CHEMISTRY LETTERS, pp. 1989-1992, 1987.

Hydrogenation of Benzene Ring by Paired Electrosynthesis with Raney-Nickel Cathode

Tsukasa YAMADA, Tetsuo OSA, and Tomokazu MATSUE[†]
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980
[†]Department of Applied Chemistry, Tohoku University, Aobayama, Sendai 980

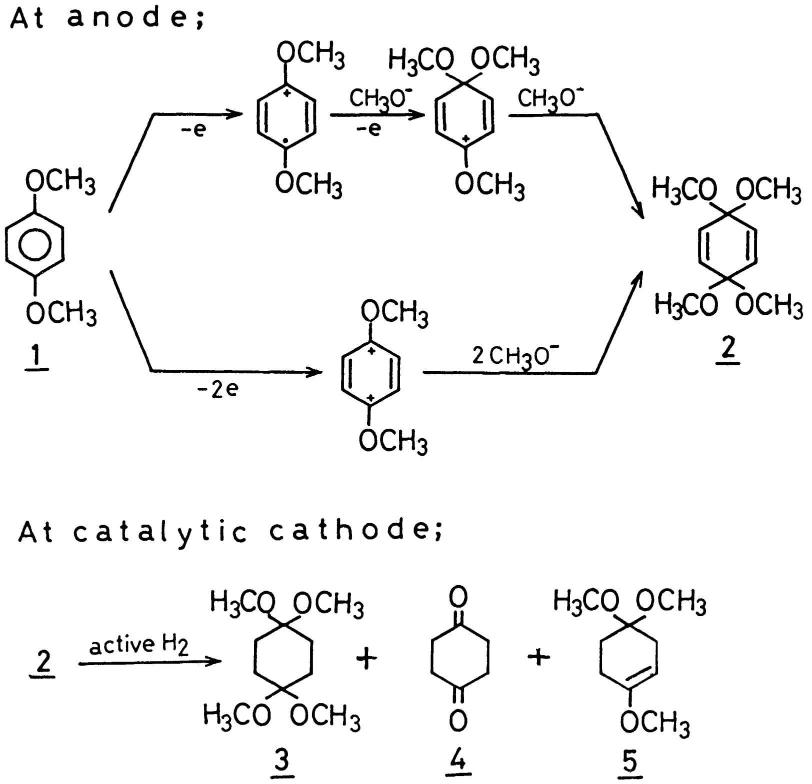
Paired electrolysis with 1,4-dimethoxybenzene (1) as a substrate was studied. Hydrogenation of the aromatic ring occurred to produce 1,4-cyclohexanedione (4) and two derivatives on Raney-nickel cathode. Two derivatives were converted into 4 by treatment of HCl aqueous solution. The total yield of 4 was 60% based on 1, whereas 4 was not formed on a platinum or lead cathode.

Paired electrosynthesis, using both cathodic and anodic reactions, sometimes provides convenient ways to produce useful compounds which are either difficult or impossible to be synthesized by one-pot chemical reactions. We have reported a one-pot addition reaction of an alcohol to a carbon-carbon double bond previously.[1)] We present here a hydrogenation reaction of the aromatic ring of 1,4-dimethoxybenzene (1) by a stepwise paired electrolysis, taking advantages of the unique characteristics[2-5)] of the Raney-nickel (R-Ni) cathode. Weinberg et al. published the electrochemical methoxylation of methoxybenzenes and related compounds.[6,7)] They obtained 1,4-benzoquinone tetramethyl acetal (2) in 88% yield in KOH/CH_3OH solution on platinum anode, and described the reaction mechanism in which 1 is converted to 2 *via* a direct discharge process and not by $CH_3O\cdot$.[7)] Nishiguchi et al. have also reported the conversion of 1 to 2 by electrooxidation process, and 2 was hydrogenated to 1,4-

cyclohexanedione tetramethyl acetal (3) by ordinary Pd-C catalytic process.8) However an electrochemical synthesis from 1 to 1,4-cyclohexanedione (4) or to its equivalent compounds have not been published. Such a direct electroreduction needs a very negative potential and does not provide a useful synthetic method. Hydrogenation of 1 is often performed by Birch reduction or catalytic hydrogenation under high H_2 pressures.

The electrolysis was carried out using a conventional divided (glass filter) H-type cell with a R-Ni powder (1.0 g) cathode and a platinum plate (50 cm^2) anode under a constant current (300 mA, which anodic potential corresponds to 2.4 V vs. SCE). The electrolyte was a methanolic solution (anolyte and catholyte; 50 ml) containing 2 M (1 M = 1 mol dm^{-3}) of CH_3ONa as a supporting electrolyte. To the anolyte 1 (40.0 g dm^{-3}) was added. The anode and the cathode were swapped after 2 x 96500 C mol^{-1} of electric charge. The final products were 3, 4, and a compound discussed later.

We have separately investigated the individual reactions. A plausible reaction mechanism of the present electrolysis is shown in Scheme 1, which is the same as presented in the anodic reaction of 1 by Weinberg et al.6,7) In anodic macro-electrolysis, 1 was converted into 2 in 83% yield. Cyclic voltammograms with platinum disk anode in 0.1 M $(C_2H_5)_4NClO_4/CH_3OH$ are shown in Fig. 1. The results show that the oxidation of CH_3O^- seems to occur at ca. 1.2 V vs. SCE, and that of 1 over 1.4 V.9) The formation of 2 was not observed when a macro-electrolysis was carried out



Scheme 1. Possible reaction mechanism.

at 1.2 V *vs*. SCE. In the first step, therefore, a cationic species (cation radical or dication) is probably formed by discharge of the aromatic ring, then reacts with CH_3O^- or $CH_3O^{\bullet}$ to yield 2, though our electrolyte of $NaOCH_3/CH_3OH$ differed from Weinberg et al's one of KOH/CH_3OH.[7)] The addition of 1 to the electrolyte solution resulted in a decrease in the peak current. This phenomenone may be due to the adsorption of the substrate, which retards the electrochemical oxidation of CH_3O^-.

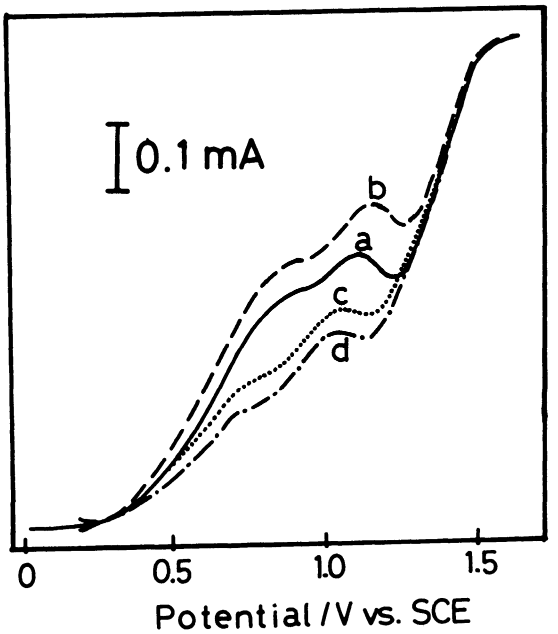


Fig. 1 Cyclic voltammograms with a platinum disk electrode.
Electrolyte; 0.1 M (1 M = mol dm^{-3}) $(C_2H_5)_4NClO_4$ in CH_3OH.
Additives; a) 1.0 mM $NaOCH_3$, b) 2.0 mM $NaOCH_3$, c) 1.0 mM $NaOCH_3$ and 1.0 mM of 1, c) 1.0 mM $NaOCH_3$ and 2.0 mM of 1.
scan rate; 100 mV s^{-1}.
Platinum disk area; 7.07 x 10^{-2} cm^{-2}.

In cathodic reaction, the catalytic hydrogenation proceeded smoothly, and 3 (45%) and a small amount of 4 (6%) were obtained on the R-Ni electrode. Another product, possibly 4-methoxy-3-cyclohexenone dimethyl acetal (5), which was changed to 4 by treatment with 3 M HCl aqueous solution, was also yielded (24%). Total current efficiency for the formation of 3, 4, and 5 was 77%. When 1 was added to the anolyte and 2 to the catholyte, 2 and the derivatives of 4 (3 and 5) were obtained in anodic and cathodic compartments, respectively, by the electrolysis in high current efficiencies. The electrolyses of 1 using a cylinder-type cell without a separator also afforded 4 and the two equivalent compounds, however the current efficiencies for the formation of the desired products were 4-10%. Therefore, a suitable structure of electrolysis cell, such as a flow-type one, will furthermore improve the current efficiencies.

We also studied the cathodic reaction of 2 on a platinum plate (50 cm^2) or a lead plate (50 cm^2) electrode, but the hydrogenation product such as 3 was not detected. The major product was the starting material 1 on both electrodes, and by-products, presumably dimerization compounds, also formed considerably on the lead electrode. These results are summarized in Table 1.

The overall reaction of the present electrolysis is to afford 4 and the equivalent compounds (3 and 5) from 1 . After the electrolysis, the catholyte was treated with 3 M HCl aqueous solution to convert 3 and 5 into 4 (isolated yield of 4 based on 1; 60%). As a result, the hydrogenation of the benzene ring of 1 is performed under mild conditions.

Table 1. Cathodic reaction of 2[a)]

Cathode	Yield / %			
	1	3	4	5
R-Ni	24	45	6	24
Pt-plate	60	trace	0	0
Pb-plate	42	0	0	0

a) Result at 4 x 96500 C mol^{-1} of electric charge.

Optimized electrolyte composition, suitable conditions of electrolysis, and other substrates to be applied are now under investigation.

This work is partly supported by a Grant-In-Aid for Special Project Research (No. 62101006) from the Ministry of Education, Science and Culture of Japan.

References

1) T. Yamada, T. Osa, and T. Matsue, Chem. Lett., 1987, 995.

2) T. Chiba, M. Okimoto, H. Nagai, and Y. Tanaka, Bull. Chem. Soc. Jpn., 56, 719 (1983).

3) M. Fujihira, A. Yokozawa, H. Kinoshita, and T. Osa, Chem. Lett., 1982, 1089.

4) T. Osa, T. Matsue, A. Yokozawa, T. Yamada, and M. Fujihira, Denki Kagaku, 53, 104 (1985).

5) T. Osa, T. Matsue, A. Yokozawa, and T. Yamada, Denki Kagaku, 54, 484 (1986).

6) B. Belleau and N. L. Weinberg, J. Am. Chem. Soc., 85, 2525 (1963).

7) N. L. Weinberg and B. Belleau, Tetrahedron, 29, 279 (1973).

8) I. Nishiguchi, T. Hirashima, H. Mizumoto, Y. Kataoka, K. Okumura, and N. Kanayama, Kagaku To Kogyo 60, 107 (1986).

9) In the reference 8, the half-wave oxidation potential of 1 is given to be 1.34 V vs. SCE in KOH/CH_3OH solution.

(Received August 8,1987)