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Photolysis of polycyclic aromatic hydrocarbons (PAHs) in dilute aqueous solutions detected by fluorescence

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Abstract

Photodegradation kinetics of anthracene, pyrene, benz[*a*]anthracene and dibenz[*a*,*h*]anthracene were studied in aqueous solutions at pH 5.6 and 7.6 with purging gases of nitrogen, oxygen or synthetic air. Photolysis of PAHs was performed in an immersion well reactor at 254 nm and was followed as decreasing fluorescence intensities. Photodegradation of PAHs was fast in all cases with anthracene and benz[*a*]anthracene being the fastest decomposed. The photochemical reactions followed a first order equation, and the apparent rate constants, k_r, varied from 10^{-3} to 10^{-4} s^{-1}. Oxygen concentration had minor effect upon the photodegradation rates of PAHs. At pH 5.6 the values of the rate constants were higher than those at pH 7.6, anthracene was an only exception of this. Based on photodegradation kinetics and fluorescence lifetime measurements, a simple scheme for a mechanism is proposed containing non-emissing excited intermediate species in equilibrium with the excited singlet state. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polycyclic aromatic hydrocarbon; Photodegradation; Fluorescence; Water

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1. Introduction

Contamination of environment with polycyclic aromatic hydrocarbons (PAHs) are considered hazardous because of carcinogenic, mutagenic and toxic effects of certain PAHs [1]. Anthropogenic activity is mainly responsible for PAH released into the environment. The major sources of PAHs are combustion of fossil fuels, heat and power generation, motor vehicle emissions, refuse burning, industrial processes, petroleum leakage and spills, fallout from urban air pollution, coal liquefaction and gasification processes and creosote and other wood preservative wastes [2].

In the environment, primary removal processes of low molecular weight PAHs are microbial degradation and evaporation. Higher molecular weight aromatics are less water soluble, which makes biodegradation difficult. Thus, these compounds are effected by sedimentation and photochemical oxidation [3]. Photooxidation is known to occur for PAHs in solution, in pure solid form or adsorbed onto solid substrates [4]. Exposure of aromatic compounds to light produces partially oxidised intermediates which are more susceptible to the biodegradation than parent compounds. Thus, photodegradation has been suggested as a pre-treatment strategy for biodegradation [5].

In order to be biodegraded, a chemical must be in an aqueous phase to enter a microbial cell [6]. Bioremediation of contaminants also permits certain growth parameters such as pH, oxygen concentration and temperature [7]. Each organism has a certain pH range where it is capable to work and an optimum pH, normally around seven. Biodegradation of unsubstituted PAHs usually involves an incorporation of molecular oxygen [2].

The photochemical reactivity of PAHs in organic solvents has been studied for almost 50 years [8]. It is generally accepted that the photodegradation of PAHs in solutions is an oxidative process which is highly accelerated by the presence of photo-initiators. Generally, the more polar the solvent is, the faster is the degradation process of PAH. Irradiation medium has also an effect on by-products formed upon irradiation [9].

Multiple studies have demonstrated that PAHs undergo fairly rapid transformations when exposed to light in organic solvents, solvent–water mixtures and in an aqueous medium in the adsorbed state [9–13]. Only few studies provide systematic results of photolysis for high molecular weight PAHs in pure aqueous solutions. The aim of this study was to investigate the photodegradation kinetics of high molecular

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weight PAHs in water solutions with different pH and oxygen concentrations.

2. Experimental details

2.1. Chemicals and media

Anthracene, pyrene, benz[*a*]anthracene (B[*a*]A) and dibenz[*a,h*]anthracene (D[*a,h*]A), were purchased from Fluka (Buchs, Switzerland) or from Merck (Schuchardt, Germany). Internal standard, pyrene-*d*10 was purchased from Ehrenstorfer (Augsburg, Germany). Dichloromethane, chloroform and *n*-hexane were from Baker (Deventer, Holland). All solvents were HPLC grade, other chemicals were reagent grade and they were used without additional purification. Water was deionised with Milli-Q Plus system (Millipore).

2.2. Photochemical experiments

2.2.1. Photolysis

Photodegradation tests were conducted in an immersion well reactor with a 16 W low pressure mercury lamp emitting >90% at 254 nm, and equipped with a water cooling system (Photochemical Reactors Ltd., UK). The lamp was allowed to stabilise for 30 min prior to experiments. The incident light intensity (I_0) was detected by a potassium ferrioxalate actinometer solution (0.006 M) at 254 nm and was 2.08×10^{-6} Einstein $\mathrm{dm^{-3}\,s^{-1}}$ (corresponding to 1.25×10^{18} photons $\mathrm{dm^{-3}\,s^{-1}}$).

In order to minimise the adsorption of the PAHs to the cell walls of the reactor, cells were cleaned by an aqua regia, then rinsed with a dilute ammonium hydroxide and prior to use with distilled water [14]. The effect of oxygen on the photolysis rate was studied by purging solutions with nitrogen, synthetic air or oxygen $0.2\,\mathrm{dm^3\,min^{-1}}$ for 30 min prior to and during irradiations. The effect of pH on the photodegradation rate was studied by irradiating PAHs at pH 5.6 (non-adjusted Milli-Q water) and at pH 7.6 (Milli-Q water adjusted with 0.1 M NaOH). Dark experiments were performed to control processes other than photodegradation under identical conditions in the absence of light.

The photolysis were conducted in an immersion well reactor at concentrations lower than the water solubility limit at 25°C, varying from 1.80 to 600 nM depending on the PAH [15]. PAHs were added to brown bottles as dichloromethane solutions and the solvent was allowed to evaporate. After that deionised water was added and the resulting solution was mixed for couple of hours before placing into the reactor.

2.2.2. Rate of the photodegradation

The photolysis in aqueous solutions was followed by measuring the fluorescence spectra (a Fluorolog 3 fluorometer, Spex Industries, Inc.) of the samples taken from the reactor every minute during 15 min irradiations. Emission spectra of PAHs were measured from 340 to 570 nm, depending on the compound. The excitation wavelengths were 340, 290, 280 and 295 nm for anthracene, pyrene, benz[*a*]anthracene and dibenz[*a,h*]anthracene, respectively.

The rate of the photodegradation was determined by fitting the fluorescence intensities of the samples to the first-order equation:

$$\ln\frac{F_0}{F_\mathrm{t}} = k_\mathrm{r}t \tag{1}$$

where F_0 and F_t are the fluorescence intensities at the monitoring wavelengths at times zero and t, respectively, and k_r is the apparent rate constant.

When the concentration, C, of the light absorbing substance is sufficiently low, especially in dilute aqueous solutions, the fraction of light absorbed, F_s, by the system, is

$$F_\mathrm{s} = 1 - 10^{-(\alpha+\varepsilon C)l} < 0.1 \tag{2}$$

where α is the absorption coefficient of the solvent, ε is the molar extinction coefficient of the photoreactive substance and l is the light pathlength. When light is weakly absorbed by the system, F_s is very nearly equal to $2.303\,(\alpha+\varepsilon C)l$ [16].

The quantum yield for the photodegradation, ϕ_Pr, can now be determined based on a relation reported by Mill et al. [10]:

$$\phi_\mathrm{Pr} = \frac{k_\mathrm{r}}{2.3\varepsilon I_0 r} \tag{3}$$

where k_r is the apparent rate constant, I_0 is the incident light intensity of the reactor, ε is the molar extinction coefficient ($\mathrm{M^{-1}\,cm^{-1}}$) and r (cm) is a reactor constant. The ε values, determined at 254 nm for anthracene, pyrene, benz[*a*]anthracene and dibenz[*a,h*]anthracene, were 1042, 18211, 69381 and 12604 $\mathrm{M^{-1}\,cm^{-1}}$, respectively. Experimentally determined value for r was 2.83 cm.

Half-lives $t_{1/2}$ were calculated using Eq. (4) which was derived from Eq. (1) by replacing F_t with $F_0/2$:

$$t_{1/2} = \frac{\ln 2}{k_\mathrm{r}} \tag{4}$$

Photolysed samples were also analysed by a Hewlett-Packard 6890 Series gas chromatograph linked to a Hewlett-Packard mass spectrometer (GC/MS). Triplicate samples for GC/MS analysis were extracted both with dichloromethane and *n*-hexane before and after 15 min irradiations. The GC was equipped with a crosslinked 5% phenyl methyl siloxane capillary column HP-5MS (30 m, 0.25 mm, 0.25 μm). Helium was used as the carrier gas. Data collection and processing were performed with an HP MSD ChemStation software.

2.2.3. Fluorescence lifetimes

The fluorescence decay curves were measured by a single-photon-counting (SPC) method with an Edinburgh Instrument 199. A synchronously pumped cavity-dumped dye laser (Spectra-Physics model 375) with a pulse duration of 5 ps was used for excitation. It was pumped with the second-harmonic output (532 nm) of mode-locked neodymium-doped yttrium aluminium garnet laser (Spectra-Physics model 390), operating at the repetition rate of 0.8 MHz. A 6 mm microchannel plate-photomultiplier tube (Hamamatsu R2809U), a time-to-amplitude converter (Ortec 567) and a constant fraction discriminator (Ortec 935) were used for detection. The time resolution of the system is 50 ps. The excitation wavelength was 300 nm. The instrumental response function was 120 ps (fwhm).

The fluorescence decays of PAHs were measured at room temperature and pressure. Measurements were done in aqueous solutions at pH 5.6 at the same concentrations as the fluorescence spectra were measured. For comparison, the decay curves of PAHs (concentrations of 10 μM) were also measured in organic solvent, for anthracene and pyrene in hexane, for benz[*a*]anthracene and dibenz[*a*,*h*]anthracene chloroform was used to ascertain solubility. The fluorescence kinetic curves were analysed by the non-linear least-squares method. The quality of the fit was judged in terms of the statistical parameter χ^2, being <1.2 for an acceptable fit.

3. Results and discussion

3.1. Photodegradation rates and quantum yields

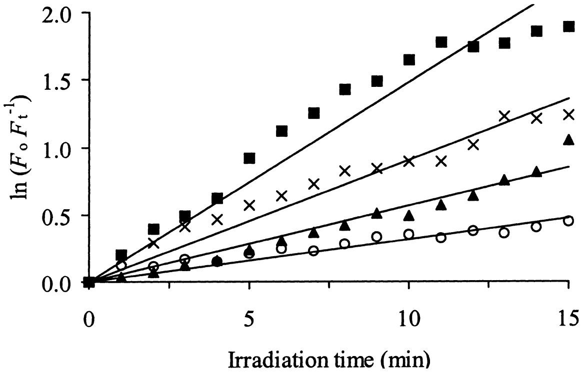


Fig. 2. First-order kinetic plot of photolysis of anthracene ($\lambda_{\text{mon.}}$=401 nm) (×), pyrene ($\lambda_{\text{mon.}}$=393 nm) (▲), benz[*a*]anthracene ($\lambda_{\text{mon.}}$=409 nm) (■) and dibenz[*a*,*h*]anthracene ($\lambda_{\text{mon.}}$=504 nm) (○) in nitrogen purged water at pH 5.6. $\lambda_{\text{mon.}}=\lambda_{\text{monitoring}}$.

The fluorescence spectra of the samples taken every minute during the irradiations are presented in Fig. 1. The decrease of the intensities were observed with time, and the data fitted to Eq. (1) followed well the first-order rate equation (Fig. 2). Intensity changes of different bands in the same spectrum were compared and no considerable differences were observed. In experiments performed under identical conditions without irradiation, only small decrease in fluorescence intensities were observed probably due to the adsorption of the PAHs on the walls and chemical oxygenation.

Table 1 lists the obtained rate constants of the irradiations performed at different oxygen concentrations and at

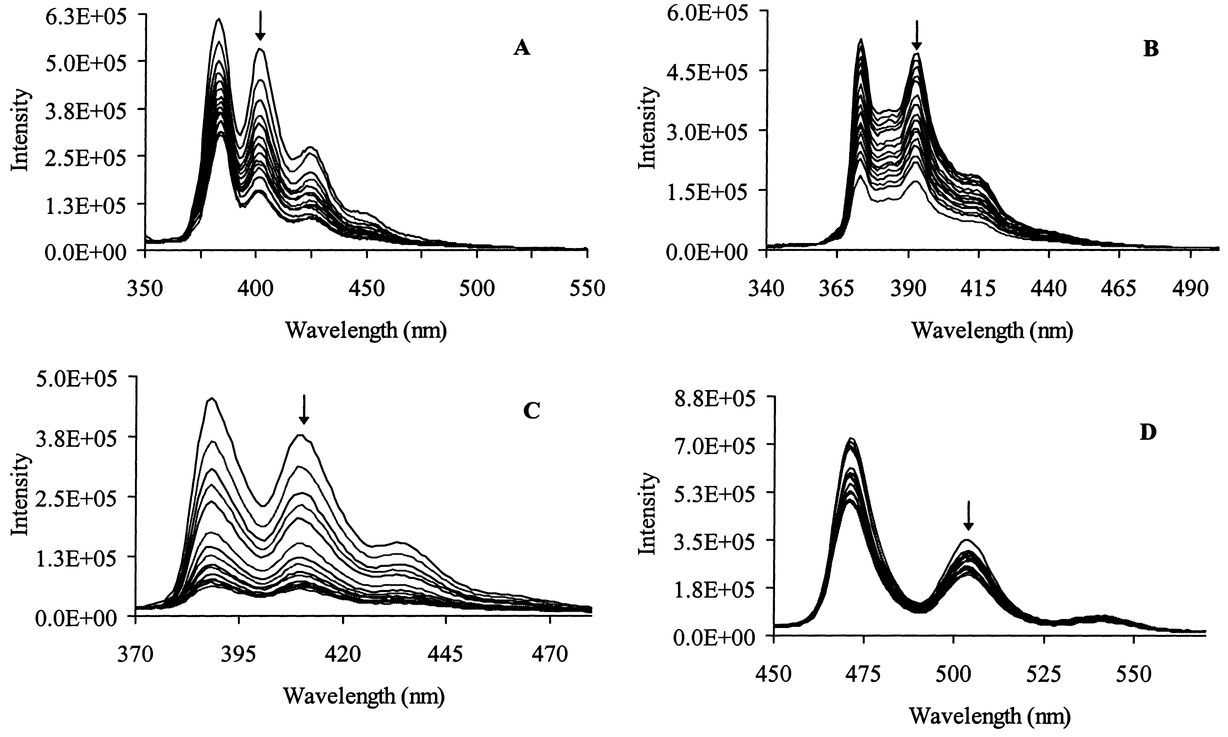


Fig. 1. Fluorescence spectra of (A) anthracene; (B) pyrene; (C) benz[*a*]anthracene; and (D) dibenz[*a*,*h*]anthracene irradiated in water at pH 5.6 purging with nitrogen 0.2 $\text{dm}^3\,\text{min}^{-1}$ for 15 min. Samples for fluorescence measurements were taken every 1 min. The order of the intensity changes vs. time is indicated by the arrow.

Table 1
The apparent rate constants, k_r, half-lives, $t_{1/2}$, and quantum yields, ϕ_{Pr}, for the photodegradation[a]

	Initial c (μM)[b]	pH	Purging gas	k_r (s^{-1})	$t_{1/2}$ (min)	ϕ_{Pr}
Anthracene	0.166	5.6	Nitrogen	2.63E−03 (±0.09)	4.39	1.87E−01
	0.140		Synthetic air	2.57E−03 (±0.25)	4.50	1.82E−01
	0.166		Oxygen	3.26E−03 (±0.11)	3.54	2.31E−01
	0.101	7.6	Nitrogen	3.39E−03 (±0.10)	3.41	2.41E−01
	0.171		Synthetic air	2.83E−03 (±0.16)	4.09	2.01E−01
	0.098		Oxygen	3.36E−03 (±0.09)	3.44	2.38E−01
Pyrene	0.166	5.6	Nitrogen	9.81E−04 (±0.06)	11.8	3.98E−03
	0.126		Synthetic air	10.7E−04 (±0.06)	10.8	4.34E−03
	0.156		Oxygen	9.32E−04 (±0.09)	12.4	3.78E−03
	0.126	7.6	Nitrogen	9.43E−04 (±0.07)	12.3	3.83E−03
	0.144		Synthetic air	9.49E−04 (±0.09)	12.2	3.85E−03
	0.389		Oxygen	8.25E−04 (±0.15)	14.0	3.35E−03
	Initial intensity[c]					
B[*a*]A	378340	5.6	Nitrogen	3.57E−03 (±0.15)	3.24	3.80E−03
	356610		Synthetic air	1.23E−03 (±0.06)	9.37	1.31E−03
	299150		Oxygen	2.50E−03 (±0.11)	4.62	2.66E−03
	388630	7.6	Nitrogen	1.79E−03 (±0.10)	6.46	1.91E−03
	319210		Synthetic air	1.14E−03 (±0.07)	10.2	1.21E−03
	283420		Oxygen	1.15E−03 (±0.04)	10.0	1.23E−03
D[*a*,*h*]A	348630	5.6	Nitrogen	4.32E−04 (±0.04)	26.8	2.53E−03
	316000		Synthetic air	4.12E−04 (±0.03)	28.0	2.42E−03
	304150		Oxygen	4.76E−04 (±0.04)	24.3	2.79E−03
	251840	7.6	Nitrogen	2.74E−04 (±0.03)	42.2	1.61E−03
	276350		Synthetic air	3.79E−04 (±0.02)	30.5	2.22E−03
	257530		Oxygen	4.09E−04 (±0.03)	28.3	2.40E−03

[a] PAHs irradiated at 254 nm in aqueous solutions at pH 5.6 and 7.6, purging with nitrogen, synthetic air or oxygen 0.2 $dm^3\,min^{-1}$; *c*: concentration.
[b] Analysed by GC/MS.
[c] Obtained with the fluorometer; by GC/MS under the detection limit.

pH values of 5.6 and 7.6 in water. The initial concentrations of benz[*a*]anthracene and dibenz[*a*,*h*]anthracene and the concentrations of anthracene and pyrene at the end of the photolysis were under detection limit of GC/MS. Hence, the extent of benz[*a*]anthracene and dibenz[*a*,*h*]anthracene prior to irradiations are presented in Table 1 as relative fluorescence intensities.

The photodegradation quantum yields presented in Table 1 are calculated by Eq. (3). For anthracene, the quantum yields are approximately two orders of magnitude higher compared with the previously obtained value. Zepp and Schlotzhauer [14] reported the quantum yield of 3.0×10^{-3} for anthracene in air-saturated water irradiated at 366 nm. It has been suggested that when organic compounds in solutions are irradiated at $\lambda<300$ nm, the rates of photodegradation can be an order of magnitude higher than those obtained at longer excitation wavelengths [9]. In the present study, a suggestion of such a tendency was observed only for anthracene.

The quantum yields for pyrene degradation agree quite well with previously observed values. Zepp and Schlotzhauer [14] reported the quantum yield for pyrene degradation in air-saturated water of 2.0×10^{-3} (±0.3) and 2.2×10^{-3} (±0.3) irradiated at 313 and 366 nm, respectively. Sigman et al. [17] reported that the quantum yield of pyrene in aerated water irradiated for hours at 300–400 nm was 2.11×10^{-3} (±0.14).

Mill et al. [10] reported that the quantum yields for the benz[*a*]anthracene photodegradation in aerated water (1% acetonitrile) irradiated at 313 nm and at 366 nm were 3.2×10^{-3} and 3.4×10^{-3}, respectively. These values are in good agreement with the values obtained in the present study.

There is limited information on photolysis of dibenz[*a*,*h*]-anthracene in aqueous solutions. Sanders et al. [18] irradiated dibenz[*a*,*h*]anthracene in acetonitrile on an exposure table unit and obtained rate constant of $1.6\times10^{-5}\,s^{-1}$ for the photodegradation. Low et al. [9] observed that the degradation rate constant for D[*a*,*h*]A at 254 nm was $1.7\times10^{-5}\,s^{-1}$ in acetonitrile and $3.2\times10^{-4}\,s^{-1}$ in methanol. The latter value determined in polar methanol is consistent with the rates we obtained in water.

3.2. *The oxygen and pH effects*

Oxygen concentration had minor or inconsistent effect upon the photodegradation rates of PAHs. It has been suggested that the primary photochemical processes in water may not involve molecular oxygen [14]. The solubility of the gas has been proposed to be limited in polar water [12]. Experimentally, singlet and triplet states can be effectively quenched by molecular oxygen. The ubiquitous nature of O_2 as a quencher may contribute to the decay of any excited state that has a fairly long lifetime. Under room atmosphere, the concentration of O_2 in typical organic solvents is $\sim 10^{-3}$ to 10^{-4} M. In water (20°C), the concentration of O_2 is 2.65×10^{-4} M and it has a diffusion constant, k_{diff}, 6.5×10^{9} M^{-1} s^{-1} [19,20]. Though, the greatest differences in the rate constants were observed for B[*a*]A, only in the case of pyrene the influence of oxygen concentration on the mutual gradation of the rate constants was consistent at both pHs (Table 1). For pyrene, the highest values were obtained by purging with synthetic air, then with nitrogen, and the lowest rates were observed by oxygen purge but the differences were small, 20% at the most.

In agreement with our observations, Sigman et al. [17] observed that removal of oxygen by argon purge slowed the photodegradation of pyrene compared to photolysis in air-saturated water. Mill et al. [10] reported surprisingly small effect of oxygen in most cases when eight PAHs, excluded pyrene, were photolysed at 313 nm and at 366 nm in water. Zepp and Schlotzhauer [14] studied the removal of dissolved oxygen in water on the photolysis rate only of 9-methylanthracene and detected no influence by degassing.

Though the operating pH range was quite narrow, a clear tendency was observed. The rate constants at pH 5.6 were a little higher than those at pH 7.6. Only in the case of anthracene, opposite results were obtained. The influence of pH was greatest for B[*a*]A; purging with oxygen, k_r was 2.2 times higher at pH 5.6 compared with that at pH 7.6. Only few studies have included the effect of pH on the photodegradation rate of PAHs. Bekbölet et al. [21] studied the effects of pH between 3 and 11 on photocatalytic detoxification of a biologically pre-treated landfill leachate. Their results showed that the concentration change of the UV-absorbing compounds, i.e. aromatics, was the lowest at pH 7. In general, the highest degradation rate was observed between pH 3 and 7 with a maximum at pH 5.

3.3. Reactive state

The fluorescence decay curves measured by a single-photon-counting method are shown in Fig. 3. Rate parameters in organic solvents followed the first-order kinetics. For the fluorescence rate parameters in aqueous solutions two-exponential decay functions were needed. The decays of anthracene and benz[*a*]anthracene were clearly at least two-exponential. For pyrene one-exponential fitting of the decay curve led to χ^2-value of 1.58, but two-exponential to a value of 1.10. For dibenz[*a,h*]anthracene, clear fluorescence formation was observed. In addition, one-exponential fitting

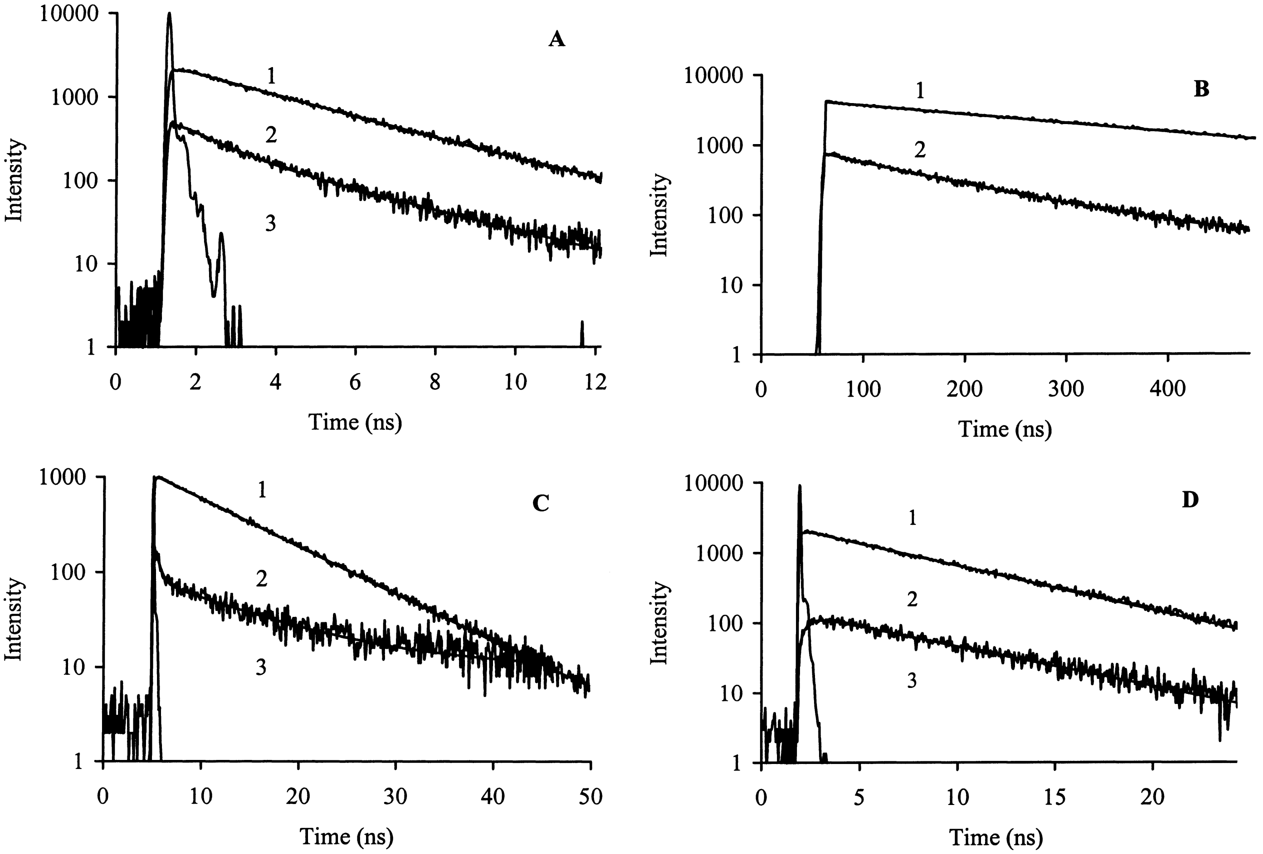


Fig. 3. Fluorescence decays and the fitted curves for (A) anthracene; (B) pyrene; (C) benz[*a*]anthracene; and (D) dibenz[*a,h*]anthracene in (1) organic solvents and (2) aqueous solutions together with (3) the instrumental response function. The excitation wavelength was 300 nm and the fluorescence decay curves were monitored at 405 nm, except for dibenz[*a,h*]anthracene in aqueous solution for which monitoring wavelength of 470 nm was used.

Table 2
Fluorescence rate parameters for PAHs in aqueous solutions, k_1 and k_2, and in organic solvent, k_d, and the χ^2-values of the fits[a]

	Anthracene	Pyrene	B[*a*]A	D[*a*,*h*]A
k_1 (s^{-1})	(2.68±0.19)E+08	(3.86±0.72)E+06	(9.43±2.47)E+07	(1.32±0.16)E+08
(%)	75.0	55.4	92.0	96.3
k_2 (s^{-1})	(9.23±1.31)E+08	(9.72±0.87)E+06	(2.07±0.08)E+09	(2.70±0.80)E+09
(%)	25.0	44.6	8.00	3.7
χ^2	1.16	1.10	1.10	0.98
k_d (s^{-1})	(3.10±0.06)E+08[b]	(2.30±0.04)E+06[b]	(1.16±0.01)E+08[c]	(1.46±0.02)E+08[c]
χ^2	1.11	1.04	0.94	21.07

[a] The decays in aqueous solutions were two-exponential and the proportion of the components are given as (%).
[b] In hexane.
[c] In chloroform.

gave χ^2-value of >1.2 for this compound. The rate parameters in water and in organic solvents and the χ^2-values of the fits are illustrated in Table 2.

In water, the observed apparent lifetimes, $\tau_{\text{app}}=k_1^{-1}$, varied from nanoseconds to hundreds of nanoseconds, depending on the PAH, and were very close to the lifetimes measured in organic solvents. If the reactive state would be the singlet excited state of a PAH, the quantum yields, $\phi_{\text{Pr}}=k_r\tau_{\text{app}}$, calculated from the obtained k_r and τ_{app} values listed in Tables 1 and 2, respectively, would differ order(s) of magnitude from the quantum yields obtained by photoirradiation (Table 1). Also the triplet states of the PAHs having lifetimes about 100 μs in a room temperature [22–24] would not be sufficiently long-lived for the relatively high quantum yields obtained. Furthermore, for naphthalene and pyrene in water, the involvement of the triplet state of the PAHs in the reaction has been ruled out [17,25]. Thus, in the present study, the singlet and triplet state reactions can be rejected.

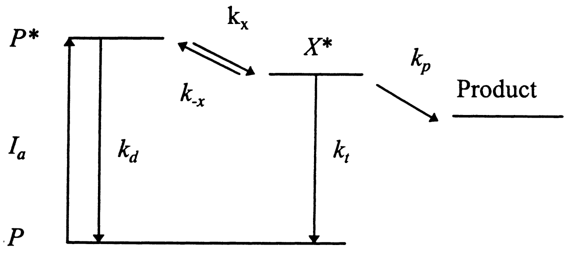
A two-exponential fluorescence decay is often an indication of an equilibrium between an emissive and a transient states. The decay of the pyrene emission, for example, at high concentration (>10^{-5} M) in organic solvents is two-exponential due to an excimer formation [19]. In aerated conditions, an electron transfer from the excited singlet state of naphthalene and pyrene to molecular oxygen in a contact charge-transfer pair has been suggested [17,25]. In a variety of degassed solvents and concentrated solutions, anthracene undergoes a photochemical 9,10,9′,10′-cycloaddition which proceeds through an excimer as intermediate [26,27]. Many aromatic molecules follow similar cycloaddition paths. Imminence of the molecules in the excimer is essential for bond formation, and steric hindrance can prevent the reaction. Unsubstituted anthracene dimerises so fast that no excimer fluorescence can be detected, whereas its derivative 9,10-dimethylanthracene shows both excimer fluorescence and photodimerisation, but 9,10-diphenylanthracene shows neither excimer emission nor photodimerisation [27].

For anthracene in the presence of air, especially in dilute solutions, photodimerisation occurs in competition with photooxidation leading to endoperoxide [26,28]. Detailed studies have shown that continued irradiation of anthracene and endoperoxide in solution ultimately leads to diones [29]. Since oxygen is ineffective in most photolyses, in aqueous solutions oxygen in the observed products has been suggested to come from water, perhaps via a radical–cation intermediate [10]. With the excitation wavelengths used in the present study, no detectable changes in the shape of the fluorescence spectra upon photoirradiation were observed. Furthermore, no new peaks indicating the formation of photodegradation intermediates were detected by GC/MS probably also due to the low concentration of the initial compounds.

The presence of excimer type intermediates have been proposed in a variety of aromatic involving photoreactions, such as photocyanation, photocycloaddition and photorearrangement reactions [26,30–32]. Thus, the most simple scheme for the behaviour observed in the present study, involving a non-emissive excited state X^* in equilibrium with the excited singlet state, is proposed (Scheme 1).

In Scheme 1, I_a is the absorbed light intensity, k_d is the sum of the rate constants of fluorescence and non-radiative decays, k_t is the rate constant of the decay of the intermediate, X^* k_p is the rate constant of the photodegradation reaction, and k_x and k_{-x} are the rate constants for the formation and the dissociation of the intermediate, X^*.

In Scheme 1, k_d can be assumed to have the same value that was obtained from the fluorescence decays in organic solvents. The actual rate constants, k_x and k_{-x}, can be calculated by applying Scheme 1 and the experimental



Scheme 1.

Table 3
Calculated rate constants, k_x and k_{-x}, obtained by applying Scheme 1 and the experimental values to Eq. (5)[a]

	Anthracene	Pyrene	B[*a*]A	D[*a,h*]A
k_x (s^{-1})	1.14E+09	7.76E+06	1.95E+09	2.25E+09
k_{-x} (s^{-1})	0.23E+09	4.25E+06	1.03E+09	1.20E+09
ϕ_x	0.78	0.77	0.94	0.94
ϕ_p	0.23	5.63E−03	1.39E−03	2.58E−03
k_p (s^{-1})	5.33E+07	2.39E+04	1.43E+06	3.09E+06

[a] The quantum yield for the formation of the intermediate X^*, ϕ_x, the quantum yield for the product formation, ϕ_p, and the rate constant for the product formation, k_p, are calculated from Eqs. (6–8).

two-exponential decay constants, k_1 and k_2 (Table 2), to a model equation first deduced by Birks et al. [33]:

$$k_{1,2} = \frac{1}{2}\{(A+B) \pm [(A-B)^2 + 4k_x k_{-x}]^{1/2}\} \quad (5)$$

where $A=k_d+k_x$, $B=k_p+k_t+k_{-x}$. Thus, the quantum yield for the formation of the intermediate X^* ϕ_x, can be calculated by Eq. (6):

$$\phi_x = \frac{k_x}{k_x + k_d} \quad (6)$$

by using the calculated k_x-value and the experimental singlet state decay constant k_d.

Knowing the photodegradation quantum yields ϕ_{Pr} (Table 1) and the values of ϕ_x, the quantum yield for the product formation, ϕ_p, can be calculated by Eq. (7):

$$\phi_{Pr} = \phi_x \phi_p \quad (7)$$

Furthermore, the rate constant for the product formation, k_p, can be obtained by the relation

$$\phi_p = \frac{k_p}{k_p + k_{-x}} \quad (8)$$

assuming that $k_p \gg k_t$. The obtained rate constants and quantum yields are summarised in Table 3. The rate constants, k_x, for the formation of the intermediate X^* are in all cases higher than the rate constants, k_{-x}, for their dissociation, and are approximately one order of magnitude higher compared with the monomer decay, k_d, in organic solvents. For pyrene both rates, however, are the same order of magnitude.

4. Conclusions

The fluorescence techniques were successfully used for monitoring the decomposition of PAHs in dilute aqueous solutions; the apparent rate constants and quantum yields for the photodegradation reaction were determined. Photolysis was most rapid for anthracene and benz[*a*]anthracene. Due to the ubiquitous nature of molecular oxygen, it requires a fairly long lifetime to quench the decay of the excited state [19]. In the present study, O_2 was only able to effect on the rate constants of pyrene. When rate constants were compared at different pHs, the values were higher at pH 5.6 than those at pH 7.6, anthracene being the only exception of this.

Since in the time resolved fluorescence measurements two-exponential decays were observed in water, the presence of a non-emissing excited specie as an intermediate for the photodimerisation was suggested. A model was proposed for determining the actual rate constants for the individual steps of the reaction scheme. The actual rate constants, k_x and k_{-x}, in Scheme 1 illustrate the formation and dissociation of the intermediate X^*.

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