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A Steady State and Laser Flash Photolysis Study of Phenanthrene Photocyanation. A Singlet and Triplet State Reaction

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Photocyanation of phenanthrene takes place *via* excited singlet state in the presence, but *via* the excited triplet state in the absence of an electron acceptor in the acetonitrile solutions. The phenomena observed by laser flash photolysis in presence and absence of the electron acceptor dicyanobenzene, and cyanide anion, are presented by a scheme involving the formation of transient ionic complexes and free cation radicals of phenanthrene. An absorption at about 420 nm observed in the presence, and at high concentration of phenanthrene, in the absence of the electron acceptor, is attributed to a cation radical of phenanthrene. The free-energy changes involved in electron-transfer processes are discussed.

In our previous studies[1,2] of photocyanation of phenanthrene in anhydrous acetonitrile we observed[1] that the main product is 9-cyanophenanthrene. The presence of an oxidizing agent (O_2) was essential for product formation. The maximum rate of the reaction was achieved at small concentration of oxygen and the rate was linearly proportional to the square of the intensity of the absorbed radiation. One of the transients observed[2] by flash photolysis decayed by second order kinetics forming another transient, the absorbance of which was proportional to the square of the intensity of the exciting light.

In the presence of an electron acceptor, dicyanobenzene (DCB), the rate of photocyanation of naphthalene and biphenyl increased[3] with increasing DCB concentration in 1:1 water–acetonitrile. We observed,[4] that the rate of reaction both in the presence and absence of DCB in anhydrous acetonitrile and in 1:1 water-acetonitrile again was linearly proportional to the square of the intensity of the absorbed radiation.

Furthermore, we found[4] that the mechanism valid for the phenanthrene reaction in dry acetonitrile[1,2] was applicable to the reactions[3] of naphthalene and biphenyl in 1:1 water–acetonitrile. The experimental data can be explained by the following reactions (Scheme 1).

$$\begin{aligned} \mathrm{ArH} &\xrightarrow{I_a} \mathrm{ArH}^* \\ \mathrm{ArH}^* &\longrightarrow \mathrm{X}+\mathrm{X}' \\ \mathrm{X}+\mathrm{X}' &\longrightarrow \mathrm{Y} \\ \mathrm{Y} &\longrightarrow \mathrm{Product} \end{aligned}$$

Scheme 1.

In Scheme 1 ArH is the reactive hydrocarbon, ArH* is its excited state (singlet or triplet) and X, X′ and Y are transients. For this type of reactions a modified quantum yield was defined:[1,4]

$$a=\frac{0.87\bar{w}_R d^2}{(I_o^2-I_t^2)D}=\frac{0.87\,\phi d}{(I_o+I_t)\,\varepsilon[\mathrm{ArH}]}, \qquad (1)$$

where ϕ is the usual quantum yield ($\phi=\bar{w}_R/I_a$), $\bar{w}_R$ is the average rate of the reaction, d is the optical path of the reaction cell, D is the absorbance of the system, ε is the molar absorption coefficient, [ArH] is the concentration of aromatic hydrocarbon and I_o, I_a and I_t are the

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incident, absorbed and transmitted light intensities, respectively.

It was shown[4] that for the cyanation reaction of the aromatic hydrocarbons the following scheme will apply (Scheme 2).

$$\begin{aligned}
&\xrightarrow{I_a} && \\
\mathrm{ArH} &\longrightarrow && \mathrm{ArH}^* \\
&\xrightarrow{k_1} && \\
\mathrm{ArH}^* &\longrightarrow && \mathrm{ArH} \\
&\xrightarrow{k_k} && \\
\mathrm{ArH}^*+\mathrm{A} &\longrightarrow && \mathrm{ArH}^{\cdot+}+\mathrm{A}^{\cdot-} \\
&\xrightarrow{k_2} && \\
\mathrm{ArH}^{\cdot+} &\longrightarrow && \text{Unproductive} \\
&\xrightarrow{k_x} && \\
\mathrm{ArH}^{\cdot+}+\mathrm{CN}^- &\longrightarrow && \mathrm{ArHCN}^{\cdot} \\
&\xrightarrow{k_3} && \\
\mathrm{ArHCN}^{\cdot} &\longrightarrow && \text{Unproductive} \\
&\xrightarrow{k_p} && \\
2\,\mathrm{ArHCN}^{\cdot}+\mathrm{Ox} &\longrightarrow && \text{Productive}
\end{aligned}$$

Scheme 2.

A relationship between the quantum yield α, and the reacting substrates could be written as eqn. (2), where c is a constant, which depends on k_3 and k_p and, in the presence of oxidizing agent, on its concentration [Ox]. In eqn. (2) [A] is the concentration of the electron acceptor, and in the absence of an added acceptor, concentration of the reacting aromatic hydrocarbon, $K_k=k_k/k_1$ and $K_x=k_x/k_2$. The constants K_k and K_x are calculated from the experimental results.

$$\frac{[\mathrm{CN}]\,[\mathrm{A}]}{\sqrt{\alpha}} = c\left(\frac{1}{K_k} + [\mathrm{A}]\right)\left(\frac{1}{K_x} + [\mathrm{CN}]\right) \qquad (2)$$

Relatively large values of K_k were observed indicating that an excited singlet state of aromatic hydrocarbon cannot be reacting and the triplet state reaction was suggested.[4] However, the reactive state of aromatic hydrocarbon in photosubstitution reactions is under discussion. Vink *et al.*[5] observed that photocyanation of biphenyl could be sensitised by benzophenone and proposed a triplet state mechanism. Hino *et al.*[6] supposed that the cation radicals of pyrene, observed in the presence of dicyanobenzene, were formed *via* the singlet state reaction. Cornelisse *et al.*[7] showed that the substitution of anisoles is a triplet state reaction. This was approved by Suzuki *et al.*,[8] but a singlet state reaction was suggested by them in the presence of dicyanobenzene. They proposed,[9] however, a singlet state reaction for photocyanation of dimethoxybenzene in the absence of dicyanobenzene and a triplet state reaction in the presence of dicyanobenzene. Yasuda[10] suggested a singlet state reaction in photocyanation of naphthalene and phenanthrene in the presence of dicyanobenzene, for the electron transfer process is an exothermic process according to calculations using the Rehm-Weller equation.[11] Bunce *et al.*[3] reached the conclusion, that photocyanation of naphthalene and biphenyl is a singlet state reaction both in the presence and in the absence of an electron acceptor.

In this work we have completed the study of photocyanation of phenanthrene by investigating its mechanism by a steady state method both in hydrous and anhydrous acetonitrile and by laser flash photolysis in anhydrous acetonitrile. We have studied the effect of dicyanobenzene and sensitized the reaction by a triplet energy transfer from benzophenone.

EXPERIMENTAL

The experimental methods used in the steady state study have been described earlier.[1] In all experiments cyanide anion was used as potassium cyanide-18-crown-6-complex. Dicyanobenzene was purified by sublimation, benzophenone was recrystallized several times and phenanthrene was purified as described in the literature.[12] No traces of anthracene were observed by UV-spectra.

Fluorescence lifetime measurements were done by SLM 4800/4800S spectrofluorometer with absorption wavelength of 346 nm and emission wavelength of 366 nm at a phenanthrene concentration of 5.0×10^{-3} mol dm^{-3}. For laser flash photolysis a frequency-doubled ruby laser (347 nm) was used for excitation.[13]

RESULTS

Assisted photocyanation of phenanthrene. The rate of photocyanation was measured in the steady state photolysis of phenanthrene in anhydrous acetonitrile in the presence of DCB and oxygen. The results are presented in Table 1. The values of $K_k=3.0\times10^3\mathrm{M}^{-1}$ and $K_x=4.5\times10^3\mathrm{M}^{-1}$

Table 1. Dependence of the rate of photocyanation of phenanthrene (5.0×10^{-3} mol dm^{-3}) on potassium cyanide (CN^-) and DCB concentrations in anhydrous acetonitrile at 25 °C.

$[CN^-]\times10^3$ / mol dm^{-3}	$[DCB]\times10^3$ / mol dm^{-3}	Rate[a] $\times10^9$ / mol dm^{-3}s^{-1}	α / mol^{-1} dm^3 s	$[DCB][CN^-]/\sqrt{\alpha}$ / mol dm s
0.5[c]	0.5	28.1	2600	4.9
1.0	0.5	33.5	3100	9.0
2.0	0.5	44.4	4100	15.6
3.0	0.5	45.8	4240	23.1
4.0	0.5	44.1	4080	31.3
5.0	0.5	47.8	4420	37.6
$K_x=4.5\times10^3$ mol^{-1} dm^3[b]				
5.0[d]	0.05	10.1	870	8.5
5.0	0.1	14.7	1260	14.1
5.0	0.2	23.3	2000	22.3
5.0	0.3	33.7	2900	27.9
5.0	0.4	38.5	3310	34.8
5.0	0.5	43.2	3710	41.0
5.0	0.65	56.8	4880	46.5
5.0	0.8	65.7	5650	53.2
5.0	1.0	79.0	6790	60.6
$K_k=3.0\times10^3$ mol^{-1} dm^3[b]				

[a] Measured rate. [b] Calculated using equations (1) and (2), $[O_2]=8\times10^{-5}$ mol dm^{-3}, $\lambda_{ex}=313$ nm. [c] $I_o=25.9\times10^{-8}$ Ein dm^{-2}s^{-1}, $I_t=0.85\times10^{-8}$ Ein dm^{-2}s^{-1}, $I_a=25.1\times25.1\times10^{-7}$ Ein dm^{-3}s^{-1}, $D=1.40$. [d] $I_o=26.7\times10^{-8}$ Ein dm^{-2}s^{-1}, $I_t=1.02\times10^{-8}$ Ein dm^{-2}s^{-1}, $I_a=25.7\times10^{-7}$ Ein dm^{-3}s^{-1}, $D=1.42$.

Table 2. Sensitization of photocyanation of phenanthrene (Ph) by benzophenone (BP) in the presence and absence of DCB in anhydrous acetonitrile at 25 °C.

$[Ph]\times10^3$ / mol dm^{-3}	$[BP]\times10^3$ / mol dm^{-3}	$[DCB]\times10^3$ / mol dm^{-3}	Rate[a] $\times10^9$ / mol dm^{-3}s^{-1}	α / mol^{-1} dm^{3}s
1.0[b]	20.0	–	1.7	40
5.0	20.0	–	8.3	260
7.0	20.0	–	12.6	305
10.0	20.0	–	16.4	395
20.0	20.0	–	41.5	1000
10.0[c]	5.0	–	16.2	1320
10.0	10.0	–	20.9	825
10.0	20.0	–	16.4	395
10.0	30.0	–	15.1	245
5.0[d]	20.0	–	8.3	260
5.0	20.0	0.2	8.0	285
5.0	20.0	0.5	8.2	290
5.0	20.0	1.0	8.3	295

[a] Measured rate, $\lambda_{ex}=366$ nm, $[CN^-]=5.0\times10^{-3}$ mol dm^{-3}, $[O_2]=8\times10^{-5}$ mol dm^{-3}. [b] $I_o=52.7\times10^{-8}$ Ein dm^{-2}s^{-1}, $I_t=2.7\times10^{-8}$ Ein dm^{-2}s^{-1}, $I_a=50.0\times10^{-7}$ Ein dm^{-3}s^{-1}, $D=1.30$. [c] $I_o=52.7\times10^{-8}$ Ein dm^{-2}s^{-1}, I_t and I_a variate. [d] $I_o=46.1\times10^{-8}$ Ein dm^{-2}s^{-1}, $I_t=3.18\times10^{-8}$ Ein dm^{-2}s^{-1}, $I_a=42.9\times10^{-7}$ Ein dm^{-3}s^{-1}, $D=1.16$.

were calculated by eqns. (1) and (2) for the relative rate of transient formation and decay, respectively.

Photosensitisation by benzophenone (BP). Exciting the reaction mixture [BP]=20×10^{-3} M, [CN^-]=5.0×10^{-3} M, [O_2]=8×10^{-5} M, and [Ph]=[$(1.0-20.0)\times10^{-3}$ M] at wavelength 366 nm, where only BP absorbs, the reaction took place with a relatively high quantum yield (α) (Table 2) and the rate of reaction depended on phenanthrene concentration. However, with increasing concentration of BP the quantum yield decreased. These observations indicate that the cyanation reaction takes place in the absence of DCB *via* the triplet state of phenanthrene, since BP is a well known energy transfer agent (the triplet state energies of BP and Ph are 2.97 and 2.69 eV, respectively); eqn. (3). In similar circumstances, but in the presence of various concentrations of DCB, the quantum yield remained the same (Table 2), indicating that DCB does not interact with the excited triplet state but only with the excited singlet state.

$$^3BP^* + {}^1Ph \rightarrow {}^1BP + {}^3Ph^* \qquad (3)$$

The effect of oxygen and water. The photocyanation reaction of unsubstituted aromatic hydrocarbons takes place in hydrous acetonitrile with high quantum yields, also in the absence of an oxydizing agent, yielding both dihydrocyano- and cyano-products.[3,10]

The rate of the reaction in acetonitrile–water solutions is also linearly proportional to the square of the intensity of the absorbed radiation.[4] Furthermore, we observed that the quantum yield (α) increases with the concentration of water in the presence, but decreases in the absence of oxygen in acetonitrile solutions (Table 3). The maximum rate is observed at a small concentration of oxygen. The value of 7.7×10^3 dm^3 mol^{-1} can be calculated for the parameter[1] $K_q=k_q\,\tau_x^o$, where τ_x^o is the lifetime of a transient quenched by oxygen, probably a neutral cyanated radical, ArHCN·,[2,4] and k_q is the quenching rate constant.

Fluorescence quenching of phenanthrene by DCB and oxygen. The fluorescence lifetime of phenanthrene in degased anhydrous acetonitrile is 45 ns. The fluorescence quenching constants K_{SV} measured by the Stern-Volmer method were

Table 3. Dependence of the rate of photocyanation of phenanthrene (5.0×10^{-3} mol dm^{-3}), in the presence of DCB (0.4×10^{-3} mol dm^{-3}), on oxygen and water concentrations in acetonitrile solutions at 25 °C.

	40 % H_2O		30 % H_2O		10 % H_2O		0 % H_2O	
$[O_2]\times10^3$ / mol dm^{-3}	Rate[a]$\times10^9$ / mol $dm^{-3}s^{-1}$	$\alpha\times10^{-3}$ / mol^{-1} dm^3	Rate[a]$\times10^9$ / mol $dm^{-3}s^{-1}$	$\alpha\times10^{-3}$ / $mol^{-1}dm^3$	Rate[a]$\times10^9$ / mol $dm^{-3}s^{-1}$	$\alpha\times10^{-3}$ / $mol^{-1}dm^3$s	Rate[a]$\times10^9$ / mol $dm^{-3}s^{-1}$	$\alpha\times10^{-3}$ / mol^{-1} dm^3s
0	10.2	1.09	11.9	1.34	16.7	1.73	0	0
0.1	87.6	9.41	83.4	7.25	57.6	5.06	38.5	3.33
1.2	30.2	3.22	26.9	2.48	18.2	1.71	12.4	1.15
K_q[b]/dm^3mol^{-1}	7.6×10^3		7.4×10^3		7.9×10^3		7.7×10^3	

[a] Measured rate. [b] Calculated from the ratios of the slopes and intercepts of the straight line when $([O_2]/\alpha)^{1/2}$ is presented as a function of [O_2], λ_{ex}=313 nm, $I_o=25.9\times10^{-5}$ Ein $dm^{-2}s^{-1}$, $I_t=0.85\times10^{-8}$ Ein $dm^{-2}s^{-1}$, $I_a=25.1\times10^{-7}$ Ein $dm^{-3}s^{-1}$, D=1.40.

1350 M^{-1} and 750 M^{-1} for oxygen and DCB, respectively. These values correspond to quenching rate constants of $k_q(O_2)=3.0\times10^{10}M^{-1}s^{-1}$ and k_q (DCB)$=1.7\times10^{10}M^{-1}s^{-1}$.

The laser flash photolysis study in the absence of DCB. By means of laser flash photolysis the triplet absorption of phenanthrene, similar to the spectrum presented in the literature,[14] was observed (Fig. 1) at phenanthrene concentrations below 1.0×10^{-3} M. It had an absorption maximum at 480 nm. The absorption decayed mainly by second order kinetics with a half life of about 4–20 μs depending on the intensity of the flash. The decay at 480 nm was faster at higher phenanthrene concentrations but independent of the concentration of cyanide anion.

At higher phenanthrene concentrations ($\geq2.9\times10^{-3}$M) a new absorption with a longer lifetime (40–60 μs) at 420 nm was observed (Fig. 1). Increasing the ground state concentration the transient absorption increased. In the presence of cyanide anion the intensity of this absorption was somewhat decreased. We suppose, that this transient is a cation radical of phenanthrene ($ArH^{\cdot+}$).

The rate of the formation of the transient at 420 nm, $(1-3)\times10^5$ s^{-1}, corresponds to the decay rate of triplet phenanthrene at 480 nm. The rate increased with increasing intensity of flash. The increase, however, became less with higher doses. This indicates a competition between second order decay of the triplet state and pseudo first order scavenging of the triplet state by the ground state of phenanthrene, forming the absorbing species. The intensity of the transient at 420 nm reached a maximum in 10–20 μs, and remained the same at least for 10 μs (Fig. 3). The presence of cyanide anion had no influence on the rate of formation of this transient.

The laser flash photolysis study in the presence of DCB. The decay of the triplet absorption at 480 nm was independent of DCB. At 400 and 420 nm similar absorptions (ArH^+) were observed (Fig. 2) as in the absence of DCB, not only at high concentration, but also at low concentration of phenanthrene.

The transient at 420 nm (ArH^+) reached a maximum during the laser pulse having a relatively higher intensity than in the absence of DCB. It decayed with a rate of $1-10\times10^5s^{-1}$ and formed a new transient with a half life of 20–50 μs (Fig. 3).

The concentrations of DCB and cyanide anion had an effect on the decay rates of both the faster and the slower decay. In the presence of cyanide anion the fast decay (ArH^+) of the transient at 420 nm was no longer observed, but a new long living transient at wavelengths between 380–460 nm was formed (Fig. 2) similar to the one we observed earlier.[2] Evidently, at wavelength of 420 nm, there are at least three different transients with different formation and decay rates depending on concentrations of phenanthrene, cyanide anion and DCB and on the intensities of flashes. Thus measured rates and lifetimes do not represent the absolute values of the processes.

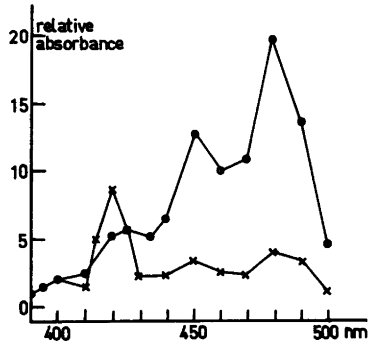


Fig. 1. Triplet-triplet absorption spectrum of phenanthrene (2.9×10^{-3} mol dm^{-3}) (○), and the transient observed 12.5 μs later (×) in acetonitrile.

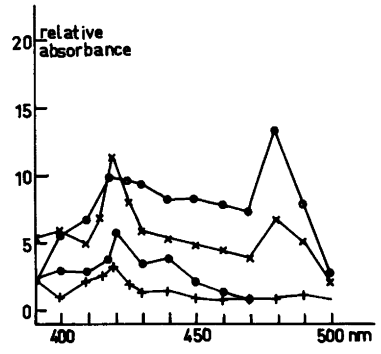


Fig. 2. Spectra of phenanthrene (2.9×10^{-3} mol dm^{-3}) in the presence of dicyanobenzene (1.0×10^{-3} mol dm^{-3}) in acetonitrile. (○) immediately after the pulse, (×) 5 μs, (+) 90 μs latter and (●) as (+), but in the presence of cyanide anion (3.6×10^{-3} mol dm^{-3}).

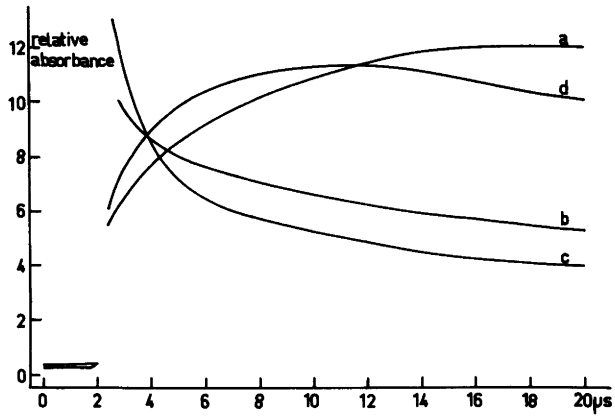


Fig. 3. Experimental traces for build-up and decay of absorptions of phenanthrene (2.9×10^{-3} mol dm^{-3}) solutions at 420 nm, (a) phenanthrene, (b) phenanthrene+DCB (1.0×10^{-3} mol dm^{-3}), (c) phenanthrene+DCB (5.0×10^{-3} mol dm^{-3}) and (d) phenanthrene+DCB (1.0×10^{-3} mol dm^{-3})+ cyanide anion (3.6×10^{-3} mol dm^{-3}).

The laser flash photolysis study in the presence of BP. Benzophenone triplet, monitored at 535 nm,[15] decayed by a second order process having a half-life of 2.7 μs at a triplet concentration of about 2×10^{-5} M in anhydrous acetonitrile. It was quenched by cyanide anion and by phenanthrene with rate constants of $k_q(CN)=3.2\times10^8 M^{-1}s^{-1}$ and $k_q(Ph)=1.3\times10^{10}M^{-1}s^{-1}$. The quenching by phenanthrene resulted in triplet formation. This state decayed mainly by second order kinetics with a half-life of about 5 μs.

No transient was observed monitoring at 640 nm, corresponding to the possible formation of benzophenone anion radical.[15] Thus benzophenone was quenched by an energy-transfer process rather than by an electron-transfer process.

At wavelengths between 500–550 nm a transient was not studied in greater detail. It is interesting to note, that its decay rate corresponds to the lifetime of singlet phenanthrene, measured by fluorescence decay, and that DCB has an effect on its decay rate, indicating that the observed transient is the singlet state of phenanthrene.

The effect of oxygen on laser flash photolysis. In the presence of air ($[O_2]\approx1.3\times10^{-3}$M) and DCB the decay of the transient at 420 nm was composed of two well separated decay processes, the first having a half-life of about 0.2 μs and the second, in the absence of cyanide anion, of about 5 μs. The former decay corresponds well to the quenching rate[16] of the triplet state of phenanthrene by oxygen ($k_q(O_2)\approx1\times10^9M^{-1}s^{-1}$ and thus $\tau_{1/2}=0.7/\Sigma k=0.7/k_q[O_2]=0.5$ μs), and the latter to the rate of the fast decay at 420 nm observed in the absence of oxygen and cyanide anion. Furthermore, in the presence of cyanide anion, another transient was formed with a rate of formation of about $4\times10^4s^{-1}$. This transient has a lifetime of about 1×10^{-4}s, which corresponds to the lifetime of the transient $ArHCN^{\cdot}$, formed in the reaction between cyanide anion and the cation radical of aromatic hydrocarbon in the presence of oxygen ($\tau_{1/2}=0.7/\Sigma k=0.7/(k_o+k_q[O_2])=0.7/(10^3s^{-1}+9\times10^6\times1.3\times10^{-3}s^{-1})=0.6\times10^{-4}$ s. Here $k_o=1\times10^3s^{-1}$ is the rate constant[2] of the decay of the reactive transient in the absence of oxygen, and $k_q=9\times10^6M^{-1}s^{-1}$ is its quenching rate constant[2] by oxygen

DISCUSSION

The photosensitization experiments done by benzophenone, and the laser flash photolysis studies show clearly that the photocyanation reaction, in the absence of DCB, takes place *via* the excited triplet state of phenanthrene. Addition of DCB does not influence this reaction, indicating that DCB does not react with the triplet. On the other hand, direct excitation of phenanthrene in the presence of DCB leads to increased photocyanation and we therefore must conclude that the important step is the reaction of DCB with singlet excited state of phenanthrene.

A transient observed under these conditions with absorption maxima at 420–430 and 400–410 nm has been attributed by Shida [17] and Asanuma [18] to the cation radical of phenanthrene and we therefore identified the transient absorbing at 420 nm, both in the presence and absence of DCB, as due to this radical.

In the presence of DCB the cation radical decayed and/or transformed into another, longer living species. The latter was identified due to its spectrum as triplet phenanthrene, formed by the electron backtransfer followed by inter-system crossing. The relatively long living transient observed in the presence of cyanide anion was a transient ArHCN·, formed in the reaction between cation radical and cyanide anion.

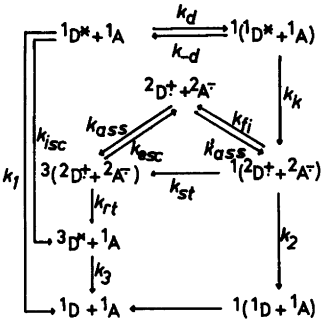
The processes which explain the observed results can be described by a scheme similar to the one proposed by Weller [19] (Scheme 3). In Scheme 3 phenanthrene is marked D (an electron donor) and A is either DCB or ground state phenanthrene (an electron acceptor). The observed transient at 420 nm can be either a radical ion pair in a singlet state $^1(^2D^+ + ^2A^-)$ or free radical ions $^2D^+ + ^2A^-$.

If the acceptor A is DCB, radical ion pairs and free ions are formed in the interaction with the excited singlet state of phenanthrene. This reaction is competing with the intersystem crossing process (k_{isc}). At high concentrations of DCB, a high concentration of radical cations is formed at the same time as a low concentration of triplet phenanthrene, and therefore the consecutive quenching of the radical cations can be observed.

Cation radicals, as ion pair or free ions, decay either to the singlet ground state (k_2) or *via* the triplet state of radical ion pair (k_{st} and k_{ass}) to the excited triplet state of phenanthrene (k_{rt}). If the rate constant for the formation of free ions (k_{fi}) is high enough, the reactive state is the radical cation. Now a high value of k_{ass} can explain the fast decaying of cation radical of 420 nm.

In the absence of DCB the ground state of phenanthrene acts as the electron acceptor. Then the formation of radical ion pairs (k_k) would be two or three orders of magnitude less than in the presence of DCB and it does not compete effectively with the intersystem crossing process (k_{isc}). High concentrations of triplet phenanthrene are formed and the intensity of absorption of the radical decreases.

As is demonstrated by the sensitization by benzophenone, the photocyanation reaction takes place in the absence of DCB, *via* the excited triplet state of phenanthrene. The reactions of the formation and decay of the benzophenone triplet, in the presence of oxygen and cyanide anion, involving the energy-transfer to ground state phenanthrene, can be schematized as follows (Scheme 4).



Scheme 3.

$$BP \xrightarrow{I_a} {}^{isc}\!\!\rightarrow {}^3BP^*$$

$$^3BP^* \xrightarrow{k_{TM}} BP$$

$$^3BP^* + BP \xrightarrow{k_q(BP)} 2\,BP$$

$$^3BP^* + O_2 \xrightarrow{k_q(O_2)} BP + O_2$$

$$^3BP^* + CN^- \xrightarrow{k_q(CN)} BP + CN^-$$

$$^3BP^* + Ph \xrightarrow{k_{etr}} {}^3Ph^* + BP$$

Scheme 4.

After the formation of triplet phenanthrene, two possible mechanisms were proposed [2,4] for reactions with cyanide anion. The first is a direct interaction of triplet phenanthrene with cyanide anion; eqn. (4).

$$^3Ph^* + CN^- \xrightarrow{k_x'} {}^3(Ph^{\cdot-}\ CN^{\cdot}) \qquad (4)$$

The second involves the formation of a transient ionic complex or free radical ions from the triplet state of phenanthrene and ground state phenanthrene, followed by the reactions according to Scheme 2; eqn. (5).

Table 4. Spectroscopic and redox potentials of the studied compounds.

Donor (D)	Acceptor (A)	$E^{o}_{A/A^{\cdot-}}$/V	$E^{o}_{D^{\cdot+}/D}$/V	E^{S}_{0-0}/eV	E^{T}_{0-0}/eV	ΔG^{S}/kJ mol^{-1}	ΔG^{T}/kJ mol^{-1}
Ph*	Ph	−2.20[a]	+1.74[a]	3.59(Ph)[a]	2.60(Ph)[a]	+27.6	+113.9
Ph*	CN−Ph	−1.92[b]	–	3.43(CNPh)[c]	2.51(CNPh)[b]	+15.1	+105.1
Ph*	p−DCB	−1.67[d]	–	4.28(DCB)[d]	3.16(DCB)[d]	−89.9	+ 18.3
Ph	BP*	−1.77[e]	–	3.20(BP)[f]	2.97(BP)[f]	+24.3	+ 46.5
CN^{-}	Ph*	−2.20[a]	+0.7[g]	3.59(Ph)[a]	2.69(Ph)[a]	−72.4	+ 14.7

Data from [a] Julliard, M. and Chanon, M. *Chem. Brit.* (1982) 558. [b] Park, S.-M. and Caldwell, R. A. *J. Electrochem. Soc. 124* (1977) 1859. [c] Lewis, Fr. D., DeVoe, R. J. and MacBlane, D. B. *J. Org. Chem. 47* (1982) 1392. [d] Baggat, J. E. and Pilling, M. J. *J. Chem. Soc., Faraday Trans. 1* (1983) 221. [e] Eriksen, J., Lund, H. and Nyvad, I. *Acta Chem. Scand. B 37* (1983) 459. [f] Scaiano, J. C. and Kim-Tkuan N. *Can. J. Chem. 60* (1982) 2286 and [g] measured in anhydrous acetonitrile as KCN−Crown complex at an Ag-electrode *vs.* SCE.

$$^{3}Ph^{*}+Ph \xrightarrow{k_k} Ph^{+} + Ph^{-} \quad (5)$$

The decision between these two mechanisms can be made by applying the stationary state hypothesis for the reactions of Scheme 4 and for each of the two mechanisms. In the latter case (eqn. 5) the rate equation can be written as eqn. (6), where C is a constant and $k_T = (k_{TM}+k_q(O_2)[O_2]+k_q(CN)[CN]+k_q(BP)[BP]) = 2.1\times10^{6}s^{-1}$, $k_{TM}=2.6\times10^{5}s^{-1}$, $k_q(O_2)=(1\times10^{9}M^{-1}s^{-1})$,[20] $k_q(CN)=3.2\times10^{8}\ M^{-1}s^{-1}$ and $k_q(BP)=(8\times10^{5}\ M^{-1}s^{-1})$.[21] Using eqn. (6) and the values of Table 2 a value of $k_{etr}=0.9\times10^{10}\ M^{-1}s^{-1}$ for the energy-transfer step is obtained. The value measured by flash photolysis is $1.3\times10^{10}\ M^{-1}s^{-1}$ close to the calculated value, confirming the proposed mechanism. On the other hand, the value of a rate constant from the mechanism of eqn. (4) is two orders of magnitudes less than the measured rate constant.

$$\frac{[CN]\ [Ph]^2}{(1+K_k[Ph])}\ \frac{1}{\sqrt{a}} = C(k_2+k_x[CN])\ (k_T+k_{etr}[Ph]) \quad (6)$$

It is worth noticing that the rate parameter $K_x=k_x/k_2$ has a value of $0.71\times10^{3}\ M^{-1}$ and $1.8\times10^{3}M^{-1}$ for naphthalene reaction in water–acetonitrile,[4] and a value of $1.6\times10^{3}M^{-1}$ and $2.9\times10^{3}M^{-1}$ for phenanthrene reaction in anhydrous acetonitrile,[4] in the absence and presence of DCB, respectively. These very similar values support the similar reactive states regardless of the solvent.

The free-energy changes involved in an electron-transfer process can be calculated by the Rehm-Weller equation.[11] The spectroscopic and redox potentials and the calculated free-energies are presented in Table 4. ΔG-value is negative in reaction between excited singlet state of phenanthrene and strong electron acceptor, DCB, and the reaction is probable singlet state reaction. Direct measurements also support the singlet state reaction.

Electron transfers from cyanide anion to excited phenanthrene are possible according to the Rehm-Weller equation both in the singlet and triplet state. However, the latter reaction is much slower. The sensitization experiments support

the triplet state reaction, but not the direct interaction between cyanide anion and an excited state of phenanthrene. According to the Rehm-Weller equation, the reaction between excited triplet state and ground state of phenanthrene is less probable than the singlet state reaction. This is also in contradiction to our experimental results.

The interaction of two cyanated neutral radicals, $ArHCN^{\cdot}$, yields a polar transient, $(ArHCN^{-} \ldots {}^{+}ArHCN)$,[1,2,4] stabilized by increasing the amount of water in the solvent mixture. In the absence of oxygen, the final product formation is retarded. Oxygen interacts with the water stabilized transient by accepting an electron from anion $ArHCN^{-}$ and a proton from cation $ArHCN^{+}$, yielding the final cyano-product at a rate which increases with the amount of water. The almost equal values obtained for K_q both in anhydrous acetonitrile[1] and in aqueous acetonitrile (Table 3) indicate the existence of the similar transient, $ArHCN^{\cdot}$, in all solutions. This is irrespective of the fact, that in aqueous acetonitrile the reaction takes place *via* the singlet state, being due to the presence of DCB, whereas in anhydrous acetonitrile, in the absence of DCB, the reaction is a triplet state reaction.

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