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Journal of Photochemistry and Photobiology A: Chemistry 110 (1997) 191–199

Photocatalytic degradation of trinitrotoluene: reductive and oxidative pathways

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Received 25 March 1997; accepted 20 May 1997

Abstract

The photocatalytic degradation of trinitrotoluene and the nitrated benzenes trinitrobenzene and dinitrobenzene on exposure to UV light, using titanium dioxide as catalyst, follows reductive and oxidative pathways. The attack by reducing species is enhanced in the presence of alcohols, such as methanol. The oxidative derivatization of trinitrotoluene in these conditions leads to trinitrobenzene, which is further degraded mainly by reduction to amino-nitro compounds. In the absence of titanium dioxide, the direct photochemical degradation of these chemicals yields the same intermediates, but with much lower reaction rates. Photocatalytic treatment appears to be a useful alternative to rid water of nitroaromatic pollution. © 1997 Elsevier Science S.A.

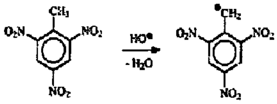
Keywords: Photocatalytic degradation; TiO_2; Trinitrotoluene

1. Introduction

The contamination of groundwater and surface water by military secondary explosives represents an ongoing worldwide problem of pollution, the full environmental consequences of which have only been recognized during recent years [1]. Since the turn of the century, 2,4,6-trinitrotoluene (TNT) has been and still is the major explosive used for ammunition throughout the world. Because of massive handling, e.g. at filling stations, and the production procedures employed for large-scale synthesis, TNT today represents a great environmental burden with respect to the location, examination, evaluation and elimination of such contamination [2]. Despite many efforts to remove TNT and the corresponding biotic and abiotic transformation and degradation products from soil and aqueous systems [3], as yet there is no accepted procedure which can be applied to laboratory and on-site requirements. Our aim is to investigate TNT degradation in aqueous systems, focusing on chemical reactions rather than biological processes [4]. To this end, we have employed well-known photocatalytic procedures, based on the reduction and oxidation potential of titanium dioxide (TiO_2) suspensions in aqueous systems [5], which have already been successfully applied to the degradation of TNT and various other nitroaromatics (see Table 1) [6–24]. These methods use radiation of short wavelength to excite electrons in the semiconductor from the valence to the conduction band in order to generate free electrons (e_{cb}^-) and free electron holes (h_{vb}^+) which result in the presence of oxidizing and reducing conditions in the same environment at the same time. For TiO_2, with an energy barrier of 3.2 eV, UVA light of 390 nm (maximum) is required.

TNT absorbs sunlight or UV radiation to produce numerous aromatic degradation products without reaching an acceptable degree of mineralization [25]. During this process, TNT is deprotonated and, with the help of electron acceptors and molecular oxygen, converted to trinitrobenzoic acid, which is finally decarboxylated to trinitrobenzene (TNB). In addition, ineffective reductive degradation pathways are known for the photolysis of TNT.

The photocatalytic degradation of TNT, using TiO_2 as catalyst and low-energy radiation of $\lambda = 290–390$ nm, is very effective in decomposing TNT [6–15]. Hydroxyl radicals on the TiO_2 surface, in addition to electron holes, seem to be the major source of oxidizing species which attack TNT at the alkyl side-chain



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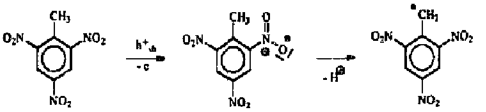
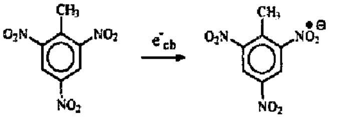
PII S1010-6030(97)00171-8

Table 1
List of recent publications on the photocatalytic treatment of nitroaromatics

Compound	Reference
2,4,6-Trinitrotoluene	[6–15]
2,4-Dinitrotoluene	[8,14]
2,6-Dinitrotoluene	[8,14]
2-Nitrotoluene	[8,14]
3-Nitrotoluene	[8,14]
4-Nitrotoluene	[8,14]
1,3,5-Trinitrobenzene	[6–8,10,14]
1,2-Dinitrobenzene	[8,14]
1,3-Dinitrobenzene	[8,14]
1,4-Dinitrobenzene	[8,14]
Nitrobenzene	[8,14,16–23]
4,6-Dinitro-*o*-cresol	[14]
Trinitrophenol	[17]
2,4-Dinitrophenol	[14,16]
2,5-Dinitrophenol	[17]
2-Nitrophenol	[14,24]
3-Nitrophenol	[14,24]
4-Nitrophenol	[14,17,21,24]
4-Nitrocatechol	[16]
2,6-Diamino-4-nitrotoluene	[14]
2-Amino-4,6-dinitrotoluene	[14]
4-Amino-2,6-dinitrotoluene	[14]
2-Amino-4-nitrotoluene	[14]



Reductive reaction, on the other hand, is initiated by electron transfer from TiO_2 to TNT



Consequently, TiO_2 suspensions continuously purged with molecular nitrogen show a significantly higher rate of TNT and TNB degradation than oxygenated systems.

The photoinduced reduction of nitro compounds in the presence of TiO_2 particles has recently been reported by Mahdavi et al. [26]. A reductive pathway for photocatalytic TNT degradation has therefore been proposed.

This study investigates the simultaneous oxidative and reductive conditions present in photocatalytic reactions. In particular, it is examined whether TNT and other nitroaromatics can be degraded under photocatalytic conditions by concomitant reductive and oxidative pathways to give non-aromatic compounds. The ultimate goal of such decontamination is to demonstrate that these potentially toxic and carcinogenic materials can be removed from the environment by converting them to simple, safe chemicals, such as water, carbon dioxide, inorganic salts, etc. Because the technical application of this method would involve sunlight as the main energy source [27], we have employed the entire wavelength band of a UV light source, rather than filtering out higher energy radiation using a cut-off filter, e.g. at 320 nm. Photolysis is the major route of natural TNT degradation with a half-life time of about 70 days [28], and photochemical reactions have been observed in water up to a depth of 90 m. An obvious disadvantage of using the complete energy bandwidth is that photocatalytic and photolytic reactions take place simultaneously.

It is shown that the degradation of TNT, as well as TNB and dinitrobenzene (DNB), occurs. Nitroaromatic material is decomposed via oxidative and reductive pathways: reducing conditions are more important for demethylated nitrobenzenes and oxidative attack is favoured for toluene derivatives.

2. Materials and methods

The starting materials and reference compounds were synthesized according to described methods, e.g. TNT [29], TNB [30], 2-amino-4,6-dinitrotoluene (2A-4,6-DNT) [31] and 4-amino-2,6-dinitrotoluene (4A-2,6-DNT) [32]. 3,5-Dinitroaniline (3,5-DNA), 1,3-dinitrobenzene (1,3-DNB), 3-nitroaniline (3-NA) and nitrobenzene (NB) were obtained from commercial sources (Aldrich).

The photocatalytic degradations were carried out with 0.3–0.5 mM solutions of nitroaromatics with or without the addition of 1 vol.% of methanol. Solutions were sonicated for 24 h in an ultrasonic bath to achieve complete solubility. An aliquot of 100 ml of solution was transferred to a 100 ml quartz round-shaped flask, supplemented with 100 mg of TiO_2 (Degussa, type P 25, 70% anatase, 30% rutile, average particle size of 21 nm, specific surface area of 50 m^2 g^{-1}), and the suspension was again treated in an ultrasonic bath for 30 min to guarantee complete suspension. Control experiments (high performance liquid chromatography (HPLC), gas chromatography (GC)) showed that there was no degradation of TNT during sample preparation. After adjustment to pH 9, these suspensions were used without flushing with nitrogen or oxygen. A low-pressure mercury lamp (Graentzel 400 W, 254 nm, Karlsruhe, Germany) was employed for irradiation; four light bulbs were arranged in a tube surrounding the reaction vessel. Typical reaction times for degradation were 120 and 240 min. During degradation, the suspension reached a maximum temperature of 65–68°C after 90 min, despite cooling by a stream of air passed through the apparatus. For analysis, aliquots of 10 ml were taken at different reaction times, and separated from TiO_2 by filtration. Analyses were carried out either with an HPLC system (Merck Hitachi L-6200 with a 655A-22 UV detector) using an RP column (YMC-Pack Explosives, 250 mm × 4.6 mm) or by GC-ECD (Shimadzu) on a silica capillary column (Supelco, PTE-5, fused silica capillary column, 30 m, 0.25 mm inner diameter, 0.25 μm film thickness). While HPLC analysis was performed directly from the aliquots, GC samples required solvent exchange from water to methanol, simultaneously concentrating the solution by a factor of five. This was achieved with Bakerbond spe columns (6 ml, high capacity RP 18, 40 μm ADP, 60 Å).

3. Results

3.1. Degradation of TNT

Photocatalytic treatment of TNT in the presence and absence of methanol yields, under the experimental conditions employed, a degradation to less than 1% of the original amount within 90 min of irradiation (Fig. 1). At any given time, this degradation is, on average, 50% more complete when no methanol is employed.

The effect of the direct photolysis of TNT was investigated, both in terms of the disappearance of TNT and of the appearance of specific intermediates. When TiO_2 is omitted from the reaction mixture, TNT degradation after 90 min amounts to only about 5% of the photocatalytic effect (Fig. 2). Degradation of TNT by photolysis alone can therefore be neglected compared with the photocatalytic reaction.

3.2. Degradation products of TNT

The investigation of the intermediates at various times during the course of the degradation reaction shows a number of unidentified species with only minor concentrations as judged from the peak heights of the high performance liquid and gas chromatograms (see, for example, Figs. 3 and 8). However, using a set of potential degradation intermediates as internal standards (reference material), we were able to characterize all of the major peaks in the chromatograms.

In this way, we established that TNB, 3,5-DNA, and the two monoamino-dinitrotoluene isomers, 2A-4,6-DNT and 4A-2,6-DNT, were the major intermediates of photocatalytic TNT breakdown (Fig. 4) when small amounts of methanol were present. Although TNB could clearly be detected as an immediate oxidation product of TNT, the corresponding TNT

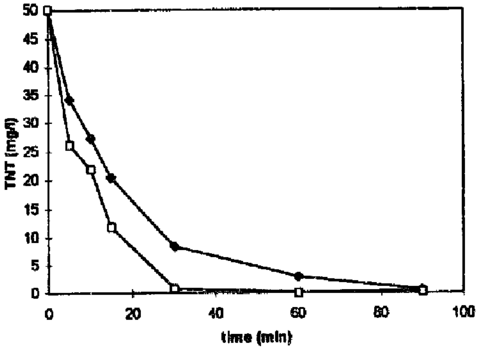


Fig. 1. Degradation of TNT in the presence (◆) and absence (□) of 1% of methanol.

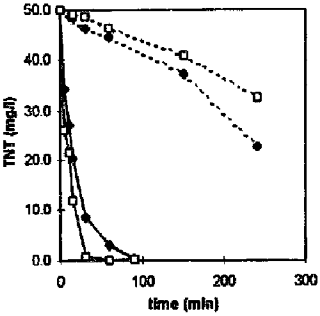


Fig. 2. Effect of photocatalytic (full lines) and photolytic (broken lines) degradation of TNT in the presence (◆) and absence (□) of 1% of methanol.

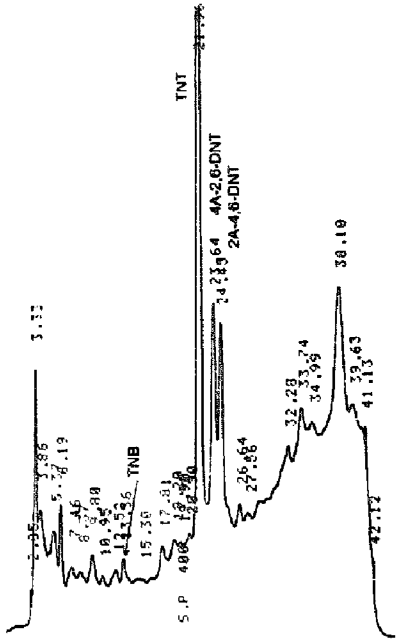


Fig. 3. Typical high performance liquid chromatogram of the photocatalytic TNT degradation after 60 min of irradiation.

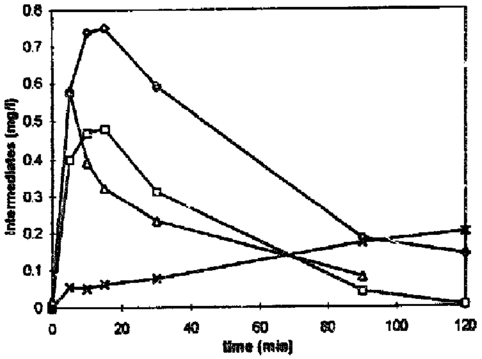


Fig. 4. Evolution of the concentration of TNB (△), 2A-4,6-DNT (□), 4A-2,6-DNT (◇) and 3,5-DNA (*) during the photocatalytic degradation of TNT in aqueous solution in the presence of 1% of methanol.

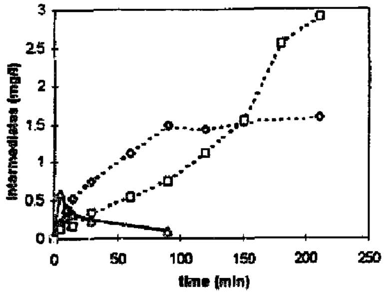


Fig. 5. Comparison of the formation of TNB by photocatalysis in the presence of methanol (△) vs. photolysis in the presence (◇) and absence (□) of methanol.

benzaldehyde and TNT acid could not be observed beyond doubt, despite the presence of small peaks with higher polarity than TNT (HPLC analysis) that overlapped with the corresponding reference material.

The relative amounts of the intermediates depend on the reaction conditions. The presence of 1% methanol enhances the appearance of these compounds, in particular the monoamino-dinitrotoluene derivatives, whereas TNB seems to be relatively unaffected. The concentration of 3,5-DNA steadily increases to about 0.2 mg l^{-1} after 90 min in the presence of methanol compared with less than 0.1 mg l^{-1} in the absence of methanol. In contrast, when methanol is omitted from the suspension, the monoamino-dinitrotoluenes, 2A-4,6-DNT and 4A-2,6-DNT, are no longer observed, but the concentration course of TNB remains unchanged.

It should also be noted that 2,4- and 2,6-dinitrotoluene (2,4- and 2,6-DNT) could not be detected as photocatalytic degradation products of TNT in the presence or absence of methanol.

Because photolysis in our experiments could not be separated from photocatalytic effects, we also investigated the generation of degradation products in the absence of TiO_2, i.e. under exclusively photolytic conditions. As shown in Fig. 5, the formation of TNB is much more prominent in the absence of TiO_2 and increases steadily at least over an illumination period of 4–5 h. However, the peak concentrations of the two isomeric monoamino-dinitrotoluenes are about 3–5 times higher in the presence of TiO_2 than the highest amounts detected during direct photolysis. Therefore, although photocatalysis undoubtedly degrades these amino-nitro aromatics in comparatively short times (e.g. within 3 h in the given apparatus), these intermediates persist much longer under photolytic conditions (Fig. 6).

3.3. Degradation of TNB and DNB

The photocatalytic treatment of TNB shows a much more dramatic effect of the presence of 1% methanol, i.e. after 60 min there is only 1% TNB remaining in the presence of methanol, whereas in the absence of methanol roughly 20% TNB is detected (Fig. 7). As observed with TNT, there are a large number of degradation products observed under photocatalytic conditions (see Fig. 8), the most prominent of which is the expected initial reduction product of TNB, i.e. 3,5-DNA (Fig. 9). Of the various other degradation products, we were able to identify 1,3-DNB in small amounts.

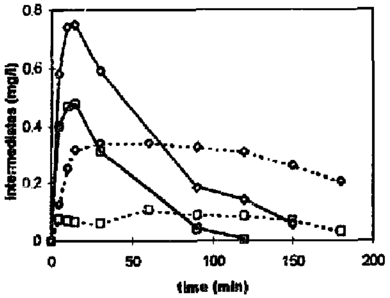


Fig. 6. Comparison of the formation of 2A-4,6-DNT (□) and 4A-2,6-DNT (◇) by photocatalysis (full lines) vs. photolysis (broken lines) in the presence of 1% of methanol.

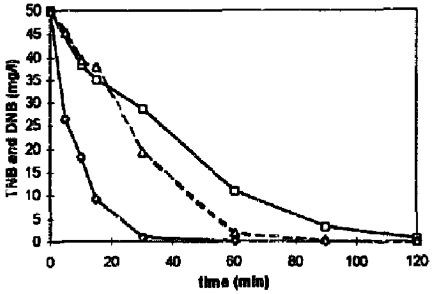


Fig. 7. Degradation of TNB in the presence (◇) and absence (□) of 1% of methanol and degradation of DNB in the presence (△) of 1% of methanol.

When 1,3-DNB is subjected to photocatalytic degradation, the initial reduction product, 3-NA, is detected as the dominant intermediate (Fig. 9), with small amounts of NB. 3-NA reaches a maximum value of about 17 mg l^{-1} after 60 min of illumination.

4. Discussion

Photocatalytic reactions were carried out with TNT, TNB and DNB in the presence and absence of methanol. While TNT is accessible to both oxidative and reductive degradation, the demethylated nitroaromatics TNB and DNB are preferentially attacked by reducing species. During their study of the photolytic degradation of tetrachloromethane, Hilgendorff et al. [33] showed that reductive photocatalytic pathways are facilitated in the presence of alcohol (specifically methanol). Therefore we investigated the photocatalytic degradation of nitroaromatic compounds in both the presence and absence of 1% methanol.

The involvement of methanol in the degradation is explained by an anodic process at the TiO_2 surface, in which hydroxyl radicals generated from electron holes react with

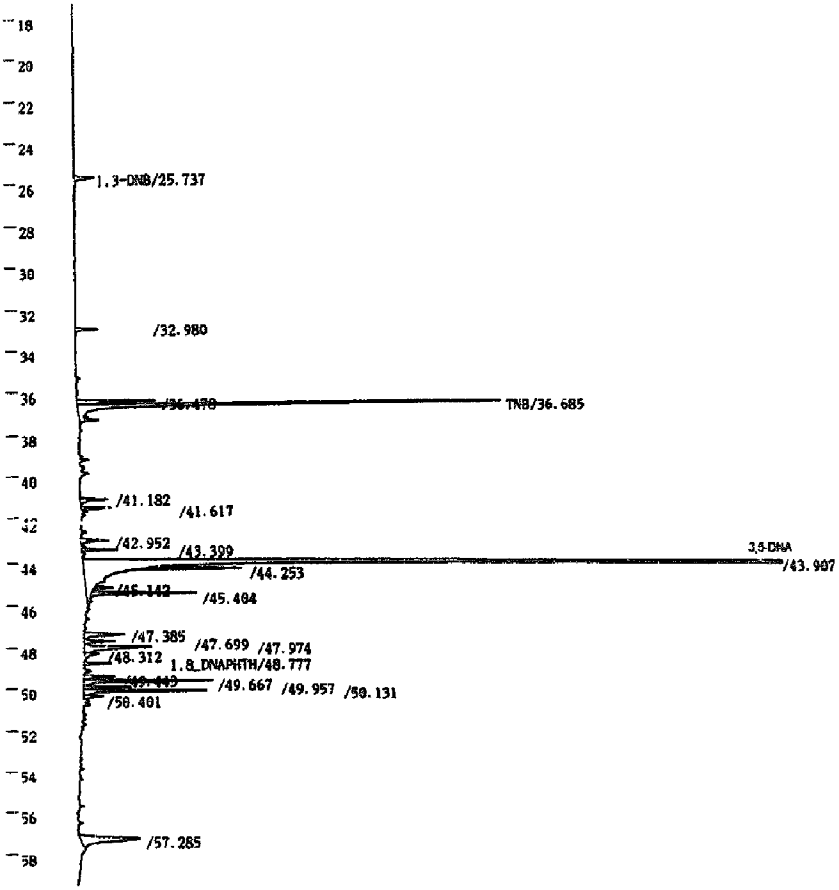


Fig. 8. Typical gas chromatogram of the photocatalytic TNB degradation after 30 min of irradiation. 1,8-Dinitronaphthalene (DNAPHTH) was added as internal standard prior to analysis.

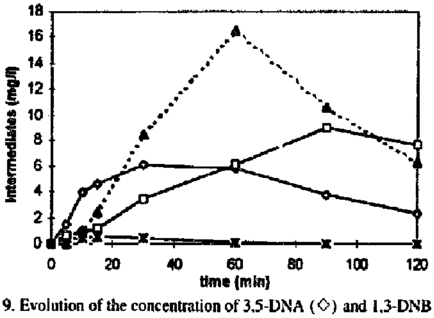


Fig. 9. Evolution of the concentration of 3,5-DNA (◇) and 1,3-DNB (*) in the presence of 1% of methanol and of 3,5-DNA (□) in the absence of 1% of methanol during the photocatalytic treatment of TNB. The appearance of 3-NA (▲) during the photocatalytic treatment of DNB in the presence of 1% of methanol is also shown.

methanol to yield α-hydroxymethyl radicals that can either react with the pollutant or inject an electron into the valence band of the catalyst (current doubling effect). In addition, the probability of undesirable e^-–h^+ recombination is diminished. The presence of methanol in the aqueous suspension is therefore believed to enhance the reductive pathways.

As can be seen from Fig. 1, TNT is readily degraded under the experimental conditions employed within 90 min of illumination in both the presence and absence of methanol. However, the degradation of TNT is faster and more complete in the absence than in the presence of methanol. In contrast, when TNB is employed in the experiments instead of TNT, the expected increase in the reductive pathway by methanol is clearly shown (Fig. 7). In addition, the number of nitro groups that can be attacked is of importance, as TNB reacts more easily than DNB. A comparison of the photocatalytic degradation of TNT, TNB and DNB (Fig. 10) in the presence of methanol reveals a decreasing reaction rate in the order TNB > TNT > DNB. Accordingly, if methanol is not present, TNT is degraded faster than TNB. These findings can be interpreted as follows.

1. The presence of methanol increases the reaction rate of the reductive degradation pathway; the number of reducible groups is also important.

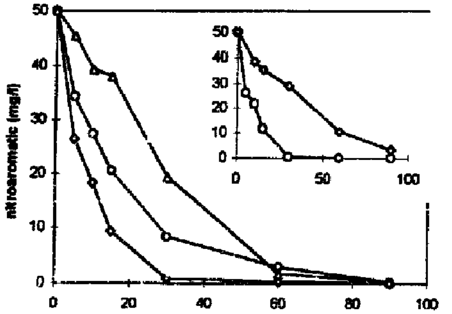


Fig. 10. Comparison of the photocatalytic degradation of TNT (○), TNB (◇) and DNB (△) in the presence and absence (inset) of 1% of methanol.

2. If methanol is omitted from the suspension, the oxidative pathway dominates the process, because under these conditions TNT is degraded more rapidly than TNB. Alternatively, the methyl group of TNT may also have a determining effect since electron-donating groups may reduce the probability of reductive attack at phenyl nitro groups. Because photocatalysis allows reductive and oxidative processes to occur simultaneously in the same reaction mixture, the degradation of TNT presumably follows initially an oxidative decarboxylation to TNB and then a fast reduction to amino-nitro compounds.

To determine the importance of photoreactions during the degradation process, we also carried out the reaction in the absence of TiO_2, i.e. under truly photolytic conditions. As can be seen from Fig. 2, photolysis does not have a significant influence on the disappearance of TNT. At any time during the experiment, photolysis amounts to less than 10% of the total degradation under photocatalytic conditions. At least for the consumption of TNT by light-induced reactions, the photocatalytic effect is much more important than photolysis.

The intermediates of the degradation process were investigated by submitting samples at various times to GC and HPLC analyses. Because of the reference material available, our method only allows the detection of intermediates resulting from the first few degradation steps which still contain an intact benzene ring. During the course of the photocatalytic experiment, the peak corresponding to TNT successively decreases, and a few prominent new peaks appear, indicating that only a few intermediates accumulate in significant amounts. A large number of smaller peaks are also observed, demonstrating that a large number of intermediates are present in very small amounts (Fig. 3).

HPLC and GC analyses demonstrate that, during the course of photocatalytic degradation of TNT in the presence of 1% methanol, TNB and isomeric 2A-4,6-DNT and 4A-2,6-DNT accumulate to measurable amounts (Fig. 4). The primary intermediates of oxidative decarboxylation of TNT, i.e. TNT aldehyde and acid, are not detected. The concentrations of TNB and the two monoamino-dinitrotoluenes reach a maximum during the first 20 min of the experiment and then constantly decay towards zero. Of the three intermediates, 4A-2,6-DNT shows the highest peak. The monoamino-dinitrotoluene isomers are not detected when the degradation is performed in the absence of methanol.

Enhanced reducing conditions therefore seem to be a requirement for the facile degradation of TNT. Otherwise, oxidative decarboxylation must precede the reductive attack of nitro groups on the aromatic ring.

It should also be noted that the concentrations of the intermediates determined at any given time during the degradation experiment actually reflect the sum of four independent processes occurring in the suspension, i.e. the formation and breakdown by photocatalytic and photolytic processes. Intermediates observed in detectable amounts during the course of photocatalytic degradation only appear because they are more slowly degraded than generated. In particular, the amino-dinitro compounds seem to have a higher generation than degradation rate under photocatalytic conditions.

To evaluate the fate of TNB and the amino-dinitro isomers, we also investigated the evolution of their concentrations under exclusively photolytic conditions, i.e. in the absence of TiO_2. As can be seen from Fig. 5, TNB is generated from TNT by a photochemical reaction. This finding supplements the results of photochemical TNT degradation (see Fig. 2). Because of its constantly increasing accumulation, we can assume that the formation of TNB under photolytic conditions has a higher rate than its degradation. The same result can also be deduced for the photolysis of amino-dinitro compounds (see Fig. 6) which, in the presence of methanol, show, after an initial increasing phase, an almost steady concentration for an extended reaction time. Again, as in the photocatalytic experiments, the concentration of 4A-2,6-DNT is higher than that of 2A-4,6-DNT. As the initial slopes of formation of the monoamino-dinitrotoluenes are quite similar, the observed concentration difference must be caused by a slower degradation of 4A-2,6-DNT than 2A-4,6-DNT. This is in accordance with the results of chemical reduction procedures which lead to the preferential reduction of TNT at the nitro group para to the methyl group rather than in the ortho position, although usually nitro groups ortho to a substituent in the aromatic ring are predominantly reduced in aqueous solution [34].

To shed further light onto the reaction mechanism, we also investigated the degradation of TNB and DNB and the appearance of intermediates derived from these processes. As can be expected from the facilitated reductive pathway under the influence of small amounts of methanol (see above), the reaction rate of TNB degradation in the presence of methanol is faster than in its absence (see Figs. 7 and 10). The degradation of DNB is slower than that of TNB, reflecting the number of groups that can be attacked by reducing species. More interesting are the degradation products derived from the photocatalytic degradation of TNB and DNB. The gas chromatogram in Fig. 8 demonstrates that, for the reaction of TNB, the major intermediate is 3,5-DNA.

Surprisingly, this intermediate is formed independent of the presence of methanol, although methanol enhances its rate of formation. However, in the absence of methanol, 3,5-DNA accumulates to higher concentrations and is more persistent. These findings are in contrast with the observation that nitro groups can only be reduced to amines when the enhancing effect of methanol is involved.

As outlined above, in methanol-containing TiO_2 suspensions, a decreasing activity is observed in the order TNB > TNT > DNB. Recently, Dillert et al. [8] have reported that, in air-saturated suspensions, reaction rates decrease in the order DNB > TNT > TNB and are negatively affected by the presence of added hydrogen peroxide [6]. These results have been explained by assuming that the photocatalytic degradation of nitroaromatic compounds occurs via two different pathways. In the oxidative pathway, the degradation is initiated by an electron hole (h_{vb}^{+}) or a hydroxyl radical ($^{\cdot}OH$), whereas, in the reductive pathway, it is initiated by electron transfer from the semiconductor conduction band to the nitroaromatic substrate. The importance of each pathway for the overall photocatalytic degradation of a given compound depends on the electron density of the aromatic system of the compound.

The electron-withdrawing effect of the three nitro groups of TNB reduces the electron density on the aromatic ring, with the consequence that the photocatalytic degradation of this compound can only be initiated by electron transfer from the semiconductor to the organic substrate. Hence the reaction rate of this compound is negatively affected by competing electron acceptors, such as molecular oxygen and hydrogen peroxide, which form radicals with poor reducing power. However, in suspensions containing methanol, the rate of photocatalytic degradation of TNB is enhanced by the combined action of the conduction band electron and the α-hydroxymethyl radical ($^{\cdot}CH_2OH$)

$$CH_3OH + h_{vb}^{+} \text{ or } {}^{\cdot}OH \rightarrow {}^{\cdot}CH_2OH + H^{+} \text{ or } H_2O \qquad (1)$$

The α-hydroxymethyl radical, formed by Eq. (1), reduces TNB, yielding formaldehyde and the TNB radical anion

$$TNB + {}^{\cdot}CH_2OH \rightarrow TNB^{\cdot -} + CH_2O + H^{+} \qquad (2)$$

In contrast with TNB, the degradation of DNB can be initiated both reductively and oxidatively.

Combining our results with the findings of Dillert et al. [8], we can conclude that the oxidative pathway is predominant in dioxygen-containing solutions and in the absence of methanol. In the presence of methanol, h_{vb}^{+} and $^{\cdot}OH$ are scavenged (Eq. (1)) and the rate of oxidatively initiated degradation is lowered. The reducing hydroxymethyl radical reacts more slowly with DNB than with TNB. However, the primary product of reduction can be quenched by molecular oxygen and, from our results, the possibility cannot be excluded that the reaction

$$DNB^{\cdot -} + O_2 \rightarrow DNB + O_2^{\cdot -} \qquad (3)$$

is favoured over

$$TNB^{\cdot -} + O_2 \rightarrow TNB + O_2^{\cdot -} \qquad (4)$$

In the case of TNT, the photocatalytic degradation can be initiated both reductively and oxidatively. On the one hand, the methyl group is oxidized after attack of h_{vb}^{+} and $^{\cdot}OH$ in subsequent steps to yield a carboxyl group, followed by the formation of TNB by decarboxylation of the intermediate benzoic acid. This degradation pathway is not feasible in methanol-containing suspensions. On the other hand, the degradation of TNT can be initiated by the action of a conduction band electron or a hydroxymethyl radical. The importance of this pathway is increased in the presence of methanol. Therefore the reaction rate as a whole is hardly affected by methanol (see Fig. 1). Thus, when the rate of the oxidative or reductive step is decreased by the addition of an appropriate scavenger, the respective counter-reaction becomes significantly faster.

Fig. 8 shows that small concentrations of 1,3-DNB are formed from TNB, which can be explained by the oxidative elimination of nitrogen from NH_2 groups via diazo compounds [35]. This process is not favoured compared with the formation of amines from nitro groups.

Principally the same processes as observed for TNB are found during the photocatalytic degradation of DNB, which yields comparatively large amounts of the corresponding nitroamine compound 3-NA (one-third of totally degraded DNB after 60 min) (see Fig. 9). With this in mind, and also in view of the 15%–20% of 3,5-DNA observed during the photocatalytic degradation of TNB, it is surprising that 3,5-DNA and 3-NA cannot be detected during the degradation of TNB. This can be explained by the easy formation of aminonitro compounds from the corresponding nitro precursors, which subsequently accumulate due to the slow further degradation by oxidative processes (e.g. via azo compounds) to the monodenitrated derivatives.

From our experiments, we deduce a reaction sequence for the photocatalytic degradation of TNT as proposed in Fig. 11. The following conclusions can be drawn:

1. TNT and other nitroaromatics (such as DNB and TNB) can readily be degraded by photocatalytic processes;
2. the reaction rate of the initial reductive step in the photocatalytic degradation of nitroaromatics decreases with the number of NO_2 groups present;
3. oxidative attack on TNT yields TNB as the first accumulating intermediate, and this process is suppressed in the presence of methanol (in accordance with the observation that methanol enhances reductive pathways);
4. methanol enhances degradation, in particular the reductive pathway to amino-nitro compounds (consequently TNB is more readily degraded in the presence than in the absence of methanol);
5. amino-nitro derivatives, at least in the presence of methanol, are more persistent, and are themselves degraded at slower reaction rates, in good agreement with the assumption that, under more reductive conditions (presence of methanol), the oxidative process leading to the elimination of the NH_2 group is inhibited;
6. nitroaromatic compounds also undergo photolytic degradation which occurs with much lower reaction rates;

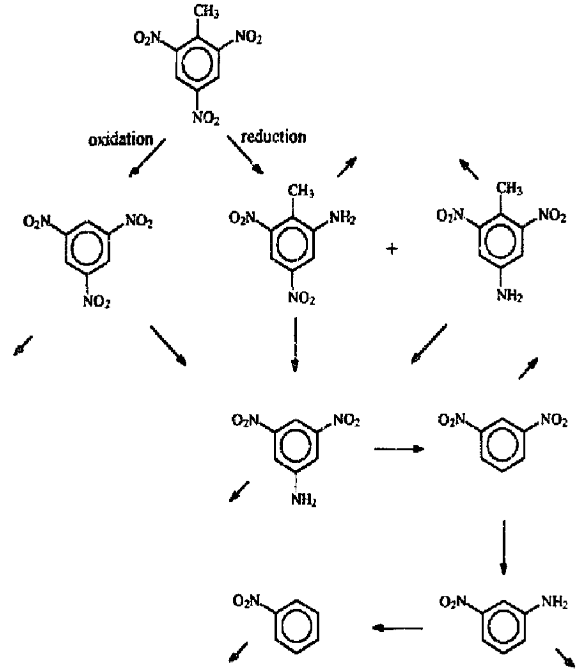


Fig. 11. Proposed sequence for the photocatalytic degradation of TNT. Short arrows denote further pathways of degradation.

7. although photochemical reactions principally produce the same intermediates as detected on photocatalytic degradation, photolysis is much slower;
8. photocatalytic degradation appears to be an attractive alternative to rid groundwater and surface water of polluting nitroaromatic compounds provided that an inexpensive technical solution can be found which allows the throughput of high flow rates.

It is of interest to study the behaviour of TNT and/or TNB under photocatalytic and photochemical conditions using a ^{14}C-uniring-labelled starting material, which will allow the complete follow-up of the entire ring carbon, thereby enabling the degradation process of these compounds to be determined. In addition, due to the elimination of nitrogen from amino-nitro compounds (e.g. 1,3-DNB from 3,5-DNA and 2,6-DNT from 4A-2,6-DNT), amino-nitroaromatic compounds must be included in the photocatalytic degradation. Experiments along these lines are currently in progress in our laboratory.

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