Chapter 11. Petrochemicals from n-Paraffins

○ Paraffin hydrocarbon (Alkanes)

- Chemical reactivity 의 감소로 인하여 용도가 그리 다양하지 않음.

(i) Acetic acid (ii) Maleic anhydride

(iii) Acetaldehyde 등 생산

○ 분자량이 낮은 hydrocarbon 의 중요한 용도 중에 하나는 Olefins 을 생산하는 것이다.

○ The lower molecular weigh n-paraffins = C_1~C_7

○ The higher molecular weight n-paraffins = C_8~C_{30}

○ 주된 용도 (syn gas 생산)

(a) $CH_4 + H_2O \rightarrow CO + 3\ H_2$

(steam reforming)

(b) $2\ CH_4 + O_2 \rightarrow 2\ CO + 4\ H_2$

(oxidation)

(1) Ethane

$C_2H_6 \rightarrow C_2H_4$

- pyrolysis cracking (750~850℃)

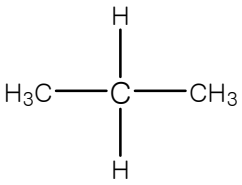
- 약 80% 의 Ethylene 을 이 방법으로 얻음 (see p.74)

(i) Vinyl chloride 생산

$$CH_2{=}CH_2 + Cl_2 \xrightarrow{\text{chlorination}} ClCH_2\text{-}CH_2Cl$$

$$ClCH_2CH_2Cl \xrightarrow{\text{pyrolysis}} CH_2{=}CHCl + HCl$$

(2) Propane : C_3H_8



(i) Nitropropanes :

- By Nitration

$$CH_3\text{-}CH_2\text{-}CH_3 \xrightarrow{HNO_3} \begin{cases} CH_3\text{-}CH_2\text{-}CH_2NO_2 & 55\sim65\ wt\% \\ CH_3\text{-}CHNO_2\text{-}CH_3 & \\ CH_3CH_2NO_2 & 20\sim25\ \% \\ CH_3NO_2 & 10\sim30\% \end{cases}$$

(용도)

Nitropropane - good solvent

Nitromethane - racing car 연료의 첨가제

(ii) Petrochloroethylene

$$CH_3\text{-}CH_2\text{-}CH_3 + 8\ Cl_2 \rightarrow CCl_2{=}CCl_2 + CCl_4 + 8HCl$$

(T=480~640℃)

(iii) Oxidation

- 촉매산화반응

$CH_3-CH_2-CH_3 + NH_3 + 2\,O_2 \rightarrow CH_2=CH-CN + 4H_2O$

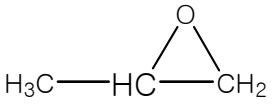
acrylonitrile

(T=500℃, 촉매 : Antimony-Uranium(5:1) + CH_3Br)

- 비촉매 산화 반응

propane을 산화반응으로 부터

propylene oxide 생산



(3) n-Butane (C_4H_{10})

- Natural gas로부터 얻어짐.
- Ethylene 생산에 이용 (minor source compare to ethane)
- Gasoline의 vapor pressure를 control 하는데 사용
- Butadiene 생산에 일어서 main feed stock임
- Propane 보다 더 활성적임.

(i) Acetic Acid

- the most important carboxylic acid
- 3가지 방법으로 acetic acid 생산

(a) carbonylation of methanol

$CH_3OH + CO \rightarrow CH_3COOH$

(b) the oxidation of acetaldehyde

$2\ CH_3CHO + O_2 \rightarrow 2\ CH_3COOH$

(c) the catalytic liquid phase oxidation (LPO) of n-butane

(the most important process)

$$C_4H_{10} \xrightarrow{O_2} CH_3COOH + \text{by products} + H_2O$$

(ii) Acetaldehyde

- by the non-catalytic vapor phase oxidation of n-butane.

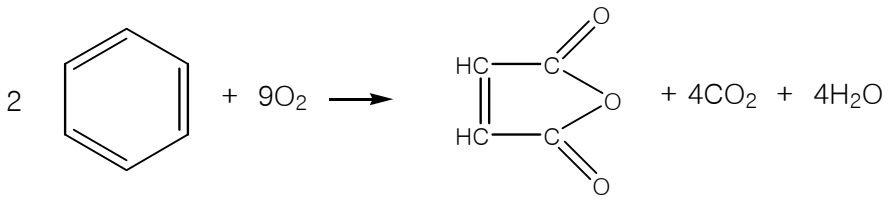
CH_3CHO (31%) HCHO (33%)

CH_3OH (20%) CH_3COCH_3 (4%)

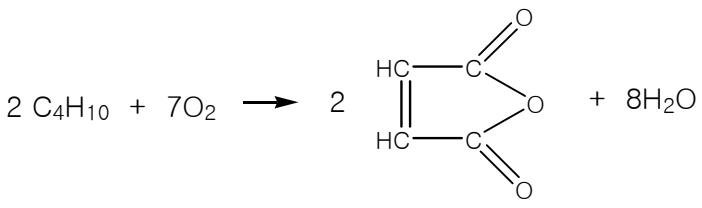
mixed solvents (12%)

(iii) Maleic anhydride

(a) catalytic oxidation of benzene



(b) oxidation of butane



(온도=500℃, 촉매 : Iron + V_2O_5-P_2O_5 on Silica-alumina)

(용도)

(a) 불포화 폴리에스터 (unsaturated polyester) 합성에 사용

- 불포화 polyester는 glass fiber와 함께 복합재료 (composite material)를 만드는데 시용.
- 즉 glass-fiber-reinforced plastics(GFRP)
- 자동차 경량화에도 이용함
- 가정에서의 욕조, 세면대등 다양하게 이용함

(4) Light Naphtha (C_5~C_7)

- feedstock for liquid phase oxidation(LPO) to produce acetic acid.

(5) High Molecular weight n-Paraffins (C_8~C_{30})

(ⅰ) Fatty acid(지방산)

- by oxidation of C_{18}~C_{30}

$R_1(CH_2)_nCH_2CH_2-(CH_2)_nR_2 + 5/2\ O_2 \rightarrow R_1(CH_2)n-COOH + R_2(CH_2)_nCOOH + H_2O$

(ⅱ) Fatty Alcohols :

- by the oxidation of n-paraffin fraction

(ⅲ) Chloroparaffins :

- by the liquid phase monochlorination using n-Octane
- used for the production of detergents

(ⅳ) Sulfonated n-Paraffins :

- by the reaction between sulfur dioxide, oxygen and n-paraffins

$$RH + 2\ SO_2 + O_2 + H_2O \rightarrow RSO_3H + H_2SO_4$$

- these sulfonates are nearly 100% biodegradable

- soft and stable in hard water - have good washing properties