Unexpected electrochemical reduction of fluoranthene in the solvents DME and HMPA: new light onto the mechanism of hydrogenation to produce tetrahydrofluoranthene

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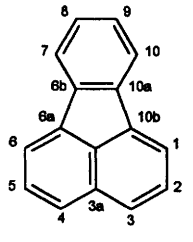
The non-alternant aromatic hydrocarbon fluoranthene (Ar^0) has been reduced, either chemically with Na or Li or by electrolysis, to the radical anion $Ar^{\cdot -}$ in the three solvents THF (tetrahydrofuran), DME (dimethoxyethane) and HMPA (hexamethylphosphoric triamide). The UV–VIS absorption spectrum of the orange–brown $Ar^{\cdot -}$ is quite similar in the three solvents and in all instances addition of H^+–H_2O has resulted in quantitative electron-back-donation along with H_2 evolution and recovery of unchanged fluoranthene Ar^0. Thus the usual Birch-type reduction to a dihydro derivative is totally inefficient in the cases under investigation. The two-electron reduction has also been achieved in these three solvents. The greenish-yellow dianion Ar^{2-} produced in THF exhibits characteristic UV–VIS absorption patterns, disproportionates with Ar^0 and reacts with H^+–H_2O only to evolve H_2.

With DME or HMPA a blood-red species is produced whose absorption spectrum is virtually the same and quite different from that observed in THF. In both solvents addition of H^+–H_2O leads to tetrahydrofluoranthene as a main reaction product but disproportionation is not observed at all in HMPA and this is not compatible with a regular dianion Ar^{2-}.

Reaction with D^+–D_2O instead of H^+–H_2O has shown that hydrogenation involves radical abstraction of H atoms from the solvent in both cases; this sheds new light onto the reaction mechanism. Furthermore, several other experiments indicate that the dianionic blood-red species is most likely a complex written as [$Ar^{\cdot -}$ ··· $^{\cdot -}$Solvent], in which the $Ar^{\cdot -}$ moiety is bound to a solvated electron localized on a solvent molecule.

Introduction

Five years ago we published[1] the unexpected observation that after electrochemical reduction of the neutral aromatic hydrocarbon fluoranthene **1** (hereafter referred to as Ar^0) in the solvent HMPA, the fluoranthene dianion Ar^{2-} so produced reacts with added aqueous HCl to yield as much as 40% of 1,2,3,10b-tetrahydrofluoranthene ArH_4 **2**.



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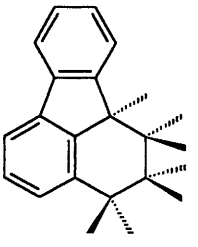

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The addition of four protons was surprising since this would require four electrons per molecule and we were led to postulate that the dianion should play the role of an electron reservoir capable of further reducing a hypothetical dihydro compound with a dibenzofulvene π structure formed in a preceding step. However no dihydro derivative was ever detected in the products.

The assumed dianion Ar^{2-}, recognizable by its blood-red colour, had been characterized by its vibronic optical absorption spectrum recorded on a dilute aliquot of the dianion, but it could not clearly be established whether we were dealing with a real dianion with two electrons occupying the aromatic LUMO.

The reaction vessel which we used at that time was not equipped with an optical cell and did not allow for the rigorous exclusion of moisture and oxygen; as a consequence the solutions had to be pre-electrolysed until complete removal of reactive impurities. For these reasons we could not follow the reaction progress through the disappearance of fluoranthene monitored by simultaneous production of $Ar^{\cdot -}$ and Ar^{2-}. We have thus designed a high vacuum electrolysis vessel fitted with an optical cell which enabled us to work under a strictly controlled atmosphere and to monitor the progressive reduction of Ar^0 by absorption spectroscopy.

This has been published in detail in a more recent paper,[2] but although we have been successful in analysing quantitatively the UV–VIS spectra of all reduced species produced in THF and HMPA, it has again not been possible to ascertain whether a real dianion Ar^{2-} is actually obtained in HMPA. Thus the blood-red species has been called 'X', but should more properly read as X^{2-}.

We now report on an extensive study of X^{2-}, a likely structure for it and a revised mechanism that accounts for the product ArH_4.

Experimental

Reagents

The solvent HMPA (99%+) from Aldrich was first dried over CaH_2 at 60–80 °C for 30 h under an atmosphere of nitrogen A28 from AIR LIQUIDE and then vacuum distilled; the middle fraction (101–102 °C/0.53 kPa) has been collected and stored under an atmosphere of nitrogen. For each experiment $LiClO_4$, ACS reagent from Aldrich, placed in the electrolysis vessel was dried by heating to 160 °C under dynamic vacuum (1.3×10^{-2} Pa) for 4–6 h. Ar 99.9996 from OXHYDRIQUE has also been used. The solvents, THF (anhydrous 99.9%) stabilized with ~0.025% butylated hydroxytoluene and DME (99%+) from Aldrich were first refluxed for 4 h over NaOH pellets and then distilled (66 and 84 °C, respectively) under atmospheric pressure of dry nitrogen and stored on sodium strips in order to remove the last traces of stabilizer and water. At the time of use, they were outgassed by freeze–pump–thaw cycles and finally introduced in the reaction cell by bulb-to-bulb transfer at 77 K. Sodium stick, dry ACS reagent, lithium rods (99.9%), deuterium chloride (20 wt% solution in D_2O, 99.5 atom% D) and deuterium oxide (99.9 atom% D) from Aldrich were used.

Apparatus and instruments

The electrolysis cell was of the two compartments and three electrodes H-type equipped with ground-joint fittings, attached 30 cm^3 bulbs for preparing solutions and high vacuum Springham stopcocks; an optical pyrex cell 4 cm^3 from HELLMA was connected perpendicular to the catholyte compartment. Bright-polished platinum plates 1 $cm^2 \times 0.05$ cm from Johnson Matthey, welded to platinum wires 0.1 cm in diameter were used as the anode and cathode. A coiled silver wire set aside the cathode worked as a satisfactorily stable comparison electrode for driving, in constant potential mode, the Princeton Applied Research model 362 scanning potentiostat. The cylindrical, *ca.* 20 cm^3, catholyte and anolyte compartments were separated by a G5 fritted glass and contained a Teflon coated magnetic bar for stirring. A photograph of this cell has been published.[2]

The current intensity was recorded with an X-t GOERZ metrawatt SE 120 instrument. When reduction is carried out chemically with Na or Li metal, a simpler type of cell is used which essentially includes a *ca.* 20 cm^3 pear-shaped Pyrex bulb connected on one side to a quartz or Pyrex 1 cm or 0.1 cm path optical cell and on the other side to Pyrex tubing with a side-arm B10 ground-joint through which Na or Li strips can be introduced and ending with a high vacuum grease stopcock.

GLC analyses and preparative separations were achieved on a twin-3 m, $\frac{1}{4}$ inch column, Intersmat IGC 16 instrument equipped with a TCD detector (W–Au wires), liquid phase DEXIL 400 15% on Chromosorb W (80–100 mesh) and He as the carrier gas.

Spectra were obtained with a Bruker WM250 spectrometer for NMR, a Bruker IFS 25 spectrometer for IR, either a Hewlett-Packard 8452A diode array or a Zeiss optical fibre MCS 320/340 combined diode array spectrometer for UV–VIS, a GC–MS ITD Finnigan MAT/Tracor 540 GC machine for relative mass measurements and a Bruker ER-200D-SRC spectrometer for EPR spectra.

Procedure

All reactions and measurements were made at 22 °C. When one wants to monitor quantitatively the reduction of Ar^0 into $Ar^{\bullet -}$ and Ar^{2-} by absorption spectroscopy, the high extinction coefficients necessitate the use of low aromatic concentrations; it is then essential to exclude residual oxidising and acidic species (oxygen and moisture) well below the 10^{-5} mol dm^{-3} limit. Thus, as a general rule, regardless of the concentration, the cells were always carefully purged with argon and then outgassed under dynamic vacuum ($< 1.3 \times 10^{-2}$ Pa) before admission of super-dry solvents and reagents; the solutions, once prepared *in situ*, were in turn outgassed by freeze–thaw cycles at 77 K under vacuum to less than 1.3×10^{-2} Pa.

Electrolyses were performed on 0.3 mol dm^{-3} $LiClO_4$ solutions, with fluoranthene added in the catholyte and within the potential range of -1.6 to -4 V *vs.* Ag wire. Chemical reduction with Na or Li was carried out in the pear-shaped cells in which strips of sodium or lithium were first introduced under a gentle flow of dry argon; measurements were usually successful when the metal strips remained mirror-bright throughout.

Results and discussion

Nature of X^{2-}

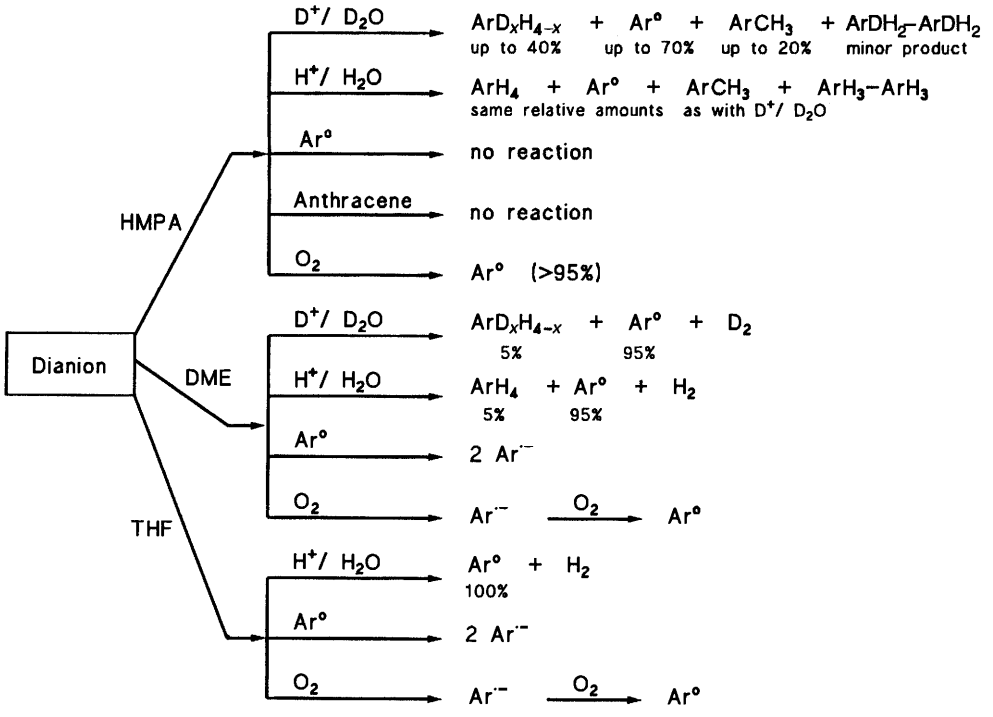
In order to elucidate the nature and structure of the blood-red species, the experiments given in Scheme 1 were performed and the results are hereafter discussed.

1. The one-electron reduction of fluoranthene by either electrolysis or reaction with Na or Li metal chips has produced the orange–brown radical anion $Ar^{\bullet -}$ in three solvents, namely THF, DME and HMPA. The UV–VIS spectrum of $Ar^{\bullet -}$ is fairly similar in the three solvents [same λ_{max} at 450, 512, 540 (sh), 592, 648 and 724 nm; similar ε values], with, however, a weak additional band at 382 nm in both THF and DME, but with the less solvated cation Na^+ only; this optical transition at higher energy indicates[3] that to some extent a contact ion-pair is produced in the poorly cation-solvating THF and even in DME with the weakly solvated Na^+, while with Li^+ or in HMPA with Na^+ and Li^+, a solvent-separated ion-pair is obtained. In the three solvents, addition of excess 1 mol dm^{-3} aqueous HCl induces quantitative electron-back-donation together with evolution of H_2 and regeneration of fluoranthene. No dihydro derivative has ever been detected. Upon addition of oxygen, $Ar^{\bullet -}$ is efficiently quenched with almost instantaneous bleaching of the solutions and $\geqslant 98\%$ recovery of unreacted fluoranthene Ar^0. At this point the strange behaviour of Ar^0 in HMPA must be emphasized: at high $[Ar^0]$ ($\sim 10^{-2}$ mol dm^{-3}) the regular sequence of reduction $Ar^0 + e_s^- \longrightarrow Ar^{\bullet -}$ followed by $Ar^{\bullet -} + e_s^- \longrightarrow Ar^{2-}$ has been observed; if $[Ar^0]$ is decreased to $\sim 10^{-3}$ mol dm^{-3}, the first reduction step to $Ar^{\bullet -}$ is observed only if the release of solvated electrons e_s^- is slow enough and if not, the reaction proceeds immediately to the blood-red X^{2-} even though there is still Ar^0 present in solution. At low $[Ar^0]$, in the 10^{-4} mol dm^{-3} range and for not exceedingly slow reduction rates, $Ar^{\bullet -}$ is not detected and the blood-red spectrum increases directly while that of Ar^0 disappears isosbestically; this is further discussed in section **2**(*b*).

2. The two-electron reduction has been performed in the same three solvents; the reduction species assumed to be the dianion Ar^{2-} has a greenish-yellow colour in THF and is blood-red in DME and HMPA; the UV–VIS spectrum is almost the same in the two latter solvents [same λ_{max} at 376, 426 (sh), 478, 512, 550 and 594 nm and similar but not identical ε values], but is distinctly different in THF [λ_{max} at 376, 440, 510 (sh), 696 and 778 nm].

The chemical behaviour of Ar^{2-} is very different in the three solvents, but is independent of the cation Na^+ or Li^+; two reactions, namely protonation and disproportionation, have been studied and the following results were obtained.

(*a*) Upon addition of aqueous HCl to the dianion, H_2 evolution and quantitative regeneration of Ar^0 occurred in THF; in DME substantial evolution of H_2 was observed but GLC analysis of the products recovered after the usual work-up (diethyl ether used as the extracting solvent) has shown the formation of about 5% of tetrahydrofluoranthene ArH_4 (GLC



Scheme 1

retention time, IR, NMR and GC–MS) in addition to 95% recovered Ar^0. In HMPA, no H_2 evolved whatsoever and after work-up, GLC revealed the presence of four compounds, three of which have been trapped and identified (NMR, IR and GC–MS) as ArH_4, Ar^0 and 3-methylfluoranthene $ArCH_3$, an unexpected product that had been overlooked in the former study.[1] From one run to another the yield of $ArCH_3$ varied with the experimental procedure and the initial [Ar^0], but in some cases the yield reached up to 20%, *i.e.* it is not a minor product (essentially $ArCH_3$ is produced when H^+–H_2O is added to the blood-red solution, but not when the solution of the anions is poured into a large excess of H^+–H_2O under vigorous stirring). ArH_4 is also often a major product amounting to 10–30% and recovered Ar^0 usually accounts for 40–70%. The fourth product seen by GC–MS is a dimer of relative mass $M_r = 410$ and base peak fragment at $M_r = 205$ which corresponds to ArH_3–ArH_3 (dimer of a trihydroradical). It could not be isolated in sufficient quantity to determine its structure.

(*b*) On account of the very different absorption spectrum obtained in THF in comparison with the spectra obtained in DME and HMPA, we have checked the dianionic nature of the reduced species by adding an excess of neutral Ar^0 to it in the different solvents. In THF and in DME immediate disproportionation took place, restoring the characteristic spectrum of $Ar^{\cdot -}$ as expected for a real dianion Ar^{2-}. In HMPA however, addition of neutral fluoranthene or even of anthracene, whose E^0 redox potential is less negative, did not bring about any change to the spectrum of the blood-red solution; this is consistent with the above-mentioned direct production of this species at low [Ar^0] and it indicates that $Ar^{\cdot -}$ competes efficiently with Ar^0 in the reaction with solvated e_s^- in this solvent.

This also means that in HMPA the $2e^-$ reduction does not lead to a conventional dianion in which two electrons occupy the aromatic LUMO for this would be thermodynamically unacceptable. Thus it is appropriate to refer to the blood-red species in HMPA as X^{2-} instead of Ar^{2-} but it must however be borne in mind that in DME the similar blood-red absorption spectrum is associated with an entity which behaves like a real dianion, at least as far as disproportionation is concerned. We will come back to this later.

3. The fact that even anthracene fails to react with X^{2-} indicates that the electron pair responsible for the dinegative charge must be strongly bound to its molecular structure and the specific action of HMPA suggests that a solvent molecule is directly involved in the structure of X^{2-}. In order to test the extent to which the electrons are trapped in X^{2-}, we carried out two experiments in which X^{2-} reacted with oxygen and with water. It turns out that reaction with neutral oxygen-free H_2O is moderately fast (seconds) whereas O_2 reacts fairly slowly (minutes). When a mixture of $Ar^{\cdot -}$ and X^{2-} in HMPA is used, O_2 instantly depletes $Ar^{\cdot -}$ leaving X^{2-} unchanged on that reaction timescale whereas, in another run, by the time that neutral oxygen-free water removes X^{2-}, $Ar^{\cdot -}$ is still almost unaffected. Thus X^{2-} behaves more like a carbanion than like a highly reducing species bearing $2e^-$ in its LUMO. This has been studied further by cyclic voltammetry (see section **10**).

4. We had previously investigated[1] the hydrogenation of fluoranthene in HMPA *via* electrochemical reduction followed by dropwise addition of aqueous HCl to the X^{2-} solution. The production of tetrahydrofluoranthene in fairly high yield (40%) had puzzled us because one had to explain the attachment of four protons on a dianion. It was suggested that, like in a Birch-type reduction, the dianion could further reduce an intermediate dihydro derivative. The first indication that this is wrong arose from the observation that just as much ArH_4 (but no ArH_2) is obtained when the X^{2-} solution is progressively introduced into a large excess of 1 mol dm^{-3} aqueous HCl solution under vigorous stirring and instantaneous dilution instead of slowly pouring H^+–H_2O into the HMPA solution, the last procedure being assumed more favourable to bimolecular e^- exchange between the proposed dianion reservoir and ArH_2 first produced [quenching of bimolecular processes by rapid dilution proved indeed efficient in the production of $ArCH_3$, see section **2**(*a*)]. Indeed this mechanism is now definitely dismissed since in HMPA the blood-red X^{2-} species does not disproportionate, does not transfer e^- even to anthracene and therefore cannot *a fortiori* act as an electron reservoir to reduce a dihydro product ArH_2 of any nature.

5. The possibility that X^{2-}, whose UV–VIS spectrum is quite fluorenyl-like,[3c] would arise from partial hydrogenation

of Ar^{2-} by traces of water or other proton donor impurities still present in HMPA, can be ruled out on the following grounds.

(*a*) For [Ar^0] up to 4×10^{-2} mol dm^{-3}, fluoranthene has been quantitatively reduced in X^{2-}; this would require much more than traces of impurities which anyway would have reacted with e_s^- or $Ar^{\bullet -}$ produced in the first step with regeneration of Ar^0 (*vide supra*). Furthermore the strictly controlled experimental procedure used for removing O_2 and H_2O makes unreasonable the assumption of such huge amounts of residual impurities.

(*b*) We reacted an authentic sample of ArH_4 (1,2,3,10b-tetrahydrofluoranthene) with Na in HMPA to produce the carbanion ArH_3^-; although the absorption spectrum of ArH_3^- resembles that of X^{2-}, it is distinctly different from it (all λ_{max} down-shifted by *ca.* 35 nm and the 426 nm band is missing). Addition of D^+–D_2O has produced 100% of $ArDH_3$ with D attached exclusively at the fluorenyl position 10b as evidenced by ^1H NMR spectroscopy and no Ar^0 could be detected, *i.e.* ArH_3^- does not aromatize through hydrogen loss; this will be further discussed in the section on the hydrogenation mechanism of X^{2-}.

(*c*) The absorption spectrum of X^{2-} in HMPA is almost identical to that recorded in DME for the well behaved assumed dianion, but it is without doubt that in this latter solvent, in which 100% disproportionation takes place, the aromatic π structure must be either essentially preserved or readily restored.

(*d*) X^{2-} in HMPA has been oxidized both chemically with O_2 and anodically [*i* is limited to a progressively decreasing value of 20–3 μA at 0 V *vs.* Ag (see section **10** on cyclic voltammetry) has permitted the selective oxidation of X^{2-} only]: more than 95% of the original fluoranthene Ar^0 has been recovered in all cases. Under these oxidising conditions X^{2-} reversed to Ar^0 without measurable production of $Ar^{\bullet -}$, *i.e.* the oxidation takes place either through a single two-electron step or *via* two one-electron steps, the first being slow and the second fast. In contrast to this, in THF and DME, the reaction of the dianion Ar^{2-} with O_2, monitored by UV–VIS spectroscopy has restored $Ar^{\bullet -}$ in a first step and only then Ar^0 in a second step.

6. Another way to produce a fluorenyl-like structure would be through radical–radical coupling[4] leading to the dimer dianion Ar^-–Ar^-. However $Ar^{\bullet -}$ has been produced in HMPA at concentrations as high as 4×10^{-2} mol dm^{-3} without alteration of its UV–VIS spectrum, *i.e.* the dimerization $Ar^{\bullet -} + Ar^{\bullet -} \rightleftharpoons Ar^-$–$Ar^-$ does not occur (at high concentrations the spectra are recorded on thin films sticking to the optical cell walls). An alternative route would be the ion–substrate coupling $Ar^{2-} + Ar^0 \rightleftharpoons Ar^-$–$Ar^-$, but anyhow on addition of H^+–H_2O one should obtain[4] the hydrodimerization product $(ArH)_2$ which in fact we have never detected [only $(ArH_3)_2$ at $M_r = 410$ has been obtained, *vide supra*]. Furthermore a dicarbanion Ar^-–Ar^- would have no tendency to regenerate Ar^0 or to disproportionate into $Ar^{\bullet -}$ in the presence of Ar^0. Still in our hands, up to 40–70% of unchanged fluoranthene has been recovered after addition of H^+–H_2O to X^{2-} in HMPA, presumably *via* protonation of the strong base[5] HMPA followed by e^- transfer [eqns. (1) and (2)] which would compete with protonation of the aromatic substrate (no H_2 has evolved, in agreement with a published result[6]).

In DME, as already mentioned, the blood-red species reacts with Ar^0 to yield quantitatively $Ar^{\bullet -}$ and this calls unambiguously for a species in which electrons are readily available as with a real dianion Ar^{2-}, although the UV–VIS spectrum is nearly identical to that of the blood-red entity obtained in HMPA. This last observation suggests that in the rather strong cation solvating DME, the dianion mainly exists as a solvent-separated ion-pair[3] where, to some extent, the aromatic framework shares electrons with solvent in a structure which should closely resemble that of the complex X^{2-} produced in HMPA.

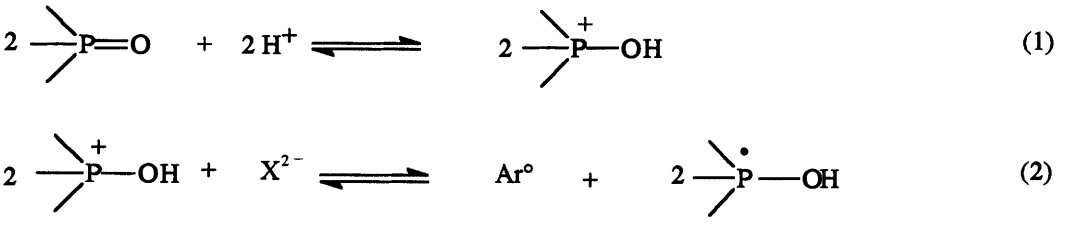
7. The unusual solvent effect associated with HMPA suggests (see section **3**) the formation of a strong Ar^{2-}·HMPA association, the existence of which calls for further evidence. Thus we have prepared the classical dianion Ar^{2-} in THF and three check-tests have been carried out on that solution.

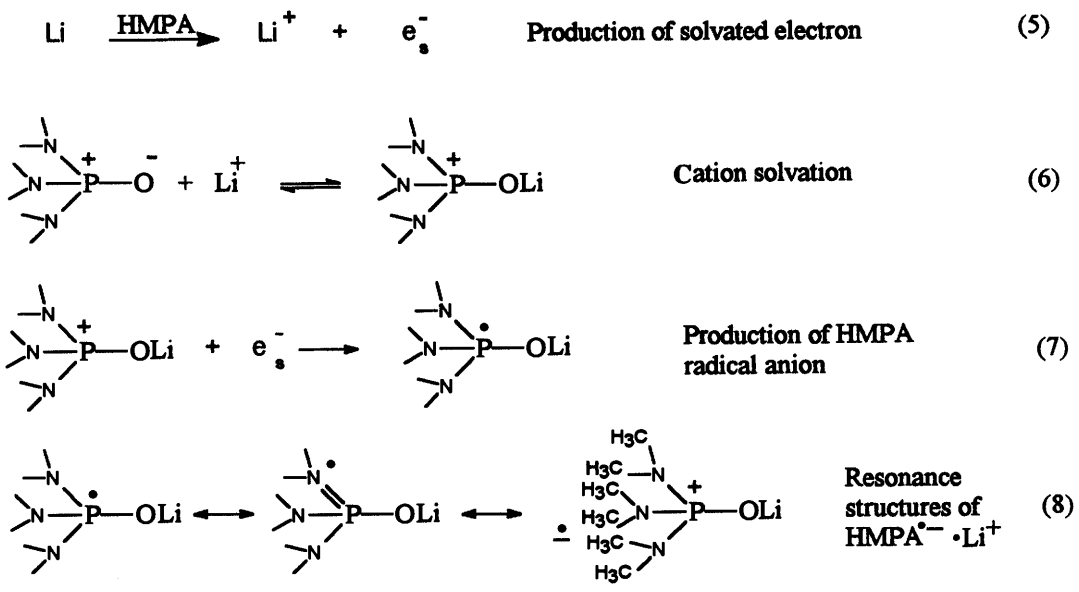
(*a*) A few drops of the Ar^{2-}–THF solution have been added to 3 cm^3 of pure superdry HMPA in an optical cell: the greenish-yellow colour of Ar^{2-} turned to blood-red instantly and the UV–VIS spectrum of that solution is identical to that of X^{2-}.

(*b*) To 4 cm^3 of the Ar^{2-}–THF solution placed in an optical cell, we have added a few drops of pure HMPA; here again the greenish-yellow colour completely vanished while the spectrum of the blood-red X^{2-} replaced that of Ar^{2-}–THF. Some fluoranthene Ar^0 has then been added to the cell but had no effect on the red species and that is consistent with the known failure of X^{2-} to disproportionate. At this point, on the basis of literature reports,[3] it is tempting to suggest that in THF one deals with a contact ion-pair $Ar^{2-}|2M^+$, whereas in the presence of the very strong cation solvating HMPA,[5,6] the solvent-separated ion-pair $M^+|Ar^{2-}$ HMPA$|M^+$ would predominate and correspond to X^{2-}. Nevertheless this explanation does not hold satisfactorily on account that due to coulombic repulsion Ar^{2-} is expected to be more reactive in the solvent-separated ion-pair than in the contact pair[3] while in fact the dianion does disproportionate with Ar^0 in THF and even DME but not in HMPA. Thus the present results lend support to the formation of a complex [Ar·HMPA]$^{2-}$ in which the two extra electrons would be shared between the aromatic species and at least one solvent molecule.

(*c*) On account of the close similarity between the UV–VIS spectra obtained by the two-electron reduction in HMPA and in DME, we have already suggested (see section **6**) that in DME, a similar complex should form and we tested in the same way how this solvent would interact with Ar^{2-} produced in THF. Thus a few drops of pure DME have been mixed with 3 cm^3 of the greenish-yellow Ar^{2-}–THF solution: indeed here too the blood-red colour appeared at once and the spectrum was identical with that of the dianion prepared in DME alone. This is a strong additional indication in favour of a solvent–solute complex that we describe as the entity [Ar·DME]$^{2-}$ by analogy with the behaviour observed in HMPA.

8. In order to substantiate even more the concept of an aromatic–solvent dinegative complex, we have relied on its production *via* a distinctly different route. We have recently shown[7] that the blue solvated electrons e_s^- produced in HMPA either by electrolysis or by dissolving Na or Li metals, can lead to the rather stable solvent radical anion $HMPA^{\bullet -}$ which proved to be a strongly reducing agent towards fluoranthene.





Thus, the pale-yellow (λ_{max} = 420 nm) $HMPA^{\bullet -}$–HMPA solution is a substitute for the blue e_s^- and reacts with Ar^0 [eqns. (3) and (4)] to produce first the orange–brown radical

$$HMPA^{\bullet -} + Ar^0 \xrightarrow{HMPA} HMPA + Ar^{\bullet -} \quad (3)$$

$$HMPA^{\bullet -} + Ar^{\bullet -} \xrightarrow{HMPA} X^{2-} \quad (4)$$

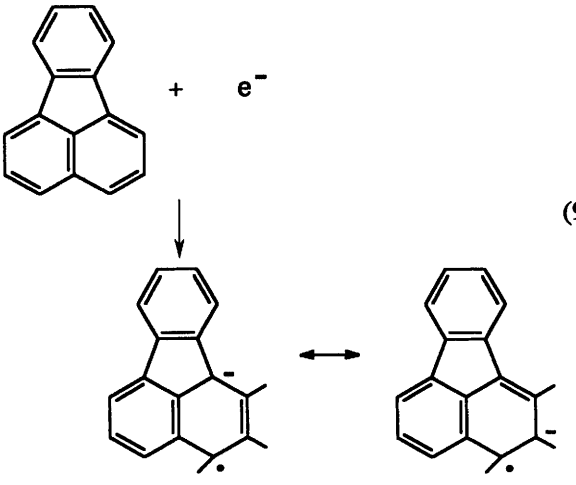
anion $Ar^{\bullet -}$ easily identified by its characteristic UV–VIS spectrum; in the presence of excess $HMPA^{\bullet -}$, the orange–brown colour turns to blood-red in a second step and the spectrum is now identical with that of X^{2-}.

At this stage one can hardly think of anything but the aromatic–HMPA complex already suggested and written as $[Ar{\cdot}HMPA]^{2-}$.

9. One more clue arose from EPR spectroscopy. In all three solvents THF, DME and HMPA the radical anion $Ar^{\bullet -}$–Na^+ produced a signal made up of three overlapping components, centred at almost the same *g* value in DME and in HMPA and at a slightly lower magnetic field in THF. These signals did not show hyperfine structure and were characterized by substantially different linewidth; in all three cases the weakest signal has the largest linewidth of 20.5 G (THF), 18.1 G (DME) and 18.1 G (HMPA). The two other signals are of similar relative intensities and characterized by linewidth values of 9.3 and 3.3 G (THF), 9.8 and 2.3 G (DME) and 10.6 and 2.5 G (HMPA). These three signals displayed by $Ar^{\bullet -}$–Na^+ are interpreted in terms of different types of ion-pairs or aggregates already recognized by UV spectroscopy;[3] they all vanished instantly upon admission of oxygen into the cell.

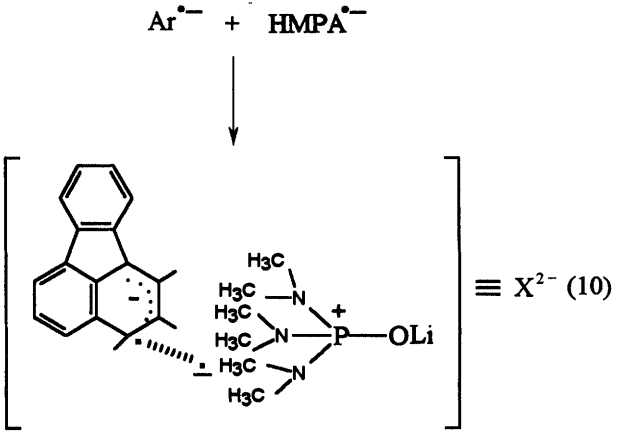
More informative were the EPR responses for the dianionic species in these solvents: none of them gave an EPR signal, indicating that they are all diamagnetic. Admission of oxygen quickly discoloured the THF and DME solutions which here again did not exhibit any EPR signal. The case of the blood-red X^{2-} produced in HMPA is however quite different: indeed whereas X^{2-} proved diamagnetic, on addition of oxygen an EPR signal with hyperfine structure appeared and increased until the red colour had vanished. The EPR spectrum of the oxidized species extended over a full range of 21.4 G, and was easily analysed as a set of 5 lines with 4.3 G splitting, each of which was further split into triplets with lines 1.07 G apart from each other. We have not been able to assign a structure to this paramagnetic species, but the essential fact is that it was produced at the expense of the dianionic diamagnetic blood-red X^{2-}; note that this paramagnetic entity eventually decomposed with regeneration of the starting fluoranthene Ar^0. These results are fully compatible with the singlet bonding complex $[Ar^{\bullet -} \cdots {}^{\bullet -}HMPA]$ that we propose, in which the e^- are no longer readily available, *e.g.* for reducing anthracene to its radical anion and for which a tentative molecular representation is presented in eqns. (5)–(10).

In the present model the radical anion $HMPA^{\bullet -}$ would possibly be stabilized through hyperconjugation with the CH_3 groups. For the aromatic moiety see eqn. (9).



(9)

One way of representing the X^{2-} complex is then through the bonding interaction between the lone e^- on the aromatic and the σ-like e^- on HMPA [eqn. (10)].



Such a complex is indeed expected to exhibit a fluorenyl-like UV–VIS spectrum while its oxidation *via* O_2 or anodic polarization should essentially restore the Ar^0 π structure as is experimentally observed.

10. Finally, to complete our study, we used cyclic voltammetry which might appear as the tool of choice in this type of work.[8] In the present case however, the reduction mechanism that could be based on it is not straightforward. Indeed, although the reversible one-electron reduction wave corresponding to $Ar^0 + e_s^- \rightleftharpoons Ar^{\bullet -}$ was easy to characterize at a standard potential of -1.0 V *vs.* Ag in HMPA–0.3 mol dm^{-3} $LiClO_4$, the reduction of Ar^0 to X^{2-} only occurred in the bulk solution at the potential of e_s^- release and was irreversible. This is coherent with our model (see section **1**) in which we propose that X^{2-} is produced *via* two distinct chemical steps, *i.e.* $Ar^0 + e_s^- \longrightarrow Ar^{\bullet -}$ followed by either $Ar^{\bullet -} + e_s^- \xrightarrow{HMPA} X^{2-}$ or $Ar^{\bullet -} + HMPA^{\bullet -} \longrightarrow X^{2-}$. Thus X^{2-} is only produced at the potential of e_s^- release (-2.2 V *vs.* Ag). It is then highly significant that cyclic voltammetry shows an oxidation wave only at a peak potential as high as $+0.06$ V *vs.* Ag (in all cases the sweep rate was 5 mV s^{-1}); this indicates that X^{2-} is a weak reducing agent or in other words that the two extra electrons are stabilized in a strongly bonding structure which is compatible with the singlet ground state of the $[Ar^{\bullet -} \cdots {}^{\bullet -}HMPA]$ complex that we propose and which of course cannot reduce even anthracene into its radical anion.

Mechanism of production of ArH_4

We have shown in section **4** that the mechanism that we have formerly proposed[1] for the production of tetrahydrofluoranthene in HMPA does not hold true anymore on account of observations made. Thus, again we face the intriguing fact that on addition of H^+–H_2O a dianionic species captures four hydrogen atoms. Of particular significance is the production of substantial amounts of 3-methylfluoranthene, which indicates that on top of its strong solvent effect HMPA comes into play as a chemically active partner able to release carbon atoms.

We attempted to trace the hydrogenation steps of X^{2-} by using a 0.5 mol dm^{-3} solution of DCl in D_2O instead of HCl–H_2O as the protonation (deuteriation) agent. Instead of the expected tetradeuteriofluoranthene, we have obtained a mixture of products of general formula ArD_xH_{4-x} where x, depending on the experimental procedure, ranges between ~ 1.3 and 1.8 as measured by ^1H NMR spectroscopy, that is up to an average of 2.7 hydrogen atoms have been incorporated; mass spectrometry provides evidence for a mixture of mono- and di-deuterio derivatives. The recovered fluoranthene Ar^0 and the methylfluoranthene are 100% deuterium-free as shown by MS, ^1H NMR and IR spectroscopy (the C–D stretching at 2176 cm^{-1} has been clearly identified in ArD_xH_{4-x}). Furthermore, the deuteriation % and positions depend on whether the X^{2-} solution is slowly poured into a large excess of D^+–D_2O under vigorous stirring or instead D^+–D_2O is slowly added to the concentrated solution of X^{2-}; in the first instance the lowest deuteriation value of x is 1.3 and deuteriation is strictly restricted to carbon atoms 10b (0.36 D), 1 (0.44 D) and 2 (0.53 D) while carbon 3 specifically catches a hydrogen atom. In contrast, when D^+–D_2O is added to X^{2-}, deuteriation increases up to an average of 1.8 atoms per molecule (*i.e.* the % of dideuterio is higher) and extensive H–D scrambling takes place resulting in a random distribution of deuterium over the four carbon atoms. While on one hand it is obvious that deuteriation involves an ionic reaction with D^+, on the other hand it is also clear that hydrogenation requires the aprotic HMPA as hydrogen donor and must be of radical nature; this along with the production of $ArCH_3$ is definite evidence for the major chemical contribution of the solvent HMPA to the reactions arising with X^{2-}. Involvement of HMPA as hydrogen donor to free radicals has in fact been reported in at least two instances.[6,9]

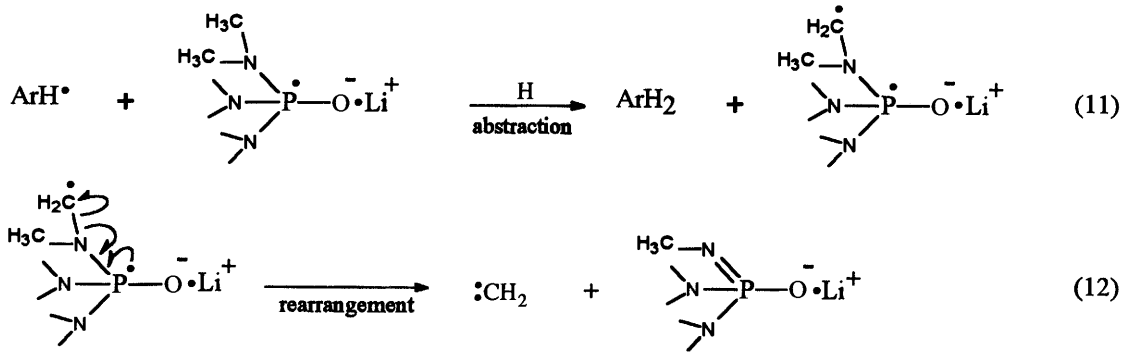
At this point, one is led to conclude that two distinct mechanisms operate: one involves a single ionic step, namely addition of D^+ on a negatively charged carbon atom, followed by three radical abstractions of H atoms from the HMPA moiety of the complex and the other implies that the two electrons of X^{2-} are eventually localized on the aromatic moiety which ends up as a dideuterio dihydrofluoranthene by addition of two D^+ and abstraction of two $H^{\bullet}$ from HMPA. Since the UV–VIS spectrum of Ar^{2-} in DME is nearly identical to that of X^{2-} in HMPA, the deuteriation experiment has also been conducted in this solvent. In DME, the blood-red species, which disproportionates with Ar^0, should have a structure close to a reactive solvent-separated ion-pair[3] such as $M^+|Ar^{2-}$ DME$|M^+$ ($M^+ = Li^+$ or Na^+). Yet addition of D^+–D_2O to the blood-red dianion in this solvent brings about results which bear some similarity to those obtained with HMPA: 95% of unchanged fluoranthene have been recovered, concomitant with D_2 evolution in this case and 5% of ArD_xH_{4-x} have been trapped by GLC (no $ArCH_3$ has ever been detected with DME). The results are even more striking here than in the case of HMPA. Indeed x only amounts to an average of 1 D distributed selectively over carbon 10b (0.4 D) and carbon 2 (0.6 D), which corresponds to a mixture of two isomeric $ArDH_3$. Thus in the aprotic DME, as many as 3 H atoms must be abstracted from the solvent by radical intermediates derived from the solvated ion-pair but again, like with HMPA, this only occurs after initiation by ionic addition of D^+.

Based on the present observations it follows that in DME the ion aggregate $Ar^{2-}\cdot 2M^+$ is strongly solvated and likely exists as a spin-paired complex, similar to that which forms in HMPA and consistent with the ionic addition of only one D^+ (solvated electrons are indeed known to form in DME,[10] although being less stable than in HMPA). However as far as disproportionation is concerned, the complex behaves as a reactive ion-pair including the dianion Ar^{2-}, in which the aromatic π structure would be essentially preserved.

The production of substantial amounts of methylfluoranthene upon addition of H^+–H_2O (or D^+–D_2O) to $M^+|Ar$ HMPA$|^{2-}M^+$ in HMPA and its total absence with the similar reaction carried out in DME is worth a comment. There is little doubt that this product arises from a carbene insertion onto an aromatic C–H bond and the only possible origin of the carbene is the solvent HMPA itself; a similar reaction on toluene to yield ethylbenzene in HMPA has been reported.[6] There is a simple way to explain this: protonation of the complex yields a free radical which abstracts a H atom from $HMPA^{\bullet -}\cdot Li^+$ and thus produces a solvent radical which rearranges with loss of $:CH_2$. The general reaction reads as eqns. (11) and (12) although hydrogenation does not actually stop at the ArH_2 stage. With DME which also undergoes H abstraction, there is no ready bond breakage that could free $:CH_2$ and the insertion is therefore not observed.

Conclusions

The fluoranthene dianion Ar^{2-}, with two electrons in its LUMO, has been produced in the solvent THF but is unstable with respect to the strong cation solvating agents DME and HMPA in which a complex solvated ion-pair is produced whose chemical reactivity involves the solvent moiety as an active partner. Although the whole reaction must be initiated by ionic addition, the subsequent steps are dominated by radical contribution and this is rather unexpected for electrochemistry carried out in highly polar media. Another major feature in these systems is the marked tendency to preserve the aromatic framework by inducing electron-back-donation rather than addition of electrophiles and this affects adversely the use of $Ar^{\bullet -}$ and Ar^{2-} as synthons in organic syntheses (electron-back-donation from charged conjugated polyenes has been reported).[11] Work is currently in progress in our laboratory to



determine whether the observations reported in the present paper are particular to the non-alternant hydrocarbon fluoranthene or apply more generally to other aromatic compounds. It has already been established that in HMPA, pyrene produces a classical radical anion, but the assumed dianion does not display the UV–VIS spectrum published[12] for the pyrene dianion and might well correspond to a [pyrene$^{\bullet-}$ ••• $^{\bullet-}$HMPA] complex analogous to that described for fluoranthene.

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