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Photocatalytic degradation of trinitrotoluene and trinitrobenzene: influence of hydrogen peroxide☆

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Abstract

The degradation of 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitrobenzene (TNB) was studied in irradiated ($\lambda > 320$ nm) homogeneous solutions and in TiO_2 suspensions by varying the concentration of hydrogen peroxide and the pH. Photodegradation of TNT occurs rapidly in both homogeneous and heterogeneous media. In TiO_2 suspensions the degradation rate of TNT is enhanced significantly compared with the homogeneous solutions at all pH values investigated. Over almost the entire pH region studied, the addition of hydrogen peroxide to the suspensions results in decreasing reaction rates. Under the experimental conditions investigated, TNB is degraded significantly slower than TNT in all cases.

Keywords: Photocatalysis; Photodegradation; Trinitrotoluene; Trinitrobenzene; Titanium dioxide; Hydrogen peroxide

1. Introduction

2,4,6-Trinitrotoluene (TNT) is a toxic explosive and is suspected to be a carcinogen [1]. In Germany it was released in high volume waste streams during its production in World War II. Consequently, several places are known where ground and surface waters are contaminated by TNT and other nitroaromatic compounds from World War II ammunition plants [2–6]. Since water supply at these sites is endangered by these contaminants [1] an efficient water treatment is necessary.

Light-induced degradation of TNT as a possible technology for the treatment of contaminated water from ammunition plants has been the topic of several research projects [7–15]. Exposure of TNT to UV radiation results in the conversion of this compound into a variety of reaction products. More than ten aromatic compounds, including 2,4,6-trinitrobenzyl alcohol, 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene (TNB) have been identified after irradiation of aqueous TNT solutions with Pyrex-filtered light [10]. Direct photolysis of TNT by 254 nm UV radiation was reported to achieve partial ring cleavage and mineralization [7]. Significant mineralization of TNT has been achieved by the combination of 254 nm UV irradiation and hydrogen peroxide [8,9,12]. Recently, it was shown that photocatalytic mineralization using TiO_2 as a heterogeneous photocatalyst can be effective for the treatment of TNT-contaminated water [13–16]. In an air-saturated suspension containing 1 g l^{-1} at pH 5, more than 95% of the initially present 100 μmol TNT l^{-1} have been degraded under illumination with 78 μmol photons min^{-1} within 90 min. During this time the concentration of dissolved organic carbon decreased by about 40% while 42 μmol nitrite l^{-1} and 132 μmol nitrate l^{-1} were formed [16].

The photocatalytic degradation of an organic pollutant is initiated by the formation of valence band holes (h_{VB}^+) and conduction band electrons (e_{CB}^-) which are formed in a semiconductor particle (e.g. TiO_2) upon band gap illumination [17]. These charge carriers migrate to the surface of the semiconductor and react by electron transfer with donors and acceptors adsorbed at this surface. Commonly, it is believed that aromatic compounds are degraded by hydroxyl radicals ($^{\bullet}OH$), formed by oxidation of adsorbed water molecules or surface bound hydroxyl groups [17–19]. It has been shown that in many cases the photocatalytic degradation of a water contaminant can be enhanced by adding hydrogen peroxide (H_2O_2) [17,19]. This effect has been explained by the formation of hydroxyl radicals during its reaction with conduction band electrons by

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☆ Dedicated to Professor H.-D. Scharf on the occasion of his 65th birthday.

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$$H_2O_2 + e_{CB}^- \longrightarrow {}^{\bullet}OH + {}^{-}OH \qquad (1)$$

or by the oxidation of reaction intermediates formed after the initial degradation step of the pollutant molecule.

In the course of a comparative investigation of advanced oxidation processes for the treatment of water contaminated by nitroaromatics from World War II ammuniation plants we have studied the effect of H_2O_2 on the degradation of TNT and TNB in aqueous homogeneous solutions and in TiO_2 suspensions under irradiation with light with wavelengths greater than 320 nm.

2. Experimental section

2.1. Materials

The photocatalyst used was TiO_2 Degussa P25. TNT was synthesized by nitrating 2,4-dinitrotoluene with an HNO_3–H_2SO_4 mixture at 80 °C and recrystallized twice from ethanol. In some experiments, recrystallized TNT from ammunition recovered at a former production site was used. All other chemicals were obtained from reputable suppliers and used as received.

2.2. Experimental procedures

The photochemical experiments were performed using the apparatus described recently [15,20].

The light source was an Osram XBO 150W xenon lamp in a Kratos lamp housing equipped with a condenser of quartz lenses and a Kratos power supply. The light beam was focused through a bore in a tempered aluminium block onto the cylindrical irradiation vessel made of borosilicate glass (Machery–Nagel vials N20-20 75.5 mm high and 23.25 mm in outside diameter). Solutions and suspensions were magnetically stirred (about 600 rev min^{-1}). The optical pathway contained a shutter and a UG1 filter (3 mm thick; Schott) to eliminate radiation with wavelengths shorter than 320 nm. All components were mounted on an optical bench.

Aqueous stock solutions, containing 100 μmol TNT or TNB l^{-1}, were prepared with diluted sulphuric acid (pH 3) by sonication for 6 h. The pH of these stock solutions was adjusted with potassium hydroxide. For photocatalytic degradation experiments the appropriate quantity of a stock solution was added to a previously weighted amount of TiO_2 resulting in a catalyst concentration of 1 g l^{-1}. These suspensions were thoroughly stirred for at least 30 min to guarantee a homogeneous distribution of the catalyst and a saturation with air. Samples of 5 ml suspension or solution were transferred into the reaction vessels. The vessels were sealed and tempered in the aluminium block to 30 ± 1 °C for about 15 min. In the experiments with hydrogen peroxide, 100 μl of a diluted aqueous solution of this oxidant was added by a syringe just before the shutter in the light beam was opened.

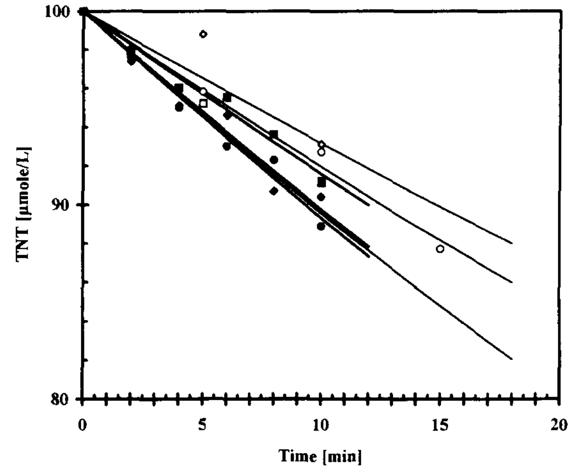

Fig. 1. Change in the concentration of TNT during irradiation in aqueous solutions and in TiO_2 suspensions under different experimental conditions: ○, no H_2O_2; ◇, 100 μmol H_2O_2 l^{-1}; □, 1000 μmol H_2O_2 l^{-1}; ●, 1 g TiO_2 l^{-1}; ◆, 1 g TiO_2 l^{-1} and 100 μmol H_2O_2 l^{-1}; ■, 1 g TiO_2 l^{-1} and 1000 μmol H_2O_2 l^{-1} ($[TNT]_0 = 100$ μmol l^{-1}; $[TiO_2]_0 = 1$ g l^{-1}; $T = 30$ °C; aerated media; pH 7; $I = 2.6$ μmol photons min^{-1}). The lines have been calculated assuming first-order kinetics.

Photon fluxes were measured by ferrioxalate actinometry [21].

2.3. Analysis

After the desired time of irradiation the reaction was quenched by addition of 1 ml of methanol and the samples were immediately centrifuged. The concentrations of the organic compounds were monitored with a high performance liquid chromatograph equipped with a UV detector. The measurements were conducted by monitoring the absorption at 254 nm. A reverse-phase column, 250 mm long and 4.6 mm in inside diameter, packed with ODS Hypersil 5 μm was used for separation and analyses. A mixture of methanol and water was used as the mobile phase (50 vol.% water; flow rate 1.0 ml min^{-1}).

3. Results

The light-induced degradation of TNT and TNB was studied in homogeneous solutions and in TiO_2 suspensions varying the concentration of H_2O_2 and the pH. In the dark, TNT and TNB were stable for several hours in air-saturated solutions. Only in oxygen-purged alkaline TNT solutions and suspensions (pH 11) was degradation in the dark observed. Under all experimental conditions investigated, a decrease in the TNT concentration was observed under irradiation. The change in concentration of TNT vs. irradiation time under different experimental conditions is shown in Fig. 1. As can be seen from this figure, the rate of disappearance of the organic compound can be described by an apparent first-order kinetic law at low conversions. Initial reaction rates r_0 have

Table 1
Initial reaction rate r_0 of the light-induced degradation of 2,4,6-trinitrotoluene ($[TNT]_0 = 100$ μmol l^{-1}; aerated solution or suspension; $T = 30$ °C; $I = 2.6$ μmol photons min^{-1})

TiO_2 ($g\ l^{-1}$)	H_2O_2 (μmol l^{-1})	r_0 (μmol l^{-1} min^{-1})						
		pH 3	pH 4	pH 5	pH 7	pH 9	pH 10	pH 11
0.0	0	< 0.10 [a]			0.84			0.92
0.0	100	0.35			0.71			0.53
0.0	1000	0.15			1.10			0.65
1.0	0	1.13	1.19	1.19	1.13	1.10	1.22	1.30
1.0	100	0.77	0.77	1.12	1.08	0.76	1.03	1.31
1.0	1000	0.55			0.88			1.53

[a] Degradation of 3% or less after irradiation for 0.5 h.

been calculated from the slopes of the plots shown in Fig. 1. The results are presented in Table 1.

The data given in Table 1 show that the degradation rate of TNT under irradiation in a homogeneous solution is a function of the initial pH and the amount of H_2O_2 initially present in the medium. In homogeneous solutions the reaction rate is increasing with increasing pH in the absence of H_2O_2. At pH 3 in absence of H_2O_2 no change in concentration of TNT was observed within the range of analytical precision during irradiation for the first 30 min in homogeneous solution. The initial reaction rate has been estimated to be smaller than 0.10 μmol l^{-1} min^{-1}. During irradiation the light-induced degradation becomes faster and after 2 h, nearly 30% of the TNT initially present in solution have been degraded. At this pH the degradation rate is enhanced drastically by the addition of hydrogen peroxide to the solution. Also, in the presence of H_2O_2 an increase in reaction rate during irradiation was observed. This effect is especially marked in the experiment with an initial H_2O_2 concentration of 1000 μmol l^{-1}; in spite of the low initial reaction rate, 48% of the initial TNT have reacted after 2 h.

In neutral and alkaline solutions, TNT is degraded photochemically very rapidly. Without added H_2O_2, 78% and 57% of the initial present TNT have reacted within 2 h at pH 7 and pH 11 respectively. At these pH values the addition of H_2O_2 to the solutions results in a decrease in initial reaction rate compared with the experiments in the absence of H_2O_2. With an initial H_2O_2 concentration of 100 μmol l^{-1}, 72% and 56% TNT have been degraded within 2 h at pH 7 and pH 11 respectively.

In TiO_2 suspensions the degradation rate of TNT is enhanced significantly compared with the homogeneous solutions at all pH values investigated. Over almost the entire pH region studied, the addition of hydrogen peroxide to the suspensions results in decreasing reaction rates. Obviously, higher concentrations of H_2O_2 result in a stronger inhibiting action of this oxidant. Only at pH 11 was a slight increase in reaction rate observed with increasing concentrations of H_2O_2.

It is noted that the initial reaction rate of the photocatalytic degradation in the absence of H_2O_2 is hardly affected by the pH of the suspension. Addition of H_2O_2 to the suspension results in a more pronounced effect of the pH on the reaction rate. However, there seems to be a pronounced influence of the pH on the degradation pathways of TNT in both homogeneous and heterogeneous media. While several degradation products can be seen in the chromatograms, the only intermediate identified was TNB. The amount of this compound found during the light-induced degradation of TNT depends strongly on the pH of the medium. Both in homogeneous solutions and in TiO_2 suspensions no TNB could be detected in media with pH values lower than pH 5. In weak acidic and neutral media, only traces of TNB were found. In TiO_2 suspensions, 0.1 μmol TNB l^{-1} and 0.5 μmol TNB l^{-1} have been found after irradiation for 10 min at pH 5 and pH 7 respectively. In the photocatalytic degradation of TNT about 2 μmol TNB l^{-1} are formed within 10 min of irradiation in the region from pH 9 to pH 11. This means that 18% of the reacted TNT is converted to give TNB in alkaline suspensions.

In homogeneous solutions at pH 11, about 6% of the degraded TNT has reacted to give TNB. Both in homogeneous and in heterogeneous media no influence of the H_2O_2 concentration on the amount of TNB formed was observed within experimental error.

The formation of TNB during the TNT photodegradation initiated a study of the behaviour of this compound under the same experimental conditions. As in the case of TNT, the rate of degradation of TNB can be described by an apparent first-order kinetic law. Initial reaction rates r_0 of the light-induced degradation of TNB are given in Table 2.

Under the experimental conditions investigated, TNB is significantly degraded more slowly than TNT in all cases. This observation is in agreement with our results from TNT photodegradation experiments, where a continuous growth in TNB concentration was observed during irradiation at pH 5 or higher. In neutral and alkaline solutions, TNB is photochemically inert also in presence of H_2O_2. In acidic homogeneous solution at pH 3, TNB is only degraded in the presence of H_2O_2. As has been observed in the case of the photocatalytic degradation of TNT, the degradation rate of TNB is significantly enhanced in TiO_2 suspensions compared with the homogeneous solutions, and addition of H_2O_2 to the suspensions results in a decrease in the reaction rate in the region from pH 3 to pH 9. However, this effect is small in neutral and weak acidic suspensions.

4. Discussion

While TNB is persistent in irradiated aqueous solutions in the region from pH 3 to pH 11, TNT is photolysed fast, as has been shown before [7,10,11,22]. The photolysis rate of TNT accelerates with time. This effect has also been reported in a previous study of the photolysis of TNT and has been

Table 2
Initial reaction rate r_0 of the light-induced degradation of 1,3,5-trinitrobenzene ($[\mathrm{TNB}]_0 = 100$ μmol l^{-1}; aerated solution or suspension; $T = 30$ °C, $I = 3.9$ μmol photons $\min^{-1}$)

TiO_2 ($g\ l^{-1}$)	H_2O_2 ($\mu mol\ l^{-1}$)	r_0 ($\mu mol\ l^{-1}\ min^{-1}$)						
		pH 3	pH 4	pH 5	pH 7	pH 9	pH 10	pH 11
0.0	0	< 0.02 [a]			< 0.02 [a]			< 0.02 [a]
0.0	100	0.16			< 0.02 [a]			< 0.02 [a]
0.0	1000	0.23			< 0.02 [a]			< 0.02 [a]
1.0	0	0.38	0.39	0.38	0.32	0.30	0.30	0.22
1.0	100	0.18	0.36	0.37	0.37	0.23	0.19	0.19
1.0	1000	0.23			0.22			0.23

[a] Degradation of 2% or less after irradiation for 2 h.

interpreted by the efficient promotion of the reaction by an indirect photolysis process through some photolysis products [22]. In homogeneous solutions the TNT photolysis rate is enhanced by an increasing pH. This effect has been observed previously during the photolysis of TNT [9,10,22] and might be due to the changes in UV–visible absorption of TNT (bathochromic shift and hyperchromie with increasing pH [23]).

The reaction rate of TNT photolysis is affected by added H_2O_2. The initial reaction rate of TNT photolysis is decreased by the addition of H_2O_2 (100 μmol l^{-1} (0.07%)) in neutral and alkaline solution but positively affected at pH 3. Increasing the concentration of added H_2O_2 to 1000 μmol l^{-1} (0.7%) results in an increase in reaction rate at pH 9 and 11 and a decrease at pH 3. Andrews and Osman [8] and Andrews [9] have also observed a non-linear behaviour of the TNT degradation rate on the concentration of the oxidant when they studied the action of H_2O_2 on the photodegradation of TNT ($\lambda = 254$ nm). They reported that the maximum degradation efficiency was achieved between 0.05 and 0.1% H_2O_2 [8,9].

For the first steps of the direct light induced degradation of TNT in homogeneous solutions the reactions given in Scheme 1 have been suggested [10,22,24–26]. Aci-TNT and the anion TNT^- are presumed to arise by an intramolecular hydrogen transfer from the methyl group to the triplet-excited nitro group attached in ortho-position followed by deprotonation [24]. TNB is formed by the oxidation of the anion via trinitrobenzyl alcohol, trinitrobenzaldehyde and trinitrobenzoic acid as the intermediates [26].

The assumption of a triplet state as the primary transient in the TNT photodegradation is supported by the observation that the reaction rate is increased in the presence of a triplet sensitiser (e.g. acetone) [8,22] and that the photolysis is faster in oxygen-free solutions than in air-saturated solutions [22].

$$
\begin{aligned}
&\mathrm{TNT} \overset{h\nu}{\rightleftharpoons} \text{aci-TNT} \\
&\text{aci-TNT} \rightleftharpoons \mathrm{TNT}^- + \mathrm{H}^+ \\
&\mathrm{TNT}^- \xrightarrow{+\mathrm{H}^+} \mathrm{TNT} \\
&\mathrm{TNT}^- \longrightarrow \text{decomposition products}
\end{aligned}
$$

Scheme 1.

On the contrary, a reductive pathway is known as an ineffective photodegradation pathway for nitroaromatics [27]:

$$\mathrm{Ar{-}NO_2} + e^- \longrightarrow \mathrm{Ar{-}NO_2}^{\bullet -} \qquad (2)$$

If we consider that the degradation of TNT in homogeneous solutions under illumination occurs both by an oxidative route via a triplet state and by a reductive route (Eq. (2)) and that in alkaline solutions a dark degradation reaction also plays a role with its reaction rate depending on the oxygen concentration, the observed influence of H_2O_2 on the TNT degradation rate in homogeneous solutions might then be explained as follows.

In alkaline solutions the oxidative route is favoured as can be seen from the appearance of trinitrobenzene. The inhibiting action of low concentrations of H_2O_2 in homogeneous solutions is then due to an energy transfer from excited TNT molecules to H_2O_2 according to

$$\mathrm{TNT}^* + H_2O_2 \longrightarrow \mathrm{TNT} + H_2O_2^* \qquad (3)$$

or an increase in the concentration of molecular oxygen as a result of a H_2O_2 decomposition according to

$$2H_2O_2 \longrightarrow H_2O + O_2 \qquad (4)$$

The increase in reaction rate at higher H_2O_2 concentrations can consequently be attributed to an acceleration of the dark reaction by a higher concentration of oxygen formed via Eq. (4). Since no TNB was detected during the photolysis of TNT at pH 3, it must be concluded that the reductive pathway is favoured in acidic media. It is known that nitroaromatic compounds such as TNT and TNB are reduced in acidic media more easily than in alkaline solutions [23,28]. From the results reported above, it can be concluded that the reduction is accelerated by H_2O_2, which is known as a poor reductant. However, the primary product of reduction can be quenched by molecular oxygen according to

$$\mathrm{Ar{-}NO_2}^{\bullet -} + O_2 \longrightarrow \mathrm{Ar{-}NO_2} + O_2^{\bullet -} \qquad (5)$$

and as in the case of alkaline solutions the O_2 concentration is higher at higher concentrations of H_2O_2.

TNB can only be degraded by the reductive route and the higher stability of TNB in homogeneous solution compared with TNT can thus be explained in this way.

The results reported above confirm that TNT and TNB can be degraded in illuminated TiO_2 suspensions. Recently, we have proposed that TNT is degraded in irradiated TiO_2 suspensions following two competitive pathways [15]. On the one hand, the methyl group is oxidized in subsequent steps to a carboxyl group. TNB is then formed by decarboxylation of the intermediate benzoic acid. The intermediary formation of TNB in the photocatalytic degradation of TNT can therefore be explained by a side-chain attack of photogenerated hydroxyl radicals or by hole oxidation:

$$\mathrm{TNT} + h_{VB}^{+} \longrightarrow \mathrm{TNT}^{\cdot +} \longrightarrow \mathrm{TNT}^{\cdot} + \mathrm{H}^{+} \quad (6)$$

$$\mathrm{TNT} + {}^{\cdot}\mathrm{OH} \longrightarrow \mathrm{TNT}^{\cdot} + \mathrm{H_2O} \quad (7)$$

On the other hand, the degradation can be started reductively by an electron transfer from excited TiO_2 to TNT:

$$\mathrm{TNT} + e_{CB}^{-} \longrightarrow \mathrm{TNT}^{\cdot -} \quad (8)$$

In the case of the photocatalytic TNB degradation, only the second pathway is possible. The inhibition of the photocatalytic degradation of TNT and TNB in TiO_2 suspensions by H_2O_2 might be due to competition between TNT and H_2O_2 for conduction band electrons (cf. reactions (1) and (8)). However, it should be noted that a charge transfer from excited TNT (or alternatively its aci form or corresponding anion) or excited TNB to TiO_2 according to

$$\mathrm{TNT\ or\ TNB} + h\nu \longrightarrow \mathrm{TNT}^{*}\ \mathrm{or\ TNB}^{*} \quad (9)$$

$$\mathrm{TNT}^{*}\ \mathrm{or\ TNB}^{*} + \mathrm{TiO_2} \longrightarrow \mathrm{TNT}^{\cdot +}\ \mathrm{or\ TNB}^{+\cdot} + \mathrm{TiO_2}(e_{CB}^{-}) \quad (10)$$

a well-known phenomenon in semiconductor photochemistry (i.e. the sensitization of semiconductors, photography) as another primary step operating in the photocatalytic degradation of nitroaromatics, cannot be excluded by the results presented above.

Compared with H_2O_2-free suspensions the more pronounced influence of pH on the initial rate of TNT degradation of TiO_2 suspension containing H_2O_2 can again be explained by the action of O_2. The primary product of reduction via Eq. (8) is quenched by a higher concentration of O_2 formed by homogeneous decay of H_2O_2 via Eq. (5), resulting in a decrease in the reaction rate. On the contrary, the dark reaction of TNT or its anion with O_2 is accelerated in suspensions at pH 1.

5. Conclusions

The results presented above clearly demonstrate that the combination of hydrogen peroxide and UV light with $\lambda > 320$ nm is not a useful method for the treatment of ground and surface water from former ammunition plants contaminated by TNT and TNB.

In contrast, photocatalysis using aqueous TiO_2 suspensions may indeed be effective for the treatment of water from World War II ammunition plants. Since TNB is degraded much more slowly than TNT in irradiated TiO_2 suspensions, conditions have to be chosen to ensure that the formation of TNB by side-chain oxidation is suppressed.

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