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Degradation of pyrene by UV radiation

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Abstract

The photodegradation of pyrene (Py) in the presence of acetic acid (AA) occurs through a radical mechanism and is faster than in organic solvents (methanol). $PyH^{\bullet}$ (absorption maximum in the UV/VIS spectra λ_{max}=395 nm in AA, lifetime τ=~2 μs in oxygen saturated solution) was identified as an intermediate in the photodegradation in AA. Absorption of a photon by ground state of Py also leads to the formation of excited states ($^1Py^*$ and ^3Py), which deexcite to the ground state without chemical changes. Singlet oxygen $^1O_2$ formed by energy transfer from ^3Py to dissolved oxygen does not react with Py. $PyH^{-\bullet}$ and $PyH^{+\bullet}$ were not found following excitation under the given conditions. The rate of photodegradation can be considerably increased by addition of water and hydrogen peroxide. The accelerating effect of hydrogen peroxide consists in photolytic formation of reactive hydroxyl radicals, which attack the pyrene nucleus. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Pyrene; Degradation; Laser kinetic spectroscopy

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) and their derivatives constitute one of the largest groups of chemical carcinogens and mutagens [1]. These are primarily anthropogenic pollutants that enter nature from industrial exhalations. The chief sources of PAH consist of household heating by coal, coal-fired power stations, automobile traffic, cigarette smoke and emissions from waste incineration plants. PAH with polar substituents were found in natural waters; the less polar compounds are important contaminants in sediments, soils and sludges [2]. The enhanced phototoxicity of PAH consists in the formation of reactive oxygen species via energy transfer from excited PAH states, which produce toxicity through oxidative stress [3]. Consequently, there is an increasing demand for the determination of trace concentrations of these substances and removal from the natural environment.

Several methods based on chemical destruction of very stable PAH have been proposed and tested [4]. These methods are based on chemical oxidation, e.g. using potassium permanganate in acidic and alkaline media, using concentrated sulfuric acid or by direct ozonation or catalytic oxidation methods. Although UV radiation in small amounts, e.g. in sunlight, can lead to increased toxicity of PAH and the formation of more toxic species, irradiation with artificial sources with higher power in the presence of radicals could lead to decomposition of the benzene rings. Methods based on photolytic degradation could be both effective and easy. In addition, information on the photolytic destruction of environmental carcinogens obtained during the development of these methods can be useful in the elucidation of the fate of these substances in the environment.

This paper is concerned with the effect of the surrounding medium (solvent) on the rate and mechanism of the photochemical degradation of pyrene (Py) as a model compound of the PAH group. Attention is paid to the initial phase of the process (to several μs following absorption of a photon), when the very stable aromatic skeleton of Py is broken. The mechanisms of photodegradation are studied primarily by methods of time-resolution spectroscopy, which permit monitoring of the individual intermediates formed following excitation of Py.

2. Material and methods

Pyrene, methanol, hydrogen peroxide and acetic acid (AA) (all Lachema, Czech Republic) were used as received. 1–500 μM solutions of Py were irradiated in a stirred

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1 cm × 1 cm quartz cuvette by continuous or pulse UV radiation. A 900 W Xenon discharge lamp with a monochromator was used for the continuous irradiation (irradiation wavelength 324±18 nm, power 30 mW, Applied Photophysics, UK). The initial rate constants k_{deg} of the photodegradation of Py were calculated from the decrease in the absorbance at wavelengths of 320 and 334 nm, assuming that there is no interference from the absorption bands of pyrene and photodegradation products. The UV/VIS absorption spectra were measured using Perkin–Elmer Lambda 10 and Pye Unicam SP8-400 spectrometers. The laser kinetic spectrometer (Applied Photophysics) and the details of procedures for measuring the time-resolved absorption and emission spectra have been described in previous papers [5,6]. A Lambda Physik LPX 205 excimer laser (308 nm, pulse length 28 ns, energy of up to 9 mJ/pulse) was used for pulse excitation and irradiation. Oxygen was removed from some of the air-saturated samples by purging with an inert gas (argon or nitrogen).

3. Results and discussion

The Py molecule with benzene rings and high symmetry (Fig. 1) is photostable in organic solvents, including methanol (Table 1). Direct photolysis of Py in organic solvents occurs according to the literature data [7] only from the highly excited triplet states by a radical mechanism. Single-photon excitation to such energy-rich states requires radiation with a wavelength less than 200 nm, which is hard to obtain in the laboratory and practically does not occur in nature. Similarly, direct ionization of Py (ionization potential 7.0 eV) by UV radiation with wavelength greater than 300 nm could occur only by a multiphoton mechanism.

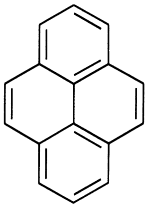


Fig. 1. Structure of Py molecule.

Table 1
Initial rate constant k_{deg} of the photodegradation of a 50 μM Py solution by UV radiation (324±18 nm) in various solvents

Solvent	10^5 k_{deg} [s^{-1}]$^{\mathrm{a}}$
Methanol	5.56
AA	22.2
AA (75%), H_2O (25%)	104
AA (50%), H_2O (50%)	117
AA (25%), H_2O (75%)	105
AA (25%), H_2O (75%) saturated by nitrogen	12.3
AA, H_2O_2 (0.5 mM)	25.4
AA, H_2O_2 (5 mM)	44.5
AA, H_2O_2 (50 mM)	181
AA(25%), H_2O (75%), H_2O_2 (0.5 mM)	104
AA(25%), H_2O (75%), H_2O_2 (5 mM)	191
AA(25%), H_2O (75%), H_2O_2 (50 mM)	366

[a] Estimated error±10%.

Absorption of (a single) photon by the ground state of Py leads to the formation of excited singlet and triplet states (Eq. (1)) and singlet oxygen $O_2(^1\Delta_g)$ (Eq. (2), (3)) with high quantum yields [8,9].

$$\mathrm{Py}\xrightarrow{h\nu}{}^1\mathrm{Py}^*\xrightarrow{\mathrm{ISC}}{}^3\mathrm{Py} \tag{1}$$

$$^1\mathrm{Py}^*\xrightarrow{^3\mathrm{O}_2}\mathrm{O}_2(^1\Delta_g) \tag{2}$$

$$^1\mathrm{Py}\xrightarrow{^3\mathrm{O}_2}\mathrm{O}_2(^1\Delta_g) \tag{3}$$

Because of the low power of the radiation (30 mW), multi-photon processes can be neglected in continuous irradiation. Similarly, multiphoton processes are not probable also in pulse spectroscopic measurements, as the instantaneous power density does not exceed $10^5\ \mathrm{W\,cm^{-2}}$ in a 28 ns pulse.

Absorption spectrum of Py is characterized by three strong bands in the UV region: ~334, ~320 and ~307 nm, used to monitor the degradation (Fig. 2a). Py is insoluble in water, but soluble in AA, a mixture of AA with water and in organic solvents, e.g. methanol. The rate constant of photodegradation of Py (k_{deg}) measured on the basis of the decrease in absorbance at 320 nm, is four times higher in AA and about 20 times higher in AA/water mixture than in methanol (Table 1). The photodegradation products are different in these two cases: in methanol, primarily products absorbing in the UV region are formed (Fig. 2b), while products, apparently of the quinone type, absorbing in the 400–500 nm region are formed in the presence of AA (Fig. 2c).

The quantum yield of singlet oxygen Φ_Δ from pyrene in methanol is greater than 0.6 [9]. Thus, if O_2 ($^1\Delta_g$) is formed only in processes (2) and (3) ($\Phi_\Delta \leq 1$), the increase of k_{deg} in 25% AA and 75% H_2O by 20 times (Table 1) cannot

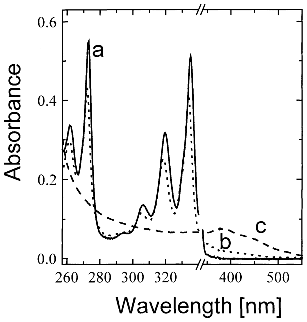


Fig. 2. UV/VIS spectrum of 12 μM Py solution in AA in the presence of hydrogen peroxide (1:1) prior to (a) and following (c, dashed line) absorption of 15 J laser radiation from an XeCl laser (λ = 308 nm). For comparison, a similar spectrum in methanol following absorption of the same energy is depicted (b, dotted line).

be explained. Moreover, the lifetime of singlet oxygen in water (~3–4 μs) is shorter than in methanol (~9–11 μs) [9]. For this reason, Py in the ground state, ^{1}Py* and ^{3}Py do not significantly react with O_2 in either the ground state or in the excited $^1\Delta_g$ state. Simultaneously, it is known that O_2 ($^1\Delta_g$) is an important mediator in photochemical and photobiological oxidations [10].

It follows from the shape of the bands in the UV/VIS spectra that a number of final products are formed during the photolysis process. The individual intermediates formed following absorption of photons can be monitored with time resolution on the basis of their characteristic bands between 400–500 nm where ground state of Py does not absorb. The absorption spectra of the unstable species formed by photolysis and radiolysis of pyrene in organic solvents are not greatly affected by the solvent and are well described in the literature: ^{3}Py (absorption maximum $\lambda_{\max}$=~415 nm) [11], radical cation $Py^{+\bullet}$ (~465 nm) [11], radical anion $Py^{-\bullet}$ (~460 nm) [12], and radical $PyH^\bullet$ (~405 nm) [13]. ^{1}Py* can be identified on the basis of emission spectra with maximum at 390 nm. The formation of excimers (Py. . . Py)* (broad emission band at 460 nm) is significant at Py concentrations greater than 50 μM.

Continuous or pulse irradiation yielded products with identical UV/VIS spectra and the same order of relative k_{deg} values. ^{3}Py was identified in differential absorption spectra following excitation by a laser pulse (λ_T=415 nm, lifetime $\tau_T = 260$ ns in air-saturated solution, quenched by oxygen to form $^1O_2$, Fig. 3b). The second intermediate is the pyrene radical, apparently $PyH^\bullet$ (λ_R=395 nm, lifetime τ_R=2 μs in oxygen saturated AA, Fig. 3a). The shift in the absorption maximum to lower wavelengths by 10 nm is apparently caused by the higher polarity of the solvents (acetic acid, water) than those used in Ref. [13]. $Py^{+\bullet}$ and $Py^{-\bullet}$, which absorb at higher wavelengths, were not found in the spectra (Fig. 3) and do not significantly affect the radical mechanism of degradation.

Because of the high quantum yields of ^{3}Py [8] and the similar lifetimes of ^{3}Py and $PyH^\bullet$ in air-saturated and argon purged AA, the band of $PyH^\bullet$ is overlapped by the band of ^{3}Py. The different reactivities of these two species can be observed in oxygen-saturated AA (Fig. 4), where lifetimes of ^{1}Py* and ^{3}Py are less than 100 ns. At times longer than 1 μs following the laser pulse, the concentration of Py no longer increases in the ground state formed by deexcitation of ^{1}Py* and ^{3}Py (see points A in Fig. 4a). The absorbance at longer times ΔA_∞ is constant and less than absorbance before absorption of radiation. These changes are caused by the decrease in concentration of ground state of Py and formation of products absorbing at higher wavelengths. Thus, $PyH^\bullet$, which is still present on the microsecond time scale, decomposes further to form products or reacts with AA in a radical reaction, but *not* with formation of the ground state of Py. At times longer than 8 μs, ΔA_∞ no longer changes at a wavelength of 390 nm (absorption band of $PyH^\bullet$). The increase in absorbance ΔA_∞ compared to the value prior to the laser pulse is caused by the formation of the final products (Fig. 2c). The first chemical processes (breakdown of benzene ring) in degradation of Py are, thus, terminated within a time period of 10 μs after photon absorption.

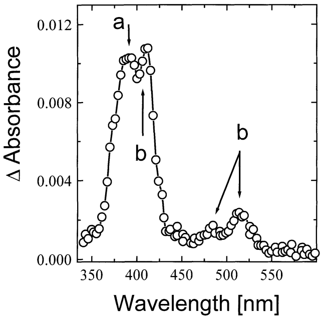


Fig. 3. Changes in the UV/VIS absorption spectrum of 8 μM Py in air-saturated AA, 100 ns following excitation by a laser pulse, the individual bands were assigned as $PyH^\bullet$ (a) and ^{3}Py (b).

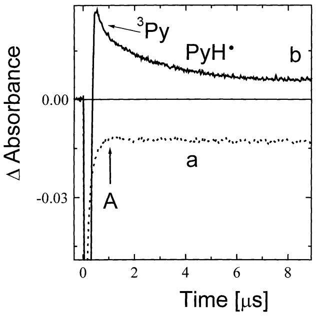
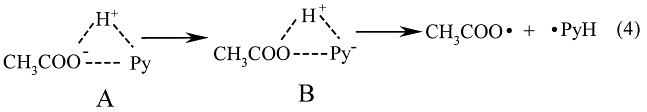


Fig. 4. Changes in the absorbance in time following the laser pulse at a wavelength of 334 nm (absorption band of ground state of Py) (a) and at a wavelength of 390 nm (^{3}Py and $PyH^\bullet$) (b), in oxygen-saturated AA. **A** designates the time when ^{1}Py* and ^{3}Py are not present in the solution (~1 μs after the laser pulse).

The single-exponential decomposition kinetics in oxygen saturated AA (Fig. 4b) indicates that $PyH^\bullet$ is no longer formed at time intervals longer than 500 ns after the laser pulse. At shorter times, the $PyH^\bullet$ band is overlapped by the ^{3}Py band and the intense fluorescence of ^{1}Py*, and thus we can only speculate on the mechanism of the formation of $PyH^\bullet$. Charge-transfer complexes of Py and the anhydride of organic acids (An), whose excitation and subsequent decomposition lead to the formation of ion pairs Py^- and An^+, are described in the literature [14]. Similar formation of ion pairs between Py^- and AA^+ could also be expected in the case of excitation of Py-AA complexes. Process of PyH formation could involve (a) formation of the excited Franck–Condon state of the charge-transfer complexes, (b) charge redistribution within the complex (formation of complexes of types A and B) and (c) subsequent dissociation with formation of $PyH^\bullet$ (Eq. (4)).



$$\underset{A}{\overset{H^+}{CH_3COO^{-}\text{----}Py}} \longrightarrow \underset{B}{\overset{H^+}{CH_3COO\text{----}Py^{-}}} \longrightarrow CH_3COO\bullet + \bullet PyH \qquad (4)$$

This process should be complete within hundreds of ps [14]. Reaction (4) could be the cause of the elevated rate constants for photodegradation of Py in AA/water solutions (Table 1). Similar to in AA, a charge-transfer complex between Py and AA is formed in the presence of water, as the concentration of AA still greatly exceeds the concentration of Py. Charge redistribution and the formation of A and B intermediates should be facilitated by the presence of polar water molecules.

The formation of $CH_3COO^\bullet$ and $^\bullet$PyH free radicals is the beginning of a chain reaction leading to decomposition of the benzene ring(s) of the pyrene chromophore and formation of polymer chains in the final stage of the radical reaction (see the UV/VIS spectra offset, Fig. 2c). In radical reactions, it can also be expected that the radicals will react with O_2, which will lead to the formation of unstable peroxide compounds (Eq. (5)).

$$^\bullet\mathrm{PyH} + \mathrm{O_2} \rightarrow {}^\bullet\mathrm{PyOOH} \qquad (5)$$

Reaction (5) can be important, as a significant decrease in k_{deg} was found in AA purged by inert gas (Table 1) and oxidation of Py by O_2 ($^1\Delta_g$) does not occur (see above). Following decomposition of the pyrene skeleton and the formation of less stable products than Py itself, the remaining Py can act as a sensitizer. The transfer of energy from ^{1}Py* and ^{3}Py to the less stable product molecules can lead to further decomposition. Similarly, attack of O_2 ($^1\Delta_g$) especially on the double bonds of the product, can be expected. In solutions saturated in air and oxygen, the final products could be CO_2 and H_2O. However, in solutions following long irradiation, the concentration of Py decreases, along with the absorbance in the UV region (300–400 nm). An increase in the efficiency of the photodegradation of Py in the final stages would require the use of a different sensitizer, that would absorb the UV radiation, that is stable, transfers its energy to the products and has a high quantum yield of singlet oxygen.

The k_{deg} value can be substantially increased by addition of hydrogen peroxide (Table 1), which can supply during irradiation hydroxyl radicals $OH^\bullet$. Systems containing benzene rings react with $OH^\bullet$ radical with a diffusion-controlled rate constant of $\sim10^9$–$10^{10}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ [15]. Unstable radicals are formed and further decomposed with opening of a benzene ring. $OH^\bullet$ can be generated by direct photolysis of H_2O_2 by UV radiation (wavelength less than 340 nm) or sensitized transfer of energy from the excited singlet state of Py to the H_2O_2 molecule. In the presence of traces of iron, the Fenton reaction (Eq. (6)) can also lead to the formation of $OH^\bullet$:

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)} + \mathrm{OH^-} + \mathrm{OH^\bullet} \qquad (6)$$

The products of the photodegradation of Py in the presence of hydrogen peroxide have similar absorption spectra to the photodegradation of Py alone. This fact also indirectly supports the radical mechanism of the reaction of Py in AA.

The photochemical method described in this paper, based on irradiation by UV lamp in the presence of acetic acid and/or hydrogen peroxide, is suitable for degradation of fused benzene ring(s) and thus can be effective also for degradation of other compounds from PAH groups. Formation of radicals in polar environment of AA in combination with attacks of $OH^\bullet$ radicals can significantly multiply rate of photochemical degradation in comparison with less polar media.

Acknowledgements

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