# The Cathodic Reduction of Anthracene in Lithium Chloride–Hexamethylphosphoramide

By **L. A. Avaca** † and **A. Bewick,*** Department of Chemistry, The University of Southampton, Southampton

The reduction of anthracene by electrochemically generated solvated electrons has been studied in LiCl–hexamethylphosphoramide using acetic acid as proton donor. The products were 9,10-dihydro-, 1,4,9,10-tetrahydro-, and 1,4,5 8 9,10-hexahydro-anthracene, and an octahydro-product that was probably reduced at the 1,2,3,4,5,8,9, and 10 positions. The variation of these products with time of electrolysis was investigated for a number of ratios of current density to substrate concentration.

AROMATIC hydrocarbons are readily reduced by electrochemically generated solvated electrons.[1-6] The products depend upon the nature of the proton donor, the temperature, the amount of electricity consumed, and the availability of basic species able to catalyse the conversion of non-conjugated polyenes to their more readily reducible conjugated isomers. Of the solvents which have been employed, systems containing hexamethylphosphoramide (HMPA) appear to provide the most strongly reducing conditions. Sternberg *et al.*[2,3] were able to obtain a high yield of cyclohexane from benzene with high current efficiency, whereas reduction in amine solvents[4] does not proceed beyond the tetrahydro-stage and, with sodium in liquid ammonia,[7,8] it stops at the dihydro-product. The sole exception is ethylenediamine in which the formation of a little of the fully reduced form has been observed.[5]

Sternberg *et al.*[2] also reported a strange result for the cathodic reduction of naphthalene in the HMPA–ethanol system. They stated that this substrate was not reducible at potentials anodic to the solvated electron region whereas in other solvents, naphthalene has been shown to be readily reduced at a potential well anodic to that required for the generation of solvated electrons. Their explanation was that the HMPA molecule was selectively adsorbed on the cathode and this blocked the reduction of the hydrocarbon as well as the evolution of hydrogen from the proton donor. However, in their experiment the current density was controlled at a value well in excess of that which could be supported by the direct reduction of naphthalene at the electrode surface. In consequence, their measurement showing the electrode potential to be within the solvated electron region does not exclude the possibility of such direct reduction. Other workers have observed direct electrochemical reduction of naphthalene in the same solvent system.[6]

For the present study, anthracene was chosen in order to investigate both direct reduction and reduction by solvated electrons.

## EXPERIMENTAL

The solvent, HMPA, was purified by vacuum distilling twice and collecting the middle fraction only. Lithium chloride, used as supporting electrolyte, was dried by melting and used at 0·3M concentration to maximise the conductivity. The solutions were prepared in a nitrogen filled dry box. The other reagents were dried in a vacuum oven and used without further purification since they were found to be free of impurities when analysed by v.p.c.

The electrolysis cell was of the conventional three-electrode type with a sintered glass diaphragm separating the anolyte from the catholyte. The reference electrode consisted of a piece of freshly cut lithium metal immersed in a saturated solution of lithium chloride in HMPA. A vitreous carbon rod of 3-mm diameter sealed in glass and with only the flat disc-shaped surface exposed, served as the cathode for most of the experiments, and a platinum foil as the anode. The aluminium foil and lead rod cathodes used for some experiments were mechanically polished before each electrolysis. During electrolysis the catholyte was stirred. For the constant-current experiments a simple H-cell with the same characteristics was used. All electrolyses were carried out using a Chemical Electronics 150V or type TR 70/20 potentiostat either connected in the usual way for potential controlled operation or as a constant current supply. For cyclic voltammetry, the potential was programmed with a Chemical Electronics waveform generator.

The identification of the products was carried out using a combination of vapour phase chromatography and mass spectroscopy. The solvent did not interfere since it had a shorter retention time than the products for the conditions employed: silicon grease at 165 and Apiezon L at 180 °C. N.m.r. spectroscopic analyses of the tetra- and hexa-hydro-derivatives were also employed following separation by preparative scale v.p.c. Quantitative analyses were by v.p.c. using three authentic samples for calibration purposes. The sensitivity was found to be the same for each of these, and this value was assumed for all of the products.

## RESULTS AND DISCUSSION

*Cyclic Voltammetry*.—The behaviour of anthracene was studied by cyclic voltammetry over a wide potential range in the absence of proton donor. The voltammograms obtained were typical of the reduction of an

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† *Present address:* Department of Chemistry, Queen Mary College, Mile End Road, London E.1.

[1] (*a*) H. W. Sternberg, R. E. Markby, and I. Wender, *J. Electrochem. Soc.*, 1963, **110**, 425; (*b*) R. A. Benkeser and E. M. Kaiser, *J. Amer. Chem. Soc.*, 1963, **85**, 2858; (*c*) A. Pullman, B. Pullman, and G. Berthier, *Bull. Soc. chim. France*, 1950, 591.

[2] H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Amer. Chem. Soc.*, 1969, **91**, 4191.

[3] H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Amer. Chem. Soc.*, 1967, **89**, 186.

[4] R. A. Benkeser, E. M. Kaiser, and R. F. Lambert, *J. Amer. Chem. Soc.*, 1964, **86**, 5272.

[5] H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Electrochem. Soc.*, 1966, **113**, 1060.

[6] T. Asahara, M. Senō, and H. Kaneko, *Bull. Chem. Soc. Japan*, 1968, **41**, 2985.

[7] A. J. Birch, *J. Chem. Soc.*, 1944, 430.

[8] A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, 1959, **81**, 3658.

aromatic hydrocarbon in an aprotic solvent, showing the reversible one electron step for the formation of the anion radical followed by its irreversible one electron reduction to form the dianion at a potential close to that for solvated electron formation as shown in Figure. 1

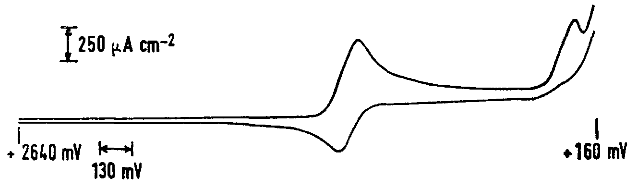

FIGURE 1 Cyclic voltammogram for a $3 \times 10^{-3}$M solution of anthracene in HMPA containing 0·3M-lithium chloride. Sweep speed 30 mV $s^{-1}$

Product distribution from the electrolytic reduction of anthracene

| Expt. no. | Starting material | Conc. (mM) | Cathode material | Constant parameter | Q | Q/mg | Coulomb yield (%) | Product composition (%) Di | Tetra | Hexa | Octa |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Anthracene | 144 | Vitreous carbon | 125 mA $cm^{-2}$ | 258 | 2·5 | 60 | 8 | 17 | 75 | |
| 2 | Anthracene | 70 | Vitreous carbon | 125 mA $cm^{-2}$ | 216 | 4·3 | 53 | | 15 | 85 | |
| 3 | Anthracene | Sat. | Vitreous carbon | 125 mA $cm^{-1}$ | 180 | 1·0 | 41 | 49 | 27 | 24 | |
| 4 | Anthracene | 67 | Vitreous carbon | −1·0 V[a] | 200 | 3·3 | 57 | 2 | 3 | 88 | 7 |
| 5 | Anthracene | 175 | Vitreous carbon | −1·0 V[a] | 189 | 1·2 | 70 | 44 | 37 | 19 | |
| 6 | 9,10-Dihydro | 112 | Vitreous carbon | 125 mA $cm^{-2}$ | 186 | 3·1 | 86 | | 6 | 72 | 22 |
| 7 | Anthracene | 59 | Al | −0·5 V[a] | 160 | 2·5 | 45 | 45 | 24 | 31 | |
| 8 | Anthracene | 74 | Al | 10 mA $cm^{-2}$ | 204 | 5·0 | 32 | 3 | 19 | 69 | 9 |
| 9 | 9,10-Dihydro | 350 | Al | 150 mA $cm^{-2}$ | 1000 | 1·0 | 36 | | 70 | 30 | |
| 10 | Anthracene | 70 | Pb | 2 mA $cm^{-2}$ | 96 | 2·0 | 65 | 100 | | | |
| 11 | 9,10-Dihydro | 70 | Pb | 2 mA $cm^{-2}$ | 153 | 3·0 | 30 | | 57 | 43 | |
| 12[b] | Anthracene | 42 | Vitreous carbon | +0·9 V[a] | | | | 100 | | | |

Concentration of acetic acid (proton donor) was approximately 1M for each expt.

[a] Potential measured against Li(metal)–$Li^+$ (sat. soln. of LiCl in HMPA). [b] The current, under normal stirring conditions, was 0·4 mA (5 mA $cm^{-2}$).

Q = Number of coulombs passed. Q/mg = Number of coulombs per mg of starting material.

The potentials of the two cathodic peaks were 1·23 and 0·33 V and the single anodic peak was at 1·29 V, all with respect to the Li–$Li^+$ (sat. LiCl) potential and measured at a sweep speed of 300 mV $s^{-1}$. The peak currents showed the expected dependence on the square root of the sweep rate and a linear dependence on anthracene concentration. On addition of a proton donor, the first reduction peak gradually doubled in size at the expense of the second one and the oxidation peak disappeared, in full concordance with the behaviour normally observed. In no circumstances was there any evidence for behaviour different to that found in other typical aprotic solvents for reduction by direct electron transfer at the electrode surface.[9,10] Results for the same system in the presence of other support electrolytes are given elsewhere.[11] The reduction of naphthalene was also found to follow the normal pattern.[9]

*Preparative Electrolysis.*—The Table gives details of the product distribution and coulomb yield for a set of preparative scale electrolyses. In all cases, acetic acid was used as the proton donor and the variables were the electrode material, the concentration of substrate, and the value of the controlled electrode potential or the current density. A further set of experiments were performed in which the course of the reduction was followed by removing samples of catholyte at intervals and analysing for the products. The results are plotted in Figures 2—4.

The molecular weights of the products were established by v.p.c. coupled with mass spectroscopy and the dihydro-compound was readily identified as the 9,10-derivative by comparison with the standard material. No other dihydro-product was formed whether the reduction was carried out directly at the electrode surface at potentials anodic to that required to form solvated electrons (Table, experiments 10 and 12) or indirectly *via* solvated electrons. In the latter case, more fully reduced products, a mixture of tetrahydro-, hexahydro-, and octahydro-anthracene, were also obtained. The structures of the tetra- and hexa-hydro-derivatives were investigated by n.m.r., which showed that the first contained aromatic, vinylic, and inner and outer methylene protons in the ratio required by structure (I), and the second possessed only vinyl and central and outer methylene protons, as in structure (II). These results fit those of Harvey[12] for the structures 1,4,9,10-tetrahydroanthracene (I) and 1,4,5,8,9,10-hexahydroanthracene (II).

The octahydro-product could not be obtained in sufficient quantity to allow structural analysis by n.m.r. spectroscopy. However, a detailed study of the cracking pattern obtained by mass spectroscopy indicates that reduction of one of the inner double bonds has occurred, *i.e.* that structure (III) rather than (IV) is correct. Both structures would be expected to give a major peak at $M - 54$, as was actually observed for the hexahydro-isomer (II), whereas only (IV) would give a peak at $M - 28$ (cleavage at the dotted lines). The cracking pattern obtained showed a very strong peak at $M - 54$ and none at $M - 28$. For comparison,

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[9] G. J. Hoijtink, ' Advances in Electrochemistry and Electrochemical Engineering,' vol. 7, ed. P. Delahay, Interscience, New York, 1970, p. 221.

[10] M. E. Peover, ' Electroanalytical Chemistry,' vol. 2, ed. A. J. Bard, M. Dekker, New York, 1967, p. 1.

[11] L. A. Avaca and A. Bewick, in preparation.

[12] R. G. Harvey, *J. Org. Chem.*, 1967, **32**, 238.

a spectrum was run on *sym*-octahydroanthracene and this had a very strong peak at $M - 28$. It must be concluded, therefore, that the outer olefinic bonds of (II) are not reduced, although this might be expected by analogy with the stepwise reduction of naphthalene.[13]

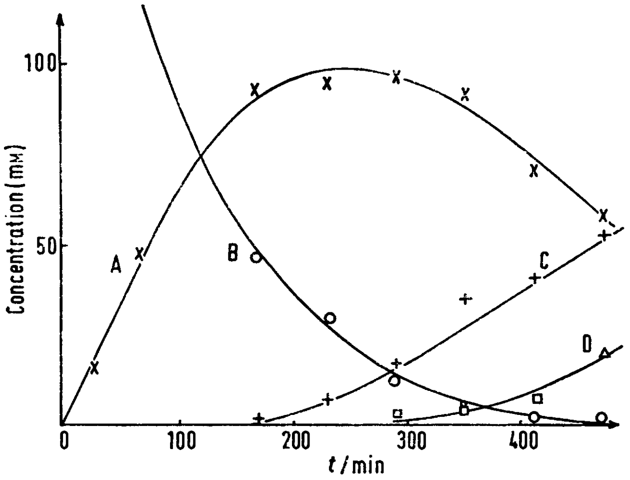


FIGURE 2 The variation with time of the product distribution from the reduction of anthracene at 125 mA cm$^{-2}$. Initial anthracene concentration 0·14M, initial acetic acid concentration 0·25M. A, Dihydro; B, anthracene; C, tetrahydro; D, hexahydro

The results shown in the Table would fit a simple stepwise mechanism involving the sequential formation of dihydro-, tetrahydro-, hexahydro-, and finally octahydro-anthracene, this route being independent of the electrode material. Such a mechanism was proposed by Harvey[12,14] to account for the results from reduction by sodium in liquid ammonia. The more detailed results of Figures 2—4 require a modification to the simple scheme. As the ratio of current density to substrate concentration is increased, the tetrahydro- and hexahydro-products appear in higher concentration compared with dihydroanthracene in the earlier stages of the experiments. In the most extreme case, Figure 4, it is clear that the major pathway to the more fully reduced products is not directly through dihydroanthracene since its concentration is at all times the lowest and it does not possess a maximum. This can be explained by the Scheme in which there is an alternative route to the tetrahydroanthracene, AnH$_4$, bypassing the dihydro-derivative. This involves further reduction of the intermediate anion AnH$^-$ instead of protonation. The relative importance of the two routes will depend upon the concentration of the solvated electrons and therefore upon the ratio of current density to substrate concentration. The alternative route will be favoured by an increase in this ratio as is observed.

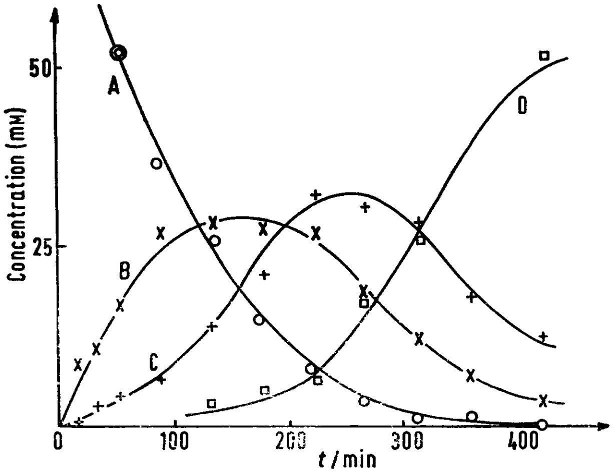


FIGURE 3 The variation with time of the product distribution from the reduction of anthracene at 125 mA cm$^{-2}$. Initial anthracene concentration 0·070M, initial acetic acid concentration 0·25M. A, Anthracene; B, dihydro; C, tetrahydro; D, hexahydro

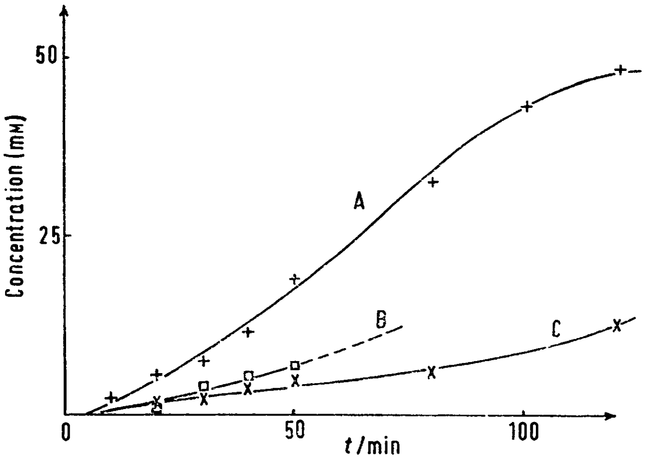
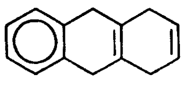
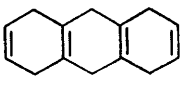


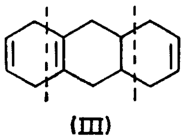
FIGURE 4 The variation with time of the product distribution from the reduction of anthracene at 125 mA cm$^{-2}$. Initial anthracene concentration 0·035M, initial acetic acid concentration 0·25M. A, Tetrahydro; B, hexahydro; C, dihydro



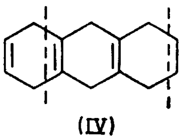
(I)



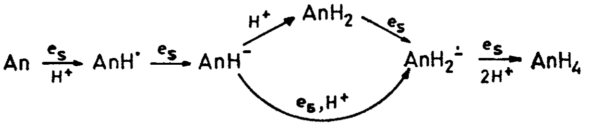
(II)



(III)



(IV)



SCHEME

The results show that it is possible to achieve appreciable selectivity of product by suitable control of

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[13] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Amer. Chem. Soc.*, 1955, **77**, 3230.

[14] R. G. Harvey and K. Urberg, *J. Org. Chem.*, 1968, **33**, 2570.

the substrate concentration, the current density, and the electrolysis time.

*The Location of the Reaction Zone.*—For a system in which reduction can occur both directly at the electrode or indirectly *via* cathodically generated solvated electrons, it is essential to control conditions so that only one of these alternative pathways is operative in a given experiment. Control of the electrode potential would be the most direct method of selection and this was employed in the study of the direct reduction process. In the solvated electron region, however, control of potential is almost impossible due to very large variations in the uncompensated resistance between the tip of the Luggin capillary and the working electrode. These variations are due to the high resistivity of the electrolyte solution which is reduced by several orders of magnitude by the generation of solvated electrons.[15] In view of this, for most experiments in the solvated electron region the current was controlled at a value well in excess of that corresponding to mass transfer control by diffusion of the anthracene. Experiment 12 gives a measure of the diffusion limited rate for a 42mM solution. Consequently in all experiments except 10, the concentration of anthracene at the electrode surface was zero and, since the reaction between solvated electrons and anthracene is very fast (disappearance of the peak for reoxidation of solvated electrons on fast cyclic voltammograms), direct reduction would not take place. It is clear that only convection could supply the anthracene at the relatively high rate required, and the indirect reduction must mainly take place in some part of the bulk environment. At the current densities employed in these experiments, the reaction will be confined to a stirred region of solution adjacent to the boundary layer. Solvated electrons were never seen away from this region, whereas at very high current densities (*ca.* 1 A $cm^{-2}$),[16] they were observed throughout the bulk volume.

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[15] L. A. Avaca and A. Bewick, in preparation.

[16] L. A. Avaca and A. Bewick, in preparation.