Chapter10. Petroleums from Methane

▪ Three major sources in petrochemical industry:

(1) carbon monoxide and hydrogen (synthesis gas) from reforming natural gas (methane)
(2) olefins from pyrolysis of ethane, propane-butane(LPG) or distillates.
(3) aromatics from catalytic reforming.

(1) Synthesis gas - a general term used to designate various mixture of carbon monoxide and hydrogen.

▪ 생산 - (i) partial oxidation of methane

$2CH_4 + O_2 \longrightarrow 2CO + 4H_2 - \triangle H$

Temp : 1,300~1,500 ℃

Press : 200 ~ 20,000 psig

non - catalytic process

(ii) steam reforming of methane

(주로사용)

$2CH_4 + O_2 \longrightarrow 3H_2 + CO$, $\triangle H_{800℃} = 54.2$ kcal

Temp = 830~850 ℃

▪ Chemicals from synthesis gas

(i) Ammonia - the parent compound of many chemicals, especially used as fertilizers.
Direct synthesis of ammonia from hydrogen and atmospheric nitrogen is a classic heterogeneous catalytic reaction.

$N_2(g) + 3H_2(g) \Longleftrightarrow 2NH_3(g), \triangle H_{25℃} = -22.08$ kcal
촉매 : iron oxide (Fe_3O_4)

(ii) Urea - a byproduct from ammonia production/carbon dioxide reacts with ammonia to produce urea. Urea is an important solid fertilizer containing about 45% nitrogen.

☞ 용도 (a) fertilizer : 75%
(b) animal feeds : 10%
(c) adhesives, plastics, and resins : 15%

▪ 생산 - two - step reaction of carbon dioxide and ammonia.

(Ⅰ)first step : $CO_2 + NH_3(g) \Longleftrightarrow NH_2COONH_4(S)$

- ammonium carbamate is formed by an exothermic reaction.

Temp = 170 ~ 190 ℃

Press = 150 atm

(Ⅱ) Second step :

$NH_2COONH_4(S) \Longleftrightarrow NH_2CONH_2(s) + H_2O(g)$

$\triangle H_{25℃} = 6.32$ kcal

- The decomposition of the carbamate to urea and water at 200 ℃

(Ⅲ) Nitric acid - produced by oxidizing ammonia with air.

촉매 : Platinum - rhodium wire gauze.

(i) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

$\triangle H_{25℃} = -21$ kcal

(ii) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

$\triangle H_{25℃} = -27$ kcal

(iii) $3\ NO_2\ (g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$

$\triangle H_{25℃} = -32$ kcal

반응온도 = -32 ℃

Press = 대기압

(IV) Hydrozine (NH_2-NH_2) - ammonia is oxidized using sodium hypochloride to produce chloramines, NH_2Cl, which further react with ammonia to produce hydrazine.

(반응)

$2NH_3 + H_2O_2 \longrightarrow NH_2\text{-}NH_2 + NaCl + H_2O$

▪ Hydrozine can also be produces from ammonia and hydrogen peroxide as the oxidizing agent.

$2NH_3 + H_2O_2 \longrightarrow NH_2\text{-}NH_2 + 2H_2O$

(용도) a rocket fuel, amino cresols, pesticide, 등

(2) Methanol

▪ Production : $2H_2 + CO \longrightarrow CH_3OH$

$\triangle H_{298} = -30.6$ (kcal/mol)

(a) High temp process :

(T = 400 ℃ , P = 4000~6500 psig)

촉매 : Zinc -Chrominum oxide ($Zn\text{-}CrO_3$)

(b) Low temp process

(T = 250~260 ℃ , P = 725~1176 psig)

촉매 : Cu, Zn

▪ Methanol로부터 얻을 수 있는 products

(i) Formaldehyde : produced by the catalyzed oxidation of methanol, and by the non-catalytic oxidation of propane-butane mixtures.

(반응) $CH_3OH \longrightarrow HCHO + H_2$

$\triangle H_{298}^{\circ} = 20.4$ kcal

$2H_2 + O2 \longrightarrow 2H_2O$

$\triangle H_{298}^{\circ} = -57.8$ kcal

Formaldehyde is usually sold as a 37% solution in water with methanol as a stabilizer. Because formaldehyde tends to polymerize in concentrated solution and in the absence of a solvent.

(ii) Acetic Acid

(반응) (a) oxidation of acetaldehyde

(b) oxidation of n-butane

(c) carbonylation of methanol

$CH_3OH + CO \longrightarrow CH_3COOH$ (Monsanto process)

(T=200 ℃, P= 215 psig)

촉매 : Rhodium iodide complex

(iii) Methyl Chloride

(반응) $CH3OH + HCl \longrightarrow CH_3Cl + H_2O$

(a) Reaction between methanol and hydrogen chloride (vapor phase)

(b) Or chlorination of methane

(iv) Methyl amines : from methanol and ammonia

$CH_3OH + NH_3 \longrightarrow CH_3NH_3 + H_2O$

$CH_3OH + CH_3NH_3 \longrightarrow (CH_3)_2NH_3 + H_2O$

$CH_3OH + (CH_3)_2NH \longrightarrow (CH_3)_3N + H_2O$

(mol%),MMA : DMA: TMA=43:24:33

MMA=살충제

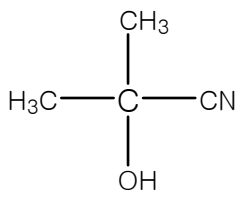
DMA= most widely needed,

살충제,제약용

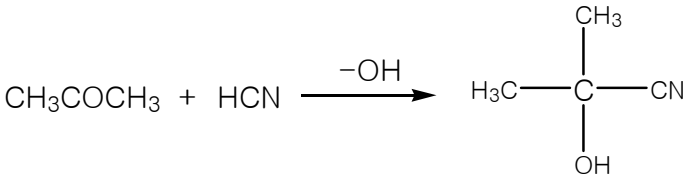
TMA=가축사료(양계)

(v) Methyl Methacrylate:

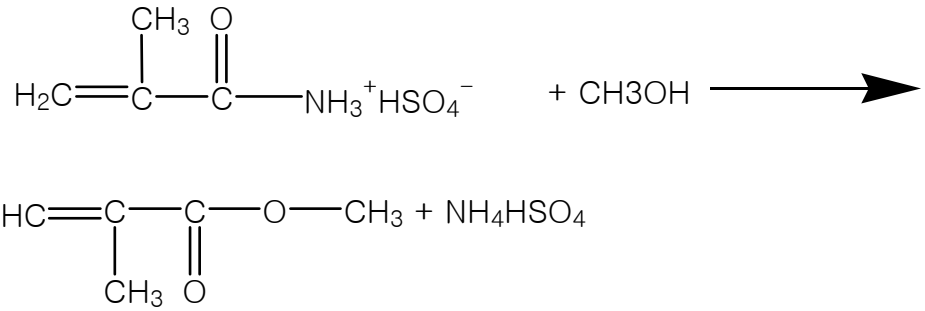
(a) starts with hydrogen cyanide and aceton in the presence of a base.

$CH3COCH3 + HCN \xrightarrow{-OH}$ 

(b) with sulfuric acid, this becomes the sulfuric acid salt of the amide of methacrylic acid.



(c) The amide salt is esterified by methanol to give methyl methacrylate.

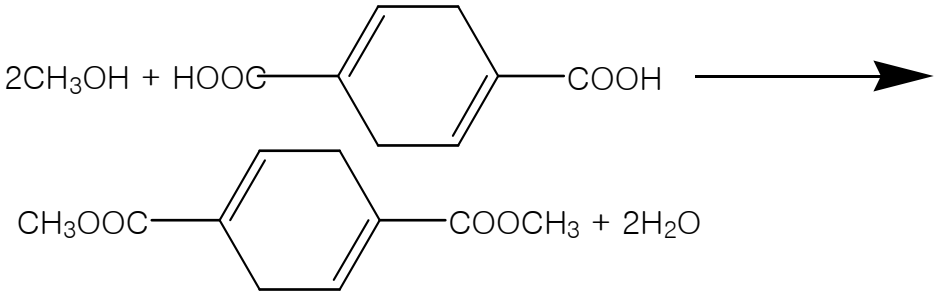


(vi) Dimethyl Terephtalate (DMT)

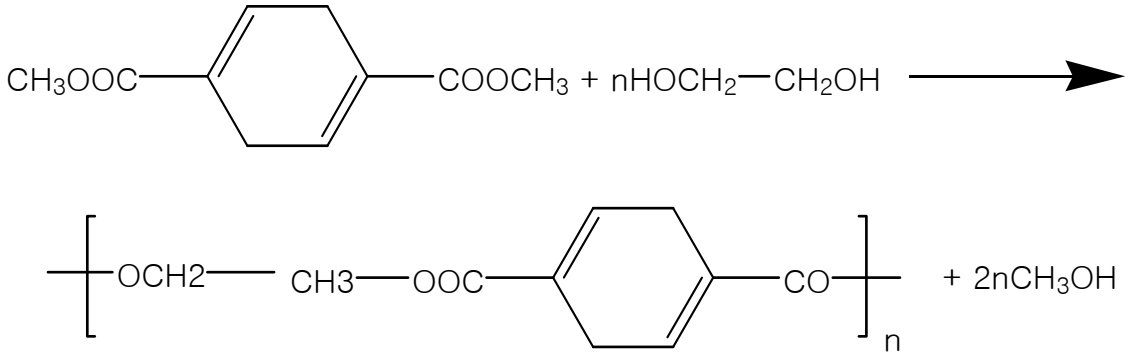
-Methanol is used for the esterification of terephthalic acid to dimethyl terephtalate transesterified with ethylene glycol to make polyester fibers.

(반응)

(a)



(b)



Poly(ethylene terephthalate) (PET) Fiber.

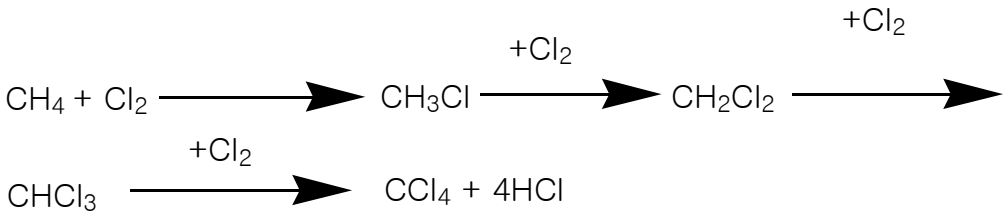
(3) Chloromethanes

- Methyl chloride, Chloromethane CH_3Cl : 58.7%
- Methylene Chloride, dichloromethane CH_2Cl_2: 29.3%
- Chloroform, trichloromethane $CHCl_3$, 9.7%
- Carbon tetrachloride, tetrachloromethane CCl_4 : 2.3%

(반응) Chlorination of methane

thermal chlorination - important

photochemical chlorination

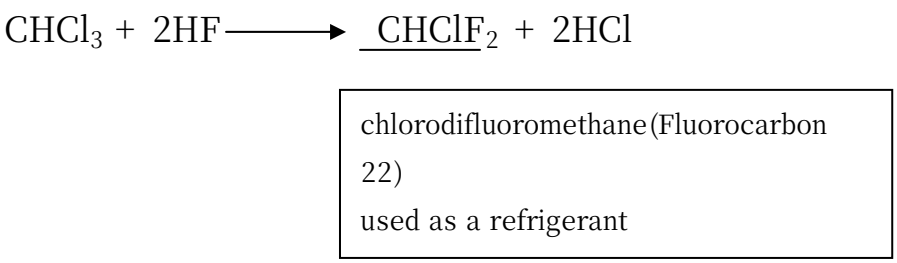


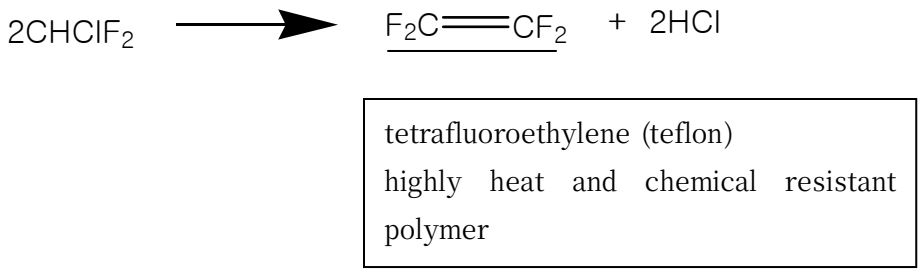
(용도) Nonflammability : chlorofluorocarbon (CFC)

polyurethane foam의 blowing agent로 이용 (ex: HCFC 141B)

slvent, paint stripping, etc.

• Chloform





• Carbon Tetrachloride

- used for the production of trichlorofluoromethane (CCl_3F, Fluorocarbon Ⅱ)
- and dichlorodifluoromethane
(CCl2F2, Fluorcarbon 12)

(반응) $CCl_4 + HF \longrightarrow CCl_3F + HCl$

$CCl_4 + 2HF \longrightarrow CCl_2F_2 + 2HCl$

(용도) ▪ aerosol product : colognes, perfume hair spray, shave cream

▪ Air conditioning,. Refrigeration (냉매)

• Carbon disulfide

$CH_4 + S \longrightarrow CS2 + 2H_2S$ (1^{st} step)

$3H_2S + 3/2O_2 \longrightarrow 3H_2O + S$ (2^{nd} step)

$CH_4 + 2S + O_2 \longrightarrow CS_2 + 2H_2O$ (net process)

Also produced by carbon and sulfur.

(용도) ▪ production of CCl_4

▪ rayon and cellophane

▪ regenerated cellulose

• Hydrogen Cyanide

$2CH_4 + 2NH_3 + 3O_2 \longrightarrow 2HCN + 6H_2O$

(용도) in the production of methyl methacrylate, acrylonitrile, etc

Also, $CH_4 + NH_3 \longrightarrow HCN + 3H_2$

(Degussa process)