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Electrochemistry of polycyclic aromatic hydrocarbons in molten tetrabutylammonium nitrate

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The oxidation and reduction of a series of polycyclic aromatic hydrocarbons have been studied in molten tetrabutylammonium nitrate at 150°C. On the oxidation side nitrated products are formed and on the reduction side butyl-substituted products were obtained. In this solvent, which is slightly unstable at 150°C, limiting cathodic process is the reduction of the NBu_4^+ ion to tributylamine and butenes and the limiting anodic process is the oxidation of NBu_4^+ to carbon dioxide. Attempts to trap the reactive intermediates produced electrochemically with added substances were unsuccessful.

It has been shown that reactive organic intermediates, useful in organic syntheses, can be easily generated in organic aprotic solvents [1]. However, the possible industrial use of such solvents in electro-organic synthesis is very limited because of the high resistance of the aprotic media resulting in very high overall voltages and very high energy costs. The purpose of this study was to investigate the possibility of electrochemically producing reactive organic intermediates in highly conducting (low resistance) aprotic molten salts. Sundermeyer [2] and co-workers have investigated many organic reactions in molten inorganic salts but unfortunately organic compounds are not very soluble in molten inorganic salts. We therefore decided to use molten quaternary ammonium salts as our solvents and in particular studied the electrochemistry of polycyclic aromatic hydrocarbons (used as model compounds) in molten tetrabutylammonium nitrate (mp = 110°C). This solvent was chosen because of its low melting point and large working voltage range.

Experimental procedure

Voltammetric measurements were performed on both a rotating platinum electrode (area $\simeq$ 3 mm^2) and a dropping mercury electrode (drop time $\simeq$ 4 s) in a standard polarographic cell heated by a silicone oil bath. Tetrabutylammonium nitrate at 150°C was used as the solvent, a tungsten electrode as the counter electrode and an Ag/AgCl/saturated NaCl electrode as the reference electrode. The reference electrode was separated from the bulk of the solution by a glass frit. The voltammetric curves were recorded on a Metrohm Polarecord fitted with an I.R. compensator.

The controlled potential electrolyses were performed in a standard H cell, with a glass electrode separating the anolyte and catholyte. The anode and cathode were 2 cm^2 platinum sheets, and the Ag/AgCl/saturated NaCl reference electrode was contained in a glass-fritted compartment dipping into the solution. Any gases evolved were trapped out in acetone/drikold traps. The products of the electrolyses were isolated by extraction of the solidified reaction mixture with water/chloroform mixtures. The ether solution was put onto an alumina column and the products separated by gradated elution with toluene/pet. ether mixtures.

The tetrabutylammonium nitrate was prepared by the stoichiometric addition of concentrated nitric acid to an aqueous solution of tetrabutylammonium nitrate. The water was taken off on a rotary evaporator and the resulting solid dried in a vacuum oven overnight. The other compounds used were purchased from B.D.H. Ltd. All analyses were performed by mass spectrometry and n.m.r.

Results and discussion

At 150°C tetrabutylammonium nitrate is slightly unstable turning brown over a period of 3-4 h and decomposing to yield tributylamine. The voltage range of the solvent was +2·4 V to −2·1 V (versus Ag/AgCl/saturated NaCl reference electrode). The limiting cathodic process was the reduction of the tetrabutylammonium cation to tributylamine and but-1-ene a quantitative yield of tributylamine being obtained. The limiting anodic process yielded carbon dioxide and a small amount of carbon deposited on the electrode as the only detectable products, but the carbon dioxide produced only accounted for 40% of the current passed. No products from the oxidation of the nitrate ion could be detected.

The base line between +2·4 V to −2·1 V was very flat with no indication of a faradaic current due to the reduction of nitrate ion. This contrasts markedly with the results found in molten alkali-metal nitrates where a hump due to the reduction of nitrate ion is observed [3]. The nature of the reduction product of the nitrate ion in the organic system is uncertain but it has been proposed that a film of inorganic oxide is formed on the platinum electrode. In the molten tetrabutylammonium nitrate system no such oxide film can be produced.

All the polycyclic aromatic compounds studied gave sharp S-shaped curves and the halfwave potentials ($E_{\frac{1}{2}}$) obtained are shown in Table 1. The oxidation potentials quoted are those for a platinum electrode and the reduction potentials those for a mercury electrode. There was very little difference between the reduction potentials found on platinum and mercury but on the oxidation side, mercury oxidizes at ≃ 0 V. Naphthalene or toluene were not oxidized or reduced in this melt.

Table 1. *Oxidation and reduction potentials* (*vs. Ag*/*AgCl*/*NaCl*) *of polycyclic aromatic hydrocarbons in molten* NBu_4NO_3 *at* 150°C

Polycyclic aromatic compound	$E_{\frac{1}{2}}$ *reduction on Hg*	$E_{\frac{1}{2}}$ *oxidation on Pt*
Anthracene	−1·87	+0·96
Perylene	−1·45	+0·94
Tetracene	−1·42	+0·76
Pentacene	−1·20	+0·74
Naphthalene	No wave	No wave

The limiting currents obtained were all diffusion controlled and of similar heights for the same concentration. However, these currents were approximately twice the limiting current obtained in this melt for the reduction of 9,10 diphenylanthracene which is known to give a 1*e* reduction in acetonitrilie [1]. E.s.r. measurements on a frozen sample from the reduction of 9,10 diphenylanthracene in molten tetrabutylammonium nitrate yielded a similar spectra to that obtained in the reduction of 9,10 diphenylanthracene in acetonitrile. Therefore it appears that more than 1*e* was being transferred in the oxidation and reduction of our model compounds.

Controlled potential oxidations and reductions were performed on anthracene. The controlled potential oxidation at +1·1 V yielded three isolatable products, 9 nitroanthracene, 9,10 dinitroanthracene and 4,9 dinitroanthracene plus some higher molecular weight solids. These products were shown not to have arisen from the oxidation of the nitrate ion followed by the attack of the nitro species thus produced on the anthracene, by performing the controlled potential oxidation on a solution of naphthalene at +1·1 V, a potential at which the naphthalene itself is not oxidized. No substituted naphthalenes were obtained from these experiments. The controlled potential reduction at −1·95 V yielded 9-butylanthracene as the only identifiable product. Again it was shown that the product did not arise from initial breakdown of the solvent, in this case the reduction of the tetrabutylammonium ion followed by attack of the resulting species on the hydrocarbon, by performing controlled potential reductions on naphthalene at −1·95 V from which substituted naphthalenes are obtained. The mechanism of these oxidations and reductions have not been determined and it is not easy to see an obvious mechanism. However, the results do show that reactive intermediates are produced in molten tetrabutylammonium nitrate. All attempts to trap these intermediates with other compounds, e.g. CO_2 and SO_2 on the reduction side and CO and anions on the oxidation side were unsuccessful, the products from reaction of the intermediates with the melt being obtained.

References

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