

¹⁴C-TRINITROTOLUENE: SYNTHESIS AND PHOTOCATALYTIC DEGRADATION

Alice Klapproth¹, Sandy Linnemann¹, Detlef Bahnemann², Ralf Dillert² and Gregor Fels¹,

¹Universitaet-Gesamthochschule Paderborn, FB 13 - Organische Chemie, Warburger Str. 100, D-33098 Paderborn, Germany and ²Institut für Solarenergieforschung GmbH (ISFH), Hameln/Emmerthal, Sokelanstr. 5, D-30165 Hannover, Germany

Trinitrotoluene and its natural metabolites display an environmental burden with respect to the contamination of soil, ground- and surface water. Photocatalytic degradation employing the semiconductor TiO₂ as catalyst has recently been found to effectively rid aqueous systems from organic pollution. We have investigated this process with respect to the conversion of the aromatic TNT-carbon by employing ¹⁴C-TNT as starting material. This way we can prove that TNT not only is degraded by the photocatalytic process but is also mineralized to yield CO₂.

Keywords: TNT, trinitrotoluene, photocatalytic degradation, mineralization, explosive

Introduction

Trinitrotoluene (TNT) and other military explosives have been identified as contaminants in ground- and surface-water at sites of former munition plants of World War II [1]. This environmental problem is due to a continuous elution of TNT from contaminated soil into the aqueous environment even 50 years after the war. In addition, because microorganisms in the soil can adopt to TNT transformation, a variety of metabolites has also been detected [2]. Attempts have been made to remove these contaminants from the aqueous system by microbiological and chemical procedures. The ultimate goal of such degradation, however, is the conversion of the pollutants to ecologically and toxicologically safe compounds like carbon dioxide (CO₂), water and inorganic nitrogen compounds. For microbiological decontamination the degradation is presently investigated under various conditions including possible ways of a mineralization [3-5]. On the other hand there are only a few attempts to degrade TNT and its metabolites by chemical procedures,

most of which rely on light induced oxidative processes [6-9]. While biological procedures could be shown to mineralize nitroaromatic compounds, for chemical processes this proof is still missing, despite some hints of CO₂ generation on photocatalytic processes [7].

We have synthesized ¹⁴C-TNT and investigated the course of the chemical degradation to CO₂ by using a photocatalytic degradation process [10] that has been shown to effectively degrade nitroaromatic contamination in aqueous systems [7-9]. The method is characterized by excitation of electrons in the semiconductor (TiO₂) from the valence- to the conduction band by radiation with short wavelength which results in the unique feature of having oxidizing and reducing conditions present in the same environment at the same time.

Results and Discussion

Uniformly ring-labeled ¹⁴C-TNT was synthesized from ¹⁴C-p-nitrotoluene adopting a procedure described by Ampleman [11]. The reaction conditions were modified to allow the complete nitration to TNT without workup of the intermediate 2,6-dinitro-toluene. Using mixed acid prepared from fuming nitric acid and conc. sulfuric acid (30 % SO₃), the first nitration step that leads to the dinitro-intermediate already immediately proceeded at room temperature on dissolving the starting material in stoichiometric amounts of the nitration mixture. Subsequent heating of the reaction mixture at 95 °C for 6 hours accomplished the nitration to TNT in 67 %. Further prolongation of the reaction time did not increase the yield, while raising the temperature to 100 °C resulted in a reduced yield.

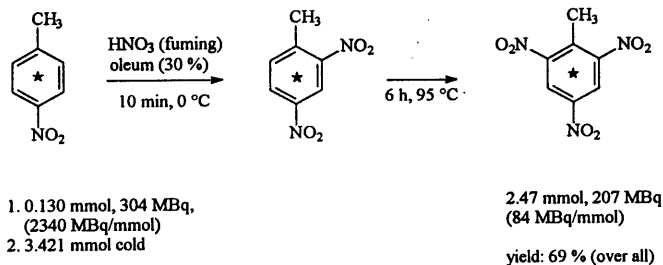


Fig. 1: Synthesis of ¹⁴C-TNT

Previous experiments had shown [9] that degradation of TNT proceeds along oxidative and reductive pathways, so that trinitrobenzene (TNB) and dinitrobenzene (DNB) as well as various aminodinitrotoluenes (ADNTs) are prominent intermediates on the TNT degradation. However only recently attempts have been made to proof the mineralization as the final stage on TNT degradation [7]. Our investigation therefore was aimed to develop an unambiguous method that allows the quantitative determination of TNT mineralization by the process of photocatalytic degradation. It is important to realize that the disappearance of TNT through photocatalytic degradation is not equivalent with total decontamination, and that at least some of the degradation intermediates are known to be much more toxic and carcinogenic than TNT itself.

Photocatalytic degradation was carried out in a special quartz reactor (see Fig. 2) using a wavelength of <390 nm (equivalent to 3.2 eV) which is necessary to overcome the energy gap between the valence- and the conduction-band of TiO_2 . Control experiments were performed without catalyst to investigate the effect of photolysis on TNT. A cutoff filter of 320 nm was used to eliminate high energetic wavelengths that would favor photolysis reactions. The reaction mixture was analysed at various times by GC- and HPLC-methods during the process to determine the time dependence of TNT degradation.

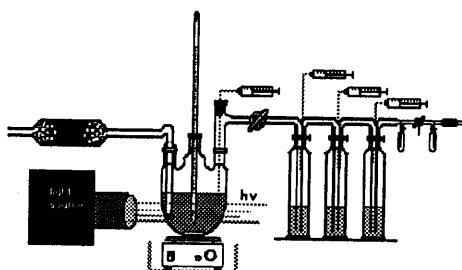


Fig. 2: Setup for the photocatalytic degradation of ¹⁴C-TNT

Using uniformly ring-labeled ¹⁴C-TNT we have balanced the degradation process by following the distribution of the radioactivity between the reactor and the CO₂ absorption medium. The reaction was carried out in aqueous suspensions of TiO₂ (1 mg/ml) that contained 0.5 mmolar amounts of ¹⁴C-TNT. Due to the irradiation, the reaction mixture warmed up slowly to 40 °C within the first two hours and then remained constant throughout the experiment.

experiment	condition	reaction vessel		absorption	carbondioxide [%]
		begin	end	flask	
		[μ Ci]	[μ Ci]	[μ Ci]	
photocatalysis	pH 4, MeOH	15.5	9.1	5.3	34.2
	pH 4	16.1	5.8	9.5	59.2
	pH 9, MeOH	16.6	14.5	1.1	6.7 *
photolysis	pH 4, MeOH	14.6	13.6	0.1	0.7

* after acidification and degassing

Tab. 1: Results from photocatalytic degradation of ^{14}C -TNT using UV-light and a cutoff filter of 320 nm. Total irradiation time was 6 hours.

The result of such degradation experiments, carried out at differing pH conditions and in the presence or absence of 1 vol % of methanol, respectively, are shown in table 1 demonstrating that ^{14}C -CO₂ is formed from ^{14}C -TNT within a few hours of radiation. The data reveal that mineralization indeed occurs during photocatalytic degradation. In particular we find that:

- photocatalysis is powerful in degrading TNT as compared to photolysis under otherwise identical condition (e.g. 0.7 % of CO₂ formation in photolysis versus 34.2 % in photocatalytic experiments)
- methanol diminishes the degree of mineralization which is in agreement with results from former investigations [9] showing that methanol enhances reductive conditions and thereby hampers the initial attack at the toluene methyl-group (e.g. CO₂ formation of 34.2 % in the presence versus 59.1 % in the absence of methanol)
- basic pH conditions also yield a reduced degree of mineralization, presumably because the amphoteric TiO₂ surface is blocked by carbonate species that prevent access of TNT or its degradation products to the semiconductor surface (e.g. 6.7 % at pH 9 versus 34.2 % of CO₂ formation at pH 4).

Balancing the radiocarbon by summing up the activity of the solution in the reactor and the absorption flasks proved that in the error range of the experiment (± 7 -8 %) no loss of radiocarbon occurred at any time during the experiments.

The time course of the experiment has also been followed and is depicted in Fig. 3 clearly indicating the influence of methanol and the pH condition. HPLC- and GC-analysis of unlabeled TNT additionally proved that TNT already has disappeared after 4-5 hours and that the expected small amounts of degradation intermediates appear as primary degradation products from

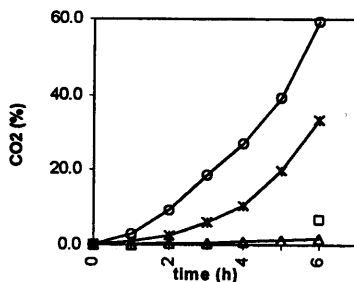


Fig. 3: Time course of the CO₂ formation during photocatalytic degradation of ¹⁴C-TNT: (o) pH4, no methanol; (*) pH4, with methanol, (Δ) pH9, with methanol, (□) pH9, with methanol, after acidification and degassing.

oxidative and reductive processes, respectively (e.g. TNB and ADNTs). At this time, however, conversion of TNT is only complete to about 50 % (under acidic conditions and in the absence of methanol), indicating that at least some of the intermediates between TNT and CO₂ are more difficult to photocatalytically degrade than TNT itself. Experiments to investigate this process in more detail are under investigation in our laboratory.

Experimental

Synthesis of ¹⁴C-TNT

The synthesis of ¹⁴C-TNT was adopted from a procedure described by Ampleman [11]. Mixed acid was prepared from 0.5 ml fuming nitric acid (100 %) and 8.1 ml sulfuric acid (30 % SO₃). 3 ml of freshly prepared mixed acid was used to dissolve 17.8 mg (0.130 mmol, 304.1 MBq, 2340 MBq/mmol) of uniformly ring-labeled ¹⁴C-p-nitrotoluene and to transfer it to an ice cooled reaction flask that contained additional 468.7 mg (3.42 mmol) of p-nitrotoluene. Immediately after transfer stirring of the solution was started. Two times 1.5 ml mixed acid were used to rinse the radioactive p-nitrotoluene and were added to the reaction mixture followed by the addition of the remaining 2.1 ml of mixed acid. The mixture was stirred for another 10 min at 0 °C followed by 6 hours at 95 °C and further 12 hours at room temperature.

Workup was initiated by the addition of 50 ml CH₂Cl₂ and stirring for 5 min at room temperature. The organic phase was separated and the aqueous phase was extracted twice with each 20 ml CH₂Cl₂. The combined organic

phases were twice stirred for 5 min with 100 ml saturated Na_2CO_3 solution and three times with 100 ml water. Separation of the organic phase and evaporation of the solvent resulted in a yellow oil from which TNT crystallized after addition of a few drops of ethanol. The crude TNT was recrystallized from ethanol to yield 560 mg (2.47 mmol, 67.1 %) of ^{14}C -TNT (206.8 ± 6.6 MBq, 83.6 ± 2.7 MBq/mmol). After recrystallization the ^{14}C -TNT was shown by HPLC and GC to have chemical and radiochemical purity of > 99.5 %. The identity of the material with an original TNT sample was shown by chromatography and ^1H -NMR.

Degradation of ^{14}C -TNT

0.5 mmol ^{14}C -TNT solutions were prepared by dissolving 11.35 mg ^{14}C -TNT (0.05 mmol, 0.1135 μCi) and 17.03 mg (0.075 mmol) unlabelled TNT in 250 ml of water. If desired, methanol was added in concentrations of 1 vol.%. The solution was sonicated for 24 hours in the dark. Control experiments (HPLC) showed that no notable TNT degradation occurs under these conditions. To 62 ml of this solution (containing 7.04 mg, 0.031 mmol, 0.0281 μCi of ^{14}C -TNT) TiO_2 (Degussa Typ P25, average particle size of 21 nm, specific surface of 50 m^2/g) was added in amounts of 1 mg/ml and the suspension was sonicated for another 20 min. 60 ml of this suspension was transferred to a quartz reactor (see Fig. 2) and the pH was adjusted to the desired value (usually pH 4 or pH 9) using a pH-device (Metrom 605, pH meter; Metrom 725, Dosimat; Metrom 614, Impulsomat). The pH stat was also employed to maintain the desired pH throughout the degradation process. The absorption flasks (scrubber) were loaded each with of 30 ml Carbosorb E (Packard). A xenon lamp was used as a light source (Müller Elektronik, SVX 1450, LAX 1450) using a cutoff filter of 320 nm. During the degradation process, a stream of air, entering through a KOH-cartridge, was slowly passed through the entire setup.

1 ml samples were taken from the reaction flask and the carbosorb, respectively, and 100 μl aliquots were measured in 3 ml of scintillation cocktail (Rotiszint ecoplus, Roth) using a Tricarb 4530 β -counter (Packard Instruments). After 6 hours the xenon lamp was shut down, the reaction mixture was adjusted to pH 2, and nitrogen was passed through the setup for another 15 min, to ensure depletion of the reaction mixture from CO_2 . At this stage the final samples were taken (6 hours sample). Control experiments were carried out to check for the effect of photolysis by running the degradation process as described but without the addition of TiO_2 .

Degradation intermediates of the photocatalytic TNT treatment were detected by HPLC- and GC-analysis as described by Nahen et.al.[9].

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