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Product-selectivity Control in Electroreduction of Aromatic Carbonyl Compounds Using Electrodes Coated with LB-films of a Quaternary Ammonium Salt[1)]

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Glassy carbon electrodes coated with LB(Langmuir-Blodgett)-films of a dimethyldioctadecylammonium salt were prepared and used for the electroreduction of aromatic carbonyl compounds to give high selectivities for the corresponding hydrodimers. The selectivities were comparable to those obtained at an uncoated electrode in catholytes containing ordinary quaternary ammonium salts(10 - 100 mM (1 M = 1 mol dm^{-3})) as co-supporting electrolytes. The coated electrodes seemed to be stable during the electrolysis.

Quaternary ammonium salts are favorably used as supporting electrolytes for reasons of their high solubility in a variety of solvents and high resistivity to cathodic reduction and anodic oxidation. It is also well-known that quaternary ammonium salt electrolytes apparently increase hydrogen overvoltages of cathodes in aqueous media and consequently increase current efficiencies for cathodic reactions. Moreover, in some kinds of electroreductive dimerization reactions of organic compounds such as activated olefins[2)] and carbonyl compounds,[3)] selectivities for the corresponding hydrodimers sre increased by using quaternary ammonium salt electrolytes. These effects may be attributed to the formation of hydrophobic layers of quaternary ammonium cations adsorbed on the cathodes.[4)] However, the use of quaternary ammonium salts as the supporting electrolytes is unfavorable from a

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practical aspect, since they are generally expensive and also must be used in high concentrations. In this viewpoint, we had an idea; that is to extremely diminish the amounts of quaternary ammonium salts used in electrolysis by fixing(coating) them in thin layers on the cathodes. In order to realize this idea, it was attempted to prepare an electrode coated with LB(Langmuir-Blodgett)-films of quaternary ammonium salts and use it for synthetic electrolysis which was chosen as an example.

A stable electrode coated with the LB-films could be prepared by the method of trial and error. A glassy carbon plate(3 x 3.5 cm) was coated with the bilayered LB-films of dimethyldioctadecylammonium poly(vinylsulfonate)5) at 38 $mN\,m^{-1}$ of surface pressure by an ordinary method.

Electrolysis for the reduction of benzaldehyde was carried out potentiostatically at -1.4 V(SCE) of cathode potential by passing 0.8 F(1F = 96484.56 C) mol^{-1} of electricity in a divided cell. The catholyte was an acetate buffer solution(pH 5, H_2O : methanol = 9 : 1, 50 cm^3) containing 1 mmol of benzaldehyde. The LB-films did not cause any significant increase in electric resistance on the electrode. The reduction products, dihydrobenzoin(hydrodimer) and benzyl alcohol(hydromonomer), were analyzed by HPLC(Zorbax-ODS column, H_2O : MeOH = 3 : 1).

Figure 1 shows relationships between product-selectivity and the number of layers of the bilayered LB-films coated. The formation ratio of dihydrobenzoin to benzyl alcohol increased approximately six times when the cathodes coated with more than three layers were used, while the stereoselectivity(*dl/meso* ratio) of dihydrobenzoin was unchanged.

As shown in Table 1, the use of an uncoated glassy carbon cathode in a similar catholyte containing tetramethylammonium chloride as a co-supporting electrolyte also resulted in an increase in the selectivity for dihydrobenzoin, but the *dl/meso* ratio decreased to 0.64. The ratio of dihydrobenzoin to benzyl alcohol obtained in a 100 mM tetramethylammonium chloride catholyte seems to be comparable to those at the cathodes coated with more than three layers of the LB-films. The decrease in the *dl/meso* ratio is interesting from a mechanistic aspect, compared with the case of the coated electrode, but the reason has not been made clear at present.

Total current efficiencies for dihydrobenzoin and benzyl alcohol were in a range of 62 - 70% and any significant change was not observed in all the electrolyses.

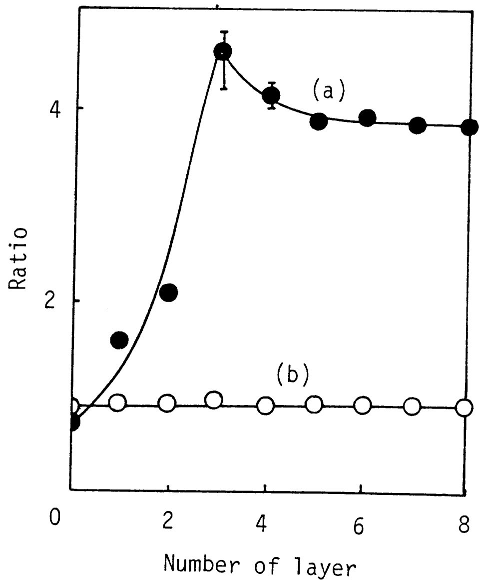

Fig. 1. Product-selectivity in the reduction of benzaldehyde at electrodes coated with various numbers of layers of LB-films of dimethyldioctadecylammonium poly(vinylsulfonate) in the absence of Me_4NCl co-supporting electrolyte. (a) Formation ratio of dihydrobenzoin/benzyl alcohol, and (b) *dl/meso* ratio of dihydrobenzoin.

Table 1. Product-selectivity in the reduction of benzaldehyde at an uncoated electrode in the presence of Me_4NCl co-supporting electrolyte

Concn of Me_4NCl / mM	Formation ratio of dihydrobenzoin/benzyl alcohol	*dl/meso* Ratio of dihydrobenzoin
0	0.7	0.90
10	1.5	0.82
100	4.4	0.64

It may be interesting to compare the numbers of quaternary ammonium molecules which cause almost the same level of the selectivity-increasing effect on being used as the LB-film and the co-supporting electrolyte. For a typical example, the numbers of the molecules in the LB-film(three layers, 7.5 cm^2) and in the catholyte (100 mM, 50 cm^3) are approximately calculated to be 9×10^{15} and 3×10^{21}, respectively: The former is one three-hundred-thousandth of the latter.

As shown in Table 2, a similar increase in the selectivity for the corresponding hydrodimers was observed in the reduction of pyridyl methyl ketones at the electrodes coated with the LB-films, though the magnitude of the increase somewhat diminished in comparison with the case of the bezaldehyde reduction.

Table 2. Product-selectivity[a] in the reduction of pyridyl methyl ketones at electrodes coated and uncoated with the LB-films[b]

Ketone	No. of layers coated	Concn of Bu_4NBr / mM	Formation ratio of hydrodimer/hydromonomer
2-Pyridyl methyl ketone[c]	0	0	0.2
2-Pyridyl methyl ketone[c]	1	0	0.3
2-Pyridyl methyl ketone[c]	3	0	0.4
2-Pyridyl methyl ketone[c]	0	10	0.4
4-Pyridyl methyl ketone[d]	0	0	1.3
4-Pyridyl methyl ketone[d]	1	0	2.4
4-Pyridyl methyl ketone[d]	5	0	2.7
4-Pyridyl methyl ketone[d]	0	10	2.3

a) *dl/meso* Ratio of the hydrodimers was not determined. b) Electrolysis was carried out in a buffer solution(pH 5) in the absence and presence of Bu_4NBr co-supporting electrolyte. c) Electrolyzed at -0.7 V(SCE). d) At -0.8 V(SCE).

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