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PHOTOCATALYTIC DEGRADATION OF TRINITROTOLUENE AND OTHER NITROAROMATIC COMPOUNDS

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ABSTRACT

The photocatalytic degradation of 2,4,6-trinitrotoluene and ten other nitroaromatic compounds in aerated TiO_2 suspensions has been studied. The following order of reactivity was observed: nitrotoluenes > nitrobenzene > dinitrotoluenes > dinitrobenzenes > 2,4,6-trinitrotoluene > 1,3,5-trinitrobenzene, which reflects the known influence of nitro groups towards the attack of electrophilic reagents on the aromatic molecule.

INTRODUCTION

Ground and surface water on or near former military sites on which explosives were produced or handled are often contaminated by the original explosives (dinitrotoluenes, 2,4,6-trinitrotoluene, and hexogen), but also by byproducts (nitrotoluenes) and compounds formed by biotic and abiotic degradation of the explosives or their byproducts (aminonitrotoluenes, nitrobenzenes, nitrophenols) [1-5]. In Germany, several places are known, where the water supply is endangered by these contaminants [1]. Thus an efficient water treatment is necessary.

Among many methods of degradation of nitroaromatic compounds, dissolved in water, a promising approach is the combination of ultraviolet (UV) irradiation and an oxidizing agent such as hydrogen peroxide [6-10], ozone [11-14] or Oxone™ [7, 11]. Recently, several groups have shown that nitro aromatics can also be degraded in irradiated TiO_2 suspensions [15-18].

In the course of a comparative investigation on advanced oxidation processes for the treatment of contaminated water from World War II ammunition plants we are studying the light induced degradation of various nitro aromatics under different experimental conditions. This paper presents results of the photocatalytic degradation of 2,4,6-trinitrotoluene, other nitrotoluenes, and nitrobenzenes in irradiated TiO_2 suspensions.

EXPERIMENTAL SECTION

Materials

The photocatalyst used was TiO_2 Degussa P25. 2,4,6-Trinitrotoluene was synthethized by nitrating 2,4-dinitrotoluene with a HNO_3-H_2SO_4 mixture at 80°C and recrystallized twice from ethanol. In some experiments recrystallized trinitrotoluene from ammunition, recovered at a former production site, was used. All other chemicals were obtained from reputable suppliers and used after cleaning by appropriate methods.

Experimental procedures

The photochemical experiments were performed in cylindrical reaction vessels made of borosilicate glass (vials N20-20, Machery-Nagel, 70206; 75,5 mm high, 23.25 mm o.d.). The reaction vessels were placed into suitable bores of a tempered aluminium block (Fig.1).

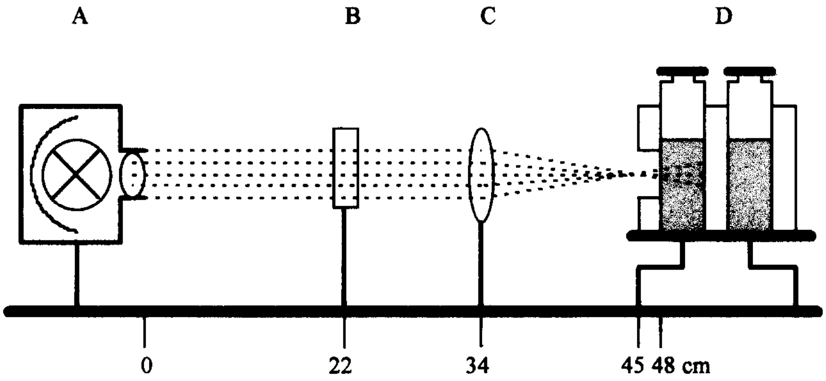

Figure 1. Experimental set-up.

(A: light source, B: shutter, filter UG 1, and neutral density filters if needed, C: quartz lens; D: aluminium block with irradiation vessels, magnetic stirrer, and thermo couple)

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 hole in the aluminium block onto the irradiation vessel. Solutions and suspensions were magnetically stirred (about 600 rpm). The optical pathway contained a shutter and an UG1 filter (3 mm thick, Schott) to minimise radiation with wavelengths shorter than 320 nm. To determine the influence of light intensity, the photon flux (I) was varied between 0.8 and 4.0 µmole photons$\times$min^{-1} using neutral density filters (Spindler & Hoyer). All components were mounted on an optical bench.

Aqueous stock solutions, containing 100 µmole$\times$L^{-1} of the organic compound, were prepared with diluted sulphuric acid (pH 3) by sonification for several hours, depending on the solubility of the organics. The pH of these stock solutions was adjusted with KOH. Prior to irradiation, 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$\times$L^{-1}. These suspensions were thoroughly stirred for at least thirty minutes. 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 ≈15 min) before irradiation.

Photon fluxes were measured by ferrioxalate actinometry [19].

Analysis

After the desired time of irradiation the samples were immediately centrifuged. The rates of disappearance of a given organic compound were monitored by a high-performance liquid chromatograph (HPLC) equipped with a UV detector. The measurements were conducted by monitoring the absorption at 254 nm or 270 nm. Reverse-phase columns, 250 mm long, 4.6 mm i.d., packed with ODS Hypersil 5 μm were used for separation and analyses. Mixtures of methanol and water were used as mobile phases (40, 45 or 50 vol.% water; flow rate 0.7 or 1.0 mL× min^{-1}).

RESULTS

The degradation of eleven nitrotoluenes and nitrobenzenes has been investigated in irradiated aqueous TiO_2 suspensions, varying the pH of the suspensions and the light intensity. As examples the change in concentration of six typical nitroaromatic pollutants *vs.* irradiation time is given in Figure 2.

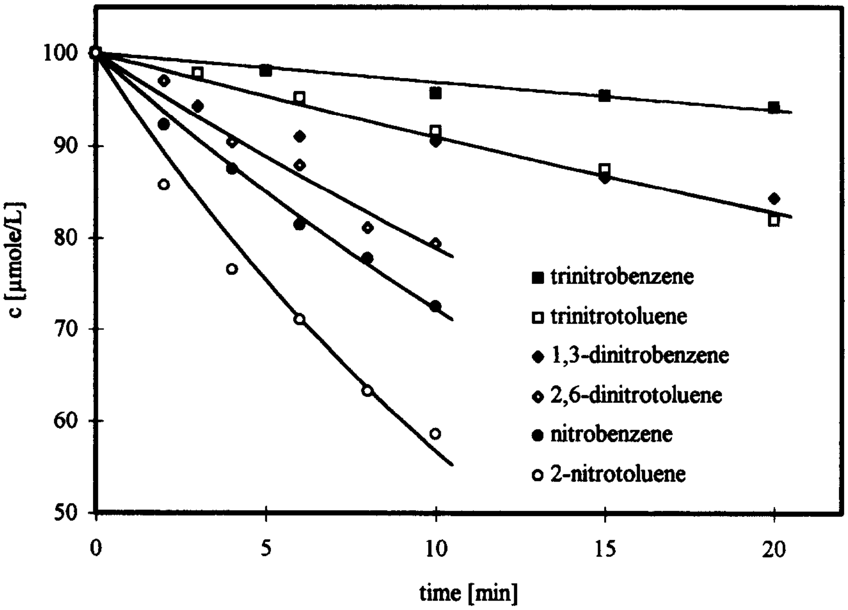

Figure 2. **Change of concentration of nitroaromatic compounds during irradiation in aqueous TiO_2 suspensions**

($[\text{aromat}]_0$ = 100 μmole×L^{-1}; $[TiO_2]$ = 1 g×L^{-1}; T = 30°C; aerated suspension, pH 3, I = 3 μmole photons×min^{-1}; The lines have been calculated assuming first order kinetics.)

In all cases the rate of disappearance of the organic solute can be described by an apparent first order rate law (correlation coefficients > 0.98). From the slopes of the respective ln c = f(t)-plots, initial reaction rates r_0 have been calculated. The results are presented in Table 1.

Table 1. **Initial reaction rates r_0 (μmole$\times$L$^{-1}\times$min^{-1}) of the photocatalytic degradation of nitroaromatic compounds**

(V_r=5 mL, $[\text{aromat}]_0$ = 100 μmole$\times$L^{-1}; $[TiO_2]$ = 1 g$\times$L^{-1}; T = 30°C; aerated suspension)

	I [μmole photons$\times$min^{-1}]	pH						
		3	4	5	7	9	10	11
2,4,6-Trinitrotoluene	3.5	1.13						1.60
	3.1	0.94	1.01	1.19	1.31	1.20	1.26	1.19
	2.6	1.13	1.19	1.19	1.13	1.10	1.22	1.30
2,4-Dinitrotoluene	3.5	3.24						2.06
2,6-Dinitrotoluene	3.1	2.37						1.66
2-Nitrotoluene	2.9	7.01						5.65
3-Nitrotoluene	3.5	6.76						6.21
4-Nitrotoluene	3.5	6.90						7.96
1,3,5-Trinitrobenzene	3.9	0.38	0.39	0.38	0.32	0.30	0.30	0.22
	2.9	0.32	0.35	0.32	0.45	0.33	0.28	0.29
1,2-Dinitrobenzene	3.2	0.83						0.76
1,3-Dinitrobenzene	3.0	0.95	0.91	0.81	0.82	0.83	0.93	0.74
1,4-Dinitrobenzene	3.1	1.20						0.83
Nitrobenzene	3.0	3.96	3.50	4.19	4.01	3.79	4.20	3.31

Aromatic nitro compounds in aqueous solutions absorb strongly in the 200 to 280 nm region and have a weak absorption extending to about 400 nm. Therefore, the homogeneous photoreactions of the nitroaromatics listed in Table 1 have been studied at different pH-values as control experiments. In the absence of TiO_2 no change in concentration within the range of analytical precision was observed for nitrobenzene, dinitrobenzenes, 1,3,5-trinitrobenzene, and 2,4-dinitrotoluene after 30 minutes of irradiation. The three isomeric nitrotoluenes, 2,6-dinitrotoluene, and 2,4,6-trinitrotoluene were degraded in homogeneous solutions under our experimental conditions, however, with reaction rates being in the case of the mono- and dinitrotoluenes one order of magnitude lower than in heterogeneous media. In the case of 2,4,6-trinitrotoluene no homogeneous degradation could be observed in acidic solution. But at pH 7 and pH 11, reaction rates of 0.84 and 0.92 μmole$\times$L$^{-1}\times$min^{-1} at a light intensity of 520 μmole photons$\times$L$^{-1}\times$min^{-1} have been determined. Thus in neutral and alkaline media the degradation rates of 2,4,6-trinitrotoluene are in the same order of magnitude as in TiO_2 suspensions.

The data given in Table 1 also show the effect of pH on the initial reaction rate r_0. It is noted that the initial reaction rate is hardly affected by the pH of the suspension. Therefore, average reaction rates r_0 have been calculated in the region between pH 3 and pH 11 for 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, 1,3-dinitrobenzene, and nitrobenzene to be 1.16±0.05, 0.33±0.02, 0.86±0.03, and 3.85±0.13 μmole×L^{-1}×min^{-1}, respectively, at light intensities of about 600 μmole photons×L^{-1}×min^{-1}.

On the other hand, there seems to be a pronounced influence of the pH on the degradation pathways. For example, at neutral and alkalinepH-values 1,3,5-trinitrobenzene has been detected as the main intermediate in the photocatalytic degradation of 2,4,6-trinitrotoluene, *i.e.*, at pH 9 and pH 11 about 18% of the reacted trinitrotoluene has been identified as trinitrobenzene after 10 minutes of irradiation. In acidic media, on the other hand, no trinitrobenzene could be found. A similar observation was made in the degradation of 2,6-dinitrotoluene where 1,3-dinitrobenzene was identified as an intermediate in alkaline but not in acidic suspensions.

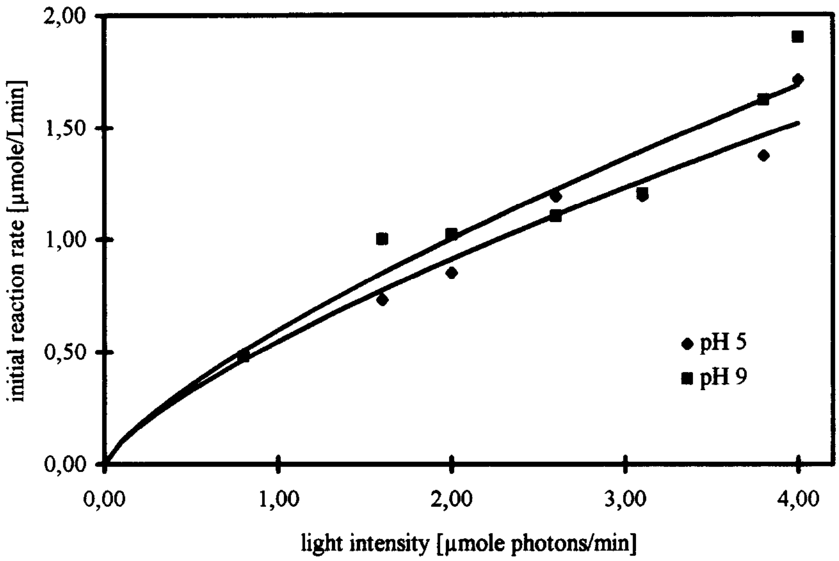

Figure 3. **Dependence of the initial reaction rate r_0 of the photocatalytic degradation of 2,4,6-trinitrotoluene on the light intensity I**

([aromat]$_0$ = 100 μmole×L^{-1}; [TiO_2] = 1 g×L^{-1}; T = 30°C; aerated suspension. The lines have been calculated using Eq. 1)

Figure 3 shows the dependence of the initial reaction rates r_0 of the photocatalytic degradation of 2,4,6-trinitrotoluene on the light intensity (0.8-4.0 μmole photons×min^{-1}) at pH 5 and pH 9. At both pH-values increasing light intensity results in an increase of the initial reaction rate but there is no linear dependence.

DISCUSSION

The results reported above show that nitroaromatic compounds can be degraded in irradiated aqueous TiO_2 suspensions. The reactivity of the compounds investigated decreased with increasing numbers of nitro groups on the aromatic ring. The methyl group of the toluenes enhanced the reactivity. The following order of reactivity was observed: nitrotoluenes > nitrobenzene > dinitrotoluenes > dinitrobenzenes > 2,4,6-trinitrotoluene > 1,3,5-trinitrobenzene. This order reflects the known influence of nitro groups towards the attack of an electrophilic reagent on the aromatic molecule.

It seems that nitrotoluenes are degraded in two competitive pathways in the presence of TiO_2. When the methyl group is the site of the initial attack it will be oxidised in subsequent steps yielding the carboxyl group. After decarboxylation (for example, following a Photo-Kolbe mechanism [20]) the corresponding nitrobenzenes are formed, which have been identified during the degradation of 2,4,6-trinitrotoluene and 2,6-dinitrotoluene. It is known that 2,4,6-trinitrotoluene is converted to 1,3,5-trinitrobenzene in natural aquatic environments under the action of light [21], and during hydrogen peroxide-UV [6] and ozone-UV treatment [12] of aqueous solutions. Ho observed the formation of 1,3-dinitrobenzene as an intermediate in the photolysis of 2,4-dinitrotoluene in the presence of hydrogen peroxide [9]. He postulated a mechanism based on the subsequent attack of photochemically generated hydroxyl radicals on the methyl group of the toluene leading to the corresponding benzene derivative *via* the detected intermediates dinitrobenzyl alcohol, dinitrobenzaldehyd, and dinitrobenzoic acid. Therefore, it seems plausible to explain the intermediacy of nitrobenzenes in the photocatalytic degradation of nitrotoluenes by a side chain attack of photogenerated hydroxyl radicals. Hydroxyl radicals have indeed been postulated by several authors as the primary oxidising species in photocatalytic reactions [22-24].

The second degradation path is either initiated by hydroxyl radical attack at the aromatic ring yielding cresols or by electron transfer from excited TiO_2 to the organic solute. As the formation of cresols from di- and trinitrotoluenes in presence of hydroxyl radicals has, to the best of our knowledge, never been reported, and 2,4,6-trinitrotoluene can not be degraded by the action of Fentons reagent [25], the reductive pathway seems to be more likely. Indeed, the light induced reduction of 4-nitrotoluene and other nitro compounds in TiO_2 suspensions has recently been reported by Mahdavi *et al.* [26]. A mechanism for the formation of amino compounds involving sequential electron transfers, protonations, and dehydration was proposed by these authors. A reductive pathway for the photocatalytic degradation of 2,4,6-trinitrotoluene has been suggested by several authors [15, 16].

Both the pH of the suspension and the chemical nature of the solute apparently influence which pathway dominates the degradation of the nitrotoluenes. In alkaline media for example, the degradation of di- and trinitrotoluenes occurs predominantly by side chain oxidation.

The reaction rate r can be described in terms of an apparent first order kinetic and depends on the incident light intensity I. Considering these facts, the rate law is given by

$$r = k' \times I^n \times c \qquad \text{(eq. 1)}$$

with the rate constant k′, and the contaminant concentration c. For $c \rightarrow c_0$, $r \rightarrow r_0$ and Eq.1 yields in a logarithmic form

$$\lg r_0 = n \times \lg I + \lg (k' \times c_0) \qquad \text{(eq. 2)}$$

Using Eq. 2, the factor n has been determined from the data presented in Fig. 3 for the degradation of 2,4,6-trinitrotoluene to be 0.73±0.06 and 0.75±0.09 at pH 5 and pH 9, respectively. Recently, Mills and Morris have determined n = 0.74±0.05 for the photocatalytic degradation of 4-chlorophenol at pH 2 and light intensities of 5 to 60 µmole photons$\times$min^{-1} using TiO_2 as the photocatalyst [27].

The degradation rate of the nitroaromatic compounds investigated here is hardly affected by the pH of the suspension between pH 3 and pH 11. This is in agreement with results of photocatalytic degradation experiments with nitrobenzene reported by D'Oliveira *et al.* [17].

CONCLUSIONS

The results presented here indicate that photocatalysis may be effective for the treatment of water from World War II ammunition plants. Because nitrobenzenes are degraded much slower than nitrotoluenes in irradiated TiO_2 suspensions, conditions have to be chosen to ensure that the formation of nitrobenzenes by side chain oxidation is suppressed. Since in any water contaminated with explosives there are many other nitroaromatic compounds, application of photocatalysis to real situations requires assessment of multicomponent systems.

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