Optimisation of electrochemical synthesis of 2-iodosylbenzoic acid

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Oxidising agents with heavy metal atom (e.g. Cr^{VI+} such as Collins reagent or pyridinium chlorochromate) were historically used for oxidising primary and secondary alcohols to correspond carbonyl compounds [1]. Moving beyond Cr-based oxidants, hypervalent iodine compounds present a promising avenue for safer and environmentally friendly oxidations. Amongst the well-known λ^3-iodanes belongs 2-iodosylbenzoic acid (2-IsBA) which proved to be valuable asset for oxidative reactions, e.g. oxyarylation [2] or oxyalkenylation [3]. When it comes to production of iodanes, toxic, and potentially dangerous substances (Selectfluor®, Oxone®, $KBrO_3$) are handled, therefore, the price and environmental footprint in form of waste is significant [4]. Alternatively, it is possible to produce iodanes utilizing electrochemical synthesis. Such alternative method of 2-IsBA synthesis (Figure 1), which is highly efficient, scalable and environmentally friendly will be presented within this contribution [5]

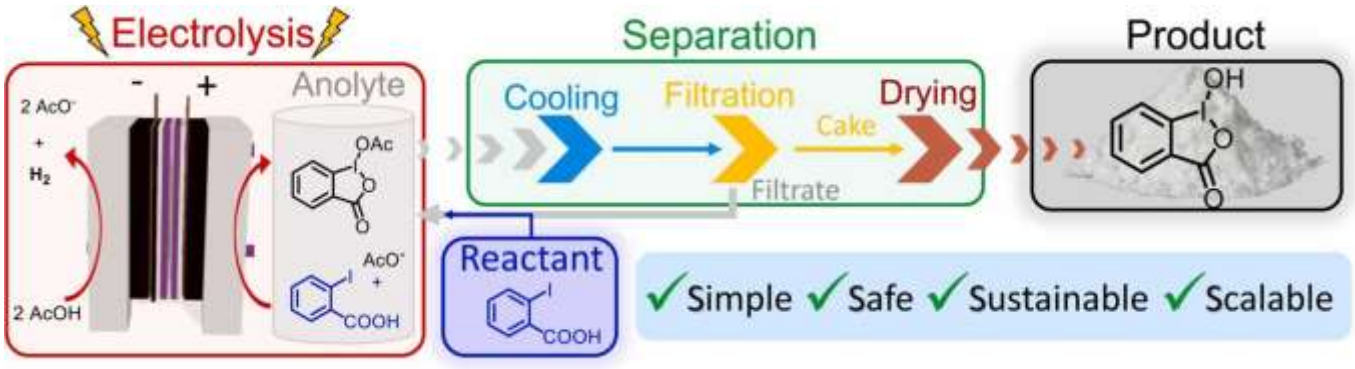

Figure 1. Scheme of electrochemical synthesis and followed up separation of solid 2-iodosylbenzoic acid [5].

Electrolysis was performed at constant potential of 1.9 V vs $Hg|Hg_2SO_4|K_2SO_{4(sat.)}$ in flow electrolyser divided by cation-exchange membrane. Electrochemical oxidation of 2-iodobenzoic acid at concentration of about 0.1 mol dm^{-3} takes place on a boron doped diamond anode in an anhydrous AcONa-AcOH solution. Electrolysis conditions such as electrode potential, time, and substrate and electrolyte concentration were examined in order to optimise the production of 2-IsBA. The optimised parameters provide excellent electrolysis yield (93%) and current efficiency (94%). The separation process exploits low solubility of 2-IsBA in AcOH resulting in 2-IsBA precipitation during the electrolysis and upon cooling the anolyte solution. The precipitate was then filtered/decanted and air-dried resulting in white solid 2-IsBA. The product was analysed utilizing iodometric titration and nuclear magnetic resonance. The analyses confirmed that the white solid product is 2-IsBA with purity of 97 wt.%. It should be pointed out that product separation was performed without any washing steps and did not require any organic solvents.

Additionally, the reusability of most involved compounds through partial recycling of both anolyte and catholyte, along with efficient product separation was confirmed. This significantly reduces waste generation compared to traditional methods, leading to lower 2-IsBA production costs and a minimized environmental footprint.

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