台灣大學開放式課程

有機化學乙

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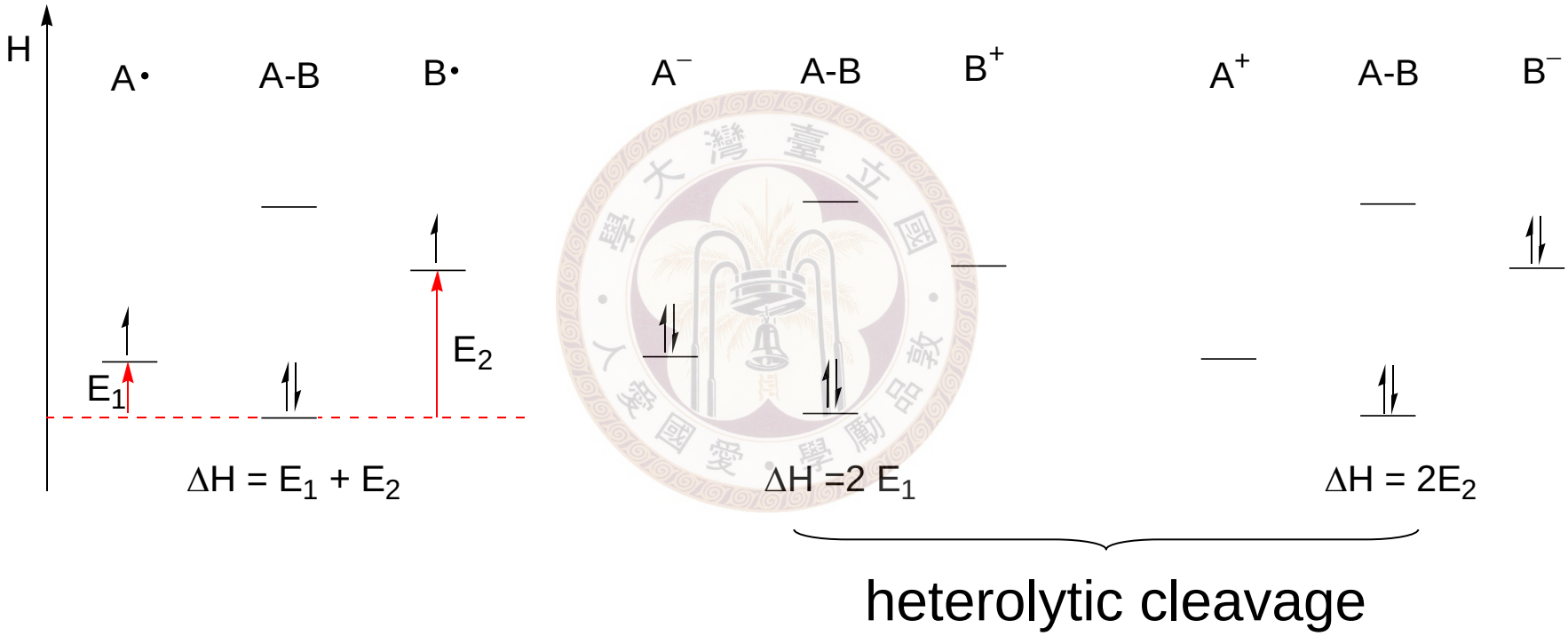
Chapter 10
Radical (自由基) reactions

※ Bond dissociation energy



$$A\text{–}B \rightarrow A\bullet + B\bullet \qquad \Delta H^o = DH^o$$

Homolytic bond cleavage

Bond energy

✓ The use of bond dissociation energy

$$H–H + Cl–Cl \rightarrow 2H–Cl$$

$DH^o = 436$ $DH^o = 243$ $DH^o = 432$ kJ/mol

assumed pathway:

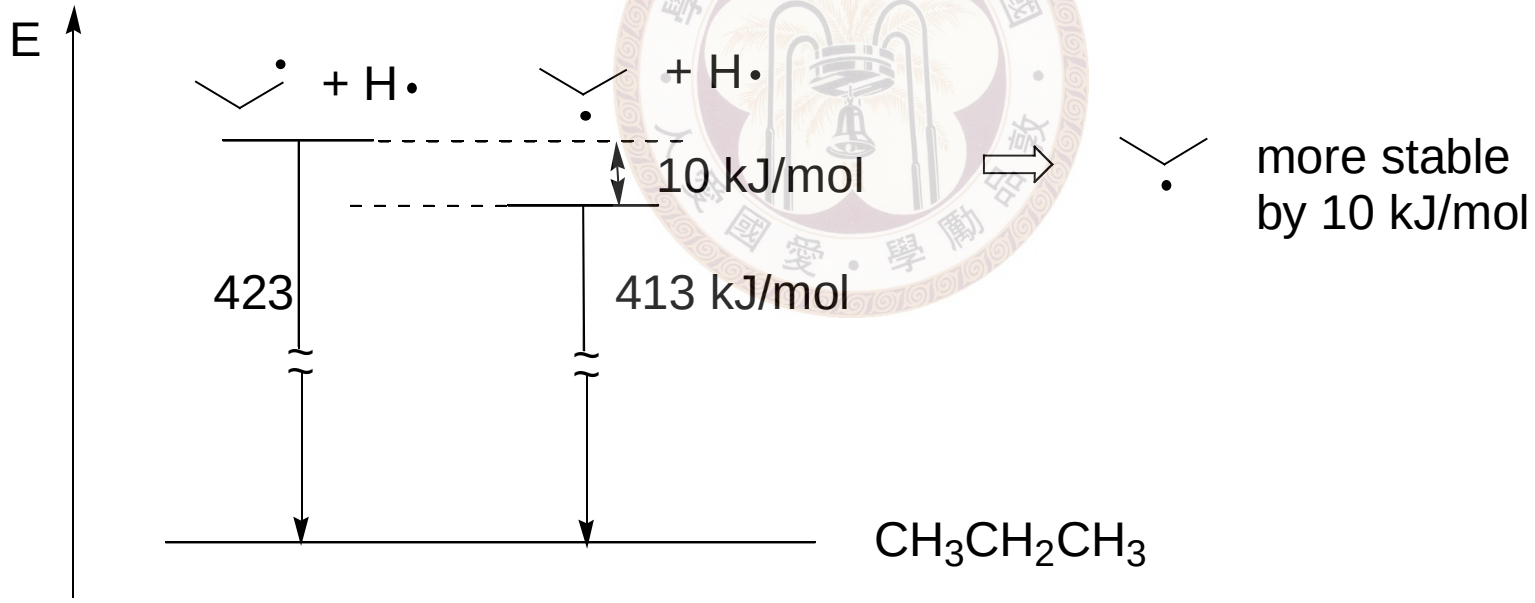
$$H–H \rightarrow H\bullet + H\bullet$$
$$Cl–Cl \rightarrow Cl\bullet + Cl\bullet$$
$$(H\bullet + Cl\bullet \rightarrow H–Cl) \times 2$$

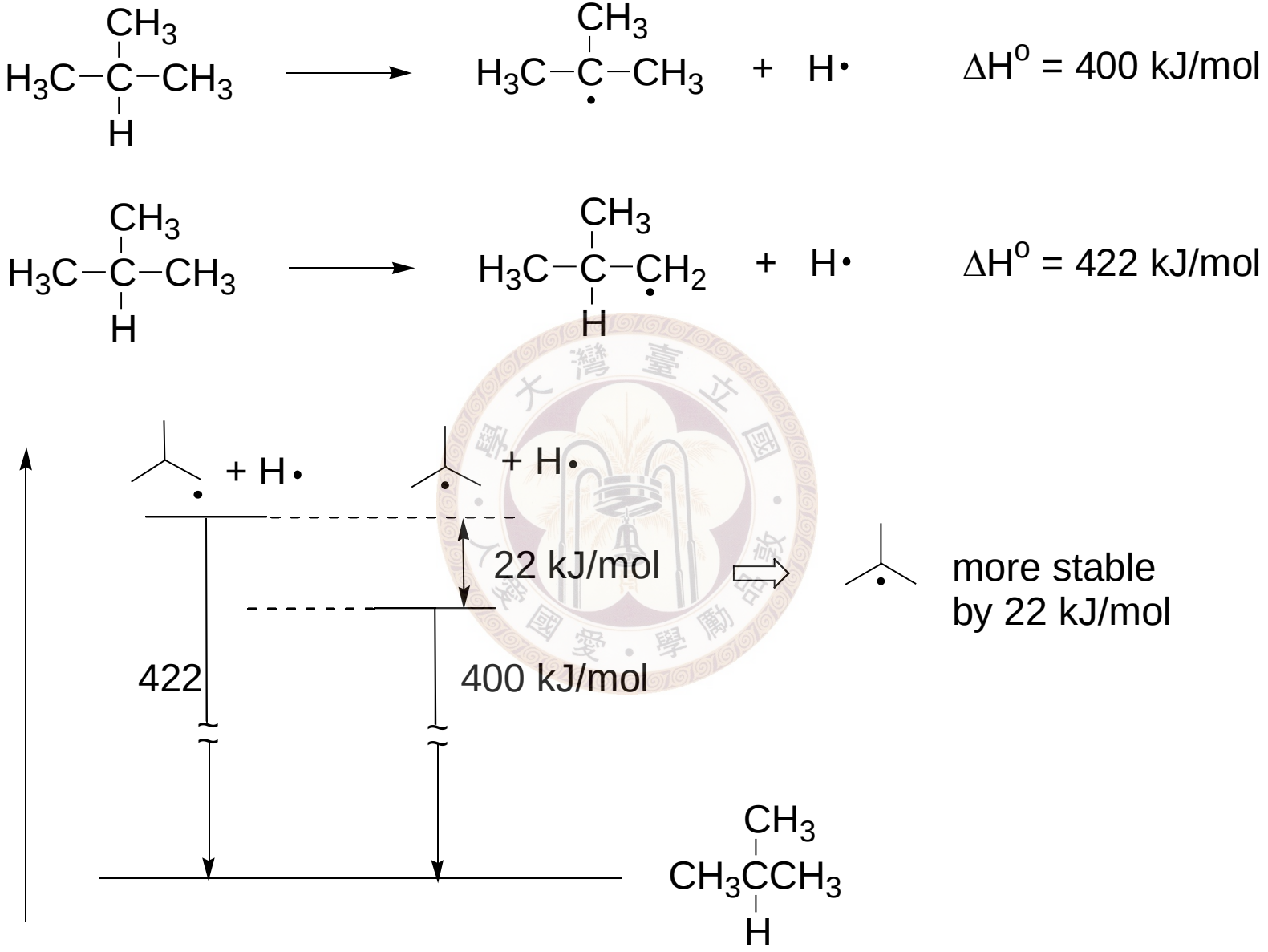
$$\Delta H^o = DH^o_{H\text{-}H} + DH^o_{Cl\text{-}Cl} - 2DH^o_{H\text{-}Cl}$$
$$= 436 + 243 - (432 \times 2) = -185 \text{ kJ/mol}$$

※ Radical stability

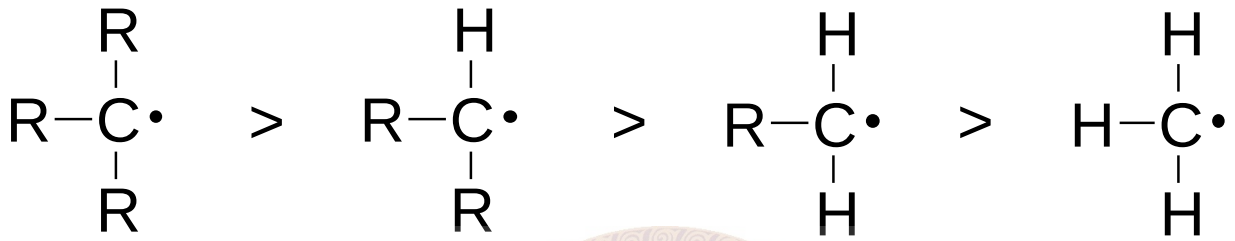
$CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2\bullet + H\bullet \quad \Delta H^o = 423$ kJ/mol

$CH_3CH_2CH_3 \rightarrow CH_3\overset{\bullet}{C}HCH_3 + H\bullet \quad \Delta H^o = 413$ kJ/mol




CH3
H3C–C–CH3
H
+ H•
ΔH° = 400 kJ/mol
CH2
ΔH° = 422 kJ/mol
E
22 kJ/mol
more stable
by 22 kJ/mol
422
400 kJ/mol

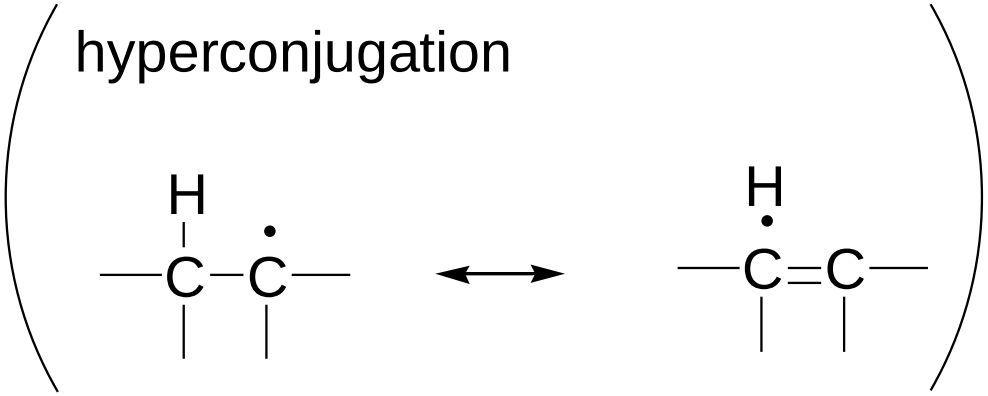
★ In general, overall stability:



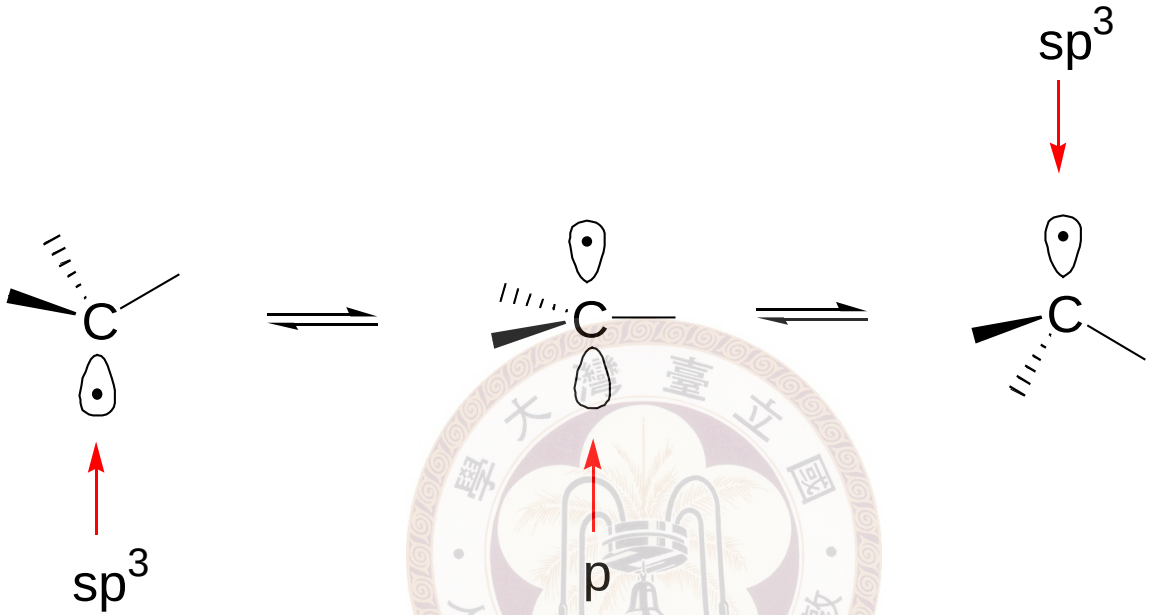
Reason (similar as carbocation):

electronically radical is electron deficient

alkyl group is considered as e^- donating group



◎ Structure of carbon radical



Low energy barrier
Interchange very quickly

※ Halogenation of alkanes

$$R\text{–}H + X_2 \xrightarrow[\text{or } h\nu]{\Delta} R\text{–}X + HX$$

a substitution reaction

X = F, Cl, Br but not I

✓ Chlorination of methane

$$CH_4 + Cl_2 \xrightarrow[\text{or } h\nu]{\Delta} CH_3Cl + HCl$$

chloromethane
(methyl chloride)

Polyhalogenation occurs:

$$CH_3Cl + Cl_2 \xrightarrow[\text{or } h\nu]{\Delta} CH_2Cl_2 + HCl$$

dichloromethane
(methylene chloride)

$$CH_2Cl_2 + Cl_2 \xrightarrow[\text{or } h\nu]{\Delta} CHCl_3 + HCl$$

trichloromethane
(chloroform)

$$CHCl_3 + Cl_2 \xrightarrow[\text{or } h\nu]{\Delta} CCl_4 + HCl$$

tetrachloromethane
(carbon tetrachloride)

Difficult to control to stop at certain stage

Except:

use large excess CH_4 → CH_3Cl major

use large excess Cl_2 → CCl_4 major

※ Mechanism of chlorination

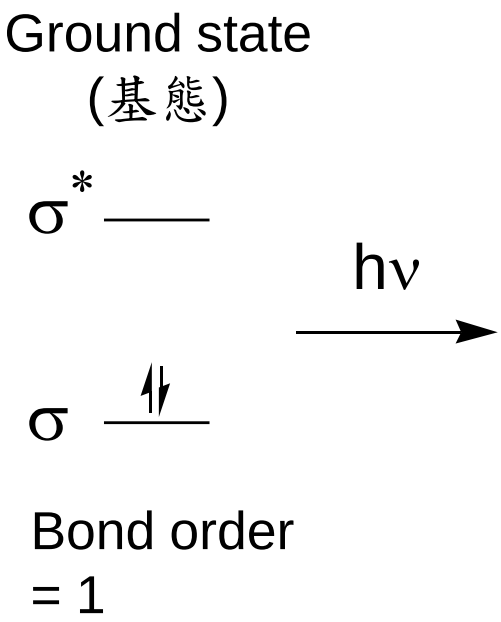
✓ Some observations:

- The reaction is promoted by heat or light
  If promoted by light, when light is turned off, reaction stops

- The light promoted process is highly efficient
  One photon → more than one product

✓ The mechanism:

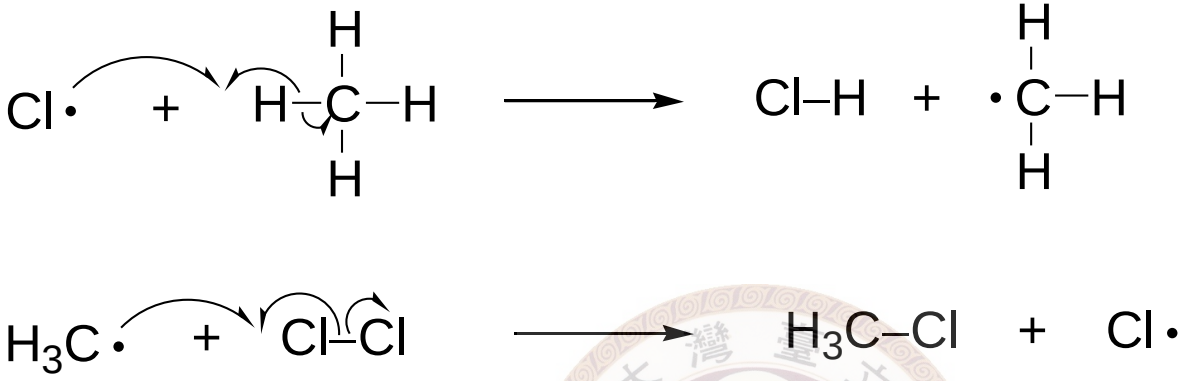
Step 1 $Cl_2 \xrightarrow[\text{or } \Delta]{h\nu} 2Cl\cdot$ an initiation step



*Some bond energy data (kJ/mol)

F-F	159	H_3C-F	461
Cl-Cl	243	H_3C-Cl	352
Br-Br	193	H_3C-Br	293
I-I	151	H_3C-I	240
HO-OH	214	H_3C-H	440
		H_3C-CH_3	378
		H_3C-OH	387

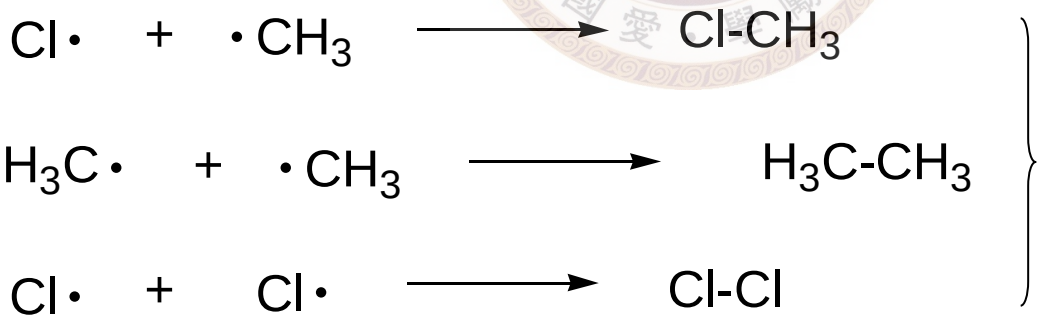
Step 2



chain propagating steps

*single-headed arrow for one electron flow

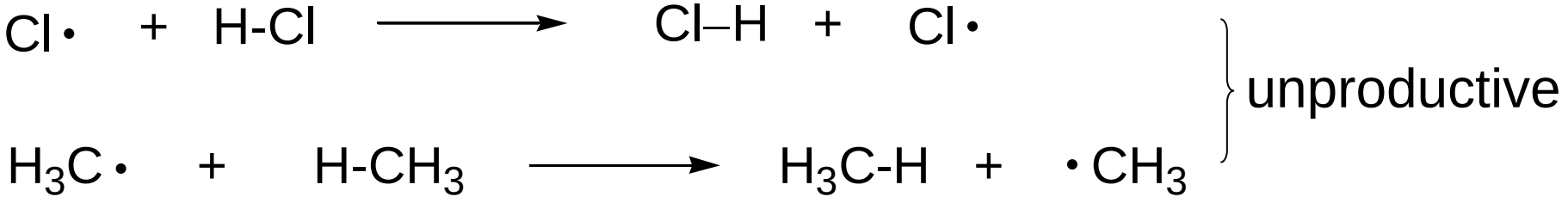
Termination steps:



radicals disappear
→ chain stops

⟹ initiation required constantly

Others:



Polyhalogenation:

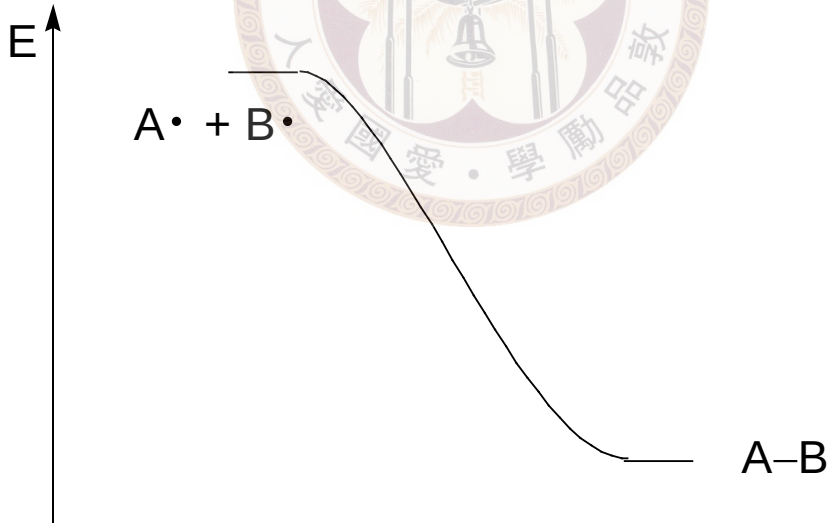
※ The energetics

◎ Chlorination

$Cl_2 \rightarrow 2Cl\cdot$ $\quad \Delta H^o = 243$ kJ/mol

$E_a = 243$ kJ/mol

*For radical combination, $E_a = 0$



$Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet$ $\Delta H^o = 8$ $E_a = 16$ kJ/mol

$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$ $\Delta H^o = -109$ $E_a = \sim 8$ kJ/mol

*For these elementary reactions:

based on Hammond-Leffler postulation, TS E resembles the SM for highly exohermic reaction

Overall: $\Delta H^o = -101$ kJ/mol for chlorination

◎ Fluorination

$F_2 \rightarrow 2F\bullet$ $\Delta H^o = 159$ $E_a = 159$ kJ/mol

$F\bullet + CH_4 \rightarrow HF + CH_3\bullet$ $\Delta H^o = -130$ $E_a = 5$ kJ/mol

$CH_3\bullet + F_2 \rightarrow CH_3F + F\bullet$ $\Delta H^o = -302$ $E_a = \sim 0$

Overall: $\Delta H^o = -432$ kJ/mol for fluorination (highly exothermic)

*Fluorination is vigorous, difficult to control
Usually performed in dilute condition
(for example, diluted with helium)

◎ Bromination

$Br_2 \rightarrow 2Br\bullet$ $\Delta H^o = 193$ $E_a = 193$ kJ/mol

$Br\bullet + CH_4 \rightarrow HBr + CH_3\bullet$ $\Delta H^o = 74$ $E_a = 78$ kJ/mol

$CH_3\bullet + Br_2 \rightarrow CH_3Br + Br\bullet$ $\Delta H^o = -100$ $E_a = \sim 0$

Overall: $\Delta H^o = -26$ kJ/mol for Bromination

*Bromination is less reactive

◎ Iodination

$I_2 \rightarrow 2I\cdot$ $\Delta H^o = 151$ $E_a = 151$ kJ/mol

$I\cdot + CH_4 \rightarrow HI + CH_3\cdot$ $\Delta H^o = 142$ $E_a = 140$ kJ/mol

$CH_3\cdot + I_2 \rightarrow CH_3I + I\cdot$ $\Delta H^o = -89$ $E_a = \sim 0$

Overall: $\Delta H^o = 53$ kJ/mol for Iodination

*Iodination is not feasible

very difficult step

Overall:

Initiation step is not a problem

The 2nd step of the chain rxn is easy

The 1st step of the chain rxn is critical

$F\bullet + CH_4 \rightarrow HF + CH_3\bullet$ $\Delta H^o = -130$ $E_a = 5$ kJ/mol

$Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet$ $\Delta H^o = 8$ $E_a = 16$ kJ/mol

$Br\bullet + CH_4 \rightarrow HBr + CH_3\bullet$ $\Delta H^o = 74$ $E_a = 78$ kJ/mol

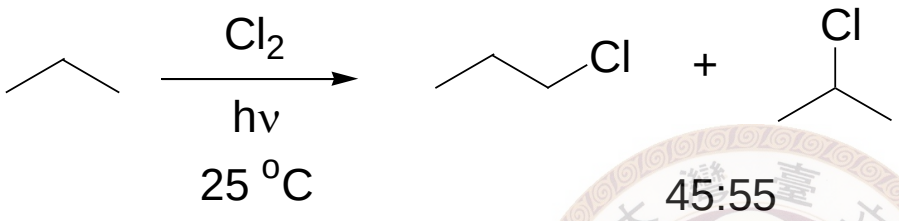
$I\bullet + CH_4 \rightarrow HI + CH_3\bullet$ $\Delta H^o = 142$ $E_a = 140$ kJ/mol

Reactivity trend:

$F_2 > Cl_2 > Br_2 > I_2$

※ Reactivity and radical stability

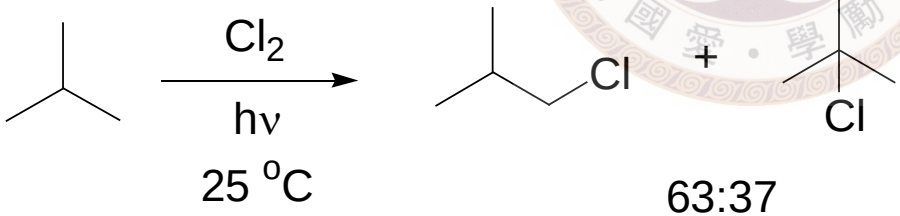
◎ Chlorination



45:55

per H $\frac{45}{6} : \frac{55}{2} = 1:3.7$

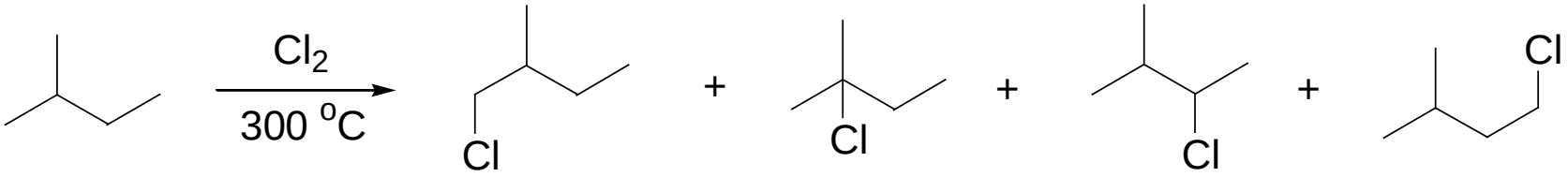
(1^o) (2^o)



63:37

per H $\frac{63}{9} : \frac{37}{1} = 1:5.3$

(1^o) (3^o)

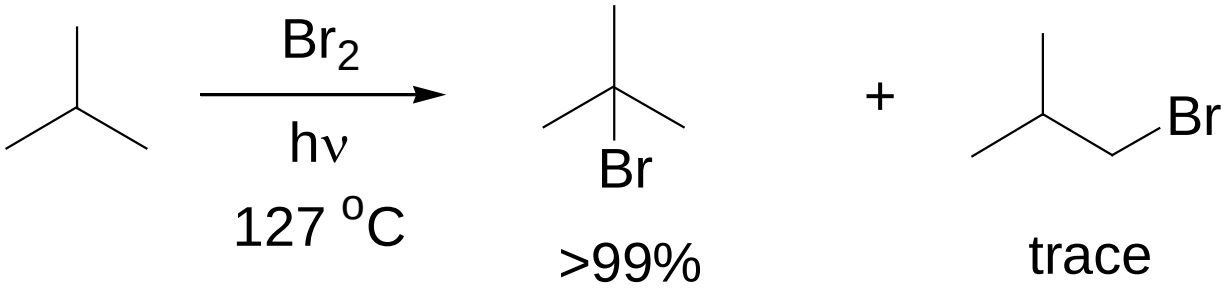


		30	:	22	:	33	:	15
per H		$\frac{30}{6}$	:	$\frac{22}{1}$	:	$\frac{33}{2}$	:	$\frac{15}{3}$
	=	5	:	22	:	16.5	:	5
	=	1	:	4.5	:	3.3	:	1

Reactivity: $3^o > 2^o > 1^o$

Parallels radical stability

◎ Bromination



The selectivity of bromination is better

Reasons:

Hydrogen abstraction by Br• is more endothermic than Cl•

According to Hammond-Leffler postulation

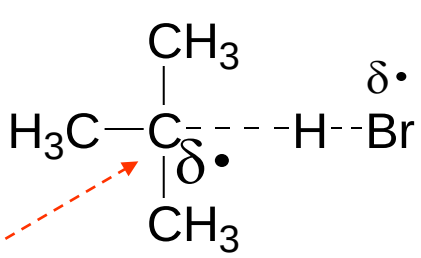
→ the TS has more product character

→ TS has more radical character

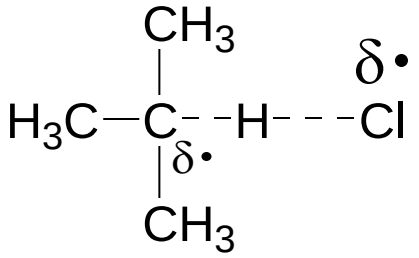
→ more stabilized radical, lower TS E

→ faster reaction

TS:

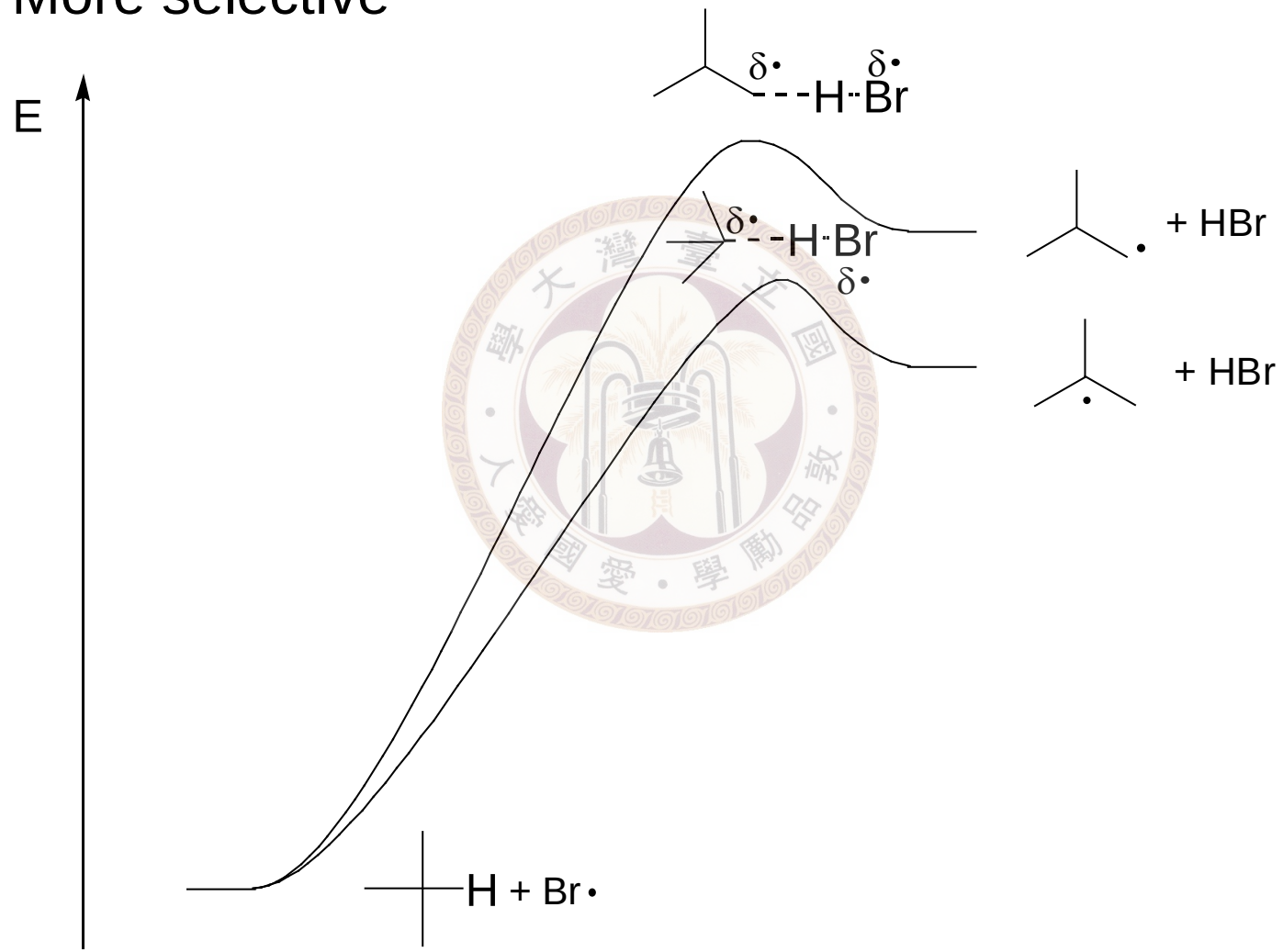


more radical character

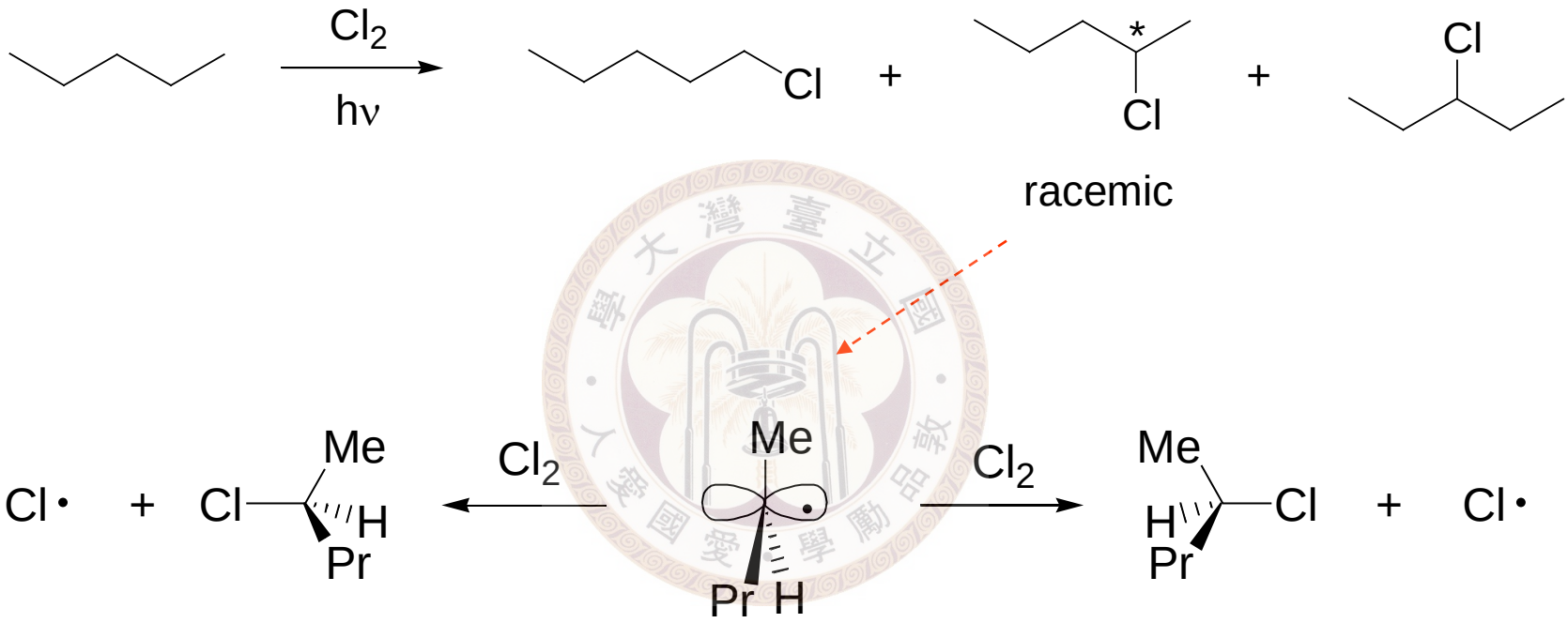


The energy difference between transition states is larger for bromination

→ More selective

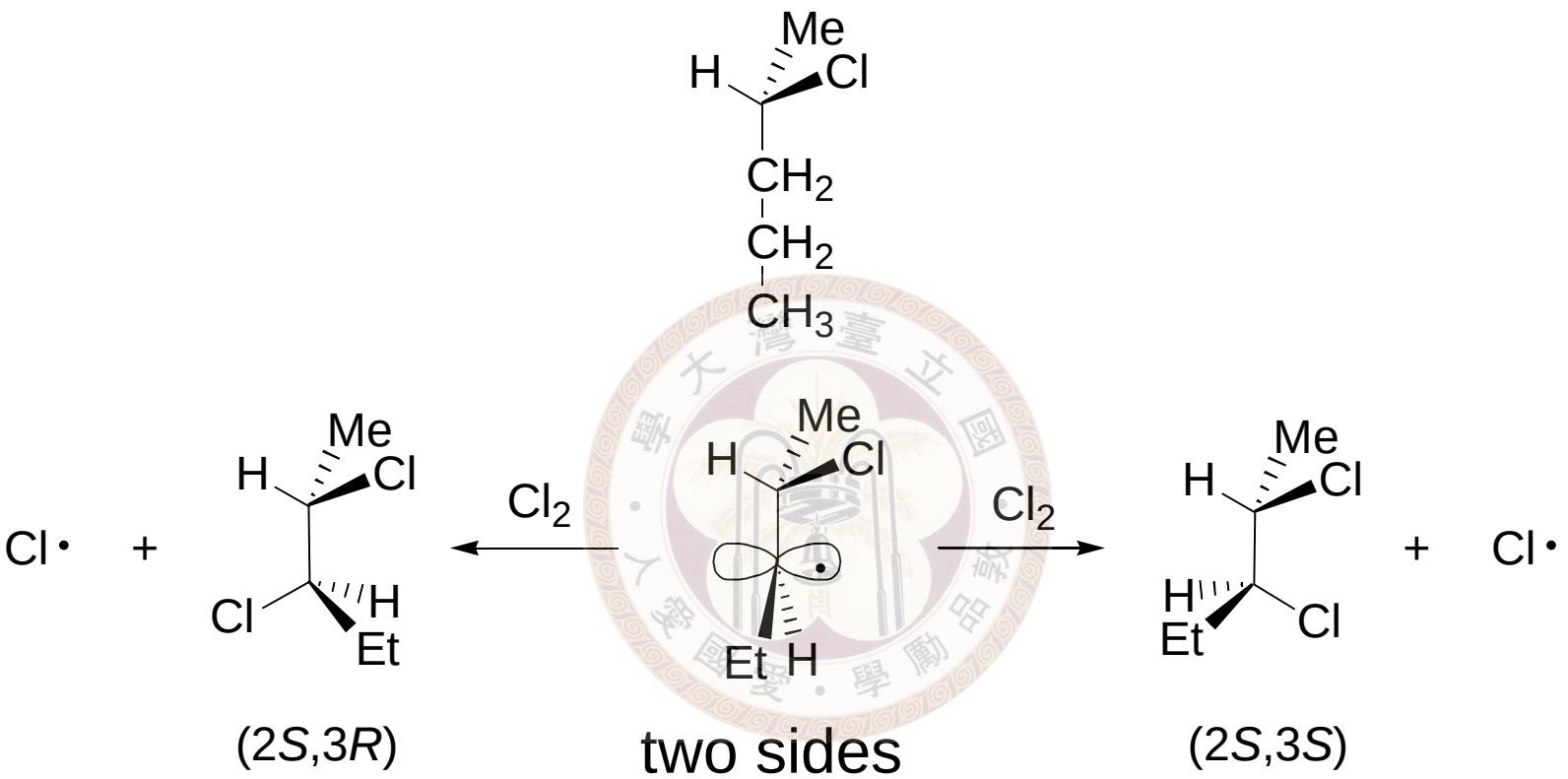


※ Stereochemistry



equal rate from both sides

✓ With existing chiral center



*Diastereoselectivity: in favor of one pair of diastereomers

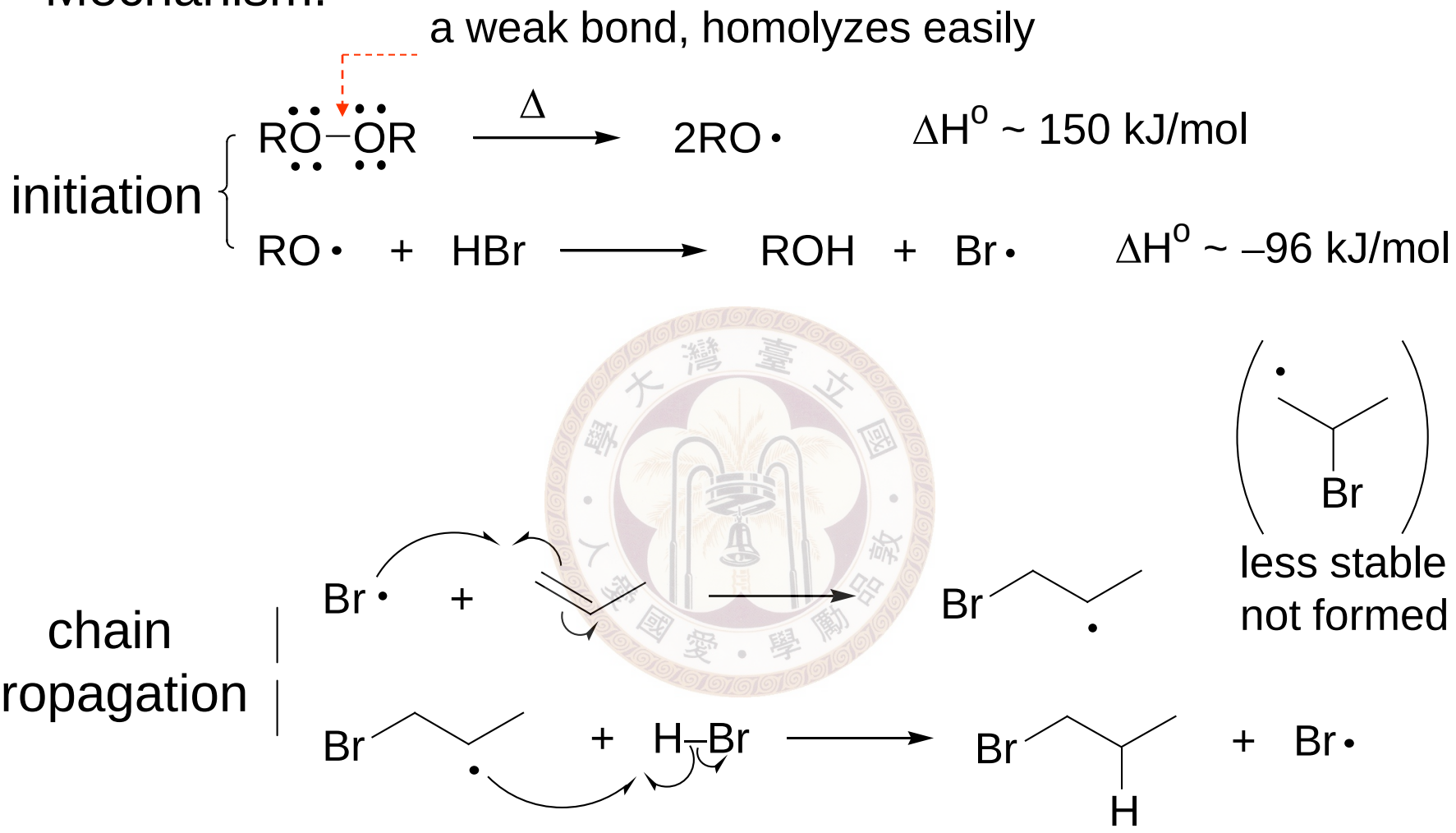
※ Anti-Markovnikov addition of HBr

a peroxide

anti-Markovnikov addition product

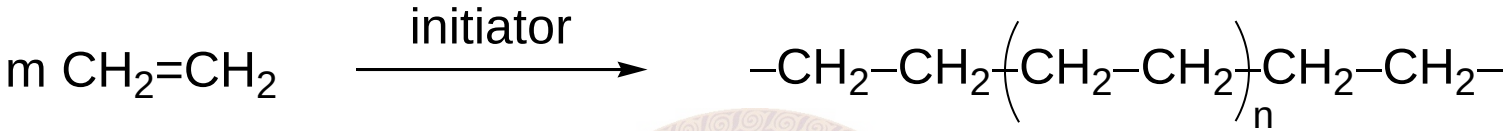
This is the result of radical addition

Mechanism:


a weak bond, homolyzes easily
initiation
RO–OR
Δ
2RO•
ΔH° ~ 150 kJ/mol
RO• + HBr
ROH + Br•
ΔH° ~ –96 kJ/mol
chain propagation
Br• +
Br
Br
less stable
not formed
Br
+ H–Br
Br
H
+ Br•

※ Radical polymerization of alkenes

Chain-growth polymers



ethylene monomer

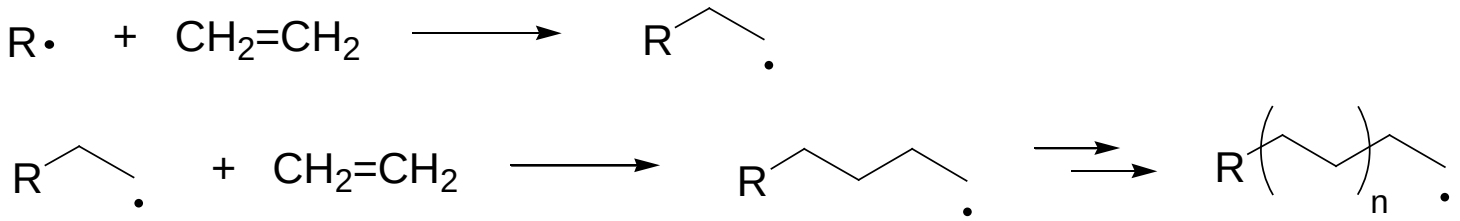
polyethylene polymer

Initiation:

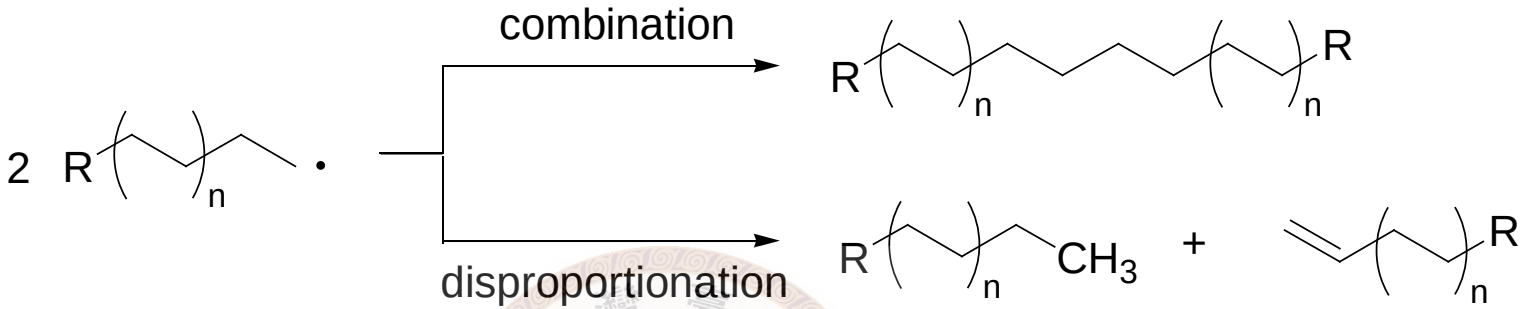
diacyl peroxide

higher conc. of initiator
→ initiates more chain
→ shorter polymer

Chain propagation:

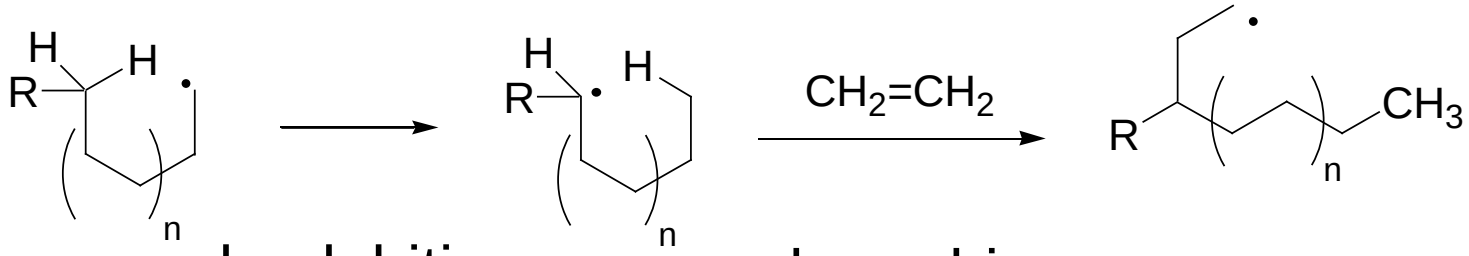


Chain termination



Branching

extends



back biting

branching occurs

※ More about chain-growth polymers

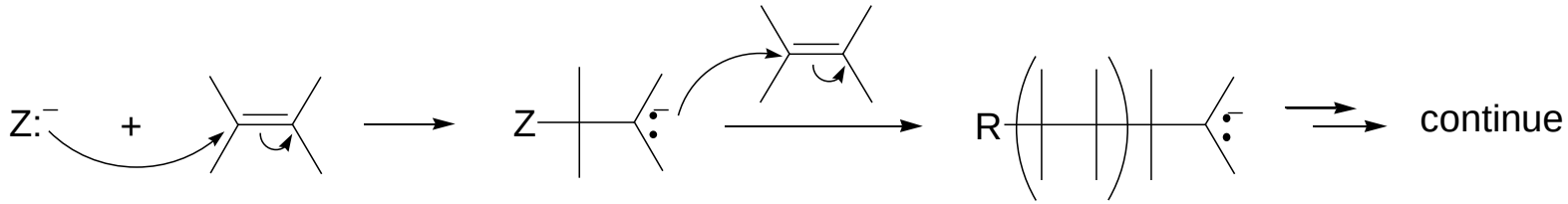
Chain-growth polymers: also called additon polymers

Three types:

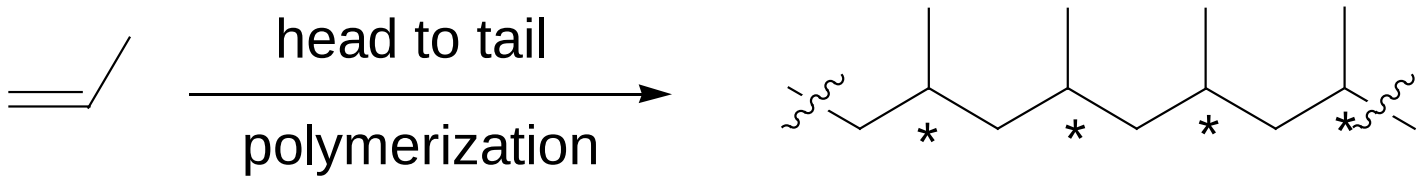
Radical polymerization

Cationic polymerization

Anionic polymerization



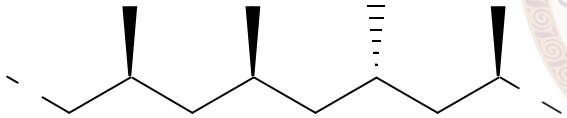
※ Stereochemistry of polymers



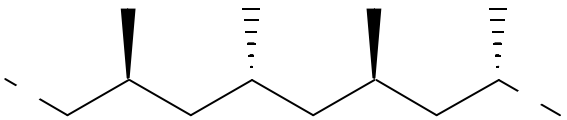
Polypropylene (PP)

Three types of stereochemistry:

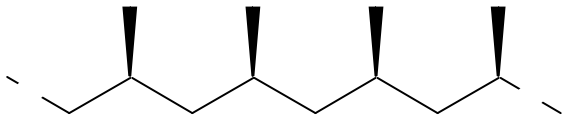
With carbon chain arranged in zig-zag form



atactic: random arrangement of the substituents (雜排)



syndiotactic: substituents arranged regularly on alternative side (間排)

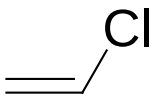


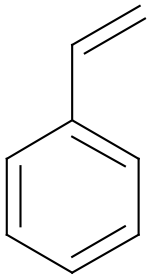
isotactic : substituents arranged on the same side (同排)

*Tacticity effects physical properties of polymers

◎ Some important polymers

$CH_2=CH_2$ → polyethylene (PE)

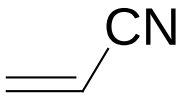
 → poly(vinyl chloride) (PVC)

 → polystyrene

$CF_2=CF_2$ → poly(tetrafluroethylene) (Teflon)

high mp, very inert

low coefficient of friction

 → polyacrylonitrile (Orlon)

※ Combustion of alkanes

Mechanism:

$RH + O_2 \rightarrow R\bullet + H\text{-}O\text{-}O\bullet$ initiation

$R\bullet + O_2 \rightarrow R\text{-}O\text{-}O\bullet$

$R\text{-}O\text{-}O\bullet + RH \rightarrow R\text{-}O\text{-}O\text{-}H + R\bullet$ } chain propagation

a hydroperoxide

$R\text{-}O\text{-}O\text{-}H \rightarrow RO\bullet + \bullet OH$

BE ~ 200 kJ/mol

initiate two more chains
→ grows like a tree
→ explosive

$RO\bullet$ / $HO\bullet$ $+ RH \rightarrow$ ROH / H_2O $+ R\bullet$

※ Reactive oxygen species (ROS): unwanted health risks

Fenton reaction

$$H_2O_2 + Fe^{2+} \rightarrow HO\bullet + HO^- + Fe^{3+}$$
$$H_2O_2 + Fe^{3+} \rightarrow HOO\bullet + H^+ + Fe^{2+}$$

$$O_2 + e^- \rightarrow O_2^-$$

superoxide

Protection mechanism in biological system:

$$2\ O_2^- + 2\ H^+ \xrightarrow{\text{superoxide dismutase}} H_2O_2 + O_2$$

$$2\ H_2O_2 \xrightarrow{\text{catalase}} 2\ H_2O + O_2$$