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Survey of Industrial Chemistry 72-145.c44

Phenol I. 1986 Xylene Derivatives 201 2/24/92

trinitrotoluene (TNT) and the polyurethane monomer toluene diisocyanate (TDI). TNT requires complete nitration of toluene. TDI is derived from a mixture of dinitrotoluenes (usually 65–80% *o,p* and 35–20% *o,o*) by reduction to the diamine and reaction with phosgene to the diisocyanate. TDI is made into flexible foam polyurethanes for cushioning in furniture (43%), automobiles (21%), carpets (14%), and bedding (12%). A small amount is used in polyurethane coatings.

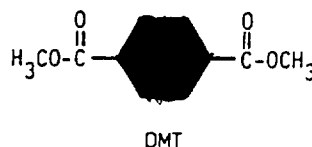
XYLENE DERIVATIVES

References

W & R 1, pp. 106–108
Kent, 969–971

There are only two top 50 chemicals, terephthalic acid and dimethyl terephthalate, derived from *p*-xylene and none from *o*- or *m*-xylene. But we also wish to discuss phthalic anhydride, which is made in large amounts from *o*-xylene.

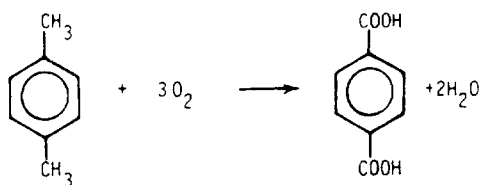
Terephthalic Acid and Dimethyl Terephthalate



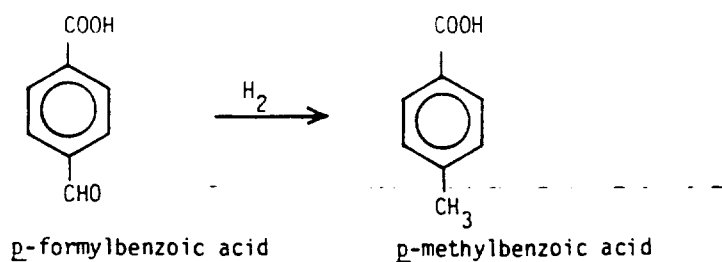
References

I. & M, pp. 807–813
KC, 11-25-85
CP, 8-8-83

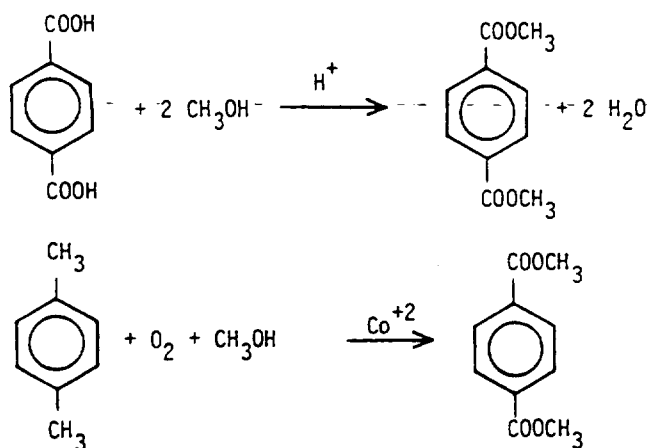
Terephthalic acid is commonly abbreviated TA or TPA. The abbreviation PTA (P = pure) is reserved for the product of 99.9% purity for polyester manufacture. For many years polyesters had to be made from dimethyl terephthalate (DMT) because the acid could not be made pure enough economically. Now either can be used. TA is made by air oxidation of *p*-xylene in acetic acid as a solvent in the presence of cobalt and manganese salts of heavy metal bromides as catalysts at 200°C and 400 psi. TA of 99.6% purity is formed in 90% yield.



The crude TA is cooled and crystallized. The acetic acid and xylene are evaporated and the TA is washed with hot water to remove traces of the catalyst and acetic acid. Some *p*-formylbenzoic acid is present as an impurity from incomplete oxidation. This is most easily removed by hydrogenation to *p*-methylbenzoic acid and recrystallization of the TA to give 99.9% PTA, which is a polyester-grade product, mp > 300°C.



DMT can be made from crude TA or from *p*-xylene directly. Esterification of TA with methanol occurs under sulfuric acid catalysis at 105°C and 50 psi. Direct oxidation of *p*-xylene with methanol present utilizes cobalt salt catalysis at 160°C and 75 psi.



The DMT must be carefully purified via a five-column distillation system, bp 288°C, mp 141°C.

TA or I
terephthal
yield poly
industry.
photograph
drink mar

Phthalic A

Reference

L & M, pp.
CP, 7-11-83

Approxim
from *o*-xyl
other 28%
petroleum
trend tow.