UV- TiO$_2$ PHOTOCATALYTIC DEGRADATION OF THE X-RAY CONTRAST AGENT DIATRIZOATE:
KINETICS AND MECHANISMS IN OXIC AND ANOXIC SOLUTIONS

BY

MATTHEW N. SUGIHARA

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Adviser:

Professor Timothy J. Strathmann
ABSTRACT

In recent years, triiodinated X-ray contrast agents (XRCs) have been widely detected in natural waters at concentrations that are often relatively high compared to other pharmaceutical micropollutants due to their extensive use and high biological recalcitrance. Diatrizoate is an ionic XRC that has been found to be especially resistant to conventional wastewater and drinking water treatment processes. This study examines the aqueous photocatalytic treatment of diatrizoate using nanophase titanium dioxide (TiO$_2$). Experiments demonstrate that diatrizoate is degraded in aqueous TiO$_2$ suspensions illuminated with ultraviolet-A (UVA) light under both oxic and anoxic conditions. Both oxidative and reductive transformation pathways for diatrizoate are initiated by photo-excited charge separation in the TiO$_2$ semiconductor, which generates a strongly oxidizing valence band hole (h$_{vb}^+$) and a strongly reducing conduction band electron (e$_{cb}^-$). In oxic solutions, diatrizoate degrades principally by oxidation with hydroxyl radicals (·OH) formed after h$_{vb}^+$ oxidizes adsorbed H$_2$O/OH·. Iodine substituents are readily liberated, but little mineralization of organic carbon and nitrogen occurs at short reaction times. Rates of photocatalytic oxidation decrease with increasing pH, attributed to unfavorable electrostatic interactions between anionic diatrizoate and the negatively charged TiO$_2$ surface at elevated pH conditions. High concentrations of bicarbonate (HCO$_3^-$), a common natural water constituent, inhibit diatrizoate oxidation by scavenging ·OH and forming less reactive carbonate radicals (CO$_3^{2-}$). In anoxic solutions, experiments demonstrate that in the absence of another exogenous electron acceptor (e.g., BrO$_3^-$), diatrizoate can also be reductively deiodinated by reaction with e$_{cb}^-$, and this pathway dominates if high concentrations of other ·OH-reactive chemicals (e.g., methanol) are present.
Photocatalytic reduction is a much more chemical-selective treatment process than oxidation with ·OH, so this pathway may be a promising strategy for selectively treating XRCs present in organic-rich wastewater streams.
ACKNOWLEDGMENTS

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CHAPTER 1
INTRODUCTION

Recent studies report widespread occurrence of a large number of pharmaceuticals and personal care products (PPCPs) in wastewater effluent-receiving water sources, raising serious concerns about impacted ecosystems and public health (Daughton and Ternes, 1999; Halling-Sørensen et al., 1998; Heberer, 2002; Hirsch et al., 1999; Kolpin et al., 2002). Although measured concentrations of these compounds are typically very low (ng L$^{-1}$ to μg L$^{-1}$), little is known about chronic exposure to sub-therapeutic levels of PPCPs over many years or potential for additive and synergistic toxicological effects when exposed to the myriad of micropollutants present in some water sources (Daughton and Ternes, 1999; Halling-Sørensen et al., 1998). Some PPCPs have been shown to be recalcitrant to conventional chemical and biological water treatment processes (Halling-Sørensen et al., 1998; Hirsch et al., 1999; Kolpin et al., 2002) so there is considerable interest in research aimed at developing more effective and sustainable technologies for treating water sources contaminated with PPCPs (Dodd and Huang, 2004; Hu et al., 2007; Hu et al., 2008; Huber et al., 2003; Paul et al., 2007).

Triiodinated x-ray contrast agents (XRCs; Table 1) are a class of medical diagnostic agents that have been found to be especially recalcitrant in wastewater and drinking water treatment facilities (Drewes et al., 2001; Seitz et al., 2006; Ternes and Hirsch, 2000). Large quantities of XRCs are administered to individual patients undergoing tests (>100 g dose$^{-1}$), which are generally excreted unmetabolized (Jekel and Reemtsma, 2006). Use of XRCs at medical facilities worldwide has been reported to be on the order of 3.5 x 10$^6$ kg yr$^{-1}$ (Pérez and Barceló, 2007). Although generally considered to be biochemically stable, some research has
shown that diatrizoate may have potential nephrotoxic effects in animals and humans (Gale et al., 1984; Humes et al., 1987).

**Table 1 - Structures of Iodinated X-Ray Contrast Agents and Structural Analogues Examined in this Study**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatrizoate (DIA)</td>
<td><img src="image" alt="Diatrizoate Structure" /></td>
</tr>
<tr>
<td>Iopromide (IOP)</td>
<td><img src="image" alt="Iopromide Structure" /></td>
</tr>
<tr>
<td>3,5-Diacetamidobenzoic Acid (DABA)</td>
<td><img src="image" alt="3,5-Diacetamidobenzoic Acid" /></td>
</tr>
</tbody>
</table>

Due to their remarkably high biochemical stability, XRC concentrations as high as 100 μg L\(^{-1}\) have been reported in natural water sources impacted by wastewater treatment plant effluent (Ternes and Hirsch, 2000). Only limited biodegradation of XRCs occurs over extended periods of time (e.g., >20 days), leading to formation of triiodinated benzoic acid metabolites that are resistant to further transformation. Among XRCs, the anionic diatrizoate has been found to be less amenable to activated sludge biodegradation than iopromide, a structurally related nonionic XRC (Haiß and Kümmerer, 2006; Kalsch, 1999). Advanced treatment processes like ozonation have shown some success in degrading XRCs, attributed to reactions with hydroxyl radicals (·OH), powerful non-selective oxidants that form during O\(_3\) decomposition (Huber et al., 2003; Ternes et al., 2003), and better XRC removal occurs during treatment with ozone-based advanced oxidation processes that promote ·OH formation (e.g., UV/O\(_3\), O\(_3\)/H\(_2\)O\(_2\)) than during O\(_3\) treatment processes where ·OH production is not specifically promoted (Ternes et al., 2003).
Photocatalytic treatment processes using semiconductors like titanium dioxide (TiO\textsubscript{2}) have emerged as a promising technology for treating waters contaminated with XRCs and other highly recalcitrant micropollutants (Hu et al., 2007; Paul et al., 2007; Hoffmann et al., 1995). TiO\textsubscript{2} materials are generally considered to be the most practical semiconductor photocatalysts for water treatment applications because they are generally considered non-toxic and are inexpensive, chemically stable, and have very low aqueous solubility (Hoffmann et al., 1995).

Ultraviolet (UV) light with energy exceeding the semiconductor bandgap energy of TiO\textsubscript{2} (\(E_{bg} = 3.2\) eV for anatase, corresponding \(\lambda < 385\) nm (Agrios et al., 2003)) excites electrons from the filled valence band to an empty conduction band, leading to charge separation and formation of strongly oxidizing valence band holes (\(h_{vb}^+\)) and strongly reducing conduction band electrons (\(e_{cb}^-\)). These species can migrate to the catalyst surface, where \(h_{vb}^+\) oxidizes adsorbed H\textsubscript{2}O/OH\textsuperscript{-} to form \(\cdot\)OH, which can then react with most organic chemicals at near diffusion-limited rates (Cermenati et al., 2000; Konstantinou and Albanis, 2003; Pandiyan et al., 2002). The photo-generated \(e_{cb}^-\) can conversely react with an adsorbed electron acceptor, typically O\textsubscript{2} in oxic waters (Hoffmann et al., 1995). Conduction band electrons in TiO\textsubscript{2} have a very low reduction potential (-0.84 V at pH = 7) (Glaze et al., 1993) and are also capable of reducing contaminants with oxidized structures, including nitroaromatic explosives and halogenated solvents (Glaze et al., 1993; Choi and Hoffmann, 1996; Low et al., 1991; Choi and Hoffmann, 1997).

Little work exists on the photocatalytic treatment of XRCs, particularly ionic XRCs like diatrizoate. Doll and Frimmel (2004; 2005a; b) reported on the susceptibility of nonionic XRCs (iomeprol and iopromide) to photocatalytic degradation, demonstrating significant rates of transformation and liberation of iodine substituents from the central ring structure, but only
limited mineralization occurs during short-term reactions. Although these studies report
degradation kinetics for XRCs during UV-TiO$_2$, experiments designed to identify the photo-
generated reacting species and the controlling reaction mechanisms and pathways were not
reported. In addition, past work was limited to photocatalytic transformation processes
occurring in oxic solutions, and potential for TiO$_2$ photocatalyzed reductive transformation
processes in anoxic solutions have not been reported. Such processes may be especially useful
for transforming the highly recalcitrant central triiodinated ring structure in XRCs to more
biodegradable products.

This contribution examines the kinetics and mechanisms for TiO$_2$ photocatalytic
transformation of diatrizoate and structurally related compounds (Table 1) in both oxic and
anoxic aqueous systems. Experimental work was conducted to (i) quantify rates of diatrizoate
photocatalytic degradation under varying solution conditions, (ii) assess the influence of key
structural features of diatrizoate on rates of photocatalytic treatment, (iii) identify the photo-
generated reactive species responsible for diatrizoate transformation, (iv) characterize organic
and inorganic transformation products, and (v) elucidate the major pathways responsible for
photocatalytic transformation of diatrizoate under both oxic and anoxic solutions. Results from
this study provide improved insights into the mechanisms and environmental factors
controlling photocatalytic transformation of XRCs, and support the further development of
practical photocatalytic treatment technologies for waters contaminated with XRCs and other
classes of recalcitrant organic micropollutants.
CHAPTER 2

EXPERIMENTAL

2.1 Materials and reagents

All reagents used were of high purity and were used as received from the suppliers. Diatrizoate (2,4,6-triiodo-3,5-diacetamidobenzoate, sodium salt) and its deiodinated analogue (3,5-diacetamidobenzoic acid; DABA), NaOH, NaClO₄, NaI, NaNO₃, NaNO₂, NH₄Cl, NaHCO₃, triethylamine, NaH₂PO₄, Na₂HPO₄, HClO₄, and ammonium acetate were purchased from Sigma-Aldrich-Fluka (St. Louis, MO). Iopromide was supplied as a gift from Schering AG (Berlin, Germany). Methanol, acetonitrile, and H₃PO₄ were obtained from Fisher Scientific (Fairlawn, NJ). Ultra-zero grade air and argon gases were obtained from S. J. Smith Welding Supply (Urbana, IL). Total organic carbon reference standards were obtained from VWR (West Chester, PA). All aqueous solutions were prepared using laboratory-grade deionized water (>17.3 MΩ cm; Barnstead Nanopure system).

Photocatalysis experiments were conducted using a nanophase TiO₂ (Type P25) supplied by Degussa (Düsseldorf, Germany). Degussa P25 has been extensively used as a model photocatalyst (Hu et al., 2007; Paul et al., 2007; Choi and Hoffmann, 1996; Low et al., 1991; Choi and Hoffmann, 1997; Doll and Frimmel, 2004; 2005a; b; Theurich et al., 1996) and is a mixed nanophase material containing approximately 70% anatase and 30% rutile with a specific surface area of 55 m² g⁻¹ (Hoffmann et al., 1995). Aqueous stock suspensions of TiO₂ were prepared >24 h prior to use to ensure hydration of the catalyst surfaces.
2.2 Light source

Reactors were illuminated using an Oriel O₃-free 450 W xenon arc lamp system (Oriel, Model 66921). Collimated light was first passed through a 10 cm water filter to remove infrared radiation followed by a reflecting mirror (to switch the light path from horizontal to vertical) and long-cutoff filters to select for ultraviolet-A + visible (referred to as UVA; \( \lambda \geq 324 \text{ nm} \)) or visible light only (Vis; \( \lambda \geq 400 \text{ nm} \)) irradiation of reaction solutions. Incident photon flux for UVA light (\( 324 \text{ nm} \leq \lambda \leq 400 \text{ nm} \)) and light from the lower end of the visible spectrum (\( 400 \text{ nm} \leq \lambda \leq 500 \text{ nm} \)) was measured by potassium ferrioxalate actinometry (Hatchard and Parker, 1956).

During the course of the study, an ignition board and reflecting mirror in the lamp system were replaced, causing a change in incident light intensity. Prior to lamp maintenance, incident photon fluxes were determined to be \( 9 \times 10^{-5} \text{ Einstein min}^{-1} \) for UVA and \( 1.6 \times 10^{-4} \text{ Einstein min}^{-1} \) for visible light. After maintenance, photon fluxes were determined to be \( 3.67 \times 10^{-5} \text{ Einstein min}^{-1} \) for UVA and \( 3.44 \times 10^{-5} \text{ Einstein min}^{-1} \) for visible light. Throughout the paper, all direct comparisons of rates shown within individual figures were conducted either before or after lamp maintenance, and a complete list of which experiments were conducted before and after lamp maintenance is provided in the Supporting Information section (Table SI-1). Experiments examining formation of diatrizoate transformation products were conducted using a similar lamp setup outfitted with an Oriel O₃-free 1000 W xenon arc lamp.

2.3 Photocatalysis experiments

Batch photocatalytic experiments were conducted in 50 mL aqueous TiO₂ suspensions that were continuously stirred in 250 mL jacketed glass beakers attached to a circulating
constant-temperature water bath maintained at 25°C. Prior to irradiation, suspensions containing the desired TiO$_2$ loading, target XRC concentration (typically 20 μM), and other solution constituents (e.g., methanol, NaHCO$_3$) were prepared and equilibrated in the dark for at least 30 min while being sparged with air (for oxic condition) or argon (for anoxic conditions). Gases were first passed through a 1 M NaOH trap to remove traces of CO$_2$ and two water traps to hydrate. Suspension pH was continuously controlled using an automatic pH stat device (Radiometer TIM854) equipped with HClO$_4$ or NaOH burettes. After collecting an initial aliquot of suspension for $t = 0$, reaction was initiated by placing the pre-equilibrated TiO$_2$ suspension under the lamp and continuing to mix and sparge with gas. Sample aliquots (1.5 mL) were then collected from the irradiated reactor at various time steps to monitor reaction progress. Collected aliquots were centrifuged for 30 min (13200 rpm; Eppendorf centrifuge 5415D) and supernatant was analyzed by high performance liquid chromatography (HPLC) to determine the concentration of target XRC remaining after differing reaction times.

For experiments examining formation of reaction products, a series of sacrificial 50 mL TiO$_2$ suspensions were prepared at pH 8 in the same manner described above and were irradiated for differing lengths of time before filtering (Millipore Millex-HN 0.45 μm) the entire reactor volume for analysis with a suite of analytical techniques. Higher initial concentrations of diatrizoate (200 μM) were used in product analysis experiments to permit easier analysis of minor reaction products.
2.4 Analytical

Concentration of diatrizoate and other target XRCs was determined by HPLC with UV photodiode array (PDA) detection (Shimadzu AVP System). For diatrizoate and DABA, a Spherisorb ODS-2 C18 column (4.6×150 mm, 5 μm packing material) and 10 mm guard column of the same material were used for the stationary phase. For diatrizoate, an isocratic mobile phase (1 mL min\(^{-1}\)) was used consisting of a 4:96 (v/v) ratio of acetonitrile and an aqueous eluent (20 mM phosphate, 10 mM triethylamine, adjusted to pH 6 with H\(_3\)PO\(_4\)). Absorbance intensity was monitored at λ = 237 nm. For DABA, a 2:98 ratio of the same eluents was used, and absorbance was monitored at λ = 231 nm. For iopromide, the stationary phase was a Novapak C18 column (3.9×150 mm, 4 μm packing material) and 10 mm guard column of the same material. A gradient method (1 mL min\(^{-1}\)) was used consisting of 5 mM ammonium acetate buffer and acetonitrile: 4% acetonitrile was maintained for the first three minutes, then increased linearly to 7.5% at 10 min and held constant for 5 min, before decreasing linearly back to 4% at 18 min and holding constant for two additional minutes. Absorbance intensity was monitored at λ = 241 nm. As reported in previous analysis (Knitt et al., 2007), doublet peaks are observed for iopromide due to stereoisomerism; quantification was accomplished by integration of both peaks.

Organic reaction intermediates and products for diatrizoate reactions were identified using liquid chromatography with tandem mass spectrometry (LC-MS/MS). Analysis was performed on an Agilent Technologies 1200 Series LC/MSD Trap XCT Ultra. An Agilent Zorbax SB-C18 column (2.1x30 mm, 3.5 μm packing material) was used as the stationary phase. An isocratic mobile phase (0.2 mL min\(^{-1}\)) was used with a 1:99 v/v ratio of two eluents (eluent A:...
95% acetonitrile, 5% H2O, and 0.1% formic acid; eluent B: 5 mM acetic acid). Mass spectral analysis was conducted in positive mode electrospray ionization (ESI+) over a mass range of 50-1300 m/z. The fragmentation amplitude used was 1.00 V conducted in auto MS(n) mode optimized for m/z = 614.

Changes in total dissolved organic carbon (DOC) concentrations during batch reactions were measured using a Shimadzu TOC-VPCH combustion analyzer. Inorganic anions (NO3−, NO2−, and I−) were quantified by ion chromatography (Dionex ICS-2000 system equipped with a conductivity detector). The stationary phase was an IonPac AS18 anion-exchange column (4x200 mm, 7.5 μm packing material), and the mobile phase (1 mL min⁻¹) was 36 mM KOH. Ammonium concentration was determined using a Hach salicylate colorimetric method (Hach method 10023) and a Shimadzu UV-2401PC UV-Vis spectrophotometer.
3.1 Reaction kinetics in oxic systems

Experimental results demonstrate that diatrizoate is photocatalytically degraded in airsaturated (i.e., oxic) aqueous TiO$_2$ suspensions irradiated with UVA light. Figure 1A shows the results of a representative batch experiment, showing degradation of diatrizoate in UVA-irradiated TiO$_2$ suspensions. More than 95% of diatrizoate is degraded within 1 h under the conditions shown. In comparison, no significant loss of diatrizoate occurs in TiO$_2$ suspensions maintained under darkness or irradiated with visible light only ($\lambda > 400$ nm), and only a small fraction (<10%) of the compound is degraded by UVA irradiation in the absence of TiO$_2$, consistent with previous reports of slow solar direct photolysis of iodinated XRCs (Doll and Frimmel, 2003). Degradation of diatrizoate during batch reactions can be described using a pseudo-first-order kinetic rate law:

$$C = C_0 e^{-k_{obs}t}$$  \hspace{1cm} (1)

where $C_0$ and $C$ represent the initial concentration of diatrizoate and its concentration remaining at time $t$, respectively, and $k_{obs}$ (min$^{-1}$) is the pseudo-first-order rate constant. Under the conditions shown in Fig. 1A, $k_{obs}$ was determined to be $2.12(\pm0.27) \times 10^{-2}$ min$^{-1}$. Results from the dark control reaction also demonstrate that diatrizoate adsorption to TiO$_2$ is minimal, with the extent of adsorption being lower than the uncertainty of the HPLC-PDA analysis method (i.e., <5% of added diatrizoate adsorbs).

Comparing the measured $k_{obs}$ values for diatrizoate with results for the antibiotic sulfamethoxazole measured in our laboratory using the same experimental setup and similar
conditions \( (k_{\text{obs}} = 2.0 \times 10^{-1} \text{ min}^{-1} \text{ for } C_0 = 21 \mu\text{M}, 100 \text{ mg L}^{-1} \text{ TiO}_2, \text{pH 9}) \) indicates that diatrizoate is significantly more recalcitrant than the antibiotic. This finding agrees with other studies on the treatment of diatrizoate and other XRCs with advanced oxidation processes in general (Huber et al., 2003; Seitz et al., 2006; Ternes et al., 2003).

Figure 1. (A) UVA-TiO\(_2\) photocatalytic degradation of diatrizoate in comparison to control experiments in oxic suspensions, and pseudo-first-order kinetic model fit; (B) comparison of pseudo-first-order rate constants for UVA-TiO\(_2\) photocatalytic degradation of diatrizoate and structural analogues listed in Table 1. Reaction conditions: \( C_0 = 20 \mu\text{M}, 1 \text{ g L}^{-1} \text{ TiO}_2, \text{pH 8}, \text{air-sparged, 25°C} \). Uncertainties represent triplicate-averaged standard deviations.
The high recalcitrance of iodinated XRCs relative to other organic micropollutants can be attributed to the stabilizing effect of the 2,4,6-triiodinated substituents on the central aromatic ring. This is supported by the much faster rate of photocatalytic oxidation observed for DABA, a structural analogue to diatrizoate that lacks the three iodine substituents (Figure 1B). The measured $k_{\text{obs}}$ value for DABA ($2.67 \times 10^{-1}$ min$^{-1}$) is more than an order-of-magnitude greater than that measured for diatrizoate under the same conditions.

The recalcitrance of diatrizoate can also be attributed partly to the ionic charge of the XRC. Results presented in Figure 1B also show that the rate constant for iopromide, a nonionic structural analogue of diatrizoate, is also more than an order-of-magnitude larger than that measured for the anionic diatrizoate under comparable conditions. This may be due, in part, to the expected weaker adsorption of diatrizoate than iopromide. Although quantitatively both compounds adsorb weakly to TiO$_2$ (e.g., <5% of added XRCs adsorb) and it is difficult to accurately measure the extent of adsorption, reactant adsorption is critical to surface-catalyzed processes, and it reasonable to expect that the anionic diatrizoate ($pK_a = 3.4$ (Lerner, 1975)) adsorbs to the negatively charged TiO$_2$ surface at pH 8 ($pH_{zpc} = 6.25$ (Hoffmann et al., 1995)) to a much lower extent than the nonionic iopromide.

The influence of diatrizoate adsorption on photocatalysis kinetics can also be used to explain the effect of solution pH. Figure 2 shows that observed rate constants are roughly constant at pH $\geq 6$, but triple when suspensions are acidified to pH 3. Although the extent of diatrizoate adsorption was small under all pH conditions examined and could not be quantified accurately using procedures employed in this study, the general pH trend is consistent with well
documented pH-dependent trends in the adsorption of benzoic acid and analogues to metal oxide surfaces (Chou and Huang, 1999; Kummert and Stumm, 1980).

3.2 Identification of photo-generated reactive species

To identify the important photo-generated reactive species for diatrizoate transformation in the presence of TiO$_2$, reaction rates were measured in batch reactors where solutions were modified by introducing known radical scavengers and electron acceptors (Figure 3). First, addition of a large excess concentration of methanol (1 M), a hydroxyl radical scavenger (Galindo et al., 2000), to an air-sparged reactor markedly inhibits the photocatalytic degradation of diatrizoate. Such marked inhibition of the reaction indicates that under oxic conditions, diatrizoate degradation occurs principally through oxidation by adsorbed ⋅OH. This finding is consistent with the dominant oxidative photocatalytic pathway identified for a diverse range of organic contaminants (Hu et al., 2007; Paul et al., 2007; Konstantinou and Albanis, 2003; Low et al., 1991; Theurich et al., 1996). The predominance of XRC reactions with ⋅OH is also supported by the relative reactivity trends already noted for diatrizoate, DABA, and iopromide. Jeong and co-workers (2010) reported that diatrizoate was significantly less reactive with ⋅OH generated in homogeneous solution (by pulse radiolysis) than DABA and iopromide. However, the relative difference in homogeneous second-order rate constants between diatrizoate and the two structural analogues (diatrizoate: 3.34 x 10$^9$ M$^{-1}$ s$^{-1}$; DABA: 6.0 x 10$^9$; iopromide: 3.34 x 10$^9$) is still smaller than the difference in apparent photocatalytic rate constants, likely due to additional variations in adsorptive interactions with the TiO$_2$ surface.
Figure 2. Effect of (A) pH and (B) dissolved carbonate on the rate of UVA-TiO$_2$ photocatalytic degradation of diatrizoate. Reaction conditions: $C_0 = 20$ μM, 25°C, air-sparged, pH 3-11 and 250 mg L$^{-1}$ TiO$_2$ (panel A), pH 8 and 1 g L$^{-1}$ TiO$_2$ (panel B). Uncertainties represent triplicate-averaged standard deviations.
The availability of photo-generated $\cdot$OH for oxidation of organic contaminants also requires an appropriate electron acceptor to react with $e_{cb}^-$ and prevent its buildup and increased rate of recombination with $h_{vb}^+$ (Hoffmann et al., 1995). Under oxic conditions, dissolved $O_2$ can adsorb to the TiO$_2$ surface and react with $e_{cb}^-$ (Hoffmann et al., 1995). Thus, it was expected that removal of dissolved $O_2$ would inhibit the photocatalytic degradation of diatrizoate, but the measured $k_{obs}$ value only decreased slightly when the TiO$_2$ suspension was made anoxic by sparging with an inert gas (argon) in place of air ($k_{obs}$ drops from $2.12 \times 10^{-2}$ to $1.64 \times 10^{-2}$ min$^{-1}$). In comparison, photocatalytic degradation of the antibiotics sulfamethoxazole and ciprofloxacin were found to be completely inhibited by removal of dissolved oxygen (Hu et al., 2007; Paul et al., 2007). In addition, when excess methanol was added to the Ar-sparged TiO$_2$ suspension, the photocatalytic degradation rate remained relatively unchanged despite the fact that methanol addition almost completely inhibits the reaction under oxic conditions. A plausible explanation for these observations is that diatrizoate, itself, can act as an electron acceptor and react with $e_{cb}^-$. So, while removal of dissolved $O_2$ and addition of excess methanol act to inhibit the $\cdot$OH-mediated oxidative degradation pathway of diatrizoate in UVA-irradiated TiO$_2$ suspensions, the same actions may be promoting reductive transformation of diatrizoate. That is, removal of dissolved $O_2$ enables diatrizoate reaction with $e_{cb}^-$ by eliminating competition from a more favorable electron acceptor, and diatrizoate can react with both $\cdot$OH and $e_{cb}^-$. Addition of excess methanol to the anoxic suspension can be expected to inhibit the former, but possibly enhance the latter by inhibiting charge recombination processes in general and effectively increasing the concentration of $e_{cb}^-$ available to react with electron acceptors (Hoffmann et al., 1995).
Although, to our knowledge, there are no previous reports of photocatalytic reduction of diatrizoate or related XRCs, the pathway is confirmed by product identification studies that will be discussed in later sections. In addition, previous literature reports support the favorability of photocatalytic reduction processes for XRCs. First, the UV-TiO$_2$ photocatalytic reductive dehalogenation of chlorinated organic compounds has been documented (Glaze et al., 1993; Lifongo et al., 2004), and, generally, reductive deiodination and debromination processes are more rapid than dechlorination processes. In addition, recent studies report reductive deiodination of XRCs by Pd-based catalysts and zerovalent iron (Knitt et al., 2007; Putschew et al., 2007). Jeong and co-workers (2010) also showed that strongly reducing hydrated electrons (e$^-_{aq}$) were much more reactive with triiodinated XRCs than with lesser iodinated and deiodinated structural analogues. Photocatalytic reductive deiodination is also confirmed by product identification experiments, discussed below.

![Figure 3. Effects of adding a hydroxyl radical scavenger (methanol) and removing dissolved O$_2$ on rate constants for UVA-TiO$_2$ photocatalytic degradation of diatrizoate. Reaction conditions: C$_0$ = 20 μM, 1 g L$^{-1}$ TiO$_2$, pH 8, 25°C, 1 M methanol, air-sparging (oxic conditions) or argon-sparging (anoxic conditions). Uncertainties represent triplicate-averaged standard deviations.](image-url)
3.3 Effects of dissolved carbonate

Increasing concentrations of bicarbonate, a common ionic constituent of natural waters, inhibit the photocatalytic degradation of diatrizoate (Figure 2B). Addition of 10 mM and 100 mM sodium bicarbonate lowers the observed rate constants by 45% and 80%, respectively, relative to control reactions conducted in an inert electrolyte (NaClO$_4$) of equivalent ionic strength. These results are consistent with previous reports that dissolved carbonate species act as hydroxyl radical scavengers in natural waters (Dhananjay et al., 2002):

\[
\begin{align*}
\text{HCO}_3^- + \cdot \text{OH} & \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \\
\text{CO}_3^{2-} + \cdot \text{OH} & \rightarrow \text{CO}_3^{2-} + \text{OH}^-
\end{align*}
\]

(2) (3)

The resulting carbonate radical is a weaker oxidizing agent that is expected to react minimally with most organic contaminants (Dhananjay et al., 2002; Haarstrick et al., 1996). However, photocatalytic degradation of diatrizoate is not completely inhibited by bicarbonate, so further studies are needed to determine the potential importance of carbonate radicals to photocatalytic and photochemical degradation processes for XRCs.

3.4 Oxidative photocatalysis reaction products and pathways

A detailed analysis of reaction products was performed for oxidative UVA-TiO$_2$ photocatalysis of diatrizoate (Figure 4) since this is the process that is likely to predominate when treating aerated source waters (e.g., surface drinking water sources). Figure 4A shows that little change in DOC occurs during photocatalytic oxidation of diatrizoate. Whereas 67% of the 200 µM initial diatrizoate concentration was degraded during the time monitored, DOC decreased by only 10%. Thus, initial reactions with \cdot \text{OH} are not leading to significant
Figure 4. Summary of products formed by UVA-TiO₂ photocatalytic degradation of diatrizoate under oxic conditions. (A) comparison of diatrizoate degradation with changes in DOC, (B) formation of inorganic ions in comparison to diatrizoate degradation, and (C) changes in LC-MS peak areas for diatrizoate and organic reaction products identified by LC-MS. Reaction Conditions: $C_0 = 200 \mu$M diatrizoate, 1 g L\(^{-1}\) TiO₂, pH 8, 25°C, air sparged.
mineralization, but instead to formation of other organic products. In addition, only minimal production of inorganic nitrogen species ($\text{NH}_4^+$, $\text{NO}_3^-$, and $\text{NO}_2^-$) was observed (Figure 4B), which implies much of the nitrogen remains bound to organic products. In contrast, measurements indicate that the 3 iodine substituents bonded to the central aromatic ring are liberated almost stoichiometrically as $\text{I}^-$ without significant lag upon diatrizoate oxidation. This is illustrated by comparing the measured production of $\text{I}^-$ with the calculated concentration of iodine associated with the concentration diatrizoate that was oxidized at each timepoint ($3x\Delta[\text{diatrizoate}]$).

Together, the observed trends in DOC and inorganic products suggest that diatrizoate was being transformed predominantly to organic products wherein the nitrogen atoms are retained, but the iodine substituents are removed. LC-MS/MS analysis was conducted to identify organic intermediates and products resulting from photocatalytic oxidation of diatrizoate, but these analyses only revealed four organic products whose proposed structures are listed in Table 2 (Products I – IV). All four products retain both of the nitrogen atoms from the parent compound, and very few carbon atoms are removed, consistent with the inorganic nitrogen and DOC measurements. However, the structures are inconsistent with the expected major reaction products because two of the four products retain all three iodine substituents in their structures and the other two retain two iodine substituents. Presumably, these compounds represent only minor products, a conclusion that is semi-quantitatively supported by plots of LC-MS/MS total ion chromatogram (TIC) peak areas for the products during the reaction (Figure 4C). Although differences in ionization do not allow for direct quantification (reference standards are not available), the observed peak areas for the four products are small.
<table>
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<th>ESI(+) MS m/z</th>
<th>ESI(+) MS² m/z</th>
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<td>VI</td>
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<td>237</td>
<td>219</td>
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1 M MeOH added to Ar-sparged suspensions to scavenge •OH
in comparison with the decrease in the peak area of diatrizoate during the reaction. Thus, if differences in ionization are not very large, it can be concluded that the products observed represent only a minor fraction of the products actually formed by photocatalytic oxidation of diatrizoate. It also follows that that the major reaction products are not amenable to HPLC-ESI(+)−MS/MS analysis. Additional techniques will be needed to identify these products. Nonetheless, because iodine liberation is near stoichiometric during the process, the major organic intermediates most likely are dehalogenated and are probably more biodegradable than diatrizoate in downstream treatment processes and in receiving waters (Jeong et al., 2010).

Jeong and co-workers (2010) recently reported on the oxidation of diatrizoate and related structural analogues by ·OH (generated by γ-irradiation) in homogeneous solution. A series of reaction products detected by LC-ESI(−)−MS/MS suggest that ipso attack of ·OH at iodo sites on the aromatic ring lead to hydroxide substitution and iodide release as shown in Scheme 1. The predominance of ipso attack at the three iodine substituents would account for the observed release of I− while maintaining DOC and retaining organically bonded nitrogen, but additional analysis is needed to confirm this pathway. Jeong and co-workers (2010) observed significantly less iodide release during homogeneous reactions of diatrizoate with ·OH, but the reaction environment at the TiO2 surface can alter the distribution of reaction products.

Scheme 1. Proposed mechanism of hydroxyl radical attack on iodo substituent (adapted from Jeong et al., 2010).
Scheme 2 illustrates proposed pathways leading to the organic products that were identified by LC-MS/MS analysis. Hydrogen abstraction from the terminal methyl group by ·OH (Hayon et al., 1970) forms a carbon-centered radical that in turn can attack the aromatic ring at the iodo position and form a cyclic product (II) and release I⁻. A second product (III) can form by ·OH attacks on the amide side chains, leading to the cleavage of the amide and formation of a primary aromatic amine (Pathirana and Maithreepala, 1997). Oxidative decarboxylation to form product IV results from ·OH attack at the carboxyl ring position on the aromatic ring (Winston and Cederbaum, 1982). Further ipso attack on one of the iodine positions and oxidation of amide side chain can then lead to product I.

Scheme 2. Proposed oxidative pathways for diatrizoate that lead to formation of minor products detected by LC-MS/MS.
3.5 Reductive photocatalysis reaction products and pathways

Kinetics experiments presented in Figure 3 suggested that diatrizoate may be reduced by photo-generated $e_{cb}^-$, so LC-MS/MS analysis was also conducted to identify organic transformation products formed when diatrizoate is photocatalytically degraded under anoxic conditions (argon-sparged, 1 M MeOH added to scavenge $\cdot$OH). This analysis confirms the formation of 3 products which differ from the parent compound only in the number of iodine substituents (Table 2, Products V-VII). Thus, as shown in Scheme 3, diatrizoate undergoes sequential reductive deiodination through reaction with photo-generated $e_{cb}^-$, similar to reactions observed with other strong reducing agents (e.g., Pd-H$_{ads}$, Fe(0)) (Knitt et al., 2007; Putschew et al., 2007).

![Scheme 3. Proposed photocatalytic reductive deiodination pathway for diatrizoate under anoxic conditions.](image-url)
CHAPTER 4

CONCLUSIONS AND ENVIRONMENTAL IMPLICATIONS

Results from this study demonstrate that UV-TiO$_2$ photocatalysis is an effective technology for degrading diatrizoate in both oxic and anoxic aqueous solutions. Experiments demonstrate that diatrizoate degradation under oxic conditions relies on reactions with hydroxyl radicals generated in accordance with the semiconductor charge separation mechanism. A variety of organic and inorganic products are detected, consistent with the non-selective reactivity of $\cdot$OH at different sites within the diatrizoate structure. At short reaction times, photocatalytic oxidation yields minimal mineralization of organic C and N in the parent molecule, but stoichiometric iodide is released. Under anoxic conditions, diatrizoate is also reductively deiodinated by reaction with e$_{cb}$, also generated by bandgap excitation. Release of iodide by both oxidative and reductive pathways is significant, because the resulting deiodinated products are expected to be much more biodegradable in downstream processes and in receiving waters. Discovery of the reductive transformation pathway for diatrizoate is also potentially useful for developing more selective treatment technologies for XRCs. Whereas the oxidative pathway, which relies on the non-selective $\cdot$OH to transform diatrizoate, is likely to be inhibited by scavenging of the radicals by a myriad of natural organic constituents that are present in natural waters and waste streams at concentrations that are orders-of-magnitude higher than the XRCs and other micropollutants (i.e., mg/L NOM vs. ng/L micropollutants), the reductive pathway relies on diatrizoate reaction with e$_{cb}$, is a much more chemically selective reactive species that should be less prone to competitive inhibition by natural organic constituents. Treatment strategies based on the reductive pathway may be particularly useful
for treating XRCs in waste streams that readily become anoxic in the absence of active aeration.

Further research is suggested to examine practical photocatalytic reduction processes for XRCs in relevant aquatic matrices.
CHAPTER 5

REFERENCES


### APPENDIX A

### SUMMARY OF BATCH EXPERIMENTS

Table SI1: Results of batch reactions for degradation of XRCs and analogue by UVA-TiO$_2$ photocatalysis

<table>
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<th>XRC</th>
<th>TiO$_2$ (mg L$^{-1}$)</th>
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<th>MeOH (M)</th>
<th>BrO$_3^-$ (mM)</th>
<th>HCO$_3^-$ (mM)</th>
<th>NaClO$_4$ (mM)</th>
<th>Sparging Gas</th>
<th>Lighting Conditions</th>
<th>Lamp</th>
<th>$k_{obs}$ (min$^{-1}$)</th>
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<td>Lamp 2</td>
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$a$ All experiments performed at 25°C  
$b$ Lamp 1 indicates lamp prior to repair. Lamp 2 indicates lamp after ignitition board and mirror replacement. UVA flux is as follows: Lamp 1 - 9 x 10$^{-5}$ Einstein min$^{-1}$; Lamp 2 - 3.67 x 10$^{-5}$ Einstein min$^{-1}$  
$c$ Uncertainty represents the triplicate-averaged standard deviation
APPENDIX B

LC-MS/MS DATA FOR DIATRIZOATE AND TRANSFORMATION PRODUCTS

Table S2: LC-MS/MS data for DIA and intermediates

DIA

P-I, m/z = 449

P-II, m/z = 485.8