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Photocatalyzed mineralization of a trimethylated phenol in oxygenated aqueous titania. An alternative to microbial degradation

Rita Terzian, Nick Serpone [1]

Laboratory of Pure and Applied Studies in Catalysis, Environment and Materials, Department of Chemistry, Concordia University, Montreal, Quebec, Canada H3G 1M8

and

Hisao Hidaka

Department of Chemistry, Meisei University, 191 Tokyo, Japan

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The most methylated phenolic substrate in coal tar creosote, 2,3,5-trimethylphenol (TMP), was mineralized photocatalytically to CO_2 and water at pH 3 in illuminated air-equilibrated titania dispersions. Trimethylhydroquinone and trimethylbenzoquinone were the two major aromatic intermediates; trace amounts of trimethylcatechol also formed. Complete mineralization was achieved in oxygenated solutions in $\sim$ 1 h; conversion of TMP was over in less than $\sim$ 25 min in aerated solutions and in less than 12 min in oxygenated solutions.

Keywords: heterogeneous catalysis; photooxidation; photomineralization; trimethylated phenol; titania suspensions

1. Introduction

Wood-preserving facilities are large users of such pesticides as creosote, pentachlorophenol, and CCA (copper, chrome, and arsenate) [1]. Accidental spillage, misuse and improper disposal of creosote and pentachlorophenol (PCP) have resulted in contaminated groundwaters in the vicinity of wood-preserving plants posing potential health risks. Coal tar creosote is a complex mixture of organic compounds comprising approximately 85% by weight of polycyclic aromatic hydrocarbons (PAHs), about 10% by weight of phenolic substances, and ca. 5% by weight of N-, S-, and O-heterocyclics [1]. The phenols constitute the bulk of the

[1] To whom correspondence should be addressed.

aqueous contaminants resulting from creosote spillage [2]. Two PCP- and creosote-contaminated sites have been reported at Pensacola, FL [2,3] and at St. Louis Park, MN [4].

Remediation techniques of such sites have employed biotic and abiotic (volatilization, leaching, and direct photolysis) processes to restore the contaminated sites with in situ biodegradation as the major method, which is not without its limitations [1]: (i) the pollutant(s) must be in a chemical form that can be degraded microbiologically, (ii) excess organic carbon robs the microbial population of oxygen and essential inorganic nutrients and thus limits its activity, and (iii) acclimatization of the microbial population that is capable of degrading the pollutant(s) is necessary. Studies by Crawford and Mohn [5] have shown that bioremediation of a PCP-contaminated site can take months to reduce the quantity of pentachlorophenol from 298 ppm (mg ℓ^{-1}) to 58 ppm. Acclimatization does accelerate the process. The specificity of a microbe to degrade a given organic pollutant is not a limitation in heterogeneous photocatalysis, since the ·OH radical is indiscriminate in its attack of organics.

Near-UV irradiation of creosote leachates in the presence of TiO_2 can rapidly and safely eliminate (mineralize) these hazardous substances in air-equilibrated aqueous media. A phenolic substance of creosote that remains to be examined [6–11] is 2,3,5-trimethylphenol (TMP); it comprises about 5% by weight of the phenolic substances in creosote [1]. We herein report the temporal course of the photomineralization of this highly methylated phenol as part of our continuing studies [6,7,12] into developing methods to destroy this and other phenols in aqueous ecosystems, with the ultimate aim to evaluate the practicality of photocatalysis in detoxifying typical multicomponent wastewater systems such as those represented by coal tar creosote leachates [2–4]. Hydroxylated aromatic intermediates formed during the photooxidative degradation was identified and rate data examined within the context of kinetic principles described earlier [13].

2. Experimental

Chemicals: 2,3,5-trimethylphenol (99%; Aldrich) was used as received; TiO_2 was Degussa P-25 (BET surface area, 55 m^2 g^{-1}; ca. 80% anatase and ca. 20% rutile). Water was doubly distilled.

The light source was a 1000 W Hg/Xe lamp; it was equipped with a water jacket to eliminate infrared radiation. The output spectrum (>220 nm) of the lamp is characterized by strong mercury lines over the xenon continuum through the visible and the ultraviolet regions.

The temporal evolution of the mineralization of TMP and identification of the respective reaction intermediates were monitored by high performance liquid chromatography (HPLC) using a Waters Associates liquid chromatograph equipped with a 501 HPLC Pump, a 441 absorbance detector, a Rheodyne 20 μl sample injec-

tion loop together with a Hewlett-Packard 3396A integrator; detection wavelengths available were 214, 254 and 280 nm. The column was a Waters reverse phase C-18 (μ-Bondapack); the mobile phase consisted of a 50/50 mixture of methanol (BDH, Omnisolv grade) and water. All samples were filtered through MSI nylon 66 filters (pore size, 0.22 μm) prior to analysis.

Procedure: UV/visible irradiation was carried out on aerated, efficiently stirred 50 ml samples. The appropriate quantity of a stock solution of TMP was added to a previously weighed quantity of TiO_2 (2 g ℓ^{-1}); the pH was adjusted with HCl. The evolution of CO_2 was monitored by gas chromatography from samples taken from illuminated and oxygenated 25 ml solutions in vials sealed with rubber septa; the pH changes during the mineralization were too small to affect the quantity of carbon dioxide measured by GC.

3. Results and discussion

HPLC chromatograms showed three detectable aromatic intermediates (**1** (traces), **2**, and **3**; wavelengths, 214 and 254 nm) formed during the course of the degradation of 2,3,5-TMP. Three aromatic species can form by reaction of ·OH radicals with TMP: 3,5,6-trimethylcatechol (TMCC), 2,3,5-trimethylhydroquinone (TMHQ), and 2,3,5-trimethylbenzoquinone (TMBQ). The retention time of TMHQ was determined from a commercially available sample; it was intermediate **2**. Intermediate **3** was identified as the TMBQ species since benzoquinones absorb little at 214 nm but show significant absorbance at 254 nm. Intermediate **1** was 3,5,6-TMCC.

In the absence of light, TMP is only slightly adsorbed ($\leqslant 10\%$; 159.3 μM of TMP and 2 g ℓ^{-1} of TiO_2; pH 3) on the semiconductor particle surface. Its transformation in aqueous irradiated TiO_2 dispersions followed good first-order kinetics: $k_{app} = 0.14 \pm 0.02$ min^{-1}; initial rate, 23 ± 2 μM min^{-1}; $t_{1/2} = 4.8$ min). The total phototransformation of TMP was complete in less than 25 min of illumination, fig. 1. The formation and transformation of the major intermediates were also monitored: TMHQ formed via first-order kinetics, $k_{app} \approx 0.1$ min^{-1}, and degraded via zero-order kinetics, $k_{app} \approx 7$ μM min^{-1}. The species TMBQ also formed via first-order kinetics, $k_{app} = 0.003$ min^{-1}, and disappeared via a zero-order process, $k_{app} \approx 2$ μM min^{-1}. In the absence of TiO_2, direct photolysis of TMP led to negligible decomposition within the time frame of our experiments and under otherwise identical conditions.

The photocatalyzed mineralization process for TMP followed the following stoichiometric reaction, as evidenced by a quantitative product analysis:

$$(CH_3)_3C_6H_2OH + \tfrac{23}{2}O_2 \xrightarrow[TiO_2]{h\nu} 9CO_2 + 6H_2O \qquad (1)$$

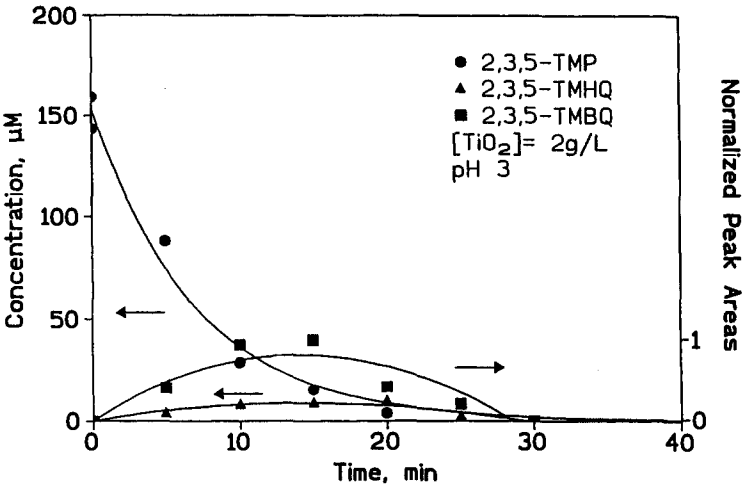


Fig. 1. Photodegradation of 2,3,5-TMP (159.3 μM) in air-equilibrated aqueous suspensions of TiO_2 (2 g ℓ^{-1}) irradiated by light at wavelengths above 300 nm; pH 3; 50 ml samples.

The presence of oxygen greatly influences the kinetics of decomposition of 2,3,5-TMP illustrated in fig. 2 for both air-equilibrated and oxygenated suspensions. Degradation is ca. 50% faster in the latter suspensions; the corresponding first-order parameters are, air versus oxygen, respectively: $k_{app} = 0.14$ and 0.21 min^{-1}; initial rates = 23 and 34 μM min^{-1}; $t_{1/2} = 4.8$ and 3.3 min. Decomposition of TMP takes place in less than 12 min in the presence of excess oxygen, fig. 2.

The quantity of CO_2 evolved as a function of irradiation time is illustrated in fig. 3 for an oxygen-saturated aqueous solution of the trimethylphenol. Approxi-

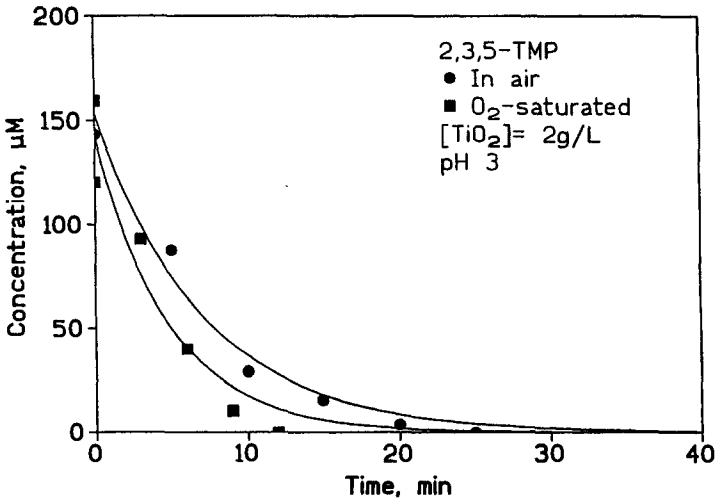


Fig. 2. Plot showing the photodegradation of ca. 20 mg ℓ^{-1} of trimethylphenol in the presence of 2 g ℓ^{-1} TiO_2 in air-equilibrated suspensions and in oxygen-saturated suspensions; initial pH 3.

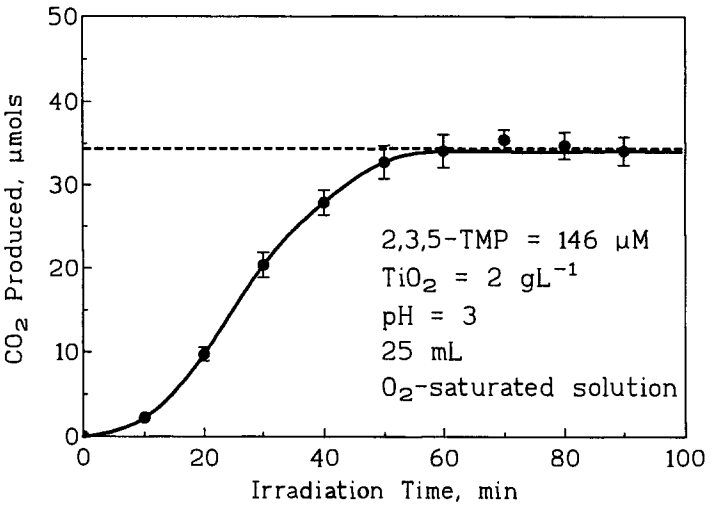


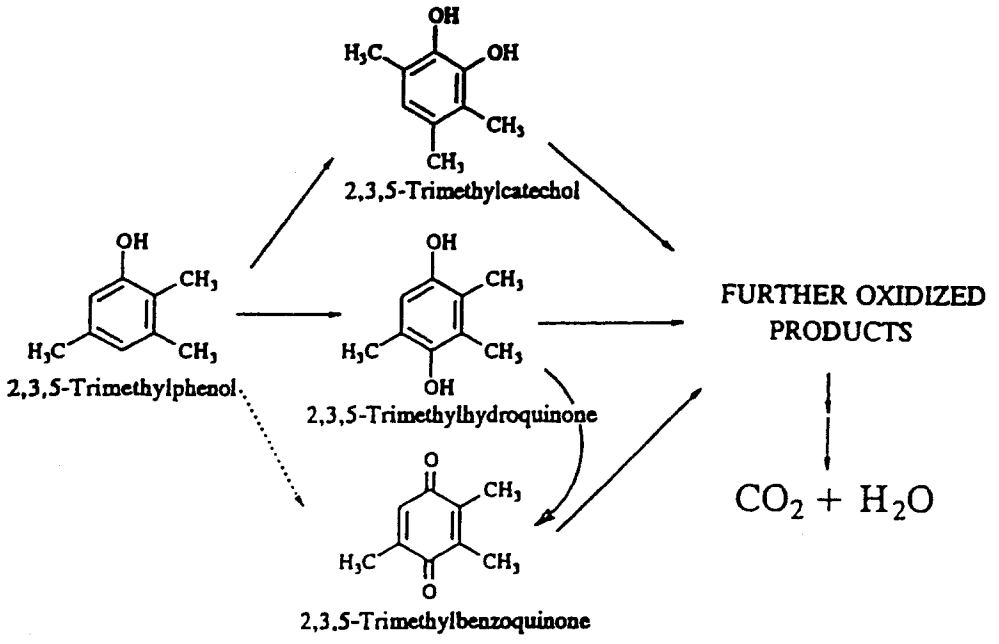
Fig. 3. Plot showing the temporal evolution of CO_2 from the photomineralization of 146 µM trimethylphenol in the presence of 2 g ℓ^{-1} TiO_2 at an initial pH of 3 in an oxygen-saturated suspension. The dotted line indicates the amount of CO_2 expected upon total mineralization.

mately 32.8 µmol of CO_2 were expected from reaction (1) for an initial concentration of TMP of 146 µM. After about 1 h of illumination, when all the TMP and the intermediates had decomposed, the expected stoichiometric amount of CO_2 was produced.

The photooxidation of TMP in illuminated TiO_2 dispersions takes place by reaction between a photogenerated active oxygen species, a surface-bound ·OH-radical [13], and TMP by formation of the ·OH-adducts [12] which on decay yield the aromatic intermediates TMHQ, TMBQ, and TMCC. Subsequent reaction of the latter with the oxidizing radical ultimately produced CO_2 and H_2O via a series of reactions that implicate ring cleavage and formation of aliphatic substrates (e.g., peroxides, aldehydes, and carboxylates [14]) of leaner carbon-to-oxygen ratios. The present results therefore suggest the first steps noted in scheme 1.

4. Conclusions

The decomposition of 2,3,5-trimethylphenol in air-equilibrated, illuminated TiO_2 suspensions takes place in less than 25 min at pH 3; in excess oxygen, the degradation is made faster (less than 12 min) and complete mineralization to CO_2 and H_2O takes place in about 1 h. Clearly, photocatalysis would be far superior to microbial degradation for such methylated phenols. In fact, 100 ppm of creosote can be mineralized to about 6 ppb (µg ℓ^{-1}) residues within 24 h by the photocatalytic method employed herein.



Scheme 1.

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