Kinetic Analysis of Aromatic Photocyanation: Naphthalene, Biphenyl, and Phenanthrene

Helge J. Lemmetyinen
Physical Chemistry Laboratory, University of Helsinki, Meritullinkatu 1 C, SF-00170 Helsinki 17, Finland

Nucleophilic photocyanation of the unsubstituted aromatic hydrocarbons, naphthalene, biphenyl, and phenanthrene, in both dry and aqueous acetonitrile can be described by a mechanism involving two photoinduced transients. The primary step of the mechanism is the formation of a transient ionic complex through triplet excimer of aromatic hydrocarbon or, when an electron acceptor is present, through triplet exciplex. The attack of cyanide ion on the transient complex yields the cyanated radical, ArHCN$^{\cdot}$, which in aqueous acetonitrile reacts with itself to yield cyano- and dihydrocyano-products or, in dry acetonitrile after being attacked by an electron, is oxidized to the cyano-product. The rate constants for the formation of radical ions and the attack of cyanide ion are calculated from the experimental results.

Mizuno,[1] and more recently Yasuda [2] and Bunce [3] investigated the photocyanation of phenanthrene, anthracene, naphthalene, and biphenyl in aqueous acetonitrile and they proposed essentially the same mechanisms as den Heijer [4] and Cornelisse [5] for reactions involving electron donating groups. Both Yasuda and Bunce propose that cation radicals are formed as a primary step when electron acceptors (A) are present, followed by the nucleophilic attack of cyanide anion [reactions (1) and (2)]. Bunce [3] measured quantum yields in the photolysis of unsubstituted aromatic hydrocarbons, suggesting that in the absence of an electron acceptor an excimer is formed which dissociates to radical ions [reactions (3) and (4)]. Both Yasuda and Bunce suggest that the final products are formed by the reaction of two neutral radicals [reaction (5)]. In aqueous acetonitrile, in the absence of oxygen, the main product is the dihydrocyano-product,[2,3]

$$\mathrm{ArH^{*} + A \longrightarrow ArH^{+\cdot} + A^{-\cdot}} \qquad (1)$$

$$\mathrm{ArH^{+\cdot} + CN^{-} \longrightarrow ArHCN^{\cdot}} \qquad (2)$$

$$\mathrm{ArH^{*} + ArH \longrightarrow excimer} \qquad (3)$$

$$\mathrm{excimer \longrightarrow radical\ ions} \qquad (4)$$

$$\mathrm{2\,ArHCN^{\cdot} \longrightarrow ArCN + ArH_2CN} \qquad (5)$$

whereas in the presence of oxygen it is the cyano-product.[2] Yasuda suggests that oxygen oxidizes the cyanated radical [reaction (6)]. The photosubstitution of the hydrogen atom in the substituted aromatic hydrocarbon is not observed in aqueous solutions in the absence of an oxidizing agent.[4]

$$\mathrm{ArHCN^{\cdot} \xrightarrow{O_2} ArCN} \qquad (6)$$

Our previous studies [6] of photocyanation of phenanthrene indicate that: (1) the main product is 9-cyanophenanthrene in dry acetonitrile and only traces of other cyano-products are present, (2) the presence of an oxidizing agent (O_2) is essential for product formation, (3) the rate of the reaction is very sensitive to the oxygen concentration and a maximum rate is observed at small concentrations of oxygen, and (4) the rate of reaction in both dry acetonitrile and 1 : 1 acetonitrile–water is linearly proportional to the square of the intensity of the absorbed radiation. We proposed [6] the mechanism of Scheme 1 for photocyanation of phenanthrene.

Flash photolysis [7] investigations support this mechanism. Two transients were observed with properties similar to those of the transients X and Y in Scheme 1.

In this work we analyse the applicability of our mechanism [6] of two photoinduced transients to the quantum yield measurement made by Bunce *et al.*[3] and study the autocatalytic photocyanation of phenanthrene and the mechanism of the reaction using nitrous oxide (N_2O) as an oxidizing agent in dry acetonitrile.

Results

In our previous work [7] we presented two possible reactions for the first step of the photosubstitution, the formation of triplet exciplex of phenanthrene and cyanide anion, or alternatively a reaction of cyanide anion with a radical cation of phenanthrene, formed either by electron photoejection or by reaction of the excited state of phenanthrene with some electron acceptor present in the solution. A choice between these two explanations would seen possible on the basis of the results obtained by Bunce.[3]

Photocyanation in Aqueous Acetonitrile.—If the formation of cation radicals is the primary step of aromatic photosubstitution Scheme 2 will apply.

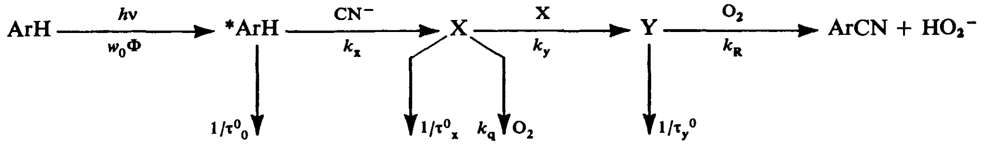
According to Scheme 2 the ionization is always assisted, either by an electron acceptor or by the ground state reactive aromate, *i.e.* self-assisted. It is suggested here that 'unassisted' photocyanation in fact involves assistance by the ground state aromatic compound. Depending on the reduction potentials of the electron acceptors and on the solvent, the transient ionic complex forms either contact ion pairs or free radical ions. Steady-state analysis gives for the formation of a reaction product relationship (7) between the quantum yield and the substrates (for details see Experimental section).

$$[\mathrm{CN^-}][\mathrm{A}]\sqrt{\frac{[\mathrm{ArH}]}{\varphi}} = a(1 + K_{\mathrm{k}}[\mathrm{A}])(1 + K_{\mathrm{x}}[\mathrm{CN^-}]) \qquad (7)$$

where $a = k_3\ [\Phi^2 . 1.15\varepsilon k_{\mathrm{p}}(I_{\mathrm{o}} + I_{\mathrm{t}})]^{-\frac{1}{2}}/K_{\mathrm{k}}K_{\mathrm{x}}$, $K_{\mathrm{x}} = k_{\mathrm{x}}/(k_2 + k_{-\mathrm{k}})$, and $K_{\mathrm{k}}[\mathrm{A}] = (k'_{\mathrm{k}}/k_1)[\mathrm{ArH}] = K'_{\mathrm{k}}[\mathrm{ArH}]$ in the absence of an electron acceptor ($[\mathrm{A}] = [\mathrm{ArH}]$) and $K_{\mathrm{k}}[\mathrm{A}] = K'_{\mathrm{k}}[\mathrm{ArH}] + K''_{\mathrm{k}}[\mathrm{A}]$ in the presence of an electron acceptor.

Applying the quantum yields, φ, obtained by Bunce [3] for the disappearance of naphthalene and biphenyl in photocyanation in water–acetonitrile the following four cases can be distinguished.

(i) *Self-assisted photocyanation of naphthalene and biphenyl.*



Scheme 1

$$ArH \xrightarrow{w_0\Phi} ArH^*$$
$$ArH^* \xrightarrow{k_1} ArH$$
$$ArH^* + A \underset{k_{-k}}{\overset{k_k}{\rightleftharpoons}} \text{ionic complex}$$
$$\text{ionic complex} \xrightarrow{k_2} ArH + A$$
$$\text{ionic complex} + CN^- \xrightarrow{k_x} ArHCN^\bullet + A^{-\bullet}$$
$$ArHCN^\bullet \xrightarrow{k_3} ArH + CN^\bullet$$
$$2\,ArHCN^\bullet \xrightarrow{k_p} ArH_2CN + ArCN$$

Scheme 2. For self-assisted reactions A = ArH, and for assisted reactions A = electron acceptor, where k_k is k'_k or k''_k, respectively. Φ is the quantum yield for the formation of a reactive excited state of ArH

Equation (7) can be written as (8). Presenting the left side of equation (8) as a function of concentration of cyanide anion

$$[CN^-]\sqrt{\frac{(ArH)}{\varphi}} = \frac{a(1 + K'_k[ArH)]}{[ArH]}(1 + K_x[CN^-]) \qquad (8)$$

(Figure 1) the values of K_x can be calculated from the ratios of the slopes and the intercepts of the straight lines (Table 1).

Rewriting equation (8) we obtain (9). A good linearity

$$\frac{1}{\sqrt{\varphi}} = \frac{a(1 + K_x[CN^-])}{[CN^-]}\left(K'_k + \frac{1}{[ArH]}\right)\frac{1}{\sqrt{[ArH]}} \qquad (9)$$

between $1/\sqrt{\varphi}$ and $1/\sqrt{[ArH]}$ is obtained, indicating that $K'_k \gg 1/[ArH]$. Thus K'_k can be calculated both for naphthalene and for biphenyl (Table 1), assuming that $(I_o + I_t)$, the sum of the incident and transmitted light intensities, is independent of the concentration of aromatic hydrocarbons. This would seem to be a correct assumption since the reactions were performed under conditions where all incident light was absorbed by the aromatic hydrocarbon.[3]

(ii) *Assisted photocyanation of naphthalene with constant concentrations of the electron acceptors.* According to the results obtained by Bunce [3] the quantum yields seem to be independent of the concentrations of hydrocarbons in the presence of the electron acceptors, dicyanobenzene and persulphate ion, and thus it is suggested here that k_k/k_{-k} have higher values for assisted cyanation than for unassisted cyanation.

(iii) *Assisted photocyanation of naphthalene with various concentrations of electron acceptors.* Equation (7) is written in the form (10). From the ratios of intercepts and slopes of the

$$[A]\sqrt{\frac{[ArH]}{\varphi}} = \frac{a(1 + K_x[CN^-])}{[CN^-]}(1 + K'_k[ArH] + K''_k[A]) \qquad (10)$$

lines drawn according to this equation (Figure 2) the values of K_k'' can be calculated (Table 1). The linearity is good for both electron acceptors.

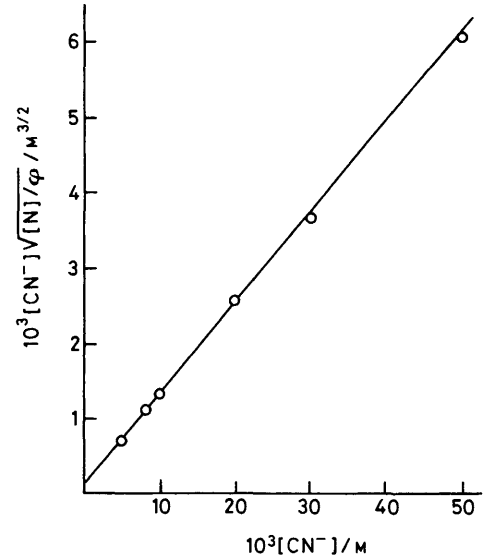


Figure 1. Dependence of the rate of self-assisted photocyanation of naphthalene (N) on cyanide anion concentration in 1 : 1 water–acetonitrile. [N] 1.0 × 10^{-3}M

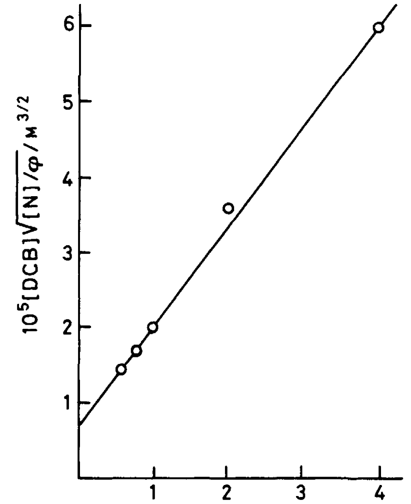


Figure 2. Dependence of the rate of assisted photocyanation of naphthalene (N) on dicyanobenzene (DCB) concentration in 1 : 1 water–acetonitrile. [N] 5 × 10^{-3}M, $[CN^-]$ 2 × 10^{-2}M

(iv) *Assisted photocyanation of naphthalene with various concentrations of cyanide anion.* When $[CN^-]\sqrt{[ArH]/\varphi}$ is presented as a function of cyanide anion concentration, according to equation (7), then in the presence of the electron acceptor (Table 1), dicyanobenzene (DCB), a straight line is obtained (Figure 3). The value of K_x for the dicyanobenzene

Table 1. Kinetic data (K/l mol^{-1}; k/l mol^{-1} s^{-1}) for photocyanation of naphthalene (N) and biphenyl (B) in aqueous acetonitrile,[3] and of phenanthrene (P) in dry acetonitrile[6]

Constant substrate	Concentration (M)	Variable substrate	Slope	Intercept	r	
N	1.0×10^{-3}	CN^-	0.118 ± 0.001^a	$(1.67 \pm 0.23) \times 10^{-4\,a}$	0.999	K_x 0.71×10^3
B	1.0×10^{-3}	CN^-	0.313 ± 0.003^a	$(1.62 \pm 0.18) \times 10^{-4\,a}$	0.999	K_x 1.93×10^3
CN^-	5.0×10^{-2}	N	0.105 ± 0.003^b	0.55 ± 0.05^b	0.999	k'_k 6.4×10^3 K'_k $0.64 \times 10^{7\,f}$
CN^-	5.0×10^{-2}	B	0.186 ± 0.021^b	4.9 ± 0.5^b	0.987	k'_k 1.5×10^3 K'_k $0.30 \times 10^{7\,f}$
N	5.0×10^{-3}	DCB	0.135 ± 0.005^c	$(6.7 \pm 1.1) \times 10^{-6\,c}$	0.998	K_k'' 660×10^3
CN^-	2.0×10^{-2}					k''_k $66 \times 10^{7\,f}$
N	1.0×10^{-3}	$S_2O_8{}^{2-}$	0.060 ± 0.002^c	$(2.02 \pm 0.24) \times 10^{-4\,c}$	0.999	K''_k 2.2×10^3
CN^-	5.0×10^{-2}					k''_k $0.2 \times 10^{7\,f}$
N	5.0×10^{-3}	CN^-	0.122 ± 0.002^e	$(6.73 \pm 2.75) \times 10^{-5\,e}$	0.999	K_x 1.81×10^3
DCB	5.0×10^{-4}					
N	1.0×10^{-3}	CN^-	0.071 ± 0.008^e	$(3.2 \pm 0.8) \times 10^{-4\,e}$	0.987	K_x 0.22×10^3
$S_2O_8{}^{2-}$	2.0×10^{-2}					
P	5.0×10^{-3}	CN^-	$(3.7 \pm 0.1) \times 10^{-5\,d}$	$(2.2 \pm 0.1) \times 10^{-8\,d}$	0.998	K_x 1.6×10^3
O_2	8×10^{-5}					
$(I_o + I_t)$	1.29×10^{-7} ein dm^{-2} s^{-1}					
CN^-	2.5×10^{-3}	P	$(6.7 \pm 0.1) \times 10^{-9\,d}$	$(7.2 \pm 0.1) \times 10^{-8\,d}$	0.991	K'_k 0.52×10^3
O_2	0.11×10^{-3}	$(I_o + I_t)$				k'_k $1.3 \times 10^{7\,f}$

Calculated by equations [a] (8), [b] (9), [c] (10), [d] (11), and according to equation [e] (7). [f] Calculated from the values of K_k using approximate triplet lifetimes τ_N *ca.* 1 ms,[8] τ_B *ca.* 0.5 ms,[9] and τ_P *ca.* 0.04 ms.[7]

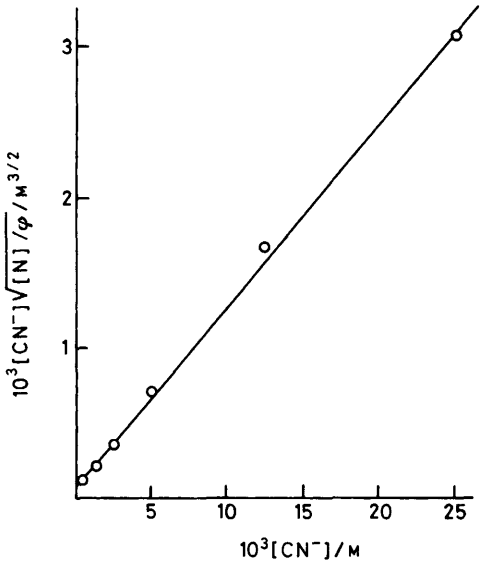


Figure 3. Dependence of the rate of assisted photocyanation of naphthalene (N) on cyanide anion concentration in 1 : 1 water–acetonitrile. [N] 5×10^{-3}M, [DCB] 5×10^{-4}M

$$ArHCN^{\cdot} + O_2 \xrightarrow{k_q} \text{unproductive}$$

$$2\,ArHCN^{\cdot} \xrightarrow{k_y} (ArHCN^{\delta-} \cdots {}^{\delta+}ArHCN)$$

$$(ArHCN^{\delta-} \cdots {}^{\delta+}ArHCN) + O_2 \xrightarrow{k_R} \text{products}$$

$$(ArHCN^{\delta-} \cdots {}^{\delta+}ArHCN) \xrightarrow{k_4} \text{unproductive}$$

or

$$ArHCN^{\cdot} + A^{-\cdot} \xrightarrow{k_y} ArHCN^- + A$$

$$ArHCN^- + O_2 \xrightarrow{k_R} \text{product}$$

$$ArHCN^- \xrightarrow{k_4} \text{unproductive}$$

Scheme 3.

assisted reaction can be calculated from the values of the slope and the intercept of this line. In a similar way the value of K_x for the persulphate anion assisted photocyanation is obtained (Table 1). The linearity is good in the former case but only reasonable in the latter case.

In the absence of dicyanobenzene K_x is 0.71×10^3 dm^3 mol^{-1}, but in the presence of the acceptor it is 1.81×10^3 dm^3 mol^{-1}. K_x is a parameter denoting the efficiency with which cyanide anion reacts with one of the transients in the reaction. The increased value of K_x in the latter case is expected because cyanation reactions are accelerated in the presence of electron acceptors, which interact with the excited naphthalene before being attacked by the cyanide anion. This supports suggestions [1-3] that cyanide anion does not react directly with the excited aromatic hydrocarbon, but attacks the cation radical of an aromatic hydrocarbon.

Photocyanation in Dry Acetonitrile.—(i) *Self-assisted photocyanation of phenanthrene.* Because only 9-cyanophenanthrene is obtained and no product is observed in the absence of oxygen, in dry acetonitrile,[6] the reactions in Scheme 3 [7] should replace the last reaction of Scheme 2. Applying the steady state approximation to Schemes 2 and 3, we obtain equation (11) where[6] $K_q = k_q/k_3$.

As above, the left side of equation (11) can be presented both as a function of cyanide anion concentration (Table 1) and of $1/\sqrt{[ArH]}$ (Table 1 assuming as before that $K'_k \gg 1/[ArH]$

$$\sqrt{\frac{[O_2][CN^-]^2(I_o + I_t)}{\varphi}} = \sqrt{\frac{k_4}{1.15\varepsilon k_R k_y}}\,\frac{k_3(1 + K_q[O_2])}{\varphi K_x K'_k}\left(K'_k + \frac{1}{[ArH]}\right)\frac{(1 + K_x[CN^-])}{\sqrt{[ArH]}} \qquad (11)$$

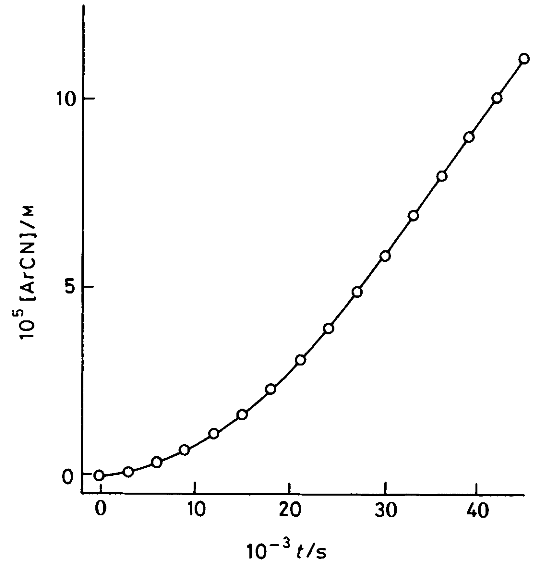


Figure 4. Formation of 9-cyanophenanthrene as a function of irradiation time in autocatalytic photocyanation of phenanthrene (P) in dry acetonitrile. (P) 5.0 × 10^{-3}M, [CN$^-$] 4.0 × 10^{-3}M and [O$_2$] 1.2 × 10^{-3}M

at high phenanthrene concentrations). Thus the values of K_x and K'_k can be calculated.

(ii) *Autocatalytic photocyanation of phenanthrene.* The autocatalytic effect of the substitution was observed by Yasuda[2] and Bunce.[3] Here this effect is studied in greater detail. As can be seen from Figure 4 the rate of formation of 9-cyanophenanthrene increases as a function of irradiation time. The rate of the autocatalytic photocyanation also depends on the square of the intensity of absorbed light. We began by studying whether the possible products peroxide, O_2^{2-}, and superoxide, $O_2^{-\cdot}$, anions affect the rate of the reaction. In the absence of oxygen but with added peroxide, Na_2O_2, or superoxide, KO_2, no reaction was observed. In the presence of oxygen, the peroxide anion had no effect on the reaction rate at concentrations between 1 × 10^{-5} and 1 × 10^{-3} mol dm^{-3}.

Superoxide radical anion decreased the rate of the reaction at concentrations higher than 5 × 10^{-5} mol dm^{-3}. This can be explained by the dual reactivity of superoxide anion: depending on the nature of the substrate it can act either as an electron acceptor or as an electron donor [reactions (12) and (13), respectively]. The autocatalytic reaction is, therefore, not due to peroxide or superoxide anions, and we proceeded to investigate the effect of 9-cyanophenanthrene.

$$ArH^{-\cdot} + O_2^{-\cdot} \longrightarrow ArH + O_2^{2-} \qquad (12)$$

$$ArH^{+\cdot} + O_2^{-\cdot} \longrightarrow ArH + O_2 \qquad (13)$$

In the presence of 1 × 10^{-5} mol dm^{-3} 9-cyanophenanthrene, in a reaction mixture containing both phenanthrene and cyanide (1 × 10^{-3} mol dm^{-3}), the photolytic reaction was observed to increase in the manner displayed in Figure 4. The autocatalysis is therefore due to the reaction product, 9-cyanophenanthrene, and the reaction can be considered as a cyanophenanthrene-assisted photocyanation.

Table 2. Quantum yields of autocatalytic photocyanation of phenanthrene (P) in dry acetonitrile

10^5[ArCN]/M	$10^3\varphi$	$10^{11}\sqrt{[O_2]/\alpha}$. [ArCN][CN$^-$]	
1.9	2.3	7.3	Slope[a]
2.7	2.8	9.6	(2.40 ± 0.04) × 10^{-6}
3.5	3.1	11.9	Intercept[a]
4.4	3.5	14.4	(3.3 ± 0.3) × 10^{-11}
5.4	4.0	16.5	r 0.999
6.4	4.5	18.7	K''_k 260 × 10^3 l mol^{-1}
7.4	5.0	20.8	k''_k 650 × 10^7 l mol^{-1} s^{-1} [b]
8.5	5.2	23.8	
9.5	5.6	25.8	
10.6	5.7	28.6	

[a] Calculated according to equation (11). [b] Calculated from the value of K''_k using the approximate triplet lifetime τ_P *ca.* 0.04 ms.[7] [P] 5.0 × 10^{-3}M, [CN$^-$] 4.0 × 10^{-3}M, and [O$_2$] 1.2 × 10^{-3}M, I_0 1.36 × 10^{-7} ein dm^{-2} s^{-1}, D_{Ph} 0.90. The values of φ and α are calculated using equations (19), (20), and (21), and using the average rates obtained from the values of Figure 4.

Presenting [ArCN]$\sqrt{[O_2][CN^-]^2/\alpha}$ as a function of the concentration of cyanophenanthrene (Table 2) a straight line is obtained and the value of K''_k for the cyanophenanthrene-assisted photocyanation reaction can be calculated from the ratio of the slope and the intercept, $K''_k/[1 + K'_k(ArH)]$, of the straight line.

Discussion

The calculated kinetic data are summarized in Tables 1 and 2. From the known lifetimes of excited singlet and triplet states of aromatic hydrocarbons the rate constants k_k can be calculated. The excited singlet states of aromatic hydrocarbons cannot be reacting, because the rate constants k_k would then be more than an order of magnitude higher than the rate constants of diffusion controlled reactions (*e.g.* K''_k 6.6 × 10^5 dm^3 mol^{-1} for the naphthalene–dicyanobenzene system and $1/k_1$ 56 ns,[3] and therefore, k''_k 1 × 10^{13} dm^3 mol^{-1} s^{-1}). The Stern–Volmer fluorescence quenching constants obtained[3] also deviate from the values obtained by the kinetic method, supporting the mechanism involving the triplet state reaction. From the approximately known triplet lifetimes,[7-9] the rate constants k_k can be calculated (Tables 1 and 2).

Quenching of the triplet state of aromatic hydrocarbon by an electron acceptor can proceed through a transient ionic complex (ArH · · · A)* regardless of its nature [reaction (14)].

$$^3ArH + A \underset{k_{-k}}{\overset{k_k}{\rightleftharpoons}} (ArH \cdots A)^* \xrightarrow{k_2} \qquad (14)$$

Quenching of this complex by cyanide anion competes with other deactivation processes described by the rate constant k_2 [reaction (15)]. The experimental quenching constant k_q for these processes is given by equation (16). Equation (16) makes it clear why the quenching of the triplet state by cyanide anion

$$(ArH \cdots A)^* + CN^- \xrightarrow{k_x} ArHCN^\cdot + A^{-\cdot} \qquad (15)$$

is difficult to observe.[7] The values of K_x describe the natures of the complexes $(\mathrm{ArH}\cdots\mathrm{A})^*$.

$$k_q = \frac{k_k k_x[\mathrm{CN}^-]}{k_2 + k_{-k} + k_x[\mathrm{CN}^-]} = \frac{k_k K_x[\mathrm{CN}^-]}{1 + K_x[\mathrm{CN}^-]} \qquad (16)$$

The relatively large value of K_x in photocyanation of phenanthrene in dry acetonitrile points to a large value of k_x when unsolvated cyanide anion is attacking a complex, for the triplet excimer of phenanthrene is known to be very weak, indicating a large value of k_{-k}. Azumi and McGlynn[10] observed a structureless emission band at 430 nm in a 10^{-3}M glassy solution of phenanthrene at 77 K, which became stronger with increasing temperature but approached zero at room temperature. They attributed this to the delayed excimer fluorescence of phenanthrene. Briegleb and his co-workers[11] observed a band at 420 nm in the triplet–triplet absorption spectrum of a phenanthrene–tetrachlorophthalic anhydride system, attributing it to a triplet excimer of phenanthrene. We found a similar band at room temperature in dry acetonitrile,[7] which was quenched effectively by cyanide anion. However, its unusually long lifetime (240 μs) does not agree with the lifetimes of intramolecular triplet excimers observed by Zachariasse *et al.*[12]

The photocyanation of aromatic hydrocarbons is proposed to occur in both acetonitrile and water–acetonitrile *via* a transient ionic complex formed from a triplet excimer or exciplex. The polarity of the complex varies with the solvent and with the reduction potential of the electron acceptor of the complex, and the complex may dissociate to solvent-separated ion pairs or free ions. An attack of the cyanide anion on the complex or on the cation radical produces a cyanated radical, $\mathrm{ArHCN}^{\bullet}$. In dry acetonitrile the reaction proceedes either by an electron transfer from the radical anion of the acceptor to the cyanated radical producing a cyanated anion, ArHCN^-, which, in the presence of oxygen, is oxidized to a cyano-product, or by disproportionation of two cyanated radicals to a transient, which interacting with the oxidizing agent, yields a cyano-product. In aqueous acetonitrile the disproportionation produces both a dihydrocyano- and a cyano-product. In the presence of an oxidizing agent it influences to the course of the disproportionation process preventing the formation of dihydrocyano-product. This explains why in the presence of oxygen[2] and persulphate ions[3] only a cyano-product is formed, and why in aqueous acetonitrile the product formation is considerably slower in the absence than in the presence of oxygen.[2]

When persulphate ion is used as an electron acceptor (Table 1) there is a deviation from the linear dependence of the quantum yield on persulphate and on cyanide anion concentrations, and the value of K_k is lower than in the absence of persulphate. The reason may be that the possible transient sulphate anion radical, $\mathrm{SO_4}^{-\bullet}$, acts as an electron acceptor or that persulphate anion behaves as an oxidizing agent similar to oxygen.

Nitrous oxide is an effective oxidizing agent in photocyanation reactions.[4] In photocyanation of phenanthrene in dry acetonitrile we found it to behave similarly to oxygen. A maximum rate of the cyanation is obtained at low N_2O concentrations and the rate decreases with increasing N_2O concentration. The quantum yields are somewhat lower than when oxygen is used.

Experimental

The rate of a photochemical reaction depending on the square of the intensity of the absorbed radiation in a thin layer of reaction mixture can be written[6] as in equation (17) where w_o

$$w_R = \alpha w_o^2 = \alpha(I\varepsilon c \ln 10)^2 \qquad (17)$$

is the rate of the excitation, α is a parameter proportional to the quantum yield, I is the light intensity, ε is the molar absorption coefficient, and c is the concentration of the absorber. The average rate of the reaction, $\bar{w}_R$, is given by equation (18) where I_o and I_t are the incident and the transmitted light intensities, d is the optical path length of the reaction cell and [ArH] = c. The quantum yield φ is obtained from equation (19). Here I_a is the absorbed light intensity.

$$\bar{w}_R = 1.15\,\alpha\left(\frac{I_o - I_t}{d}\right)(I_o + I_t)\varepsilon[\mathrm{ArH}] \qquad (18)$$

$$\varphi = \bar{w}_R/I_a = 1.15\,\alpha(I_o + I_t)\varepsilon[\mathrm{ArH}] \qquad (19)$$

The experimental methods used in the photocyanation of phenanthrene have been described[6] earlier. Oxygen (150 Torr) was added to the sample in a reaction vessel from which air had been removed by repeated freezing and pumping. Samples from the reaction mixture were taken through a septum with an injection syringe and analysed by g.l.c. The reaction was followed up to a product concentration of *ca.* 2% (1×10^{-4} mol dm^{-3}) of the initial reactant concentration.

The stock solutions of potassium superoxide and sodium peroxide were prepared by dissolving $\mathrm{KO_2}$ or $\mathrm{Na_2O_2}$ (2.0×10^{-4} mol) and 18-crown-6 ether (2.0×10^{-4} and 4.0×10^{-4} mol, respectively), in dry oxygen-free acetonitrile (25 ml). The undissolved complex was removed from the solvent by centrifugation. The concentration of superoxide radical was determined photometrically.[13] The absorption remained unchanged for several weeks after the preparation of the solutions, indicating the absence of water.

9-Cyanophenanthrene absorbs more strongly (ε 1 430 mol^{-1} m^2 at 310 nm) than phenanthrene (ε 16.5 mol^{-1} m^2 at 313 nm) at the irradiation wavelength 313 ± 3 nm. An average molar absorption coefficient for cyanophenanthrene, $\varepsilon_{\mathrm{CPh}}$, was determined between the wavelengths 310 and 316 nm. The value obtained was 1 030 mol^{-1} m^2.

The absorbance of phenanthrene and cyanophenanthrene in the reaction mixture, $\bar{D}$, and the light intensity absorbed by phenanthrene, I_a, for the time interval from i to j, were calculated by equations (20) and (21) where D_{Ph} is the absorbance of phenanthrene, d is the optical path (1.0 cm) of the reaction cell, c_i and c_j are the concentrations of cyanophenanthrene at times i and j, and I_o is the incident light intensity.

$$\bar{D} = \mathrm{D_{Ph}} + \varepsilon_{\mathrm{CPh}} d(c_i + c_j)/2 \qquad (20)$$

$$I_A = D_{\mathrm{Ph}} I_o (1 - 10^{-\bar{D}})/\bar{D} \qquad (21)$$

Nitrous oxide was added to the sample in the reaction vessel at 25.0 °C. The solubility of nitrous oxide is 8.7×10^{-3} mol dm^{-3} when its partial pressure is 60 Torr. The time of irradiation was selected to yield *ca.* 0.5% product.

Acknowledgements

This work was supported by the Finnish Cultural Foundation. I thank Mr. E. Pulkkinen for the measurements where nitrous oxide was used as oxidizing agent and Mr. J. Niiranen for the measurements where phenanthrene was photocyanated in aqueous acetonitrile.

References

1 K. Mizuno, C. Pac, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 1975, 553.

2 M. Yasuda, C. Pac, and H. Sakurai, *J. Chem. Soc., Perkin Trans. 1*, 1981, 746.

3 N. Bunce, J. Bergsma, and J. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 1981, 713.

4 J. den Heijer, O. Shadid, J. Cornelisse, and E. Havinga, *Tetrahedron*, 1977, **33**, 779.

5 J. Cornelisse, G. Lodder, and E. Havinga, *Rev. Chem. Intermed.*, 1979, **2**(**3**), 231.

6 H. Lemmetyinen, J. Koskikallio, M. Lindblad, and M. Kuzmin, *Acta Chem. Scand., Ser. A*, 1982, **36**, 391.

7 H. Lemmetyinen, J. Koskikallio, V. Ivanov, and M. Kuzmin, *J. Photochem.*, 1983, **22**, 115.

8 J. Langelaar, R. Rettschnick, and G. Hoijtink, *J. Chem. Phys.*, 1971, **54**, 1.

9 J. Birks, ' Photophysics of Aromatic Molecules,' Wiley, London, 1970, p. 637.

10 T. Azumi and S. McGlynn, *J. Chem. Phys.*, 1964, 3131.

11 G. Briegleb, H. Schuster, and W. Herre, *Chem. Phys. Lett.*, 1971, **4**, 53.

13 K. Zachariasse, R. Busse, U. Schrader, and W. Kühnle, *Chem. Phys. Lett.*, 1982, **89**, 303.

12 T. Ozawa, A. Hanaki, and H. Yamamoto, *FEBS Lett.*, 1977, **74**, 99.

Received 12*th November* 1982; *Paper* 2/1898