Mechanisms of Electrochemical Hydrogenation of Fluoranthene in HMPA with Ethanol and Aqueous HCl as Proton Donors

Yves Dassas, Stéphane Boué, and André Fontana *
Service de Chimie Générale et Carbochimie, Faculté des Sciences Appliquées, CP165, Université Libre de Bruxelles, 50, avenue F. D. Roosevelt, B-1050 Brussels, Belgium

The electrochemical hydrogenation of the non-alternant aromatic hydrocarbon fluoranthene has been investigated in $LiClO_4$–hexamethylphosphoric triamide; it has been found that hydrogenation cannot be achieved satisfactorily, not even to the dihydro derivative, when ethanol is used as the proton donor, whether present during or added after electrolysis. On the other hand, reaction of a stock of fluoranthene dianion with aqueous hydrochloric acid proves to be a clean, easy way to prepare 1,2,3,10b-tetrahydrofluoranthene, a product which requires donation of four electrons to fluoranthene. A mechanism is discussed to account for such a transfer of electrons.

Since it was discovered that in the solvent HMPA (hexamethylphosphoric triamide) electrons can be released from a cathode to produce solvated electrons,[1] in much the same way as *via* dissolution of alkali metals in liquid ammonia, several studies have been undertaken[2–4] in connection with the mechanism of electrochemical hydrogenation of unsaturated hydrocarbons and, more particularly, polycyclic aromatic compounds in this remarkable solvent.[5] However, in spite of the numerous investigations performed in the field,[6] most results are still controversial at present.

In particular, there are two fundamental discrepancies between the reports presented by Sternberg[3] and by Avaca.[4] According to Sternberg *et al.*, the solvent HMPA is so strongly adsorbed on the cathode that no dissolved species can reach it and be reduced at potentials anodic to the value required for the generation of solvated electrons, which turns out to be more cathodic than the reduction potential of an isolated carbon–carbon double bond, thus permitting reduction not only of polycyclic aromatics but also of benzene derivatives and even of mono-alkenes.

Opposing these results, Avaca *et al.* claim that reduction of anthracene in HMPA–LiCl–acetic acid mixtures occurs either by direct electron transfer at the cathode interface to yield 9,10-dihydroanthracene at potentials less cathodic than for producing solvated electrons, or preferentially in the bulk environment when the cathode potential is driven down to values more negative than that corresponding to solvated electrons. Furthermore, it was shown that whereas hydrogenation up to 1,4,5,8,9,10-hexahydroanthracene is readily achieved with solvated electrons, further reduction of isolated double bonds is just observable and in any case does not proceed to a detectable extent beyond 1,4,5,8,9,10,11,12-octahydroanthracene.

Obviously more work needs to be done before light is shed on this subject, and this induced the study reported here, namely, reinvestigation of the electrolysis of aromatic hydrocarbons in HMPA while aiming at the production of perhydro compounds which are of interest in the course of coal and heavy oils processing.[7] However, the authors were struck by the fact that former electrochemical studies have been mostly restricted to alternant aromatic compounds, and have therefore chosen the non-alternant aromatic hydrocarbon fluoranthene as the substrate in the present work.

Experimental

Reagents.—The solvent HMPA 99% from Aldrich was vacuum distilled under an atmosphere of nitrogen A28 from Air Liquide and the middle fraction (103–105 °C/5 mmHg) collected. Lithium perchlorate ACS reagent from Aldrich was dried by melting at 270 °C. Absolute ethanol 99.8% from Bruggeman, azeotropic ethanol of analytical grade, and fluoranthene 98% from Aldrich were used without further purification.

Apparatus and Instruments.—The electrolysis vessel was a classical three electrode H-cell with ground-joint fittings for external connections; catholyte and anolyte compartments (80 cm^3 capacity each) were separated by a G4 fritted glass and stirred by means of a magnetic bar. Platinum flags 1 cm × 1 cm × 0.05 cm were used as anode and cathode. A Pt wire placed in a separate compartment plugged with fritted glass and set close to the cathode served as a comparison electrode (indeed Ag^+ ions proved unstable in the presence of HMPA, in agreement with an earlier report,[8] and the $Ag|Ag^+$ reference was thus discarded). Although not having clearly defined thermodynamic significance, the mere platinum wire was characterized in the chosen medium by a remarkably stable and reproducible potential.

A Princeton Applied Research model 362 scanning potentiostat was used either to record the polarization curves on a Goertz Metrawatt SE 790 X–Y recorder or to run the preparative electrolyses in the potentiostatic mode. GLC analyses were performed on a Perkin-Elmer Sigma-3 chromatograph fitted with an FID detector and two 2 m, $\frac{1}{8}$ in columns: Apiezon L (15%) on Chromosorb W (80–100 mesh) for separation of low molecular masses, and Dexsil 300 (1%) on Supelcoport (100–120 mesh) for separation of dimers. Mass spectra were obtained using either a VG-70-70 spectrometer or a Finnigan ITD 800 GC–MS instrument. NMR spectra were recorded using a Bruker WM 250 spectrometer and visible spectra using a Varian–Cary 2300 spectrometer.

Procedure.—Both compartments of the H-cell were first purged with nitrogen and then filled with 50 cm^3 (each) of the appropriate solution, *i.e.*, 0.3 mol dm^{-3} $LiClO_4$ in HMPA with or without added ethanol and fluoranthene, depending on the type of experiment. The atmosphere was always kept oxygen-free by means of a gentle flow of nitrogen passing through the

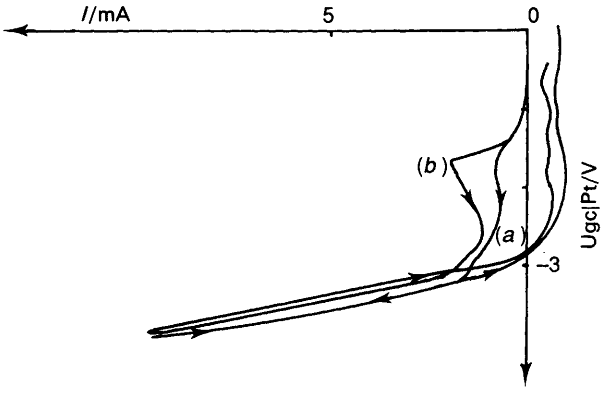


Figure 1. Cathodic polarization curves for Pt electrode *vs.* Pt wire (100 mV s^{-1}). (*a*) solvent, HMPA; electrolyte, $LiClO_4$ (0.3 mol dm^{-3}); (*b*) as (*a*), but with fluoranthene (0.02 mol dm^{-3}).

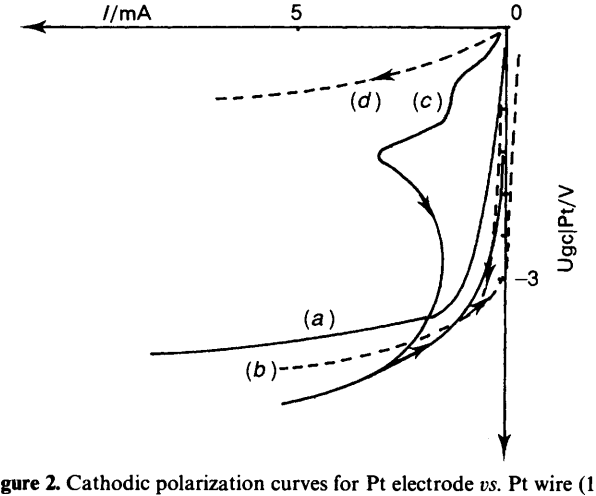


Figure 2. Cathodic polarization curves for Pt electrode *vs.* Pt wire (100 mV s^{-1}). Solvent, HMPA; electrolyte, $LiClO_4$ (0.3 mol dm^{-3}); ethanol concentration (*a*) 0.007; (*b*) 0.1; (*c*) 0.15; (*d*) 0.66 mol dm^{-3}.

cell. In order to determine the optimum conditions for preparative electrolysis, polarization curves were successively analysed for HMPA–$LiClO_4$, HMPA–$LiClO_4$–ethanol, HMPA–$LiClO_4$–fluoranthene, and HMPA–$LiClO_4$–ethanol–fluoranthene mixtures. For preparative electrolyses carried out at −4.0 V *vs.* Pt wire (J = 6–8 mA cm^{-2}), the proton donor ethanol was either present at the start or added after exhaustive generation of anions; aqueous HCl as the proton donor was only added to the anions at the end of a run. Electrolyses were interrupted after transfer of 4–5 F per mole of fluoranthene, and the crude mixture (after reaction with the proton donor) was poured into a large excess of distilled water which was then extracted three times with benzene. The benzene extract was carefully washed with water until complete removal of HMPA was achieved; the benzene was evaporated and the solid residue dried under vacuum before being analysed by GLC, mass spectrometry, and NMR spectroscopy.

Results and Discussion

Polarization Curves.—The cathodic polarization of the HMPA–$LiClO_4$ system has been explored by cyclic voltammetry between zero and −4.0 V *vs.* Pt wire for a number of experimental conditions which include addition of fluoranthene and/or ethanol and water as proton donors. The polarization curves obtained for 0.3 mol dm^{-3} $LiClO_4$ in HMPA at the sweep rate of 100 mV s^{-1} showed only a weak reduction wave with an ill-defined broad maximum at about −1.75 V *vs.* Pt and a very intense wave the threshold of which lay at *ca.* −2.85 V *vs.* Pt and which is assigned to the solvation of electrons released from the cathode [Figure 1 (*a*)]. If extended pre-electrolysis was allowed to proceed at −1.75 V *vs.* Pt, the corresponding weak wave progressively vanished and was thus ascribed to a residual impurity. When the potential sweep reversed, an oxidation wave appeared, consistent with the reversible capture of solvated electrons by the platinum electrode; thus the standard potential for $(e^-)_{Pt}|(e^-)_{solvated}$ was estimated at −2.8 V *vs.* Pt wire and varied by not more than ±100 mV regardless of experimental conditions.

Upon addition of fluoranthene to the solvent–electrolyte solution there was observed a new small wave with peak current at −1.6 V *vs.* Pt and also an intense wave starting at −2.8 V [Figure 1(*b*)]; this will be discussed later. The quite unusual behaviour observed in this system needs to be stressed, namely that the current intensity measured at potentials more cathodic than −2.8 V *vs.* Pt always decreased by as much as 25% if the solution was stirred, the original current value being quickly restored when stirring stopped. This is contrary to the expectation for a diffusion-controlled process, but does not hold true for the wave at −1.6 V *vs.* Pt which, in contrast, was enhanced by stirring. It must also be noted that the concentration of fluoranthene was found to be important: at values $\leqslant 0.02$ mol dm^{-3} under stirring, a current density of *ca.* 8 mA cm^{-2} could be maintained for hours at −3.6 V *vs.* Pt, whereas in a 0.06 mol dm^{-3} solution the cathode, at the same potential, was quickly covered with a brown resin layer while the current dropped to zero.

The influence of proton donors such as ethanol and water in the absence of fluoranthene was then investigated. When ethanol was added to HMPA–$LiClO_4$ up to a concentration of 0.10 mol dm^{-3}, the cathodic polarization curves were similar to those obtained without alcohol except that the wave at −2.85 V *vs.* Pt was shifted downward to more negative potentials and was no longer reversible, *i.e.*, the anodic current was suppressed probably because solvated electrons had reacted with ethanol, although no gaseous hydrogen was detected [Figure 2 (*a*), (*b*)]. With ethanol concentrations above 0.10 mol dm^{-3}, reduction waves began to show up at less negative potentials [Figure 2, curves (*c*), (*d*)], and for the literature-reported mixture containing 66 mol% alcohol[3] a vigorous hydrogen evolution dominated over the whole range of cathodic potential; furthermore, potential sweeps made in rapid succession resulted in a fast decrease of the current intensity, indicating a cathode passivation of unknown origin but fully reversible when the current was interrupted for a short while.

The influence of water much resembles that of ethanol but in a more drastic way (as shown in Figure 3). At very low concentrations [Figure 3(*a*), (*b*)], the wave assigned to solvated electrons was still present but appeared at more cathodic potentials and was totally irreversible. As the water concentration increased up to 0.07 mol dm^{-3}, a new reduction wave developed with a threshold at −1.0 V *vs.* Pt [curve (*c*)] and became dominant with hydrogen evolution for 0.15 mol dm^{-3} [curve (*d*)]; a passivation phenomenon similar to that reported with ethanol was also observed here.

Finally, it was found that when fluoranthene is present at a concentration of 0.02 mol dm^{-3}, even in the presence of azeotropic or absolute ethanol up to at least 4 mol dm^{-3}, the cathodic polarization curves were practically identical with those obtained in the absence of a proton donor, exhibiting only a weak reduction wave at −1.6 V *vs.* Pt aside of that of solvated electrons at −2.8 V *vs.* Pt. Moreover, there was no significant evolution of hydrogen even at a potential as negative as −4.0 V *vs.* Pt. It was thus concluded that preparative electrolysis of fluoranthene to produce anions should *a priori* be possible in the presence as well as in the absence of ethanol.

Table. Products yielded by electrolysis of fluoranthene on Pt cathode.[a]

Proton donor used/concentration in HMPA		Current density, J/mA cm^{-2}	Products
During electrolysis	After electrolysis		
Ethanol[b]/2 mol dm^{-3}		5–6	Unchanged fluoranthene (*ca.* 85%) Dimer M_r 408 (*ca.* 10%) Numerous unidentified (tot < 5%)
	Ethanol[b]/2 mol dm^{-3}	8	Unchanged fluoranthene (*ca.* 20%) Dimer M_r 408 (< 2%) Polymers (*ca.* 80%) Several unidentified (traces)
	Aqueous HCl/0.02 mol dm^{-3}	8	Unchanged fluoranthene (*ca.* 50%) 1,2,3,10b-tetrahydrofluoranthene (*ca.* 40%) Dimer M_r 410 (*ca.* 10%)

[a] Solvent, HMPA; [LiClO$_4$] = 0.3 mol dm^{-3}; [fluoranthene] = 0.02 mol dm^{-3}; volume electrolysed, 50 cm^3; duration of electrolysis, 9 h with stirring; constant cathode potential, −4.0 V *vs.* Pt wire; cathode area, 2 cm^2; T = 15–20 °C. [b] Absolute or azeotropic.

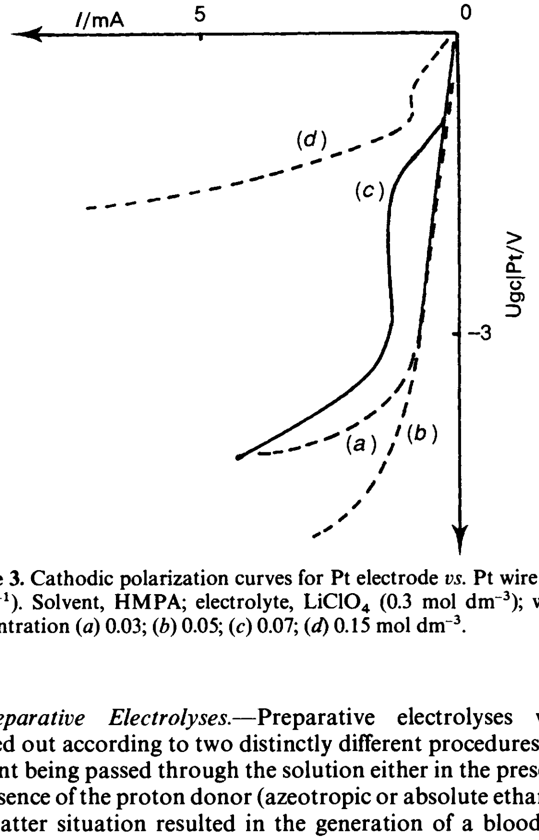


Figure 3. Cathodic polarization curves for Pt electrode *vs.* Pt wire (100 mV s^{-1}). Solvent, HMPA; electrolyte, LiClO$_4$ (0.3 mol dm^{-3}); water concentration (*a*) 0.03; (*b*) 0.05; (*c*) 0.07; (*d*) 0.15 mol dm^{-3}.

Preparative Electrolyses.—Preparative electrolyses were carried out according to two distinctly different procedures, the current being passed through the solution either in the presence or absence of the proton donor (azeotropic or absolute ethanol). The latter situation resulted in the generation of a blood-red stock of fluoranthene anions, which at the end of a run were reacted with a large excess of either absolute ethanol or aqueous (0.2 mol dm^{-3}) hydrochloric acid.

Whatever the procedure used, the crude reaction mixture was then worked up as described in the experimental section and the solid residue thus obtained was analysed by GLC, mass spectrometry, and NMR spectroscopy. The most informative outcome of this work is summarized in the Table, and the results are discussed at length below.

*Electrolyses in the Presence of Ethanol.**—When an attempt is made to pass current through a solution containing fluoranthene, whether ethanol is present or not, a weak current wave is recorded at −1.6 V *vs.* Pt wire while a faint orange colour appears on the cathode and vanishes in the bulk solution; this has been assigned to the direct formation of the radical anion $\mathrm{Ar}^{-\bullet}$ (see the section on polarization curves above). If the potential is made more negative, solvated electrons are eventually released into the catholyte without hydrogen evolution, and it might be expected that with this strongly reducing species it should be feasible to produce in solution either the radical anion $\mathrm{Ar}^{-\bullet}$ or the dianion Ar^{2-}. However, in the presence of ethanol, where neither the blue solvated electrons nor the red or orange aromatic anions can be accumulated (as evidenced by visual examination), it seems reasonable to rule out the contribution of Ar^{2-} to the formation of products. In the present study it was found by GLC analysis, mass spectrometry, and NMR spectroscopy that electrolysis of a 0.02 mol dm^{-3} fluoranthene solution in HMPA at −4.0 V *vs.* Pt, involving up to 4 F mol^{-1} but carried out in the presence of 2 mol dm^{-3} ethanol, produced mostly unchanged fluoranthene (**1**) along with small amounts (total < 5%) of numerous unidentified compounds and roughly 10% of a dimer of relative molecular mass 408 but little, if any, polymer. Only scant traces of dihydro- and tetrahydro-fluoranthene were detected by GLC.

Thus, in contrast with the results obtained for other aromatics,[3,4] hydrogenation of fluoranthene by electrolysis in HMPA in the presence of ethanol proved definitely unsatisfactory and no attempt was made to determine the structure of the products. One can, however, reasonably speculate that the dimer arises from reactions (1)–(5) (ready dimerization of 2,3-dihydrofluoranthene in basic medium has been reported[9]) and

$$\mathrm{Ar} + e^- \longrightarrow \mathrm{Ar}^{-\bullet} \qquad (1)$$

$$\mathrm{Ar}^{-\bullet} + \mathrm{ROH} \longrightarrow \mathrm{ArH}^{\bullet} + \mathrm{RO}^- \qquad \text{slow} \quad (2)$$

$$\mathrm{ArH}^{\bullet} + \mathrm{Ar}^{-\bullet} \longrightarrow \mathrm{ArH}^- + \mathrm{Ar} \qquad \text{fast} \quad (3)$$

$$\mathrm{ArH}^- + \mathrm{ROH} \longrightarrow \mathrm{ArH}_2 + \mathrm{RO}^- \qquad (4)$$

$$2\,\mathrm{ArH}_2 \xrightarrow{\mathrm{RO}^-} \mathrm{Ar}_2\mathrm{H}_4 \qquad \text{dimer } (M_r = 408) \quad (5)$$

the high current loss might be explained by the competing reduction of ethanol as suggested by Parker.[10]

$$\mathrm{Ar}^{-\bullet} + \mathrm{ROH} \longrightarrow \mathrm{Ar} + \mathrm{RO}^- + \mathrm{H}^{\bullet} \qquad \text{(regeneration of hydrocarbon)} \quad (6)$$

$$\mathrm{H}^{\bullet} + \text{HMPA or ROH} \longrightarrow \text{volatile decomposition products } (\textit{e.g.}, \mathrm{Me_2NH}, \text{as hinted by smell}) \quad (7)$$

---

* Note that for all experiments the same results were obtained with absolute as with azeotropic ethanol.

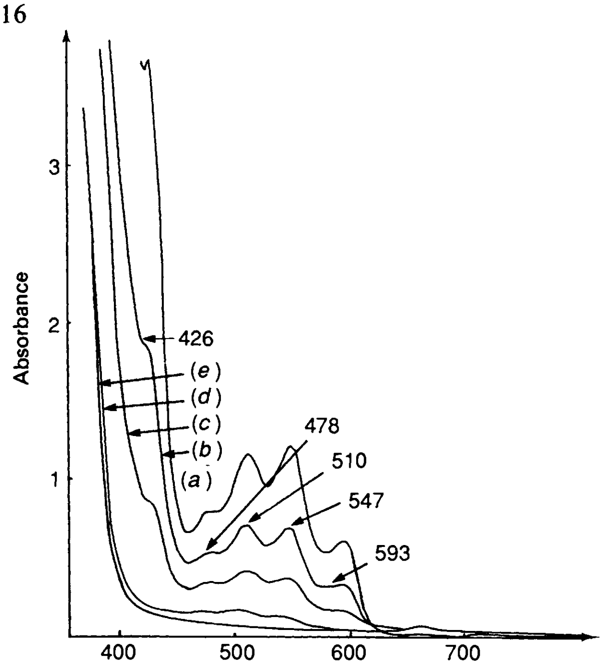


Figure 4. Absorption spectra of the anions produced by electroreduction of a 0.02 mol dm^{-3} solution of fluoranthene in HMPA–$LiClO_4$ at -4.0 V *vs.* Pt. Optical path, 1 cm; original solution diluted 100 times. (*a*) Spectrum recorded after passage of 4.7 F mol^{-1} through the solution; (*b*), (*c*), (*d*), and (*e*) as (*a*), but after progressive additions of oxygen.

Preparation of Anions by Electrolysis in the Absence of a Proton Donor.—The direct reduction of fluoranthene on the cathode at -1.6 V *vs.* Pt has already been mentioned above, but the current associated with this process is so weak that it may not play a significant role under the experimental conditions that were used.

In order to remove any reactive impurity, HMPA–$LiClO_4$ solutions were first pre-electrolysed at potentials between -3.1 and -4.0 V *vs.* Pt wire until irregular dark blue spots characteristic of solvated electrons developed on the cathode surface; fluoranthene was then added and the colour on the cathode turned from blue to blood-red and rapidly extended into the bulk of the solution. (Alternatively, the current was passed directly through the HMPA–$LiClO_4$–fluoranthene solution which, after the pre-electrolysis period, became red without the blue colour of solvated electrons being noticed on the cathode.)

It is worth at this point mentioning some unusual behaviour always observed in the production of solvated electrons and of fluoranthene anions as well. Upon stirring of the solution, at constant voltage, the current drops substantially (typically from 20 mA down to 15 mA) but quickly resumes its original value if the system is left at rest; this is the opposite of what is expected for a diffusion-controlled process. This is possibly due to a surface activation phenomenon of unknown origin involved in the release of electrons from the cathode, the surface being more active when an electron layer is already present.

During electrolysis the solution was sampled and electronic spectra of the fluoranthene anions were recorded (see Figure 4); aside of the maxima at 593, 547, 510, and 478 nm, two other transitions at 426 and 386 nm were revealed by subtracting curve (*e*) from curve (*c*), and there exists at least one more transition at shorter wavelength (but the spectrometer response at $A > 3.5$ is not sufficiently reliable to estimate a maximum for it).

It is of utmost interest to note that while all transitions decrease in intensity upon progressive exposure to oxygen [Figure 4(*b*)–(*e*)], the bands at 426 and 386 nm disappear more rapidly than those at lower frequency; as a cross-check for this observation it was found that a decrease in the amount of charge Q transferred per mole also reduces the intensity of the band at 426 nm relative to absorptions at longer wavelengths. Based on this, the absorptions at 593, 547, 510, and 478 nm are tentatively assigned to the radical ion $A^{-\bullet}$ and those at 426 and 386 nm to the dianion Ar^{2-}. In keeping with this it is also hypothesized that at high Q per mole transferred, the species that reacts subsequently with a proton donor is the dianion.

Reaction of Anions with the Proton Donor Ethanol.—Upon addition of an excess of absolute ethanol under an oxygen-free atmosphere, the dark red solution yielded by electrolysis (5 F mol^{-1}) turns to orange and then becomes slowly discoloured. After the usual work-up, GLC analysis and mass spectrometry evidenced the formation of several unidentified products in trace amounts, some dimer of relative molecular mass 408, and a substantial amount of unchanged fluoranthene (**1**), although a polymeric material was mainly obtained, in contrast with the results reported by Streitwieser,[9] who recovered up to 50% of a single dimer (M_r = 408) on addition of methanol to [fluoranthene$^{-\bullet}$ Na^+] in liquid ammonia.

The predominant polymerization reaction, which is not observed to occur when electrolysis is performed in the presence of ethanol, is readily accounted for by reactions (8)–(11) in which fluoranthene dianion is assumed to be the starting reagent. As

$$Ar^{2-} + ROH \longrightarrow ArH^- + RO^- \quad \text{fast and irreversible} \quad (8)$$

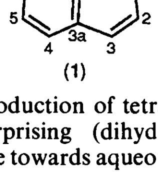
$$ArH^- + ROH \rightleftharpoons ArH_2 + RO^- \quad \text{slow and reversible}^9 \quad (9)$$

$$2ArH_2 \xrightarrow{RO^-} Ar_2H_4 \qquad \text{dimer } (M_r = 408) \quad (10)$$

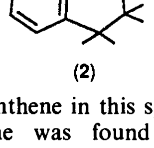
$$ArH^- \xrightarrow{ArH_2} Ar_2H_3^- \xrightarrow{ArH_2} Ar_3H_5^- \longrightarrow\longrightarrow \text{polymers} \quad (11)$$

far as hydrogenation of fluoranthene is concerned, the outcome is no better than that for electrolysis carried out in the presence of ethanol.

Reaction of Anions with Aqueous HCl *as the Proton Donor.*—The addition of an excess of 0.2 mol dm^{-3} aqueous hydrochloric acid to the red electrolysed solution (5 F mol^{-1}) resulted in its immediate discolouration. The solid residue recovered after work-up, analysed by GLC, mass and NMR spectrometry as a remarkably clean mixture of 50% unchanged fluoranthene (**1**), 10% dimer of relative molecular mass 410 (the GLC retention time of which is considerably shorter than that of the dimer produced with ethanol as the proton donor), and 40% tetrahydrofluoranthene (**2**) [checked against an authentic sample: δ($CDCl_3$) 7.69 (1 H, d, J = 7.5 Hz), 7.47 (2 H, d, J = 7.7 Hz), 7.26 (3 H, br m), 6.99 (1 H, dq, J = 7.5 and 1.0 Hz), 3.56 (1 H, dd, J = 12.2 and 5.2 Hz), 2.95 (1 H, dt, J = 17.4 and 5.2 Hz), 2.66 (1 H, br m), 2.47 (1 H, br m), 2.04, (2 H, br m), and 1.11 (1 H, br m).



(1)



(2)

The production of tetrahydrofluoranthene in this system is most surprising (dihydrofluoranthene was found to be unreactive towards aqueous HCl) since it requires four electrons per fluoranthene molecule. This leads to the conclusion that the postulated starting dianion plays the role of an electron

$$\left.\begin{array}{l}\mathrm{Ar}^{2-} + \mathrm{H}^{+} \longrightarrow \mathrm{ArH}^{-}\\ \mathrm{ArH}^{-} + \mathrm{H}^{+} \longrightarrow \mathrm{ArH}_2\\ \mathrm{ArH}_2 + \mathrm{Ar}^{2-} \longrightarrow \mathrm{ArH}_2^{-\bullet} + \mathrm{Ar}^{-\bullet}\end{array}\right\}\begin{array}{c}\text{fast}\\ \text{and}\\ \text{irreversible}\end{array}\quad\begin{array}{c}(12)\\ (13)\\ (14)\end{array}$$

$$2\mathrm{Ar}^{2-} + 2\mathrm{H}^{+} \longrightarrow \mathrm{ArH}_2^{-\bullet} + \mathrm{Ar}^{-\bullet} \qquad \text{balance} \qquad (15)$$

$$\mathrm{ArH}_2^{-\bullet} + \mathrm{H}^{+} \longrightarrow \mathrm{ArH}_3^{\bullet} \qquad (16)$$

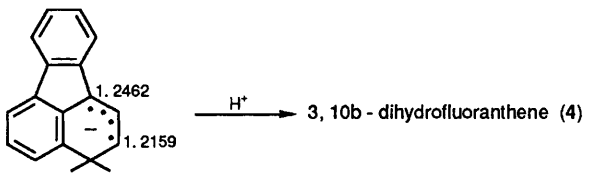
$$\mathrm{ArH}_3^{\bullet} + \mathrm{ArH}_3^{\bullet} \longrightarrow \mathrm{Ar}_2\mathrm{H}_6 \qquad \text{dimer } (M_r = 410) \qquad (17)$$

$$\mathrm{ArH}_3^{\bullet} + \mathrm{Ar}^{-\bullet} \longrightarrow \mathrm{ArH}_3^{-\bullet} + \mathrm{Ar} \qquad \text{(regeneration of fluoranthene)} \qquad (18)$$

$$\mathrm{ArH}_3^{-\bullet} + \mathrm{H}^{+} \longrightarrow \mathrm{ArH}_4 \qquad \text{tetrahydro-fluoranthene } (\mathbf{2}) \qquad (19)$$

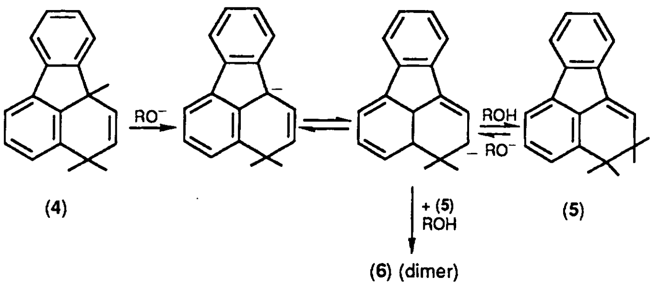
reservoir able to transfer efficiently half of its charge to a species formed in previous reduction steps. This could be consistently accommodated by reactions (12)–(15) and (16)–(19). However, for reaction (14) to hold fast and irreversible requires that the reduction potential of ArH_2 be less cathodic than the oxidation potential of Ar^{2-}.

At this point one should reflect on the predictions based on HMO theory. Calculations have been performed[9] which indicate that fluoranthene dianion has the highest electron density at position 3 and should first protonate to yield the anion (**3**), in which the two positions of highest electron densities [given in (**3**)] are 2 and 10b, with 10b preferred over 2 for protonation.



(**3**)

Thus (**4**) has been proposed as the actual reduction product of fluoranthene, but in the presence of the strong base RO^- it would rapidly isomerize to the more conjugated compound (**5**) which in turn would quantitatively dimerize to produce (**6**) (M_r 408). Our results however do not support this view; indeed if (**4**) were formed in the first place, it would not isomerize into (**5**) with HCl as the proton donor. Now with its π structure of 9-vinylfluorene and based on reduction potentials, (**4**) is not expected to be reduced by the fluoranthene dianion,[11] *i.e.* reaction (14) would not take place, but even more if the radical anion of (**4**) were formed all the same it would lead to hydrogenation of the fluorene moiety and would not produce (**2**) as the major reduction product. Therefore we must conclude that, although MO calculations for (**3**) indicate a slightly higher electron density at position 10b, actual protonation takes place at position 2 to yield (**5**), which with its dibenzofulvene π-structure is a likely candidate[11,12] for electron transfer from Ar^{2-} and stands as a reasonable intermediate on the route to (**2**) and to the dimer $\mathrm{Ar}_2\mathrm{H}_6$.



Acknowledgements

We thank Dr. B. Bettens for his kind assistance in performing the GLC analyses.

References

1 L. I. Krishtalik, *Electrochim. Acta*, 1976, **21**, 693.
2 (*a*) H. W. Sternberg, R. E. Markby, and I. Wender, *J. Electrochem. Soc.*, 1963, **110**, 425; (*b*) N. M. Alpatova and S. E. Zabusova, *Electrokhimiya*, 1980, **16**, 1262; (*c*) R. A. Misra and A. K. Yadav, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 347.
3 H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Am. Chem. Soc.*, 1967, **89**, 186; *ibid.*, 1969, **91**, 4191.
4 L. A. Avaca and A. Bewick, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1709.
5 H. Normant, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 1046.
6 R. Dietz, 'Organic Electrochemistry,' ed. M. M. Baizer and H. Lund, Marcel Dekker, New York, 1983, p. 237.
7 R. W. Coughlin and G. Kreysa, *Chem. Ing. Tech.*, 1983, **55**, 8; P. S. Moon, *J. Electrochem. Soc.*, 1984, **131**, 363; W. Kochkanek and G. Kreysa, *Chem. Ing. Tech.*, 1986, **58**, 372; G. Kreysa, *Nachr. Chem. Tech. Lab.*, 1986, **34**, 967.
8 M. D. Mackey and R. Peat, *J. Electroanal. Chem.*, 1982, **137**, 321.
9 A. Streitwieser, Jr. and S. Suzuki, *Tetrahedron*, 1961, **16**, 153.
10 M. F. Nielsen, O. Hammerich, and V. D. Parker, *Acta Chem. Scand., Ser. B*, 1984, **38**, 809.
11 (*a*) G. J. Hoijtink and J. van Schooten, *Recl. Trav. Chim. Pays-Bas*, 1952, **71**, 1089; (*b*) G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, *ibid.*, 1956, **75**, 487.
12 A. Streitwieser, Jr., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.

Paper 9/04198B
Received 2*nd October* 1989
Accepted 14*th November* 1989