SELECTIVE OXIDATION OF XYLENES TO TOLUIC ACIDS

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ABSTRACT: *A mixture of manganese, cobalt and lead para-amino benzoates supported on silica gel is used to catalyze oxidation of xylenes to toluic acids in presence of oxygen or air. Reactions are clean and catalysts can be recovered easily and reused.*

KEY WORDS: *Selective oxidation, Xylenes, Toluic acid, Oxygen, Cobalt and manganese salts.*

The oxidation of alkylarenes to aromatic mono and poly carboxylic acids were attracted much interests [1]. A great number of oxidizing agents can effect this conversion, the oxidants commonly used are alkaline permanganate [2], chromic acid [3], aqueous sodium dichromate [4], peroxydisulfate copper (II) in acetic acid [5] and electrolytic oxidation by Co(II) acetate [6].

Synthetic chemists are faced with a limited methods for selective oxidation of dialkylarenes to mono carboxylic acids such as oxidation of xylenes to toluic acids. It has been reported that the isomeric xylenes could be oxidized to respective toluic acids in presence of oxygen catalyzed by cobalt ion, initiated by ozone [7]. A mixture of Co, Mn, Cr and Ni salts of fatty acids and oxygen oxidized *p*-xylene to *p*-toluic acid [8]. *o*-Xylene was oxidized to *o*-toluic acid using oxygen and Pt anode at 2.3 V in acetonitrile [9].

Recently we have reported the selective oxidation of allylic and benzylic alcohols to their corresponding carbonyl compounds using oxygen or air catalyzed by a mixture of the manganese and cobalt *p*-amino benzoates supported on silica gel [10].

Now we have extended our studies with this catalyst and we wish to report that it selectivity oxidizes xylenes to touic acids.

Xylene 25 mL (21.7 g, 204.4 mmol) was oxidized by oxygen at the rate of 15 mL per minute at reflux temperature and under atmospheric pressure in presence of cobalt (2 g), manganese (2 g) and lead (2 g) of *p*-amino benzoates supported on silica gel [10]. The reaction progress was monitored by collection of water in a Dear-Stark apparatus. The generation of water ceased after 40 minutes and the reaction mixture was cooled to room temperature and diluted with xylene (25 mL). The mixture was filtered and the solid material was washed with ether (2 × 20 mL). The ethereal solutions were combined together with the filtrate. The solvent was evaporated to give 13.27 g (97.5 mmol, 47.7%) of toluic acid.

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The same oxidation was also proceeded by blowing the air (35 mL per minute) to give 8.72 g (64 mmol, 31.3%) of toluic acid (Table 1).

The recovered solid material was dried in an oven at 135 °C for 4 hours and was used as the calalyst for the next experiment. The activity of the recovered catalyst was decreased around 10% in each repeating experiment.

Table 1: Oxidation of xylenes to toluic acids

Starting material	Product	Yield (Oxygen)	Yield (Air)
p-xylene	*p*-toluic acid	47.7	31.3
m-xylene	*m*-toluic acid	36.0	23.6
o-xylene	*o*-toluic acid	29.8	20.5

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REFERENCES

[1] The preparation of carboxylic acids has been rereviewed in "*Methodene Organischen Chemie*", Vol. VIII, Part 3, E. Mullen, Ed. George Thieme, Verlage,Stuttgart, (1952).

[2] Mills, W. H., *J. Chem. Soc.*, 3191(1912).

[3] Jacobson, O., *Chem. Ber.*, **18**, 1701(1885).

[4] Friedman. F., Fishel, D.L. and Shecter, H.J., *Org. Chem.*, **30**, 1453(1965).

[5] Walling, C., Chengxue, Z. and El. Taliawi, M. G., *J. Org. Chem.*, **48**, 4910(1983).

[6] Bakir., U. and Pekel, A.T., *Bull. Electrochem.*, 5, 452(1989).

[7] Hay, A. S., Eustance, J. W., Banchard, H. S., *J. Org. Chem.*, **25**, 616(1960).

[8] Koval. J., *Czech. Patent* 209 ,102,Nov, 30(1981).

[9] Mastsuda, Y., Nishiki, T., Nakagawa, K. and Dehara, M., *C. A.* 190859 m, **101**(1984).

[10] Hashemi. M. M. and Ghazanfari D., *Iranian J. Chem. & Chem. Eng.*, **13**, 77(1995).