

A Mechanism Involving Two Photoinduced Transients for the Photocyanation of Phenanthrene in the Presence of Oxygen and Potassium Cyanide-18-crown-6 Ether in Anhydrous Acetonitrile

H. LEMMETYINEN,^a J. KOSKIKALLIO,^a M. LINDBLAD^a and M. G. KUZMIN^b

^a Physical Chemistry Laboratory, University of Helsinki, SF-00170 Helsinki 17, Finland and ^b Laboratory of Photochemistry, Faculty of Chemistry, Lomonosov Moscow State University, 11234 Moscow, USSR

The dependence of the quantum yield, of the photocyanation of phenanthrene by potassium cyanide-18-crown ether, on the exciting light intensity, and the concentrations of the reagents was studied in the presence of oxygen in anhydrous acetonitrile. The proposed mechanism involves two transients. The first transient is formed by interaction of triplet phenanthrene with a cyanide anion and transformed into the second transient by second order reaction. The latter is oxidized by molecular oxygen into the reaction product 9-cyanophenanthrene. The rate constants of the reactions are estimated from the concentration dependences.

Photochemically-induced nucleophilic reactions, among them the cyanation of aromatic hydrocarbons, have been studied extensively during the last decade.¹

Nilsson² and Lok and Havinga³ found that the methoxy group activates nucleophilic hydrogen atom photosubstitution of an aromatic compound. Mizuno⁴ reported photocyanation of phenanthrene and naphthalene in the presence of 1,4-dicyanobenzene.

Photocyanation is usually carried out in a mixture of organic solvent and a small amount of water in which cyanide salts are dissolved. Beugelmans⁵ found that the photosubstitution is more efficient in aprotic organic solvents than in protic solvents when the reaction takes place in the presence of cyclic polyether, 18-crown-6. Recently it has been shown⁶ that photocyanation of anisole is also enhanced when crown ether is replaced by poly-

ethylene glycol. Polyethylene glycol and crown ether both activate anions in non-polar aprotic solvents by increasing the ion-dissociation. On the other hand, anions are strongly solvated by protic solvents⁷ and by small amounts of water, which retards the nucleophilic reactivity.

Den Heijer⁸ showed that the presence of an oxidizing agent is essential for hydrogen atom substitution reaction. Oxygen, nitrous oxide and ammonium persulfate can be used for this purpose.

Cornelisse¹ suggested that photoionization of the hydrocarbon is the primary step in nucleophilic photosubstitution of an aromatic hydrocarbon activated by an electron donating group. The radical cation formed then reacts with a nucleophile to form the product. Bunnett and his group⁹ have shown that the primary step in many nucleophilic photosubstitutions is formation of a radical anion, which then reacts with a nucleophile.

We have investigated photocyanation of phenanthrene in anhydrous acetonitrile in the presence of potassium cyanide-18-crown-6 ether and oxygen at 25 °C. Variations in the intensity of the exciting radiation and the concentrations of cyanide anion and oxygen are found to influence the rate of product formation in a complex way. A simplified mechanism is proposed which explains the experimental results.

EXPERIMENTAL

Materials. Acetonitrile was purified by stirring it with calcium hydride, decanting, distilling with

phosphorous pentoxide, refluxing with calcium hydride and distilling. It was protected against moisture and stored under nitrogen. Phenanthrene was recrystallized several times. Potassium cyanide-18-crown-6 complex was prepared by dissolving equivalent amounts of 18-crown-6 ether and KCN in dry methanol, refluxing the solution 30 min and removing the solvent at reduced pressure. The resulting complex was dissolved under nitrogen in dry acetonitrile by stirring the solution in the dark. The undissolved complex was removed from the solvent by centrifugation. The concentration of cyanide anion was determined by titration.⁷ By this method a 4.2×10^{-2} mol dm⁻³ solution of the cyanide was obtained.

Methods. The reaction mixture was prepared in a 3.0 cm³ quartz cuvette, with optical path of 1.0 cm, from known amounts of phenanthrene and cyanide solutions. Air was removed from the solution by repeated freezing and pumping to about 5×10^{-6} Torr. Oxygen of a known pressure (10–150 Torr) was added to the reaction vessel containing the frozen reaction solution. The gas volume in the reaction vessel was 12 cm³. Equilibrium between the gas and liquid phases was established by stirring the solution in the dark. The solubility of oxygen in the reaction mixture (5.0×10^{-3} mol dm⁻³ of both KCN-crown ether complex and phenanthrene) was determined separately by measuring the drop in pressure when oxygen was dissolved in 100 cm³ of reaction mixture. The solubility of oxygen is $(1.2 \pm 0.1) \times 10^{-3}$ mol dm⁻³ at 25 °C when the partial pressure of oxygen is 150 Torr, and this corresponds to an oxygen concentration of 8×10^{-5} mol dm⁻³ at an oxygen pressure of 10 Torr.

The intensities of the exciting radiation and

quantum yields of photosubstitution were measured with a potassium ferrioxalate actinometer, using the method of Calvert and Pitts.¹⁰ As light sources we used a 100 W high pressure Hg lamp (254 nm and 313 nm) from Illumination Ind. Inc. and a 450 W Xe lamp (270 nm, 330 nm and 346 nm) from Osram GmbH in combination with an MDR-2 High Intensity Monochromator. The linear dispersion of the monochromator was 6 nm. The intensities of the exciting radiation varied, depending on the wavelength, between $(1.0$ and $17.0) \times 10^{-8}$ einsteins dm⁻² s⁻¹. The intensities were measured during each experiment. The yield of the product, 9-cyanophenanthrene, was determined by liquid chromatography with a Perkin-Elmer Series 1 chromatograph and Model LC-15 UV-detector attached to a HC-ODS Sil-x-1 column. A 60% CH₃OH-water eluent was used. As internal standard we used toluene, which was added to the reaction mixture after irradiation. The time of irradiation was selected to yield about 1–5% of product. Two unidentified products, less than 10% the amount of the main product, 9-cyanophenanthrene, were also obtained. The ratio of the three products was constant in all experiments.

RESULTS AND DISCUSSION

Our investigations showed that the rate of nucleophilic photosubstitution of phenanthrene to 9-cyanophenanthrene in dry acetonitrile depends on the concentrations of both cyanide anion and oxygen (Tables 1 and 2) and is proportional to the square of the intensity of the absorbed radiation

Table 1. Dependence of the rate of photocyanation of phenanthrene on potassium cyanide concentration at phenanthrene concentration 5.0×10^{-5} mol dm⁻³ in acetonitrile at 25 °C.

$(\text{CN}^-) \times 10^3$ mol dm ⁻³	Rate ^a $\times 10^{11}$ mol dm ⁻³ s ⁻¹	$\alpha^b \times 10^{-2}$ mol ⁻¹ dm ³ s	$\sqrt{(\text{O}_2)(\text{CN}^-)^2/\alpha} \times 10^8$ mol ² dm ⁻⁶ s ^{-1/2}
0.1	5.9	1.70	6.9
0.2	13.4	3.84	9.2
0.3	14.9	4.27	13.1
0.4	14.4	4.12	17.7
1.0	23.8	6.54	35.0
2.0	31.0	8.92	59.8
3.0	28.4	8.15	94.1
4.0	28.8	8.29	124.2

^a Measured rate. ^b Calculated using eqn. (3). $(\text{O}_2) = 8 \times 10^{-5}$ mol dm⁻³, $\lambda_{\text{ex}} = 254$ nm, $I_0 = 4.18 \times 10^{-8}$ ein dm⁻² s⁻¹, $I_a = 4.06 \times 10^{-7}$ ein dm⁻³ s⁻¹, $I_t = 0.075 \times 10^{-8}$ ein dm⁻² s⁻¹, $\log(I_0/I_t) = 1.74$.

Table 2. Dependence of the rate of photocyanation of phenanthrene on oxygen concentration at phenanthrene concentration $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ in acetonitrile at 25 °C.

$(\text{O}_2) \times 10^3$ mol dm ⁻³	Rate ^a $\times 10^{11}$ mol dm ⁻³ s ⁻¹	$\alpha^b \times 10^{-2}$ mol ⁻¹ dm ³ s	$\sqrt{(\text{O}_2)(\text{CN}^-)^2/\alpha} \times 10^8$ mol ² dm ⁻⁶ s ^{-1/2}
0.01	4.0	1.13	21.4
0.02	18.7	5.37	17.0
0.08	20.8	5.97	29.2
0.16	21.3	6.12	40.9
0.32	13.9	3.99	71.8
0.75	8.3	2.36	142.4
1.20	6.4	1.85	203.8

^a Measured rate. ^b Calculated using eqn. (3). $(\text{CN}^-) = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda_{\text{ex}} = 254 \text{ nm}$, $I_0 = 4.18 \times 10^{-8} \text{ ein dm}^{-2} \text{ s}^{-1}$, $I_a = 4.06 \times 10^{-7} \text{ ein dm}^{-3} \text{ s}^{-1}$, $I_i = 0.075 \times 10^{-8} \text{ ein dm}^{-2} \text{ s}^{-1}$, $\log(I_0/I_i) = 1.74$.

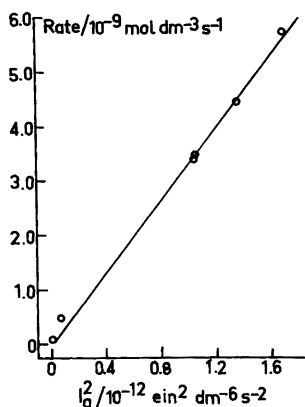


Fig. 1. Dependence of the rate of photocyanation on the square of the intensity of the absorbed radiation at phenanthrene concentration $5.0 \times 10^{-3} \text{ mol dm}^{-3}$.

(Table 3 and Fig. 1). Two transients were observed¹¹ by flash photolysis. One of the transients decayed by second order kinetics in the absence of oxygen, and the optical density of the absorption of the another transient was proportional to the square of the intensity of the exciting light.

Eqn. (1) gives the dependence of the total reaction rate, w_R , on the square of the absorbed light intensity,

$$w_R = \alpha w_o^2 = \alpha(I\epsilon c)^2, \quad (1)$$

where α is a parameter similar to quantum yield and a function of the concentrations of cyanide anion and oxygen, w_o is the rate of the excitation, ϵ is the molar absorption coefficient, c is the concentration of the absorber and I is the light intensity at any point in the system. Along the pathway the light intensity decreases exponentially, $I = I_0 \exp(-\epsilon c l \ln 10)$, where I_0 is the incident light intensity

Table 3. Dependence of the rate of photocyanation of phenanthrene on the exciting radiation at phenanthrene concentration $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ in acetonitrile at 25 °C.

Rate ^a $\times 10^9$ mol dm ⁻³ s ⁻¹	$I_a \times 10^7$ ein dm ⁻³ s ⁻¹	$I_a^2 \times 10^{12}$ ein ² dm ⁻⁶ s ⁻²	λ_{ex} nm
0.10	0.6	0.004	313 ^b
0.53	2.7	0.073	313 ^c
3.47	10.2	1.04	313
3.47	10.2	1.04	330
4.47	11.6	1.35	313
5.73	13.0	1.68	346

$(\text{CN}^-) = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $(\text{O}_2) = 8 \times 10^{-5} \text{ mol dm}^{-3}$. ^a Measured rate. ^b Pyrex filter 2.0 mm. ^c Pyrex filter 1.0 mm.

and l is the distance from the front of the reaction cell. Thus the rate of the reaction decreases along the reaction cell. The average rate of the reaction is given in eqn. (2), where d is the optical path of the

$$\begin{aligned}\bar{w}_R &= \alpha \frac{(I_0 \varepsilon c \ln 10)^2}{d} \int_0^d \exp(-2 \varepsilon c l \ln 10) dl \\ &= \alpha \frac{I_0^2 \ln 10}{2 d^2} D (1 - 10^{-2D}) \\ &= 1.15 \frac{\alpha}{d^2} (I_0 - I_t)(I_0 + I_t) D,\end{aligned}\quad (2)$$

reaction cell, $D = \varepsilon c d$ is the optical density of the system and I_t is the transmitted light intensity. Eqn. (2) can be rewritten to eqn. (3).

$$\frac{0.87 \bar{w}_R d^2}{(I_0^2 - I_t^2)} = \alpha D \quad (3)$$

The linear dependence of the reaction rate on the optical density according to equation (2) explains the observed dependence of the rate on phenanthrene concentration (Fig. 2, Table 4) and it confirms the dependence of the substitution reaction on the square of the absorbed light intensity.

The squared dependence of the reaction rate on the absorbed light intensity indicates either that the formation of the reaction intermediate is a two-photon process or that the product is formed in the reaction between two transients, both formed by monophotonic processes. The flash photolysis experiments support the latter mechanism.

We propose a mechanism (Scheme 1) involving the formation of a transient X in the primary step,

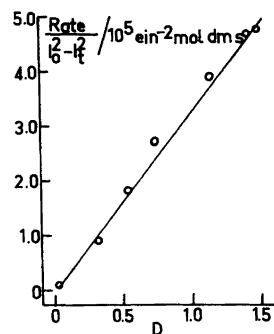
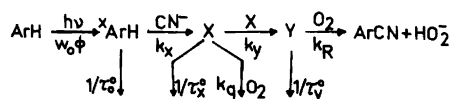


Fig. 2. Dependence of the rate of photocyanation on the optical density.



Scheme 1.

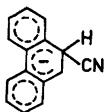
followed by its transformation into another transient Y by a second order process. The transient Y reacts with oxygen and yields the final reaction product 9-cyanophenanthrene.

The fluorescence of phenanthrene is not quenched by cyanide anion at the concentrations used in our experiments ($< 10^{-2}$ mol dm $^{-3}$). Obviously the triplet state of phenanthrene reacts with cyanide anion. The transient X is probably a triplet exciplex or a radical anion formed from phenanthrene and a cyanide radical. Its nature will

Table 4. Dependence of the rate of photocyanation of phenanthrene on the optical density in acetonitrile at 25 °C.

(ArH) ^a × 10 ³ mol dm ⁻³	Rate ^b × 10 ⁹ mol dm ⁻³ s ⁻¹	I ₀ × 10 ⁸ ein dm ⁻² s ⁻¹	I _t × 10 ⁸ ein dm ⁻² s ⁻¹	I _a × 10 ⁷ ein dm ⁻³ s ⁻¹	D
1.0	0.03	13.5	12.3	1.2	0.04
2.0	1.29	13.6	6.5	7.1	0.32
3.3	2.78	13.5	3.9	9.6	0.54
5.0	4.52	13.5	2.5	11.0	0.73
10.0	8.76	15.0	1.1	13.9	1.14
16.7	10.48	15.0	0.6	14.4	1.40
20.0	10.65	15.0	0.5	14.5	1.48

^a Concentration of phenanthrene. ^b Measured rate. (CN⁻) = 2.5 × 10⁻³ mol dm⁻³, (O₂) = 0.11 × 10⁻³ mol dm⁻³, λ_{ex} = 346 nm.



Scheme 2.

be discussed in greater detail in the next paper.¹¹ The transient Y is assumed to be a σ -complex (Scheme 2). This σ -complex can be formed due to a recombination of the phenanthrene radical anion and the cyanide radical or through an interaction of two triplet exciplexes. Oxidation of the σ -complex by molecular oxygen yields 9-cyanophenanthrene and the peroxide anion HO_2^- .

The rates of the formation of transients X and Y are given in eqn. (4), where ϕ is the quantum yield for

$$w_x = w_o k_x \phi (\text{CN}^-) \tau_o \quad (4)$$

$$w_y = k_y w_x^2 \tau_x^2$$

the formation of reactive excited state of phenanthrene, τ_o is its lifetime and τ_x is the mean real lifetime of the transient X. w_x and w_y are the rates of the formation of transients X and Y, and k_x and k_y are the rate constants of these reactions. The local rate of the final product formation is given by eqn. (5). Here τ_y is the real lifetime of the transient Y and

$$w_R = k_R (\text{O}_2) (Y) = k_R (\text{O}_2) w_y \tau_y \quad (5)$$

$$= k_R k_y \tau_y (\text{O}_2) [w_o \phi \tau_o \tau_x k_x (\text{CN}^-)]^2$$

k_R is the reaction rate constant. The real lifetime of the excited phenanthrene, in the presence of cyanide anion, is determined by the Stern-Volmer relation in eqn. (6), where $K_x = k_x \tau_o$. If the real lifetime of the

$$\tau_o = \tau_o^o / [1 + K_x (\text{CN}^-)], \quad (6)$$

transient X is determined mainly by first order processes (the unimolecular decay and the quenching by oxygen) then $k_y(X) \ll [1/\tau_x^o + k_q(\text{O}_2)]$, where k_q is the quenching rate constant of X by oxygen. Furthermore, if the rate of oxidation of the σ -complex is smaller than the rate of its decomposition into phenanthrene and cyanide anion, eqn. (7), then we have eqns. (8) and (9), where $K_q = k_q \tau_x^o$.

$$k_R (\text{O}_2) \ll 1/\tau_y^o, \quad (7)$$

$$\tau_x \approx \tau_x^o / [1 + K_q (\text{O}_2)], \quad (8)$$

$$\tau_y \approx \tau_y^o \quad (9)$$

Thus eqn. (5) can be written in the form (10).

Applying eqn. (1) we obtain eqns. (11) or (12).

$$w_o (\text{CN}^-) \sqrt{\frac{(\text{O}_2)}{w_R}} = \frac{[1 + K_x (\text{CN}^-)] [1 + K_q (\text{O}_2)]}{\phi \tau_o^o k_x \tau_x^o (k_y \tau_y^o k_R)^{1/2}} \quad (10)$$

$$\sqrt{\frac{(\text{CN}^-)^2 (\text{O}_2)}{\alpha}} = (\phi^2 k_R k_x^2 k_y \tau_x^{o2} \tau_o^{o2} \tau_y^o)^{-1/2} [1 + K_x (\text{CN}^-)] [1 + K_q (\text{O}_2)] \quad (11)$$

$$\sqrt{\frac{(\text{CN}^-)^2 (\text{O}_2)}{\alpha}} = a [1 + K_x (\text{CN}^-)] = b [1 + K_q (\text{O}_2)] \quad (12)$$

Thus the inverse of the square root of the rate can be presented as a function of substrates (CN^- and O_2). Applying eqn. (12) to the experimental results in Tables 1 and 2 we get straight lines for the functions of both cyanide anion and oxygen concentrations at phenanthrene concentration $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ (Figs. 3 and 4).

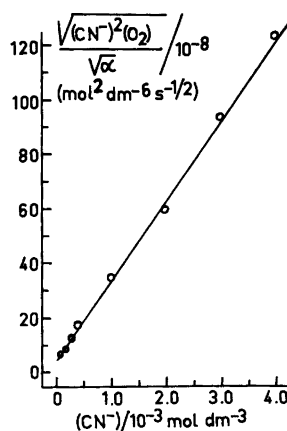


Fig. 3. Dependence of the rate of photocyanation on cyanide concentration according to eqn. (12) at phenanthrene concentration $5.0 \times 10^{-5} \text{ mol dm}^{-3}$.

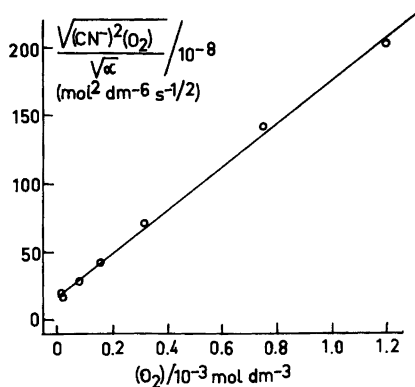


Fig. 4. Dependence of the rate of photocyanation on oxygen concentration according to eqn. (12) at phenanthrene concentration 5.0×10^{-5} mol dm $^{-3}$.

The values obtained for the coefficients are given in Table 5. The values of $(\phi^2 \tau_o^{\circ 2} k_x^2 \tau_x^{\circ 2} k_y \tau_y^{\circ} k_R)$ obtained from the dependence of the quantum yield on both cyanide anion and oxygen concentrations are quite close to each other. This confirms the proposed kinetic scheme. Similar linear relationships were obtained at phenanthrene concentration 5.0×10^{-3} mol dm $^{-3}$ (Tables 6 and 7) with some different values of the coefficients (Table 5). This is probably due to the observed increase of the rate of the cyanation reaction when some reaction products are formed or to some more complex mechanism at higher concentration of phenanthrene.

Also at cyanide concentration higher than 10×10^{-3} mol dm $^{-3}$, the dependence on the cyanide concentration begins to deviate from linearity (Table 6). This may be due to an additional

Table 5. Values of the coefficients in eqns. (11) and (12) obtained at phenanthrene concentrations 5.0×10^{-5} mol dm $^{-3}$ and 5.0×10^{-3} mol dm $^{-3}$.^a

(ArH)	mol dm $^{-3}$	5.0×10^{-5}	5.0×10^{-3}
<i>a</i>	mol 2 dm $^{-6}$ s $^{-1/2}$	4.0×10^{-8}	9.5×10^{-8}
K_x	mol $^{-1}$ dm 3	7.4×10^3	1.6×10^3
$(\phi \tau_o^{\circ} k_x \tau_x^{\circ})^2 k_y \tau_y^{\circ} k_R$	mol $^{-4}$ dm 12 s	1.8×10^{15}	0.5×10^{15}
<i>b</i>	mol 2 dm $^{-6}$ s $^{-1/2}$	1.8×10^{-7}	4.0×10^{-7}
K_a	mol $^{-1}$ dm 3	9.0×10^3	13.0×10^3
$(\phi \tau_o^{\circ} k_x \tau_x^{\circ})^2 k_y \tau_y^{\circ} k_R$	mol $^{-4}$ dm 12 s	1.5×10^{15}	0.5×10^{15}

^a At phenanthrene concentration 5.0×10^{-5} mol dm $^{-3}$ the concentrations of oxygen and cyanide anion were 8×10^{-5} mol dm $^{-3}$ and 8.0×10^{-4} mol dm $^{-3}$ and at phenanthrene concentration 5.0×10^{-3} mol dm $^{-3}$ they were 8×10^{-5} mol dm $^{-3}$ and 5.0×10^{-3} mol dm $^{-3}$, respectively.

Table 6. Dependence of the rate of photocyanation of phenanthrene on potassium cyanide concentration at phenanthrene concentration 5.0×10^{-3} mol dm $^{-3}$ in acetonitrile at 25°C.

$(CN^-) \times 10^3$ mol dm $^{-3}$	Rate ^a $\times 10^9$ mol dm $^{-3}$ s $^{-1}$	$\alpha^b \times 10^{-2}$ mol $^{-1}$ dm 3 s	$\sqrt{(O_2)(CN^-)^2/\alpha} \times 10^8$ mol 2 dm $^{-6}$ s $^{-1/2}$
0.5	1.90	6.9	17
1.0	4.37	15.9	22
2.0	4.90	17.9	42
2.0	5.03	18.4	42
3.5	6.88	25.1	63
5.0	7.50	27.4	86
7.1	7.94	28.9	118
14.1	6.75	24.6	254
21.4	5.29	19.3	436

^a Measured rate. ^b Calculated using eqn. (3). $(O_2) = 8 \times 10^{-5}$ mol dm $^{-3}$, $\lambda_{ex} = 313$ nm, $I_o = 12.52 \times 10^{-8}$ ein dm $^{-2}$ s $^{-1}$, $I_a = 12.14 \times 10^{-7}$ ein dm $^{-3}$ s $^{-1}$, $I_t = 0.37 \times 10^{-8}$ ein dm $^{-2}$ s $^{-1}$, $\log(I_o/I_t) = 1.52$.

Table 7. Dependence of the rate of photocyanation of phenanthrene on oxygen concentration at phenanthrene concentration $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ in acetonitrile at 25°C .

$(\text{O}_2) \times 10^3$ mol dm^{-3}	Rate ^a $\times 10^9$ $\text{mol dm}^{-3} \text{ s}^{-1}$	$\alpha^b \times 10^{-2}$ $\text{mol}^{-1} \text{ dm}^{-3} \text{ s}$	$\sqrt{(\text{O}_2)(\text{CN}^-)^2/\alpha} \times 10^8$ $\text{mol}^2 \text{ dm}^{-6} \text{ s}^{-1/2}$
0.08	5.71	26.5	86
0.16	4.94	23.1	131
0.25	4.13	19.3	180
0.36	2.72	12.6	266
0.56	2.02	9.4	385
0.80	1.11	5.2	688
1.60	0.60	2.8	1195

^a Measured rate. ^b Calculated using eqn. (3). $(\text{CN}^-) = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda_{\text{ex}} = 313 \text{ nm}$, $I_0 = 10.88 \times 10^{-8} \text{ ein dm}^{-2} \text{ s}^{-1}$, $I_a = 10.60 \times 10^{-7} \text{ ein dm}^{-3} \text{ s}^{-1}$, $I_t = 0.28 \times 10^{-8} \text{ ein dm}^{-2} \text{ s}^{-1}$, $\log(I_0/I_t) = 1.58$.

quenching of some excited state by the cyanide anion.

It is possible to evaluate $(\phi\tau_x^0)^2 k_y$ from the value obtained for $(\phi\tau_x^0 k_x \tau_x^0)^2 k_y \tau_y^0 k_R = 1.7 \times 10^{15} \text{ mol}^{-4} \text{ dm}^{12} \text{ s}$. Using the approximation (7) and the obtained value of $K_x = k_x \tau_x^0$ (Table 5)

$$\phi^2 \tau_x^0 k_y = \frac{1.7 \times 10^{15} \text{ mol}^{-4} \text{ dm}^{12} \text{ s}}{(k_x \tau_x^0)^2 k_R \tau_y^0}$$

$$> 3.1 \times 10^7 (\text{O}_2) \text{ mol}^{-2} \text{ dm}^6 \text{ s}.$$

Because $k_y \leq 1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $(\text{O}_2) > 0.08 \times 10^{-3} \text{ mol dm}^{-3}$ and $\phi \leq 1$, $\tau_x^0 > 5 \times 10^{-4} \text{ s}$. Furthermore, because $K_a = k_a \tau_x^0 = 9.0 = 10^3 \text{ mol}^{-1} \text{ dm}^3$, $k_a < 2 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Acknowledgement. This work has been done within the framework of the scientific collaboration between the University of Helsinki and Lomonosov Moscow State University.

REFERENCES

- Cornelisse, J., Lodder, G. and Havinga, E. *Rev. Chem. Intermed.* 2 (3) (1979) 231.
- Nilsson, S. *Acta Chem. Scand.* 27 (1973) 329.
- Lok, C. M. and Havinga, E. *Proc. K. Ned. Akad. Wet. B* 77 (1974) 15.
- Mizuno, K., Pac, C. and Sakurai, H. *J. Chem. Soc. Chem. Commun.* (1975) 553.
- Beugelmans, R., Le Goff, M.-T., Pusset, J. and Roussi, G. *J. Chem. Soc. Chem. Commun.* (1976) 377.
- Suzuki, N., Shimazu, K., Ito, T. and Izawa, Y. *J. Chem. Soc. Chem. Commun.* (1980) 1253.

- Lemmettyinen, H., Lehtinen, L. and Koskikallio, J. *Finn. Chem. Lett.* (1979) 72.
- Den Heijer, J., Shadid, O. B., Cornelisse, J. and Havinga, E. *Tetrahedron* 33 (1977) 779.
- Kim, J. K. and Bunnett, J. F. *J. Am. Chem. Soc.* 92 (1970) 7463.
- Calvert, J. G. and Pitts, J. N., Jr. *Photochemistry*, Wiley, New York 1966, p. 780.
- Lemmettyinen, H., Ivanov, V. L., Kuzmin, M. G. and Koskikallio, J. *To be published.*

Received August 26, 1981.