



Photodegradation of 1-nitropyrene in solution and in the adsorbed state

Alexander Muck^a, Pavel Kubát^b, Anabela Oliveira^c,
Luis Filipe Vieira Ferreira^c, Josef Cvačka^d, Svatopluk Civiš^{b,*},
Zdeněk Zelinger^b, Jiří Barek^a, Jiří Zima^a

^a UNESCO Laboratory of Environmental Electrochemistry, Department of Analytical Chemistry,
Charles University, 128 43 Praha 2, Czech Republic

^b J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,
Dolejškova 3, 182 23 Praha 8, Czech Republic

^c Centro de Química-Física Molecular, Instituto Superior Técnico, Universidade Técnica de Lisboa.,
Complexo Interdisciplinar, Av. Rovisco Pais 1049-001, Lisboa, Portugal

^d Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,
Flemingovo namesti 2, 166 10 Prague 6, Czech Republic

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Abstract

The photodegradation of the 1-nitropyrene (NPY) has been studied using conventional (Xe and medium pressure Hg lamps) and laser sources (XeCl excimer and Nd-YAG UV). Low energy monochromatic light sources were used to study the early stages of degradation (up to 50% conversion). The medium pressure Hg lamp was used for longer periods of irradiation (up to 6 h) and for greater degradation of NPY. The results of our work confirm that degradation occurs by radical mechanism. Aromatic hydroxymethyl, methoxy, hydroxy and nitroso derivatives of pyrene (Py) are created by low energy UV irradiation. After a massive UV irradiation, the Py aromatic system is destroyed and more polar low-molecular compounds are generated. The photochemical method described in this paper, based on irradiation by UV lamp, is therefore, suitable for degradation of fused benzene ring(s) and thus should also be effective for degradation of other nitrated polycyclic aromatic compounds.

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* Corresponding author. Tel.: +420-2-66-053085; fax: +420-2-8591766.

E-mail address: civis@jh-inst.cas.cz (S. Civiš).

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives constitute one of the largest groups of chemical carcinogens and mutagens [1,2]. The increased interest in nitrated polycyclic aromatic hydrocarbons (NPAHs) dates from the work of Jäger [3] and Pitts et al. [4], who independently found out that PAH may react with nitrogen oxides with the formation of NPAH, under conditions that can be expected in a polluted environment and/or with combustion processes [5–7]. Hence, NPAH are often found in the industrial and general environment especially in ambient, urban and work-place air, diesel and petrol engine exhausts, exhausts from industrially important combustion processes, cigarette smoke, and in drinking, water rain, surface and waste waters [8,9]. Moreover, NPAH can be formed via atmospheric reactions either by light initiated reaction of PAH with hydroxyl radicals followed by NO₂ addition and elimination of H₂O or by reaction with N₂O₅, which prevails at night. These two radical reactions generally lead to products with different position of a nitro group than in products of normal electrophilic substitution. NPAH can be also formed in soil from parent PAH and various nitrogen sources under light irradiation [10].

The development of methods suitable for destruction of NPAH and their metabolites and for decontamination of laboratories working with these substances is a prerequisite for any large-scale monitoring involving a greater number of analytical laboratories and it is strongly recommended by the International Agency for Research on Cancer. Methods based on photolytic degradation could be both effective and easy to implement. In addition, information on the photolytic destruction of environmental carcinogens obtained during the development of these methods can provide useful information for clarifying the fate of these substances in the environment.

Photodegradation of NPAHs was investigated recently in simple models of organic aerosols [11]. The results show that photodegradation is significantly accelerated by the presence of anthraquinone, an atmospherically relevant photochemical radical sensitizer. Our results [12] also show that photodegradation of nonsubstituted pyrene (Py) in solution of acetic acid (AA) occurs by a radical mechanism, which is accelerated by the presence of hydroxyl radicals. In the present studies, we selected 1-nitropyrene (NPy) as a model compound of the NPAH group and considered the effect of the surrounding medium (solvent, oxidant) on the rate and mechanism of the photochemical degradation of NPy in solution and in the adsorbed state. We found that long irradiation of samples containing NPy by UV photons initiates radical reactions that lead to the destruction of the aromatic skeleton and to the formation of low-molecular products.

2. Experimental

1-Nitropyrene (97%, Sigma–Aldrich), cellulose (microcrystalline cellulose powder, Fluka DS-0), methanol (HPLC-grade, Sigma–Aldrich), hydrogen peroxide and AA (all Lachema, Czech Republic), TiO₂ (anatase structure, Lachema p.a.) and TiO₂ (P25, Degussa) were used as received. The 1×10^{-6} to 1×10^{-3} M solutions of NPy in methanol were irradiated by continuous or pulse UV radiation while stirring in a quartz cell of 1 cm width. Samples of NPy adsorbed on cellulose were prepared by evaporation of solvent from cellulose–NPy–(TiO₂,

H₂O₂)–solvent mixture and irradiated in a quartz cuvette of 0.2 cm width. This technique was described in detail elsewhere [13].

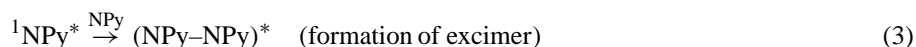
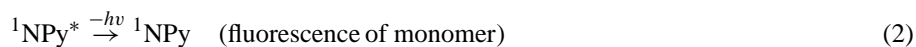
Four irradiation sources were used to study the degradation process. A Lambda Physik LPX 205 excimer laser (308 nm, pulse width 28 ns, energy of up to 100 mJ per pulse) for experiments in solution and Nd-YAG laser (B.M. Industries, Thomson-CSF, model Saga 12–10, 355 nm, 5 ns pulse width, energy up to 350 mJ per pulse) for degradation of NPy adsorbed on cellulose were used for pulse excitation and irradiation. A 900 W xenon discharge lamp with a monochromator (irradiation wavelength 324 ± 18 nm, power 30 mW, Applied Photophysics, UK) was selected for continuous irradiation. These three monochromatic light sources were used for irradiation to obtain a semiquantitative description of the early stages of photodegradation (up to 50% conversion). We also used a medium pressure mercury lamp without monochromator for longer irradiation and “deeper” degradation of NPy. The UV–VIS absorption spectra were measured using a Perkin-Elmer Lambda 19 and a Pye Unicam SP8-400 spectrophotometers. The laser flash photolysis apparatus for measurement in a transmission (Applied Photophysics) and in a diffuse reflectance arrangement [13], and the details of procedures for measuring the time-resolved absorption and emission spectra have been described in previous papers [13–15]. Resonance light-scattering (RLS) experiments were conducted using simultaneous scans of the excitation and emission monochromators of a Perkin-Elmer LS 50B luminescence spectrophotometer. Oxygen was removed from some of the air-saturated samples by purging with an inert gas (argon or helium).

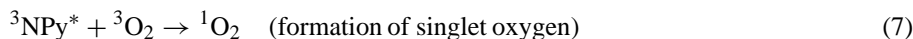
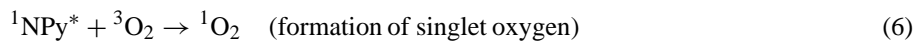
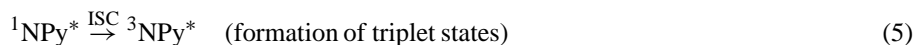
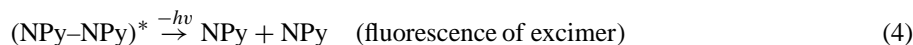
P 4000 pump, SCM 1000 vacuum degasser (all Finnigan Inc.) and analytical high performance liquid chromatography (HPLC) column LiChrospher[®] 100 RP-18, 5 μ m, 125 \times 4 mm i.d. (Merck) were used for chromatographic separation of irradiated samples in methanol–water (85:15 (v/v)) mobile phase. Isocratic mode was used for analysis, the flow rate was 0.5 ml min⁻¹ and 20 μ l of methanolic solution was sampled. An LCQ mass spectrometric detector equipped with an ion-trap analyser, atmospheric pressure chemical ionization and UV 6000 LP diode array UV spectrometric detector were used for detection (all Finnigan). The mass spectrometer worked in a full-scan mode with $m/z = 50$ –1000 Da range of analyzed ions. The capillary was heated to 200 °C, temperature of evaporator was set at 475 °C, ionization time was 5 ms with 6 kV high voltage power supply, 37 V on capillary.

3. Results and discussion

3.1. Photodegradation of NPy in solution

The principal photophysical processes occurring in Py derivatives after absorption of photons are well described in the literature [16] (Eqs. (1)–(7)).





Any of these processes (Eqs. (1)–(7)) does not lead to direct photodegradation of Py derivative. Singlet oxygen, a well known mediator of photochemical reactions does not significantly react with condensed aromatic rings [17].

The formation of free Py radicals like $\bullet\text{PyH}$ [18] or $\text{PyO}\bullet$ is the beginning of a chain reaction leading to decomposition of the fused benzene ring(s) of the Py chromophore [12,18]. Py radicals are formed with significantly lower quantum yield than products described by Eqs. (1)–(7). The process of radical formation is completed in a few picoseconds and it is facilitated in polar media such as AA. The presence of Py radicals starts a chain reaction where substitution or opening of one aromatic ring can take place. It can also be expected that the radicals will react with O_2 , which will lead to the formation of unstable peroxide compounds $\text{PyOO}\bullet$. If NPy photodegradation occurs via radical mechanisms, the presence of radical sources like H_2O_2 or anthraquinone, which start a radical chain reaction, will facilitate photodegradation [11,12].

Absorption spectrum of NPy is characterized by three well resolved vibronic absorption bands in the UV region: ~ 398 , ~ 375 and ~ 287 nm (Fig. 1a). Three irradiation sources were used for photodegradation—XeCl excimer laser, Xe lamp and medium pressure Hg lamp—all emit UV photons that are effectively absorbed by NPy. NPy is insoluble in water, but soluble in organic solvents, e.g. methanol or AA. After irradiation by UV photons in methanol or AA, absorption maxima of NPy in UV–VIS spectra were decreased and a new broadband spectrum was formed with absorption maxima below 300 nm (Fig. 1b).

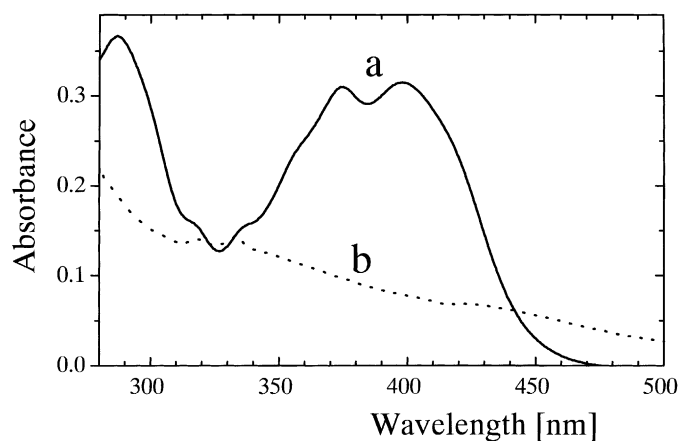


Fig. 1. Absorption spectra of 50 μM NPy in methanol before irradiation (a) and after irradiation (b) by XeCl laser (330 J in total).

Table 1
Apparent first-order decay rate constants k_{deg} of the photodegradation of a 50 μM NPy solution by UV radiation of 900 W Xe lamp in methanol and in acetic acid (AA)

Irradiated pyrene	Solvent	Rate constant (10^4 s^{-1})
NPy	Methanol	1.83
	AA	1.41
	75% AA, 25% H ₂ O	0.63
	50% AA, 50% H ₂ O	0.24
	AA, 5×10^{-4} M H ₂ O ₂	2.8
	AA, 5×10^{-3} M H ₂ O ₂	1.7
	AA, 5×10^{-2} M H ₂ O ₂	1.7
	50% AA, 50% H ₂ O, 5×10^{-2} M H ₂ O ₂	0.75
Py ^a	AA	2.2

^a From [12].

The initial rate constants k_{deg} of the photodegradation were estimated from the decrease of the NPy absorption bands. We obtained similar results (error $\pm 10\%$) calculated from the changes in the absorbance at several wavelengths between 398 and 350 nm, assuming that there is no interference between the absorption bands of NPy and the photodegradation products. This assumption is supported by low intensity spectra of products after long irradiation (Fig. 1b). Rate constants of degradation of NPy, and of nonsubstituted Py (Py) in the same condition under irradiation by Xe lamp are summarized in Table 1.

Most experiments were performed in methanol and in AA that accelerated photodegradation of nonsubstituted Py [12]. However, this effect was not observed in NPy degradation where k_{deg} , for degradation of NPy in methanol, is comparable with that for degradation in AA. These results show that the rate of NPy photodegradation is controlled by another processes rather than simple Py photodegradation. Addition of a more polar solvent (water) to the reaction mixture significantly decreases k_{deg} . NPy in a concentration above 10 μM precipitates in a mixture of 50% AA.

If the principal processes leading to NPy degradation are radical reactions, the k_{deg} value should substantially increase in the presence of hydrogen peroxide, which can supply hydroxyl radicals OH^\bullet during irradiation. Systems containing benzene rings react with OH^\bullet radicals with a diffusion-controlled rate constant of $\sim 10^9$ to $10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ [19]. Unstable radicals are formed and further decomposed resulting in the opening of a benzene ring. The OH^\bullet can be generated by direct photolysis of H_2O_2 by UV radiation (wavelength $< 340 \text{ nm}$) or sensitized transfer of energy from the excited singlet state of $^1\text{NPy}^*$ to the H_2O_2 molecule. Addition of small amount of H_2O_2 increased k_{deg} (see Table 1). This fact indirectly supports the idea of radical mechanisms of photodegradation. The accelerating effect of H_2O_2 is less significant, than in the case of nonsubstituted Py decomposition [12]. However, the contribution of a parasitic reaction of OH^\bullet with H_2O_2 (rate constant of $4 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$) increases at higher concentrations of H_2O_2 . The product of this reaction $\text{O}_2^{\bullet-}$ is known to be a less efficient oxidant of organic compounds than OH^\bullet [19]. Laser energy is absorbed in a limited volume near the entrance window of reactor, where radicals can be formed. Thus, the overall rate constant k_{deg} is decreased even if local concentration of OH^\bullet is increased.

Taking into account the absorption spectra of individual Py species and the emission spectrum of Xe lamp, we can compare the amount of NPy and Py photodegradation. Rate constants k_{deg} for degradation of NPy and Py are of the same order of magnitude (Table 1). However, NPy can be photolyzed by UV radiation with longer wavelengths (up to 400 nm) than nonsubstituted Py (up to 340 nm) due to different UV–VIS absorption spectrum.

3.2. Photodegradation of NPy adsorbed on cellulose

Photodegradation of NPy adsorbed on cellulose was studied using fluorescence spectroscopy with samples prepared from solution of NPy in methanol and in AA. Three bands in the fluorescence spectrum of adsorbed NPy were resolved: fluorescence of monomeric $^1\text{NPy}^*$ (390 and 406 nm) and fluorescence of excimer $(\text{NPy-NPy})^*$ (515 nm). Intensity of individual fluorescence bands varied during irradiation (Fig. 2).

Figs. 3 and 4 show the dependence of $(\text{NPy-NPy})^*/^1\text{NPy}^*$ (a) and $^1\text{NPy}^*$ emission (b) as a function of absorbed energy. $(\text{NPy-NPy})^*$ is the expected product of excitation only at high concentration of NPy. Thus, a decreasing concentration of $(\text{NPy-NPy})^*$ formed after excitation indicates a decreasing concentration of NPy (or other Py derivatives formed during irradiation) in the ground state. $^1\text{NPy}^*$ emission (Fig. 2b) in the early stages of photodegradation increases with absorbed energy. The reason for this is that laser radiation penetrates deeply into the sample and $(\text{NPy-NPy})^*$ cannot be formed due to lower concentrations of $^1\text{NPy}^*$ and NPy (Eq. (3)) near the entrance window of the reactor. Concentration of NPy adsorbed on cellulose substantially decreases in the final stages of photodegradation resulting in lower emission of $^1\text{NPy}^*$ (Fig. 3b).

Blank experiments without NPy show that cellulose itself decomposes under strong irradiation by Nd-YAG laser. Products of cellulose decomposition have different fluorescence spectra and lifetimes of the excited singlet states than spectra measured after irradiation of NPy adsorbed on cellulose. Photodegradation of cellulose itself is a very complicated

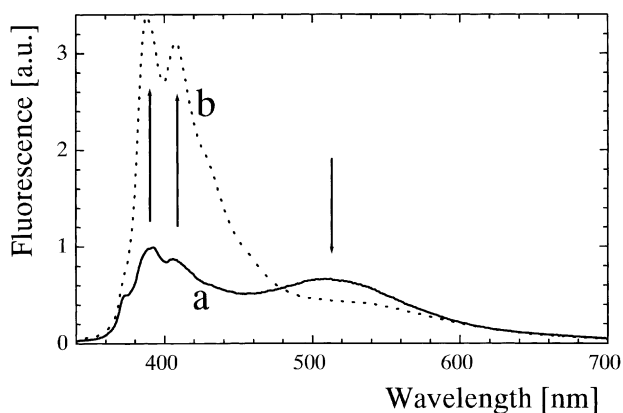


Fig. 2. Fluorescence spectra of NPy (6.1 $\mu\text{mol/g}$ of cellulose) before (a) and after irradiation by Nd-YAG laser ((b) dotted line, wavelength 355 nm, absorbed energy 18 J). Arrows designate increase of $^1\text{NPy}^*$ fluorescence (390 and 406 nm) due to deeper penetration into the sample and decrease of $(\text{NPy-NPy})^*$ fluorescence at 515 nm due to lower concentration of NPy.

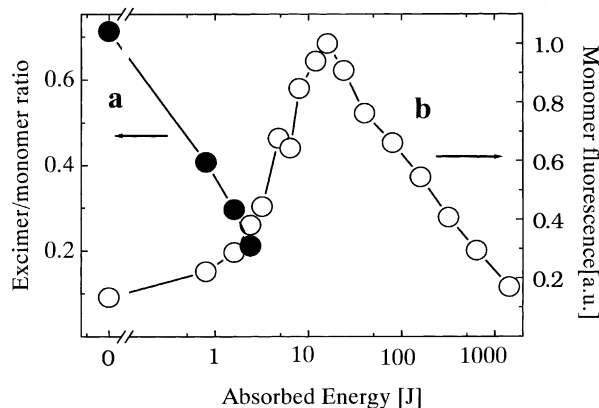


Fig. 3. Dependence of $(\text{NPY-NPy})^*/{}^1\text{NPY}^*$ ratio (a, left axis) and ${}^1\text{NPY}^*$ fluorescence (b, right axis) on absorbed energy of Nd-YAG laser (wavelength 355 nm, energy output 80 mJ/puls), 6.1 μmol of NPY on 1 g of cellulose, prepared from NPY dissolved in methanol.

process. Many factors such as the presence of dye, various oxidants, as well as the ambient atmosphere and the wavelength of the irradiation may affect the rate of photodegradation and product distribution [20]. Some radicals especially hydroxyl radicals are shown to be important intermediates in these oxidative processes. The presence of any radical could significantly accelerate the rate of destruction of Py aromatic rings that occurs by a radical mechanism [12].

We prepared also samples from solution of AA, which accelerate radical decomposition of Py skeleton and with addition of oxidants (H_2O_2 and TiO_2), which produce hydroxyl radicals under irradiation. Small influences of oxidants on the rate constant of degradation can be explained by small concentrations of hydroxyl radical formed from H_2O_2 and AA

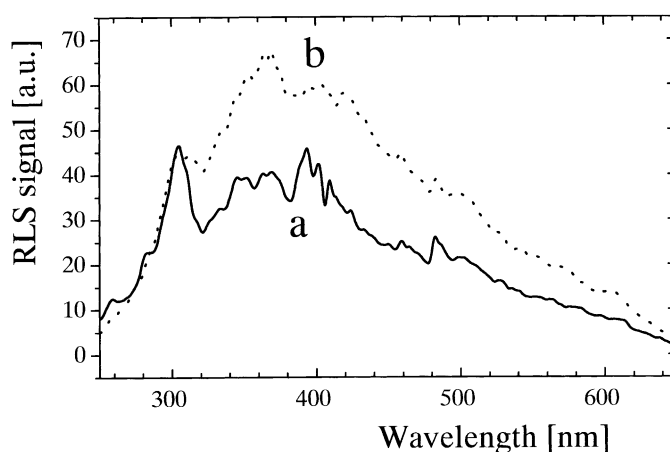


Fig. 4. RLS spectra of 5×10^{-5} M NPy (a) and product of degradation after 6 h irradiation by 200 W Hg lamp (b).

in comparison with radicals that are produced by cellulose photolysis. On the other hand, TiO₂ has a strong absorption band matched to the irradiation wavelength. UV photons were absorbed only by the surface layer of TiO₂ and this did not allowed degradation in the overall volume of the sample.

Quantitative comparison of NPy photodegradation in the adsorbed state and in solution is not easy. We found changes in the emission and absorption spectrum of NPy adsorbed on cellulose after absorption of <0.1 J of UV radiation. Irradiation in the adsorbed state is very effective for degradation of NPy in the surface layer due to the high extinction coefficient of the sample. On the other hand, photodegradation of NPy in solution occurs more slowly (visible changes in absorption and fluorescence spectra after more than 1 J) but is sufficient for the degradation of NPy in the bulk of the reactor.

3.3. Products of photodegradation

The irradiated samples were analyzed and identified by HPLC, mass, UV–VIS absorption, fluorescence and RLS spectroscopies. After irradiation of NPy in solution and in the adsorbed state we found a large number of products, especially after long irradiation. The reaction mechanism of NPy photodegradation is very complicated and consists of many radical reactions.

Based on the spectra recorded and on injections of 1-hydroxypyrene and of several model compounds (*m*-hydroxymethylnitrobenzene, methoxybenzene) we assume that several Py derivatives were formed by irradiation of NPy in methanol (Table 2). The same product was observed in degradation of NPy adsorbed on cellulose. It could be seen from the chromatograms that more polar methoxypyrene isomeric derivatives are produced by UV irradiation in the presence of oxygen. Hydroxymethylpyrene derivative formation is less dependent on oxygen presence in solution than that of methoxyderivatives, and that nitrosopyrene and hydroxynitropyrene formation is enhanced by the absence of oxygen. The presence of one methoxy group on the Py ring supports a mechanism that starts with PyO• radical formation and NO [11] and continues by the transfer of CH₃ group from methanol or AA.

After long irradiation (Hg lamp, 6 h) NPy and the reaction products are photolyzed more efficiently (Fig. 2b). The results show that aromatic structure of Py was totally destroyed, resulting in low-molecular compounds. These results were confirmed by a direct injection of the solution after irradiation to a mass spectrometer with electron impact ionization. The species with high *m/z* were not detected (Fig. 5). Following decomposition of the Py skeleton

Table 2
Identified products of NPy photodegradation

Products	Ret. time (min)	<i>m/z</i>	Comments
(1) Methoxypyrene	4.09	233.6	Isomer
(2) Methoxypyrene	4.34	233.6	Isomer
(3) Methoxypyrene	4.76	233.6	Isomer
(4) Hydroxymethylpyrene	5.63	279.0	
(5) Hydroxypyrene	5.88	218.5	
(6) 1-Nitropyrene	11.68	248.2	Standard
(7) Nitrosopyrene	14.90	232.4	

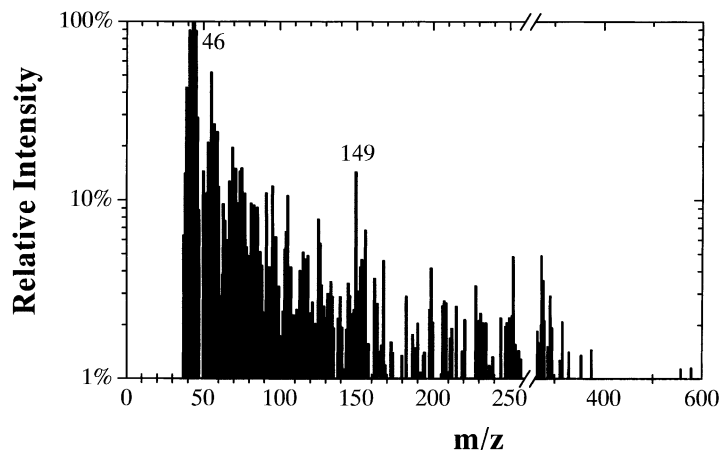


Fig. 5. Mass spectrum of 0.5 mM NPy in methanol after 6 h of irradiation by mercury lamp, products were not separated on HPLC column.

and the formation of less stable products than NPy or similar Py derivative themselves, the remaining Py derivatives can act as sensitizers. The transfer of energy from $^1\text{NPy}^*$ and $^3\text{NPy}^*$ to the less stable products and oxidation of double bonds by singlet oxygen can lead to further decomposition.

It should be noted that the analysis of photolytic reactions of aromatic systems, electron impact ionization is more efficient than chemical ionization due to the fact that more fragment ions are formed by impact ionization. Since there are no spectra databases available for HPLC–mass spectroscopy (MS) systems, these limitations need to be taken into account when choosing the analysis technique.

The high number of low-molecular products was confirmed by measurement of UV–VIS absorption spectra. Typical spectra of the resulting products absorb below 290 nm. These changes show that the fused aromatic system of NPy was destroyed and small fragments are produced. Only an extremely small fraction of products exhibit a larger π -conjugation than NPy, which results in a red shift in UV–VIS spectrum.

The absorption bands of products with higher molecular weight than NPy (aggregates or polymers) could be also visualized by another technique: RLS [21] however, higher light scattering in resonance depicts only a small increase of light scattering in samples containing products of degradation when compared with the RLS spectrum of pure NPy (Fig. 4a and b).

This observation is in good agreement with results of MS, where only a very small fraction of high molecular products was found (Fig. 5).

4. Conclusion

We have studied the photodegradation of solutions of NPy in methanol or AA, and when adsorbed on cellulose, by UV irradiation. We found that aromatic hydroxymethyl, methoxy,

hydroxy and nitroso derivatives of Py are created by low energy UV irradiation. After a massive UV irradiation, the Py aromatic system is destroyed and more polar low-molecular compounds are created. The photochemical method described in this paper, based on irradiation by UV lamp, is therefore, suitable for degradation of fused benzene ring(s) and thus should also be effective for degradation of other nitrated polycyclic aromatic compounds.

Acknowledgements

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