Comparative analysis of the photocatalytic reduction of drinking water oxoanions using titanium dioxide

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Journal: *Water Research*

Revision Date: July 19, 2016

Keywords: Oxoanion; photocatalysis; titanium dioxide; nitrate; bromate; chlorate

Abstract

Regulated oxidized pollutants in drinking water can have significant health effects, resulting in the need for ancillary treatment processes. Oxoanions (*e.g.*, nitrate) are one important class of oxidized inorganic ions. Ion exchange and reverse osmosis are often used treatment processes for oxoanions, but these separation processes leave behind a concentrated waste product that still requires treatment or disposal. Photocatalysis has emerged as a sustainable treatment technology capable of catalytically reducing oxoanions directly to innocuous byproducts. Compared with the large volume of knowledge available for photocatalytic oxidation, very little knowledge exists regarding photocatalytic reduction of oxoanion pollutants. This study investigates the reduction of various oxoanions of concern in drinking water (nitrate, nitrite, bromate, perchlorate, chlorate, chlorite, chromate) using a commercial titanium dioxide photocatalyst and a polychromatic light source. Results showed that oxoanions were readily reduced under acidic conditions in the presence of formate, which served as a hole scavenger, with the first-order rate decreasing as follows: bromate > nitrite > chlorate > nitrate > dichromate > perchlorate, corresponding to rate constants of 0.33, 0.080, 0.052, 0.0074, 0.0041, and 0 cm²/photons x 10¹⁸, respectively. Only bromate and nitrite were reduced at neutral pH, with substantially lower rate constants of 0.034 and 0.0021 cm²/photons x 10¹⁸, respectively. No direct relationship between oxoanion physicochemical properties, including electronegativity of central atom, internal bond strength, and polarizability was discovered. However, observations presented herein suggest the presence of kinetic barriers unique to each oxoanion and provides a framework for investigating photocatalytic reduction mechanisms of oxoanions in order to design better photocatalysts and optimize treatment.

Introduction

Oxoanions are present in water sources and treated drinking water and examples include nitrate, nitrite, bromate, chromate, perchlorate, chlorate, chlorite, iodate, selenate, tungstate, and molybdate. Oxo- (or oxy-) anions have a central atom (*e.g.*, N) bonded to oxygen atoms (*e.g.*, NO_3^-). Currently, the United States Environmental Protection Agency (USEPA) regulates nitrate, nitrite, dichromate, perchlorate, bromate, and chlorite under the Safe Drinking Water Act. Removing these oxoanions using traditional drinking water treatment processes (*e.g.*, coagulation, filtration) is ineffective because of their high stability in water. Consequently, oxoanions are problematic pollutants requiring the use of other treatment technologies or strategies.

The most commonly used treatment technologies are physical separation processes such as ion exchange (IX) and reverse osmosis (RO), or changes in oxidant addition processes (*e.g.*, chlorine dioxide for chlorate/chlorite, ozone for bromate). While effective at removing oxoanions from the drinking water source, IX and RO treatment produces concentrated waste brines that require additional costs for treatment or disposal. For some oxoanions such as nitrate, this also unbalances its natural cycle (*i.e.*, returning NO_3^- to N_2). Technologies that sustainably treat oxoanions directly to innocuous byproducts are ideal. Catalytic technologies (*i.e.*, heterogeneous, photo-, electro-) have received attention for their ability to efficiently treat oxoanions to innocuous and stable byproducts (Mori et al. 1999, 2000, Kominami et al. 2005a, Zhang et al. 2007, Lozovskii et al. 2009, Li et al. 2010, Mishra et al. 2011, Hirayama et al. 2014, Pan et al. 2012, Gekko et al. 2012, Cappelletti et al. 2008, Liu et al. 2012, Tanaka et al. 2013, Gherbi et al. 2011, Qu et al. 2013, Noguchi et al. 2002, Zhao et al. 2011, Ye et al. 2013). Photocatalysis in particular is appealing because it could be operated using solar light.

A photocatalyst converts light energy (*i.e.*, photons) to electrons in order to facilitate oxidation and reduction reactions. The use of metal oxides as photocatalysts for treating organic

compounds has been known for nearly a century,(Keidel 1929) and much progress has been made to advance photocatalysis for environmental applications, with a substantial effort dedicated to reduced compounds and microorganisms (*e.g.*, synthetic organic compounds, bacteria).(Di Paola et al. 2012, Hoffmann et al. 1995) Photocatalytic transformation of oxidized species has been studied extensively for energy related applications, such as the reduction of water to H₂ (Kudo and Miseki 2009) and carbon dioxide to hydrocarbons (Roy et al. 2010), Study of oxidized contaminants including halogenated disinfection byproducts (Gerrity et al. 2009) and oxoanions has been less comprehensive, and understanding of the relevant principles remains incomplete.

Investigation of these photocatalytic reduction processes, largely using TiO₂, for oxoanions has been reported for nitrate (Li and Wasgestian 1998, Gao et al. 2004, Soares et al. 2014, Rao and Murty 1936, Ranjit and Viswanathan 1997, Kominami et al. 2005b, Sa et al. 2009a, Wehbe et al. 2009, Sa et al. 2009b, Anderson 2011, Doudrick et al. 2012a, Yang et al. 2013a, Doudrick et al. 2013a) nitrite,(Gekko et al. 2012, Liu et al. 2009, Ranjit and Viswanathan 2003, Kominami et al. 2010) bromate,(Noguchi et al. 2002, Mills et al. 1996, Noguchi et al. 2003, Zhang et al. 2010), chromate,(Cappelletti et al. 2008, Tanaka et al. 2013, Gherbi et al. 2011, Testa et al. 2004, Wang et al. 2008, Zhang et al. 2013, Kuncewicz et al. 2012, Cheng et al. 2015, Meichtry et al. 2014, Chenthamarakshan and Rajeshwar 2000, Liu and Sun 2004, Sun et al. 2005, Hsu et al. 2007, Xu et al. 2008, Mu et al. 2010, Wang et al. 2010, Sridharan et al. 2013) and perchlorate(Ye et al. 2013). Studies of removal of oxoanions from real water sources indicate that photocatalytic reduction occurs, although at a reduced rate in comparison to deionized water studies (Doudrick et al. 2012a, Luiz et al. 2015, Huang et al. 2014). These studies demonstrate that photocatalysis is an appropriate technology for removal of aqueous oxoanions from drinking water. However, modification of experimental conditions (*e.g.*, pH and hole scavenger addition) away from natural

water conditions remains a necessary process in order to achieve satisfactory removal rates and by-product selectivity. These studies tend to focus on the role of the chemical and physical structure of the photocatalyst in driving the reduction process and influencing formation of different byproducts (*i.e.*, byproduct selectivity), with less emphasis on the role of the oxoanion itself in the process. Consequently, the reduction schemes of the various oxoanions are poorly understood.

The goal of this study was to compare photocatalytic oxoanion (*e.g.*, nitrate, nitrite, bromate, perchlorate, chlorate, chlorite, dichromate) reduction rates in the presence of a polychromatic light source and relate these rates to oxoanion physicochemical properties. This is the first comparative analysis on the photocatalytic reduction of similar oxoanions using identical conditions. Results were used to 1) investigate trends in oxoanion reduction rate with respect to physicochemical properties, 2) determine the impact of reaction conditions (*e.g.*, pH and hole scavenger) on oxoanion reduction, and 3) probe mechanistic steps of the reduction process for individual oxoanions. The findings are useful for the rational design of advanced photocatalysts for selective treatment of oxidized pollutants.

1. Experimental Methods

2.1 Chemicals and Materials

All chemicals were used as received. Sodium or potassium salts were used as sources for the oxoanions (Sigma Aldrich: NaNO₃ (S5506, >99%), NaNO₂ (237213, 97+%), NaBrO₃ (02151, >99%), NaClO₄ (410241, >98%), NaClO₃⁻ (403016, >99%), NaClO₂ (71388, 80%), NaBr (3588-01, 99%), NaCl (S9625, >99%), NaHCOO (S648, >99%), and K₂Cr₂O₇ (207802, >99%). Evonik (formally Degussa) P90 TiO₂ (>99.5%) was used as a photocatalyst. Characterization for this

material can be found elsewhere.(Doudrick et al. 2012a) Briefly, P90 contains both anatase (88%, 12 nm) and rutile (12%, 18 nm) crystal structures, has a surface area of approximately 104 m²/g, and has an average isoelectric point (IEP) of 6.4 in water. Ultrapure deionized water was used for all experiments and prepared using a Nanopure® (18.3 MΩ-cm) treatment system.

2.2 Analytical Measurement

Bromate (BrO₃⁻), perchlorate (ClO₄⁻), chlorate (ClO₃⁻), chlorite (ClO₂⁻), bromide (Br⁻), chloride (Cl⁻), and formic acid (HCOO⁻) concentrations were measured using ion chromatography (IC) (Dionex DX-120 with AS12A column; Dionex DX-500 with an AS16 column for perchlorate). Hexavalent chromium concentrations were measured by ultraviolet-visible light (UV-Vis) spectroscopy using colorimetric measurement 8023 (Hach DR5000, Loveland, CO). Total chromium in solution was measured using inductively coupled plasma atomic emission spectroscopy (ICP-OES). For IC measurement using the AS12A column, the formic acid retention time overlaps with ClO₂⁻ retention times, resulting in inaccuracy for ClO₂⁻ measurements when high concentrations of formic acid were used as a hole scavenger. As such, formic acid was not used as a hole scavenger for this compound, and only the photocatalytic mechanisms using water as a hole scavenger were investigated. TDN and DOC were measured using a total organic carbon/total nitrogen (TOC/TDN) analyzer (Shimadzu TOC-V/ASI-V/TNM-1). UV-Vis absorption spectra for the oxoanions were obtained from 190-600 nm at a 1 nm resolution (Hach DR5000, Loveland, CO).

2.3 Photocatalytic Experiments

Photocatalytic experiments were performed using a 200-mL annular photoreactor with a UV lamp located in the center, following methods used previously (Doudrick et al. 2012a, Yang et al. 2013a, Doudrick et al. 2013a, Cheng et al. 2015). A borosilicate sleeve was placed around the lamp to filter out light wavelengths less than 280 nm to minimize direct photolysis of oxoanions or formate. The UV light source was a 450-W (Ace Glass power supply, 7830-60) medium-pressure mercury-vapor lamp (Ace Glass, 7825-34; Hanovia PC451.050) that was placed in a double-walled quartz immersion well (Ace Glass, 7854-25). The system temperature was maintained at 25°C using a chiller. To overcome possible kinetic control of the water oxidation reaction and focus on the reduction reaction, experiments were conducted for select oxoanions with the addition of an organic hole scavenger. A hole scavenger serves as an electron donor by interacting with the photogenerated hole on the excited catalyst. Formate ion was selected as the hole scavenger as it has been shown to serve as an effective hole scavenger for the reduction of nitrate (Sa et al. 2009b, Doudrick et al. 2012a, Luiz et al. 2012, Yang et al. 2013b, Doudrick et al. 2013b), and dichromate (Sun et al. 2005). For each run, the photocatalyst was suspended using magnetic stirring in a solution of ultrapure water containing oxoanion and formate. The oxoanion concentration was 7 mM (bromate 7.8 mM) and the formate concentration was determined on the basis of stoichiometry as presented in Equations 1-8 (formate to oxoanion molar ratios were 0.76 to 2.91). Prior to irradiation, the sample was stirred in the dark for 1 hr to account for non-photocatalytic removal (*i.e.*, adsorption). During kinetic photocatalysis experiments, samples were collected at periodic intervals, filtered using a 0.45- μ m nylon membrane to remove the photocatalyst, and stored in amber glass vials in the dark at ~4°C until analysis within 48 hours.

2.4 Lamp Irradiance Measurements

The lamp irradiance at the point of photocatalytic reaction was measured using a UV-Vis fiber optic spectrometer (Avantes AvaSpec-2048) adapted with a cosine corrector. Irradiance was measured in solution at a distance halfway between the lamp and reactor wall (1 cm) and at multiple points from the bottom to the top of the reactor to obtain the average irradiance. For this study, the total lamp irradiance in ultrapure water from 280 to 1050 nm was 29.2 mW/cm². With a bandgap of ~3.2 eV for TiO₂ (Doudrick et al. 2012b), the total irradiance absorbable by P90 (280–388 nm) was 6.5 mW/cm², or approximately 22% of the total lamp irradiance (Figure SI-1). Only the wavelengths absorbed by P90 were used for reporting irradiance doses in all the experiments. To make the results comparable with other materials and similar studies, results are reported as a function of irradiation rather than time. Irradiation for the polychromatic light source is reported not as an energy fluence (*e.g.*, J/cm²) but as a photon fluence (TiO₂ absorbable) to account for differences in photon energies.

3. Results and Discussion

3.1 Oxoanion removal with an organic hole scavenger at acidic pH

The removal of the oxoanions using TiO₂, formate (*i.e.*, hole scavenger) and a polychromatic UV light source (> 280 nm) under acidic (pH~2.5) conditions is shown in Figure 1. Byproducts for bromate, chlorate, nitrate/nitrite, and dichromate were bromide, chloride, nitrogen gases/ammonium (70%/30%), and trivalent chromium, respectively. Analysis of oxoanion removal rates indicated first-order kinetic behavior. The removal rates decreased in the following order: bromate > nitrite > chlorate > nitrate > dichromate, with no removal observed for perchlorate, corresponding to first-order rate constants of 0.33, 0.080, 0.052, 0.0074, 0.0041, and 0 cm²/photons x 10¹⁸, respectively (Table 1). The units for the first-order rate constants are

179 $\text{cm}^2/\text{photons} \times 10^{18}$, which is equal to inverse photon fluence and equivalent to inverse time with
180 regards to standard rate constant units (*e.g.*, s^{-1}). Rates constants are reported in this unit to allow
181 for meaningful comparison of rates among studies using various lamps and photocatalysts.

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The oxoanion multi-electron reduction half reactions under acidic conditions (pH = 0) and their respective reduction potentials are given in Equations 1-8. The reduction potentials of the tested oxoanions are shown in Figure 2 with respect to the conduction band of TiO₂. As the reduction potentials of all tested oxoanions are more positive than the conduction band of TiO₂, photocatalytic reduction of each of these oxoanions is thermodynamically feasible. With regards to thermodynamics, the reduction of nitrate to nitrite is the least favored, while reduction of chlorite to chloride is the most favored (*e.g.*, Figure 2). It may be expected that rate of reduction of the oxoanions, which share similar structure and chemical properties, could be related to the reduction potential of the oxoanions. A similar relationship has previously been reported for the photocatalytic reduction of chloroplatinate compounds.(Mahlamvana and Kriek 2014).

- (1) $2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$ ($E^\circ = 1.25 \text{ V}$)
- (2) $\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{Cl}^- + 4\text{H}_2\text{O}$ ($E^\circ = 1.29 \text{ V}$)
- (3) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ ($E^\circ = 1.38 \text{ V}$)
- (4) $\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$ ($E^\circ = 1.44 \text{ V}$)
- (5) $2\text{NO}_2^- + 4\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{N}_2 + 8\text{OH}^-$ ($E^\circ = 1.11 \text{ V}$ at pH = 7; $\text{pK}_a \sim 3.4$, $\sim 100\% \text{ NO}_2^-$)
- (6) $2\text{HNO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O}$ ($E^\circ = 1.52 \text{ V}$ at pH = 0; $\text{pK}_a \sim 3.4$, $\sim 100\% \text{ HNO}_2$)
- (7) $\text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O}$ ($E^\circ = 1.46 \text{ V}$)
- (8) $\text{ClO}_2^- + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$ ($E^\circ = 1.61 \text{ V}$)

In this case, it was found that the oxoanion reduction rate trend at acidic pH does not directly correlate to the variation in reduction potentials for multi-electron reactions. The theoretical trend in reduction rate extrapolated from standard reduction potentials at acidic pH decreases as follows: nitrous acid > chlorate > bromate > dichromate > nitrate. The experimental trend was found to be: bromate > nitrous acid > chlorate > nitrate > dichromate. There appears to be a loose relationship, as oxoanions with relatively high reduction potentials, including bromate ($k=0.330 \text{ cm}^2/\text{photons} \times 10^{18}$) and nitrous acid ($k=0.0802 \text{ cm}^2/\text{photons} \times 10^{18}$) were reduced more

rapidly, while oxoanions with relatively low reduction potentials, including nitrate ($k=0.0074$ cm²/photons x 10¹⁸) and perchlorate (no removal) were reduced at a slower rate, if at all.

While the trend in reduction rate loosely correlates with the reduction potential of the various oxoanions, the inexact correlation provides little evidence that the reduction rates are governed by the thermodynamic potential. Further, the absence of perchlorate removal indicates that simple thermodynamic control is not the functional limitation on photocatalytic oxoanion reduction as this reduction is thermodynamically allowed, yet does not occur.

No correlation between physicochemical properties and reduction rate was observed for the tested oxoanions. Chaplin et. al showed that reduction rates over palladium catalysts cannot be related to relative bond strength,(Chaplin et al. 2012) and our results with TiO₂ echo this. Bromate and perchlorate have a bond strength of 242 kJ/mol and 197 kJ/mol, respectively,(Chaplin et al. 2012) yet bromate is much more readily reduced than perchlorate. Similarly, we found no correlation between central atom properties of oxoanions such as electronegativity and reduction rate. For example, bromate, chlorate, and nitrate all have three oxygens and similar structures, but their electronegativity, 2.96, 3.16, 3.04, respectively, did not correlate with their rate constants, 0.33, 0.052, and 0.0074 cm²/photons x 10¹⁸, respectively. Therefore, the trend in reduction rates is unlikely to be dominated by a trend in oxoanion properties such as thermodynamic potential or bond strength, but rather it appears that the reduction rates are governed by reduction schemes of individual oxoanions that vary in mechanism and are independently controlled by unique intermediary reaction steps. This hypothesis is further supported by observations under near neutral conditions (pH ~6.8 to 7).

3.2 Oxoanion removal with an organic hole scavenger at neutral pH

For oxoanion reduction, pH can significantly affect the photocatalytic reduction rate, generally with acidic conditions promoting rapid reduction.(Kominami et al. 2005a, Soares et al. 2014, Doudrick et al. 2013a) Photocatalytic reduction experiments were repeated at near neutral pH under similar conditions presented in [Figure 1](#); [Figure 3](#) shows the photocatalytic reduction of oxoanions in the presence of TiO₂ and formate at neutral pH. A small amount of nitrite and dichromate removal (~10%) was observed, while only bromate was removed to any significant degree; the rate constant for bromate removal was an order of magnitude slower (0.034 cm²/photons x 10¹⁸) compared to acidic conditions (0.330 cm²/photons x 10¹⁸). Our results confirm that solution pH has a clear effect on the oxoanion reduction rate, with acidic pH generally improving reaction rate.

For oxoanion reduction, the pH plays multiple roles – it provides a source of protons required for the reduction half-reaction (*e.g.*, [Equations 1-8](#)), it controls the surface charge of the photocatalyst and it changes speciation of both starting oxoanions and unstable intermediate species. The strong acid oxoanions (perchlorate, nitrate, chlorate, bromate), are deprotonated at all experimental pH, so their speciation will not change with an increase in pH. However, for the weak acids (nitrite, chlorite, hypochlorite, chromate), the change in pH may affect speciation. While chlorite has a pK_a value (1.96) less than all experimental pH, nitrite, hypochlorite, and chromate have pK_a values of 3.2, 7.54, and 5.9, respectively, which results in their protonation under neutral pH conditions.

The role of pH on reduction mechanisms has been demonstrated by us previously for TiO₂/Ag, which indicated that nitrate was reduced to nitrite under acidic and neutral conditions, but further reduction was dependent on pH and this correlated with the pK_a of NO₂⁻/HNO₂.(Doudrick et al. 2013a). Only nitrous acid was further reduced, while nitrite was not

reduced. This dependency is confirmed in this study by the lack of significant nitrite reduction at neutral pH (Figure 3). Chlorate shows a similar protonation dependence, as it is rapidly reduced in acidic conditions, but largely unchanged in neutral conditions. Because these are catalytic reactions that presumably occur on the photocatalyst surface, this protonation dependence may indicate the need for localized protons at reactions sites, and thus control the overall kinetics.

In this study, the decrease in reduction rate with increasing pH may be attributed to changes in the photocatalyst behavior as pH varies. The point of zero charge for TiO₂ (P90) is approximately 6.4 (Doudrick et al. 2012a). Thus, negatively charged photocatalyst surfaces have little affinity for oxoanions at neutral pH (Noguchi et al. 2003). The lack of interaction between negatively charged oxoanions and the photocatalyst surface likely retards the reduction rate and may contribute to the lack of reduction of oxoanions at neutral pH.

Photolysis may also provide an alternative explanation to the proton dependence. UV-Vis absorption spectra and molar absorptivities for the oxoanions are shown in Figure SI-2, and intermediate oxoanion absorption behavior is summarized in Table SI-1. For bromate, chlorate, and nitrate, the intermediate oxoanion species – bromite/bromous acid, chlorite/chlorous acid, nitrite/nitrous acid, respectively – all have protonated species that absorb light at wavelengths used in this study (e.g., Figure SI-1). Bromate was the one exception to the observed pH dependence, as bromate reduction occurred at neutral pH and the byproduct selectivity remained bromide (Figure SI-3). This unique behavior could possibly be attributed to photon absorption behavior of BrO⁻, which has a significantly higher molar absorptivity (130 M⁻¹ cm⁻¹) at 365 nm than other oxoanion intermediates, compared to its protonated version (10 M⁻¹ cm⁻¹). However, extremely slow rate of bromate reduction in the absence of any organic hole scavenger (Figure SI-4) indicates that the reduction pathway requires an electron scavenger and that bromate photolysis likely does

not play a significant role in the mechanism of bromate reduction in the presence of a hole scavenger.

3.3 Kinetic limitations of photocatalytic reduction of oxoanions

In a photocatalytic system, there are additional kinetic restraints to the reaction beyond those imposed by the redox reaction itself. The relevant photocatalytic processes and their associated rates are shown in [Figure 4](#). Ignoring the excitation rate, the three main rates in the photocatalytic process that control the overall reaction rate (k_o) are the reduction rate (k_{red}) with conduction band electrons, the oxidation rate with holes (k_{ox}), and the recombination rate (k_{recomb}). Recombination refers to the tendency of a photo-excited electron to recombine with a hole before reacting with adsorbed species. On a single, heterogeneous photocatalyst, oxidation and reduction rates work in tandem, and if just one is slow, charge buildup can occur on the photocatalyst, increasing the probability of recombination (and k_{recomb}), thus reducing the overall photocatalytic activity, k_o .

TiO₂ is notoriously poor at photocatalytically oxidizing water (Cowan et al. 2011), thus k_{ox} will be slow, preventing photocatalysis. Addition of an easily oxidized hole scavenger relieves the risk that k_{ox} of water oxidation may cause kinetic limitation of the photocatalytic reaction. Therefore, kinetic limitation of the redox reaction occurs when $k_{red} < k_{rec}$. Competitive reduction of dissolved oxygen may also interfere with oxoanion reduction and serve as a kinetic limitation (Gerischer and Heller 1991).

Bromate was the only oxoanion with measurable photocatalytic reduction activity observed at both acidic and neutral pH. We therefore hypothesize that bromate reduction, which was an order of magnitude more rapid than other oxoanions at acidic pH, remains rapid enough to prevent

significant interference from recombination or oxygen reduction, while reduction rates of other oxoanions fell near or below the rate of electron-hole recombination and were therefore retarded. Additional experimentation including determination of the recombination rate and a study of the adsorption kinetics with respect to pH are necessary to investigate this hypothesis fully. Preliminary sorption data taken from this experiment indicates that oxoanion sorption on TiO₂ is negligible with respect to concentration in the bulk, however further investigations into surface interaction are currently underway.

While proton concentration is clearly influential with respect to the rate of the photocatalytic reduction process, the pH dependency alone cannot effectively explain the relative reduction rates experienced by the oxoanions. As these relative reduction rates also cannot be satisfactorily correlated to any physicochemical trends, the kinetic limitations are presumably unique to the specific oxoanion and are likely influenced by the reduction pathways available to that oxoanion. This is demonstrated in the case of the chlorine oxoanions. The relevant reduction reactions and their standard reduction potentials (at pH = 0) are given in [Equations 9-13](#).

Despite perchlorate having a relatively low thermodynamic barrier to reduction ([Eq. 9](#)), its reduction is extremely challenging due to the slow kinetics of the reaction mechanism. The tetrahedral structure of the perchlorate ion distributes the negative charge evenly across the anion and makes it largely unsuceptible to attack by reducing electrons. (Mahmudov et al. 2008)

Chlorate, the two-electron reduction product of perchlorate, does not have this structural barrier and is reduced to chloride under acidic conditions despite an increased thermodynamic potential barrier (Eq. 10). This suggests that the two electron reduction of perchlorate to chlorate is the limiting reaction under the investigated photocatalytic conditions. These results are in good agreement with observations from previous studies providing evidence for this kinetic barrier.(Urbansky et al. , Lang and Horanyi 2003)

A similar kinetic restriction on the reduction of nitrate has been suggested previously. Nitrate reduction over noble metal catalysts proceeds via stepwise multi-electron transfers with the two electron reduction of nitrate to nitrite being a rate limiting intermediate step.(Chaplin et al. 2012) This kinetic barrier is further illustrated in this study (Figure 5). Nitrite is efficiently removed under acidic conditions (Figure 5a; $k = 0.080 \text{ cm}^2/\text{photons} \times 10^{18}$). The significant loss of dissolved nitrogen indicates that the major byproducts were gases (*e.g.*, N_2 , N_2O). The more gradual removal of nitrate under similar conditions (Figure 5b; $k = 0.0074 \text{ cm}^2/\text{photons} \times 10^{18}$) indicates that the conversion of nitrate to nitrite is a slow kinetic step that limits overall nitrate conversion. Further, the lack of nitrite buildup during the nitrate reduction process indicates that any generated nitrite was rapidly converted to another nitrogenous product. These results demonstrate the limitations on the reduction of nitrate are a consequence of the kinetic barriers for the two electron reduction of nitrate to nitrite, which serves as the rate limiting step of the nitrate reduction process under tested conditions.

3.4 Oxoanion reduction without added hole scavenger

Assuming formate oxidation proceeds via a two-electron oxidation to carbon dioxide (Doudrick et al. 2013b), the theoretical moles of formate required would be the number of electrons

required (Equations 1-8) divided by two. Table 2 shows the theoretical required molar ratio of formate to oxoanion derived from Equations 1-8 and compares this ratio to the experimental ratios that were observed. These ratios are largely in agreement, indicating that (1) formate proceeds via a two-electron oxidation, presumably from hole oxidation, and (2) the assumed byproducts in Equations 1-8 are correct. One exception was nitrite, which did not consume the molar requirement for formate (*i.e.*, 1.5), indicating that electrons are provided from some other source, most likely nitrite itself, as will be discussed below.

In order to further investigate possible self-oxidation as a source for electrons in the redox scheme, oxoanion reduction was investigated without the addition of an organic hole scavenger (*e.g.*, formate). Photocatalytic reduction, albeit slow, was only observed for bromate, nitrite, and chlorate (Figure SI-4). The initial pH was 5.72, 5.50, and 7.15, respectively. Nitrite and chlorite removal can likely be attributed to self-oxidation at the hole (*i.e.*, self-hole scavenging). However, it is unlikely that bromate could be oxidized under these conditions due to the extreme difficulty of forming perbromate.(Pisarenko et al. 2011) Therefore, it is assumed that bromate reduction is favored enough to overcome recombination even when water must be used as the hole scavenger.

Chlorate reduction was not observed under these conditions, which can be presumably be attributed to the slower reduction rate of chlorate resulting in recombination dominating. Further, chlorate oxidation to perchlorate is similarly challenging to bromate oxidation, eliminating self-oxidation as a possible source of electrons. Therefore, we selected chlorite as an additional oxoanion to investigate under these conditions, as the oxidation of chlorite to chlorate is more accessible than chlorate oxidation to perchlorate. These results (Figure 6), show that chlorite was rapidly removed from aqueous solution under tested conditions. During the reaction, chlorate and

chloride were formed at roughly equal rates, indicating that chlorite was being both oxidized and reduced during the reaction process. The electrons that are generated by chlorite oxidation to chlorate are available to drive the reduction to chloride, and chlorite effectively serves at its own hole scavenger. Because the oxidation of chlorite is significantly more thermodynamically favored than the oxidation of water ($E^0(\text{ClO}_3^-/\text{ClO}_2^-) = 0.71\text{V}$), chlorite oxidation occurs preferentially and prevents kinetic limitation of the reaction.

Photolysis may also play a role in this scenario because photolysis of chlorite forms perchlorate, chlorate, and chloride.(Kang et al. 2009). Under our irradiance conditions (*i.e.*, [Figure SI-1](#), peak at 365 nm), no direct photolysis of chlorite is observed. However, the intermediate compound, hypochlorite/hypochlorous acid, absorbs photons within the irradiance range used in our experiments. At a starting experimental pH of 7.15, hypochlorite/hypochlorous acid were present at an approximate ratio of 46/54 ($\text{pK}_a = 7.54$). Hypochlorite has a molar absorptivity of $10\text{ M}^{-1}\text{ cm}^{-1}$ ([Table SI-1](#)), yet hypochlorous acid has no absorption at this wavelength. While the molar absorptivity for hypochlorite is very small, some photolysis may assist with the redox reactions.

Nitrite appears to undergo a similar process at a reduced rate. In [Table 2](#), the photocatalytic reduction of nitrite is shown to oxidize significantly less formate than theoretically required, indicating that nitrite may preferentially oxidize to nitrate ($E^0(\text{NO}_3^-/\text{NO}_2^-) = 0.43\text{V}$) over formate oxidation, a process that has been reported previously.(Zhu et al. 2005) Nitrate concentrations reported in [Figure 5a](#) confirm this behavior. A small amount of nitrate is continuously formed even as nitrite and total nitrogen levels decline throughout the experiment. Oxidation of these intermediate species allows for increased removal during the photocatalytic process; however, this oxidation forms oxidized species (*e.g.*, nitrate, chlorate) that remain problematic and are more

challenging to remove by photocatalytic means. Advancement of photocatalysis as a treatment method for oxidized contaminants will likely require steps to minimize inadvertent oxidation of target species and intermediates.

5. Conclusions

In the presence of an appropriate hole scavenger and under acidic conditions, P90-TiO₂ is capable of photocatalytically reducing a number of oxoanions to innocuous byproducts. However, under relevant water treatment conditions (*i.e.*, water as a hole scavenger, neutral pH), P90-TiO₂ is not an active photocatalyst for the reduction of oxoanions (with the exception of chlorite, bromate, and nitrite), despite meeting the thermodynamic requirements to drive these reactions. This inactivity appears to be driven by the hole reaction (*i.e.*, water oxidation) rather than the electron transfer at the conduction band. The exception to this behavior was oxoanions that served as self-hole scavengers, undergoing simultaneous oxidation and reduction. Perchlorate was not reduced even in the presence of an efficient hole scavenger and under acidic conditions. Because chlorate reduction to chloride was observed, the one- or two-electron reduction of perchlorate has been identified as the limiting step in perchlorate reduction.

While no correlation (*e.g.*, electronegativity of central atom, bond strength, polarizability) between similar oxoanions (*e.g.*, bromate, nitrate, chlorate) and reaction rates was found, observations presented herein suggest the presence of unknown kinetic barriers that are unique to each oxoanion, likely related to the intermediate pathways available for transformation. Also playing a role may be the presence of protonated intermediates and photolysis assisted reduction of these compounds. While no direct relationship between physicochemical properties and reduction behavior was discovered, the study provides a basis for the developing a framework for

investigating photocatalytic reduction of oxoanions in order to design better photocatalysts and optimize treatment. Effective photocatalysis requires the identification of the limiting step in the reduction scheme of individual oxoanions (i.e. perchlorate reduction to chlorate) in order to overcome this barrier. Future research on photocatalytic oxoanion reduction should focus on the development of new photocatalysts that are capable of overcoming the thermodynamic (*i.e.*, negative conduction band potentials) and kinetic barriers (*e.g.*, high water oxidation rate, retarding recombination) of specific oxoanions while maintaining innocuous byproduct selectivity. Making photocatalysts that are visible light active is also important, but this is a secondary goal behind synthesizing a photocatalyst that can achieve the former.

6. Acknowledgements

Doudrick acknowledges the University of Notre Dame and the College of Engineering for startup funding. This research was partially supported by the National Science Foundation (CBET 1132779).

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Table 1. 1st order rate constants for photocatalytic reduction of oxoanions using different hole scavengers. pH of formic acid and sodium formate solutions was approximately 2.5 and 6.8, respectively.

Oxoanion	k (cm²/photons x 10¹⁸)		
	Formic Acid	Sodium Formate	Water
Bromate	0.330	0.034	0.0023
Nitrate	0.0074	NR	NR
Nitrite	0.0802	0.0021	0.0021
Chlorate	0.0516	NR	NR
Chlorite	NA	NA	0.0203
Cr(VI)	0.0041	<0.0010	<0.0010
Perchlorate	NR	NR	NR

NA = Not Analyzed, NR = No Removal

Table 2. Theoretical proton dependence and ratio of formate to anion consumption as well as the experimental formate to anion consumption ratio.

Anion	Theoretical Formate Ratio	Experimental Formate Ratio
Nitrate	2.5	2.7
Nitrite	1.5	0.76
Chlorate	3	2.89
Bromate	3	2.91
Dichromate	1.75	1.45

Figure 1. Use of TiO_2 and UV light for reduction of oxoanions (perchlorate, dichromate, nitrate, chlorate, nitrite, and bromate) under acidic conditions (*i.e.*, formic acid as electron donor)

Figure 2. Standard reduction potentials of oxoanions (Bard 1985) and their relationship to the TiO_2 CB potential (Gratzel 1989) (at pH = 0). Scale is in order from top to bottom. Potentials change with an approximate Nernstian relationship (*i.e.*, +0.059 V/pH).

Figure 3. Photocatalytic removal of various oxoanions in the presence of P90 and formate at neutral pH.

Figure 4. Simplified schematic of a single, heterogeneous photocatalytic process showing relevant rate (k) parameters.

Figure 5. Removal of a) nitrite and b) nitrate with P90, UV and formate under acidic conditions.

Figure 6. Removal of chlorite and formation of by-products using P90 and UV light (> 280 nm) at pH = 7.15.