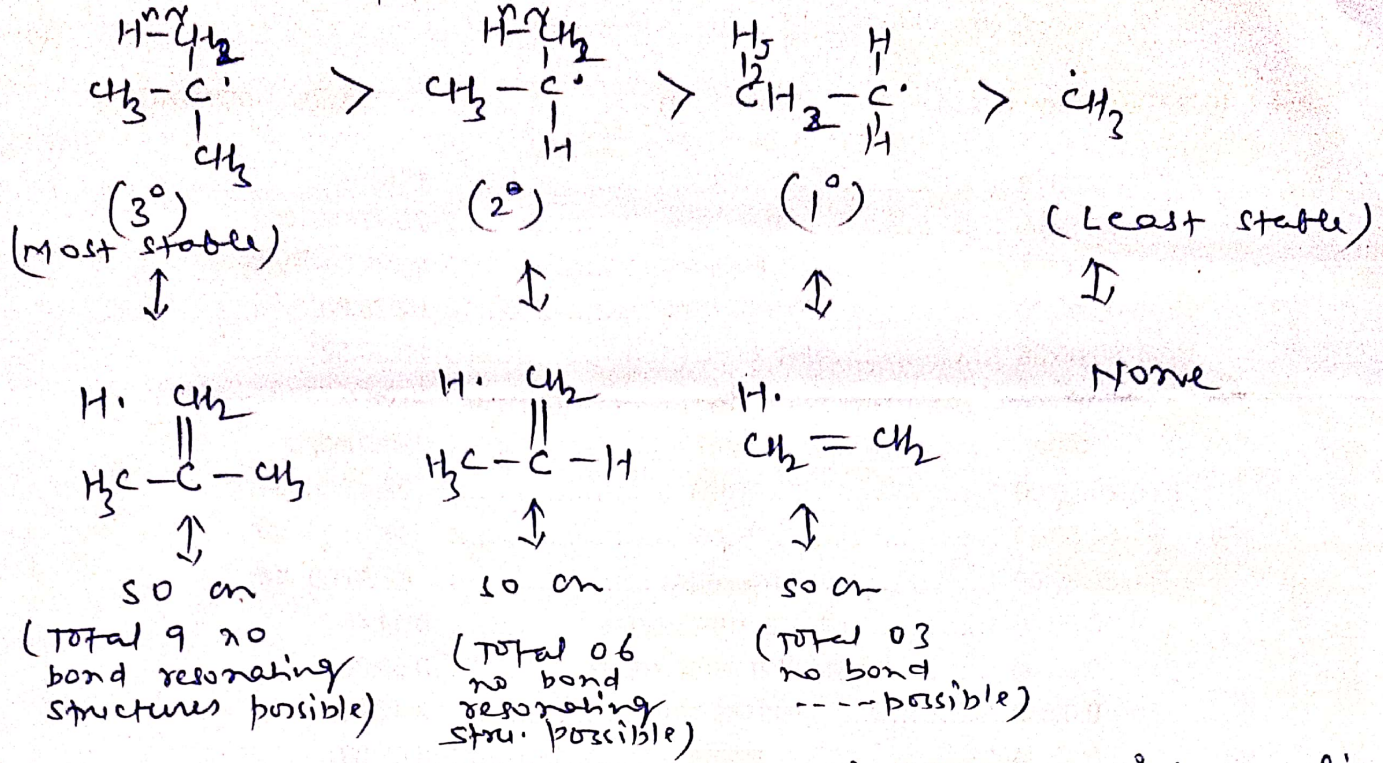
while for,

$2°C^+$ ion, only 6 no-bond Str. are possible,

$1°C^+$ ion, " 3 " " " " "

$CH_3^{\oplus}$ ", no such structures is possible.

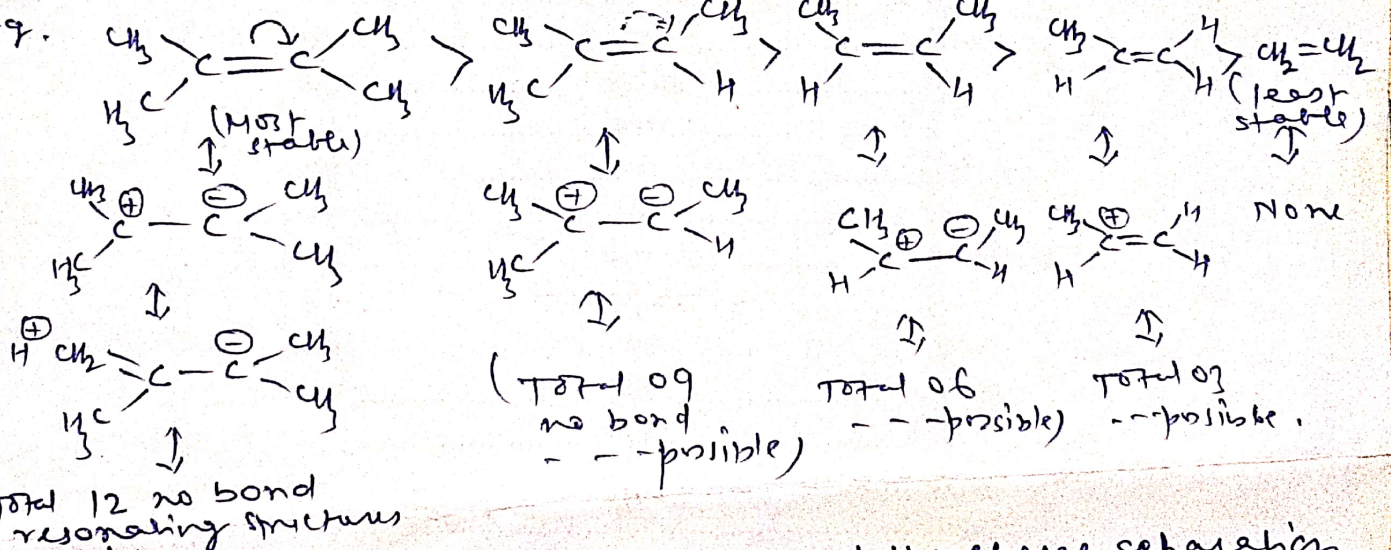
(ii) Similarly stability of free radicals can also be explained as under



In this case also the electron deficiency on 3° free radical is dissipated to a maximum extent on the α-H atoms, while in $-CH_3$ free radical it is localised, so the above order of stability is obtained.

(iii) stability of substituted alkenes w.r.to ethene can also be explained by the concept of Hyperconjugation.

e.g.



Due to delocalisation of π-electron cloud the charge separation may take place as shown above and the resulting transient electron deficiency may get dissipated to α-H-atoms, making the system more stable. As a result Tetramethyl Tetramethyl ethene is found to be the most stable while ethene, the least on the basis of physical parameters (like enthalpy of hydrogenation ---etc).