

Photolysis of Pyrene and Chloropyrene in the Presence of Triethylamine in Acetonitrile: Dehalogenation Assisted by Potassium Cyanide

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Kinetics and transient absorption spectra of pyrene- and 1-chloropyrene-triethylamine (TEA) systems, in the presence and absence of cyanide ions, have been studied by a nanosecond time-resolved laser flash photolysis method in dry acetonitrile at room temperature. Schemes for chloropyrene-triethylamine- and chloropyrene-triethylamine-CN⁻ systems have been developed and individual rate constants determined either by direct measurements or by use of computer analysis of the experimental decay curves. The reaction results in the dehalogenation of chloropyrene to yield pyrene as the reaction product, but high quantum yields (0.2–0.4) are obtained only in the presence of cyanide ions. The hydrogen atoms which replace the chlorines originate from the solvent. This was determined by deuterium labelling. The reaction proceeds *via* an exciplex to radical ions, which recombine to form ion pairs. Cyanide ions attract chlorohydropyrene radicals, which are mainly formed in the reaction between chloropyrene anion radicals and the solvent. The cyanohydropyrenyl radicals formed are in equilibrium with the relatively stable cyanopyrene anion radicals and, by cleavage of the cyano radicals, yield the reaction product.

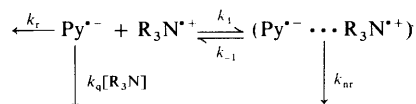
The formation of radical anions is an important step in many reactions of aromatic compounds. The interaction of electronically excited arenes with aliphatic amines results in the formation of short-lived exciplexes^{1,2} followed by an electron transfer from the amine to the arene and yields, in many cases, a radical ion pair.^{3,4} Aryl compounds often yield products in which a hydrogen, cyano or methoxy group is replaced by an alkylamino group^{3,5–11}. Haloaromatics are dehalogenated and yield substituted aryl compounds.^{12,13} Ohashi *et al.*¹⁴ have reported the photoreduction of chlorobiphenyl by amines which proceeds *via* a charge-transfer complex formed from a singlet excited state. Bunce *et al.*^{15,16} have studied halogenated biphenyl, benzene and naphthalene and presented strong arguments for a triplet state reaction *via* a charge-transfer complex.

Various methods have been used to activate the substrate by the injection of an electron producing the anion radical. This can be achieved either photochemically,^{17,18} or electrochemically,^{19,20} and by alkali metals dissolved in liquid ammonia.¹⁷ Anion radicals are often produced in liquid ammonia either electrochemically²⁰ or photochemically,^{18,21–23} but, particularly in cases when photochemical reactions are being investigated, other solvents such as tetrahydrofuran, dimethoxyethane, benzene,²¹ dimethyl sulfoxide,²⁴ acetonitrile, methanol and cyclohexane,²⁵ have been used. In photochemically induced reactions anion radicals are often formed by electron transfer from a nucleophile to an excited arene.^{18,22,23} This reaction is usually carried out in liquid ammonia. It is also possible for an excited arene to accept an electron from a specific electron donor,^{25,26} in this case the role of the nucleophile becomes important only in the later stages of the reaction path. These types of reaction have not been studied in any great detail.

Mataga has made intensive studies of different types of photoinduced electron transfer reaction in polar solutions.²⁷ According to his results some aromatic amines may act as electron donors when reacting with arenes in polar solvents. The formation of several kinds of ion pair and exciplex is possible. In the case of the aliphatic amine, triethylamine (TEA), the geminate ion pairs undergo dissociation into free ions without back electron-transfer deactivation in polar solutions

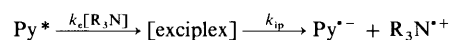
such as acetonitrile, acetone and pyridine.²⁷ The efficiency of free-ion formation is *ca.* 0.5 which means that the efficiency of geminate ion pair formation is also 0.5. This difference as compared with aromatic amines may be due to the planar structure of the cation radicals of aliphatic amines.

Recently Mataga *et al.* described²⁶ pyrene-trialkylamine systems in polar solvents, where long-lived ion pairs are formed *via* the recombination of free ions. The observations were made using time-resolved transient absorption and conductivity measurements on a nanosecond time scale. The proposed mechanism for the ion activation is shown in Scheme 1.



Scheme 1

In this scheme the free ions, $\text{Py}^{\cdot-}$ and $\text{R}_3\text{N}^{\cdot+}$, are formed by a fast picosecond process from an exciplex of pyrene and amine (Scheme 2).



Scheme 2

Reaction k_r does not take place in acetonitrile and reaction k_{nr} is most important for 1-hydroxyphenyl formation. The pyrene anion radical itself reacts with amines by reaction k_q . This scheme might be very important for the elucidation of chemical reaction mechanisms *via* exciplex systems.²⁶

We have studied carefully the photochemistry of pyrene- and chloropyrene-TEA systems, in the absence and presence of a strong nucleophile (cyanide ion) in acetonitrile by laser flash photolysis. The study was based on the following hypothesis.

(1) If the dissociation of the exciplex takes place on a picosecond time scale, then the rate-determining step for the formation of free ions is the reaction between excited pyrene and TEA, and this can be determined directly by measuring the fluorescence quenching of pyrene and the rate of the formation of pyrene anion radicals.

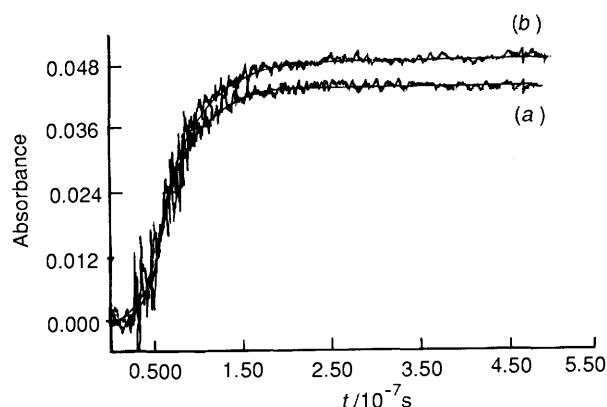


Fig. 1 Formation of the anion radicals of chloropyrene at 493 nm in the presence of [TEA], (a) $3.7 \times 10^{-3} \text{ mol dm}^{-3}$ and (b) $4.5 \times 10^{-3} \text{ mol dm}^{-3}$. The calculated first-order formation rate constants are (a) $2.1 \times 10^7 \text{ s}^{-1}$ and (b) $2.5 \times 10^7 \text{ s}^{-1}$.

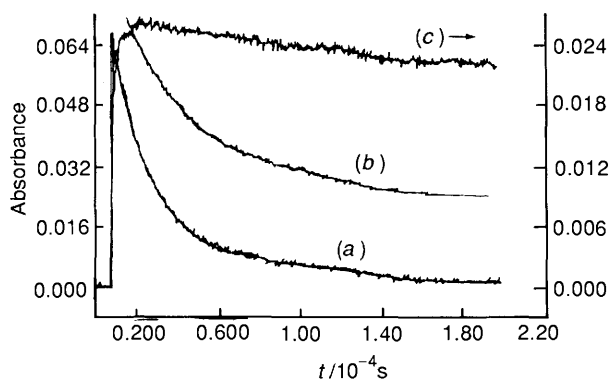


Fig. 2 Time dependences of the decays of chloropyrene anion radicals at TEA concentrations of $8.3 \times 10^{-3} \text{ mol dm}^{-3}$ (a) in the absence of cyanide ions at 493 nm, (b) at a cyanide anion concentration of $4.8 \times 10^{-3} \text{ mol dm}^{-3}$ at 493 nm and (c) at a cyanide anion concentration of $4.8 \times 10^{-3} \text{ mol dm}^{-3}$ at 508 nm.

(2) If the main reaction of the free ions is recombination to an ion pair ($\text{Py}^{\cdot-} \cdots \text{R}_3\text{N}^{\cdot+}$), then the decay of pyrene anion radical should, at low TEA concentrations, follow second-order kinetics.

(3) At high TEA concentrations a first-order term can be attached to the reaction between the anion radical and TEA.

(4) If, in the case of chloropyrene, the anion radical is cleaved to an aryl radical, which is typical of *e.g.* the $\text{S}_{\text{RN}}1$ mechanism,²⁸ a first-order reaction should also be observed at low TEA concentrations.

(5) In the presence of cyanide ions the formation of a new transient, anion radical of cyanopyrene, should be observed.

(6) An electron transfer from the anion radical of cyanopyrene to the ground state chloropyrene may initiate a chain reaction, where either cyanopyrene, pyrene, dihydro-pyrene or aminopyrene would be the main reaction product produced in high quantum yield.

Results and Discussion

Qualitative Analysis of Transient Spectra and Decay Curves.—The decay curves were measured at wavelengths of 400–430 nm and 480–510 nm. The time-resolved transient absorption spectrum of chloropyrene was measured at wavelengths between 360 and 520 nm.

(i) *Pyrene fluorescence.* The fluorescence lifetime at 399 nm in acetonitrile was determined to be 303 ns. A Stern–Volmer plot gave a value of $550 \text{ dm}^3 \text{ mol}^{-1}$ for the quenching by TEA. Thus the quenching rate constant is $1.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

(ii) *Pyrene–TEA system at 492 nm.* In the absence of TEA no absorption at 492 nm was observed, but in its presence an intense narrow band due to the pyrene anion radical²⁶ was formed. Its rate of formation depended on the TEA concentration, but was independent of excitation light intensity. It was possible to determine the Stern–Volmer constant for its formation and a value of $610 \text{ dm}^3 \text{ mol}^{-1}$ was obtained. Using the measured fluorescence lifetime for pyrene of 303 ns, a rate constant, k_e , for the reaction between the excited pyrene molecule and TEA, and for the exciplex formation reaction could be calculated. A value of $2.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was obtained. This value is in good agreement with the fluorescence-quenching rate constant.

The decay of the anion radical followed second-order kinetics at low TEA concentrations. The experimental rate parameter was $k_{\text{exp}} = 1.2 \times 10^5 \text{ s}^{-1}$. When a value of 0.5 for the efficiency of the anion radical formation was used,²⁷ the molar absorption coefficient ϵ was calculated to be $5.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The second-order rate constant for ion recombination is thus $k_1 = k_{\text{exp}}\epsilon d = (1.2 \times 10^5 \text{ s}^{-1})(5.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})(2 \text{ cm}) = 1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The same value was obtained by Mataga *et al.*²⁶

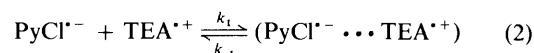
When the decay of the anion radical was analysed at higher TEA concentrations ($\geq 3.5 \times 10^{-3} \text{ mol dm}^{-3}$) the response functions also involved a first-order term. This term, which corresponds to the reaction between the anion radical and TEA, $k_q^{\text{exp}} = k_q[\text{TEA}]$, increased linearly with TEA concentration. An average of several measurements gave a value of $5.0 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for k_q .

(iii) *Cl–Pyrene fluorescence.* The measured fluorescence lifetime for chloropyrene was 58.3 ns. In the presence of TEA, the lifetimes were shorter and a value of $330 \text{ dm}^3 \text{ mol}^{-1}$ was obtained for the Stern–Volmer constant, which corresponds to a quenching rate constant of $5.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

(iv) *Cl–Pyrene–TEA system at 493 nm.* The observed transient with a maximum at 493 nm is in some ways analogous to that found in pyrene due to the anion radical of chloropyrene. The rate of its formation depends on the TEA concentration (Fig. 1) increasing with its concentration. By dividing the measured first-order rate constants by the TEA concentrations the second-order rate constants for chloropyrene anion radical formation was calculated. The average value of measurements at different TEA concentrations determined was $5.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value is the same as was measured for fluorescence quenching by TEA. Furthermore, because the rate of the triplet formation, $2.3 \times 10^6 \text{ s}^{-1}$ for chloropyrene, is about one order of magnitude lower than that for the formation of the anion radical, the possibility of a triplet-state reaction can be ruled out. Thus the reaction is evidently a singlet-state reaction and is given by eqn. (1).



The decay response function of the anion radical involves both a first- and a second-order term [Fig. 2 (a)]. These are independent of TEA concentration. Using the rate of the second-order term, $4.5 \times 10^5 \text{ s}^{-1}$, a value of $2.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ was measured for the molar absorption coefficient ϵ , when the efficiency for free-radical formation is taken to be 0.5.²⁷ From this it follows that the rate constant for the radical recombination is, in the case of chloropyrene, $k_1 = k_{\text{exp}}\epsilon d = 1.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This step of the mechanism can be presented as in eqn. (2).



The first-order term of the decay response function of the anion radical of chloropyrene can be identified as a cleavage

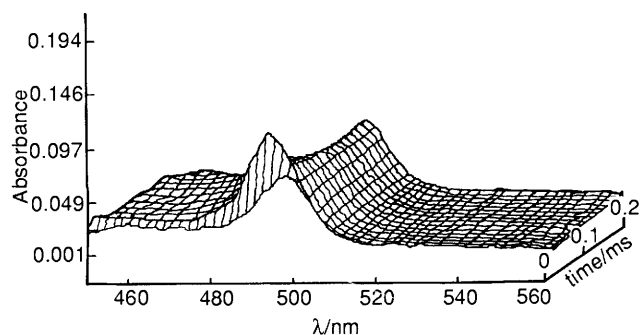
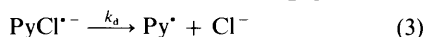


Fig. 3 Time-resolved transient absorption spectrum of the chloro- and cyano-pyrene anion radicals in acetonitrile. $[TEA] = 4.8 \times 10^{-3} \text{ mol dm}^{-3}$, $[CN^-] = 1.3 \times 10^{-2} \text{ mol dm}^{-3}$. The total delay time is 0.2 ms after the laser pulse excitation.

reaction of the anion radical to an aryl radical and chloride ion with a measured rate constant of $1.8 \times 10^3 \text{ s}^{-1}$ [eqn. (3)].



(v) *Cl-Pyrene-TEA system at 415 nm*. In the absence of TEA, an absorption, with formation and decay rate constants of 2.3×10^6 and $3.2 \times 10^4 \text{ s}^{-1}$, respectively, was observed at 415 nm. This was due to triplet-triplet absorption.

When TEA was added to the reaction solution the band at *ca.* 415 nm broadened and its formation rate increased. This indicates that a second transient is formed in a reaction of TEA with an excited state of chloropyrene. Since the triplet-triplet absorption was also present at this wavelength the formation rate constant was not detected satisfactorily. In the pyrene-TEA system in acetonitrile a band at 400 nm was assigned²⁶ to the absorption of 1-hydropyrenyl radical formed from the ion-pair state *via* a proton transfer from the amine cation to the pyrene anion. Analogously, in the case of chloropyrene, all the features of the transient observed at *ca.* 415 nm indicate that the transient can be assigned to a hydropyrenyl radical of chloropyrene [eqn. (4)].



The decay of the hydrochloropyrene radical at 415 nm largely followed second-order kinetics, but a first-order term was also observed, which was independent of TEA concentration. At high TEA concentrations ($\geq 3.8 \times 10^{-3} \text{ mol dm}^{-3}$) the second-order term increased with concentration.

(vi) *Cl-Pyrene-TEA-CN⁻ system at wavelength ranges from 400 to 430 nm and from 480 to 510 nm*. In order to study the reactivity of the anion radical of chloropyrene, a strong nucleophile, CN^- , was added to the reaction solution. Cyanide ions reduced the decay rate of the 493 nm transient [Fig. 2 (b)] and the maximum of the band shifted to a wavelength of 498 nm (Fig. 3). At longer wavelength, the profile of the decay curve changed and the formation of a new transient was observed [Fig. 2 (c)]. This is also demonstrated in Fig. 4 when measured on a faster timescale. This transient can be identified as a cyanopyrene anion radical.

The rate of the cleavage reaction of the anion radical, $1.8 \times 10^3 \text{ s}^{-1}$ [eqn. (3)], is evidently several orders of magnitude too slow to take place before the formation of the cyanopyrene anion radical (Fig. 4). The rate for this reaction was determined to be $0.35 \times 10^6 \text{ s}^{-1}$ at a cyanide concentration of $4.8 \times 10^{-3} \text{ mol dm}^{-3}$. Thus a reaction between the cyanide ion and the aryl radical, which is often suggested²⁸ to take place *via* the $S_{RN}1$ mechanism, can in the present mechanism be ruled out.

In order to demonstrate the role of the chlorohydropyrenyl radical in the mechanism, the system was carefully studied in the wavelength range 400–430 nm in the presence of cyanide ion.

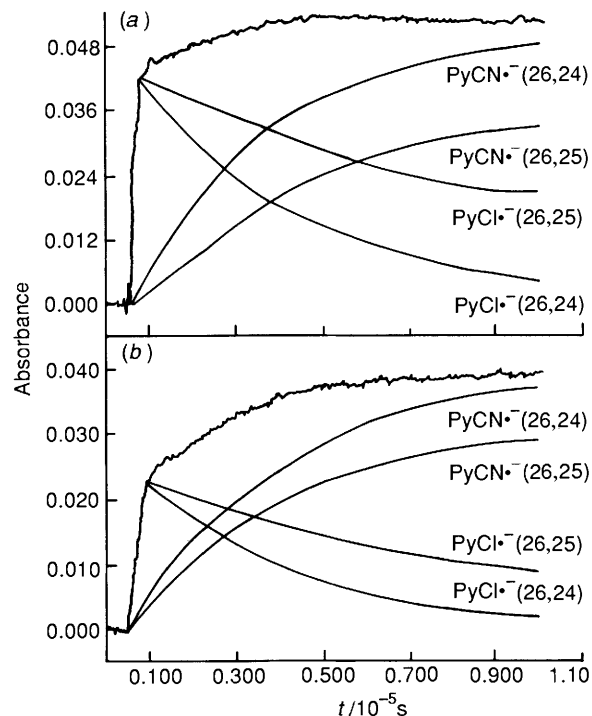


Fig. 4 Formation of cyanopyrene anion radicals from chloropyrene anion radicals (a) at 498 nm and (b) at 503 nm in the presence of $[TEA] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[CN^-] = 4.8 \times 10^{-3} \text{ mol dm}^{-3}$. The calculated absorbances of the transients using either the model eqns. (26) and (24) or (26) and (25) are indicated.

The kinetics of the band at 415 nm, assigned to a chloropyrenyl radical, was practically the same as in the absence of cyanide ions. Only a small increase in intensity was observed. The decay lifetime of the absorption, however, increased gradually with wavelength from a value of 36 μs at 415 nm, in the absence, to 71 μs at 425 nm, in the presence of cyanide ion. This lifetime is considerably shorter than that of the cyanopyrene anion radical at 498 nm. Thus a new transient, which can be assigned to a cyanohydropyrenyl radical, is formed with a maximum at 421 nm [eqn. (5)]. At shorter wavelengths its formation overlaps the



increased decay rate of the chlorohydropyrenyl radical and the kinetics remain the same.

Quantitative Analysis of the Experimental Results.—(i) *Quantum yields for the disappearance of pyrene and chloropyrene*. Quantum yields for the disappearance of the starting arenes were measured at different reactant concentrations. For pyrene the quantum yields were relatively low, < 0.01 , both in the presence and absence of the cyanide ion and accurate values were not determined. Dependences of quantum yields on the concentrations of all the reactants were observed for $PyCl$ (Table 1). In the absence of cyanide ions the quantum yields for disappearance were very low (less than 0.01). At the CN^- concentration range from 0 to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ the quantum yields increased and produced constant values. The dependency of the quantum yield on the chloropyrene concentration indicates that a chain reaction might be involved.

The obtained quantum yields were remarkably lower than those measured for chlorobiphenyl^{14,16} or chloronaphthalene¹⁶ in acetonitrile or for chlorobenzene¹⁶ in cyclohexane or in its mixture with acetonitrile. The triethylamine concentrations, used in these experiments were, however about one magnitude of order higher than those used by us. Quantum yields³ for hydrogen addition to phenanthrenecarbonitrile were

Table 1 Measured quantum yields for the disappearance of PyCl

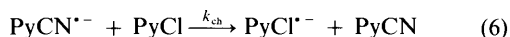
[TEA]/10 ⁻³ mol dm ^{-3a}	Φ	[PyCl]/10 ⁻⁵ mol dm ^{-3b}	Φ	[CN ⁻]/10 ⁻³ mol dm ^{-3c}	Φ
1.0	0.18	0.9	0.09	1.0	0.15
1.6	0.23	1.8	0.15	2.8	0.18
3.2	0.31	3.0	0.20	5.6	0.22
5.6	0.37	4.5	0.23	7.0	0.23
8.0	0.40	6.0	0.26	12.6	0.23
9.0	0.40	6.9	0.27	18.2	0.23

^a [PyCl] = 4.5 × 10⁻⁵, [KCN] = 7.0 × 10⁻³. ^b [KCN] = 47.0 × 10⁻³, [TEA] = 1.6 × 10⁻³. ^c [PyCl] = 4.5 × 10⁻⁵, [TEA] = 1.6 × 10⁻³ mol dm⁻³.

as low as 0.003 in acetonitrile, but increased to a value of 0.03 in non-polar solvents, when diethylamine acted as an electron donor. In these reactions the formation of a contact radical-ion pair, the anion radical of cyanophenanthrene and the cation radical of the amine, was suggested as a reaction intermediate. In our studies where the formation of the free ion radicals was observed, the quantum yields increased to a value as high as 0.4. Thus, there is a difference between the reactions of the cyanopyrene and cyanophenanthrene anion radicals in the latter stages of the mechanism.

(ii) *Product analysis.* Reaction products for the chloropyrene reaction were analysed by gas chromatography. The results showed that the main reaction product was pyrene. The amounts of the products were analysed only qualitatively, but the yields of the products corresponded approximately to the yields of the consumed starting material.

A chain-initiated reaction between the anion radical of cyanopyrene and the ground-state chloropyrene, eqn. (6), can



be ruled out, as cyanopyrene was not observed as a reaction product.

Much experimental evidence shows that photodehalogenation of chloropyrene is mechanistically very closely related to the photohalogenation of chloro-benzene, -naphthalene and -biphenyl,¹⁶ where three pathways have been suggested for the steps following the electron transfer from the amine to the halide. These are (a) loss of a chloride ion followed by hydrogen abstraction, (b) protonation by an external proton donor and (c) protonation within the exciplex, eqn. (7).

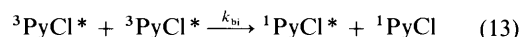
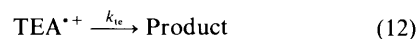
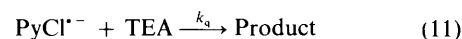
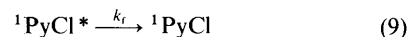
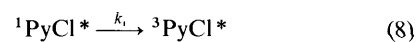


The differences in the results of that study with those of the present work are that (a) the dechlorination of chloropyrene is assisted by cyanide ions, (b) both the formation and (c) the recombination of free anion radicals of chloropyrene and cyanopyrene were observed. The loss of Cl⁻ from PyCl^{·-} [reaction (3)] was observed to be a slow process, and thus inefficient from the point of view of product formation. The loss of CN⁻ from PyCN^{·-} would be even slower because CN⁻ is a stronger nucleophile than Cl⁻.

(iii) *Deuteration studies.* Deuterium labelling was used to determine the origin of the hydrogen atom replacing the chlorine atom. When CD₃CN was used as the solvent more than 90% deuterium incorporated into the product was observed. Thus the hydrogen is mainly the result of hydrogen abstraction from the solvent or protonation by the solvent [eqn. (4)].

(iv) *Kinetic analysis.* In order to develop the mechanism of the reaction studied a kinetic computer-assisted analysis was made. In the absence of cyanide ions a mechanism based on that presented by Mataga *et al.*²⁶ was used to describe simultaneously a set of several decay curves at wavelengths of

415 and 492 nm on different timescales. The following reactions [(8)–(13)], in addition of the reactions (1)–(4) and (7) were taken into account.



In the time region 1–360 μs, where it was not necessary to take reactions (1) and (8) into account, the following rate equations at time *t* after excitation can be written:

$$(dx_1/dt) = (-k_1/\epsilon_1)x_1x_2 + k_{-1}x_3 - (k_d + k_h)x_1 \quad (14)$$

$$(dx_2/dt) = (-k_1/\epsilon_1)x_1x_2 + k_{-1}x_3 - k_{ie}x_2 \quad (15)$$

$$(dx_3/dt) = (k_1/\epsilon_1)x_1x_2 - (k_{-1} + k_n)x_3 \quad (16)$$

$$(dx_4/dt) = (k_n\epsilon_3/\epsilon_1)x_3 + (k_h\epsilon_3/\epsilon_1)x_1 - k_d x_4 - 2k_{bi}x_4x_4/\epsilon_2 \quad (17)$$

where $x_1 = [\text{PyCl}^{\cdot-}]_{\epsilon_1}$, $x_2 = [\text{TEA}^{+\cdot}]_{\epsilon_1}$, $x_3 = [\text{PyCl}^{\cdot-} \cdots \text{TEA}^{+\cdot}]_{\epsilon_1}$, and $x_4 = \{[{}^3\text{PyCl}^*]_{\epsilon_2} + [\text{PyClH}^{\cdot}]_{\epsilon_3}\}$. ϵ_1 is the molar absorption coefficient of PyCl^{·-} at 492 nm and ϵ_2 and ϵ_3 are the molar absorption coefficients of transients ³PyCl* and PyClH[·], respectively, at 415 nm.

In order to calculate the unknown kinetic parameters we estimated their values by minimizing the following residual functions, eqn. (18).

$$F = \sum_{i=1}^{N_1} [(x1_{i,\text{exp}} - x1(t_i))]^2 + \sum_{j=1}^{N_2} [(x4_{j,\text{exp}} - x4(t_j))]^2 \quad (18)$$

where $x1(t_i)$ and $x4(t_j)$ are the calculated values of the transient absorption of PyCl^{·-} and of the sum of absorbances of the transient A and ³PyCl*, respectively, at times $t = t_i$ and $t = t_j$, and $x1_{i,\text{exp}}$ and $x4_{j,\text{exp}}$ are the corresponding experimental absorbances at 492 and 415 nm, respectively. N_1 and N_2 are the numbers of experimental points at observation wavelengths of 492 and 415 nm.

The initial values of the differential equations system (14)–(17) were considered to be unknown and they were estimated during the minimization of the residual function. The starting channels of the registration system corresponding to the time equal to zero were chosen for both experimental curves separately and iteratively to obtain the best description of the experimental data. The transient absorptions at 415 nm and 492 nm were taken to be of the same accuracy and to be independent of each other in the different measurements and channels. Thus the residuals are included in the residual function with equal weights.

The values of the kinetic parameters producing the minima of the residual function are presented in Table 2.

At the time region 0–600 ns, where reactions (1)–(4) and (7)–(13) are taken into account the rate equations (14)–(17) become eqns. (19)–(22).

$$(dx_1/dt) = (-k_1/\epsilon_1)x_1x_2 + k_{-1}x_3 - (k_d + k_h)x_1 + k_e[\text{TEA}][{}^1\text{PyCl}^*]_0 \epsilon_1 \exp[-t(k_e + k_i + k_f)] \quad (19)$$

Table 2 The measured and calculated kinetic parameters for Py-TEA and PyCl-TEA systems. The accuracy of the last figure is ± 1 .

Parameter	Py ²⁶	Py	PyCl (decay)	PyCl (formation)
$k_e/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		0.20×10^{10a}	5.7×10^9a	5.7×10^9
$k_1 \epsilon_1^{-1}/\text{cm s}^{-1}$			3.4×10^5	
$k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	1.4×10^{10}	1.4×10^{10}	1.0×10^{10b}	
k_{-1}/s^{-1}	2.5×10^5		1.0×10^7	9.2×10^6
k_i/s^{-1}			2.3×10^{6c}	
k_f/s^{-1}		$3.3 \times 10^{6a,c}$	$1.7 \times 10^{7a,c}$	
k_{dt}/s^{-1}			3.2×10^{4c}	
k_d/s^{-1}		0.0	1.8×10^3	
$k_a/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	3.3×10^{4d}	5.0×10^6	—	
k_n/s^{-1}	2.5×10^5		1.0×10^4	
$k_n \epsilon_3 \epsilon_1^{-1}/\text{s}^{-1}$			0.3×10^2	
k_h/s^{-1}			6.4×10^4	
$\epsilon_3/\text{mol dm}^{-3} \text{ cm}^{-1}$			83	
k_{te}/s^{-1}			4.1×10^3	
$k_{bi} \epsilon_2^{-1}/\text{cm s}^{-1}$			4.3×10^5	
$k_{bi}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			1.6×10^{10e}	

^a By single-photon-counting method. ^b Calculated assuming $\epsilon_1 = 2.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. ^c Measured in the absence of TEA. ^d $k_a[\text{TEA}]$. ^e Calculated using a value of $\epsilon_2 = 3.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ for triplet-state pyrene, (I. Carmichael, W. P. Helmen and G. L. Hug, *J. Phys. Chem. Ref. Data*, 1987, **16**, 255).

$$\begin{aligned} (dx_2/dt) = & (-k_1/\epsilon_1)x_1x_2 + k_{-1}x_3 - k_{te}x_2 \\ & + k_e[\text{TEA}][^1\text{PyCl}^*]_0 \epsilon_1 \exp[-t(k_e + k_i + k_f)] \quad (20) \end{aligned}$$

$$(dx_3/dt) = (k_1/\epsilon_1)x_1x_2 - (k_{-1} + k_n)x_3 \quad (21)$$

$$\begin{aligned} (dx_4/dt) = & (k_n \epsilon_3/\epsilon_1)x_3 \\ & + (k_h \epsilon_3/\epsilon_1)x_1 - k_{dt}x_4 - 2k_{bi}x_4x_3/\epsilon_2 \\ & + k_i \epsilon_2 [^1\text{PyCl}^*]_0 \exp[-t(k_e + k_i + k_f)] \quad (22) \end{aligned}$$

Applying the initial conditions $x_1(0) = x_2(0) = x_3(0) = x_4(0) = 0$ and fixing the parameters calculated in the slow time region (Table 2) the other unknown parameters included in the equations (19)–(22) can be calculated. Kinetic descriptions of the most important parameters obtained by the solution, eqns. (19)–(22), are presented in Table 2.

(v) *Evaluation of the mechanism in the presence of cyanide anions.* The cyanide anion did not have any influence either on the lifetimes of the singlet or the triplet states or on the formation of the anion radical of chloropyrene. Because the dissociation rate of $\text{PyCl}^{\cdot-}$ was measured to be relatively slow ($k_d = 1.8 \times 10^3 \text{ s}^{-1}$) as compared with the relatively fast formation of the new transient (Figs. 3 and 4) the possibility of hydrogen abstraction by the aryl radical ($\text{Py}^{\cdot} + \text{RH} \longrightarrow \text{PyH} + \text{R}^{\cdot}$) from the solution can be ruled out.

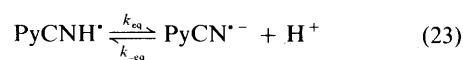
Thus at first sight the possible reactions of the CN^- ions are (a) attack at the anion radical $\text{PyCl}^{\cdot-}$ or (b) attack at the ion pair ($\text{PyCl}^{\cdot-} \cdots \text{TEA}^{+\cdot}$), or (c) attack at the chlorohydroxyrenyl radical formed *via* these transients.

In case (a), a dianion radical is formed as a transient.

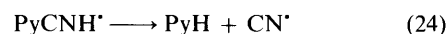


Formation of such radicals appears, however, to be improbable although kinetically possible.

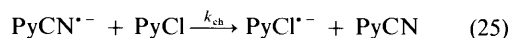
Protonation within the exciplex^{3,4,16} or in the ion pair [reaction (7)],²⁶ and halogenated aryl radical formation [case (b)] does not produce high values for quantum yields in the absence of cyanide ions. On the other hand, if the most important step of the cyanide-assisted dechlorination is attack of the cyanide ion on the chlorohydroxyrenyl radical and a formation of a cyanohydroxyrenyl radical, eqn. (5), the formation of the cyanopyrenyl radical anion can easily be explained in terms of a reversible deprotonation of the cyanohydroxyrenyl radical, eqn. (23).



Finally, by analogy with the dechlorination of biphenyl,¹⁶ the product formation can be depicted as shown in eqn. (24), which



yields the final product, or by reaction (25), which initiates the possible chain reaction.



Because observed transient absorption curves were measured for $\text{PyCl}^{\cdot-}$ and $\text{PyCN}^{\cdot-}$ at 498 and 503 nm, reactions (4), (5) and (23) can be kinetically combined as reaction (26):



This reaction also includes the formation of the cyanohydroxyrenyl radical *via* reaction (7).

Thus four sets of kinetic differential equations can be written to describe the reactions; these are presented in Table 3.

The experimental transient absorption curves measured at 498 and 503 nm were used in the calculations as the most accurate experiments. These two experimental curves are thought to be the sums of the absorbances of $\text{PyCl}^{\cdot-}$ and $\text{PyCN}^{\cdot-}$ with different absorption coefficients. The response functions were constructed as the sums of $x_1(t)[\epsilon'_1(498)/\epsilon_1(492)] + x_5(t)$ at 498 nm and $x_1(t)[\epsilon''_1(503)/\epsilon_1(492)] + x_5(t)[\epsilon'_5(503)/\epsilon_5(498)]$ at 503 nm, where $x_5 = \epsilon_5[\text{PyCN}^{\cdot-}]$, ϵ'_1 and ϵ''_1 are the molar absorption coefficients of $\text{PyCl}^{\cdot-}$ and ϵ_5 and ϵ'_5 are those of $\text{PyCN}^{\cdot-}$ at 498 and 503 nm, respectively. As estimations of the parameters those values were taken which minimized the sum of squares of the residuals between the experimental and the response functions. The parameters k_{-1} , k_d , k_i , k_n and k_n obtained in the absence of CN^- , were fixed. The initial values for the unknown parameters $x_1(0) = x_2(0)$ and $x_3(0)$ were estimated during the minimization. $x_5(0)$ was assumed to be zero time $t = 0$. The parameters obtained as a result of the minimization processes are listed in Table 4.

Fitted response functions and its components, $\text{PyCl}^{\cdot-}$ and $\text{PyCN}^{\cdot-}$, at wavelengths 498 and 503 nm are shown in Fig. 4. The calculated response functions fit the experimental decay curves of the models well. The values, 0.71×10^{10} and 0.74×10^{10}

Table 3 Differential equations for equations (1)–(4) and (5)–(13) supplemented with the possible reaction combinations (26, 24) or (26, 25).

Rate equations	Coefficients for parameters:				
	x_1	x_2	x_1x_2	x_3	x_5
(dx_1/dt)					
(26, 24)	$-(k_d + k_h + k_c[\text{CN}^-])$	—	$(-k_1/\epsilon_1)$	k_{-1}	—
(26, 25)	$-(k_d + k_h + k_c[\text{CN}^-])$	—	$(-k_1/\epsilon_1)$	k_{-1}	$(k_{ch}\epsilon_1/\epsilon_5)[\text{PyCl}]$
(dx_2/dt)					
(26, 24, 25)	—	$-k_{te}$	$(-k_1/\epsilon_1)$	k_{-1}	—
(dx_3/dt)					
(26, 24, 25)	—	—	(k_1/ϵ_1)	k_{-1}	—
(dx_5/dt)					
(26, 24)	$(k_h + k_c[\text{CN}^-])\epsilon_5/\epsilon_1$	—	—	—	$-k_{pr}$
(26, 25)	$(k_h + k_c[\text{CN}^-])\epsilon_5/\epsilon_1$	—	—	—	$-k_{ch}[\text{PyCl}]$

Table 4 Calculated kinetic parameters for ClPy-TEA-CN⁻ systems using reaction combinations (26, 24) or (26, 25). The accuracy of the last figure is ± 1 .

Model reactions	(26, 24)	(26, 25)
ϵ_1/ϵ_5	1.10	1.15
$[\text{PyCl}^{\cdot-} \cdots \text{TEA}^+]_0 \epsilon_1$	0.0046	0.0043
$[\text{PyCl}^{\cdot-} \cdots \text{TEA}^+]_0^a/\text{mol dm}^{-3}$	1.6×10^{-7}	1.5×10^{-7}
$k_c[\text{CN}^-]/\text{s}^{-1}$	0.25×10^6	0.35×10^6
$k_c/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1 b}$	5.2×10^7	7.3×10^7
$k_1\epsilon_1^{-1}/\text{s}^{-1}$	2.4×10^5	2.6×10^5
$k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1 a}$	0.71×10^{10}	0.74×10^{10}
$k_{ch}[\text{PyCl}]/\text{s}^{-1}$		6.7×10^4
$k_{ch}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1 c}$		2.2×10^9
k_{pr}/s^{-1}	0.20×10^5	
ϵ'_5/ϵ_5	0.76	0.76
$x_1 = [\text{PyCl}^{\cdot-}]_0 \epsilon_1$	0.060	0.060
$[\text{PyCl}^{\cdot-}]_0/\text{mol dm}^{-3 a}$	2.1×10^{-6}	2.1×10^{-6}

^a Calculated assuming $\epsilon_1 = 2.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. ^b $[\text{CN}^-] = 4.8 \times 10^{-3} \text{ mol dm}^{-3}$. ^c $[\text{PyCl}] = 4.8 \times 10^{-3} \text{ mol dm}^{-3}$.

$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, calculated for the rate constant k_1 using reaction (26) are about the same as the value calculated in the absence of cyanide ion and are very near the maximum value of the rate constant of a diffusion-controlled reaction in acetonitrile. This fact supports the mechanism (26), it is the combination of the reactions (4), (5) and (22).

The calculated molar absorption coefficients ϵ_1/ϵ_5 (the ratio of absorption coefficients of transients $\text{PyCl}^{\cdot-}$ and $\text{PyCN}^{\cdot-}$ at wavelengths 493 and 498, respectively) for the combinations of reactions (26, 23), and (26, 24) are 1.10 and 1.15 which is consistent with the experimental observations. This is another fact supporting the mechanism (26). Because $\epsilon_1/\epsilon_5 = 1.10$ (Table 4) the molar absorption coefficient for the transient $\text{PyCN}^{\cdot-}$, $\epsilon_5(498 \text{ nm}) = 26\,400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. By using the calculated value (Table 4) $\epsilon'_5(503 \text{ nm})/\epsilon_5(498 \text{ nm}) = 0.76$ a value $20\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ is obtained for $\epsilon'_5(503 \text{ nm})$. Furthermore, by using an estimated value $[\text{PyCl}^{\cdot-}]_0 = 2.1 \times 10^{-6} \text{ mol dm}^{-3}$ (Table 4) at $t = 0$ and experimental absorption intensities from Fig. 4, the molar absorption coefficients for anion radical of chloropyrene at wavelengths of 498 and 503 nm are calculated to be 10 000 and 5500 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. These values are consistent with the experimental spectrum (Fig. 3).

Conclusion

The calculated rate constants (Tables 2 and 4) are consistent with those presented in the literature^{3,4,16,27} and are physically possible.

The results show that the kinetic scheme derived²⁶ for the pyrene-TEA system is also applicable to a chloropyrene-TEA system in acetonitrile. The kinetic analysis gave very similar results in both cases. Predictable differences were observed in the later stages of the reaction, when the reaction was studied in the presence of cyanide ions. These were firstly, the influence of the nucleophile on the anion radical behaviour was only observed for the chloropyrene reaction, not for pyrene. Secondly, the quantum yield for chloropyrene disappearance increased markedly when cyanide was added showing that the formation of the cyanohydropyrenyl radical is the yield-determining step.

Experimental

Pyrene (Fluka AG, *purum*) was recrystallized several times from ethanol and sublimated under vacuum. 1-Chloropyrene was purchased from Alfa and used without further purification. Triethylamine (Merck) was purified by fractional distillation under reduced pressure. Acetonitrile was purified by being stirred with calcium hydride, decanted, distilled with phosphorus pentoxide, refluxed with calcium hydride and distilled. It was protected from moisture and stored under dry nitrogen. Deuteriated acetonitrile (99.5% D) was obtained from Aldrich and used without further purification.

To increase its solubility in acetonitrile, potassium cyanide was added to the solution as the crown-ether salt.²⁹ Potassium cyanide-18-crown-6 complex was prepared by dissolution of equivalent amounts of 18-crown-6 and KCN in dry methanol, reflux of the solution for 30 min and removal of the solvent under reduced pressure. On dissolution of this complex in dry acetonitrile a $4.2 \times 10^{-2} \text{ mol dm}^{-3}$ solution of cyanide was obtained.

The compounds studied by the flash-photolysis method were dissolved in acetonitrile and the sample solutions were prepared from these solutions so that the concentration of pyrene was 1.4×10^{-5} and that of chloropyrene between $(0.9-6.9) \times 10^{-5} \text{ mol dm}^{-3}$. In the flash photolysis experiments their absorbances at 308 nm were about 0.1. The samples were degassed by several freeze-pump-thaw cycles.

The preparative irradiations were performed as follows.

Chloropyrene (100 mg) and triethylamine (250 mg) were dissolved to 25 cm³ in CH₃CN or CD₃CN containing 4.2 × 10² mol dm⁻³ of cyanide ions. The samples were degassed by several freeze-pump-thaw cycles and irradiated using a 100 W Hg lamp with a monochromator at 254 or 313 nm. It was halted at >90% conversion of chloropyrene. The products were determined by GC analysis. The solvent was then removed by rotary evaporation and layer chromatography was used to separate the products. Deuterium incorporation into products was determined by NMR spectroscopy and confirmed by GC-MS analysis, where attention was focused on the peaks at *m/e* 202 and 203.

The flash-photolysis experiments were carried out with an excimer laser focused on the sample (ELIM 72, Special Design Bureau of the Estonian Academy of Science) at 308 nm. The laser pulse width was about 10 ns fwhm and it had a maximum energy of about 60 mJ per pulse. When the effect of the light intensity on the reaction was studied the laser energy was attenuated by 20–70% using gray filters. The excitation light was focused to a beam 2 cm long and 2.0 mm wide, which coincided with the monitoring beam. Transient absorptions were monitored with a 100 W pulsed xenon lamp. The width of the xenon lamp pulses were 2 ms and they were stable at their maximum height to within 2% for 100 μs. When the intensity of the pulsed xenon lamp was constant the laser was fired. The excitation and monitoring pulses were at right angles. The detection wavelength was selected for each sample by a monochromator (MDR 23). The monitoring beam was focused on the sample on an area of about 5 mm² coinciding with the region excited by the laser. After passing through the sample the monitoring beam was focused on the entrance slit of the second monochromator (MDR 23). The signal was detected by a photomultiplier (FEU-106), which was connected to the differential amplifier (Tektronix 7 A 7) of a 500 MHz transient digitizer (Tektronix 7912 AD). The intensity of the monitoring light was measured at the same time as the laser excitation in each experiment and its value was used to calculate the absorbance of the transient studied. In cases of low signal intensities, averages of several measurements were used to calculate the decay curves and the instrumental noise due to variations in the monitoring light intensity and the transient digitizer. These were then subtracted from the measured decay curves. The influence of fluorescence on transient absorption was reduced in a similar way. When recording the transient absorption spectra, decay curves were measured automatically at each wavelength used. The curves were stored and presented as a function of the wavelength. The data were stored by a computer (Olivetti 24M) for further manipulation. A least-squares fitting procedure was used to calculate the rate parameters from the experimental decay curves. The values obtained for the goodness to the applied fits were between 1.0 and 1.4, which are all acceptable. Analyses which produced poorer goodness-of-fit were neglected.

The fluorescence lifetimes were determined by a single-photon-counting method with an Edinburgh Instrument 199

fluorescence time-domain spectrometer using a coaxial flashlamp (fwhm time of 1.5 ns). The decay curves were analysed using a non-linear last-squares iterative reconvolution method.

The quantum yields of the reaction were measured with a potassium ferrioxalate actinometer, using the method of Calvert and Pitts.³⁰ The time of irradiation was selected to convert about 1–3% of chloropyrene into the product. Details of the quantum-yield measurements are given elsewhere.²⁹

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