Chapter 2

Experimental

Apparatus:

A flow diagram of the apparatus used for the study of oxidation of xylene is shown in Fig. 1. The apparatus comprised of three main units, viz., the feeding unit for introduction of desired quantities of purified air and xylene vapours; the reactor unit containing the catalyst kept at the required temperature and the product recovery unit for condensing the solid products and storing the gases.

Air from a compressed air cylinder was passed through a purification tower $P_1$, metered through a calibrated flowmeter $F_1$, redried and then introduced to a xylene evaporator $S$. The xylene evaporator was kept at a desired constant temperature in a glycerine bath $G_3$. The purification tower was packed with calcium chloride, activated charcoal, potassium hydroxide pellets, indigo sillen gel and finally a pad of glass wool. The glycerine bath was provided with a stirrer, a thermometer and an immersion heater regulated by a 'variva' and a micric energy regulator. The rate of evaporation of the xylene was calibrated for different bath temperatures and primary air flow rates.

A stream of secondary air, similarly purified and metered was mixed with the xylene vapours and the mixed gases were passed through the reactor $R$. A mercury manometer $M$ recorded the pressure in the system. The reactor was made from 22 cm. pyrex tubing and was provided with an 8 cm. coil around it. The catalyst was packed in the reactor around a central sealed thermocouple tube between two purified asbestos plugs. The upper end of the reactor was closed with a cork and sealed with collodion. The reactor was kept in an electrically heated molten salt bath $S_3$ containing a mixture of sodium nitrite, potassium nitrate and sodium nitrate in the ratio 34:53:3 as recommended by Kirt et al.
for the temperature range required in these studies. The tempera-
ture of the salt bath was regulated by a rheostat and a servic
energy regulator. The gases, preheated by passage through the
coil, entered the reactor at the bottom and the reaction products
were let out through a side tube provided at the top of the
reactor. The temperatures of the salt bath and the catalyst
bed at different zones were recorded by two thermocouples
(TC₁ and TC₂).

The tube connecting the xylene evaporator to the bubbler
was heated by a nichrome wire wound around it to prevent condensa-
tion of xylene vapours.

The exit gases from the reactor were conducted through
a long air condenser (AC), two ice cooled condensers (C₁ and C₂)
and then scrubbed through a series of water bubblers (B₁ and B₂).
The gases from the bubblers, after being passed through a water
condenser, could either be collected over saturated brine in the
calibrated gas reservoir (CR) or passed through a Set Test
Meter (SM).

**Experimental Procedure:**

A known quantity of the catalyst, normally 20.0 cc, was
packed in the reactor which was then fitted in the reaction unit.
After taking its initial weight, the bubbler containing xylene was
placed, in an outer glass jacket, in the glycerine bath. The salt
bath and the glycerine bath were heated to the desired tempera-
tures and a stream of primary and secondary air, corresponding
to the desired space velocity and air/xylene ratio, was started.
Solid products started condensing almost immediately. The air
and xylene vapours were passed for a definite period, usually 2
hours, keeping the flow rates and bath temperatures constant
throughout the run. The exit gases from the scrubbers were passed
through the Set Test Meter except for ten minutes in the middle
of the run when these were collected in the gas carboy. The
total volume of the exit gas as recorded by the flowmeter and
the carboy was noted.

At the end of the run, the primary air was cut off first to stop the xylene feed and the secondary was continued for another ten minutes to flush the catalyst. The xylene bubbler was removed, cooled to room temperature and weighed. The condensers and the water bubblers were all washed with hot water and the washings collected together for analysis.

Analysis of Reaction Products:

The reaction products obtained from the oxidation of ortho xylene over a vanadium bearing catalyst, V$_2$O$_5$-Ir., were on testing found to contain phthalic anhydride, maleic anhydride and quinone besides carbon dioxide. Benzoquinone and toluic aldehyde were present in traces in some experiments.

The sublimation of the solid products collected in the air condenser gave pure white needle like crystals of phthalic anhydride having a sharp m. pt. of 130.2°C. Mixing of these crystals with pure phthalic anhydride did not lower the m. pt. These crystals when fused with resorcinol and a little concentrated sulphuric acid gave fluorescence. The maleic anhydride in the residue was identified by converting the acid in water solution to fumaric acid in sunlight, in the presence of traces of bromine. The fumaric acid had a closed tube m. pt. of 226°C., the mixed m. pt with pure acid being 285.5°C. The quinone in the reaction product was detected by the liberation of iodine from potassium iodide in the presence of sulphuric acid. It was extracted from the water solution of the products with carbon tetrachloride.

For the estimation of these, the reaction products were dissolved in hot distilled water and the solution was heated to boiling to drive off dissolved carbon dioxide. There was no water insoluble portion. After cooling, the solution was made to known volume. An aliquot portion was titrated against standard alkali using phenolphthalein as an indicator. From the alkali titre the total amount of ortho xylene converted to phthalic and maleic
was calculated. Both these acids are dicarboxylic and one molecule of either results from one molecule of ortho xylene. The maleic acid was estimated according to the method given by Marisic. A measured portion of the solution was repeatedly extracted with carbon tetrachloride till the extract was colourless. The water solution was then titrated at 60°C against standard potassium permanganate solution in presence of sulphuric acid. The end point was taken when the pink colour lasts for one minute. The permanganate solution was standardized against a maleic acid solution of known strength. From the permanganate titration value the amount of ortho xylene oxidized to maleic anhydride was calculated and by subtraction from the amount of total ortho xylene converted to acids, the conversion to phthalic anhydride was found out. The method of estimation was checked on known mixtures made from pure compounds.

The quinone in the product was determined by estimating the iodine liberated from potassium iodide in presence of sulphuric acid according to the equation:

$$C_6H_4O_2 + 2 KI + H_2SO_4 \rightarrow C_6H_4(OH)_2 + K_2SO_4 + I_2$$

The liberated iodine was titrated against standard sodium thiosulphate solution using starch as an indicator towards the end point.

Whenever required, the estimation of carbon dioxide in the product gases was done by passing the exit gases through a number of bubblers containing potassium hydroxide or barium hydroxide solutions of known strength and back titrating the solutions with standard acid. No carbon monoxide was detected in the reaction products.

**Preparation of Catalysts:**

The methods used for the preparation of the different catalysts, employed for the oxidation of ortho xylene are given in detail at suitable places in the various chapters of this section. A.R. grade chemicals were generally used for the
preparations except where otherwise mentioned.

Indian kieselguhr which was generally employed as catalyst support, was washed several times with water, boiled with nitric acid and rewarshed till free of nitrate ions. It had light pale colour. Its apparent bulk density was about 0.5 ga/cc. when moderately packed.

The prepared catalysts were of '6 + 10' mesh size and 20.0 cc. volume was used in each case. All the catalysts, when freshly prepared were treated with air-ortho xylene mixture for 2-4 hours before the start of experimental runs.

Ortho xylene used was of L.R. grade obtained from British Drug House (London). It was redistilled over sodium before use.

**Nomenclature:**

The nomenclature used in the presentation of the experimental data on the oxidation of xylenses is defined below:

1. **Air rate** : Litres of air at room temperature passed per hour (for both primary and secondary streams)

2. **Bath temperature** : Temperature of the salt bath (°C.)
   **Bed temperature** : Temperature of the hottest part of the catalyst bed (°C.)

3. **Space Velocity** : Volume of gas mixture (air and xylene vapour) at N.T.P. passing per hour per volume of catalyst; cc./hr./cc.

4. **Molar air/xylene ratio** : Volume of air at N.T.P./hr. Volume of xylene (as hypothetical gas) at N.T.P./hr.

5. **Contact time** : Volume of catalyst Volume of gases (at catalyst temp.) passing per sec.

6. **Per cent conversion** : gm. xylene converted (per pass) to phthalic or maleic anhyd. x 100 gm. xylene passed

7. **Per cent selectivity** : Xylene converted to phthalic anhyd. Xylene converted to phthalic and maleic anhyd. x 100.
8. Space Time Yield: g. phthalic anhyd. produced/hr/litre of catalyst.

9. Per cent Process Yield: \( \frac{\text{g. phthalic anhyd. produced}}{\text{g. xylene passed}} \) x 100

Sample Calculations:

Catalyst: Fused Vanadium Pentoxide on Pumice.
Volume of catalyst: 20.0 cc.
Initial wt. of o-xylene bubbler = 66.529 g.
Final wt. of o-xylene bubbler = 64.731 g.
Wt. of o-xylene evaporated = 1.798 g.

Primary air rate = 14.0 l/hr. Secondary air rate = 111.0 l/hr.
Total air rate = 125.0 l/hr.

Temperature:
- Bubbler = 100°C.
- Bath = 470°C.
- Bed = 490°C. (Perfectly uniform temp. throughout the catalyst bed)

Time of run = 1.0 hr. Room temp. = 30°C.
Atm. pressure = 76.0 cm.

A. Products in the condensers and washers made to 500 cc.
Acid (0.0674 N) required = 24.12 x 10 = 241.2 cc.
Potassium permanganate solution required = 17.45 x 10 = 174.5 cc.
1 cc. of 0.0674 N Acid = 0.004597 g. o-xylene
1 cc. of permanganate soln. = 0.001039 g. o-xylene (as maleic acid)

Ortho xylene oxidized to phthalic and maleic anhyd. = 241.2 x 0.004597 = 1.1090 g.
Ortho xylene oxidized to maleic anhyd. = 174.5 x 0.001039 = 0.1812 g.
Ortho xylene oxidized to phthalic anhyd. = 0.9278 g.

Per cent Conversion to phthalic anhyd. = \( \frac{0.9278}{1.798} \times 100 = 51.54 \)

Per cent Conversion to maleic anhyd. = \( \frac{0.1812}{1.798} \times 100 = 10.09 \)
Per cent selectivity phthalic anhyd. = \( \frac{51.54}{51.54 + 10.09} \times 100 \) = 83.62

Space Time Yield of phthalic anhyd.

\[ \text{(gm./hr./l.)} = \left( \frac{\text{gm. o-xylene converted to phthalic anhyd./hr.}}{\text{cc. of catalyst}} \right) \times \frac{\text{mol. wt. phthalic anhyd.}}{\text{mol. wt. o-xylene}} \times \frac{1000}{106} \]

= \( 0.9270 \times 148 \times \frac{1000}{106} \times \frac{1000}{20} = 64.71 \)

Per cent Process Yield of phthalic anhyd

\[ \left( \frac{\% \text{ conversion to phthalic anhyd.}}{\text{phthalic anhyd.}} \right) \times \frac{\text{mol. wt. of phthalic anhyd.}}{\text{mol. wt. of o-xylene}} \]

= \( 51.54 \times 148 \times \frac{1000}{106} = 71.96 \)

Air/hr. at N.T.P. = \( 125 \times \frac{273}{(273 + 50)} = 112.7 \text{ l./hr.} \)

Vol. of o-xylene vapour/hr. = \( 1.798 \times 22.40 \times \frac{1000}{106} = 0.37 \text{ l./hr.} \)

Space velocity = \( (112.7 + 0.37) \times 1000 \times \frac{1}{20} = 5653 \text{ cc./hr./cc.} \)

Molar air/xylene ratio = \( \frac{112.7}{0.37} = 296 \)

B. Estimation of CO₂

350.0 cc. of KOH soln. (5 bubblers) and 50.0 cc. Ba(OH)₂ soln. (1 bubbler) were taken for CO₂ absorption.

Normality of HCl soln. = .07957 N

Original titre value :

350.0 cc. KOH soln. = 2473.1 cc. HCl
50.0 cc. Ba(OH)₂ soln. = 95.55 cc. HCl.

Total = 2568.45 cc. HCl

Final titre value (after CO₂ absorption) :
Pot. hydroxide = 1605.2 cc. HCl
Barium hydroxide = 93.95 cc. HCl
Total = 1699.05 cc. HCl

CO₂ formed = 2568.45 - 1699.05 - 31.80
             = 837.6 cc. HCl (.07957 H)
             = 1.4202 gm. CO₂

CO₂ due to
maleic anhyd. formation = .3216 gm.
Balance CO₂ = 1.0986 gm.
1.0986 gm. CO₂ = .3310 gm. o-xylene

Per cent o-xylene completely oxidized to CO₂ = 18.41

Summary of Results:

Space velocity = 56.52     Molar air/xylene ratio = 296
Per cent conversion to phthalic anhyd. = 51.54
Per cent conversion to maleic anhyd. = 10.09
Per cent selectivity = 85.62
Space time yield (phthalic anhyd.) = 64.71.
Per cent process yield (phthalic anhyd.) = 71.96
Per cent conversion to CO₂ = 13.41