Transients Formed during Reduction of Polynuclear Aromatics: A Pulse Radiolysis Study

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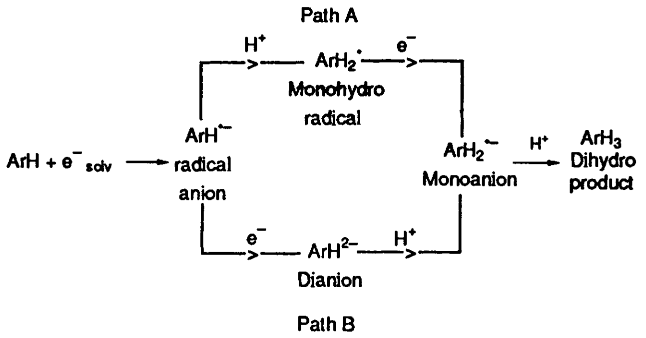
Pulse radiolysis studies of the reduction of polynuclear aromatic hydrocarbons naphthalene, anthracene, pyrene and pentacene (ArH) with solvated electron and H atom have been carried out on the nanosecond time scale, using 7 MeV electron pulses in polar organic solvents, both protic and aprotic. Kinetic results of reactions of ArH with e^-_{solv} show high reactivity (k *ca.* 10^{10} dm^3 mol^{-1} s^{-1}) to form the respective radical anions ($ArH^{\bullet -}$), with increasing yields in the presence of primary low molecular weight aliphatic amines and alcohols. In an attempt to follow the individual radical anion reactivity in these solvents, their decay to form the respective monohydro radicals ($ArH_2^{\bullet}$) were observed. The measured pseudo-first-order formation rate constants of the respective $ArH_2^{\bullet}$ (k_f *ca.* 10^5 to 10^3 s^{-1}) indicate that, in the presence of dissolved alkali metal in THF and amines/ammonia, as in the Birch synthesis, the reduction of these hydrocarbons follows this mechanism.

In organic synthesis, reduction of polynuclear aromatic hydrocarbons (ArH) is conveniently carried out at reduced temperature by treatment with alkali metals or calcium (M) in the presence of liquid ammonia or amines dissolved in an ether solvent (THF), and is commonly known as Birch reduction.[1-3] The reduction proceeds *via* carbanionic intermediates which ultimately take up protons either from the solvent matrix or added cosolvents like alcohols to form the dihydrogenated species. As shown in Scheme 1, from the initially produced radical anion ($ArH^{\bullet -}$) that is always formed in the first step, this process has been postulated to occur by one or both of the following pathways.

(i) Addition of a proton to the radical anion and then repeated addition of another electron and proton involving the monohydro radical intermediate ($ArH_2^{\bullet}$) as in path A.

(ii) The dianion intermediate (ArH^{2-}) is produced from further reduction of $ArH^{\bullet -}$, and undergoes addition of two protons in two steps as in path B. The monoanion ($ArH_2^{\bullet -}$) is a common intermediate before the final protonation in both the pathways mentioned above.



Scheme 1

Since addition of even one electron to any ArH will result in the loss of its aromatic stability, simultaneous addition of the second electron to this negatively charged radical anion to form the dianion may be difficult in terms of energetics, unless stabilization of the excess charge by solvation, delocalization or possible counter ion binding (originating from dissolved alkali metal M^+ as in the Birch process) also takes place simultaneously.[4] In smaller ArH molecules, whose effective electron affinity in solution is low,[4] preferential addition of the second electron before protonation therefore seems less probable. Thus, depending on the specific hydrocarbon (ArH) being reduced, the relative propensity of these two processes would be influenced by the prevailing concentrations of the solvated H^+/e^- as well as by the individual reaction rates of H^+ (or the matrix donating H^+) and e^-_{solv} addition to the corresponding radical anion. Both these processes will be strongly dependent on the ease of charge stabilization in any anion/radical formed, as well as the relaxation and rearrangement of solvent matrix aggregation around it with respect to its changing charge. Therefore, the formation of dianions is expected to gain importance with those ArH that have high electron affinity and the possibility of rapid charge delocalization over a large 'molecular area', resulting in their slow protonation rates, or for compounds like cyclooctatetraenes ($4n$ π electron system) where the dianion acquires aromatic stability ($4n + 2$ π electron).[5]

Using pulse radiolysis techniques, characterization studies of transients (anions and excited states) of various aromatic hydrocarbons have been carried out at room and low temperatures in different solvents and glassy matrices.[6] However, elucidation of any reaction mechanism, as in the Birch process in the presence of aliphatic amines in these solvents, where solvated electrons play an important part, has not been reported. In our study, a quantitative evaluation of the decay pathways followed by transient radical anions ($ArH^{\bullet -}$) of four aromatics naphthalene(NP), anthracene(AN), pyrene(PY) and pentacene(PE) has been attempted, to confirm the possibility of the existence of one or both pathways of Scheme 1. The intermediates to which each of these radical anions decay further, in various solvent matrices relevant to Birch reduction, have been studied. The spectral characteristics in the UV–VIS range and relevant kinetic parameters for all these intermediates are also presented. The radical anions for this purpose have been generated separately in each matrix at room temperature using the technique of pulse radiolysis. The primary reducing species in this case is the same as obtained in the Birch reduction process, namely $e^-_{ammonia/amine}$ (ammoniated or aminated electron). Unlike the Birch conditions, however, stabilization of the radical anion by ion pairing with a solvated cation arising from the solublized metal ion, M^+_{solv} was not possible.

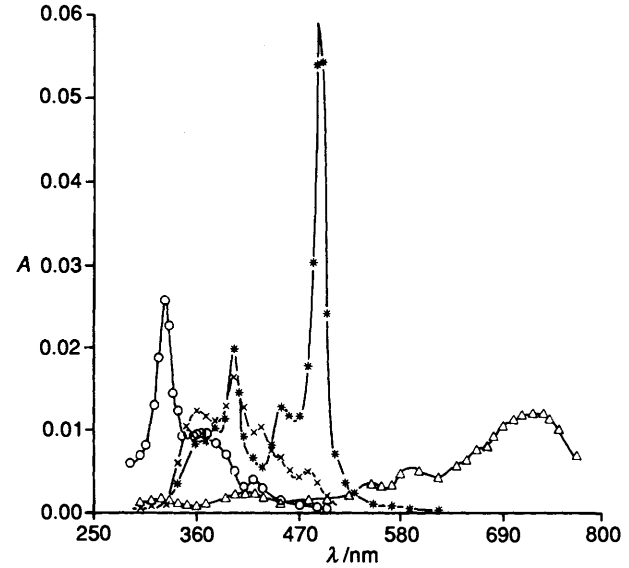


Fig. 1 Optical absorption spectra of transients of NP (—○—), AN (—△—), PY (—*—) and PE (—×—) in deoxygenated TB at [e^-_{solv}] = 1.2×10^{-6} mol dm^{-3}

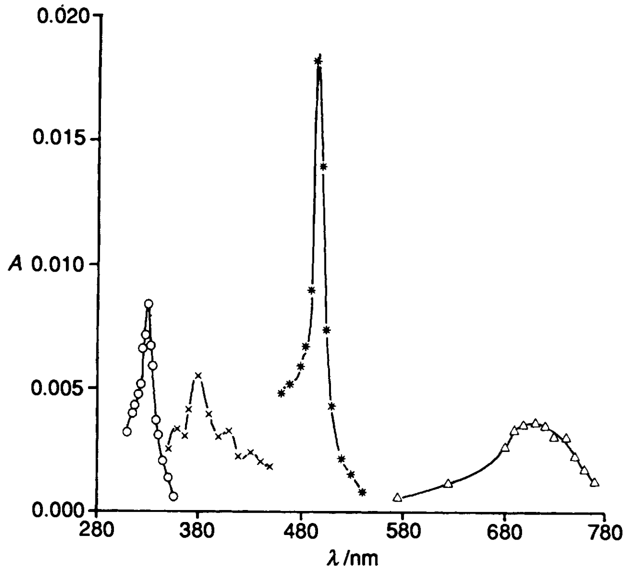


Fig. 2 Optical absorption spectra of radical anion ($ArH^{\bullet -}$) transients of NP (—○—), AN (—△—), PY (—*—) and PE (—×—) in deoxygenated THF at [e^-_{solv}] = 3.8×10^{-7} mol dm^{-3}

Experimental

Naphthalene, anthracene and pyrene were obtained from Fluka AG and used after recrystallization from benzene. Pentacene, obtained from KK laboratories, was first dissolved in tetrahydrofuran and its saturated solution was filtered. Its concentration was checked spectrophotometrically[7] and later diluted in appropriate solvent matrices for further studies. Solvents used in the study were AR grade *tert*-butyl alcohol (TB), obtained from M/s SISCO, India and spectro grade tetrahydrofuran (THF) and ethanol, obtained from M/s BDH, England. While TB was used after drying and distillation, THF was used after removal of peroxide residue, repeated drying and final distillation over sodium metal. Iolar grade gasses N_2, O_2 and N_2O, obtained from M/s Indian Oxygen Ltd. were used for saturating the solutions.

The pulse radiolysis experimental set-up used in this study has been described in detail earlier.[8a] Single pulses of 7 MeV electrons used for different set of experiments were of either 50 ns or 2 μs duration and the dosimetry was carried out using air saturated 0.01 mol dm^{-3} KCNS solution in water using the value of $G(CNS)_2^-\varepsilon = 2.23 \times 10^{-4}$ m^2 J^{-1} at 500 nm from literature.[8b] Typical maximum possible doses obtained were for 50 ns pulses 15 Gy and for 2 μs pulses 120 Gy. The kinetic spectrophotometric detection system was capable of measurement in the range of 250–800 nm. Dry ammonia for these experiments was generated from a mixture of solid NaOH and NH_4Cl and was used with N_2 carrier gas. The amines 1,2-diaminoethane (ED) and 1,2-diaminopropane (PD) obtained from M/s SISCO, India were purified by refluxing and distilling over KOH in a N_2 stream. Spectra of $ArH_2^{\bullet}$ species in organic media were recorded separately in the presence of dissolved HCl gas that was generated from a mixture of solid NaCl and conc. H_2SO_4 and was used with N_2 carrier gas. Unless otherwise stated, all the solutions were saturated with N_2 gas prior to irradiation. Whenever required fresh solutions were used to keep solute decomposition within the limits of experimental error and minimize interference from radiolysis products.

Results

Formation of Radical Anion.—Solvated electron, e^-_{solv}, reactions in TB and THF with the aromatic hydrocarbons NP, AN, PY and PE produced transients absorbing in the UV–VIS range. As seen later, these were assigned to the respective radical anion structures. Employing *ca.* 10^{-4} mol dm^{-3} solutions of each of these ArH, with 50 ns electron pulses, their formation was observed to be complete within a few μs. The optical absorption spectra of the various $ArH^{\bullet -}$ measured in TB are shown in Fig. 1 while Fig. 2 represents their spectra obtained in THF solvent. As explained later, compared to Fig. 2, Fig. 1 also shows some additional peaks not due to the radical anions of the corresponding solutes. These peaks belong to the monohydro radicals of the respective solutes which are also formed simultaneously in protic TB by the addition of primary $H^{\bullet}$ radical to solutes.

Under these experimental conditions, electron radiolysis is also expected to generate solute triplets (^3ArH) on the μs time scale though their yields in solvents like TB and THF may be quite low.[9] In μs time scales as employed for all measurements, the contribution from any singlet excited state of solute/solvent is expected to be insignificant. In earlier studies[6a,b] the triplet absorption of NP, AN and PY have been characterized. In our experiments no significant absorption due to these solute triplets were observed in TB, while in THF a small peak, probably due to ^3AN was present. From the reported values of λ_{max} for ^3ArH of NP, AN and PY (values lie between 414 and 425 nm for all in different solvents), it is observed that these values are very different from the λ_{max} values of the respective radical anions ($ArH^{\bullet -}$, Figs. 1 and 2) and the intermediates to which these were observed to decay, as discussed later. Similarly, for any ^3PE produced the same argument is expected to hold, causing minimum interference in later studies.

As the solvated electron yield varies with the relative permittivity of the solvent, it is expected to be more in TB and in the presence of ammonia/amines, as compared to THF. In THF the e^-_{solv} absorption peak has been measured at 2100 nm[10] and in the current range of transient absorption measurements (*i.e.* 250–800 nm) its molar extinction coefficient value is reported to be low. Therefore, comparison of its decay kinetics with that of transient ($ArH^{\bullet -}$) formation was not possible. In THF, accepting the reported extinction coefficient (ε) values of radical anions from literature[6a] (PY: 4.95×10^4 dm^3 mol^{-1} cm^{-1} at λ_{max} = 497 nm and AN: 0.99×10^4 dm^3 mol^{-1} cm^{-1} at λ_{max} = 720 nm) and from the observed yields of these transients in the present set of experiments, the Ge^-_{solv} value was calculated to be 0.25. In TB, assuming the respective ε values of these radical anions to be same as in THF, the calculated value for Ge^-_{solv} is

Table 1 Formation of $ArH^{\bullet -}$ in TB and THF as compared to decay of e^-_{solv} in TB

ArH	$k(e^-_{solv})_{decay}$/ 10^{10} dm^3 mol^{-1} s^{-1}	$k_{1\,form}/10^{10}$ dm^3 mol^{-1} s^{-1}		$k_{1\,decay}/10^3$ s^{-1}		λ_{max}/nm	
		TB	THF	TB	THF	$ArH^{\bullet -}$	$ArH_2^{\bullet}$
NP	2.1	1.9	1.5	83	73	325, 365	335
AN	2.6	2.4	2.0	550	240	730	275, 320, 405
PY	2.5	2.2	1.5	630	300	495	405
PE	1.2	1.0	0.5	33	1.8	370–390	425, 480

0.8 and is close to the value expected in low molecular weight aliphatic alcohols.[6a] In both the aliphatic amines used as solvent, the observed Ge^-_{solv} value was of the order of 1.2. In the presence of dissolved ammonia (saturated in the solvents), both in TB and THF, while the absorption spectra remained very similar, the transient yields increased *ca.* fourfold compared to neat THF and *ca.* 1.5-fold compared to neat TB as the solvents and, for example, PY as the solute. For the other three solutes the increases in transient yield were of a similar order. Due to the practical difficulties in obtaining solutions of standard concentration of ammonia in these solvents, primary aliphatic amines (1,2-diaminoethane and 1,2-diaminopropane) were used in all subsequent studies. Observations indicate that, as compared to neat THF, the presence of even small amounts of amine (*ca.* 5% v/v) increased the yield of the radical anions substantially, to almost the values observed when pure amines were used as solvents. Unless otherwise stated, amine concentrations in later studies were maintained at 25% v/v level in THF as it closely resembled the solvent matrix of the actual Birch reduction process mentioned earlier.

The e^-_{solv} optical absorption characteristics in neat amine solvents showed a monotonous increase with increasing wavelength over the entire range of measurement but no peaks were observed within the measurement range as reported in the literature.[11] Solvated electron in TB has a broad absorption profile with its peak above 800 nm and its optical absorption at 650–700 nm allowed its easy spectrophotometric detection[12] in the present case. In the presence of electron scavengers like dissolved O_2 and N_2O, the yields of these transients, as measured at the respective λ_{max}, reduced drastically. This happened as both O_2 and N_2O are known electron scavengers and left a very small fraction of e^-_{solv} for reaction with the aromatics. The spectral absorption profiles of the transients

$$O_2 + e^-_{solv} \longrightarrow O_2^-$$

$$N_2O + e^-_{solv} \longrightarrow N_2 + O^-$$

and their λ_{max} values were observed to be fairly similar to the reported spectral details of the radical anion for each of these aromatics in low temperature studies in a glassy matrix.[6c,d] It confirmed that radical anions were always produced quantitatively from e^-_{solv} reaction with these aromatics, both in protic (TB), amines and aprotic (THF) polar solvents. For each of the above mentioned solute–solvent combinations 50 ns electron pulses have been used at a dose of 15 Gy per pulse.

The radical anion ($ArH^{\bullet -}$) species from these aromatics were observed to have absorption maxima close to the values (λ_{max}) 325 and 365 nm for NP, 730 nm for AN, 495 nm for PY and multiple peaks at 370–390 nm for PE. From the closely matching decay rates of e^-_{solv} in TB (and in some cases amine or amine/THF) and the rate of formation of the respective radical anions of these solutes, the bimolecular rate constants for their formation were determined to have values of the order of 10^{10} dm^3 mol^{-1} s^{-1}.

To avoid repetition in all subsequent discussions, unless otherwise stated, PY has been chosen as the representative solute as its behaviour was observed to be similar to NP, AN and PE. Table 1 summarizes the measured kinetic and spectral parameters of the radical anions and the transients formed from its decay.

Decay of Radical Anion.—Under the present experimental conditions any radical anion transient is expected to react or disappear by one or more of the following pathways.

(I) Abstract a proton from the surrounding matrix of solvent that may include dissolved ammonia/amines and alcohol to form the monohydro adduct (same as $ArH_2^{\bullet}$ in path A of Scheme 1).

(II) Interact with any other positively charged ions formed by radiolysis of the matrix.

(III) Disproportionate to generate a dianion and the solute molecule: $2ArH^{\bullet -} \longrightarrow ArH^{2-} + ArH$.

(IV) Molecular rearrangement including fragmentation.

(V) Under favourable conditions it can also take up another e^-_{solv} and form the dianion (same as ArH^{2-} in path B of Scheme 1).

In processes II and III above the decay of the radical anion is expected to follow second-order kinetics owing to the prevailing low concentration of the reacting cations and anions, whereas in processes I or IV the expected decay kinetics are first order. In this study it was observed that the respective radical anion decay characteristics measured at λ_{max} of its absorption always showed a first-order decay. For these measurements 50 ns as well as 2 μs electron pulses were used. From Table 1, the measured kinetic parameters in all cases indicate that processes II and III may be ruled out under the conditions of this study for these selected aromatics. In an earlier pulse radiolysis study of THF–PY as the solvent–solute[13] no transient cations arising from its radiolysis could be detected thus indicating a very low possibility of process II above.

Process IV may not be a favourable mode of decay of the radical anions arising from aromatics like NP, AN, PY and PE owing to their structural characteristics where minimal strain exists. However, some dimerization has been reported to take place under steady state solvated electron reaction in liquid ammonia at a very slow rate in the presence of high concentrations of suitable acceptors.[5] Such changes on the μs time scale, as in this study, can be ruled out in the absence of any acceptors other than the parent ArH molecules.

Observed Radical Anion Decay.—From Scheme 1, the protonation of the radical anion by the solvent matrix would result in the formation of the monohydro adduct, $ArH_2^{\bullet}$. This is same as the $H^{\bullet}$ radical adduct of the parent compound and therefore should be the intermediate formed in a reaction of the same with the primary $H^{\bullet}$ radical. By selective generation of this radical, produced by protonation of e^-_{solv} with dissolved HCl gas at a concentration of 10^{-3} mol dm^{-3}, the reaction of each of these aromatics was studied in THF.[14] The absorption spectra of $ArH_2^{\bullet}$ transients obtained from NP, AN, PY and PE are presented in Fig. 3. The peaks assigned to the respective adducts ($ArH_2^{\bullet}$) are 335 nm (NP), 275, 320 and 405 nm (AN), 405 nm (PY) and 425 and 480 nm (PE). From the time resolved

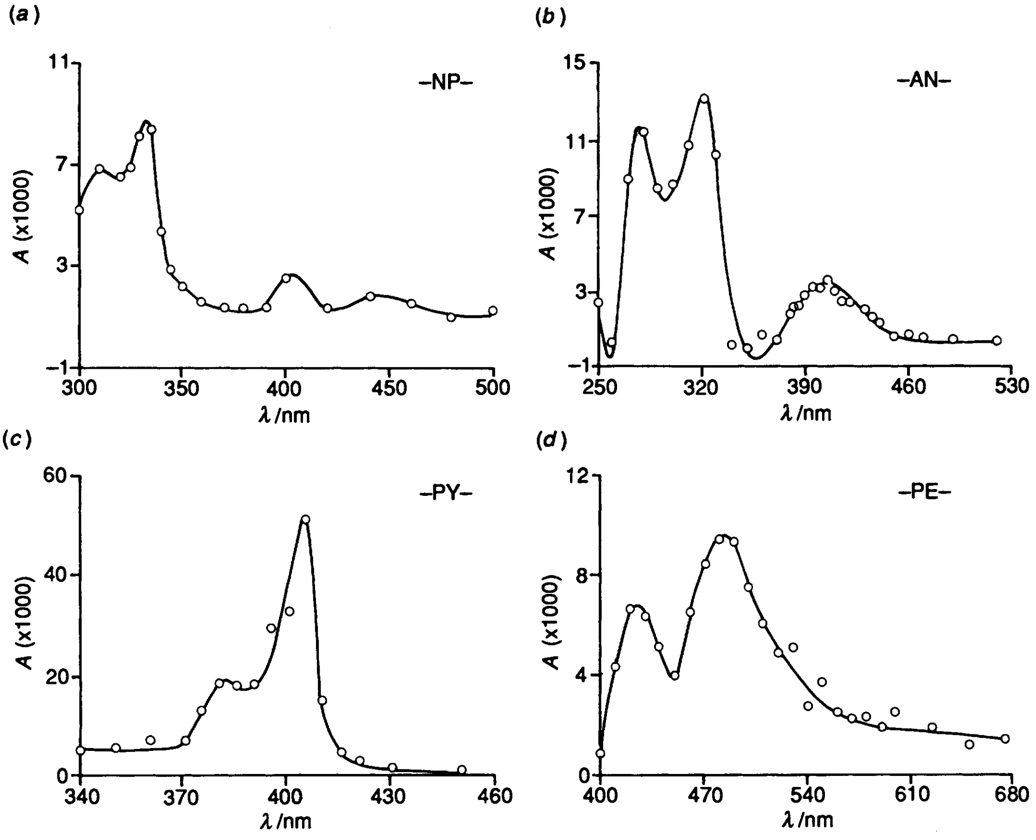


Fig. 3 Optical absorption spectra of monohydro radicals ($ArH_2^{\bullet}$) of (*a*) NP, (*b*) AN, (*c*) PY and (*d*) PE in deoxygenated THF containing dissolved HCl (10^{-3} mol dm^{-3}) for 15 Gy/50 ns e^- beam pulse

absorption spectra of each of the radical anions in TB and THF solvents, it was observed that the decay of the radical anions due to solvent protonation resulted in the simultaneous formation of the hydrogen adducts confirming process I above. Thus all these radical anions were protonated by the matrix, both in the absence and presence of dissolved alcohols, ammonia and amines, as well as by neat amines, stressing the monohydro radical pathway (path A of Scheme 1). In this context it is pertinent to discuss briefly the situation where THF alone was used as the solvent. Even after drying the THF as discussed earlier, in all probability, traces of water either remained or were introduced from the atmosphere during its subsequent handling or when making up the solutions. This resulted in the radical anion decays becoming pseudo first order in THF; these are otherwise expected to follow a second-order decay kinetics as protionation should have taken place exclusively with the help of protons formed during each pulse.

Formation of a $H^{\bullet}$ adduct in the case of pyrene in THF at 405 nm, taken as a representative for other solutes, is here discussed in detail. Using 50 ns pulses and a PY concentration of 10^{-3} mol dm^{-3}, the time resolved spectra obtained in deoxygenated THF are presented in Fig. 4 with the transient formation/decay traces, monitored at 405 nm and 495 nm on the oscilloscope, shown separately in the inset. While the after-pulse peak at 495 nm is observed to decay continuously and reach the base line, the trace at 405 nm due to the $H^{\bullet}$ adduct of PY ($PYH^{\bullet}$) at first gains height (in two stages as explained below) and then starts decaying only after elapse of a few μs. The two stage formation of $PYH^{\bullet}$ resulted from: (a) first by direct reaction of PY with $H^{\bullet}$ (from matrix radiolysis during the pulse on the ns time scale), and (b) second by subsequent decay (protonation) of the radical anion initially formed by reaction of e^-_{solv} (on the μs time scale).

Path (a) resulted in a non-zero after pulse absorbance due to $PYH^{\bullet}$ that subsequently decayed following first-order kinetics [decay $\tau_{1/2}$ = 19 μs, as measured separately in N_2O-saturated THF by selectively omitting step (b) above]. Initial non-zero absorbance at 405 nm at the end of electron pulse (50 ns) suggests that in neat THF, as discussed later, radiolysis also produced a substantial amount of $H^{\bullet}$ radical as the primary species that generated the monohydro radical of PY.

Path (b) resulted in continuous formation of fresh $ArH_2^{\bullet}$ (for a duration of *ca.* 12 μs, assuming it to be the only channel of $ArH^{\bullet -}$ decay, with a measured first-order value of $\tau_{1/2}$ = 1.8 μs). With the progress of time, as the radical anion concentration reduced considerably, the contribution of step (b) became insignificant. Then the monotonous decrease of absorbance at 405 nm became prominent as depicted in the inset trace. In the intermediate time scale the inset trace at 405 nm depicts an overall increase in absorbance in the first few μs when faster formation of $ArH_2^{\bullet}$ [from step (b) above] dominates its slower decay. Next, as the formation and decay seem to balance each other, the trace maxima at 405 nm remains fairly constant resulting in a broad peak for the absorbance *vs.* time plot as shown in the inset. Similar observations were made for AN and PE at their respective wavelengths of interest, and are not discussed separately. Under similar experimental conditions, oscilloscope traces for naphthalene as solute did not produce very well defined formation and decay patterns. Since the absorption maxima of $NP^{\bullet -}$ and $NPH^{\bullet}$ are very close together, such behaviour is expected. However, the same argument for the decay of its radical anion still holds.

Addition of 25% of either of the amines to THF increased the radical anion yield significantly, while the yield of $H^{\bullet}$ adduct decreased considerably. This occurred because, in the presence of amines that have large relative permittivity compared to THF, the solvation of secondary electrons was assisted, increasing its yield. This observation also suggests that during THF radiolysis a significant fraction of the secondary electrons

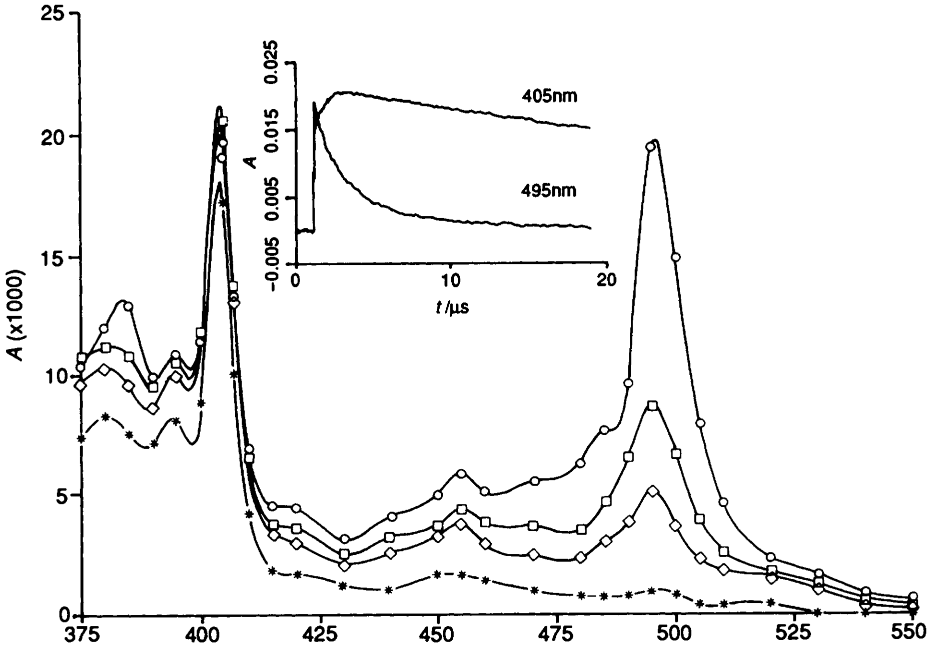


Fig. 4 Time resolved optical absorption spectra of PY radical anion formed in 50 ns e⁻ beam pulsed deoxygenated solution of 10^{-3} mol dm^{-3} PY in THF at a dose of 15 Gy/50 ns e⁻ beam pulse. Elapsed time in μs represented are as follows: —○— (after pulse = 0), —□— (2), —◇—(4) and —*— (12). Inset: Plot of time *vs.* *A* traces at 405 nm and 495 nm from the same spectra.

produced initially recombined with the cations in a spur reaction before these were solvated. The resulting H• probably became the source for the monohydro adduct $\mathrm{ArH_2}^\bullet$ that gave rise to a non-zero initial (after pulse) yield. Qualitatively these reaction steps can be represented as in Scheme 2, where THF^+

$$\mathrm{THF} \dashrightarrow \mathrm{THF}^+ + e^- \quad \text{generation} \qquad (1)$$

$$e^- + \mathrm{solv}(=\mathrm{THF}) \longrightarrow e^-_{\mathrm{solv}} \quad \text{solvation} \qquad (2)$$

$$\mathrm{THF}^+ + e^- \longrightarrow \mathrm{THF}^* \dashrightarrow \mathrm{TF}^\bullet + \mathrm{H}^\bullet \quad \text{spur combination} \qquad (3)$$

$$\mathrm{THF}^+ + \mathrm{THF} \longrightarrow \mathrm{THFH}^+ + \mathrm{TF}^\bullet \qquad (4)$$

$$\mathrm{THFH}^+ + e^-_{\mathrm{solv}} \longrightarrow \mathrm{THF} + \mathrm{H}^\bullet \qquad (5)$$

$$\mathrm{H}^\bullet + \mathrm{ArH} \longrightarrow \mathrm{ArH_2}^\bullet \qquad (6)$$

$$\mathrm{RNH_2} + \mathrm{THFH}^+ \longrightarrow \mathrm{RNH_3}^+ + \mathrm{THF} \qquad (7)$$

$$\mathrm{RNH_2} + \mathrm{THF}^+ \longrightarrow \mathrm{TF}^\bullet + \mathrm{RNH_3}^+ \qquad (8)$$

$$\mathrm{RNH_2} + \mathrm{THF}^* \longrightarrow \mathrm{THF} + \mathrm{RNH_2}^* \quad \text{quenching} \qquad (9)$$

Scheme 2

is the cation prior to solvation, THFH^+ is the protonated THF or solvated proton, TF• is the deprotonated THF^+ or dehydro THF. In presence of a H• scavenger like cyclohexa-1,4-diene (CHD) at millimolar concentration levels in THF the after-pulse yield at 405 nm showed a decrease, while in the presence of 3% v/v ED the after-pulse yield at 405 nm vanished completely. These observations are presented in Fig. 5 which indicates the validity of the above reaction scheme. It is observed that the time scale of the formation trace at 405 nm matches the decay trace at 495 nm more closely when the initial after-pulse yield of the monohydro radical is almost nil, as in the case of 3% v/v ED/THF used as the solvent. The presence of CHD in THF produced a result close to it. In THF, the presence of electron quenchers like dissolved N_2O and O_2 decreased the radical anion yield considerably (*ca.* 95%) as measured at 495 nm, while the decrease in absorbance due to the monohydro adduct was

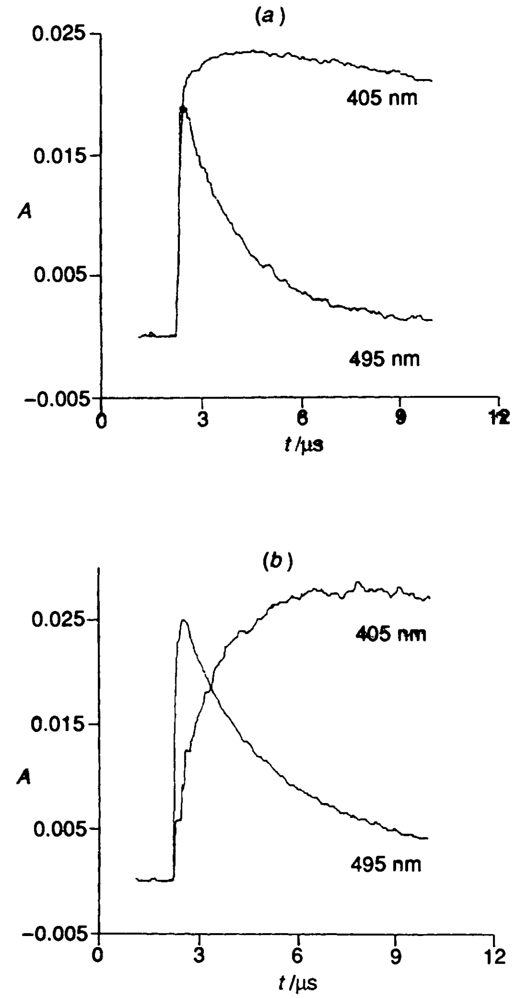


Fig. 5 Plot of time *vs.* *A* traces at 405 nm and 495 nm for PY at a dose of 15 Gy/50 ns e⁻ beam pulse. (*a*) Deoxygenated THF containing millimolar cyclohexa-1,4-diene. (*b*) Deoxygenated THF containing 3% v/v 1,2-diaminoethane.

Table 2 Effect of added alcohol on yield of ArH$^•$ from pyrene

[PY]/ 10^{-3} mol dm^{-3}	Added alcohol concentration[b]	Increase in ArH$^•$ yield of PY at 405 nm w.r.t. PY in neat THF (%)
2	0.1 mol dm^{-3} TB	4
2	0.1 mol dm^{-3} ET	5
2	1% v/v TB	4
2	1% v/v ET	11
2 + 25% ED[a]	0.1 mol dm^{-3} TB	40
2 + 25% ED	0.1 mol dm^{-3} ET	36
2 + 25% ED	1% v/v TB	150
2 + 25% ED	1% v/v ET	170

[a] ED = 1,2-diaminoethane. [b] TB = *tert*-butyl alcohol, ET = ethanol.

comparatively less (*ca.* 50%), confirming the importance of THF$^+$ cation recombination before solvation as shown in Scheme 2. As amines are known to be efficient scavengers of H$^+$, the presence of even 3% v/v ED in THF helped in the reduction of the after-pulse H$^•$ yield [compare step (7) against step (5) above] resulting in decreased after-pulse formation of ArH$_2^•$ and a very good resemblance between the decay trace of ArH$^{•-}$ and formation trace of ArH$_2^•$ was obtained. In this context it needs to be mentioned that in the presence of amines that are efficient quenchers of excited states, the decrease in the yield of H$^•$ may take place as in step (9) as a result of the quenching of the excited THF [THF* as in step (3)] which generates H$^•$. Additionally, as shown in step (8), even a significant fraction of radiolytically generated THF$^+$ producing THF* (and finally H$^•$) inside the spurs may instead transfer a proton to the amine, thus reducing the after-pulse PYH$^•$ yield further, while at the same time increasing the PY$^{•-}$ yield [reducing inside-spur quenching of e$^-$ as in step (3) thus effecting its increased solvation]. It may be noted that with increasing amine concentration in the matrix the relative importance of these processes may change and this simplified post radiolysis scheme may not be strictly followed as the radiolysis products of amine may get involved in a similar way. The kinetic studies showed that the decay of radical anion in the presence as well as in the absence of amines always remained first order and from the rate constant values it is inferred that its protonation may be effected by the solvent matrix consisting mainly of THF.

In some of the metal–ammonia reduction schemes of ArH discussed earlier low molecular weight aliphatic alcohols are used as co-solvents. Under the present experimental conditions it was observed that addition of even 1% v/v of protic alcohols like ethanol and TB increased the hydrogen adduct (ArH$_2^•$) formation rate as well as its yield considerably. Table 2 gives the details of these studies. The increase in the hydrogen adduct yield is expected as the alcohols are well known protonating agents[15] with increasing ability from TB to ethanol and their presence during the Birch reduction is expected to result in the protonation of the radical anion. Data given in Table 2 indicate that the radical anion was effectively protonated in the presence of these alcohols. When the amines were present it was observed that in the presence of 1% ethanol the yield of hydrogen adduct ArH$_2^•$ had almost doubled. However their presence had no significant effect when amine was absent.

Conclusions

From our studies on the decay modes of the radical anions, and taking into consideration the kinetic parameters in different solvent matrices, the possibility of dianion formation, as in path B of Scheme 1, from NP, AN, PY and PE as solutes seems to be remote. During Birch reduction of these ArHs, protonation of radical anion by the solvent matrix thus offers the most favourable channel for the ultimate formation of the dihydro species. However, the possibility that similar reactions occur in the presence of dissolved alkali metal in a matrix of ammonia (or amine) in THF at low temperature needs to be investigated separately. It is expected that under such reduction conditions, where a steady concentration of e$^-_{solv}$, which is of the same order as the concentration of the solute, is available,[16] shifting of the following equilibrium towards dianion formation may take place, as in process V of the decay mode of radical anions.

$$\mathrm{ArH^{•-} + e^-_{solv} \rightleftharpoons ArH^{2-}}$$

It has been argued that the presence of solvated metal ions (M$^+_{solv}$) under such conditions may provide a stabilizing effect on the dianion by the mode of ion pairing, thus shifting the above equilibrium towards the right hand side.[5] In our study, using ArH concentrations in the range of 2×10^{-6} to 2×10^{-5} mol dm^{-3} and 2 µs electron pulses from the accelerator at maximum dose, a steady concentration of e$^-_{solv}$ over this time period was generated in these solvent matrices and the possibilities of the formation of dianions were explored. Relatively high concentration of e$^-_{solv}$ (in the order of 4–20 × 10^{-6} mol dm^{-3} in different matrices) thus generated remained steady for the period of 2 µs. Under this condition, the radical anions formed immediately after the beginning of the electron pulse were exposed to the environment of solvated electrons still forming. Even for a [e$^-_{solv}$]/[solute] ratio value of 10 no confirmation of dianion formation could be obtained in 1 ms in terms of appearance of new peaks due to the dianions of each of these solutes in any solvent matrix. The dianion spectral details have been well characterized in low temperature studies in a glassy matrix[6c,d] and the peak values reported therein were taken as reference. While formation of a dianion transient could never be confirmed the other possible pathway (A of Scheme 1) was always observed to occur. In the Birch reduction, where hydrogenation of these ArHs is effected by the addition of two electrons and two protons, the second electron will therefore, in all certainty, add to the monohydro radical ArH$_2^•$, forming the monoanion (ArH$_2^{•-}$) as in Scheme 1, path A.

Since the formation of dianion takes place by the addition of an e$^-_{solv}$ to the radical anion, a pulse radiolysis study starting with radical anion already existing in the solvent matrix as the solute, is expected to provide the necessary kinetic and other details on the formation of dianions. Radicals and dianions in such studies can be obtained by two methods.

(1) Low temperature reactions of e$^-_{solv}$ generated by alkali metal in THF or THF/ammonia with ArH that may persist for sufficient time to be used for a pulse radiolysis study as above.

(2) Using two LINAC beams with a suitable delay interval. The radical anions formed from the e$^-_{solv}$ reaction with a solute will be exposed to the electron pulse from the second beam and the decay kinetics of the radical anion to generate the dianion may be quantitatively studied in the presence of solvents of choice. Here it is important to realize that the solute concentration needs to be maintained at a level less than the effective concentration of e$^-_{solv}$ produced from the first beam, to minimize competition between ArH and ArH$^{•-}$ for e$^-_{solv}$ from the second beam. Then, for any ArH, the comparison of the relative rates of formation of monohydro species and the dianion will help in confirming the actual path followed. Our qualitative study using 2 µs electron pulses mentioned earlier was conducted along these lines where a high concentration of e$^-_{solv}$, maintained for the fairly long time of *ca.* 2 µs, was expected to give an effect similar to using two beams delayed by an interval of time of similar magnitude. The present study highlights the importance of path A of Scheme 1 and path B needs to be quantified separately for actual comparison for the present set of aromatics, and these studies may be extended to other related hydrocarbons.

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