

Coupling of electrochemical activation and oxygenation for aldehydes synthesis from toluenes in acetic acid

Dorin Bejan, André Savall*

savall@chimie.ups-tlse.fr

Laboratoire de Génie Chimique,

CNRS, Université Paul Sabatier

118, rte de Narbonne, 31062 Toulouse, France

Stéphane Trévin, Mohamed Mellah

EDF R&D – Les Renardières - E23/EPI

77818 Moret sur Loing, France

Oxidation of methylbenzenes in the liquid phase, by dioxygen is the basis of several industrial processes of great importance.¹ The available methods of activation having a practical interest for the action of dioxygen are (i) catalytic reactions with metal ions, and (ii) reaction with free radicals. Recent work carried out in our laboratory has shown that the autoxidation reactions of toluenes catalyzed by cobalt(II) acetate (path (i)) can be favorably assisted by electrochemistry.^{2,3}

Having as an objective the improvement of the aldehyde selectivity, we focused our study on the action of dioxygen during the direct electro-oxidation of alkylaromatics in solution in acetic acid in the absence of metal catalyst; this makes us hopeful that the process may be ended with the formation of aldehyde. Since the work of Ebersson⁴ it is admitted that the direct anodic oxidation of methylated aromatics can generate, under soft conditions, benzylic cation radicals and radicals (Scheme 1). The present work was undertaken with the aim of developing the coupling reaction between dissolved dioxygen and radicals generated by anodic oxidation of methylated aromatics dissolved in acetic acid (path (ii)). The oxygenation reaction expected can be summarized by Scheme 1.⁵ The peroxide radical $\text{ArCH}_2\text{O}_2^\bullet$ is able to lead to valuable products.¹

The direct electrochemical oxidation of toluenes in solution in acetic acid on a graphite anode under oxygen saturation conditions leads to the formation of benzaldehydes (Fig. 1). On a graphite anode the acetate/aldehyde ratio varies from values higher than 20 under an oxygen-free atmosphere to 2 under oxygen saturation (1 atm, 80 °C, 63 A m⁻²). The acetate/aldehyde ratio increased with the temperature; however, the proportion of aldehyde was not greatly influenced by the temperature.⁵ A reaction mechanism is proposed for the process conducted under oxygen saturation in the basis of the results of voltametric studies⁵ and large scale electrolyses. Accordingly, it is assumed that the benzyl radicals generated on the anode, from *p*-methoxytoluene or *p*-*tert*-butyltoluene in acetic acid, can react directly with dissolved molecular oxygen. The generated peroxide radicals, $\text{ArCH}_2\text{O}_2^\bullet$, undergo chemical reactions leading to the formation of the corresponding aldehyde and alcohol (Scheme 1). Under the reaction conditions, most part of the alcohol is electro-oxidized into aldehyde. The selectivity of the aldehyde in this oxidation process could be improved by operating under conditions increasing the dioxygen solubility (low temperature) and by using a convenient electrode material favoring the desorption of the reaction intermediaries.

Fig. 1 A- under N₂; B- under O₂; 1. *p*-*tert*-butyl toluene; 2. acetate; 3. aldehyde; 4. faradaic yield (Y); 5. faradaic contribution (Y⁻¹). I = 0.2 A (S_{an.} = 32cm²). T = 80°C. 100 mL AcOH 0.2M *p*-*t*-butyl tol. 0.1M Et₄NBF₄.

Scheme 1.

The reaction has been applied to the synthesis of 4-*t*-butyl 3-methoxy benzaldehyde used as intermediate in perfumery and cosmetic industry. The process has been satisfactorily extended to the synthesis of benzaldehyde from toluene at the scale of 10 moles in a reactor of 20 liters.

References

1. R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, 1981.
2. G. Falgayrac, A. Savall, *J. Appl. Electrochem.* 29 (1999) 253.
3. D. Bejan, J. Lozar, G. Falgayrac, A. Savall, *Catalysis Today* 48 (1999) 363.
4. L. Ebersson, *J. Am. Chem. Soc.* 89 (1967) 4669.
5. a) D. Bejan, A. Savall, *New Directions in Organic Electrochemistry, Proceedings Volume 2000-15*, Edit. A. J. Fry and Y. Matsumura, The Electrochemical Society, Pennington, NJ, pp. 45-48. b) D. Bejan, A. Savall, *J. Electroanal. Chem.* 507 (2001) 234.



