A Note of the Preparation of Terephthalic Acid

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From the time of the discovery of terephthalic acid by Hofmann [1] in 1856, to the present [2], the only practical method of obtaining this substance from *p*-cymene has been oxidation with chromic acid in sulphuric acid solution.

$$C_{10}H_{14} + 4\ H_2Cr_2O_7 \rightarrow C_6H_4(COOH)_2 + 4\ H_2O + 2\ CO_2$$

This method is both slow and inefficient. In two separate runs, using 80 g $K_2Cr_2O_7$ and 65 ml conc. H_2SO_4 in 350 ml of water for 10 ml cymene, the following yields of terephthalic acid were obtained:

	Yield after 12 h refluxing	Yield after 36 h refluxing
Run I	18.0 %	—
Run II	13.5 %	24.8 %

It can thus be seen that the yield, even after 36 hours, is far from satisfactory, to say nothing of the expenditure in time required.

This oxidizing procedure utilizes a two phase system, *i. e.*, the cymene is insoluble in the chromic acid mixture. It was believed that if a suitable solvent could be found, the reaction could be made to take place in a one phase system, and the procedure vastly improved. Such a solvent was found in acetic acid.

The following procedure was followed in the single phase oxidation of cymene:

Approximately 30 g of CrO_3 was dissolved in 40 ml of water. To this was added a mixture of 160 ml glacial acetic acid and 50 ml of conc. sulphuric acid. This oxidizing mixture was then placed in a flask equipped with a reflux condenser. Two ml cymene were dissolved in 50 ml of glacial acetic acid and this solution was slowly dropped into the heated oxidizing mixture. Uusually 25 to 30 minutes were allowed for the complete introduction of the cymene solution.

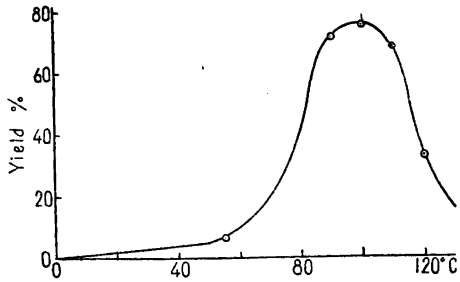

Fig. 1. Yield of terephthalic acid at various temperatures.

The excess chromic acid was then completely reduced by sulphurous acid, and the solution was shaken with ether, in which terephthalic acid is insoluble, and filtered. The precipitate was washed with hot water, dried at 105° C for one hour, and weighed.

The following results were obtained by oxidation at various temperatures:

Run	Temp. °C	Yield %	Titration equivalent
I	55	6.4	87.8
II	90	71.5	84.2
III	100	75.6	83.2
IV	110	68.5	83.2
V	120	33.0	86.0

These results, when plotted, show that the maximum yield of terephthalic acid is obtained at approximately 100° C.

In conclusion it may be stated that the single phase oxidation of *p*-cymene to terephthalic acid using acetic acid as a solvent, decreases the time required by the older method by 95 % and, at the same time, increases the yield by over 400 %.

1. Hofmann, A. W. *Ann.* **97** (1856) 206.
2. Kirjakka, P. *Suomen Kemistilehti* **A 13** (1940) 62.

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