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# Photocatalytic oxidation mechanism of benzonitrile in aqueous suspensions of titanium dioxide

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## Abstract

The photocatalytic oxidation of benzonitrile was carried out in aqueous suspensions (pH 11) of commercial polycrystalline $TiO_2$ (Merck and Degussa P25) irradiated by ultraviolet light.

The rate of decomposition was dependent on the concentration of benzonitrile and followed a pseudo-first order kinetics. The complete mineralization of a 0.70 mM benzonitrile solution was achieved in ca. 8 h by using $TiO_2$ Degussa P25, whereas the substrate was only partially mineralized even after 14 h of irradiation in the presence of $TiO_2$ Merck. The final oxidation products were carbonate and nitrate. The appearance and the evolution of organic and inorganic intermediate species were also investigated and allowed to hypothesize the reaction pathways.

*Keywords:* Heterogeneous photocatalysis; Benzonitrile; Titanium dioxide

## 1. Introduction

Benzonitrile is a very toxic molecule extensively used as a solvent due to its high stability. Very few works concerning the benzonitrile abatement or its chemical modification are reported in the literature [1–3], although benzonitrile compounds are widely used as herbicides and fungicides and their fate in the environment is not completely known [4]. Anyway benzonitrile is a very interesting model molecule for photooxidation studies because it possesses an aryl and a nitrile group that may undergo different oxidation routes. Ehrich et al. [3] studied the direct oxidation of benzonitrile to its hydroxyderivates using $N_2O$ as oxidant. The reaction was carried out in gas-solid regime on ZSM-5 type zeolites. They found mainly $CO_2$ but the three monohydroxybenzonitrile derivatives were also detected.

Heterogeneous photocatalysis is a technology successfully used to oxidise or reduce organic and inorganic species present both in vapour and in liquid effluents [5–8]. The photocatalytic process requires mild conditions and the degradation of recalcitrant, very toxic and non-biodegradable compounds is almost always achieved. $TiO_2$ is commonly used as photocatalyst due to its low cost, high activity and stability [9]. Photodegradation of *N*-containing compounds has been widely studied to investigate the relation between the inorganic species produced (in particular ammonium and nitrate ions) and the chemical structure of the starting molecule [10–13]. The heterogeneous photocatalytic degradation of benzonitrile at acid pH has been recently investigated [14]. Some papers have concerned the photodegradation of nitrile or amide functionalized molecules as acetonitrile [15–20], methanamide [10,13], ethanamide [21] and benzamide [22–24].

In this work, we report a study of the photocatalytic degradation of benzonitrile in the presence of $TiO_2$. The experiments were carried out at pH 11 in aqueous suspensions of two kinds of commercial polycrystalline $TiO_2$, i.e. Merck and Degussa P25, irradiated by ultraviolet light. The abatement of the substrate and of the total organic carbon (TOC) was monitored. The influence of the benzonitrile concentration on the photooxidation rate was investigated. Moreover, intermediate species and final degradation products were monitored throughout the photocatalytic experiments in order to study the fate of the nitrile group and of the aromatic ring.

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## 2. Experimental

The study of the photocatalytic degradation of benzonitrile was carried out by using a discontinuous Pyrex batch photoreactor of cylindrical shape containing 1.5 L of aqueous suspension of $TiO_2$. The photoreactor was provided with ports in its upper section for the inlet and outlet of gases, for sampling and for pH and temperature measurements. In selected runs, the outlet gas was bubbled in a trap containing an aqueous solution of NaOH at pH 12 to fix the hydrogen cyanide stripped from the reacting system and then in a trap containing an aqueous solution of HCl at pH 2 to fix the ammonia that could escape from the reactor. A magnetic stirrer guaranteed a satisfactory suspension of the photocatalyst and the uniformity of the reacting mixture. A 500 W medium pressure Hg lamp (Helios Italquartz, Italy) was axially immersed within the photoreactor. The irradiance reaching the photoreactor (15.5 mW $cm^{-2}$) was measured in the 300–400 nm range by means of a radiometer UVX Digital leaned against the external wall of the photoreactor containing only pure water. The lamp was cooled by water circulating through a Pyrex thimble and the irradiated suspension had a temperature of about 300 K. Pure oxygen was continuously bubbled into the suspension for ca. 0.5 h before switching on the lamp and throughout the occurrence of the photoreactivity experiments. $TiO_2$ Merck (100% anatase, BET surface area: 10 $m^2$ $g^{-1}$) and $TiO_2$ Degussa P25 (≈80% anatase, 20% rutile, BET surface area: 50 $m^2$ $g^{-1}$) were used as the photocatalyts. For all of the runs the catalyst amount was 0.4 g $L^{-1}$ and the initial pH of the suspension was adjusted to 11 by addition of NaOH. Initial benzonitrile concentrations were in the 0.14–0.77 mM range. All the reagents were analytical grade Fluka.

The photoreactivity runs lasted at least 5 h, but some selected runs lasted until 14 h. The analyses of the samples (5 ml volume) withdrawn from the suspensions at fixed intervals of time were performed after separation of the catalyst by filtration through 0.45 μm cellulose acetate membrane filters (HA, Millipore). A HPLC instrument constituted by a Varian 9012 Solvent Delivery System pump coupled with a Varian 9050 variable wavelength UV–vis detector was used to analyse benzonitrile and its organic degradation intermediates. A column Phenomenex Synergi 4 μm Fusion RP 80 (150 mm long × 2 mm i. d.) allowed an optimal separation of the peaks. A mixture of acetonitrile, water and an aqueous solution (80 mM) of $KH_2PO_4$ (42/30/28, v/v/v) was used as the eluant with a flow rate of 0.2 ml $min^{-1}$. The UV–vis detector was setted at 224 nm.

TOC analyses were carried out for all of the runs by using a 5000A Shimadzu total organic carbon analyser in order to follow the mineralization of the organics. The quantitative determination of the anions present in the reaction mixture during the runs was carried out by using an ionic chromatograph (Dionex DX 120) equipped with an ION PAC AS14A column (250 mm long × 4 mm i. d.). An aqueous solution of $NaHCO_3$ (2.8 mM) and $Na_2CO_3$ (2.2 mM) was used as eluant at the flow rate of 0.5 ml $min^{-1}$.

The concentrations of cyanide and ammonium ions were determined by means of selective electrodes connected to an Orion 720A+ analyser using calibration graphs of solutions of KCN and $NH_4Cl$ as the authentic standards.

## 3. Results and discussion

Some preliminary experiments were carried out in order to investigate the adsorption of benzonitrile into the surface of the catalysts. The benzonitrile concentration was measured in liquid phase before and after the addition of the $TiO_2$ powders in dark conditions. The concentration values did not change significantly even after long times of contact under stirring indicating that benzonitrile scarcely adsorbs in the dark at pH 11 into both $TiO_2$ surfaces. Blank tests performed in the absence of catalyst but in the presence of UV light evidenced that no decrease of the substrate concentration occurred. The abatement of benzonitrile was observed only during the photocatalytic experiments. Fig. 1 shows the benzonitrile concentration versus irradiation time for runs carried out in the presence of the two $TiO_2$ samples.

Benzonitrile completely disappeared after 1–2 h, when $TiO_2$ Degussa P25 was used as the photocatalyst; whereas, its degradation was slower in the presence of $TiO_2$ Merck. The photocatalytic reaction followed a pseudo-first order kinetics under our experimental conditions.

The variation of the TOC concentration during two selected photodegradation runs is illustrated in Fig. 2. Benzonitrile was

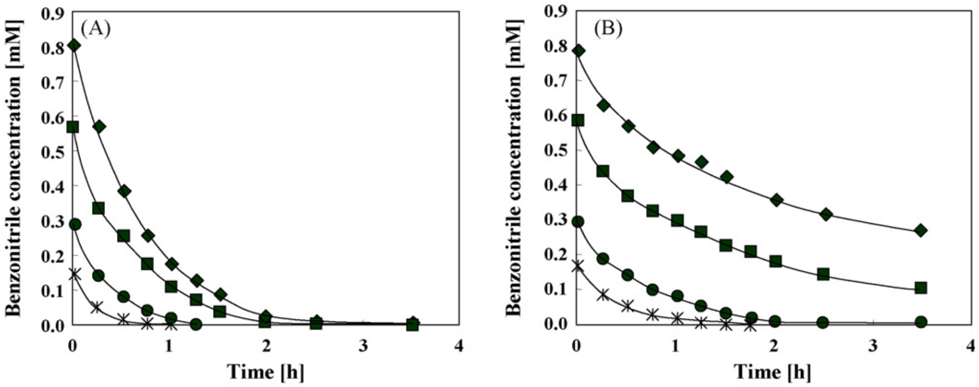

Fig. 1. Benzonitrile concentration vs. irradiation time for runs carried out in the presence of $TiO_2$ Degussa P25 (A) and $TiO_2$ Merck (B).