

# HIGH THROUGHPUT APPROACH FOR DEVELOPMENT OF O-XYLENE ELECTROCHLORINATION

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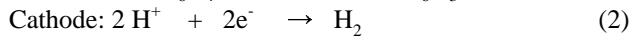
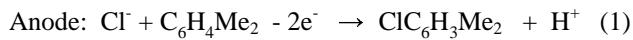
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Commercially valuable chloroaromatic compounds are produced by chlorination of the aromatic starting material with chlorine. This reaction requires a Lewis catalyst (e.g.  $\text{FeCl}_3$ ) and generates  $\text{HCl}$ , which should be recycled. In addition, para/ortho regioselectivity of this reaction is low. For chlorination of o-xylene in the presence of  $\text{FeCl}_3$  the para (or 4-) selectivity is within 55 – 60 % range. Shape-selective solid catalysts improve para-selectivity up to 85 % [1] but their activity and stability are low.

Electrohalogenation of aromatic compounds is well known. However, low current density prevents their industrial use. Generally, electrochemical chlorination routes are less regioselective than chemical ones [2]. Current density of electrochlorination of aromatic compound with aqueous  $\text{HCl}$  is not high enough (e.g. up to 65 mA/cm<sup>2</sup> for o-xylene) [3].

This paper describes a novel process for synthesis of predominantly 4-chloro-1,2-dimethylbenzene by electrochlorination of o-xylene according Eqs. 1-3.



Electrochlorination was carried out in an undivided beaker type electrochemical cell or in the Electrolytica MicroFlow cell using graphite electrodes. To accelerate discovery and optimization steps, a high throughput unit containing 16 beaker type cells with replaceable electrodes was used. The cells can be connected in series or parallel to run experiments with constant current or potential respectively. Validation of this unit shows that the position of a vial in the array is not important (t-tests) and relative standard deviations are reasonably low (within 7 % for reaction rate and less than 0.5 % for reaction selectivity).

Electrolysis of biphasic mixture of aqueous  $\text{HCl}$  and o-xylene takes place only at rather low current density (up to 50 mA/cm<sup>2</sup>). The increase of current density causes the electrode passivation. Addition of phase transfer catalysts (PTA) (e.g.  $\text{Me}_3\text{BuNCl}$  or  $\text{Me}_3\text{CtNCl}$ ) allowed increasing of current density and alleviated the passivation problem. It was found that addition of a small amount of acetonitrile to the reaction mixture containing PTA slows down the electrode passivation at high current density but current efficiency remains low (~ 70 %).

Electrolysis of mono- or biphasic systems o-xylene – aqueous  $\text{HCl}$  – organic solvent allows high current density (up to 250 mA/cm<sup>2</sup>) and current efficiency (90 – 95 %). Reaction rate for different solvents is similar (Fig.1) and depends mostly on concentration of reagents. For example, for acetonitrile the reaction rate is linear function of hydrochloric acid concentration even when system becomes biphasic. The influence of different solvents on reaction selectivity is shown on Fig. 1. In general, para-selectivity of electrochlorination is the same

or better than that of chlorination in the presence of Lewis acids. Acetonitrile and ethanol have the best combination of reaction rate and para-selectivity. However, ethanol as well as methanol demonstrate low current efficiency and promote chain chlorination with formation of the alpha-isomer and overchlorination with formation of dichloro- and trichloroxylanes. The nuclear selectivity (3- and 4-isomers vs. alpha isomer) for other solvents is in the range 90 – 96 %. It was found that if to carry out electrolysis in the absence of light, electrochlorination occurs practically only in aromatic nucleus. Addition of salts of some metals, especially cerium, noticeably increases chain chlorination even in the dark.

Optimization of o-xylene electrochlorination in mixed solvents MeCN – tetraglyme and MeCN – acetic acid in the presence of PTC was done using high throughput experiments. It was showed that para-selectivity decreases with the increase of reagent concentration and with the decrease of MeCN content in the mixed solvents. PTC has no effect on para-selectivity and little effect on reaction rate if the concentration of a solvent is high enough but increases the current efficiency and absolutely necessary in the flow cell to stabilize the biphasic emulsion.

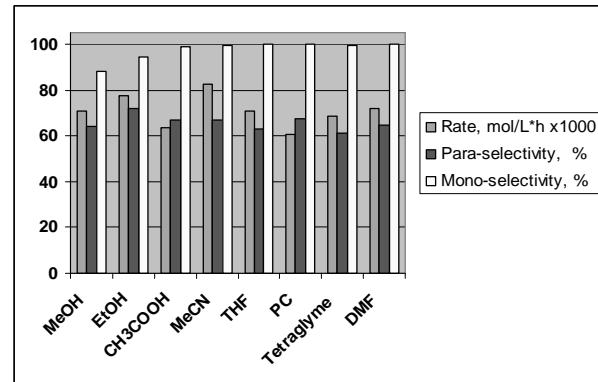


Fig. 1. Rate and reaction selectivity for o-xylene electrochlorination in the presence of different solvents.

DESIGN-EXPERT Plot

4-Selectivity, %  
X = A: HCl, M  
Y = C: TG

Actual Factor  
B: TMBAC = 0.00

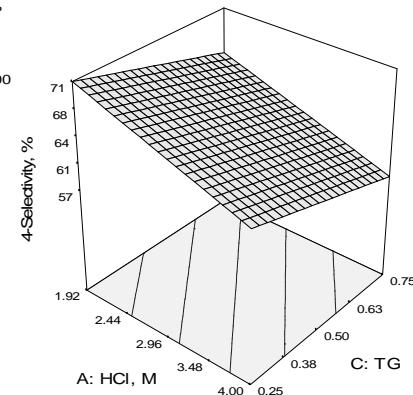


Fig. 2. Para-selectivity as function of HCl concentration and tetraglyme content in acetonitrile:tetraglyme mixed solvent.

## Reference:

- [1] S. Matsuoka, K. Tada, and H. Minomya, JP Patent 03081234 A2 to Toray Industries, Inc., 1991.
- [2] A. Muthukumaran, T. Raju, and V. Krishnan, *Bulletin of Electrochemistry*, **1996**, 12, 320.
- [3] M. M. Atamov, Yu. A. Yuzbekov, S. N. Borisov, and Z. T. Sultanova, *Azerb. Khim. Zhurnal*, **1984**, 24.