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*An electrolysis cell with close consecutive flow-through porous electrodes for particular organic electrosynthesis**

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Intermediates involved in ECE mechanisms cannot generally be obtained in a one-step electrosynthesis. A continuous two-step preparation can be achieved in a particular redox electrolysis cell using two closely consecutive flow-through porous electrodes of opposite polarities. For instance, with such a cell, nitroso compounds can be prepared with efficient yields from the corresponding nitrobenzenes.

1. Introduction

ECE mechanisms, involving a chemical reaction (C) between two electron transfer reactions (E) as shown in reaction 1 are frequently observed in organic electrochemistry.

$$S \overset{E}{\rightleftharpoons} I_1 \xrightarrow[\text{fast}]{C} I_2 \overset{E}{\rightleftharpoons} P \tag{1}$$

The I_2 intermediate can be obtained in two steps as observed by cyclic voltammetry (Fig. 1): the reduction of S to P (for a first cathodic process) and, after polarity reversal of the working electrode, the oxidation of P to I_2. However, in a classical electrolysis cell using a single working electrode the duration of each step is too large to prepare I_2 from S if the P intermediate is chemically unstable; moreover, a chemical reaction between P and I_2 can take place.

For instance, in aqueous acidic media, the cathodic reduction of nitrobenzenes leads to the corresponding arylhydroxylamine, according to an ECE mechanism [1]:

$$\mathrm{ArNO_2} \overset{+2e+2\mathrm{H}^+}{\rightleftharpoons} \mathrm{ArN(OH)_2} \xrightarrow{-\mathrm{H_2O}} \mathrm{ArNO} \overset{+2e+2\mathrm{H}^+}{\rightleftharpoons} \mathrm{ArNHOH} \tag{2}$$

If the arylhydroxylamine is sufficiently stable, it can be oxidized to nitrosobenzene but, generally, formation of an azoxy derivative is observed:

$$\mathrm{ArNO} + \mathrm{ArNHOH} \longrightarrow \mathrm{Ar{-}N{=}}\underset{\displaystyle\overset{\downarrow}{\mathrm{O}}}{\mathrm{N}}\mathrm{{-}Ar} + \mathrm{H_2O} \tag{3}$$

Preliminary studies have shown that it is possible to carry out continuous reduction of S to P and the further oxidation of P to I_2 by using an electrolysis cell in which the solution flows through two consecutive porous electrodes with opposite polarities ('redox cell' with two working electrodes).

The first redox cell with solution flowing through two closely spaced electrodes was described by

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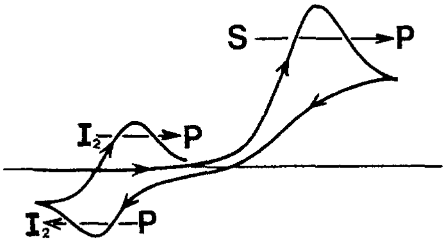

Fig. 1. Voltammogram for an ECE mechanism.

Braun and co-workers [2, 3] for voltammetric measurements. The cell of Kihara *et al.* [4] used two porous, glassy carbon electrodes and was developed for rapid determination of plutonium ions in solution; the disposition of two counter electrodes respectively associated to the working electrodes made the current field perpendicular to the electrolyte flow. In the cell described by Kenkel and Bard [5] for electroanalysis the two working electrodes were separated by a ring, and upstream and downstream counter electrodes were associated with the working electrodes.

We have studied various arrangements for redox cells with two porous working electrodes with or without auxiliary counter electrodes. First [6, 7], we described a cell with only two separated working electrodes for the synthesis of nitroso compounds from nitrobenzenes with stable hydroxylamine intermediates. Then, we used a cell with two porous working electrodes spaced by a thin porous insulator for the preparation of substituted butadienes by oxidation of unstable intermediate dianions resulting from the reduction of enol ethers [8].

Generally, for an ECE mechanism, the amount of electricity involved at the first working electrode is higher than that at the second. In order to avoid secondary electrochemical reactions at the second working electrode a counter-electrode must be used. Therefore, we proposed a general laboratory electrolysis cell [9] with a particular device especially adapted to carry out consecutive and opposite reactions: two closely consecutive porous working electrodes and an upstream counter electrode provide a good current distribution. More recently [10] we investigated (theoretically and experimentally) an analytical electrolysis cell using two closely consecutive flow-through electrodes and one (upstream) or two (upstream and downstream) counter electrodes. According to the same general design we built cells for preparative electrosynthesis. In the present paper, results obtained with these cells are compared to those obtained previously with analytical cells in the preparation of nitroso compounds from the corresponding nitrobenzenes.

2. General cell design and current distribution

The schematic diagram of the cell is shown in Fig. 2; it corresponds to a cathodic process followed by an anodic process. The general device is the same for preparative cells as for the previously described analytical cell [10].

The porous working electrodes (26.5 mm diameter for the analytical cell, 40 and 52.5 mm for the preparative cells) are made with graphite felt and are isolated by a thin glass microfibre filter. Fritted glass discs separate the working compartments and the two auxiliary upstream and downstream compartments.

The redox cell can be used with the following.

(i) One electrical circuit between the two porous working electrodes. The current intensities are the same at the working cathode and at the working anode ($i_{\mathrm{red}} = i_{\mathrm{ox}} = i_{\mathrm{v}}$; see Fig. 2).

(ii) Two electrical circuits, the first between the two porous working electrodes and the second between the upstream counter electrode and the first porous electrode, and the third between the intensity at the working cathode ($i_{\mathrm{red}} = i_{\mathrm{K}} + i_{\mathrm{v}}$; see Fig. 2) is higher than the current intensity at the working anode ($i_{\mathrm{ox}} = i_{\mathrm{v}}$); this disposition provides a good distribution of currents for cathodic

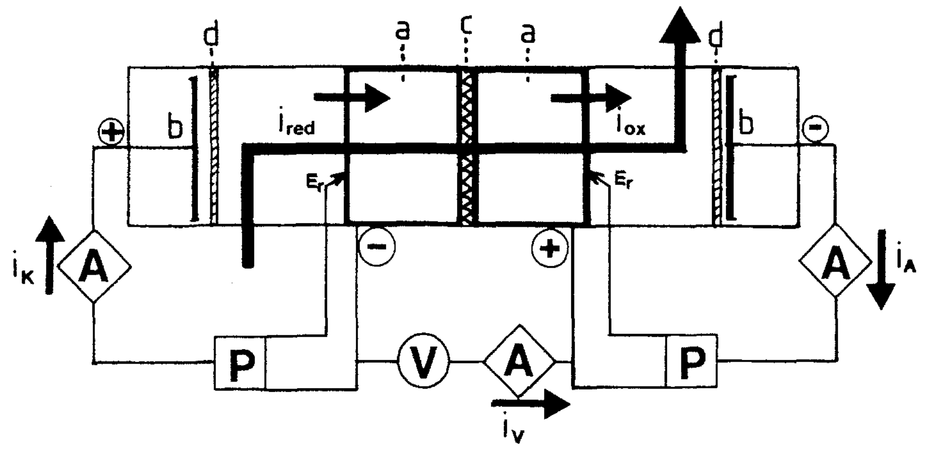

Fig. 2. Schematic diagram of the cell and current distribution with one ($i_K = i_A = 0$), two ($i_K \neq 0$ and $i_A = 0$) or three ($i_K \neq 0$ and $i_A \neq 0$) electrical circuits. A, ammeter; P, potentiostat; V, power supply; a, porous working electrode; b, auxilliary counter electrode; c, porous insulator; d, fritted glass separator; E_R, reference electrode; →, electrode flow circuit. $i_{red} = i_K + i_v$; $i_{ox} = i_A + i_v$.

and anodic processes (see Introduction). Also, a good potential distribution at the working cathode is obtained because this electrode is located between two counter electrodes (the upstream counter electrode and the working anode) [10–12].

(iii) Three electrical circuits, the first between the two porous working electrodes, the second between the upstream counter electrode and the first porous electrode, and the third between the second porous electrode and the downstream counter electrode. In this disposition it is possible to obtain a better potential distribution at the working anode than with only two electrical circuits; it is also possible to make the cathodic current intensity ($i_{red} = i_K + i_v$) higher than the anodic current density ($i_{ox} = i_A + i_v$).

However, a disposition with two electrical circuits generally leads to good results because the second working electrode is located after its counter electrode (the first working one) [6–10]. Because a steady-state is usually reached, the cell can be used with potentiostats or with power current supplies. The working potentials can be controlled at the inlet or at the outlet of the porous electrodes as shown in Fig. 2.

3. Experimental details

The electrolyte was deaerated with nitrogen gas and pumped through the cell from a reservoir using a peristaltic pump. The outlet solution was collected under N_2 gas for polarographic analysis (chemical yield determination) before isolation of the final product. The electrolyte flow rate was measured from the outlet solution.

For the isolation of 3,4-dichloronitrosobenzene a large amount (two parts) of water was added to the outlet solution to precipitate the nitroso compound. After filtration the crude residue was quickly steam-distilled.

For the isolation of 3-nitrosophthalic acid from the outlet solution, the following procedure was used. Between 70 and 80% of the water was removed *in vacuo* from the buffer solution, then a concentrated HCl aqueous solution was added to the residual solution. The acidic solution was quickly extracted with ether or ethylacetate and the extract was dried over $MgSO_4$. After removal of the solvent the crude 3-nitrosophthalic acid was obtained.

Table 1. Use of electrolysis cell with two close consecutive porous electrodes and two electrical circuits (graphite felt electrodes; 26.5 mm diameter for A cell, 40 mm for B cell and 52.5 mm for C cell; 6 mm thickness for each electrode) in synthesis of 3-nitrosophthalic acid from 3-nitrophthalic acid ($2\,g\,l^{-1}$ in acetic buffer 0.5 M CH_3CO_2H + 0.5 M CH_3CO_2Na). Electrolyte flow rate, v

Cell	v ($cm^3\,mm^{-1}$)	i_K (mA)[a]	i_v (mA)[a]	y^{ch}_{red} (%)[b]	y^{e}_{red} (%)[b]	$(NO)/(NO_2)_0$ (%)[c]
A	2.7	81	83	95	95	95
B	6.0	180	185	92	92	92
C	9.8	290	310	89	89	89

[a] For current distribution see Fig. 2.
[b] y^{ch}_{red} and y^{e}_{red}: chemical and electrical yields for cathodic process (polarographic analysis).
[c] $(NO)/(NO_2)_0$: nitroso chemical yield relative to the starting material (polarographic analysis).

4. Application for the synthesis of aromatic nitroso compounds from nitrobenzenes

General methods for the chemical synthesis of nitroso compounds from nitrobenzenes involve two steps (see e.g. [13]). The first step, the reduction of nitrobenzene in aqueous medium with zinc powder, yields phenylhydroxylamine:

$$ArNO_2 + 2Zn + H_2O \longrightarrow ArNHOH + 2ZnO \qquad (4)$$

and in the second step the nitroso compound is obtained from phenylhydroxylamine by acidified sodium dichromate (or $FeCl_3$) oxidation:

$$3ArNHOH + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3ArNO + 2Cr^{3+} + 7H_2O \qquad (5)$$

To prepare nitroso compounds with a good chemical yield, hydroxylamine intermediates must be stable and the last reaction must be fast and complete to avoid the azoxy formation according to reaction 3. The cathodic reduction of nitrobenzenes can be a convenient method of preparing stable hydroxylamines [14], but the anodic oxidation of the latter in a classical electrolysis cell is too slow compared with the rate of condensation [15] (reaction 3) to avoid the formation of a large amount of azoxy derivatives.

The use of an electrolysis cell with closely consecutive flow-though porous electrodes of opposite polarities (see Introduction) is of interest for the synthesis of nitroso compounds from nitrobenzenes according to the following sequence

$$ArNO_2 \xrightarrow[-H_2O]{+4e+4H^+} ArNHOH \xrightarrow{-2e-2H^+} ArNO \qquad (6)$$

Because of the high efficiency of three-dimensional porous electrodes, high rates of chemical transformations are obtained for very short contact times between the solution and the cathode or the anode. Thus, it is possible to prepare nitroso compounds with high yields resulting from relatively unstable hydroxylamines and also to avoid azoxy formation.

4.1. *Analytical study of nitroso compound synthesis in a redox electrolysis cell*

4.1.1. The hydroxylamine intermediate is relatively stable. To compare the efficiency of electrolysis cells of different sizes (analytical cell, 26.5 mm diameter [10], and scale-up cells 40 and 52.5 mm diameters) we studied the synthesis of 3-nitrosophthalic acid from 3-nitrophthalic in aqueous acetic buffer according to reaction 6.

Results are shown in Table 1. The electrolyte flow rates and the current intensities are adjusted to the same value per unit area of the working electrode. We generally observe good chemical and electrical yields, but the electrical yields, and as a result chemical yields, decrease slightly with increase of electrode size.

Table 2. Use of electrolysis cell with two close consecutive porous electrodes and two or three electrical circuits (carbon felt electrodes; 26.5 mm diameter; 6 mm thickness for each electrode) in synthesis of 2-nitroso acetanilid from 2-nitro acetanilid; ($2\,g\,l^{-1}$ in $1\,N\ H_2SO_4$ + 50% ethanol by volume). Electrolyte flow rate, $2.9\,cm^3\,min^{-1}$

i_K (mA)[a]	i_v (mA)[a]	i_A (mA)[a]	y^{ch}_{red} (%)[b]	y^{ch}_{ox} (%)[b]	$(NO)/(NO_2)_0$ (%)[c]
180	0	90	89	57	51
140	40	50	94	62	58
90	90	0	92	59	54

[a] For current distribution see Fig. 2.
[b] y^{ch}_{red} and y^{ch}_{ox}: chemical yields for cathodic and anodic process (polarographic analysis).
[c] $(NO)/(NO_2)_0$: nitroso chemical yield relative to the starting material (polarographic analysis).

4.1.2. The hydroxlylamine intermediate is relatively unstable. In hydroalcoholic medium ($1\,N\ H_2SO_4$ + 50% ethanol by volume) the evolution of hydroxylamine resulting from the reduction of 2-nitroacetanilid is fast ($t^{1/2} = 3s$) [10]. However, it is possible to prepare the nitroso compound, according to reaction 6, with relatively good yields (Table 2). The chemical yields depend on the current distribution and the best yield is obtained with three electrical circuits; a better potential distribution at the two working electrodes is probably then achieved.

4.2. *Large-scale preparation of nitroso compounds in a redox electrolysis cell*

A redox cell with electrodes of diameter 52.5 mm was used to perform large-scale preparation of nitrosobenzenes according to reaction sequence 6. Two nitrobenzenes were selected for the experiments: 3,4-dichloronitrobenzene is soluble in hydroalcoholic solutions (acetic buffer, 2.5 M CH_3CO_2H + 2.5 M CH_3CO_2Na + 80% ethanol by volume) and 3-nitrophthalic acid is soluble in aqueous solution (acetic buffer, 0.5 M CH_3CO_2H + 0.5 M CH_3CO_2Na or phosphate buffer, 0.25 M NaH_2PO_4 + 0.25 M Na_2HPO_4).

4.2.1. Electrosynthesis of 3,4-dichloronitrosobenzene. (NB. The produced nitroso derivative is less soluble than the starting nitro compound and can precipitate in the working anode compartment for concentrations higher than $3\,g\,l^{-1}$.) The results are shown in Table 3. Good yields are obtained and were controlled by polarographic analysis of the electrolysed outlet solution; however, the yield notably decreases after precipitation and steam-distilled purification of the crude 3,4-dichloronitrosobenzene (see Experimental details).

4.2.2. Electrosynthesis of 3-nitrosophthalic acid. In acetic and phosphate buffers the 3-nitrosophthalic acid is prepared with relatively good yields (Table 4). However, in the more acidic buffer the

Table 3. Electrosynthesis of 3,4-dichloronitrosobenzene from 3,4-dichloronitrobenzene (2 g in 1 litre of acetic buffer 2.5 M CH_3CO_2H + 2 .5 M CH_3CO_2Na + 80% ethanol by volume). Electrolysis cell with two close consecutive porous electrodes and two electrical circuits (graphite felt electrodes, 52.5 mm diameter, 6 mm thickness for each electrode). Electrolyte flow rate, $10\,cm^3\,min^{-1}$

i_K (mA)[a]	i_v (mA)[a]	y^{ch}_{red} (%)[b]	Weight (yield) (g) (%)[c]	Purity (%)	m.p. (°C)
300	310	78	0.87 (47)	99.5	90

[a] For current distribution see Fig. 2.
[b] y^{ch}_{red}: chemical yield for cathodic process (polarographic analysis).
[c] Weight of isolated compound from 2 g of starting nitrocompound (see Experimental details).

Table 4. Electrosynthesis of 3-nitrosophthalic acid from 3-nitrophthalic acid (4 g in 1 litre of acetic buffer 0.5 M CH_3CO_2H + 0.5 M CH_3CO_2Na (A) or phosphate buffer 0.25 M NaH_2PO_4 + 0.25 M Na_2HPO_4 (B)). Electrolysis cell with two close consecutive porous electrodes and two electrical circuits (graphite felt electrodes, 52.5 mm diameter; 6 mm thickness for each electrode). Electrolyte flow rate, v

Medium	v *(cm^3 mn^{-1})*	i_K *(mA)*[a]	i_v *(mA)*[a]	y^{ch}_{red} *(%)*[b]	*Weight (g)*[b]	*Purity (%)*	*m.p. (decomposition) (°C)*
A	8.9	490	500	94	3.3	86	185
B	5.1	310	310	89	3.6	85	220

[a] For current distribution see Fig. 2.
[b] y^{ch}_{red}: chemical yield for cathodic process (polarographic analysis).
[c] Weight of isolated compound from 4 g of starting material (see Experimental details).

formation of trace amounts of 3-aminophtalic acid at the cathode could explain the presence of 3-azophthalic acid as by-product in the isolate compound:

$$ArNO + ArNH_2 \longrightarrow ArN{=}NAr + H_2O \qquad (7)$$

In the less acidic buffer, no 3-azophthalic acid was indicated by polarography in the electrolysed outlet solution or in the isolated compound (see Experimental details).

The purity of the crude 3-nitrosophthalic acid is approximately 85%; the major by-product is the starting 3-nitrophthalic acid. No method was found to purify the crude product.

5. Conclusion

An electrolysis cell with close consecutive flow through porous electrodes has been shown to be efficient for the electrochemical preparation of nitrosobenzenes from the corresponding nitrobenzenes. Good yields are achieved in a one-step operation. It is worth noting that such compounds are difficult to obtain using classical chemical or electrochemical methods. Such a redox electrolysis cell might well be useful for the electrosynthesis of intermediates involved in various ECE mechanisms.

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