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Reduction of Aromatic Compounds by Solvated Electrons Generated at Cathode

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Synopsis. Phenol, anisole, and toluene can be reduced electrochemically to cyclohexanol, methoxycyclohexane, and methylcyclohexane respectively, in ethanol containing hexamethylphosphoric triamide (HMPA) at aluminium cathode. The reduction of these aromatics is believed to occur due to electrochemically generated solvated electrons.

The electrochemical reduction of benzene has been reported in variety of reaction conditions.$^{1-5)}$ In some reports$^{4,5)}$ it has been observed that direct electron transfer from cathode to aromatic nucleus does not take place, but the electron is introduced into the solution as solvated electrons, which may cause the reduction of benzene away from the electrode in the bulk of the solution.

$$e^-_{(\mathrm{cathode})} + \text{solvent} \rightleftharpoons e^-_{(\mathrm{solvent})}$$

The use of solvated electrons is of particular significance because the reported chemical methods involve high temperature and pressure. Furthermore, the yield of the reduced product in chemical hydrogenation depends upon a number of factors such as acid concentration, catalyst, hydrogen pressure, mode of addition and presence of water soluble quaternary ammonium compounds.$^{6-9)}$ Fichter and Stocker$^{10)}$ reported the reduction of phenol to cyclohexanol in 2 mol dm^{-3} sulfuric acid at platinized platinum electrode in poor yield. The use of solvated electrons in reduction of benzene has been reported by Sternberg and coworkers.$^{11,12)}$ Recently Misra and Sharma$^{13)}$ investigated the cathodic reduction of phenol and 2-naphthol to cyclohexanol and *trans*-2-dacalol respectively, at platinum foil in 2 mol dm^{-3} perchloric acid in good yield. In the present communication, we report the electrochemical reduction of phenol, anisole, and toluene in EtOH–HMPA (67:33). Lithium chloride was used as supporting electrolyte.

Experimental

Materials. Phenol, toluene, and anisole (all B.D.H.), lithium chloride (SISCO) and hexamethylphosphoric triamide(Fluka) were used without further purification.

Cell Assembly. A 400 ml beaker with provision to hold the cathode, porous diaphragm, thermometer, and magnetic bar, was used as electrolysis cell. Aluminium sheet was used as cathode and a carbon plate inside the diaphragm served as anode. A constant current was passed from a current regulated power supply (0-10 A/0-100 V).

Electrolysis, Work Up, and Analysis. Following is the detail of electrolysis: catholyte 125 ml, 3% lithium chloride solution in EtOH–HMPA (67:33), and 0.025 mol dm^{-3} of organic compound, anolyte 35 ml, 3% lithium chloride solution in EtOH–HMPA (67:33), current (0.3 A, current density 0.0326 A/C m^2), cell temperature (28±2 °C).

After the theoretical time corresponding to 6 F/mol, the catholyte was filtered and poured into 200 ml of water and acidified with dilute hydrochloric acid. The organic material was extracted with hexane (in case of phenol, the remain is also extracted with ether), and the organic layer was fractionally distilled to separate the reduced product and unreacted aromatic compound. The reduced product thus obtained was redistilled to get pure product. Their bp, yield, IR, and NMR data are given in Table 1.

Results and Discussion

The aromatics *viz.*, phenol, anisole, and toluene in EtOH–HMPA at aluminium cathode in a divided cell afforded the corresponding hexahydro derivatives. The cathodic potential which initiates the reduction of phenol, anisole, and toluene was −2.4, −2.10, and −2.00 V (*vs.* saturated calomel electrode) respectively. A blue colouration during the reaction indicates the formation of solvated electrons whose existence has been proved and detected by electron

Table 1. Physico-chemical and spectral characteristics of cyclohexanol, methoxycyclohexane, and methylcyclohexane

Product	Bp θ_b/°C Found (reported)	Yield %	IR$^{a)}$ $\nu_{\mathrm{O-H/O-CH_3}}$ cm^{-1}	$\nu_{\mathrm{C-H}}$ cm^{-1}	^{1}H NMR$^{b)}$ δ
Cyclohexanol	160—161 (161)$^{c)}$	51.7	3450—3300 $\nu_{\mathrm{O-H}}$	2825, 2750	1.1—2.9 (m, 10H; CH$_2$) 3.8 (s, 1H; CH) 5.4 (s, 1H; CH)
Methoxycyclohexane	134—136 (135—136)$^{d)}$	45.8	3060—3010 $\nu_{\mathrm{O-CH_3}}$	2825, 2750, 2725	1.0—2.9 (m, 10H; CH$_2$) 3.45 (s, 1H; CH) 3.85 (s, 3H; CH$_3$)
Methylcyclohexane	98—101 (100)$^{e)}$	45.4	—	2950, 2920, 2850	1.0 (s, 3H; CH$_3$) 1.1—2.1 (m, 11H; CH$_2$ and CH)

a) IR were recorded on Perkin-Elmer-577 Grating IR Spectrophotometer. b) NMR were recorded on Perkin-Elmer RB 12 Spectrometer using TMS as internal Standard. c) Ref. 17(i). d) Ref. 17(ii). e) Ref. 17(iii).

spin resonance studies.[4,11] The solvated electrons formed by the reduction of metal ion followed by a dissolution step, interact with the monosubstituted benzene to give the dihydro derivative by the same mechanism reported previously.[14] Further reduction of dihydro product depends upon reaction conditions. For example, electrochemical reduction of benzene in methylamine[15] and tetralin in ethylenediamine[16] produces di- and tetra- hydro derivatives *viz.*, cyclohexadiene and cyclohexene in case of benzene, hexahydronaphthalene and octahydronaphthalene in case of tetralin. The non reducibility of benzene from olefin stage in amine solvent is due to the reason that the reduction of isolated double bond is much slower than the reduction of benzene to cyclohexadiene. But in our case fully reduced products of aromatics were isolated, indicating thereby that hydrogen evolution reaction 1 is suppressed, because HMPA is selectively adsorbed on the metal surface and hence preventing the decomposition of ethanol.

$$e^{-}_{\mathrm{cathode}} + C_2H_5OH \longrightarrow C_2H_5\bar{O} + 0.5\,H_2 \qquad (1)$$

In addition to suppressing the hydrogen evolution at cathode, HMPA must also suppress the hydrogen evolution in solution. This is corroborated by the fact that when the reduction of phenol is carried out in absence of HMPA, the yield of cyclohexanol is very low (≈5%). Hence it is reasonable to deduce that the reduction of phenol (also anisole and toluene) is possible if the electron and proton transfer reactions 2 and 3 are faster

$$\bar{e}_{C_2H_5OH} + R \longrightarrow R^{\overset{\cdot}{-}} + C_2H_5OH \qquad (2)$$

$$R^{\overset{\cdot}{-}} + C_2H_5OH \longrightarrow RH^{\cdot} + C_2H_5\bar{O} \qquad (3)$$

than the two competing hydrogen forming reactions 4 and 5.

$$\bar{e}_{C_2H_5OH} + \bar{e}_{C_2H_5OH} \longrightarrow H_2 + 2\,C_2H_5\bar{O} \qquad (4)$$

$$\bar{e}_{C_2H_5OH} + C_2H_5OH \longrightarrow 0.5\,H_2 + C_2H_5\bar{O} \qquad (5)$$

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