

Photolysis of 2,4-dinitrotoluene in various water solutions: effect of dissolved species

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Abstract

This work investigates the photolysis of 2,4-dinitrotoluene (2,4-DNT) in the presence of different dissolved species. Initial experiments revealed that the direct photolysis of 2,4-DNT in deionized water solutions under sunlight and artificial light followed a pseudo-first order kinetic. Humic acids (HA) appeared to act as sensitizers in the aqueous photolysis of 2,4-DNT and the calculated half life was found to be approximately 2 h, which is faster than the half life calculated in the case of deionized water (~4 h). The presence of salt (NaCl) in the deionized water solutions was found to have a more pronounced sensitizing effect upon the photolysis of 2,4-DNT, yielding half lives of the order of 1 h. Investigations on seawater and groundwater spiked with 2,4-DNT, revealed that photolysis is enhanced in the order seawater > groundwater ~ deionized water. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Nitroaromatic compounds can be found in a variety of products, including pesticides and explosives. Their presence in fresh water, marine environments, drinking water supplies and industrial effluents poses serious environmental concerns due to the toxicity and persistence associated with these compounds [1,2].

In general, nitroaromatic compounds exhibit similar broad absorption spectra extending from the ultraviolet (UV) into the short-wavelength visible region. These spectra overlap the spectrum of ground-level sunlight and photolysis through direct absorption of sunlight is generally expected to be rapid [3]. A previous report examining the effect of structure variation of monocyclic nitroaromatics upon their direct photoreaction under sunlight concluded that photolysis rates of nitroaromatic compounds are strongly dependent on the nature of the substituent on the nitroaromatic ring [3]. This variability was found to be mainly attributable to differences in the reaction quantum efficiencies of the compounds. Substitution of the aromatic ring with methyl groups greatly enhances photolysis rates, especially when the methyl group is ortho to the nitro group. For example, nitrobenzene was the most inefficient of all compounds studied and substitution by methyl groups was found to particularly

enhance the photolysis efficiency of the nitroaromatic system. Furthermore, substitution adjacent to the nitro group resulted in decreased quantum efficiencies, and this apparent steric effect was most pronounced in the case of 2,3- and 3,4-dinitrotoluenes (DNT). Accordingly, the structural configuration of 2,4-DNT is expected to enhance photolysis by increasing quantum efficiencies.

Natural waters contain various substances that influence the rates of sunlight-induced reactions of pollutants. A previous report concluded that fulvic acid (isolated from different natural water bodies) enhance the sunlight-induced photodegradation rates of nitrobenzenes, nitrotoluenes, and nitroxylenes when compared to the rates observed in distilled water [3]. The phototransformation of 2,6-DNT in seawater subject to simulated solar radiation was recently published and the authors reported a 89% phototransformation in 24 h and a complete removal after 72 h [4].

Regarding 2,4-DNT, several reports evaluate the efficiency of different photodegradation treatment technologies such as advanced oxidation processes [1,5–10] or surfactant-assisted UV-photolysis [11,12]. However, to the best of our knowledge, scarce information [3] exists regarding the indirect or “sensitized” photolysis processes initiated via light absorption by natural substances for 2,4-DNT which is considered to be the most toxic explosive compound as evidenced by its extremely low drinking water and effluent discharge limits set by USEPA [13].

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The primary objective of this work was to investigate the photolysis of 2,4-DNT in natural waters as well as to evaluate the effect of different dissolved species (sodium chloride and humic substances) on 2,4-DNT aqueous solutions subject to artificial light. The results obtained in deionized water containing the target pollutant were used for comparison. Solid-phase microextraction (SPME) was used as a sample pre-treatment method [14] enabling photolytic investigation of dilute 2,4-DNT water solutions.

2. Experimental

2.1. Chemicals and sample preparation

2,4-DNT was purchased from Riedel-de-Haën. An acetonitrile stock solution was prepared and used daily for spiking aqueous solutions at the concentration level of interest. The stock solution was stored at 4 °C in the dark when not in use. All solvents were pesticide-grade (Merck KGaA). Deionized water was prepared on a water purification system (EASYpure RF, Barnstead/Thermolyne). Sodium chloride (>99.5% pure) was obtained from Merck and humic acid, sodium salt (technical grade) was purchased from Aldrich.

2.2. Photolytic experiments

Photolysis experiments under artificial light were conducted in a 500 mL Pyrex vessel in the center of which a glass cylindrical tube (17 × 3.5 cm) was placed housing a 9 W UV-A lamp (Radium Ralutec, 9 W/78, 350–400 nm). In a typical run, a 200 mL of a 1 mg/L 2,4-DNT aqueous solution containing the amount of dissolved species as described in the text was prepared daily and loaded in the vessel. The reactor and its content were covered with aluminum foil during all experiments. The reactor's temperature was left uncontrolled (22 °C initial temperature). Five millilitre samples periodically drawn from the vessel were analysed using the SPME sample pre-treatment method coupled to a gas chromatographer equipped with a flame ionisation detector (GC-FID). Previous investigations revealed that pH did not affect the photolysis rates of TNT and other nitroaromatics present in natural waters [9,15]. Accordingly, pH studies were not included in the present investigations.

Seawater (Sougia, south part of Crete) and groundwater (well in Agia Triada, Chania, Crete) samples, collected few days before conducting the photoexperiments, were initially analysed and found free of nitroaromatic contamination. Each sample was spiked at 1 mg/L with 2,4-DNT and the resulting synthetic solutions were exposed to artificial light according to the procedure described previously.

An outdoor photolysis experiment under natural sunlight irradiation was conducted on the roof of the department of Environmental Engineering (Technical University of Crete, Chania, Crete, 35°31'N, 24°1'E) between 10 a.m. and 6 p.m. on the sunny summer days in July. The total exposure time was 40 h in five days. The hydrolysis extend, was investigated by running a parallel experiment where an identical spiked demonized

water solution was left in the dark for the same period of time.

2.3. SPME procedure

The 65- μ m polydimethylsiloxane–divinylbenzene (PDMS–DVB) SPME fibre type and SPME fibre holder assembly, purchased from Supelco, were used for extraction. Overall, a five millilitre aqueous sample, was placed in a seven millilitre clear glass vial (Supelco), fitted with aluminium foil and screw cap with hole (Supelco). Extraction was performed at room temperature and under intensive magnetic stirring (1000 rpm) using a glass-coated mini-impeller. The SPME fibre holder assembly was clamped and allowed to sit on top of the seven millilitre glass vials and the SPME fibre was then exposed to the aqueous phase for 15 min at room temperature. After sampling the aqueous sample, the fibre was retracted and transferred to the heated injection port of the GC-FID for desorption, where it remained for 5 min.

2.4. GC-FID analysis

Analyses were performed on a Shimadzu GC-17A, Version 3, GC equipped with an FID and a 30 m × 0.25 mm 0.25 μ m SPB-1701 (14%-(Cyanopropyl-phenyl)-methylpolysiloxane) capillary column (Supelco). The split/splitless injector operated at 260 °C with the split closed for 5 min and the detector temperature was maintained at 280 °C. Helium was used as a carrier gas at a flow-rate of 1.2 mL/min. The oven temperature was initially held at 60 °C for 1 min, programmed to 250 °C at a rate of 10 °C/min where it stayed for 5 min.

Quantification was achieved by using the external standard calibration method. The linearity of the SPME method was evaluated over the concentration range 0.05–1 mg/L and was found to be very good having a 0.995 correlation coefficient (r^2). Repeatability, expressed in terms of relative standard deviation (R.S.D.), was determined by extracting five consecutive water samples spiked at the 1 mg/L during the same day and was found to be very good (R.S.D. = 2.6%).

3. Results and discussion

3.1. Direct photolysis of 2,4-DNT under sunlight and artificial light

The direct photolysis of 2,4-DNT in deionized water and under sunlight and artificial ultraviolet light was initially investigated. For the purpose of the present studies, an outdoor experiment under natural solar irradiation was initially carried out by exposing for 40 h in five days, 200 mL of deionized water spiked at a concentration level of 1 mg/L. A control experiment was run in parallel, where an identical solution was kept in the dark at ambient temperature for the same period of time. The concentration of 2,4-DNT was monitored in both solutions as a function of time and the results are depicted in Fig. 1. The control experiment showed that hydrolysis did not take place and hence photolysis is the predominant process for the dinitroaro-

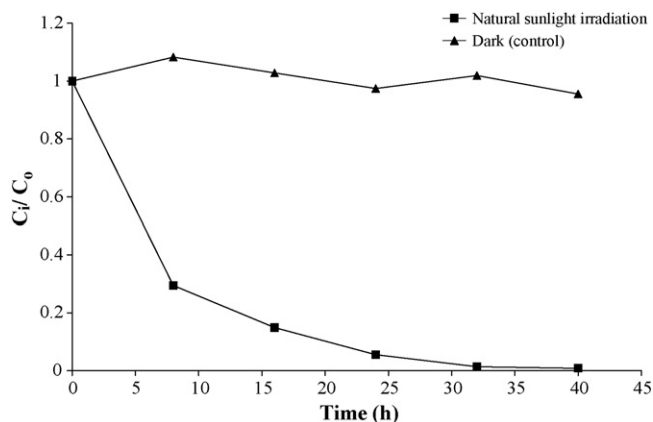


Fig. 1. Extend of direct photolysis of 200 mL deionized water solution spiked with 1 mg/L 2,4-DNT when exposed to natural sunlight irradiation or when left in the dark (control) for five days (total exposure 40 h).

matic compound removal. In addition, Fig. 1 revealed that the direct photochemical degradation of 2,4-DNT is of first order with respect to the substrate concentration, i.e.,

$$-\frac{dC_t}{dt} = kC_t \quad (1)$$

Rearranging and integrating Eq. (1) yields:

$$\ln(C_t) = \ln(C_0) - kt \quad (2)$$

where k is an apparent reaction rate constant, and C_0 and C_t is the substrate concentration at time zero and t respectively. If the concentration–time profiles are plotted in the form of Eq. (2), the rate constants can be calculated from the slopes of the respective straight lines. Linear regression of the logarithm of concentration against time, revealed that the apparent kinetic was first order ($r^2 = 0.98$) and the calculated half-life ($t_{1/2} = \ln 2/k$) was approximately 16 h.

Next, three deionized water solutions having different 2,4-DNT concentrations were exposed to UV-A (spectral domain 350–400 nm) and the reduction in concentration was monitored as a function of exposure time (Fig. 2). Overall, direct photolysis revealed a 39.3, 42.6 and 57.8% 2,4-DNT removal, after exposing for 4 h to UV-A aqueous solutions initially spiked at

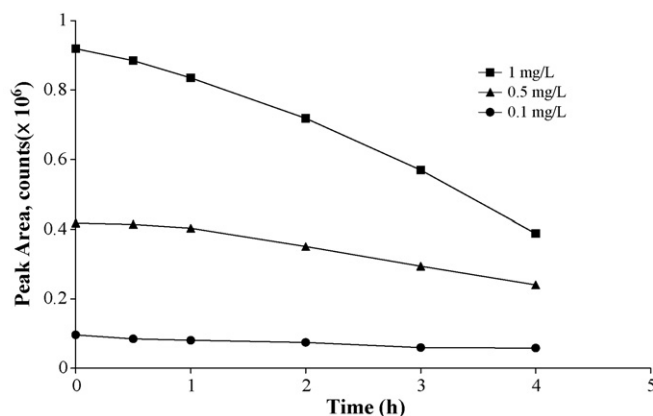


Fig. 2. Direct photolysis under artificial light of deionized water solutions spiked at 0.1, 0.5 and 1 mg/L with 2,4-DNT as a function of time.

0.1, 0.5 and 1 mg/L respectively. The data presented in Fig. 2 were then used to investigate the kinetics of the removal process taking into consideration the kinetic expressions describing zero and first order reactions. A zero-order reaction has a rate which is independent of the concentration of the reactant(s). Increasing the concentration of the reacting species will not speed up the rate of the reaction and the general equation describing the process is given by

$$-\frac{dC_t}{dt} = k \quad (3)$$

Upon integrating Eq. (3) yields:

$$C_t = C_0 - kt \quad (4)$$

Linear regression of the concentration (C_t) data versus exposure time and comparison with the results from the regression of $\ln(C_t)$ versus time, revealed that the phototransformation is best described by a pseudo-first order model with an approximate half-life ($t_{1/2}$) of 4 h.

3.2. Sensitized photolysis of 2,4-DNT under artificial light

Photolysis of organic compounds in aqueous solutions can be altered by various chemicals. Depending on the compound, these chemicals may act as sensitizers or on the contrary they may exhibit quenching and scavenging effects [16,17].

In a previous report dealing with 2,4,6-trinitrotoluene (TNT), Mabey et al. [15] found that the photolysis of this compound was strongly accelerated in aqueous solutions of humic substances. In addition, Simmons and Zepp [3], produced results on the influence of humic substances (fulvic acid isolated from different natural water bodies) on direct excitation of 19 nitroaromatics in aqueous systems under sunlight exposure. The results revealed that humic substances enhanced the rates of photolysis.

In light of this, the effect of humic acids (HA) upon the photoreaction of 2,4-DNT was investigated. Accordingly, in a separate set of experiments 1 mg/L 2,4-DNT deionized water solutions containing 10 mg/L of HA were exposed UV-A (spectral domain 350–400 nm) for 4 h and the reduction in concentration was monitored as a function of exposure time. The results are given in Fig. 2. As seen, HA had the ability to catalyse the 2,4-DNT photoreaction, enhancing 2,4-DNT removal (73.8%) when compared to the one found in the case of deionized water (57.8%). Assuming pseudo-first order reaction kinetic ($r^2 = 0.99$), the calculated half-life ($t_{1/2}$) was found to be approximately 2 h, which is faster than the half-life calculated in the case of deionized water (~ 4 h). This positive influence of HA on the photodegradation of 2,4-DNT is attributed to the sensitisation effect of HA [18,19] (Fig. 3).

Next, the effect of salt upon the photolysis of 2,4-DNT was investigated using sodium chloride as model salt. For the purpose of these studies, NaCl concentrations ranging from 0–15%, w:v were investigated and the photolysis of 1 mg/L deionized water solutions were monitored as a function of time. As seen (Fig. 4) the presence of salt had a dramatic effect on the photodegradation of the dinitroaromatic compound investigated here. After 4 h of irradiation, removals were found to be 57.8, 91.3, 94.6 and

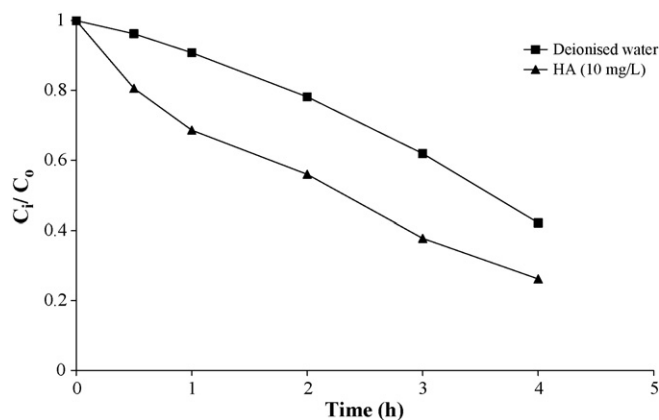


Fig. 3. Photolysis of 2,4-DNT in deionized water and in the presence of humic acid (10 mg/L) under artificial light (UV-A spectral domain).

95.0% for aqueous solutions containing 0, 4, 8, and 15% NaCl (w:v) respectively, demonstrating thus the sensitisation effect of NaCl on the photolysis of 2,4-DNT. Application of linear regression of the logarithm of concentration against time, yielded an apparent first order kinetic with correlation coefficients 0.99, 0.98 and 0.98 for the reaction mixtures containing 4, 8, and 15% NaCl (w:v), respectively. In addition, the calculated half-lives were found to be approximately 1 h. Indeed the presence of salt at these concentrations had a particularly strong effect upon the photolysis of 2,4-DNT.

In a separate set of experiments the effect of dissolved species upon the phototransformation of 2,4-DNT was investigated. Seawater and groundwater samples initially containing 1 mg/L 2,4-DNT were subject to artificial light (UV-A) and the substrate removal was monitored as a function of exposure time. The results revealed (Fig. 5) that after irradiating the solutions for 4 h, removals were found to be 57.8, 62.2 and 92.2% for the deionized water, groundwater and seawater solutions respectively. Clearly, photolysis of 2,4-DNT under artificial light is greatly enhanced when seawater is used as matrix. Overall, the photoremoval of 2,4-DNT in deionized water and groundwater was about three times slower than in spiked seawater solutions exposed to UV light. If a pseudo-first order kinetic reaction is

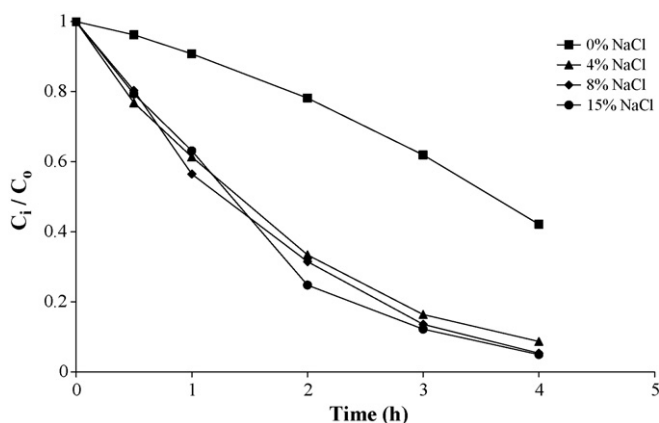


Fig. 4. The effect of different NaCl concentrations on the aqueous photolysis of 1 mg/L 2,4-DNT under artificial light (UV-A spectral domain).

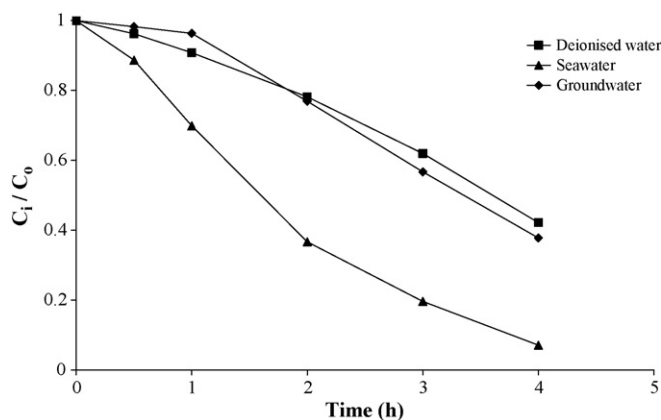


Fig. 5. Photolysis of 1 mg/L 2,4-DNT in deionized water, groundwater and seawater under artificial light (UV-A spectral domain).

assumed (with respective r^2 values of 0.98, 0.94 and 0.98), the calculated half-lives are approximately 4 h in distilled deionized water, 3 h in groundwater and 1 h in seawater.

The present findings are in accordance with previous reports dealing with the photolysis of organic micropollutants in seawater. Nipper et al. recently reported the phototransformation of picric acid and 2,6-DNT in seawater under simulated solar radiation (SSR) [4]. No significant photolysis of picric acid in seawater was observed for up to 47 days, but phototransformation of 2,6-DNT began soon after the initial exposure to SSR, with 89% being phototransformed in 24 h and none remaining after 72 h. The loss of 2,6-DNT from seawater solutions kept under similar conditions, but in the absence of UV, was negligible (3.2%) after a 96-h exposure period, thus confirming that the loss observed under SSR was due to phototransformation. In addition, the beneficial sensitizing effect of seawater upon the photolysis of carbofuran (an active acetylcholinesterase inhibitor) has been recently reported [20]. According to this report, photolysis of carbofuran was approximately 31 times faster in seawater than in fortified distilled deionized water under 300 nm light exposure. Finally, in the case of triclosan (a widely used bactericide), a 12-days photolysis experiment performed in freshwater and seawater under a low intensity artificial white light source, revealed that photodegradation was approximately two times faster when triclosan was present in the seawater matrix [21]. Although the exact mechanism is unknown, all the above references point the strong sensitization effect of dissolved species on the photolysis of seawater samples containing small amounts of organic compounds.

4. Conclusions

The studies reported here indicate that photolysis rates of 2,4-DNT are strongly dependent on the dissolved species present in the aqueous solution. Humic substances enhanced the photolysis rate and the sensitization effect was enhanced when NaCl was present in the reaction mixture. The photolysis of 2,4-DNT in distilled deionized water and groundwater was approximately three times slower than in seawater when exposed to UV light.

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