

Article ID: 1001-0742(2001)03-0361-04

CLC number: X12

Document code: A

Photodegradation of α -naphthaleneacetic acid in aqueous solution

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Abstract: Kinetic processes of α -naphthaleneacetic acid (NAA) photolysis were studied under different conditions. The results showed that the ultraviolet light was more effective than fluorescent light in promoting degradation, and the degradation of NAA under ultraviolet light followed the first order kinetics with the photolysis rate constant of $1.15 \times 10^{-2} \text{ min}^{-1}$ and half-life time ($t_{1/2}$) of 60 min. Further, it was proved that the photolysis rate was higher in the presence of oxygen, titanium dioxide (TiO_2), and low pH (acidic solution). At last, two photolysis intermediates were identified by GC-MS and possible photolysis pathways were proposed.

Key words: α -naphthaleneacetic acid; photolysis; aqueous solution

Introduction

α -naphthaleneacetic acid (NAA) is an important plant growth regulator used not only to prevent the preharvest drop of apples but also as a fruit thinning agent (Worthing, 1991). Much research work about the effect of NAA on plant tissues (Speer, 1993; Hideyoshi, 1993; Prasad, 1994), plant growth and synthesis of RNA and proteins (Joshi, 1993) etc, has been published. Pispipa B. *et al.* have investigated the photophysical behavior of NAA by steady-state and time-resolved fluorescence as a function of pH (Pispipa, 1994). But the photolysis of NAA are scarcely studied.

The influence of wavelength of the lamp, carrier gas, pH of the solution and titanium dioxide (TiO_2) on photolysis of NAA are reported here; its photoproducts were identified, and possible pathways of photodegradation in aqueous solution were established.

1 Materials and methods

1.1 Reagents and materials

NAA (98%) was purchased from Caoyang Second Reagent Factory, Shanghai, China. TiO_2 (anatase) also from Shanghai was used as a photocatalyst. All solvents used were of analytical grade. Doubly distilled water was used throughout this study.

1.2 Photoreactor

The basic photoreactor geometry is shown in Fig. 1. The reactor consisted of a 40 cm i. d. aluminum tube, three ultraviolet lamps (main wavelength at 254 nm) and three fluorescent lamps (main wavelength at 365 nm). The ultraviolet lamps and the fluorescent lamps were fixed on the wall of aluminum tube at equal distance, so that the aqueous solution in the photoreactor can be irradiated uniformly (Liu, 1995).

The distance between the lamps and the reactor wall was 10 cm. The water temperature at inlet tube was kept at 25°C. Nitrogen or oxygen at 300 ml/min was used as the carrier gas and the suspension in the reactor was constantly stirred magnetically.

1.3 Analytical determination

Concentration of unreacted NAA was determined as follows: the irradiation was stopped at fixed times, the suspension was centrifuged at high speed (1000 r/min) for 20 min, the centrifuged solution was analyzed by High Performance Liquid Chromatography (HPLC; Blswanath, 1988; Sajid, 1991). 10 μl centrifuged solution was injected into the chromatograph, composed by an isochrom pump, a spectra 100 UV-Vis detector, and SPHERI-5 RP18 (220 mm \times 4.6 mm i. d.) column. A mixture of methanol/water (70/30, v/v) at 0.5 ml/min was used as a mobile phase. The NAA absorption was monitored at 281 nm, which corresponds to one of the λ_{max} value of the compound. Its measured retention time was 4.03 min.

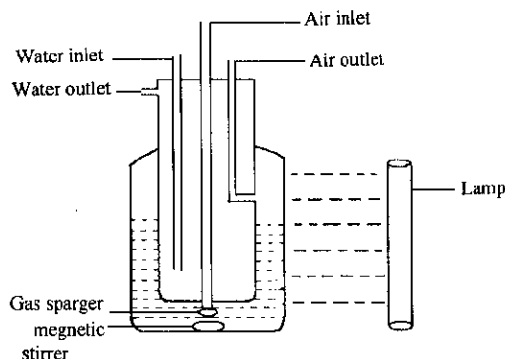


Fig. 1 Basic geometry of photoreactor

1.4 Photoproducts identification

An aqueous solution of NAA (10 mg/L) was irradiated for 2h in the photoreactor. The photolysis products obtained were extracted with equal volume of methyl trichloride (CHCl_3), the organic extract was analyzed with GC-MS, composed by a Finnigan MAT model SSQ-7000 chromatograph-mass spectrometer using electron impact ionization at 70 eV and a 30m SE-54 quartz capillary column. The GC oven temperature was programmed to increase from 80°C to 250°C at a rate of 6°C/min.

2 Results and discussion

2.1 Effect of wavelength

The UV absorption spectra of NAA indicate that NAA has only two major absorption bands, one at 223 nm, and the other at 281 nm, no absorption at wavelength longer than 320 nm. But the wavelength of sunlight is above 290 nm, so NAA hardly photodegrades under sunlight radiation. This expectation was supported by our experiment. After one day under the sunlight, the concentration of NAA was decreased from 50 mg/L to 42.5 mg/L, which indicates only 15% decomposed, including a part of thermodegradation.

Similar results were observed when the sample was irradiated under fluorescent light (main wavelength at 365 nm) for 3h with only 5.3% NAA decomposed, whereas after 3h irradiation under ultraviolet light (main wavelength at 254 nm), 86% was decomposed (Fig. 2). Many organic molecules are excited by light of 254 nm and degraded as a result of direct action (Ralph, 1992). NAA has no absorption at 365 nm, so it is hard to break the chemical bond with fluorescent light. Therefore the degradation rate of NAA is slower under fluorescent light as compared to under ultraviolet light.

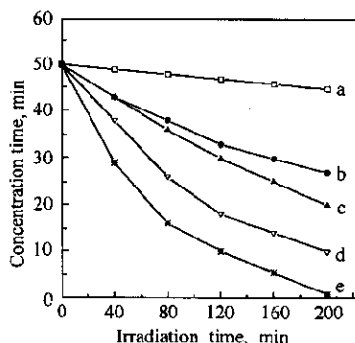


Fig.2 Photodegradation of α -naphthal enacetic acid in different conditions

a.365 nm; b.365 nm + TiO_2 ; c.254 nm + N_2 ; d.254 nm; e.254 nm + TiO_2

The degradation of NAA under ultraviolet light followed a first-order kinetics and the following equation was derived experimentally.

$$\ln C = -0.011509t + 3.963.$$

The photolysis rate constant, $1.15 \times 10^{-2} \text{ min}^{-1}$, the related coefficient (γ), 0.9961, and the half-life time of degradation ($t_{1/2}$), 60 min, were determined.

2.2 Effect of carrier gas

The photolysis rate and the products of NAA were varied with different carrier gas, i.e. oxygen and nitrogen. Aqueous solution of NAA (50 mg/L) was irradiated for 1.5h under UV light (254 nm) in different carrier gas and then analyzed by HPLC. The results are shown in Fig. 3, which indicate that not only the photolysis rate in nitrogen (absence of oxygen) was obviously slower than that in oxygen, but also the number of photoproducts in nitrogen were less than that in oxygen. According to the identified photoproducts, the photo reaction of NAA in aqueous solution can be expressed as oxidation process because the dissolved oxygen in the aqueous solution act as an electron neutralizer to form O_2^- that changed to H_2O_2 , which formed the active oxygen species such as OH^\cdot and O_2^- . It can be

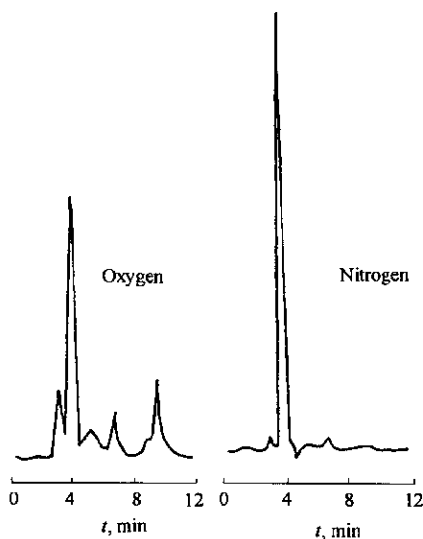
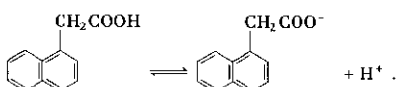


Fig.3 HPLC pattern of photoproducts

concluded that the hydroxyl radical, OH^\cdot , is the primary oxidant in this photo-catalytic system (Craig, 1990).

2.3 Effect of pH

NAA is a weak acid and its ionization equation in aqueous solution is shown as below:



The pH of aqueous solution of NAA was 3.41. HCl and NaOH were used to adjust the pH of the aqueous solution. The effect of pH on the photodegradation of NAA was determined and the results are shown in Fig. 4. It can be seen that the photolysis rate increased with a decrease in pH of the aqueous solutions. At pH > 9.0, the photolysis rate was slower due to the increase of hydroxyl ions (OH^-). The decrease of photolysis rate by increasing pH of the aqueous solution can be explained by assuming competition between ionization and photodegradation of NAA for the active sites.

2.4 Effect of TiO_2

The effect of TiO_2 (anatase) as a catalyst on the photolysis of NAA was also determined with adding various amounts of TiO_2 into aqueous solution, 100 mg/L TiO_2 was found to be the optimum dose for NAA photolysis. The reaction rate coefficient (k) was found to be $1.9 \times 10^{-2} \text{ min}^{-1}$ under 254 nm radiation with 100 mg/L TiO_2 and the photolysis rate was 1.7 times higher than that without TiO_2 . The half-life time in the presence of TiO_2 was only 39 min, which is shorter as compared with 60 min without TiO_2 . It was also observed that TiO_2 can promote photolysis rate of NAA under 365 nm radiation (Fig. 2). This can be explained as TiO_2 particles can absorb light heavily and reduce the penetration distance of photons from the NAA particles. The photoelectrons and holes are formed closer to the surface of TiO_2 particles and take less time to reach the surface of the NAA particles, and hence find less time to participate in energy wasting recombination reactions before useful surface (or near-surface) reactions could take place (Ralph, 1992). The electron-hole pairs can make almost every organic compound to undergo some oxidation-reduction reactions (Ralph, 1990; Edmondo, 1993).

2.5 Photoproducts identification and possible pathways of photo degradation

Under 254 nm UV light, the color of the NAA aqueous solution in the photo-reactor was changed from white to light yellow, which deepened with the increase of the irradiation time. According to the HPLC spectra (Fig. 3), there were four

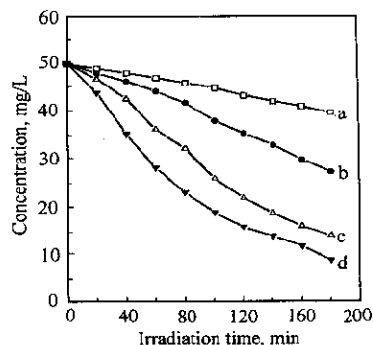


Fig. 4 Effect of pH on the photodegradation of α -naphthaleneacetic acid
a. pH = 11.07; b. pH = 9.07; c. pH = 6.70;
d. pH = 2.63

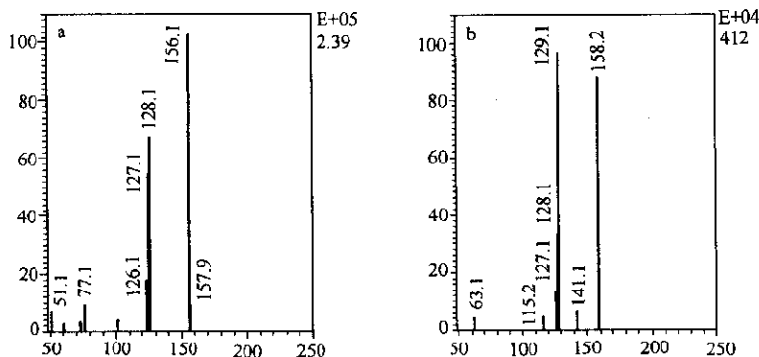


Fig. 5 EI mass spectrum of intermediate photoproducts

more peaks along with NAA peak. The first photoproduct appeared after irradiated for 9.95 min and the others were in succession, and their concentration increased gradually.

To identify the structure of these photoproducts, the photolytic solution was assayed by GC-MS. Several compounds having structure related to NAA were identified as possible degradation photoproducts. α -naphthaldehyde (Fig. 5a, Fig. 6 (2)) and α -naphthalenemethanol (Fig. 5b, Fig. 6 (3)) were found to be the main photoproducts when irradiated by the light. The possible pathway for the degradation of NAA can be suggested as an oxidative process involving the attachment of

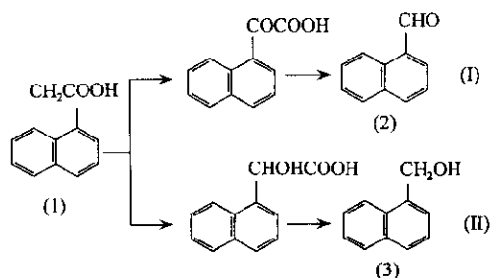


Fig. 6 Proposed photodegradation pathways of α -naphthaleneacetic acid

OH^\cdot radicals.

3 Conclusion

The photodegrade rate of α -naphthaleneacetic acid was slower in visible light than in 254 nm UV light. The degradation of NAA under ultraviolet lamp followed a first-order kinetics having a photolysis rate constant $1.15 \times 10^{-2} \text{ min}^{-1}$ and the half-life time ($t_{1/2}$) 60 min. The photolysis rate decreased with the increase of pH. TiO_2 (anatase) proved to be a good catalyst for photolysis of α -naphthaleneacetic acid with the half-life time ($t_{1/2}$) only 39 min, which is shorter as compared with 60 min without TiO_2 . The photoreactions of NAA in aqueous solution can be attributed as oxidation process. α -naphthaldehyde was identified as the main photoproduct.

Acknowledgment: The author thanks Akbar Ali (Pakistan Institute of Nuclear Science and Technology) for his technical help.

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(Received for review May 8, 2000. Accepted July 12, 2000)