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Discussion

Comments on the paper "Low-bromide containing MC catalyst for the autoxidation of *para*-xylene" by B. Saha and J.H. Espenson [J. Mol. Catal. A 271 (2007) 1–5]

Walt Partenheimer

Central Research and Development, E.I. DuPont de Nemours & Co., Inc., Experimental Station, Wilmington, DE 19880-0328, USA

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I wish to point out that this publication [1] describes phenomena that I described 3 years earlier in greater detail and were generalized to a number of different methylaromatic compounds.

The publication [1] describes the Co/Mn/Br catalyzed aerobic oxidation of *p*-xylene in acetic acid solvent. They describe a decreasing rate of reaction which then ceased and the color changed from pink to light brown. They presumed that the rate of reaction ceased because of benzylic bromide formation. The addition of sodium bromide immediately restored the rate of reaction and changed the color back from brown to pink.

Identical phenomena and very similar experiments were reported earlier [2] for *p*-toluic acid and 4-tolylaldehyde (intermediates in *p*-xylene oxidation) as well as for toluene and 4-chlorotoluene. In this paper, the formation of benzylic bromides were not assumed, but measured during the reactions. When all of the bromide was converted to a benzylic bromide, the reaction essentially ceased. The absorbance values were measured during reaction via UV–vis and ascribed partially to Mn(III) formation. Finally addition of hydrogen bromide changed the color of solution and restored the rate and selectivity of the reaction. All of these phenomena are strongly dependent upon water concentration since the restoration of the ionic bromide occurs by solvolysis of the benzylic bromides, as well as by oxidation.

Also reference 19 in the paper [1] is incorrect. The authors are probably referring to one of my later papers [3] which also describes the effect of benzylic bromides on the rate of formation of carboxylic acids.

References

[1] B. Saha, J.H. Espenson, Low-bromide containing MC catalyst for the autoxidation of *para*-xylene, J. Mol. Catal. A 271 (2007) 1–5.
[2] W. Partenheimer, The complex synergy of water in the metal/bromide autoxidation of hydrocarbons caused by benzylic bromide formation, Adv. Synth. Catal. 346 (2004) 297–306.
[3] Novel catalytic characteristics of the Co/Mn/Cl/Br liquid phase oxidation catalyst, in: F.E. Herkes (Ed.), Catalysis of Organic Reactions, Marcel Dekker, Inc., 1998, pp. 357–368.

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E-mail address: wpartenheimer@msn.com.

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