On the Primary Reaction Pathways in the Photochemistry of Nitro-Polycyclic Aromatic Hydrocarbons

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Abstract
The primary reaction pathways in the photochemistry of nitro-polycyclic aromatic hydrocarbons under specific laboratory conditions are briefly summarized. In addition, photochemical data is presented for 2-nitronaphthalene, 1-nitronaphthalene, and 2-methyl-1-nitronaphthalene in cyclohexane and acetonitrile solutions under aerobic and anaerobic conditions. It is shown that molecular oxygen significantly reduces the photodegradation quantum yield of 1-nitronaphthalene and 2-methyl-1-nitronaphthalene by 63% and 81%, respectively, whereas 2-nitronaphthalene is photoinert in both solvents under aerobic and anaerobic conditions. In addition, it is proposed that recombination of the aryl and nitrogen (IV) dioxide geminate radical pair within the solvent cage or internal conversion of an initially formed intramolecular charge transfer state may play an important role in the fraction of excited molecules that returns to the ground state in 1-nitronaphthalene and 2-methyl-1-nitronaphthalene. Scavenging of radical species by molecular oxygen and the generation of singlet oxygen in high yield are proposed to contribute to the photochemistry of these nitro-naphthalene derivatives in solution.

Keywords: Photochemistry of nitro-polycyclic aromatic compounds; Radical pair recombination; Excited-state dynamics; Environmental photochemistry; Ultrafast spectroscopy; Computational chemistry

Introduction
Nitro-polycyclic aromatic hydrocarbons (NPAHs) constitute one of the most troubling classes of environmental pollutants. Concern about these compounds arises partly from their ubiquity: NPAHs are released to the environment directly from a variety of incomplete combustion processes [1] and are also formed in situ by atmospheric reactions of polycyclic aromatic hydrocarbons (PAHs) [2-5]. They have been identified as components of grilled food as well as in diesel, gasoline, and wood smoke emissions, and are also commonly found in aquatic systems and in sediments [5-9].

Despite the potential negative impact of NPAHs to human health, the emission of NPAHs to the environment continues, primarily from municipal incinerators [10], motor vehicles (particularly from diesel exhausts) [11,12], and industrial power plants [13] among other sources. These emissions are likely to rise with the increasing consumption of petroleum and coal particularly in developing countries. It is estimated that NPAHs are released to the ground atmosphere by both volatile and particulate processes [1] and are also formed in situ by atmospheric reactions of polycyclic aromatic hydrocarbons (PAHs) [2-5]. They have been identified as components of grilled food as well as in diesel, gasoline, and wood smoke emissions, and are also commonly found in aquatic systems and in sediments [5-9].

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Photocatalytic transformation is thought to be one of the main routes of natural removal of NPAHs in the environment [8,16-19]. Importantly, NPAHs are frequently more toxic than their parent PAHs [8,20], and photochemical degradation of a number of NPAHs leads, in turn, to photoproducts, some of which are more toxic than their parent compounds [8,20,21]. However, the light-induced transformation mechanisms of NPAHs are still under debate and knowledge of their fates in the environment is of current interest [22-39]. Fundamental gaps remain in our knowledge of the elementary steps that lead to product formation with regard to the competition among available reaction pathways, the intermediate species involved in the photochemical transformations, and the degradation rates as a function of compound structure, added co-solutes, and micro-environment [26,34,35,40-43]. Consequently, development of laboratory models enabling accurate and quantitative measurements of these photochemical properties is essential for modeling the concentration and persistence of NPAHs in the environment and to understand their overall contribution to air quality [44-46]. Moreover, laboratory studies can facilitate the development of quantitative structure-activity relationships (QSARs), which connects photophysical and photochemical data to the physicochemical and structural properties of NPAHs [20,22,23,30,32,38,39,47]. In recent years, QSARs have been successfully developed [19,48,49], relating the toxicity, carcinogenicity, and mutagenicity of NPAHs with their physicochemical and structural properties.

The present work summarizes the primary reaction pathways that have been identified in the photochemistry of NPAHs under specific laboratory conditions. In addition, photochemical results of 2-nitronaphthalene, 1-nitronaphthalene, and 2-methyl-1-nitronaphthalene in cyclohexane and acetonitrile solutions are presented that provide new insights about the photochemical fate of these nitro-aromatic compounds in the environment.

Materials and Methods
Chemicals
Cyclohexane (99.9%) was obtained from Fisher Scientific. Acetonitrile (99.6%) was obtained from Acros. Both solvents were used as received. 2-Nitronaphthalene, 1-nitronaphthalene and 2-methyl-1-nitronaphthalene were obtained from Sigma-Aldrich (99.7%, 99% and 99%, respectively). 2-nitronaphthalene, 1-nitronaphthalene and 2-methyl-1-nitronaphthalene are moderately toxic compounds.

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Proper safety precautions were taken at all times to limit health risks. Due to the presence of a minor impurity in the commercial sample of 2-nitronaphthalene [39], recrystallized samples of 2-nitronaphthalene from methanol were used in the experiments reported in this work.

**Steady-state measurements**

Steady-state absorbance measurements were performed using a Cary 100 UV/Vis spectrometer (Varian, Inc.). Photodegradation experiments were performed using a 150 W Xe lamp (Newport-Oriel, Apex Source Arc, source model 66453, lamp model 6255), as reported recently [39]. The wavelength range of 275-375 nm was selected for irradiation by using a FGUVS11S colored glass filter (Schott), except for the determination of photodegradation rates, where a Pyrex filter was also used to restrict the irradiation wavelengths to the 300 to 375 nm range. The polychromatic light was focused through a 450 mm lens placed at 5 cm from the front of the lamp source. The sample was placed at 41 cm from the front of the lens. The beam width at the sample was 0.95 cm. Solutions were contained in a 1 cm quartz cuvette (Starna, Inc.) and stirred continuously with a magnetic stir bar (Starna, Inc.) to assure a homogeneous irradiation of the solutions at all times.

For the determination of the polychromatic photodegradation quantum yields, the change in concentration of the nitronaphthalene derivatives as a function of irradiation time was obtained using a HPLC (Shimadzu LC-20AD) with an amide column (Ascentis RP-Amide, 5 μm, 25 cm×4.6 mm). The HPLC was used in order to separate the parent compounds from the photoproducts. Calibration curves were obtained for each nitronaphthalene derivative. At least 5 data points were used for each of the calibration curves, giving area under the chromatographic fraction versus concentration, as described recently [39]. An isocratic elution was used with a solvent composition of 80% acetonitrile and 20% water. A photodiode array detector (Shimadzu SPD-M20A) was used to measure the absorbance of the eluting compounds. Potassium ferrioxalate was used as an actinometer to measure the lamp intensity used to measure the absorbance of the eluting compounds. Potassium ferrioxalate was used as an actinometer to measure the lamp intensity used to measure the absorbance of the eluting compounds.

**Results and Discussion**

**Brief summary of the primary photochemical pathways in NPAHs**

In 1966, Chapman et al. correlated the probability of photoreactivity of NPAHs with the out-of-plane arrangement of the nitro group relative to the plane of the aromatic moiety [47]. NPAH compounds with parallel nitro substituents were proposed to be more stable to light degradation than those with perpendicular nitro substituents. This correlation is known as the Chapman's orientation-photoreactivity relationship. In general, nitro groups peri to two hydrogen atoms are expected to be in a perpendicular orientation (Figure 1a), while nitro groups peri to one hydrogen atom are expected to stay in a parallel orientation relative to the aromatic rings (Figure 1b) [48,52-54]. The preferred perpendicular orientation of the nitro group peri to two hydrogen atoms is due to steric forces acting between the hydrogen atoms on the aromatic rings and the oxygen atoms on the nitro group, which restrict the torsion angle of the nitro group to an out-of-plane conformation.

Chapman proposed that the first step after excitation of compounds with nitro groups that are perpendicular to the aromatic rings is rearrangement of the nitro group to a nitrite intermediate (Figure 2 (2)). It was further proposed that perpendicular orientations increased probability of overlap between the half-vacant, non-bonding orbital of the nitro group and the adjacent orbital of the aromatic ring in the excited state [47]. This orbital overlap leads to the formation of an oxaziridine-type transition state (Figure 2 (1)) that can collapse to the nitrite intermediate (Figure 2 (2)). A dissociation reaction then produces nitrogen (II) oxide (NO₂⁻) and aryloxy (ArO⁻) radicals (Figure 2 (3)). Oxidation products such as quinones and hydroxyl compounds are expected to be formed subsequently from secondary reactions of the aryloxy radical intermediate. In parallel orientations, orbital overlap between the π-orbitals of the aromatic ring and the half-vacant, non-bonding orbital of the nitro group is unfavorable in the excited state, precluding the formation of the oxaziridine-type transition state (Figure 2).

However, it is still unclear which excited state is responsible for the formation of the nitrite intermediate and of the NO and ArO radicals. Figure 3 summarizes the primary electronic-energy relaxation pathways that have been proposed in the photochemistry of NPAH compounds. A generic NPAH compound (NO₂-Ar) is used as example. A direct dissociation-recombination mechanism from the excited singlet state was first proposed by Brown [55]. In this mechanism, the C-N bond is weakened in the excited singlet state leading to the formation of the aryl (Ar•) and nitrogen (IV) dioxide geminate radical pair. This radical pair was suggested to rearrange to a nitrite intermediate, which then forms the aryloxy radical (pathway 2b in Figure 3). Subsequently, Chapman proposed that an upper nπ* triplet state (pathway 2a in Figure 3) is another plausible candidate for the formation of nitrogen (II) oxide and the aryloxy radicals but did not provide spectroscopic evidence of its participation [47].

Spectroscopic studies, mainly by Hamanoue [56-60], and Testa and their co-workers [61,62] were subsequently performed in an effort to detect the proposed excited states and reactive intermediate species participating in the photochemistry of NPAH compounds. Studies by Hamanoue et al. using 9-nitroanthracene and several meso-substituted nitroanthracene derivatives suggested that NPAH compounds decay through two simultaneous pathways after light absorption [29,56-60]. Singlet-to-triplet intersystem crossing was proposed as one of the relaxation pathways (path 1 in Figure 3). A second pathway involves the formation of nitrogen (II) oxide and the aryloxy radicals through a photoinduced dissociation reaction of the NPAH compound from an intermediate triplet state (path 2a in Figure 3). Electron spin resonance and transient absorption studies have been used to detect the radical

![Figure 1: The nitro-group in (a) 6-nitrobenzo[a]pyrene is peri to two hydrogen atoms while in (b) 1-nitropyrene is peri to one hydrogen atom.](image-url)
intermediates formed from the dissociation reaction [57,59,63]. The lowest-energy excited triplet state has been detected using transient absorption, Raman spectroscopy, and steady state phosphorescence at low-temperature [26,34,56,59,64,65]. However, direct evidence of the population of the intermediate excited triplet state and of the excited state responsible for the formation of the nitrogen (II) oxide and the aryloxy radicals were not obtained because of the limited time-resolution and detection sensitivity used in those works. It has also been suggested that the lowest-energy excited triplet state in NPAH compounds may undergo intermolecular electron transfer or hydrogen abstraction depending on the solvent used (Figure 3) [34,35,61,65,66], but direct spectroscopic evidence of these reactive intermediates is lacking (Figure 3).

Several groups have recently challenged Chapman’s orientation-reactivity relationship [23,25,26,29,30]. Warner et al. studied the photodegradation of several NPAH pollutants in solution and solid particles [23]. The authors grouped the NPAHs in three different categories based on their photoreactivity in solution. While several NPAH compounds followed Chapman’s relationship others do not. It was concluded that the nitro group orientation is not the only factor controlling the photoreactivity of the NPAH pollutants [23], and recent works support this idea [25,29,32,34,38,39]. For instance, femtosecond broadband transient absorption spectroscopy in combination with computational methods has been recently used to study the excited state dynamics in 1-nitropyrene [25]. Ground state optimization of 1-nitropyrene results in a nitro group torsion angle of 32.8° relative to the aromatic rings. Optimization of the lowest-energy excited singlet state resulted in a nitro group torsion angle of 0.07°. The transient absorption spectra revealed that the rotation of the nitro group in the excited singlet state occurs in ~100 femtoseconds [25]. Based on Chapman’s relationship (Figure 2), the nitro to nitrite rearrangement should not be favored in the photochemistry of 1-nitropyrene. However, 1-hydroxypyrene is the major product in the photochemistry of 1-nitronaphthalene and in 2-methyl-1-nitronaphthalene, whereas a ca. 5 kcal/mol energy barrier prohibits the population of the intramolecular change transfer state in 2-nitronaphthalene [38]. This energy barrier explains the lack of photoreactivity in 2-nitronaphthalene in the solvent used [39]. The dissociative channel is proposed to be responsible for the dissociation-recombination mechanism proposed originally by Brown [55], leading to the formation of the aryl radical (Ar•) and nitrogen (IV) dioxide geminate radical pair (Figure 3). This radical pair rearranges to a nitrite intermediate (2 in Figure 2), which then form the nitrogen (II) oxide (NO) and arylxylo (ArO) radicals (3 in Figure 2 and pathway 2b in Figure 3). The formation of the NO and ArO radicals has been proposed to be the primary photochemical pathway leading to the observed photochemistry in 1-nitronaphthalene and 2-methyl-1-nitronaphthalene under anaerobic conditions [39].

Role of aryl and nitrogen (IV) dioxide geminate radical pair recombination in the photochemical fate of nitronaphthalene derivatives

An important aspect in the development of the kinetic model discussed above for the nitronaphthalene derivatives [29,38,39] is the fact that internal conversion from the lowest-energy excited singlet state to the ground state is negligible, as time-resolved anisotropy measurements for 1-nitronaphthalene indicated [24]. This is further supported by recent CASPT2//CASSCF(12/12) calculations in which conical intersections between the S1 and excited singlet states were not found [37]. These nitronaphthalene derivatives also exhibit negligible fluorescence quantum yields of ca. 10⁻⁴ or less [38,39]. However, the
reported photodegradation yield of 1-nitronaphthalene is ca. $10^{-3}$ and its triplet yield is only 64% under anaerobic conditions [39], leaving a large fraction of the initial excited singlet state population unaccounted for. This result seems counterintuitive because it implies that close to 36% of the excited singlet state population in 1-nitronaphthalene should return back to the ground state. Similarly, the photodegradation yield of 2-nitronaphthalene is practically zero and the reported triplet yield is only 93% [39]. This implies that 7% of the excited singlet state population should decay back to the ground state. In the case of 2-methyl-1-nitronaphthalene, the triplet yield is 33% and the photodegradation yield is 12% [39]. This leaves 55% of the excited-state population returning to the ground state unaccounted for.

To reconcile the fact that the time-resolved and the photochemical results available to date cannot account for the decay of all of the excited singlet state population, we propose that a large fraction of the aryloxy radical after hydrogen abstraction from the solvent or from a reaction of singlet oxygen with 1-nitronaphthalene. However, more work is needed to characterize the photoproducts of 1-nitronaphthalene and those resulting from the photolysis of 2-methyl-1-nitronaphthalene in different solvents and in the presence of different additives. While this is out of the scope of the present work, below we explore what can be learned regarding the primary photochemical pathways in these nitronaphthalene compounds from the determination of photodegradation rates and quantum yields in the presence or absence of molecular oxygen (Figure 4).

The photodegradation rates for 2-nitronaphthalene, 1-nitronaphthalene, and 2-methyl-1-nitronaphthalene were estimated from the changes in absorbance as a function of irradiation time for each nitronaphthalene derivative using absorption spectroscopy under air-saturated conditions. A Pyrex filter was used to block the radiation wavelengths below 300 nm (see the methods section for details). Precautions were taken to ensure that the integrated area of the initial absorption band above 300 nm (i.e., before the irradiation experiments began) were similar for the three nitronaphthalene derivatives.

The changes in absorbance were converted to changes in concentration using the extinction coefficients reported in the literature for each compound [39]. A kinetic, zero-order rate equation was used to determine the photodegradation rates because the percent of degradation of each nitronaphthalene derivative was kept at 15% or less. In the case of 2-nitronaphthalene, no detectable changes in absorption spectrum were observed even after more than 6 hours of continuous irradiation in cyclohexane or acetoneitrile solutions. Hence, it is assumed to be photoinert under the air- and $O_2$-saturated conditions used in this study.
work. Similar results were obtained recently for the photochemistry of 2-nitronaphthalene in acetonitrile under anaerobic conditions [39] (Figure 5).

Figure 5 shows the estimated photodegradation rates as a function of the calculate ground-state torsion angle for each compound. The torsion angles were obtained from density functional calculations in vacuum at the B3LYP/6-31+G(d,p) level of theory, as reported previously [29,39]. The photodegradation rates increase with an increase in the nitro-group torsion angle of the nitronaphthalene derivatives independent of the solvent used. This is in general agreement with Chapman’s orientation-reactivity relationship (Figure 2) [47] and in good agreement with the photodegradation rates previously measured in the gas phase [22]. While the photodegradation rate of 1-nitronaphthalene does not vary significantly in cyclohexane versus acetonitrile, the photodegradation rate of 2-methyl-1-nitronaphthalene is twofold higher in cyclohexane than in acetonitrile. The latter observation correlates with the smaller rate of intersystem crossing reported for this compound in cyclohexane ($2.7 \times 10^{12}$ s$^{-1}$) relative to acetonitrile ($4.8 \times 10^{12}$ s$^{-1}$) [38]. In other words, assuming that the solvent-dependent intersystem crossing rates equal to a decrease in the triplet yield of 2-methyl-1-nitronaphthalene in cyclohexane versus acetonitrile, an increase in the yield of the dissociative pathway would be expected (Scheme 1), which can lead to the observed increase in the photodegradation rate in cyclohexane. Another possibility is that there is a higher formation of singlet oxygen in cyclohexane than in acetonitrile for 2-methyl-1-nitronaphthalene [67], which leads to a significant increase in the formation of oxidative products. However, the participation of singlet oxygen in the formation of oxidation products seems to be insignificant. A more quantitative analysis of the potential participation of singlet oxygen in the photochemistry of 1-nitronaphthalene and 2-methyl-1-nitronaphthalene requires the determination of photodegradation yields in the presence and absence of molecular oxygen, which are reported next (Table 1).

Table 1 collects the photodegradation yields of 2-nitronaphthalene, 1-nitronaphthalene, and 2-methyl-1-nitronaphthalene in acetonitrile under N$_2$-, O$_2$-, and air-saturated conditions. The photodegradation quantum yields were determined using a HPLC to separate the photoproduts from the parent compound, as explained in the method section. Analogous measurements in cyclohexane were impractical because the higher volatility of this solvent. As in the case of the photodegradation rate reported above, no photodegradation was observed in the irradiation experiments for 2-nitronaphthalene in the presence or absence of molecular oxygen and thus its photodegradation yield is reported as zero in Table 1. On the other hand, the photodegradation quantum yield of 1-nitronaphthalene and 2-methyl-1-nitronaphthalene decreases with an increase of molecular oxygen concentration. This might be indicative of quenching of the triplet state in the presence of molecular oxygen, leading to large yields of singlet oxygen generation in 1-nitronaphthalene [67] and 2-methyl-1-nitronaphthalene solutions. However, this will also suggest that singlet oxygen is unable to oxidize 1-nitronaphthalene or 2-methyl-1-nitronaphthalene in acetonitrile, as has been observed in nitropyreno derivatives [68].

The suggestion above that singlet oxygen cannot oxidize the nitronaphthalene derivatives would also imply at first glance that the triplet state should play a large role in the photochemistry of 1-nitronaphthalene and 2-methyl-1-nitronaphthalene in acetonitrile, contrary to what has been recently proposed [39]. However, the reduction in the photodegradation yield under aerobic conditions can also be explained by assuming that molecular oxygen can scavenge one or more of the radicals formed in the intramolecular charge transfer pathway (Scheme 1). In fact, Garcia-Berrios and Arce have recently proposed that molecular oxygen can scavenge the pyrenylxoyl radical of 1-nitropyrene efficiently [39], thus reducing by 67% the formation yield of 1-hydroxypyrene, one of the major photoproducts [26]. If molecular oxygen can also scavenge one or more of the radicals formed in 1-nitronaphthalene and 2-methyl-1-nitronaphthalene, then this would explain part or all of the reduction in the photodegradation yield reported in Table 1 under aerobic conditions. For instance, recent experiments in aqueous solutions have shown that the radical anion of 1-nitronaphthalene can be scavenged by molecular oxygen [69]. Clearly, however, the experiments presented herein cannot prove or rule out the participation of the triplet state in the photoreactivity of these nitronaphthalene derivatives or the direct scavenging by molecular oxygen of one or more of the radical species proposed in Scheme 1. Altogether, it is clear that the photochemistry of these nitronaphthalene derivatives is more complex than previously thought and further stead-state and time-resolved photochemical investigations in the presence of triplet quenchers and radical/electron scavengers are warranted.

Experiments aimed at measuring and quantifying the generation of singlet oxygen in the photochemistry of 2-nitronaphthalene and 2-methyl-1-nitronaphthalene are essential to evaluate their potential phototoxicity, as has been recently shown for other NPAHs [20]. A high yield of singlet oxygen has been reported for 1-nitronaphthalene in both acetonitrile and cyclohexane solutions [67]. In particular, 2-nitronaphthalene might prove to be an excellent singlet oxygen generator upon UVA excitation, which can explain its high toxicity [19]. If so, 2-nitronaphthalene has the potential to be used in photosensitization and therapeutic applications, where the use of a photochemically-robust, photoinert sensitizer is required.

**Conclusions**

The major reaction pathways in the photochemistry of NPAHs under specific laboratory conditions have been presented. Readers interested
in a broader discussion about the photochemistry of nitro-aromatic compounds are referred to previous monographs [8,19,70,71]. Despite recent progress at understanding the photodegradation mechanism of NPAHs, fundamental gaps remain in our knowledge of the elementary steps that lead to product formation. This is particularly evident regarding the competition among available reaction pathways, the intermediate species involved in the photochemical transformations, and the degradation rates as a function of compound structure, added co-solutes, and micro-environment.

New insights regarding the primary reaction pathways participating in the photochemistry of 2-nitronaphthalene, 1-nitronaphthalene, and 2-methyl-1-nitronaphthalene in cyclohexane and acetonitrile solutions under aerobic and anaerobic conditions were presented. It was shown that molecular oxygen significantly reduces the photodegradation quantum yield of 1-nitronaphthalene and 2-methyl-1-nitronaphthalene, whereas 2-nitronaphthalene is essentially photoinert. Recombination of the aryl and nitrogen (IV) dioxide germinate radical pair within the solvent cage was suggested to play an important role in the fraction of excited singlet state molecules that returns to the ground state in 1-nitronaphthalene and 2-methyl-1-nitronaphthalene. An alternative ground-state recovery pathway was proposed, where a fraction of the intramolecular charge transfer state internally converts to the ground state before the dissociation-recombination process occurs. Scavenging of radical species by molecular oxygen and the generation of singlet oxygen in high yield were proposed to contribute to the photochemistry of these nitro-naphthalene derivatives in solution. Singlet oxygen did not seem to oxidize the nitronaphthalene derivatives under the experimental conditions used in this work. The triplet state was suggested to play a minor role in the photochemistry of 1-nitronaphthalene and 2-methyl-1-nitronaphthalene. Further studies are needed to corroborate or refute this latter hypothesis using triplet quenchers other than molecular oxygen.

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68. Arce R personal communication.

