Chapter 2

Hydrocarbon (from C & H)
- Aliphatic ; alkane, alkene, alkyne, cyclic
- Aromatic

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the simplest ; CH_4 ⇒ relatively inert

- structure :p40
- nonpolar
- low m.p.&b.p. (van der Waals force)
- density:0.4
- solublility
  - slightly soluble in H_2O
  - very soluble in organic liq.

heat of combustion : 213kcal NH_3 alcohol

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fuel , H_2 , CO & H_2 ⇐ oxidation

acetylene

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halogenation

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HCl + CCl_4 ← HCl + $CHCl_3$ ← HCl + CH_2Cl_2 ← HCl + CH_3Cl ← ($h\nu$ or Δ) $CH_4 + Cl_2$

(substitution)

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can be the major product with a large excess of CH_4

$$CH_4 + Br_2 \xrightarrow[\text{or } \Delta]{h\nu} CH_3Br \rightarrow CH_2Br_2 \rightarrow CHBr_3 \rightarrow CBr_4$$

reactivity for halogenation $F_2 > Cl_2 > Br_2 > I_2$

Rxn mechanism ; the detailed step-by-step decription of a chemical rxn
- difficult to prove
- explain many results, offer good predictions and have consistency ⇒ well established

From rxn mechamisms ⇒ easily understand the complicated rxns.
- improve the yield.
- change the rxn courses ro get the desired products.

For halogenation, the mechanism should expain

1) no rxn in the dark at RT
2) rxn over 250°C or under UV at RT
3) λ to induce chlorination = λ to dissociate Cl_2
4) O_2 slows down the rxn
5) one photon produces many CH_3Cl molecules

$Cl_2 \longrightarrow 2\,Cl\cdot$ initiation ⇒ require energy ⇓ supplied by heat or hν

$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot$

$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$

propagation ⟹ chain rxn

$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6$

$Cl\cdot + Cl\cdot \longrightarrow Cl_2$

$Cl\cdot + CH_3\cdot \longrightarrow CH_3Cl$

termination

free radical ; unpaired odd electron, very reactive

$CH_3\cdot + O_2 \longrightarrow CH_3{-}O{-}O\cdot$; slow down or stop the rxn ⇓ inhibitor , inhibition period

exothermic rxn ; readily occur

endothermic rxn ; not readily occur

$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl \quad \Delta H = -25kcal$ ⇒ occur only at a high temp. ⇓ due to the cleavage of Cl_2

$Cl_2 \longrightarrow 2\,Cl\cdot \quad \Delta H = +58$

$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot \quad \Delta H = +1$

$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot \quad \Delta H = -26$

$Cl\bullet + CH_3{-}H \longrightarrow H{-}Cl + CH_3\bullet \quad \Delta H = +1$

(104) (103) $E_a = 4$

⇓

proper orientation ⇐ activation energy ⇐ a collision must provide a minimum amount of energy for an effective rxn

$Br\bullet + CH_3{-}H \longrightarrow H{-}Br + CH_3\bullet \quad \Delta H = +16$

(104) (88) $E_a = 18$

Fig 2.3 , 2.4 & 2.5

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(no bond-breaking or bond-forming)

chemical rxn ⇒ collisions of sufficient energy and proper orientation

rate = collision frequency × energy factor × probability factor (orientation factor)

⇓ ⇓ ⇓

size and weight are not important ⇐ concn or P, size, speed (weight & T) ; T (controllable), E_a ; not vary widely for closely related rxns.

Fig 2.7 ⇒ $E_a\uparrow$ the fraction of effective collcsions ↓

$rate = PZe^{-E_a/RT}$

at 275°C	E_a	5	10	15	⇒ to increase a rxn rate: T↑ E_a↓ concn↑
	rate	10000	100	1	
250°C ⟶ 300°C	rate	1.5	2	3	

$E_a\uparrow$ the effect of $\Delta T\uparrow$

$Cl\bullet + CH_3{-}H \longrightarrow H{-}Cl + CH_3\bullet$ $\Delta H = +1$, $E_a = 4$

$Br\bullet + CH_3{-}H \longrightarrow H{-}Br + CH_3\bullet$ $\Delta H = +16$, $E_a = 18$

different relative rate. why?

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similar collision frequency probability factor

defferent energy factor

the order of reactivity

$F_2 > Cl_2 > Br_2 > I_2$

$X_2 \longrightarrow 2\,X\bullet$

$X\bullet + CH_4 \longrightarrow HX + CH_3\bullet$

$CH_3\bullet + X_2 \longrightarrow CH_3X + X\bullet$

X	F	Cl	Br	I
ΔH	38	58	46	36
	-32	1	16	33
	-70	-26	-24	-20

⇒ explained by this step

⇓

chain length

F Cl Br I ⟶ shorter

↓

longer chain more chain

alternative mechnism

$Cl\bullet + CH_4 \longrightarrow CH_3Cl + H\bullet$ $\Delta H = 20$, $E_a > 20$ ⇒ can not compete

$H\bullet + Cl_2 \longrightarrow HCl + Cl\bullet$

$CH_3\bullet$; C—H ⇒ $sp^2 \sim sp^3$

C ⇒ $p \sim sp^3$

continuous process

a chemical rxn ⇒ reactants ⟶ products

intermediate structure

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transition state
(the top of the energy hill)

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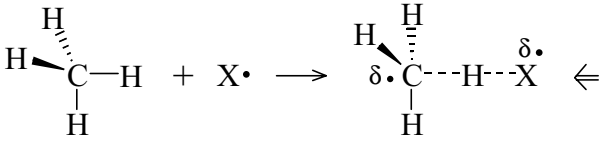
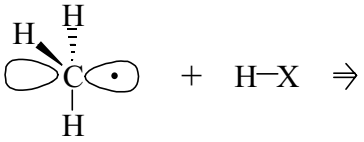


(reactant) (transition state)

⇐ any factor to stabilize the transition state relative to the reactants lowers E_a



(product)

How much does the trasition state resemble the products?

How far have bond-breaking and bond-forming gone?

How flat is the methyl group?

How much does the methy group carry the odd electron?

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difference in structure

late transtion state ⟵ E_a ↑ reactant-like ↓

early transition state ⟵ E_a ↓ reactant-like ↑

⇐ difference in electronic distribution

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difference in energy

ex) $Cl\cdot + CH_4$ $\quad E_a = 4$

$Br\cdot + CH_4$ $\quad 18$

⇓

highly reactive reagents ; early transition state, reactant-like trasition state

poorly reactive reagents ; late transition stae, product-like trasition state

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Molecular formula ⇒ (qualitative elementary analysis / quantitative elementary analysis / molecular weight determination) Fig 2.12

400 ~ 750 nm visible IR

UV 250 nm 300 nm

absorbed by N_2 & O_2 absorbed by O_3

⇒ $O_2 + h\nu \longrightarrow O\cdot + O\cdot$ initiation

$O\cdot + O_2 + M \longrightarrow O_3 + M^*$

$O_3 + h\nu \longrightarrow O_2 + O\cdot$ propagation

($M = O_2$, N_2)

$O\cdot + O\cdot + M \longrightarrow O_2 + M^*$

$O\cdot + O_3 \longrightarrow O_2 + O_2$ termination

CFC : CF_3Cl, $CFCl_2$ etc

$CF_3Cl + h\nu \longrightarrow F_3C\cdot + Cl\cdot$

$Cl\cdot + O_3 \longrightarrow ClO + O_2$

$ClO + O\cdot \longrightarrow Cl\cdot + O_2$

break the ozone-producing chain