

Presented By:

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CARBOCATIONS & STABILITY

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- A carbocation is a species where a carbon atom bonds to three carbon atoms and has a positive charge.
- Carbocations are electron deficient species and therefore very reactive and unstable.
Anything which donates electron density to the electron-deficient center will help to stabilize them.

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Factors that stabilize them are the following:

- Neighboring carbon atoms (inductive effect)
- Neighboring carbon-carbon multiple bonds (resonance effect)
- Neighboring atoms with lone pairs (resonance effect)

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How carbocations are stabilized by neighboring carbons atoms?

The stability of carbocations decreases as the number of carbons attached to the C⁺ decreases.

That means that tertiary carbocations are more stable than secondary that in turn are more stable than primary (Fig. 1)

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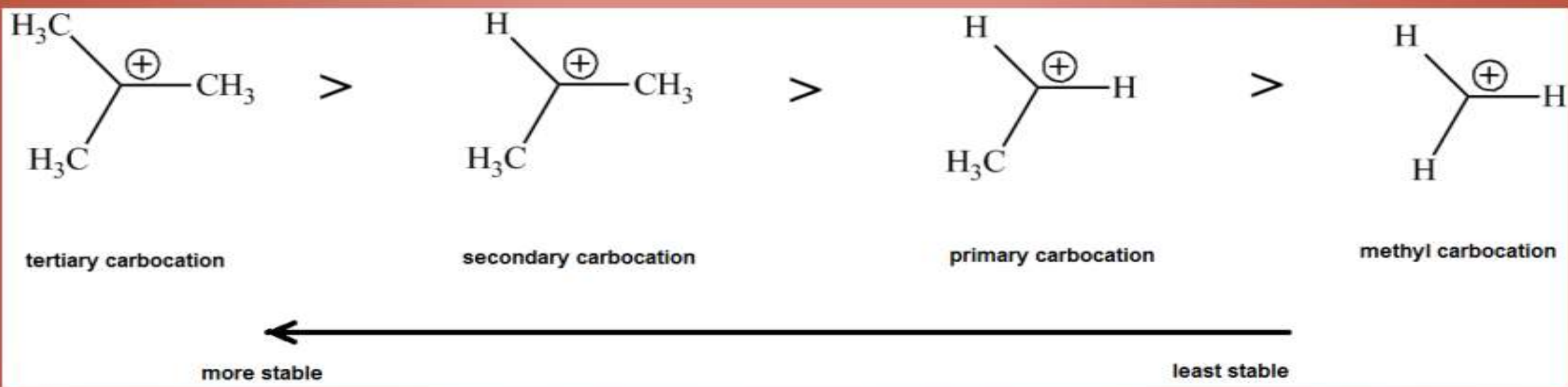


Fig. 1: Carbocation stability increases as methyl substitution increases around the electron deficient carbon C^+ . The methyl groups ($-\text{CH}_3$) are electron donating and therefore stabilize the positive charge (inductive effect).

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An explanation for this is that the methyl group (-CH₃) acts as an electron-donor and therefore stabilizes the positively charged cation.

Remember that the C atom has an electronegativity of 2.5 and that H 2.2.

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A better explanation is that electrons are donated from the C-H bonds to the empty p orbital of the C⁺ therefore stabilizing the carbocation through hyperconjugation (the more the -CH₃ groups attached to the C⁺ the more stable the carbocation becomes).

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How carbocations are stabilized by carbon-carbon multiple bonds (resonance)?

Carbocations where the C^+ is adjacent to another carbon atom that has a double or triple bond have extra stability because of the overlap of the empty p orbital of the carbocation with the p orbitals of the π

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bond. This overlap of the orbitals allows the charge to be shared between multiple atoms – delocalization of the charge - and therefore stabilizes the carbocation.

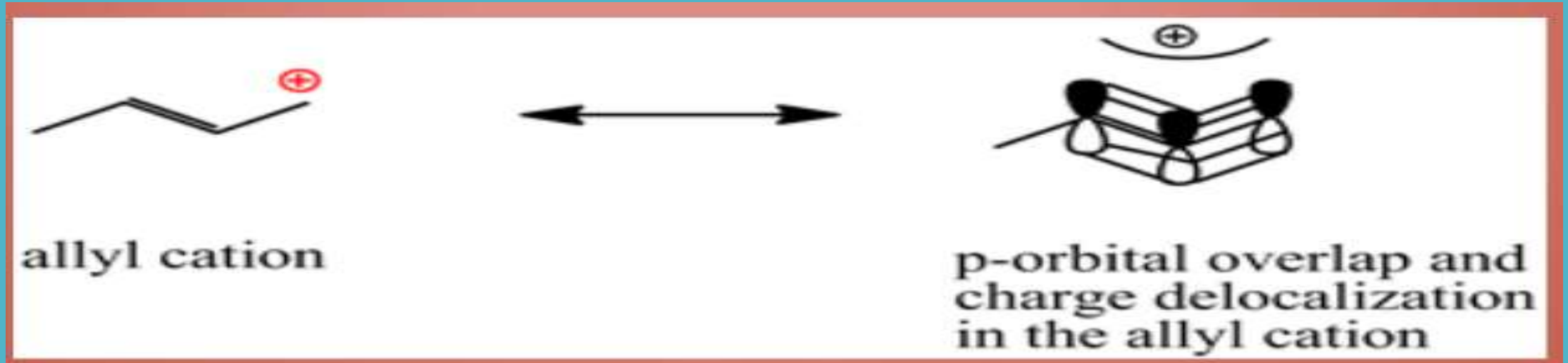


Fig. 2: Carbocation stabilization by multiple bonds adjacent to the C⁺ atom through p-orbital overlap

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This effect is called charge delocalization and is shown by drawing resonance structures where the charge moves from atom to atom.

It greatly stabilizes even primary carbocations – normally very unstable – that are adjacent to a carbon-carbon multiple bond.

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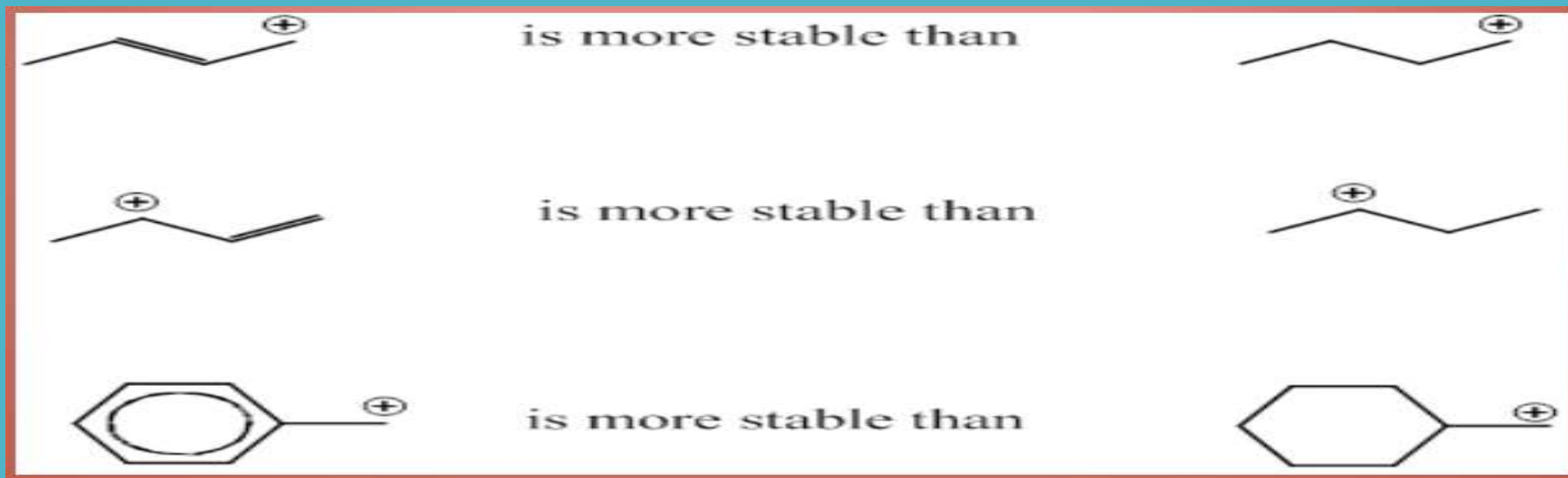


Fig. 3: Carbocation stabilization by multiple bonds adjacent to the C⁺ atom

How carbocations are stabilized by adjacent atoms with lone pairs?

Adjacent atoms with lone pairs act as electron donors to the electron-poor carbocation.

This results in forming a double bond (π bond) and the charge is delocalized to the atom donating the electron pair (π donation). Nitrogen and oxygen atoms are the most powerful π donors. However, even halogen atoms stabilize carbocations through donation of a lone pair

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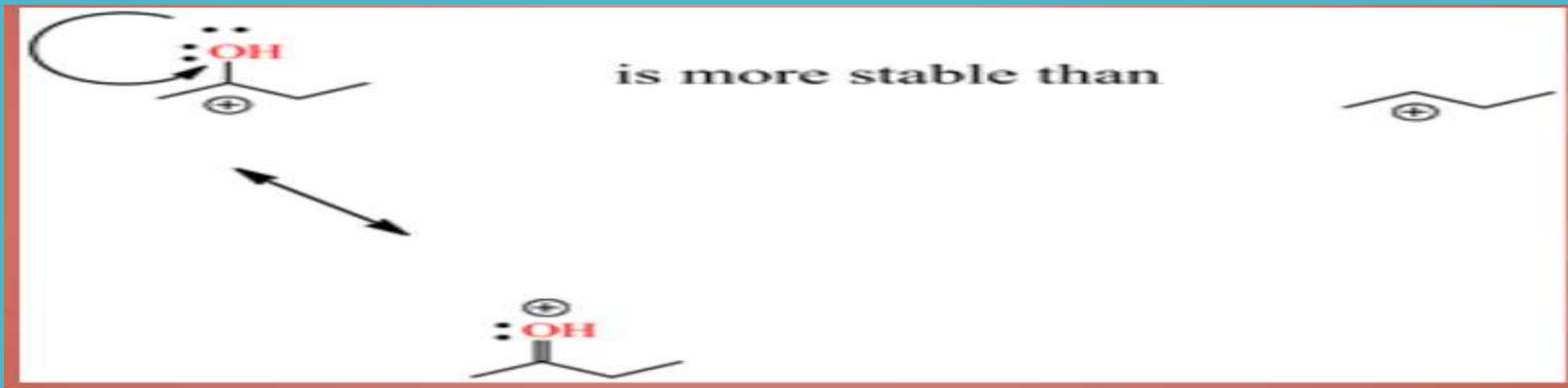


Fig. 4: Stabilization of the carbocation by lone pair donation. The O atom donates an electron pair to the C⁺ atom and a double bond is formed. The positive charge is delocalized to the oxygen atom providing extra stability.