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Highly Selective Formation of 1-Phenylethanol by Indirect Electroreduction of Acetophenone on a Lead Cathode in the Presence of Catalytic Amounts of Antimony(III) Chloride

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In the presence of antimony(III) chloride, acetophenone is selectively electroreduced to 1-phenylethanol on a lead cathode in protic medium at low current densities.

It has been well known that acetophenone (1) is electrolytically reduced to 1-phenylethanol (2), 2,3-diphenyl-2,3-butanediol (3) and ethylbenzene (4), and the product distribution depends on the reaction condition.[1,2] In the case of direct macroscale electroreduction, in general, 3 was a major product. Recently, several electroreduction methods for the formation of 2 has been proposed, and they are based on chemically modified electrodes and electrocatalysts.[3,4] Some problems arise in the cathode material, the amounts of catalyst and the yield.

In this paper, we report that an indirect electroreduction of 1 in the presence of $SbCl_3$ afforded smoothly 2 in excellent yield under mild conditions.

A typical procedure is as follows: The cell used was a 100 ml beaker divided by a porous cup (15 ml) serving as the anode compartment. The cathode was a Pb plate (ca. 21.3 cm^2) and the anode was a Pt plate (ca. 4.0 cm^2), respectively. A solution containing 1 (1.0 g, 8.3 x 10^{-3} mol) and catalytic amounts of $SbCl_3$ (1.7 x 10^{-5} mol) dissolved in a mixed solvent (50 ml) of aqueous 2M-HCl, EtOH, and n-BuOH (2.5 : 1.0 : 1.5 v/v) were put into the cathode compartment. The solution was electrolyzed at a constant current density (-3.7 mA/cm^2) corresponding to the reduction potential of $SbCl_3$ (-0.25 V vs. Ag/AgCl) with stirring at room temperature. After passage of 3F/mol, the catholytes were neutralized with alkali and then extracted with ether. The extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was analyzed by GLPC and 2 was obtained in the yield of 99%.

When $SbCl_3$ was used in amount much more than 1.5 x 10^{-3} mol vs. 1, no reduction product other than 2 was obtained (Fig. 1). In the absence of $SbCl_3$, the major product was 3. The efficiency of antimony(III) leading to the drastic change of the reduction products was the highest so far obtained for among 11 kinds of metal chlorides investigated.[5] The results were as follows: (Metal chloride, Yield of 2, mA/cm^2, F/mol) $SbCl_3$, 82%, 4, 8; $FeCl_3$, 27%, 2, 8; $ZnCl_2$, 25%, 16, 8; $MnCl_2 \cdot 2H_2O$, 13%, 17, 8; $NiCl_2$, 12%, 10, 8; $CoCl_2$, 11%, 4, 8; $CrCl_3 \cdot 6H_2O$, 11%, 16, 8; $CuCl_2$, 7%, 5, 8; $InCl_3 \cdot 4H_2O$, 6%, 6, 8; $SnCl_2$, 2%, 5, 2;

$CdCl_2$, 2%, 13, 2. On the other hand, it was also sensitive to the cathode materials applied. The accelerative effects of the cathode materials decreased in the order: Pb (Yield of 2, 99%) > Hg (98%) > Cd (97%) > Cu (90%) > Pt (89%) > Zn (63%). The same results were obtained in the range of 1.7, 8.0, 15.0 mA/cm^2 of current density, respectively. And also high yields (88 to 98%) were obtained in the range of 2 to 4 F/mol of electricity.

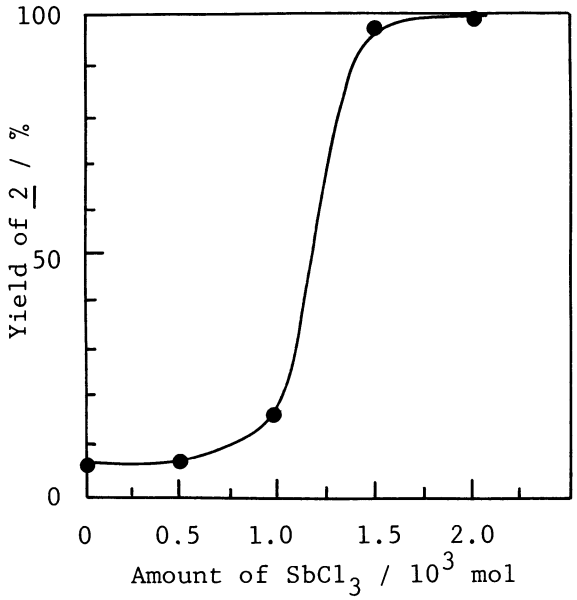

Fig. 1. The yield of 2 as a function of the amount of $SbCl_3$. Pb cathode, -3.7 mA/cm^2, 4F/mol.

At present, the function of $SbCl_3$ to induce the formation of 2 is not understood clearly. However, it is likely that the electrogenerated zerovalent Sb plays a significant role in the selective reduction of 1.

In conclusion, we successfully developed a new electrochemical method for the selective reduction of 1 to 2, which could not have been easily produced through various studies.[6,7] Further works on the utility of this method for other organic materials are now in progress.

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