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PHOTOCHEMICAL REACTION OF NITRO-POLYCYCLIC AROMATIC HYDROCARBONS: EFFECT BY SOLVENT AND STRUCTURE

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Abstract

Photochemical degradation of 1-nitropyrene, 2-nitrofluorene, 2,7-dinitrofluorene, 6-nitrochrysene, 3-nitrofluoranthene, 5-nitroacenaphthene, and 9-nitroanthracene were examined in CHCl_3 , CH_2Cl_2 , DMF, DMF/ H_2O (80/20), CH_3CN , or $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (80/20). The degradation follows mostly the 1st order kinetics; but a few follow 2nd order kinetics or undergo self-catalysis. The photodegradation rates follow the order: $\text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{DMF} > \text{DMF}/\text{H}_2\text{O} > \text{CH}_3\text{CN} > \text{CH}_3\text{CN}/\text{H}_2\text{O}$. DMF is an exceptional solvent because 3 of the 7 compounds undergo self-catalytic reaction. 9-Nitroanthracene, which has a perpendicular nitro group, is the fastest, while the more compact 1-nitropyrene and 3-nitrofluoranthene, are the slowest degrading compounds.

Keywords

Light; Degradation; Nitro Polycyclic Aromatic Hydrocarbons; Solvent Effect; Structure Activity Relationship

INTRODUCTION

Nitro-polycyclic aromatic hydrocarbons (Nitro-PAHs) are generated as a result of incomplete combustion of organic materials and petrochemicals, or formed by the reaction of PAHs with NO_2 or NO_3^- in the atmosphere [1]. Nitro-PAHs are of primary concern because many of them are much more carcinogenic than their parent PAHs, and display a greater degree of mutagenicity although they appear in the environment one to two orders of magnitude lower than their parent PAHs [2]. They are found in the environment in the vapor and aqueous phase, and are absorbed onto particulate matters. Nitro-PAHs undergo various chemical reactions in the environment including photochemical reactions when exposed to light. It has been proposed that the photochemical reaction rate and mechanism of Nitro-PAHs depends on the orientation of the nitro group, whether it is parallel (co-planar) or perpendicular to the aromatic rings [3]. The nitro group is forced out of the plane into a perpendicular position by the *peri* hydrogens to minimize energy due to steric hindrance. Co-planar Nitro-PAHs usually undergo photochemical oxidation of the aromatic rings, while the perpendicular Nitro-PAHs are proposed to undergo rearrangement of the nitro group first to a nitrite and then to a nitroso substituted ketone. The nitroso substituted ketone is not stable, and is easily oxidized further to quinones [4,5].

There have been a number of studies performed on the degradation of Nitro-PAHs, and numerous techniques to determine their concentration in the environment or their photoproducts. Warner et al examined the relationship between nitro group orientation and photochemical degradation of Nitro-PAHs [6]. Fourteen different Nitro-PAH samples were dissolved in CH₃CN or absorbed onto a surface (silica, alumina, carbon, and cellulose) and irradiated. Their results showed that not all Nitro-PAHs in solution demonstrated a relationship between nitro group orientations. The compounds absorbed onto a surface showed that the nature of the particle had more of an influence on degradation than the structure of the Nitro-PAHs.

It is common knowledge that solvents have different effects on the rate of degradation, and affect the formation of photoproducts [7,8]. Moeini-Nombel and Matsuzawa investigated the effect of solvents and substituent groups on the photo-oxidation of fluorene [7]. This research compared the rate constants, degradation half-lives, and quantum yield of fluorene and its derivatives when irradiated with UV light. The photodegradation varied based on the solvent used with CH₂Cl₂ giving a faster rate, and 50/50 CH₃CN/H₂O giving a slower rate. Fluorene and 1-methylfluorene displayed similar photostabilities, while 2-nitrofluorene was more resistant to photodegradation. In this paper, we will present the photoreaction kinetics and the effect by solvents and position/orientation of the nitro group on the photodegradation rate of seven Nitro-PAHs.

EXPERIMENTAL METHODS

1-Nitropyrene (1-NP), 2-nitrofluorene (2-NF), 3-nitrofluoranthene (3-NFA), 5-nitroacenaphthene (5-NAN), 6-nitrochrysene (6-NC), 9-nitroanthracene (9-NA), and 2,7-dinitrofluorene (2,7-DNF) were purchased from Sigma-Aldrich Chemical Company (Milwaukee, WI) and used without further purification. The solvents used were: CH₃CN, CH₃CN/H₂O (80/20), CH₂Cl₂, CHCl₃, N,N-dimethyl formamide (DMF), DMF/H₂O (80/20), and MeOH. All solvents were HPLC grade purchased from Fisher Scientific (Fairlawn, NJ, USA) and used without further purification. Water used (18 Ω) in this experiment was deionized with a Barnstead Nanopure Infinity water deionization system (Dubuque, IA). All of the selected Nitro-PAHs were prepared in each solvent at 100 μM concentration, and were irradiated with a UVA Lamp (Spectraline SB-100P, 365±20 nm, Spectronics Corporation, Westbury, NY, USA) at 8 cm distance with an output energy of 144 J/cm²·h.

A Nitro-PAHs solution in a quartz cuvet (1 cm light path) was irradiated and the degradation was monitored using a CARY 300E UV-Vis absorption spectrophotometer from Varian Inc. (Houston, TX). The absorption at a certain wavelength, $[A]_0$ and $[A]_t$ at the start and at time t , respectively, were recorded. The wavelength selected to record the absorption (relative concentration of the starting compound) was carefully chosen so that there is no absorption from the photoproducts to interfere with the measurement. Specifically, the wavelength used for each compound was: 1-NP: 405 nm; 2-NF: 336 nm; 2,7-DNF: 346 nm; 3-NFA: 377 nm; 5-NA: 374 nm; 6-NC: 373 nm; 9-NAN: 364 nm. A plot of $\ln([A]_0/[A]_t)$ vs. irradiation time t was used for first order reactions and a plot of $1/[A]$ versus t for second order reactions. For first order reactions, $\ln([A]_0/[A]_t) = kt$ was used to determine the rate constant (k). Once k was calculated, the degradation half-life ($t_{1/2}$) was determined by $t_{1/2} = 0.693/k$. For second order reactions, $1/[A] = 1/[A]_0 + kt$ was used to determine k . Once k was calculated, the degradation half-life was determined by $t_{1/2} = 1/(k[A]_0)$.

RESULTS

Photodegradation Rates of Nitro-PAHs

Irradiation by UVA light of the solutions of Nitro-PAHs in various solvents was carried out. The absorption spectra at each irradiation time interval and the absorption value at the peak were recorded. The progress of the photodegradation was analyzed by either fitting to a 1st or a 2nd order reaction. Their degradation half lives were calculated. Some did not fit well with either the 1st or the 2nd order reaction and the $\ln([A]_0/[A])$ versus t plot curved upward. We classified these as self-catalytic reactions. Due to solubility problem, some of the degradation could not be accomplished. There were also a few cases that did not appear to have any degradation during the period irradiated. The results are summarized in Table 1.

1-NP degraded in all of the selected solvents; however, there was only 60% degradation after 75 min of UV irradiation in CH₃CN, 37% after 180 min in CH₃CN/H₂O, and 60% after 60 min in CH₂Cl₂, not enough degradation to calculate the degradation half-lives. 1-NP has a $t_{1/2}$ of 37 min in DMF, 69 min in DMF/H₂O, and 12 min in CHCl₃. The rate of degradation of 1-NP is CHCl₃ > DMF > DMF/H₂O. The nitro group in 1-NP has one *peri*-hydrogen and should be co-planar to the pyrene rings.

2-NF degraded in all solvent systems used for this study. It showed 21% degradation after 160 min of irradiation in CH₃CN, and 15% degradation after 60 min in CH₃CN/H₂O, not enough to determine a half-life. 2-NF in CH₂Cl₂ followed a zero order reaction and a half-life was determined to be 90 min. The degradation of 2-NF in CHCl₃ is a 2nd order reaction with a half-life of 1.6 min calculated by $t_{1/2} = (1/k[A]_0)$. 2-NF underwent self-catalysis in DMF and DMF/H₂O, and a half-life could not be determined. The plot of $\ln([A]_0/[A]_t)$ vs. t curved upward, indicating the reaction speeded up during the irradiation. It is known that photolysis of 2-NF produces 2-nitrofluorenones [9], which can be the photosensitizer to catalyze the further reaction of 2-NF.

2,7-DNF was insoluble in nearly all solvents except in DMF, although Warner et al used CH₃CN for 2,7-DNF [6]. 2,7-DNF in DMF and DMF/H₂O became intensely yellow after 1 min of irradiation while it was clear before irradiation. The solution became darker as time lapsed. The $t_{1/2} = 7$ min when 2,7-DNF is irradiated in DMF/H₂O. The half-life of 2,7-DNF in DMF could not be determined due to not enough degradation after 60 min of irradiation.

3-NFA was one of the most resistant to photodegradation in that it showed little or no degradation in CH₃CN, CH₃CN/H₂O, or CH₂Cl₂. It did show 85% degradation in CHCl₃ (Figure 2) or DMF. However, it only degrades 52% after 150 min of irradiation in DMF/H₂O. 3-NFA was sparingly soluble in MeOH. The half-life of 3-NFA in CHCl₃ was 24 min and was a 1st order reaction. However, 3-NFA underwent self-catalysis in DMF and the half-life could not be determined. The orientation of the nitro group of 3-NFA is parallel to the ring, and is more stable under light irradiation [3,6].

5-NAN degraded in all selected solvents. 5-NAN has a λ_{max} between 372 – 376 nm. 5-NAN in CHCl₃ was a 2nd order reaction with $t_{1/2} = 8.5$ min. The degradation in CH₃CN, CH₃CN/H₂O, and DMF/H₂O are 1st order reactions. The half-life of 5-NAN in these solvents are: CH₃CN = 63 min, CH₃CN/H₂O = 88 min, DMF/H₂O = 37 min. The half-life could not be determined in CH₂Cl₂ due to slow degradation. 5-NAN in DMF underwent self-catalysis and a half-life could not be determined (Figure 3). 5-NAN has one *peri*-hydrogen and the nitro group is co-planar. The rate of degradation of 5-NAN from fastest to slowest was: CHCl₃ > DMF > DMF/H₂O > CH₃CN > CH₃CN/H₂O. As an example for the three types of photoreaction kinetics, 1st order, 2nd order and self-catalysis, figure 3 plots the $\ln([A]_0/$

$[A]_t$ vs. t for 5-NAN in all of its solvents. As can be seen, the upward curvature in DMF signifies self-catalysis.

The plot of $\ln([A]_0/[A]_t)$ versus t for 6-NC in CHCl_3 , CH_2Cl_2 , and $\text{DMF}/\text{H}_2\text{O}$ are straight lines while it curves upward in DMF, signifying self-catalysis (not shown). 6-NC showed a minimum of 80% degradation in DMF, $\text{DMF}/\text{H}_2\text{O}$, and CH_2Cl_2 . 6-NC degraded rapidly in CHCl_3 , and showed 87% degradation within 8 min. 6-NC was sparingly soluble in MeOH, and it did not generate enough data in CH_3CN , and $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ to plot. The half-lives of 6-NC are 2 min in CHCl_3 , 18 min in CH_2Cl_2 , 17 min in DMF, and 35 min in $\text{DMF}/\text{H}_2\text{O}$. The rate of degradation of 6-NC from fastest to slowest is: $\text{CHCl}_3 > \text{DMF} \approx \text{CH}_2\text{Cl}_2 > \text{DMF}/\text{H}_2\text{O}$.

The plot of $\ln([A]_0/[A]_t)$ versus t for 9-NA yielded straight lines in the initial stages of the irradiation and became curved after a significant of degradation had occurred. 9-NA degraded very rapidly in all selected solvents, and was the fastest of all Nitro-PAHs studied here. The majority of the starting material had totally degraded within 10 min of irradiation in most solvents. 9-NA in MeOH was also soluble. The formation of photoproducts of 9-NA in $\text{DMF}/\text{H}_2\text{O}$ solvent were observed and they are known as 9,10-anthraquinone and bianthrone [4,10–12]. The half-lives for 9-NA are as follows: $\text{CHCl}_3 = 1$ min, $\text{CH}_2\text{Cl}_2 = 2$ min, $\text{CH}_3\text{CN} = 6$ min, DMF = 3 min, $\text{DMF}/\text{H}_2\text{O} = 4$ min, $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 6$ min.

DISCUSSION

From the data in Table 1, we found that the photoreaction rates of Nitro-PAHs are governed by several factors related to solvent and their intrinsic structure. Solubility and polarity of a solvent affect the photochemical reaction rate. Structure, both the PAH ring arrangement and position or orientation of the nitro-group, play important roles in the photoreaction of Nitro-PAHs. In addition, photoreactions of Nitro-PAHs follow different kinetics, 1st and 2nd order or self-catalytic reaction.

Solubility

Nitro-PAHs are relatively insoluble in water, but soluble in organic solvents. Six of our selected Nitro-PAHs were soluble in DMF and $\text{DMF}/\text{H}_2\text{O}$, but were only sparingly soluble in MeOH. 2,7-DNF was soluble only in DMF and $\text{DMF}/\text{H}_2\text{O}$ although Warner et al was able to carry out the photolysis in CH_3CN . 6-NC was soluble in majority of the solvents, but was sparingly soluble in CH_3CN and $\text{DMF}/\text{H}_2\text{O}$. 1-NP, 2-NF, 3-NFA, 5-NAN, and 9-NA were all soluble in CH_3CN , $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, CH_2Cl_2 , CHCl_3 , DMF, and $\text{DMF}/\text{H}_2\text{O}$. Solvent rank based on solubility is as follows: $\text{DMF} > \text{DMF}/\text{H}_2\text{O} > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{CH}_3\text{CN} > \text{CH}_3\text{CN}/\text{H}_2\text{O} \gg \text{MeOH}$. Although DMF seems to be the best solvent to dissolve the Nitro-PAHs, chloroform is the best solvent for kinetics study.

Effect by Solvent: Photoreaction is faster in less polar solvents

If the degradation half-lives are compared for a chosen Nitro-PAH in all the solvents, it degrades fastest in CHCl_3 , followed by CH_2Cl_2 and DMF. For 9-NA, which has a degradation half-life in all solvents, the degradation rate rank is: $\text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{DMF} > \text{DMF}/\text{H}_2\text{O} > \text{CH}_3\text{CN} > \text{CH}_3\text{CN}/\text{H}_2\text{O}$. The other Nitro-PAHs have a similar pattern. This seems that the degradation rate is anti-parallel to the polarity of the solvents, which is $\text{CHCl}_3 < \text{CH}_2\text{Cl}_2 < \text{CH}_3\text{CN} \approx \text{CH}_3\text{CN}/\text{H}_2\text{O}$, except for DMF and $\text{DMF}/\text{H}_2\text{O}$. The rate of degradation of our selected Nitro-PAHs in the various solvents may be attributed to the solubility of dissolved oxygen (O_2). In general, the solubility of O_2 increases as the solvent polarity decreases [7,13]. CHCl_3 is the least polar solvent while water is the most polar. The results indicate that the oxygen content decreases with increasing water content which

explains why the rate of degradation is slower with the addition of water to CH_3CN or DMF. The presence of oxygen oxidizes the parent compound leading to photodegradation.

In DMF, three Nitro-PAHs, 2-NF, 3-NFA and 5-NAN, follow a self-catalytic kinetics, indicating that DMF is different from other solvents. The degradation reaction starts slow, but picks up speed as more and more starting compound is converted to photoproducts, resulting in an upward curvature for the $\ln[A_0]/[A]$ versus irradiation time t plot. The logical explanation is that one or more of the photoproducts are photosensitizers. Possible photosensitizers are quinones since they are known to catalyze PAH photodegradation [14]. 2-NF may produce 2-nitrofluorenone [9]. 5-NAN may produce acenaphthene-5,6-dione and 3-NFA may produce of fluoranthene-2,3-dione. However, these photoproducts have not been isolated and characterized.

Effect by Nitro-PAH Structure

Using the degradation rates (half-lives) of Nitro-PAHs in CHCl_3 in Table 1, the rank of the degradation rates is: 9-NA > 2-NF \approx 6-NC > 5-NAN > 1-NP > 3-NFA. Similar ranking can be achieved in other solvents, although the data are not as complete as in CHCl_3 due to solubility or slow degradation. It is known that the nitro group in 9-NA is in the perpendicular conformation to the anthracene ring and undergoes rearrangement to nitrite very quickly due to photolysis. This is followed by transformation to a nitroso ketone intermediate, which converts to anthraquinone [4,10]. None of the other Nitro-PAHs has two *peri*-hydrogens as 9-NA and would not likely follow this reaction mechanism. The likely photoreaction is oxidation of the aromatic rings. These are slower reactions than the nitro to nitrite rearrangement reaction [3,15]. The relatively faster rate for 2-NF and 6-NC may be due to the quick conversion to the respective quinones [9]. Finally, 1-NF and 3-NFA are the slowest degrading nitro-PAHs due to the more compact ring systems that are difficult to be oxidized.

Complex Photoreaction Kinetics

The photoreaction of the seven selected Nitro-PAHs in six solvent systems follows three kinetics models: 1st order, 2nd order, or self-catalysis. The complexity of the photoreaction kinetics of Nitro-PAHs is reflective of the variety of reaction pathways the Nitro-PAHs can take: rearrangement reaction, oxidation of the ring, reaction with molecular oxygen or solvent molecules, and bi-molecular reactions [3]. The fact that most photoreactions are 1st order indicates that the rate determining step for the photoreaction involves one Nitro-PAH molecule. The 2nd order reaction is reflective of the bi-molecular reaction or complex parallel reactions. The self-catalytic reaction is reflective of the photosensitizing effect or the reactive nature of the photoproducts that can facilitate degradation of the original Nitro-PAHs. Another issue is the concentration of molecular oxygen in the solvent. Since most of the degradation of the Nitro-PAHs in solution requires molecular oxygen [3], the concentration differences of molecular oxygen in the solvents will contribute to the complexity of the photoreaction kinetics.

Conclusions

In conclusion, the photoreaction of Nitro-PAHs is complex with various pathways, kinetics models, and photoproducts. Solvent polarity, concentration of oxygen in the solvent, orientation of the nitro group, and the ring structure of the PAH are main contributors to the complexity. Degradation rate ranks as $\text{CHCl}_3 > \text{CH}_2\text{Cl}_2 \approx \text{DMF} > \text{DMF}/\text{H}_2\text{O} (80/20) > \text{CH}_3\text{CN} > \text{CH}_3\text{CN}/\text{H}_2\text{O} (80/20)$. 5-NAN degradation starts slow in DMF, but becomes faster after 30 min due to self-catalysis. The rate of degradation of the seven selected Nitro-PAHs in various solvents is attributed to the solubility of dissolved oxygen and how solvents facilitate the photoreaction. In general, the solubility of O_2 increases as the solvent polarity

decreases [7,13]. CHCl_3 is the least polar solvent while water is the most polar. This explains why the rate of degradation is slower with the addition of water to CH_3CN or DMF. The presence of oxygen oxidizes the parent compound leading to photodegradation.

Acknowledgments

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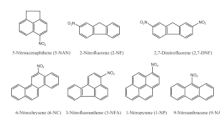


Figure 1.
Names and structures of nitro-polycyclic aromatic hydrocarbons selected for this study.

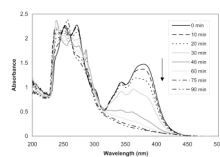


Figure 2. Absorption spectra of 3-nitrofluoranthene (100 μM) in CHCl₃ irradiated with UVA light showing steady degradation.

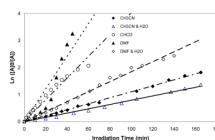


Figure 3. Plot of $\ln([A]_0/[A]_t)$ vs. t for 5-nitroacenaphthene in selected solvents. As shown in the graph that the reasonable straight line fits in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, CH_3CN , and $\text{DMF}/\text{H}_2\text{O}$, and downward curved fit in CHCl_3 signifying 2nd order reaction, and upward curved fit in DMF signifying self-catalysis.

Table 1

Degradation half-lives (min) of Nitro-PAHs in selected solvent systems*

	1-NP	2-NF	2,7-DNF	3-NFA	5-NAN	6-NC	9-NA
CH₃CN	NED	NED	Insoluble	ND	63	Insoluble	5.9
CH₃CN/H₂O	NED	NED	Insoluble	ND	88	Insoluble	6.1
CH₂Cl₂	NED	90(zero)	Insoluble	ND	NED	18	1.7
CHCl₃	12	1.6 (2 nd)	Insoluble	24	8.5 (2 nd)	1.8	0.8
DMF	37	SC	NED	SC	SC	17	2.6
DMF/H₂O	69	SC	7.3	NED	38	35	3.6

* All half-lives are based on 1st order reaction except those indicated for 2nd order or zero order (it means that the plot of $\ln[A]$ versus t is a straight line); SC = Self-catalysis; for self-catalytic reactions, no half-life is determined; ND = No degradation; NED = Not enough degradation.