Quadrant II – Transcript and Related Materials

Programme: F.Y.B.Sc. (Chemistry)

Subject: Chemistry

Course Code: CHC 101 Section B

Course Title: Inorganic Chemistry and Organic Chemistry

Unit: 03- Aliphatic Hydrocarbons

Module Name: Alkanes (upto 5 carbons): Reactions: Free Radical Substitution: Halogenation (2)

Module No: 39

Name of the Presenter: Ms. Anuja B. Naik

Notes

Transcript of the video

Hello students, I am Ms. Anuja Naik from Ganpat Parsekar College of Education, Harmal, Pernem Goa and I will be dealing with Alkanes (upto 5 carbons): Reactions: Free Radical Substitution: Halogenation (2)

The lecture deals with,

- ✓ Halogenation of alkanes
- Relative Reactivities of the Halogens
- Relative Reactivities of Alkanes toward Halogenation
- Ease of abstraction of hydrogen atoms
- Stability of free radicals
- Ease of formation of free radicals
- Reactivity and Selectivity in halogenation

So, at the end of the lecture, the student will be able to:

- Understand the Relative Reactivities of the Halogens

- Understand the Relative Reactivities of Alkanes toward Halogenation
- Explain the ease of abstraction of hydrogen atoms
- Explain the stability of free radicals
- Explain the ease of formation of free radicals
- Learn the Reactivity and Selectivity in halogenation

Relative Reactivities of the Halogens

- The halogens vary in their reactivity towards alkanes in free radical reactions.
- Fluorine is highly reactive toward hydrocarbons.
- Only chlorine and bromine are useful as free-radical halogenating agents.
- Iodine is nonreactive toward alkanes.
- The observed order of reactivity of halogen is $F_2 > Cl_2 > Br_2 > I_2$

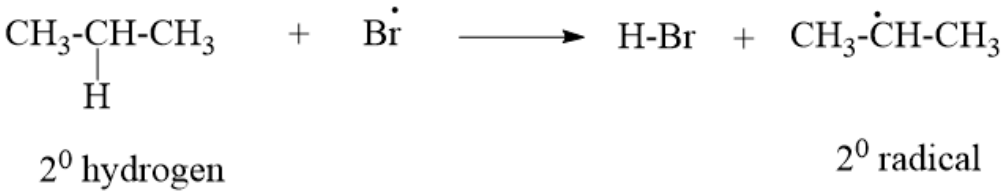
Relative Reactivities of Alkanes toward Halogenation

- The reactivity of a hydrogen depends chiefly upon its class, and not upon the alkane to which it is attached.
- Different types of hydrogens-Primary, secondary and tertiary have different reactivities towards halogens.
- It can be concluded that reactivity of an alkane in halogenation depends on the type of hydrogen is being extracted.

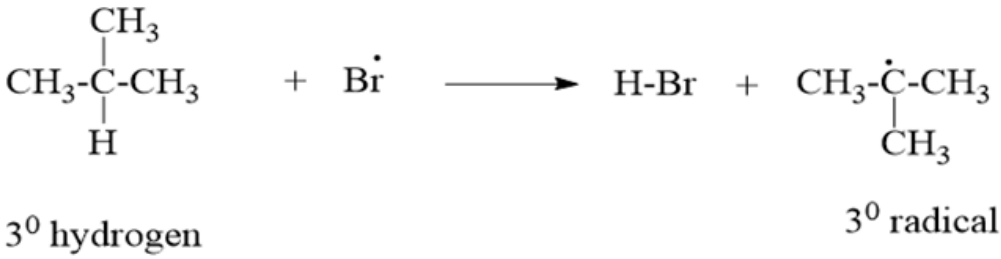
Ease of abstraction of hydrogen atoms

- The different types of hydrogen are not abstracted at identical rates by free radicals.
- The abstraction of a primary hydrogen forms a primary alkyl radical.

- Abstraction of a secondary hydrogen forms a secondary alkyl radical.



- Abstraction of a tertiary hydrogen forms a tertiary alkyl radical.



➢ The order of relative ease of abstraction of hydrogen atoms is

$$3^0 > 2^0 > 1^0 > CH_4$$

<u>Stability of free radicals</u>

- The order of stability of free radicals is $3^0 > 2^0 > 1^0 > \cdot CH_3$
- The stability of the radicals follows the same order as their ease of formation i.e. $3^0 > 2^0 > 1^0$
- Therefore, the more stable the free radical, the more easily it is formed.
- It requires more energy to form a primary radical, less to form a secondary radical and least to form a tertiary radical.

Ease of formation of free radicals

- ✓ The ease of formation of free radicals is

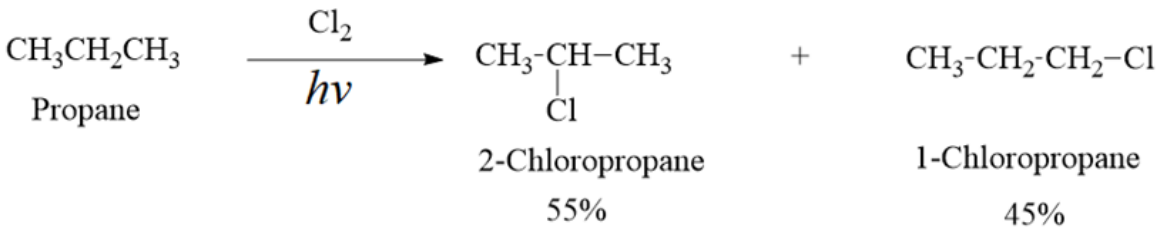
$$3^0 > 2^0 > 1^0 > \cdot CH_3$$

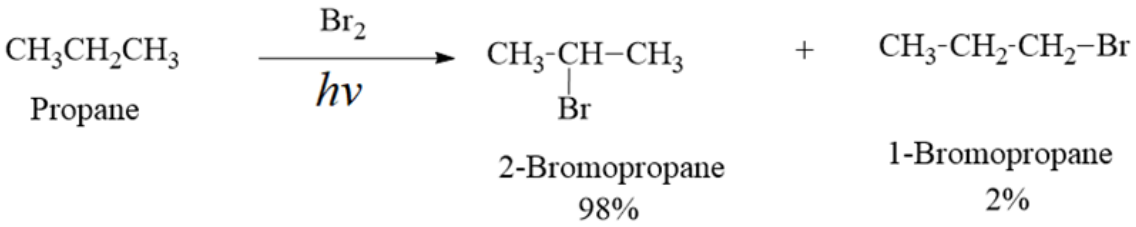
- ✓ The more stable the free radical, the more easily it is formed.
- ✓ And this is the same as the order of abstraction of hydrogens

$$3^0 > 2^0 > 1^0$$

Reactivity and Selectivity in halogenation

- ✓ We have seen that different types of hydrogens-Primary, secondary and tertiary have different reactivities towards halogens.
- ✓ We have learnt the order of reactivity of halogens toward alkane i.e. $F_2 > Cl_2 > Br_2 > I_2$
- ✓ We have also learnt the order of ease of abstraction of hydrogen atoms i.e. $3^0 > 2^0 > 1^0 > CH_4$





- ✓ The reaction of propane with chlorine under free radical conditions yields two monochlorinated products, 2-Chloropropane and 1-Chloropropane in the ratio 55:45.
- ✓ Whereas in case of bromine, 2-Bromopropane and 1-Bromopropane are formed in the ratio 98:2.
- ✓ Bromine which yields 98% 2-Bromopropane, is more selective about abstracting a secondary hydrogen than is chlorine.
- ✓ The selectivity of bromine arises from the fact that bromine is less reactive than chlorine in free radical halogenations.
- ✓ It is easier to remove a hydrogen atom from a secondary carbon to form a secondary radical than it is to remove a hydrogen atom from a primary carbon to form a primary radical. Because a secondary radical is more stable than a primary radical.
- ✓ The reaction of a bromine radical with an alkane is endothermic. The transition state is reached late in the reaction process. As a result, the transition state resembles the product- an alkyl radical.
- ✓ Whereas, the reaction of a chlorine radical with an alkane is exothermic. The transition state for chlorination is reached early. As a result, the transition state resembles the reactant- propane.
- ✓ Chlorination reaction does not show selectivity as far as formation of primary or secondary radicals.
- ✓ In case of bromination, since secondary radical is more stable than a primary radical, more of the secondary radical is formed and therefore more (98%) of the final product is formed.
- ✓ Since the bromination reaction is slower than chlorination, there is time available to form the more stable radical.
- ✓ Chlorination being fast, there is no time to make a decision between the more or less stable radicals and therefore an almost equal product ratio is seen (55:45).
- ✓ This explains why bromine is more selective than chlorine in its reaction with alkanes.
- ✓ Therefore it can be concluded that, the less reactive the reagent, the more selective it is.
- ✓ The Bromine atom is less reactive and more selective than the chlorine atom.

Summary of the video (Abstract of the transcript)

- ✓ The observed order of reactivity of halogen is $F_2 > Cl_2 > Br_2 > I_2$
- ✓ Only chlorine and bromine are useful as free-radical halogenating agents.
- ✓ Different types of hydrogens-Primary, secondary and tertiary have different reactivities towards halogens.
- ✓ The order of relative ease of abstraction of hydrogen atoms is
  $3^0 > 2^0 > 1^0 > CH_4$
- ✓ The order of stability of free radicals is $3^0 > 2^0 > 1^0 > \cdot CH_3$
- ✓ The stability of the radicals follows the same order as their ease of formation i.e. $3^0 > 2^0 > 1^0$
- ✓ The more stable the free radical, the more easily it is formed.
- ✓ The less reactive the reagent, the more selective it is.
- ✓ The Bromine atom is less reactive and more selective than the chlorine atom.