Anodic oxidation of o-toluenesulphonamide to saccharine on a NiO(OH)-coated nickel anode

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o-Toluenesulphonamide has been electrolytically oxidized at low current density to saccharine in aqueous solutions of alkali carbonates on anodes coated with NiO(OH). This electrolytic oxidation led to a 40% yield of saccharine. The application of carbon and glassy-carbon counter electrodes or of various supports for the working electrodes did not result in improved saccharine yield. Moreover, the choice of a different potential and a different current density or the use of organic co-solvents did not substantially affect the course of the electrolytic oxidation.

In the electrolytic oxidation of o-toluenesulphonamide a parasitic evolution of oxygen occurred which caused a partial degradation of the starting material. In strongly alkaline media, i.e. in aqueous solutions of alkali hydroxides, a fission of the NH₂ group with formation of o-toluenesulphonate occurred during the electrolysis.

1. Introduction

The production of saccharine is still important in the technology of artificial sweeteners. The oxidative transformation of o-toluenesulphonamide, representing the last production step, is carried out either with potassium permanganate in alkaline media or with dichromate in approximately 70% H₂SO₄. Both oxidation processes have been optimized [1, 2] in such a way that yields of 86–90% are reached. The dichromate oxidation, although leading to a higher yield and to less side products, is a less suitable and more delicate operation because of the carcinogenic and toxic properties of chromium. The permanganate process, on the other hand, consumes the expensive oxidant whose regeneration from the resulting manganese dioxide is costly. A number of electrolytic oxidation processes [3–6] have been suggested among which the oldest directly oxidizing procedures made use of an anode formed by a thin PbO₂ layer formed on a platinum support with a lead counter electrode [3, 5]. The fundamental objection to this method of oxidation is based on the necessity to work with toxic lead and the possibility of lead contamination of the product. This shortcoming is also the fundamental disadvantage of further indirect oxidation [4] performed with redox systems such as Cr⁶⁺/Cr³⁺ or Ce⁴⁺/Ce³⁺.

In the present work, the possibility of direct electrolytic oxidation of o-toluenesulphonamide (o-TSA) to saccharine was investigated, making use of an electrocatalytically modified nickel anode. The electrocatalytic anode, prepared by depositing a black NiO(OH) layer on a nickel support with a nickel counter electrode, was successfully applied [7] to the production of vitamin C [8], and also in the oxidation of some primary aliphatic amines to nitriles and primary aliphatic alcohols to carboxylic acids [9]. This paper presents the results of our attempts to achieve a conventional electrolytical transformation of TSA to saccharine.

2. Experimental details and results

The o-TSA was donated by Spolana Factory Neratovice; its quality corresponded to an intermediate in chemical saccharine production. All other chemicals were AR quality. Distilled water
was used for preparing the electrolytes and the activation solution. The working electrodes were made either from available sheets of thickness from 0.3 to 0.4 mm or from sintered nickel electrodes used in alkaline batteries (product of Bateria at Slaný). The auxiliary electrodes were produced either from nickel or from graphite (produced by Elektrokarbon at Topolčany) or glassy-carbon (by Sigri Elektrographit, FRG).

In the present experiments a spiral ‘Swiss-roll’-type cell made from a nickel sheet was used. The nickel roll was placed in a vinyl flow-through cartridge with electrical screw contacts and molded inlet and outlet tubes for the electrolyte. A further all-glass, flange-mounted (sandwich) cell was also used (Fig. 1). This consisted of two symmetrical dish-shaped chambers with circular cross-section, a wide sealing edge and a double jacket bottom.

A separator or a Nafion membrane or both were placed in the sealing ring between the two halves of the cell. In this case, different disc-shaped electrodes with a diameter of about 60 mm were used. For aqueous media (even with co-solvents) a seal of silicon rubber proved satisfactory. The divided cell contained a cationic Nafion 901 membrane (DuPont, USA). The electrode system in the undivided cell consisted of parallel, connected plates of the working and auxiliary electrodes with total areas of about 7.5 and 8 dm², respectively, separated by polypropylene nets. The cells were connected into a circulation loop containing a storage flask, a magnetic pump and a regulating valve as shown in Fig. 2.

The two-phase electrolyte-gas mixture passed via a cooler to the storage vessel. The CO₂ content was assessed by absorption in a saturated aqueous solution of Ba(OH)₂, and O₂ concentration was determined polarographically by bubbling through 50% ethanolic 0.1 M NaOH. A polarograph enabled monitoring of oxygen during the experiment. A flow-through extraction cartridge made of PVC, filled with the starting TSA, was installed in the electrolytical circuit. This ensured a continuous saturation of the circulating electrolyte with the sparingly soluble starting substance.

Before the electrolysis proper the surface of the working electrode was activated with a solution of nickel(II) ions prepared according to [8]. On applying a voltage of 3–4 V a current of about 3–12 A passed through the cells. Before each experiment the working electrode was activated, after which both the cells and the circuit were rinsed with distilled water. The current and the charge were measured using a coulometric counter [10]. The potential of the working electrode was measured using an HP 3466 A multi-