

HALOGENATION

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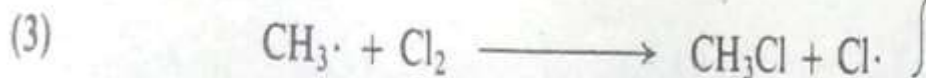
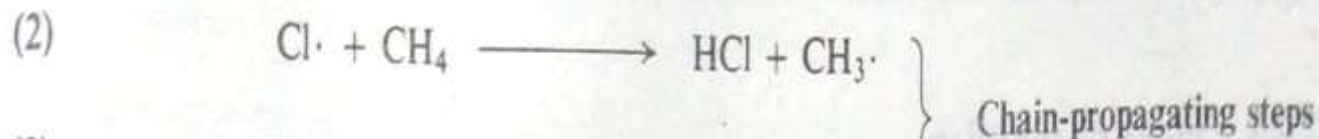
INTRODUCTION

- ▶ **DEFINITION-** Halogenation is defined as the process in which one or more halogen atoms are introduced in into an organic compound
- ▶ Halogen atom include F, Cl, Br etc

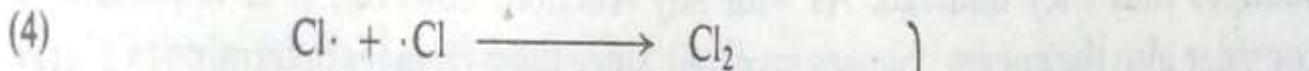
TYPES OF HALOGENATION

- ▶ Free radical halogenation
- ▶ Addition of halogen to alkenes and alkynes
- ▶ Halogenation of aromatic compounds
- ▶ Other Halogenation method
 - a) Fluorination
 - b) Chlorination
 - c) Bromination
 - d) Iodination

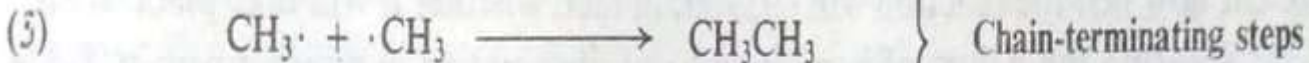
Free radical halogenation



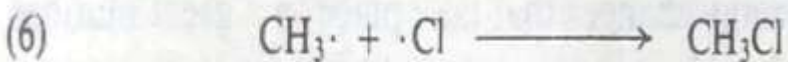
then (2), (3), (2), (3), etc., until finally:



or



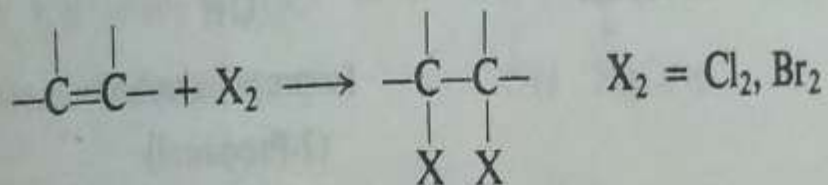
or



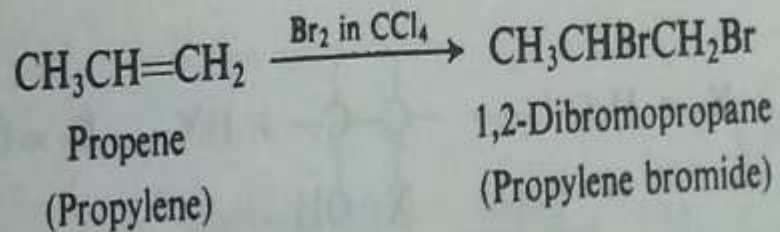
Addition of halogen to alkenes

(Propylene)

2. Addition of halogens. Discussed in Secs. 9.12-9.13 and 10.2-10.3.



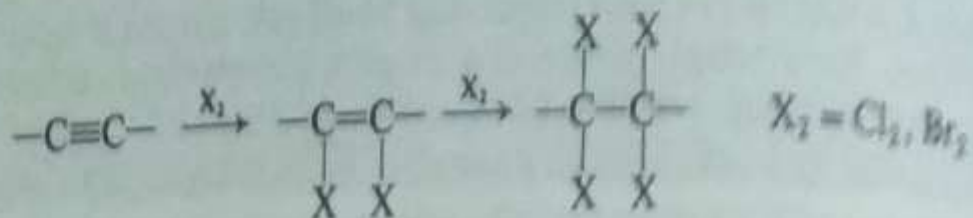
Example:



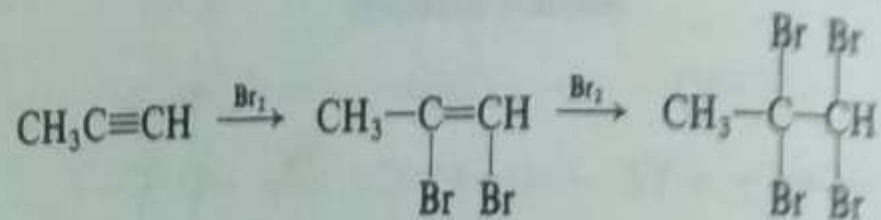
Addition of halogen to alkynes

CONTINUED

2. Addition of halogens. Discussed in Sec. 12.9.



Example:



Kinetics-1)Heats of reactions 2) Energy of activation
 3) Progress of reaction 4) Rates of reaction

fig: Relative reactivities of halogen towards methane.

		X =	F	Cl	Br	I
(1)	$X_2 \longrightarrow 2X\cdot$	$\Delta H =$	+38	+58	+46	+36
(2)	$X\cdot + CH_4 \longrightarrow HX + CH_3\cdot$		-32	+1	+16	+33
(3)	$CH_3\cdot + X_2 \longrightarrow CH_3X + X\cdot$		-70	-26	-24	-20

... disociation of molecules into atoms, we may

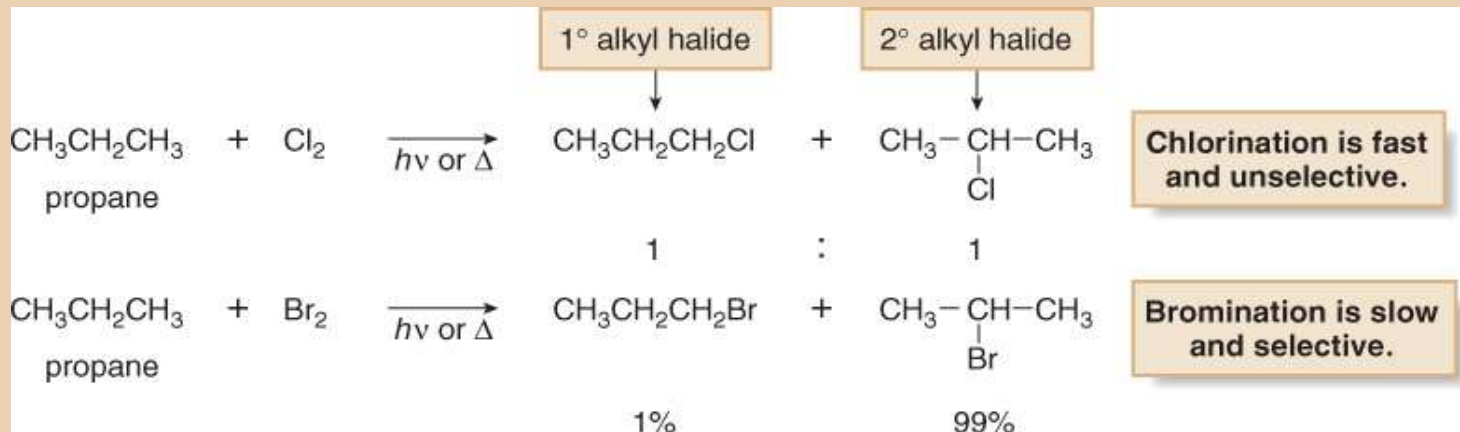
KINETICS OF HALOGENATION

Chlorination versus Bromination

• Although alkanes undergo radical substitutions with both Cl_2 and Br_2 , chlorination and bromination exhibit two important differences.

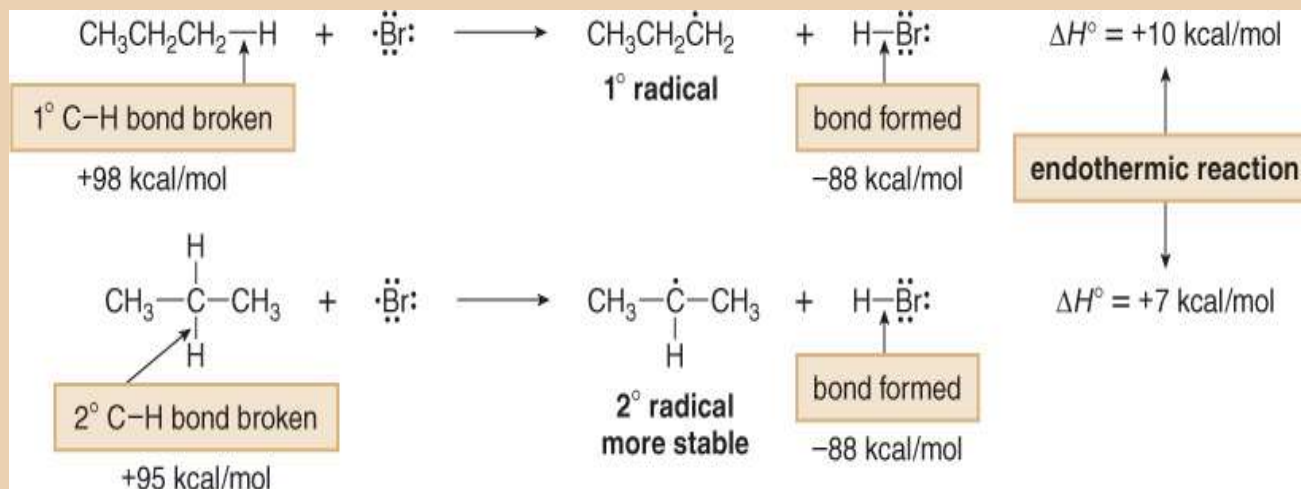
1. Chlorination is faster than bromination.

2. Chlorination is unselective, yielding a mixture of products, but bromination is often selective, yielding one major product.



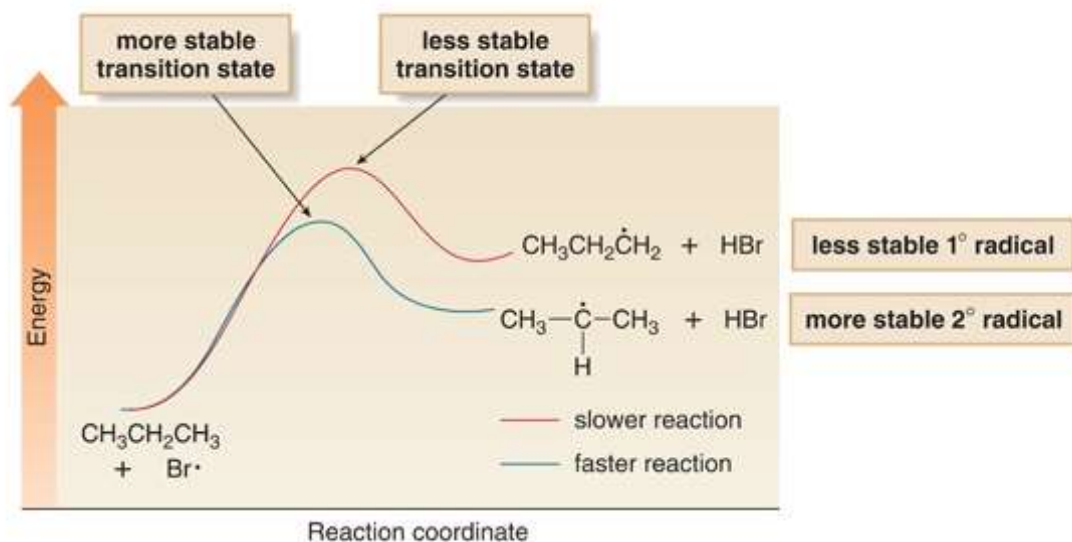
ENERGETICS OF THE BROMINATION RXN.

- The differences in chlorination and bromination can be explained by considering the energetics of each type of reaction.
- Calculating the ΔH^0 using bond dissociation energies reveals that abstraction of a 1^0 or 2^0 hydrogen by $\text{Br}\cdot$ is endothermic, but it takes less energy to form the more stable 2^0 radical.



TRANSITION STATE IN THE BROMINATION OF PROPANE

Figure 13.5 Energy diagram for the endothermic reaction: $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Br}^\bullet \rightarrow \text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}_2 + \text{HBr}$ or $(\text{CH}_3)_2\dot{\text{C}}\text{H} + \text{HBr}$

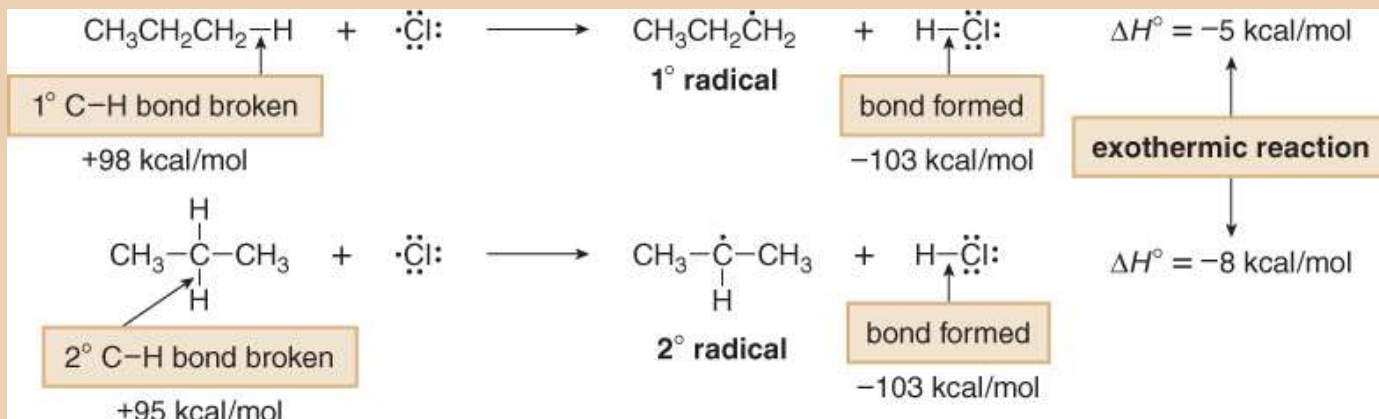


- The transition state to form the less stable 1° radical ($\text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}_2$) is higher in energy than the transition state to form the more stable 2° radical [$(\text{CH}_3)_2\dot{\text{C}}\text{H}$]. Thus, **the 2° radical is formed faster.**

Conclusion: Because the rate-determining step is endothermic, the more stable radical is formed faster, and often a single radical halogenation product predominates.

ENERGETICS OF THE CHLORINATION RXN.

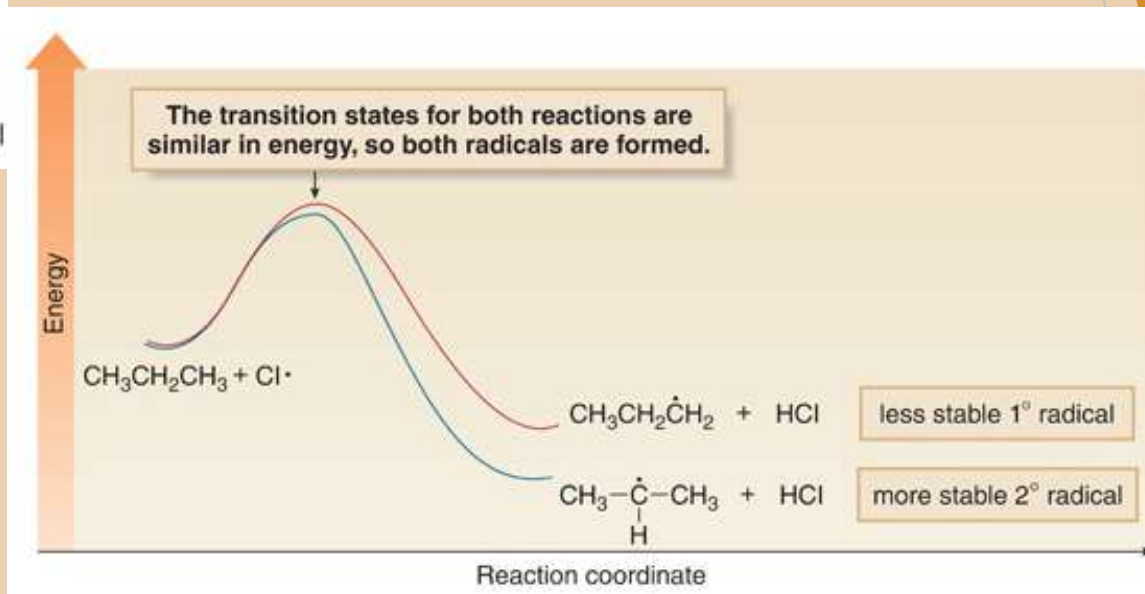
- Calculating the ΔH° using bond dissociation energies for chlorination reveals that abstraction of a 1° or 2° hydrogen by $\text{Cl}\cdot$ is exothermic.



- Since chlorination has an exothermic rate-determining step, the transition state to form both radicals resembles the same starting material, $\text{CH}_3\text{CH}_2\text{CH}_3$. Thus, the relative stability of the two radicals is much less important, and both radicals are formed.

TRANSITION STATE IN THE CHLORINATION OF

Figure 13.6 Energy diagram for the exothermic reaction: $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}^\bullet \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^\bullet$ or $(\text{CH}_3)_2\text{CH}^\bullet + \text{HCl}$

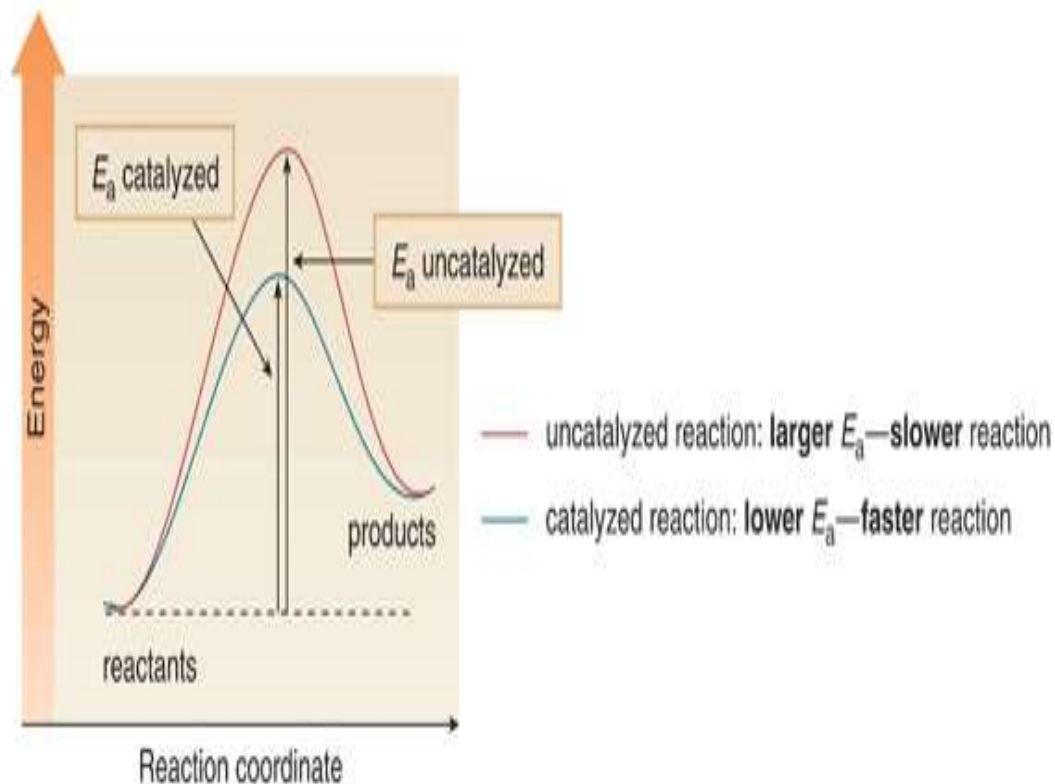


Conclusion: Because the rate-determining step in chlorination is exothermic, the transition state resembles the starting material, both radicals are formed, and a mixture of products results.

CATALYSTS

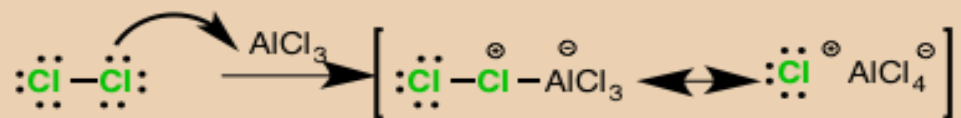
Figure 6.7 The effect of a catalyst on a reaction

- The catalyst lowers the energy of activation, thus **increasing the rate of the catalyzed reaction.**
- The energy of the reactants and products is the same in both the uncatalyzed and catalyzed reactions, so the **position of equilibrium is unaffected.**

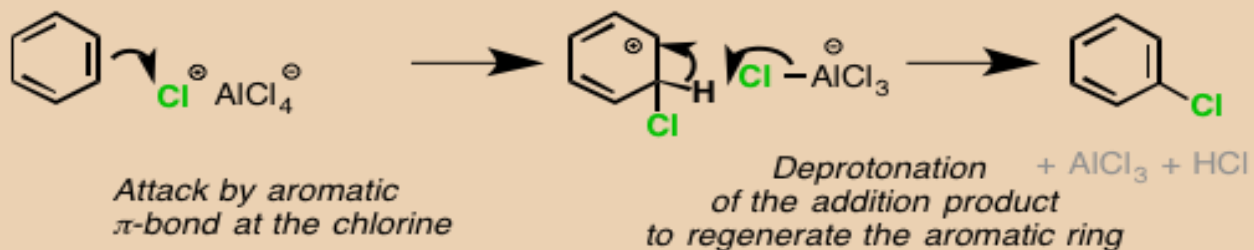


CATALYTIC HALOGENATION

How it works: Mechanism for activation of chlorine by AlCl_3



... and subsequent chlorination





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