JOURNAL OF APPLIED ELECTROCHEMISTRY **17** (1987) 1228–1233

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

JAROMÍR HLAVATÝ, VIKTOR BAKOS, JIŘÍ VOLKE

J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 118 40 Prague 1, Vlašská 9, Czechoslovakia

Received 23 January 1987; revised 16 May 1987

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 NH_2 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 bichromate in approximately 70% H_2SO_4. Both oxidation processes have been optimized [1, 2] in such a way that yields of 86–90% are reached. The bichromate 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 PbO_2 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 Cr^{6+}/Cr^{3+} or Ce^{4+}/Ce^{3+}.

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

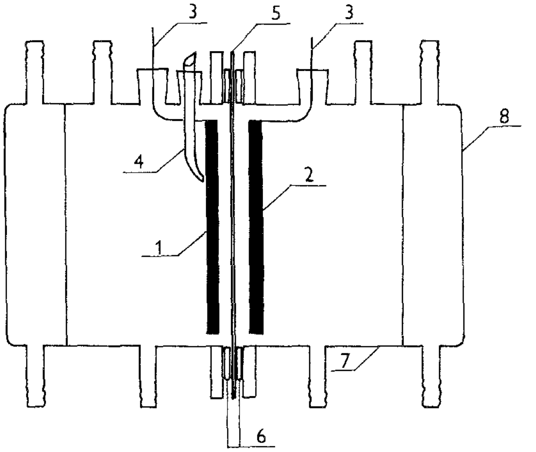


Fig. 1. Divided electrolytic cell: 1, Disc-shaped working electrode; 2, disc-shaped counter electrode; 3, electrode contact; 4, reference electrode; 5, Nafion 901 membrane; 6, gasket; 7, cell vessel; 8, thermostated jacket.

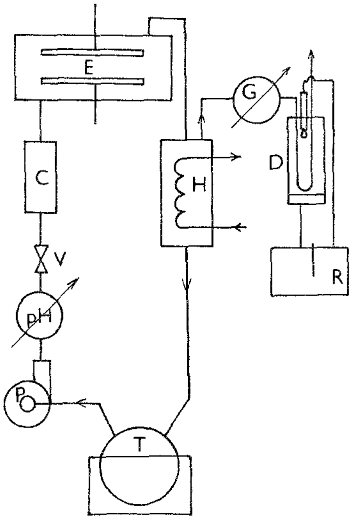


Fig. 2. Flow-sheet of the electrolytic loop with the undivided cell: C, extraction cartridge; E, undivided cell; D, vessel with a dropping mercury electrode; G, gasometer; H, heat exchanger; pH, pH meter; P, pump; R, polarograph; T, storage tank; V, valve.

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 dm^2, 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 CO_2 content was assessed by absorption in a saturated aqueous solution of $Ba(OH)_2$, and O_2 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 multimeter versus a Hg/HgO reference electrode (in approximately 1 M NaOH).

During the electrolysis, samples were taken for determining saccharine by polarography. The reduction wave of saccharine [11] did not prove useful, so the cathodic wave of the catalytic reduction of hydroxonium ions in unbuffered media was used instead. The analysis of the electrolyte containing Na_2CO_3 or NaOH was convenient because, upon diluting the sample with ethanol and treating it with a cation exchange resin (Dowex 50 W), CO_2 was liberated and the sample contained only the starting substance and possibly saccharine as an H-acid.

The sample, treated in this way, could also be used for TLC analysis. A 0.1 ml volume of the sample was added to 4.9 ml of an 0.1 M ethanolic solution of LiCl in the polarographic cell. In an unbuffered ethanolic LiCl solution saccharine yielded a reproducible cathodic wave at -1.3 V to -1.4 V (versus SCE), the height of which was directly proportional to the concentration over the range from 5×10^{-4} to 5×10^{-3} mol l^{-1}. Qualitative tests of the composition of the electrolyte were carried out by TLC with the following solvent system: CH_2Cl_2 + 10% (by volume) diethyl ether.

In electrolysis performed in NaOH solutions, sodium *o*-toluenesulphonate was the main product. This compound is easily soluble in water and crystallizes from concentrated solutions as colourless foil-like crystals which do not melt up to 360° C. The H^1-NMR and C^{13}-NMR spectra of this product suggested an intact CH_3 group in its structure ($\delta_{CH_3} = 20.37$). Elemental analysis yielded the following values: 39.64% C, 4.45% H, 11.8% S. The values calculated for sodium toluenesulphonate were as follows: $C_7H_7SO_3Na \cdot H_2O$ (molecular weight 212.23): 39.62% C, 4.28% H, 15.11% S.

In the polarographic analysis of electrolyte samples from experiments in NaOH a cathodic wave of hydroxonium ions was obtained which did not differ from that due to the presence of saccharine. Coincidentally, the spot given by the free toluenesulphonic acid in TLC appears at the same distance from the start as the spot of the saccharine standard. A differentiation was effected only by determination of the melting points.

The preparative electrolytic experiments were carried out in the following manner. The electrodes comprised a sintered nickel foil as the working anode and a glassy–carbon auxiliary cathode and were placed in an undivided glass cell. After activation both the cell and the electrolytic loop were rinsed with distilled water. In the next step the extractor cartridge with 30 g TSA was connected and an electrode for measuring the pH was inserted. The storage flask was filled with 1300 ml of a solution containing 50 g K_2CO_3. This solution was heated up to 50–60° C and the electrolyte was continuously saturated with the starting substance via the cartridge. The current density was 0.31 A dm^{-2} and the working electrode potential was $+0.76$ V (versus Hg/HgO/1 M NaOH electrode).

The course of electrolysis was followed by polarography, by TLC and by measurement of the electrical charge passed through the solution. The gaseous phase was passed through a wash bottle containing a $Ba(OH)_2$ solution. From the wash bottle the gas proceeded into the polarographic cell in which, after preceding deaeration, the dissolved oxygen was determined. The gaseous phase always contained about 10% (by volume) O_2. After 32 h of electrolysis a charge of 41.8 A h had passed, which corresponded to the calculated charge of 40.5 A h at 70% current efficiency referred to the quantity of the starting TSA. The electrolysis was stopped and the whole circuit loop, after discharge of the yellowish electrolyte, was rinsed with 1200 ml of hot distilled water. The electrolyte was cooled below 10° C and, by adding concentrated hydrochloric acid, its pH was adjusted to 5–6.

After removing the solvent and desiccating the product, 5.6 g of the non-reacted starting material crystallized (melting point from 140° C). A further acidification of the mother liquor with concentrated hydrochloric acid to pH 1–2 and cooling to 0–5° C led to the deposition of small colourless crystals of saccharine which, when filtered off and dried, weighed 4 g and gave a melting point of 222–224° C. After reducing the mother liquor volume by means of vacuum evaporation a mixture of the starting material and saccharine (weight 5.5 g) was deposited. The pure saccharine was isolated from the

Table 1. Preliminary electrolysis in water solutions

Cell type; working–auxiliary electrode	*Electrolyte*	*Current density ($A\,dm^{-2}$)*	*Temperature (° C)*	*Change in pH during electrolysis*	*Charge passed (A h)*	*Yield of saccharine (%)*
'Swiss roll' cell; NiO(OH)–Ni/Ni	0.66 M Na_2CO_3 0.35 M TSA added in portions	1	60–65	10.1 to 9.3	147	15
Flange-type cell; NiO(OH)–Ni/Ni	0.66 M Na_2CO_3	3.7	60	9.35 to 8.45	136.8	10
Flange-type cell; NiO(OH)–Ni/graphite	0.61 M Na_2CO_3	1.7	59–60	9.91 to 9.05	63	10
Stacked cell; NiO(OH)–Ni/carbon	0.85 M NaOH	0.53	40–44	12.15 to 8.65	266	–

mixture by the following procedure. The mixture and the residue, after evaporation of the washing water from the rinsing of the electrolytic circuit loop, was extracted with approximately 1 M NH_4OH at room temperature. After neutralizing and then acidifying the liquor with concentrated HCl to pH 1–2, 5.5 g of saccharine crystals resulted. The melting point was again 224–225° C.

Data for electrolyses under different conditions are summarized in Tables 1–3.

The oxidation to saccharine also proceeds at a slower rate at a lower temperature, such as 30° C. The use of co-solvents aimed at improving the solubility of the substrate and attaining a more favourable adsorption equilibrium did not increase the saccharine yield to the desired value (cf. Table 3). The electrolysis in a divided cell containing a Nafion membrane led to the evolution of oxygen in the separated anodic chamber and to the decomposition of the starting material. The yield was about 15% and 50–60% of the starting substance was recovered. With a lower voltage (1.5 V) the yield amounted to 30%. The starting *o*-TSA was, in part, oxidized to CO_2. The catalytic effect of black, active NiO(OH) on the oxidation of the methyl group in the *o*-TSA structure has also

Table 2. Electrolysis in water solutions with balance control

Cell type; working–auxiliary electrode	*Electrolyte*	*Current density ($A\,dm^{-2}$)*	*Temperature (° C)*	*Change in pH during electrolysis*	*Charge passed (A h)*	*Yield of saccharine (%)*
Stacked cell; NiO(OH)–Ni/graphite	0.71 M Na_2CO_3 0.175 M TSA	0.63	57–60	10.6 to 9.9	72	15
'Swiss roll' cell; NiO(OH)–Ni/Ni	0.43 M K_2CO_3 0.35 M TSA	1.0	60	10.5 to 8.1	195.6	15.5
'Swiss roll' cell; NiO(OH)–Ni/Ni	0.21 M Na_3PO_4 0.175 M TSA	0.75	52–56	10.2 to 9.9	63.2	20
Flange-type cell; NiO(OH)–Pt/Ni	0.58 M K_2CO_3 0.175 M TSA	0.8	57–59	10.6 to 10.1	67.8	15
Flange-type cell; NiO(OH)–sintered Ni/glassy-carbon	0.36 M K_2CO_3 0.175 M TSA	0.31	59–60	10.5 to 10.1	41.8	40
	0.36 M K_2CO_3 0.35 M TSA	0.28	59–60	10.5 to 9.3	85	37.5

Table 3. Electrolysis with co-solvents

Cell type; working–auxiliary electrode	*Electrolyte*	*Current density ($A\,dm^{-2}$)*	*Temperature (°C)*	*Change in pH during electrolysis*	*Charge passed (A h)*	*Yield of saccharine (%)*
Flange-type cell; NiO(OH)–sintered Ni/glassy–carbon	0.36 M K_2CO_3, 10% (vol.) dioxane, 0.175 M TSA	1.0	60	10.4 to 9.5	36.2	30
	0.36 M K_2CO_3, 5% (vol.) t-butanol, 0.175 M TSA	0.72	56–59	10.5 to 9.8	49.5	33
	0.36 M K_2CO_3, 5% (vol.) dioxane, 0.175 M TSA	0.51	60	10.4 to 9.8	40	35
Flange-type cell; NiO(OH)–Ni/glassy–carbon	0.36 M K_2CO_3, 24% (vol.) THF, 0.175 M TSA	0.36	30	10.5 to 9.7	47.4	30

been proved in the chemical oxidation by t-butylhypochlorite. In this reaction, proceeding in alkaline media (NaOH), saccharine was detected. The procedure, however, has not been studied in detail.

3. Discussion

The introductory experiment performed with a suspension of finely ground *o*-TSA in a sodium carbonate solution (Table 1) demonstrated the low solubility of the starting material, even at increased temperature and difficulties, due to its deposition on the active surface of the working electrode and in the meshes of the separator. When using the extractive dissolution of the starting material the crystallization of the starting substance in the electrolyser was considerably suppressed.

Table 1 shows the results of these experiments in which the influence of different current densities and also the application of a glassy–carbon counter electrode instead of a nickel one were investigated. During electrolysis most of the starting sulphonamide in the extractor cartridge was dissolved, but the highest yields of saccharine achieved amounted to only 15%.

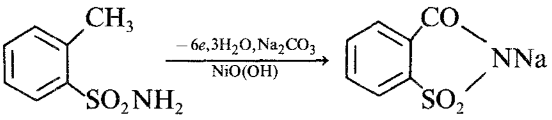
The use of different cells in the experiments detailed in Table 2 did not improve the yields. Sodium hydroxide, used as supporting electrolyte, easily dissolved the starting sulphonamide but, instead of saccharine, only *o*-toluenesulphonate resulted to a considerable degree. Its identity was confirmed by elemental analysis and NMR spectra; the white crystals do not melt up to 360° C. During the experiments with NaOH, ammonia could be smelt. The production of ammonia from the starting sulphonamide is caused by electrolysis, because a long-term treatment of the starting substance with NaOH at the same temperature without electrolysis does not affect the amidic group.

The cathodic wave of the catalytic reduction of hydrogen ions, applied for a quantitative assessment of the saccharine content in the electrolyte, increased during the electrolysis in NaOH solutions. However, this favourable result appeared to be false because it only corresponds to an increase in the concentration of the undesired *o*-toluenesulphonic acid formed as shown above. Since in the material balances, both of organic and inorganic components, there were a number of discrepancies, we turned our attention to systematically isolating all components of the electrolyte. A survey of experiments performed in this way is found in Table 2.

At the same time it was confirmed that even at a low current density and at a voltage of 2 V the gaseous phase also contained a considerable percentage of CO_2 in addition to O_2. Doubtless this was due to the aggressive action of O_2 evolved on the starting substance, resulting in its total degradation. This conclusion concerning the full degradation of organic compounds leading to

CO_2, H_2O, SO_2, NH_3 etc. through anodic oxygen effects has been discussed for various organic compounds [12]. The reported yield of 15–20% are referred to all the starting substances. After passing an electric charge corresponding to a 70% current efficiency with respect to the applied quantity of TSA, an average of 10–20% of the starting material was recovered. Ammonia cannot be used as the supporting electrolyte because it dissolves the active layer on the electrode with the formation of green solutions containing nickel.

The overall mechanism can be formulated as follows:



4. Conclusion

In the electrolytical oxidation of *o*-TSA in alkaline media at an electrode coated with NiO(OH), saccharine is formed. This attractive finding of the catalytic activity of NiO(OH) was also confirmed by an experiment in which a chemical oxidant was used. Further experiments revealed, however, that by direct electrolytic oxidation in an undivided cell and in alkaline carbonate media, 40% saccharine is the highest yield attainable. Strongly alkaline solutions of hydroxides lead to the splitting off of NH_3 in the electrolytic oxidation and to the formation of the *o*-toluenesulphonate. Even at the lowest current densities attainable (at +0.7 V versus Hg/HgO electrode) oxygen is formed at the anode and this contributes to a degradation of larger amounts of the starting substance. Attempts to remove these difficulties by using co-solvents in concentrations from 5–20% (by volume) in the electrolysis did not result in better yields.

References

[1] M. Grayson and Kirk-Othmer, 'Encyclopedia of Chemical Technology' Wiley and Sons, New York (1984) Vol. 14, p. 833; Vol. 6, p. 92.
[2] W. Gerhartz, 'Ullmanns Enzyklopädie der Technischen Chemie', Verlag Chemie Weinheim (1982) pp. 22, 356.
[3] H. Löwe, Schwz. Pat. P 94223 (1921).
[4] K. Durkes, Ger. Pat. 920 186 (1954); *Chem. Abstr.* **52** (1958) 19624.
[5] F. Fichter and H. Löwe, *Helv. Chim. Acta* **5** (1922) 60.
[6] N. V. Industrieelle Maatashappij, Holl. Pat. P 41 338 (1935); *Chem. Abstr.* **31** (1937) 8399.
[7] P. Seiler and P. M. Robertson, *Chimia* **36** (1982) 7–8, 305 and references cited therein.
[8] P. M. Robertson, Pat. D 2503819 Int. Cl^3 C 25 B 11/00 (1975).
[9] J. Klauen and H. J. Schäfer, *Tetrahedron* **38** (1982) 3299.
[10] J. Chaloupka, *Chem. Listy* **79** (1985) 762.
[11] V. Stará, *ibid.* **79** (1985) 992.
[12] F. Fichter, 'Organische Elektrochemie', Steinkopff, Dresden (1942) pp. 12–13, 75–85.