ELECTROLYTIC GENERATION OF SOLVATED ELECTRONS IN A SOLVENT OF HIGH PROTON DONOR CAPABILITY; ELECTROLYTIC REDUCTION OF THE BENZENE RING

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Until now, electrolytic generation of solvated electrons could be achieved only in solvents of low donor capability such as liquid ammonia[1,2] or certain amines,[3-5] a fact which imposed severe restrictions on the choice of solvent and reaction conditions. Attempts, described below, to generate solvated electrons electrolytically in a solvent of relatively high proton donor capability such as ethanol were doomed to failure due to hydrogen evolution at a potential far below that required for release of electrons into the solvent. The recently published discovery[6] that hexamethylphosphoramide (HMPA), $[(CH_3)_2N]_3PO$, is capable of dissolving alkali metals prompted us to investigate whether electrolytic generation of solvated electrons in a solution of ethanol containing HMPA was possible.

EXPERIMENTAL

Reagents. Lithium chloride, tetralin, 1-octene and HMPA were of the highest purity available commercially. HMPA was purified by vacuum distillation and the fraction boiling between 89° and 92° at 4-5 mm was used.

Apparatus. The electrolysis vessel, described previously,[4] consisted of an H-cell of 150 ml total capacity. The two compartments were separated by a coarse, 25 mm glass frit. A carbon rod (spectroscopic grade), 3.5 cm long and 0.5 cm in diameter served as the anode. A rectangular piece of sheet aluminum of 4.5 cm^2 total immersed surface served as the cathode. Reproducible cathode potentials during current flow were obtained by inserting the Luggin capillary into a sleeve formed by folding over one edge of the aluminum electrode.[4]

Electrolytic Reduction. The electrolytic reduction of tetralin (1 ml, 7.35 mmole) and 1-octene (1 ml, 6.37 mmole) was carried out at a constant current of 500 ma in 60 ml of ethanol-HMPA solution containing 33 mole pct HMPA, 0.3 M in LiCl. At the start of the electrolysis, the cathode potential was -2.5 volts (vs. Ag wire) and slowly changed to -2.4 volts in the course of 25 minutes at which point the electrolysis was interrupted. The solution in the cathode compartment was diluted with water and the aqueous solution was extracted with pentane. The pentane extract was warmed in a current of nitrogen to remove the solvent and the residue was analyzed by mass spectrometric and GLC methods.

RESULTS AND DISCUSSION

When a solution of HMPA, 0.3 M in LiCl, is electrolyzed, dark blue globules, characteristic of solvated lithium, form at the cathode surface at a potential of -2.3 volts (vs. Ag wire) and the solution in the cathode compartment becomes deep blue, visual evidence that the reaction $Li^+_s + e^- \rightarrow Li^+_s \ldots e^-_s$ is taking place. The half-life of the solvated electron at room temperature was determined by dissolving lithium in HMPA and measuring the decrease in ESR signal peak height with time. The half-life was 38 minutes,[7] a value which compares well with that of 15 hours found for the half-life in liquid ammonia as reported by J. Corset and G. Lepoutre.[8] In the presence of ethanol, the intensity of the color is lower and the cathode potential is different, depending on the amount of alcohol present. In ethanol containing 33 mole pct. HMPA, for example, the blue color appears at a cathode potential of -2.5 volts (vs. Ag wire). However, in the presence of both alcohol and benzene the solution remains colorless during electrolysis, with only

a small amount of blue color visible at the cathode surface. Proof that electrolytic reduction of the benzene ring in ethanol-HMPA solution is possible was obtained by electrolysis of tetralin in a solution composed of 67 mole pct. ethanol and 33 mole pct. HMPA, 0.3 M in LiCl. The electrolysis was carried out at a cathode potential of -2.5 to -2.4 volts (vs. Ag wire). After completion of the electrolysis, analysis of the recovered product by mass spectrometric and GLC methods showed that it consisted of (vol. pct): tetralin (80), hexalin (2), octalin (1) and decalin (17), and that tetralin had been hydrogenated at a current efficiency of 54 pct. Under the same conditions, 1-octene was reduced to octane at a current efficiency of 26 pct. When the electrolysis of tetralin is carried out under the same conditions but in the absence of HMPA, copious hydrogen evolution takes place and the cathode potential during electrolysis is now -1.5 volts (vs. Ag wire), i.e., 0.8 to 1.0 volt more anodic than that at which release of electrons was observed into HMPA or ethanol-HMPA solution. Under these conditions not even traces of reduced tetralin could be detected in the recovered material. It is remarkable that the strong hydrogen evolution that occurs during electrolysis of ethanol at -1.5 volts is drastically reduced in the presence of as little as 33 mole pct. HMPA. This suggests adsorption of the aprotic but highly polar[9] HMPA at the electrode surface to the near exclusion of ethanol. In the presence of HMPA, the charge transfer process is release of electrons into the solvent and not hydrogen evolution. The high percentage of decalin in the reaction product is probably due to the high proton availability in the solution containing 67 mole pct. ethanol, since electrolytic reduction of tetralin in ethanol-HMPA containing only 25 mole pct. ethanol gave hexalin as the main product. Tetralin is not reduced when the electrolysis is carried out in HMPA in the absence of ethanol. Under these conditions, the catholyte becomes dark green colored during electrolysis. Mass spectrometric analysis of the recovered reaction product indicates the presence of considerable amounts of mono- and dimethyltetralin and small amounts of dimers of these methyltetralins in addition to unchanged starting material, tetralin.

On the basis of these results and previous work on the reduction of the benzene ring in ethylenediamine,[4] we believe that electrochemical reduction of the benzene ring in ethanol-HMPA involves addition of the solvated electron, e_s^-, to the solvated benzene ring, B_s,

$$S + e^- = e_s^-$$

$$B_s + e_s^- = S + B_s^-$$

where S indicates the solvent molecules required to solvate an electron. Subsequent protonation of the benzene anion, B_s^-, and further addition of electron and proton completes the hydrogenation of a double bond as has been pointed out previously.[10] Apparently, the cathode in ethanol-HMPA solution containing alkali halide functions in the same way as in liquid ammonia[2] and amines,[4] i.e., as an electron electrode.

The present results demonstrate for the first time that electrolytic generation of solvated electrons in a solvent of relatively high proton donor capability is feasible and that these electrons are available for addition to organic compounds.

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