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INVESTIGATION OF THE MECHANISM OF PHENANTHRENE PHOTOCYANATION BY FLASH PHOTOLYSIS IN DRY ACETONITRILE

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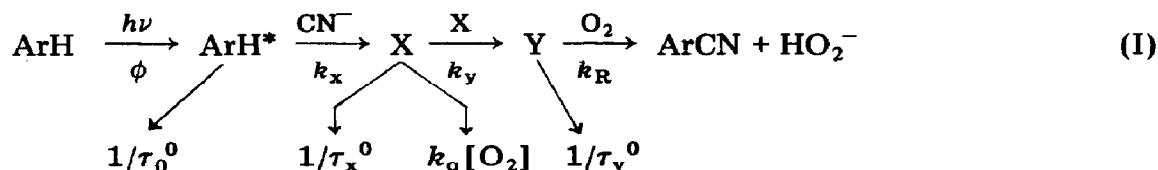
Summary

The mechanism of photocyanation of phenanthrene was studied by flash photolysis. Two transients were observed in the presence of the cyanide anion. One decayed by second-order kinetics and the intensity of absorption of the other was linearly proportional to the square of the intensity of the exciting light. Two possible mechanisms based on the experimental results are presented for the formation and quenching of the transients.

1. Introduction

The photolysis of aromatic hydrocarbons in the presence of the cyanide anion and oxidizing agents is known to yield cyanosubstituted compounds [1]. Crown ethers have been used to study the reaction in dry acetonitrile [2, 3]. The rate of the reaction has been found to be proportional to the square of the light intensity and dependent on the concentrations of both the cyanide anion and oxygen [3]. The proposed mechanism involves two photoinduced transients X and Y:

$$\text{ArH} \xrightarrow[\phi]{h\nu} \text{ArH}^* \xrightarrow[k_x]{\text{CN}^-} \text{X} \xrightarrow[k_y]{\text{X}} \text{Y} \xrightarrow[k_R]{\text{O}_2} \text{ArCN} + \text{HO}_2^- \qquad (\text{I})$$

$$1/\tau_0^0 \qquad\qquad 1/\tau_x^0 \quad k_q[\text{O}_2] \quad 1/\tau_y^0$$

To elucidate the mechanism of the reaction further we studied the transients formed by flash photolysis.

2. Experimental details

Acetonitrile was purified and dried before use. Phenanthrene was re-crystallized several times. Potassium cyanide 18-crown-6 complex was prepared as described earlier and stored under nitrogen [3]. It was dissolved in dry acetonitrile by stirring. The concentration of cyanide anion was determined by titration [4]. The reaction mixtures were prepared from stock solutions of potassium cyanide and phenanthrene. Degassed solutions of phenanthrene (2.5×10^{-3} mol dm^{-3}) and potassium cyanide 18-crown-6 complex (($0 - 1$) $\times 10^{-2}$ mol dm^{-3}) were irradiated in cylindrical quartz cells (diameter, 15 mm; length, 80 mm). Flash photolysis experiments were carried out with a flash energy of 400 J and a pulse duration of 10 μs. The exciting light was filtered by a UFS-6 glass filter. The flash energy was varied by neutral density filters. The fluorescence spectra were measured using a Jobin–Yvon spectrofluorometer.

3. Results and discussion

The flash photolysis of a degassed solution of phenanthrene in dry acetonitrile in the absence of the cyanide anion caused the formation of two different transients (Fig. 1). The absorption spectrum of one of them, with a lifetime of about 36 μs, is due to the triplet–triplet absorption of phenanthrene [5]. In the presence of the cyanide anion the absorption spectrum of this transient does not change and its lifetime remains about the same. The other transient, which absorbs at 420 nm, has a lifetime of 230 μs and is quenched by potassium cyanide (Fig. 1). Two new transients with broad absorptions at 390 - 450 nm and lifetimes of about 1 ms and 0.6 s are formed (Figs. 2 and 3).
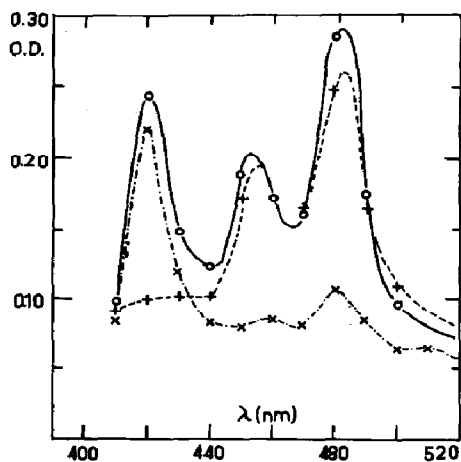

Fig. 1. Absorption spectra 20 μs after the flash pulse excitation of a solution of phenanthrene (2.5×10^{-3} mol dm^{-3}) in acetonitrile: ○, [CN$^-$] = 0; +, [CN$^-$] = 10 $\times 10^{-3}$ mol dm^{-3}; ×, [CN$^-$] = 0 (60 μs after the pulse). The relative intensity of the flash pulse is 3.
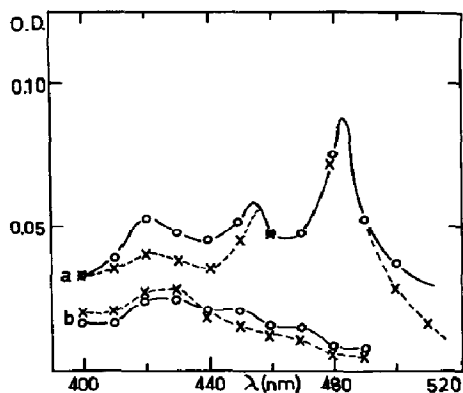
Fig. 2. Absorption spectra of a solution of phenanthrene (2.5×10^{-3} mol dm^{-3}) in aceto-nitrile 20 μs (curves a) and 500 μs (curves b) after flash pulse excitation: $\bigcirc$, [CN$^-$] = 1×10^{-3} mol dm^{-3}; $\times$, [CN$^-$] = 10×10^{-3} mol dm^{-3}. The relative intensity of the flash pulse is unity.
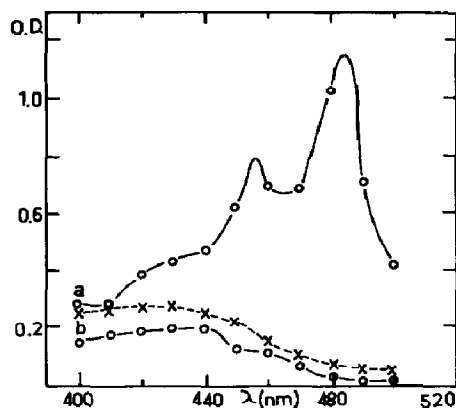
Fig. 3. Absorption spectra of a solution of phenanthrene (2.5×10^{-3} mol dm^{-3}) in aceto-nitrile 20 μs (curve a) and 500 μs (curves b) after flash pulse excitation: $\bigcirc$, [CN$^-$] = 1×10^{-3} mol dm^{-3}; $\times$, [CN$^-$] = 10×10^{-3} mol dm^{-3}. The relative intensity of the flash pulse is 12.
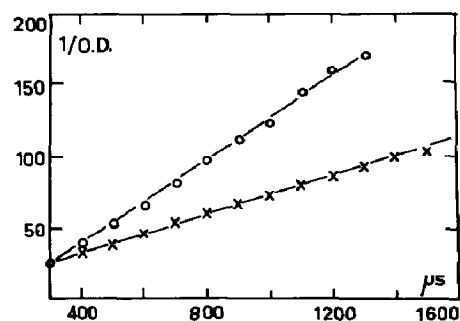

Fig. 4. Inverse of the absorbance of transient X at 420 nm as a function of the time after pulse excitation of a solution of phenanthrene (2.5×10^{-3} mol dm^{-3}) in acetonitrile: $\bigcirc$, [CN$^-$] = 1×10^{-3} mol dm^{-3}; $\times$, [CN$^-$] = 10×10^{-3} mol dm^{-3}. The relative intensity of the flash pulse is unity.

The transient with a lifetime of about 1 ms decays by second-order kinetics (Fig. 4), and the transient with a lifetime of 0.6 s decays by first-order kinetics. Absorption of the former transient depends linearly on the energy of the exciting flash, but absorption of the latter is proportional to the square of the flash energy. These results confirm the mechanism proposed in ref. 3, the former transient being X and the latter Y in reaction scheme (I). The observed lifetimes for transients X and Y and the calculated rate constants are presented in Table 1. The values are in good agreement with those suggested earlier [3].

Experimental data obtained by flash photolysis and by continuous irradiation can be explained in terms of the following reactions:

TABLE 1

Lifetimes τ_x^0, τ_0^0 and τ_y^0 of the transients X, ArH* and Y respectively obtained by flash photolysis, rate constants obtained by continuous radiation [3] and calculated rate constants [a]

Lifetime [b]	Measured rate constant (continuous irradiation) [c]	Calculated rate constant
$\tau_x^0 = 1 \times 10^{-3}$ s	$k_q\tau_x^0 = 9.0 \times 10^3$ mol^{-1} dm^3	$k_q = 9.0 \times 10^6$ mol^{-1} dm^3 s^{-1}
$\tau_0^0 = 36 \times 10^{-6}$ s	$k_x\tau_0^0 = 7.4 \times 10^3$ mol^{-1} dm^3	$k_x = 2.0 \times 10^8$ mol^{-1} dm^3 s^{-1}
$\tau_y^0 = 0.6$ s	$(\phi\tau_0^0 k_x\tau_x^0)^2 k_y\tau_y^0 k_R =$ 1.65×10^{15} mol^{-4} dm^{12} s	$\phi^2 k_y k_R = 5.0 \times 10^{13}$ mol^{-2} dm^6 s^{-2}
$\tau = 230 \times 10^{-6}$ s [d]		

[a]The symbols are as given in reaction scheme (I).
[b]At a phenanthrene concentration of 2.5×10^{-3} mol dm^{-3}.
[c]At a phenanthrene concentration of 5×10^{-5} mol dm^{-3}.
[d]Band at 420 nm observed in the absence of oxygen and the cyanide anion.

$$A \xrightarrow{h\nu} A^*$$

$$A^* \xrightarrow{CN^-} X + X'$$

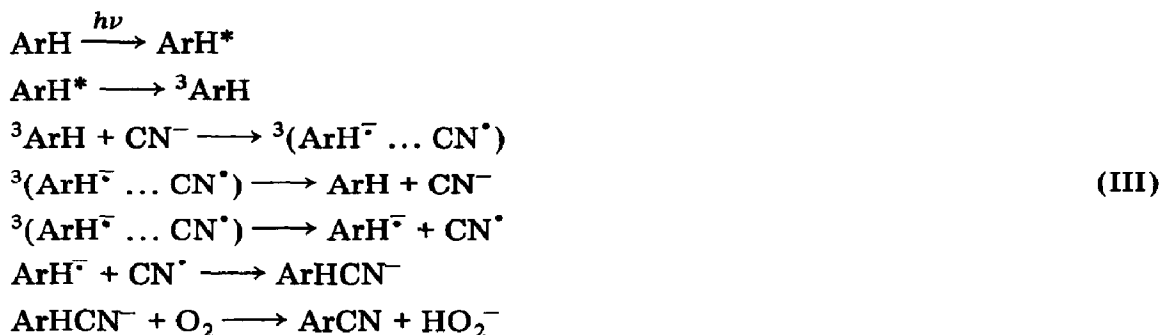$$X + X' \longrightarrow Y \qquad\qquad\qquad (II)$$

$$Y \longrightarrow B$$
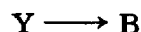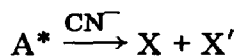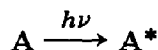
where A is the ground state of phenanthrene, A* is an excited molecule of phenanthrene, X and X' are transients and B is the final product. To explain the second-order dependence of the reaction rate on the intensity of the exciting light we have to assume that in steady state experiments transients X and X' would decay mainly by first-order processes to yield the original reagents.

No quenching of the fluorescence of phenanthrene was observed at varying concentrations of the cyanide anion. The observation that the cyanide anion does not quench either the singlet excited state of phenanthrene or its triplet state was unexpected. One possible explanation could be the formation of a triplet exciplex of phenanthrene and the cyanide anion which has an absorption spectrum and lifetime very similar to the triplet state of phenanthrene. The second possibility is a reaction of the cyanide anion with the radical cation of phenanthrene which is formed either by electron photo-ejection or by reaction of the singlet excited state of phenanthrene with an electron acceptor present in the solution.

The first explanation can be shown schematically as follows:

$$ArH \xrightarrow{h\nu} ArH^*$$

$$ArH^* \longrightarrow {}^3ArH$$
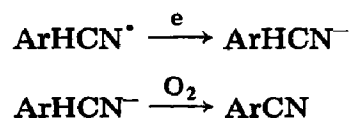
$${}^3ArH + CN^- \longrightarrow {}^3(ArH^{\bar{\cdot}} \ldots CN^{\bullet})$$

$${}^3(ArH^{\bar{\cdot}} \ldots CN^{\bullet}) \longrightarrow ArH + CN^- \qquad\qquad\text{(III)}$$

$${}^3(ArH^{\bar{\cdot}} \ldots CN^{\bullet}) \longrightarrow ArH^{\bar{\cdot}} + CN^{\bullet}$$

$$ArH^{\bar{\cdot}} + CN^{\bullet} \longrightarrow ArHCN^-$$

$$ArHCN^- + O_2 \longrightarrow ArCN + HO_2^-$$

where transient X is the radical anion of phenanthrene and X' is the radical $CN^{\bullet}$ which is formed by the dissociation of the triplet exciplex ${}^3(ArH^{\bar{\cdot}} \ldots CN^{\bullet})$. The reaction of the radical anion of phenanthrene with the radical $CN^{\bullet}$ yields the σ complex $ArHCN^-$ which is transient Y in reaction scheme (I). The cyanide anion, however, reacts directly with triplet excited phenanthrene only if the spectrum of the exciplex is very similar to the triplet–triplet absorption spectrum of phenanthrene. They usually have rather different spectra [6].

The other possible photocyanation mechanism involves the formation of the phenanthrene radical cation:
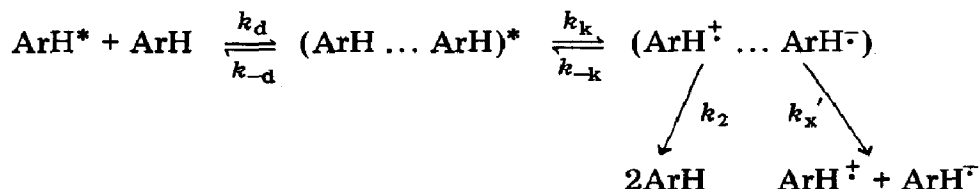
$$ArH \longrightarrow ArH^*$$

$$ArH^* \longrightarrow ArH^{\dot{+}} + e$$

$$ArH^{\dot{+}} + CN^- \longrightarrow ArHCN^{\bullet}$$

$$2ArHCN^{\bullet} \longrightarrow (ArHCN^- \ldots ArHCN^+) \qquad\qquad\text{(IV)}$$

$$(ArHCN^- \ldots ArHCN^+) \xrightarrow{O_2} ArCN$$

or

$$ArHCN^{\bullet} \xrightarrow{e} ArHCN^-$$

$$ArHCN^- \xrightarrow{O_2} ArCN$$
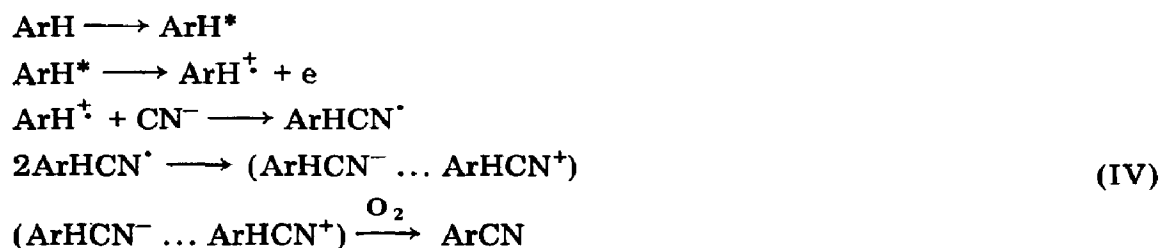
This photocyanation pathway has been proposed earlier [7] for the primary process. In this scheme transient X is the radical $ArHCN^{\bullet}$ which reacts with itself (X'), with a solvated electron or with a product (X') due to its interaction with an electron acceptor, and transient Y is either the complex $(ArHCN^- \ldots ArHCN^+)$ formed by the interaction of two neutral radicals or the σ complex $ArHCN^-$ as in reaction scheme (III). The reaction product is formed by the interaction with oxygen.

In addition, the radical $ArHCN^{\bullet}$ must decay by a first-order reaction. The decay of transient X by a first-order process and the decrease of its decay rate by a second-order process (Fig. 4) with increasing cyanide anion concentration can be explained as follows:

$$ArHCN^{\bullet} + CN^- \longrightarrow ArH + (CN)_2^{\bar{\cdot}}$$

$$(CN)_2^{\bar{\cdot}} + e \longrightarrow 2CN^-$$
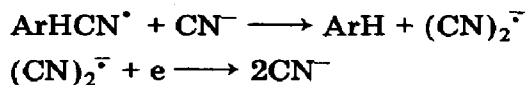
The formation of the cation radical proposed in reaction scheme (IV) can take place by electron photoejection or by interaction between an excited and a ground state molecule of an electron donor and an electron acceptor. In the absence of other electron acceptors, ground state phenanthrene can act as an acceptor. The interaction between the excited and the ground states of phenanthrene may yield an excimer, which in a polar solvent dissociates to a radical anion and a radical cation. To investigate the formation of radical ion pairs and free radical ions we consider the following reaction scheme:

$$\text{ArH}^* + \text{ArH} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (\text{ArH} \ldots \text{ArH})^* \underset{k_{-k}}{\overset{k_k}{\rightleftharpoons}} (\text{ArH}^{\stackrel{+}{\cdot}} \ldots \text{ArH}^{\bar{\cdot}})$$

$$\swarrow k_2 \qquad k_x' \searrow$$

$$2\text{ArH} \qquad \text{ArH}^{\stackrel{+}{\cdot}} + \text{ArH}^{\bar{\cdot}}$$

The formation of the encounter complex between the acceptor and the donor, in either the singlet or the triplet state, is followed by electron transfer. The radical ion pair produced either returns via back electron transfer to the ground state (k_2) or dissociates into separate radical ions (k_x'). According to the stationary state approximation, the experimental rate constant is

$$k_q = \frac{k_d k_k (k_2 + k_x')}{(k_2 + k_x')(k_k + k_{-d}) + k_{-d} k_{-k}} \tag{1}$$

There is a difference in the reaction depending on whether the reacting molecules are in the excited singlet or the excited triplet state [8]. The back electron transfer (k_2) to the ground state is spin forbidden in the case of the triplet reaction, and therefore is slow compared with dissociation into radicals (k_x') or with competing reactions (e.g. $k_x[\text{CN}^-]$). This yields a higher concentration of free radicals than the singlet state reaction for which k_2 is larger than k_x'. It is common to set $k_d/k_{-d} = 1 \text{ mol}^{-1} \text{ dm}^3$ and $k_d \approx k_{\text{diff}} \approx 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ in both the singlet and the triplet reactions. In the singlet reaction, where $k_2 \approx 10^{10} \text{ s}^{-1}$ which is much greater than k_x' and k_{-d} is much greater than k_k, eqn. (1) reduces to

$$k_q \approx \frac{k_k k_2}{k_2 + k_{-k}} \approx k_k \text{ mol}^{-1} \text{ dm}^3 \tag{2}$$

and in the triplet reaction, where k_2 is much less than k_x' and k_{-d} is much greater than k_k, eqn. (1) reduces to

$$k_q \approx \frac{k_k k_x'}{k_x' + k_{-k}} \text{ mol}^{-1} \text{ dm}^3 = \frac{k_k(k_x'/k_{-k})}{1 + (k_x'/k_{-k})} \text{ mol}^{-1} \text{ dm}^3 \approx k_k \text{ mol}^{-1} \text{ dm}^3 \tag{3}$$

when k_x'/k_{-k} is much greater than unity. The quenching of the triplet or the singlet state of excited phenanthrene by ground state phenanthrene, where the rate constant $k_q \approx k_k$ mol^{-1} dm$^3 \leqslant 10^7$ mol^{-1} dm^3 s^{-1}, is thus difficult to observe. When the cyanide ion is present it reacts with either the radical ion pair or the radical cation. Then in the triplet reaction

$$k_q = \frac{k_k(k_x/k_{-k})[CN^-]}{1 + (k_x/k_{-k})[CN^-]} \tag{4}$$

It is clear on the basis of this equation that the quenching of the triplet state by the cyanide anion cannot be observed for $k_x[CN^-]/k_{-k} \gg 1$. Thus the radical cation may be formed from the excited triplet state without any quenching of the triplet–triplet absorption of phenanthrene being observed.

The formation of an excimer was suggested by Bunce *et al.* [9] for the unassisted photocyanation of naphthalene and biphenyl although they did not observe quenching of the monomer fluorescence. The relatively long-lived transient observed by us at 420 nm (Fig. 1) in the absence of the cyanide anion and oxygen could be the radical cation formed by the interaction of the excited singlet or triplet state and ground state phenanthrene. It is quenched by the cyanide anion and disappears at cyanide anion concentrations above about 10^{-2} mol dm^{-3}. A broad absorption by the radical cation of phenanthrene was observed at 420 nm on irradiation in a rigid solution [10] and also in the presence of dicyanobenzene in acetonitrile [11].

The primary step in the photocyanation of phenanthrene could be the formation of an excimer in the singlet or triplet state followed by electron transfer from the excited state to the ground state of phenanthrene. The possibility of direct interaction between the cyanide anion and triplet state phenanthrene cannot definitely be ruled out.

Acknowledgment

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