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ASYMMETRIC SYNTHESIS BY MODIFIED RANEY NICKEL POWDER ELECTRODES

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A new enantioselective electrochemical hydrogenation of achiral ketones by Raney nickel powder electrodes modified with optically active tartaric acids is described. 2-Hexanone was reduced to 2-hexanol at ca. -1.0 V vs. SCE in a high current efficiency of more than 67%. The reduction on the unmodified Raney nickel powder electrodes gave alcohol with no optical rotation, whereas on the modified powders with (R,R)-(+)-tartaric acid, the optical purity between 2-6% (av. 4%) for (S)-(+)-2-hexanol was obtained. When Raney nickel was modified with (S,S)-(-)-tartaric acid, the enantiomer, (R)-(-)-2-hexanol, was formed with almost the same optical purity. The similar results were obtained for the reduction of 2-heptanone and 2-octanone.

This letter deals with the enantioselective hydrogenation of achiral ketones by Raney nickel powder electrodes modified with optically active tartaric acids. For these several years, the study of chemically modified electrodes (CME)1) has been one of the most attractive fields in electrochemistry. Several attempts have been made to fabricate the CMEs for various kinds of applications such as electrocatalysis2), photosensitization3,4), protection of semiconductor electrodes from photocorrosion5), photoelectrocatalysis6), analytical sensors4,7), display devices8), and selective electrosynthesis9-12). However, progress in the last application has been slow so far in spite of the pioneering work in the field on chiral electrodes by Miller and co-workers10). After their early publications, only our studies of regio-11) and species-selective12) electrosyntheses by cyclodextrin modified electrodes have been added in the literature.

In so far as chiral synthesis is concerned, miscarriage of the strategy may have been the cause of failure to attain satisfactory results. In a sense, Miller and co-workers10) followed the idea developed by Grimshaw13), Horner14), and others 15,16), who used optically active supporting electrolytes which are involved in the construction of the electrical double layer and influence the mode of adsorption of the substrate and therefore the stereochemical course of the reaction. These investigators10, 13-16) have used the electrode materials catalytically inactive for hydrogen such as Hg, Pb, Cd, carbon, etc., and consequently the electrochemical reduction proceeded *via* a so-called EC (or ECEC) mechanism, i.e., hydrogenation was attained by the successive transfer of electrons and protons17,18). However, even in the alcohol formation the whole process by transfer of two electrons and two protons *in toto* does not necessarily occur in the double layer for all products. In other words, the thickness of the reaction layer may be greater than that of the dimension of the double layer and therefore part of the reaction may proceed outside of the double layer[18].

On the other hand, hydrogenation proceeds always at the electrode surface when we use a catalytically active electrode for hydrogen which is made of nickel or a metal of the platinum group. On these metals, atomic hydrogen chemisorbed on the metal is formed first from protonic solvent, e.g., alcohol, at a more positive potential than the potential for the reduction of the carbonyl compounds *via* the EC mechanism and then hydrogenation is completed by the attack by the surface atomic hydrogen upon the carbonyl moiety of the substrate as proceeds in catalytic hydrogenation.[19] Consequently we can expect that the control of the stereochemical course of the reaction by the chemical modification of the electrode surfaces is more effective on the catalytically active electrodes than on the inactive electrodes. The enantioselective catalytic hydrogenation by modified Raney nickel has already been successfully attained by the pioneering work done by Izumi and coworkers[20].

Preparation of chiral Raney nickel with tartaric acid was carried out according to these authors' method[21]. The electrochemical cell was a conventional divided H-type cell. For making contact with the nickel powder, a nickel plate electrode (15 cm^2) with a nickel lead was first placed on the bottom of cathodic chamber on which then ca. 1.4 g of the modified powder was stacked in the presence of an electrolyte solution of ca. 60 cm^3 methanol containing 0.5 mol dm^{-3} LiCl and 2 cm^3 of substrate 2-hexanone. The electrolysis was carried out under nitrogen by the controlled current (with an auxiliary electrode made of Pt gauze) or the controlled potential conditions (with an additional saturated calomel electrode (SCE)) using a Yanaco VE-8 controlled potential electrolyzer. After electrolysis, the catholyte was first neutralized by HCl and then extracted with ether. The ether solution was concentrated with a rotary evaporator, and the residue was finally distilled. The products were identified by comparison of the gas chromatographic peaks and their boiling points with those of authentic samples. The main product was 2-hexanol with b.p. of 138 °C; the amounts of by-products except hydrogen gas were very small. The optical purities (P_o) defined as $100\times[\alpha]_D^{20}/[\alpha]_{D,max}^{20}$ were determined with a JASCO DIP-4 polarimeter on the basis of $[\alpha]_{D,max}^{20} = +12.7°$ (0.0524 g cm^{-3} in absolute ethanol) reported[22] for optically pure (S)-(+)-2-hexanol.

The reduction of aliphatic ketones in alcoholic solutions on mercury cathode usually takes place at potentials more negative than -2.0 V vs. SCE[23]. However, on the present Raney nickel powder electrodes 2-hexanone was reduced to 2-hexanol at ca. -1.0 V vs. SCE in a high current efficiency of more than 67%. Here current efficiency is defined as the percentage of the total electrons transferred which are utilized in the formation of the desired product. Namely, about 1.5 times of the theoretical charge on the basis of two electrons per ketone molecule was enough to complete the reduction. Most of the ineffective charge was consumed for the formation of hydrogen gas escaping from the catholyte.

The reduction on the unmodified Raney nickel electrode gave the alcohol with no optical rotation, whereas on the powder electrode modified with (R,R)-(+)-tartaric acid, the P_o value between 2-6% (av. 4%) for (S)-(+)-2-hexanol was obtained under the controlled current (0.05A or 0.1A) or controlled potential (-1.0 V vs. SCE) conditions. The P_o values were affected by the modification and electrolysis conditions.

The higher P_o values were obtained when Raney nickel powders were modified twice; the same modification procedure was repeated twice by the newly prepared modifying solution, and/or when a lower current was passed in the controlled current electrolysis. In Table 1 is shown the effect of current on the P_o values of 2-hexanol formed on the twice-modified Raney nickel powder electrodes in the controlled current electrolysis. As shown in Table 2, the similar P_o values were obtained for the reduction of other 2-alkanones such as 2-heptanone and 2-octanone.

Table 1. Effect of current on optical purities of 2-hexanol formed on twice-modified Raney nickel powder electrodes in the controlled current electrolyses

pH[a)]	0.03 A	0.05 A	0.10 A
	P_o / %		
3.2	6.7	2.8	2.9
3.3	5.1	2.3	3.6
3.6	6.4	5.9 3.4	2.7
3.8	6.5	4.5	1.9
3.9	4.0	9.3 3.5 5.0 5.0	3.0
4.2	9.0	6.1	2.5
av.	6.3	4.8	2.8

a) pH of modifying solution

Table 2. Enantioface-differentiating electrochemical hydrogenation of 2-alkanones on Raney nickel powder electrodes modified with (R,R)-(+)-tartaric acid[a)]

Substrate	pH[b)]	$[\alpha]_D^{20}$	P_o /%[c)]
2-Heptanone	3.90	0.67	5.9
	3.80	0.48	4.2
2-Ocatnone	3.80	0.51	5.2
	3.20	0.62	6.3

a) controlled current electrolysis (0.05 A). b) pH of modifying solution. c) calculated on the basis of reported $[\alpha]_{D,max}^{20}$ values.[22,24)]

When Raney nickel was modified with (S,S)-(−)-tartaric acid, an optical rotation of the opposite sign was observed and the P_o value of (R)-(−)-2-hexanol was almost the same as observed for (S)-(+)-2-hexanol described above.

The P_o values obtained in the present experiment were less than those obtained in the catalytic hydrogenation, although its current and chemical efficiencies were high. However, even in the catalytic hydrogenation, 2-hexanol also gave a lower P_o value (ca. 30%) compared with other substrates[25)]. As a cause of the low P_o value the following interpretation is now presented[26)] : 2-hexanone can interact strongly with tartaric acid adsorbed on the nickel surface only through one hydrogen bonding between its one carbonyl group and one of two hydroxyl groups of tartaric acid and consequently the enantioface-differentiating ability of the modified surface is low, while the higher enantioface-differentiation is attained for the substrates forming two hydrogen bonds with the surface tartaric acid. Such compounds of two hydrogen bonds as acetylacetone, methyl acetoacetate, and 4-hydroxy-2-butanone are now under investigation.

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