

# Free Radicals

By

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# Radical addition of HCl, HBr, HI

- It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H–Cl bond being stronger ( $430.5 \text{ kJ mol}^{-1}$ ) than H–Br bond ( $363.7 \text{ kJ mol}^{-1}$ ), is not cleaved by the free radical, whereas the H–I bond is weaker ( $296.8 \text{ kJ mol}^{-1}$ ) and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

# Radical addition of HCl, HBr, HI

- **Hydrogen iodide addition**
- Endothermic step in the chain propagation of HI addition.



- In the case of hydrogen iodide, the addition of the iodine radical to the double bond is the endothermic step of the chain propagation.

# Radical addition of HCl, HBr, HI

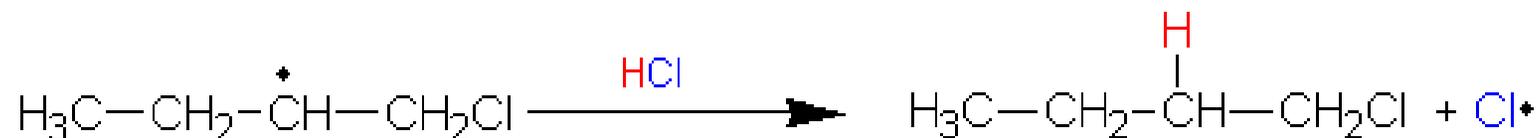


Halogen	Bond strength of the C-C $\pi$ bond	Bond strength of the C-X bond	$\Delta H$ (kJ/mol)
Cl	276	343	-66
Br	276	289	-13
I	276	226-276	+50

# Radical addition of HCl, HBr, HI

- **Hydrogen Cl addition**
- in the chain reaction of radical **HCl** addition to alkenes, the **second** chain propagation step is energetically unfavourable, since the amount of energy that must be applied in order to cleave the strong H-Cl bond considerably exceeds the amount of energy that is released during the new C-H bond's formation. As a result, this step is an endothermic reaction

# Radical addition of HCl, HBr, HI



Halogen	Bond strength of the H-X bond	Bond strength of the C-H bond	$\Delta H$ (kJ/mol)
Cl	431	410	+ 21
Br	376	410	-34
I	297	410	-113

# Radical addition of HCl, HBr, HI

- **HBr addition**
- in the radical HBr addition to alkenes, both chain propagation reactions are exothermic, while in radical HCl as well as HI addition, in each case one propagation step is endothermic. Therefore, only the HBr addition actually occurs.

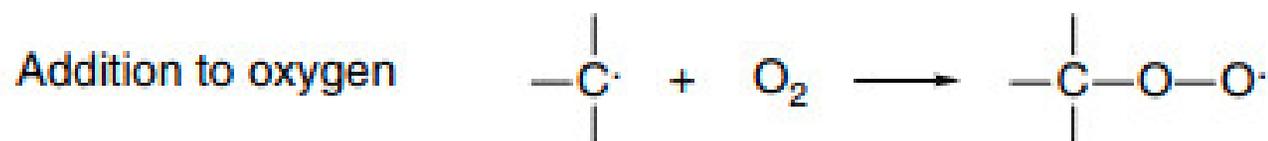
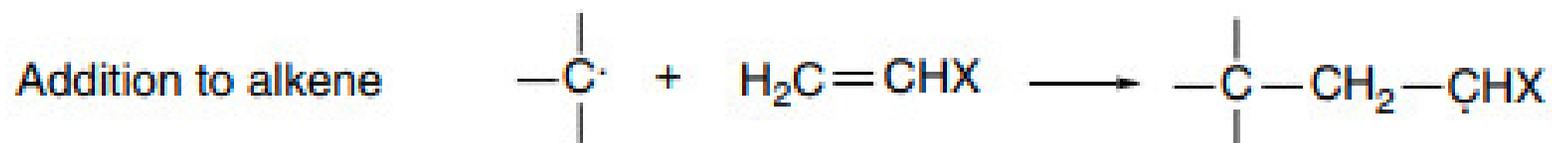
# Radical addition of HCl, HBr, HI

In association with the HCl and HI addition, the polar HX addition with an ionic intermediate stage largely exceeds the radical addition, which results, contrary to the radical addition, in the Markovnikov product.

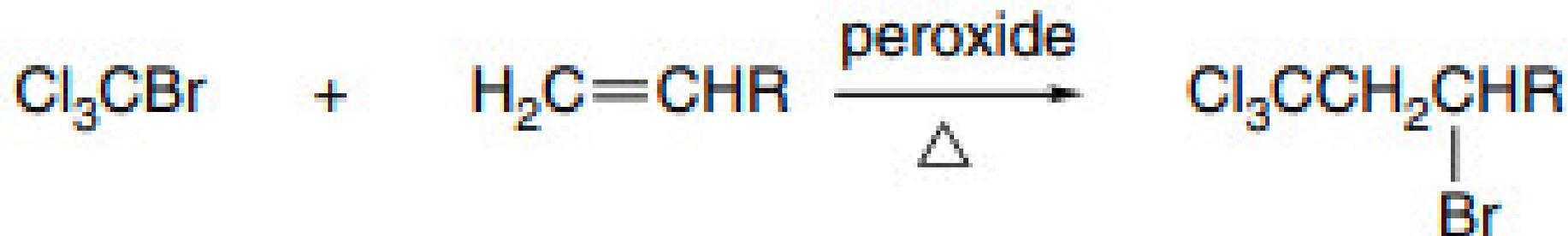
# Radical addition on alkene

In addition to HBr, many other reagents, such as thiols and some methyl halides, may also be added to alkenes in a radical addition.

# Radical addition on alkene

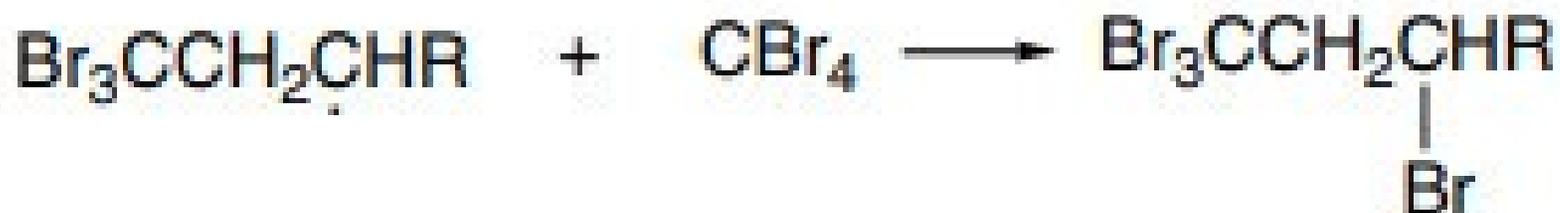
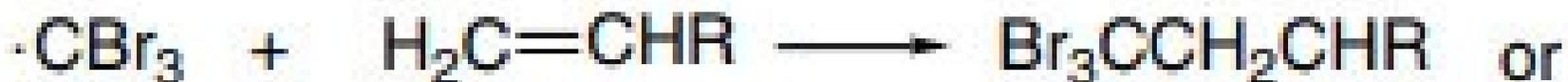
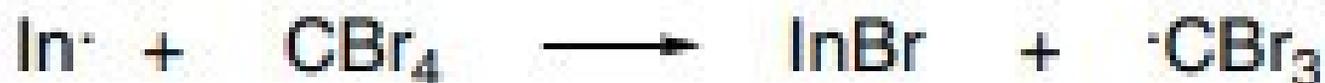


# Radical addition on alkene



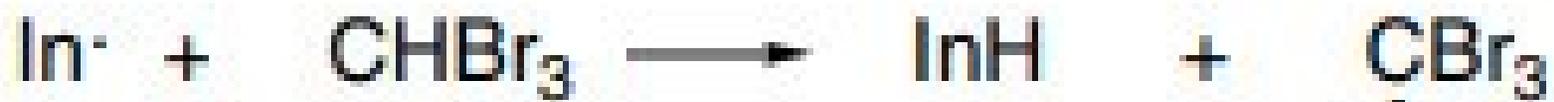
# Radical addition on alkene

## ADDITION OF TETRABROMOMETHANE



# Radical addition on alkene

## ADDITION OF TRIBROMOMETHANE



# Radical addition on alkene

- The order of reactivity of the halomethanes is  $\text{CBr}_4 > \text{CBrCl}_3 > \text{CCl}_4 > \text{CH}_2\text{Cl}_2 > \text{CHCl}_3$ .

# Radical Allylic Bromination

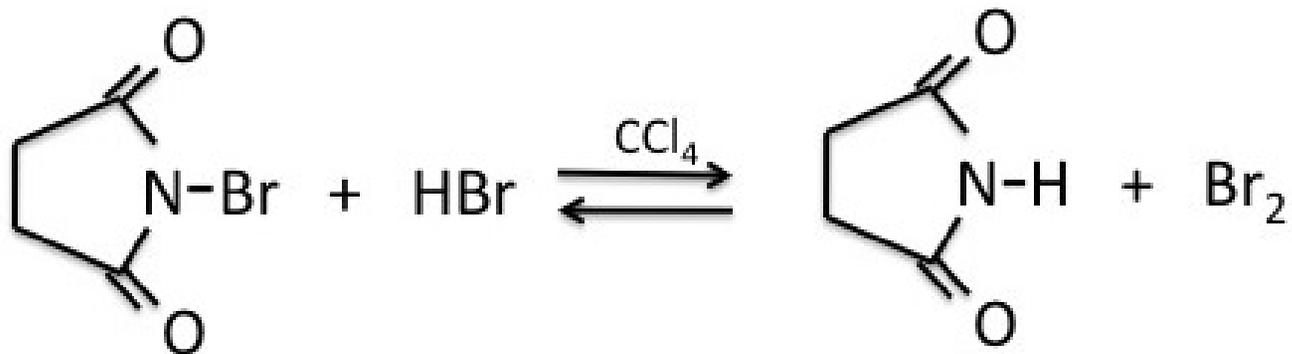
(Wohl-Ziegler Reaction)

## Preparation of Bromine (low concentration)

NBS (N-bromosuccinimide) is the most commonly used reagent to produce low concentrations of bromine.

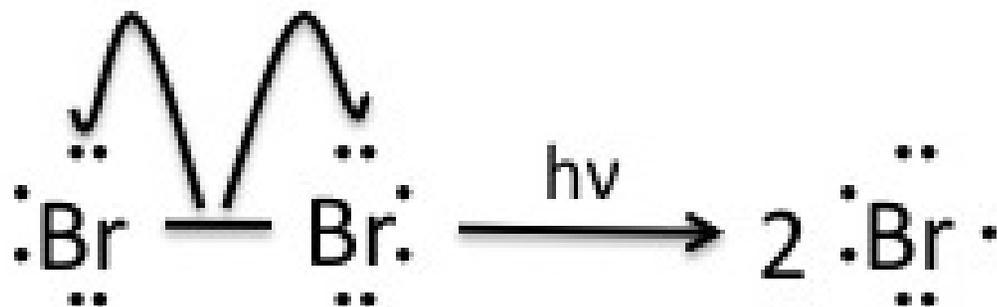
When suspended in tetrachloride ( $\text{CCl}_4$ ), NBS reacts with trace amounts of HBr to produce a low enough concentration of bromine to facilitate the allylic bromination reaction.

# Radical Allylic Bromination



# Radical Allylic Bromination

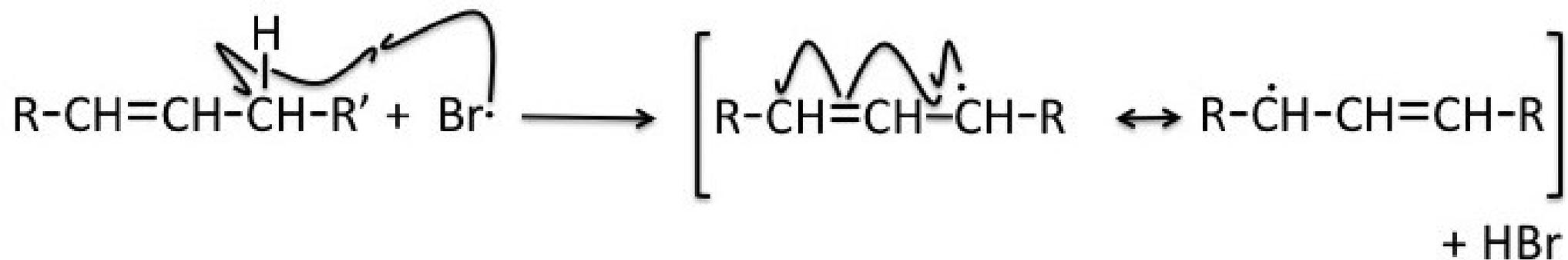
- **Step 1: Initiation**
- Once the pre-initiation step involving NBS produces small quantities of  $\text{Br}_2$ , the bromine molecules are homolytically cleaved by light to produce bromine radicals.



# Radical Allylic Bromination

- **Step 2: Propagation:** One bromine radical produced by homolytic cleavage in the initiation step removes an allylic hydrogen of the alkene molecule. A radical intermediate is generated, which is stabilized by resonance.
- The stability provided by delocalization of the radical in the alkene intermediate is the reason that substitution at the allylic position is favored over competing reactions such as addition at the double bond.

# Radical Allylic Bromination

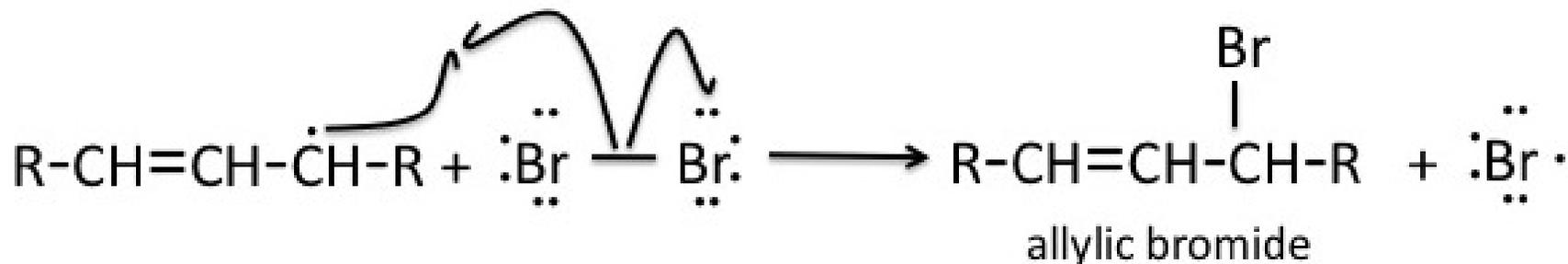


# Radical Allylic Bromination

- **Step 2: Propagation:**
- The intermediate radical then reacts with a  $\text{Br}_2$  molecule to generate the allylic bromide product and regenerate the bromine radical, which continues the radical chain mechanism.
- If the alkene reactant is asymmetric, two distinct product isomers are formed.

# Radical Allylic Bromination

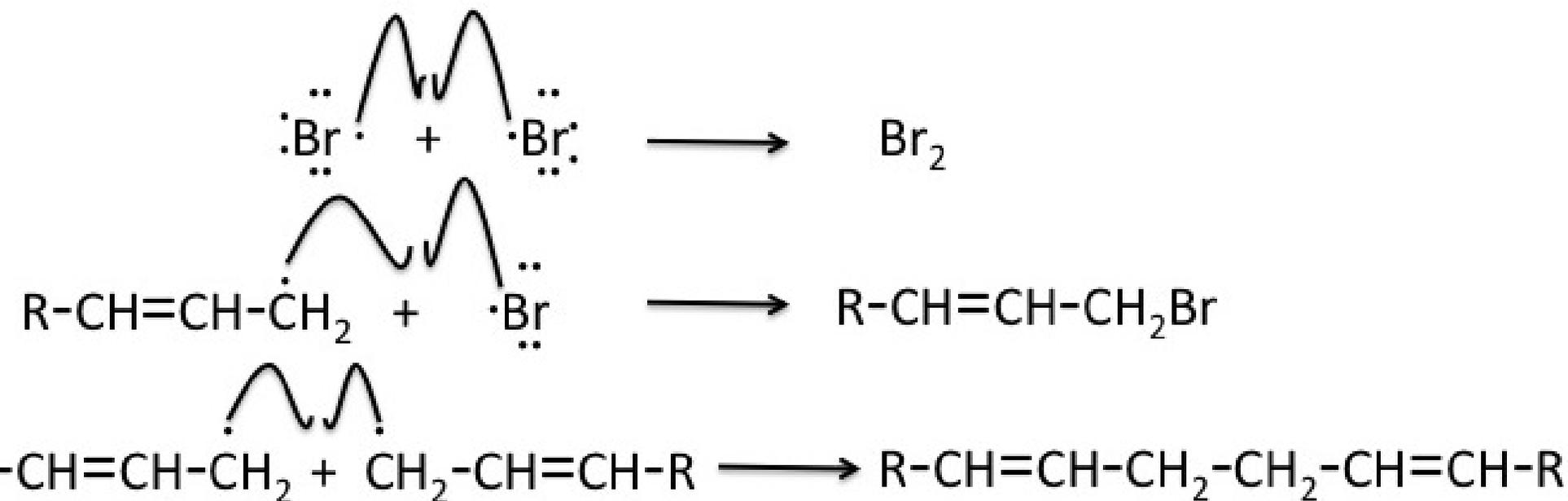
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# Radical Allylic Bromination

- **Step 3: Termination**

- The radical chain mechanism of allylic bromination can be terminated by any of the possible steps shown below.



# Radical Allylic Chlorination

- Like bromination, chlorination at the allylic position of an alkene is achieved when low concentrations of  $\text{Cl}_2$  are present. The reaction is run at high temperatures to achieve the desired results.

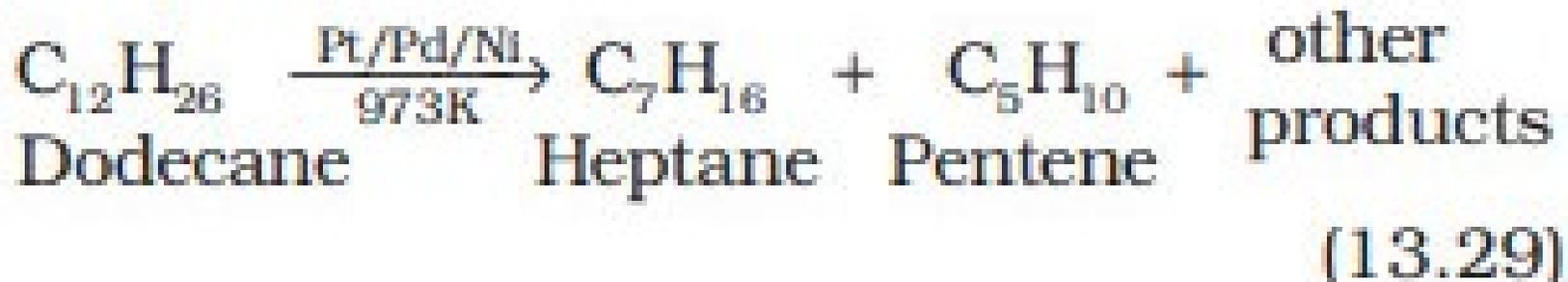
# Radical Stability

**Table 3.17. Thermochemical Stabilization Energies for Some Substituted Radicals (in kcal/mol)**

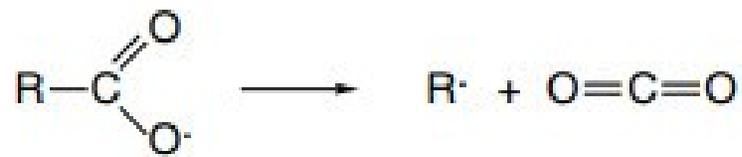
	RSE <sup>a</sup>		RSE <sup>a</sup>
CH <sub>3</sub> ·	-1.67	CH <sub>3</sub> (OH)CH·	2.15
CH <sub>3</sub> CH <sub>2</sub> ·	2.11	(NC)FCH·	-2.79
NCCH <sub>2</sub> ·	6.50	F <sub>2</sub> CH·	-4.11
NH <sub>2</sub> CH <sub>2</sub> ·	3.92	(CH <sub>3</sub> ) <sub>3</sub> C·	4.35
CH <sub>3</sub> NHCH <sub>2</sub> ·	12.18	CH <sub>3</sub> Ċ(CN) <sub>2</sub>	3.92
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> ·	14.72	CH <sub>3</sub> Ċ(OH) <sub>2</sub>	0.15
HOCH <sub>2</sub> ·	3.13	CH <sub>3</sub> Ċ(CN)(OH)	2.26
CH <sub>3</sub> OCH <sub>2</sub> ·	3.64	CF <sub>3</sub> ·	-4.17
FCH <sub>2</sub> ·	-1.89	CCl <sub>3</sub> ·	-13.79
(CH <sub>3</sub> ) <sub>2</sub> CH·	2.57	CH <sub>2</sub> =CH-CH <sub>2</sub> ·	13.28
(NC) <sub>2</sub> CH·	5.17	C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> ·	12.08
(HO) <sub>2</sub> CH·	-2.05	CH <sub>2</sub> =CH·	-6.16
		HC≡C·	-15.57
		C <sub>6</sub> H <sub>5</sub> ·	-10.27
		C <sub>5</sub> H <sub>5</sub> ·	19.24
		CH <sub>3</sub> C·	7.10
		O	

# Radical Pyrolysis

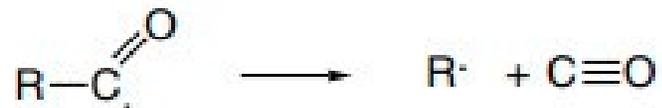
Pyrolysis of alkanes is believed to be a free radical reaction. Preparation of oil gas or petrol gas from kerosene oil or petrol involves the principle of pyrolysis. For example, dodecane, a constituent of kerosene oil on heating to 973K in the presence of platinum, palladium or nickel gives a mixture of heptane and pentene.



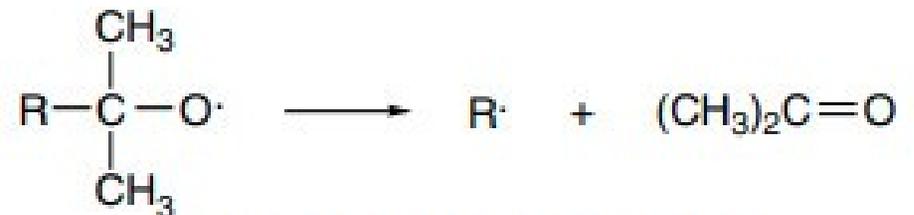
# Radical Fragmentation



decarboxylation

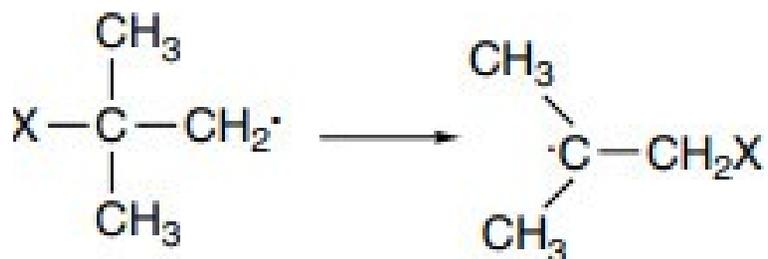


decarbonylation



$\beta$ -fragmentation of alkoxy radical

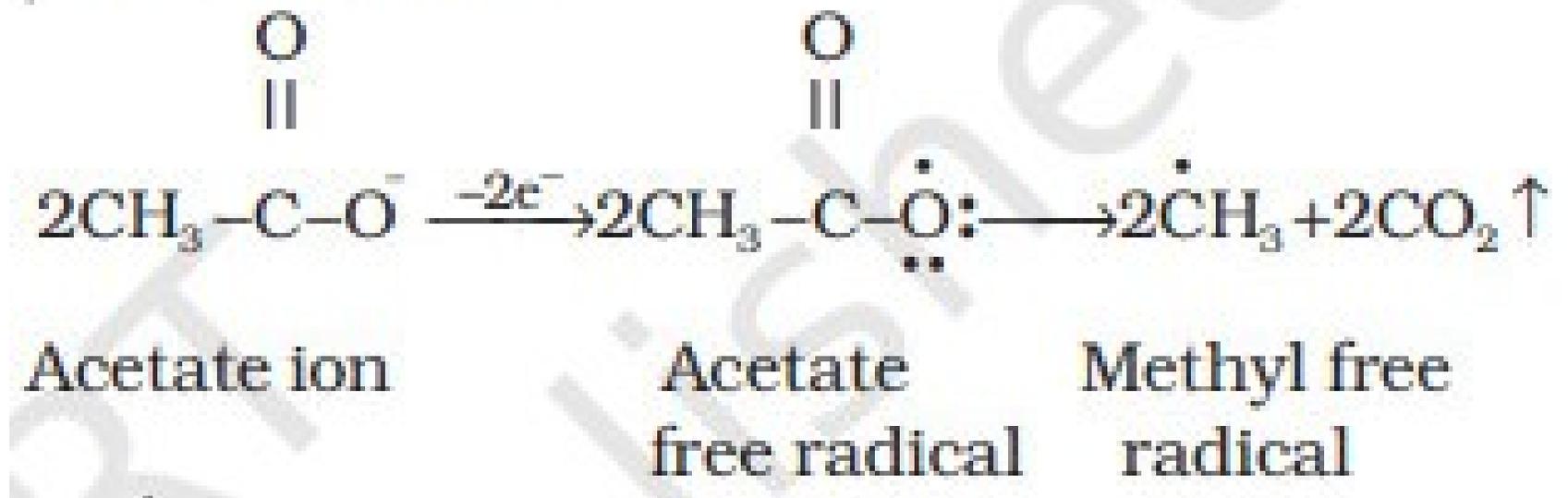
# Radical Rearrangement



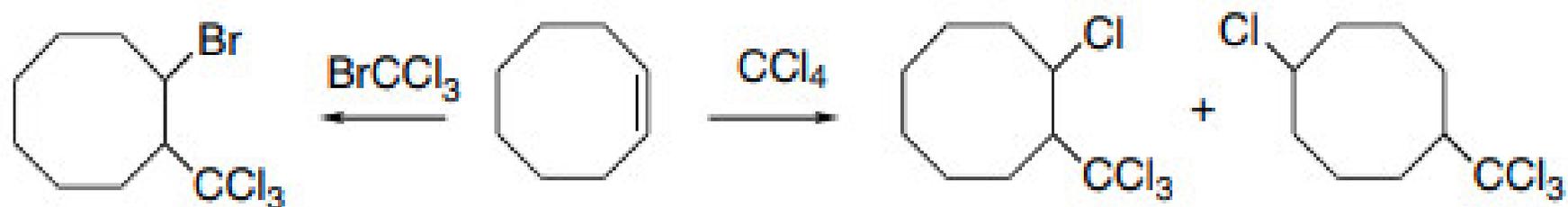
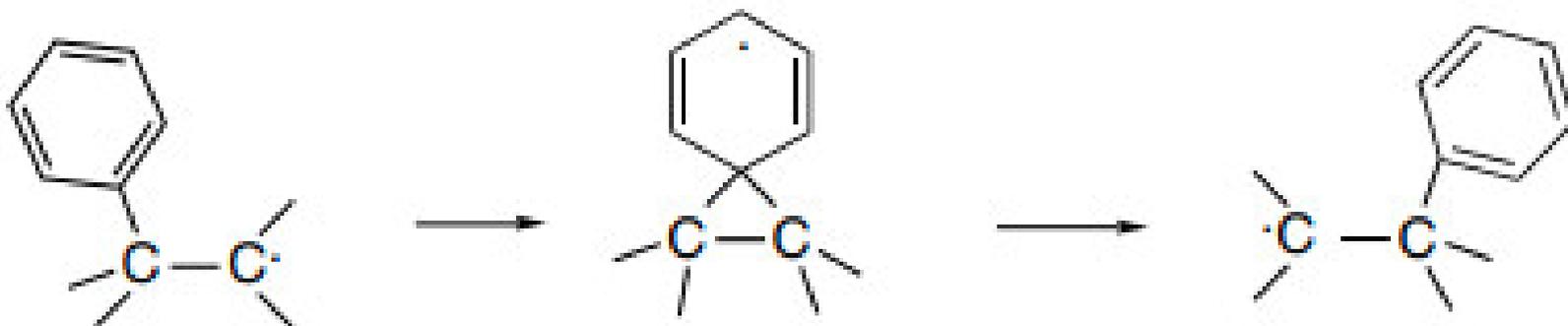
X	$k$ ( $\text{s}^{-1}$ )	$E_a$ (kcal/mol)
Ph	$7.6 \times 10^2$	11.8
$\text{CH}_2=\text{CH}$	$10^7$	5.7
$(\text{CH}_3)_3\text{CC}\equiv\text{C}$	9.3	12.8
$(\text{CH}_3)_3\text{CC}=\text{O}$	$1.5 \times 10^5$	7.8
$\text{N}\equiv\text{C}$	9.0	16.4

# Radical Rearrangement

ii) **At anode:**



# Radical Rearrangement



# Radical Dimerization

