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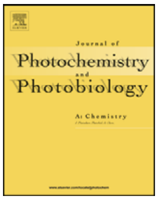

Steady-state and transient photolysis of p-nitroaniline in acetonitrile

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ABSTRACT

Both transient photolysis and steady-state photo-degradation experiments were performed to gain insight into the kinetics and mechanisms of degradation of p-nitroaniline (p-NA) in acetonitrile (MeCN) solutions. Complete degradation of p-NA was observed at diverse irradiation conditions under 254 nm UV light. Once H_2O_2 was added into the experimental system, degradation of p-NA was enhanced remarkably. The removal rate increased rapidly with increment of the irradiation time and reached 90% at 30 min. p-NA could be totally removed after 90 min in UV/H_2O_2 process. In the presence of O_2 and H_2O_2, removal rate increased linearly with increment of the irradiation time and reached 90% at 10 min. p-NA could be totally removed after 20 min in UV/($O_2 + H_2O_2$) process. For transient photolysis, excited states of p-NA were observed after 355 and 266 nm laser flash photolysis (LFP). The transient absorption spectra were recorded and bimolecular rate constant of $6.89 \times 10^9\ M^{-1}\ s^{-1}$ was calculated for the self-quenching of ^{3}p-NA*. Production of ^{3}p-NA* in MeCN and H_2O mixed solution was also studied. LFP of p-NA with addition of H_2O_2 was investigated for the first time.

1. Introduction

p-Nitroaniline (p-NA) is an important compound either manufactured or used as an intermediate such as in the synthesis of dyes, antioxidants, pharmaceuticals, gum inhibitors, poultry medicines, pesticides, etc. As a consequence, a plethora of p-NA is leaked out with industrial wastewater into the environment. Unfortunately, p-NA has been found to be harmful to aquatic organisms and may cause long-term damage to the environment. It is highly toxic with a TLV (threshold limit value) of 0.001 kg m^{-3}, which is lower than that of aniline (0.002 kg m^{-3}). The presence of a nitro group in the aromatic ring enhances its stability to resist chemical and biological oxidation degradation, while the anaerobic degradation produces nitroso and hydroxylamines compounds which are known as carcinogenic [1–3]. Nowadays, p-NA has been considered as one kind of persistent organic pollutants (POPs) due to its toxicity, potential carcinogenic and mutagenic effects, and treatments of p-NA containing wastewater have attracted world-wide attention [3–5].

In recent years, advanced oxidation processes (AOPs) have been identified as an attractive option for wastewater purification, particularly in cases where the contaminant species are difficult to be removed using biological or physicochemical processes. The processes involve the generation of highly reactive hydroxyl radical ($^\bullet$OH), which can oxidize and mineralize almost all organic molecules owing to its high oxidation potential ($E^\circ = +2.8$ V) [6–8]. UV light or sunlight has been used in the direct photo-degradation of contaminants in aqueous environments, but neither is considered as an efficient method. Since the late 1960s, many studies have indicated that the UV/H_2O_2 process is able to oxidize a wide variety of organic pollutants in aqueous solutions [9–11]. Generally, the effectiveness of homogeneous light-driven oxidation processes is associated with $^\bullet$OH radicals generated in the reaction mixture by the direct photolysis of an added component (e.g., H_2O_2) under UV irradiation.

$$H_2O_2 \xrightarrow{h\nu} 2^\bullet OH \qquad (1)$$

The success of direct photolysis is highly dependent on the photo-reactivity of the organic compounds. Hence, the properties of the pollutants and the photo-degradation mechanism should be investigated beforehand because the degradation mechanism of organic substances is often complex, especially in diverse reaction conditions. Consequently, individual degradation systems must be designed to study the properties of target pollutants. Besides, some reactive intermediates might undergo further reactions and be present at undetectable concentrations. Hence, their transient existence can only be inferred from the kinetic data and/or other means. Laser flash photolysis (LFP) and pulse radiolysis techniques have been used to study the mechanism involved. The intersystem cross-

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ing (ISC), internal conversion, and vibrational relaxation of p-NA in water and 1,4-dioxane have been studied using ultrafast transient absorption spectroscopy. The data reveal that relaxation on the excited singlet state surface, followed by internal conversion to the ground-state and intersystem crossing to the triplet state [1]. In this paper, excited states of p-NA were studied in MeCN solution, whose polarity is higher than 1,4-dioxane and lower than water. Transient photolysis of p-NA in MeCN was investigated using 355 and 266 nm LFP. And photochemical properties of p-NA were studied. Furthermore, LFP of p-NA with H_2O_2 was investigated for the first time. Early in the year 1977, Van Der Linde had determined the reaction rate constant of p-NA with $^{\bullet}OH$ using pulse radiolysis [12]. However, the data have never been used to associate with any practical degradation research. Although some researches such as photo-catalytic degradation has been done to understand the degradation mechanism [5], to the authors' knowledge, there is little information available in the literature about the detailed degradation mechanism of p-NA in MeCN solution, especially the cooperation of $^{\bullet}OH$ with O_2. In this study, both steady-state photo-degradation and transient photolysis experiments of p-NA were performed to gain insight into the kinetics and mechanisms of photo-induced degradation of p-NA in MeCN. The main objectives of the present work are to elucidate the mechanisms of photo-induced degradation of p-NA and consequently to provide kinetic insight into utilization for remediation of p-NA-laden wastewaters.

2. Experimental

2.1. Chemical reagents

p-Nitroaniline, tert-butanol (t-BuOH) and 30% H_2O_2 were of analytical grade purchased commercially. Acetonitrile (MeCN) was chromatographic purity grade. O_2 and N_2 gases were of high purity (99.99%). Other reagents were used directly without further purification. All solutions were fresh prepared using water from a Milli-Q purification system just before experiment.

2.2. Laser flash photolysis experiments

LFP experiments were performed with a ND:YAG laser which provided 266 and 355 nm pulses with a duration of 5 ns. The maximum laser power was 50 and 80 mJ/pulse, respectively. The samples for photolysis experiments were all bubbled with high-purity (99.99%) N_2 or N_2O in quartz cuvettes for 20 min before use. The time-resolved experiments were all carried out at $15 \pm 2\,^{\circ}C$. The detailed description of the facility and experimental conditions can be found elsewhere [13,14].

2.3. Photo-degradation procedures and analysis

The irradiation source is hexagonal in cross section of 9 cm side length. Six low-pressure Hg lamps (8 W), which emit 253.7 nm UV light, are arranged on each side of the device made of stainless steel and coated by aluminum foil for light reflection. Samples in quartz cuvettes were located in the center of the lamps. Details of the device can be referred to a Chinese Patent [15].

Concentrations of p-NA were determined by gas chromatography (Varian CP 3800) with a column (VF-5MS, $30\,m \times 0.25\,mm \times 0.25\,\mu m$). The column temperature was initially held at $50\,^{\circ}C$ for 2 min and then programmed up to $300\,^{\circ}C$ at $20\,^{\circ}C\,min^{-1}$. UV–vis absorption spectra were measured by a Hitachi UV-3010 spectrophotometer. All experiments were carried out at ambient temperatures ($25 \pm 2\,^{\circ}C$).

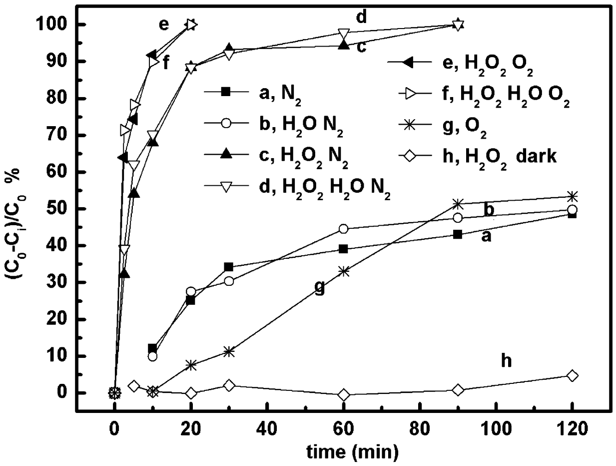

Fig. 1. Removal rates of 1 mM p-NA in MeCN solutions at different conditions: (a) N_2 saturated; (b) N_2 saturated with H_2O; (c) N_2 saturated with H_2O_2; (d) N_2 saturated with H_2O_2 and H_2O; (e) O_2 saturated with H_2O_2; (f) O_2 saturated with H_2O_2 and H_2O; (g) O_2 saturated; (h) with H_2O_2 in dark.

3. Results and discussion

3.1. Remove of p-NA in MeCN under 254 nm UV light

3.1.1. Direct remove of p-NA in MeCN

Series of p-NA MeCN solutions were irradiated at 254 nm UV light; and the removal rate is shown in Fig. 1. In N_2 saturated experimental system, removal rate increased slowly along with increment of the irradiation time and reached 50% after 120 min (Fig. 1a). When p-NA solution was saturated with O_2, removal rate was reduced slightly at the beginning of the irradiation but also reached 50% after 120 min (Fig. 1g). With the progress of photolysis the color of the solution became brownish gradually and precipitates were obtained.

The following content will expound that p-NA can be photo-excited directly to produce its excited states in N_2 saturated MeCN solution. Then excited states of p-NA interact with its ground-state spontaneously to form dimers, trimers (Eqs. (2)–(4)), and eventually result in higher oligomers and polymers of low solubility, which can be easily separated from the solution. In O_2 saturated experimental system, excited states of p-NA can be quenched by O_2 to produce singlet oxygen ($^1O_2^*$) (Eq. (5)). Accordingly, the yield of triplet states of p-NA (^{3}p-NA*) will be reduced. Hence, the removal rate was a little lower than that of N_2 saturated experimental system at the very beginning of the irradiation. However, $^1O_2^*$ is also one of the most oxidizing and reactive species. It is extensively involved in the degradation of organic pollutants as the result of its high oxidative activation ($E^{\circ} = +2.2\,V$). Obviously, both N_2 and O_2 experience the increase in color intensity and form precipitates during reaction, and they are both oxidation processes, which lead removal of p-NA in MeCN solution with lower rate.

3.1.2. Effect of $^{\bullet}OH$ and cooperation with O_2 in photo-degradation of p-NA

Once H_2O_2 was added into the experimental system, removal rates of p-NA were enhanced remarkably. In N_2 saturated solution with addition of 0.147 M H_2O_2, removal rate increased rapidly along with increment of the irradiation time and reached almost 90% in 30 min. p-NA could be totally degraded after 90 min (Fig. 1c and d). In order to rule out direct oxidative of H_2O_2 in the photo-degradation process, p-NA solution with addition of 0.147 M H_2O_2 was kept in dark. And p-NA could not be degraded (Fig. 1h). This means that $^{\bullet}OH$ generated from H_2O_2 by 254 nm UV light-induced photo-degradation of p-NA in MeCN. The mechanism of $^{\bullet}OH$-