Enhancement of Oxyanion and Diatrizoate Reduction Kinetics Using Selected Azo Dyes on Pd-Based Catalysts

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Azo dyes are widespread pollutants and potential cocontaminants for nitrate; we evaluated their effect on catalytic reduction of a suite of oxyanions, diatrizoate, and N-nitosodimethylamine (NDMA). The azo dye methyl orange significantly enhanced (less than or equal to a factor of 5.24) the catalytic reduction kinetics of nitrate, nitrite, bromate, perchlorate, chlorate, and diatrizoate with several different Pd-based catalysts; NDMA reduction was not enhanced. Nitrate was selected as a probe contaminant, and a variety of azo dyes (methyl orange, methyl red, fast yellow AB, metanil yellow, acid orange 7, congo red, eriochrome black T, acid red 27, acid yellow 11, and acid yellow 17) were evaluated for their ability to enhance reduction. Hydrogenation energies of azo dyes were calculated using density functional theory, and a volcano relationship between hydrogenation energies and reduction rate enhancement was observed. A kinetic model based on Brønsted–Evans–Polanyi (BEP) theory matched the volcano relationship and suggests sorbed azo dyes enhance reduction kinetics through hydrogen atom shuttling between reduced azo dyes (i.e., hydrazo dyes) and oxyanions or diatrizoate. This is the first research that has identified this synergetic effect, and it has implications for designing more efficient catalysts and reducing Pd costs in water treatment systems.

Introduction

Pd-based catalytic reduction with hydrogen has emerged as a promising approach to treat a variety of contaminants including nitrate (NO$_3^-$) (1–7), N-nitosodimethylamine (NDMA) (8, 9), perchlorate (ClO$_4^-$) (10), and trichloroethylene (TCE) (11–13). Relevant Pd-based catalysts for these contaminants include Pd (11, 12), Pd–In (1, 2, 4, 9), Pd–Cu (3, 7), Pd–Sn (7, 14), and Pd–Re (10). The economic feasibility of Pd-based catalysts was recently demonstrated in a pilot study by Davie et al. (13); Pd-based catalytic treatment of TCE in groundwater at Edwards Air Force Base California was potentially less expensive than treatment with activated carbon ($8/1000$ gal versus $10–$336/1000 gal). Also, activated carbon and other competing technologies such as ion exchange, electrodialysis, and reverse osmosis produce concentrated residues that require subsequent treatment or disposal. Another promising alternative, biological treatment, is less robust to system interruptions and engenders concerns for pathogens in drinking water (13, 15).

Catalytic reduction can be affected by the presence of multiple contaminants. They may compete for reactive sites or hydrogen on the catalyst surface and lower reduction rates (16), or they may provide synergistic effects that enhance reduction rates (17). In this work, we investigated the effects of selected azo dyes on catalytic reduction rates for a suite of natural water pollutants; nitrate, nitrite, perchlorate, chlorate, bromate, NDMA, and diatrizoate. The suite of pollutants was selected because of their presence in drinking water resources, and their negative ecological and health impacts (18–28). Nitrate and nitrite come from fertilizers (29); perchlorate is used as an oxidant in rocket fuel, munitions, or blasting materials (23); chlorate, bromate, and NDMA are associated with disinfection processes in water treatment (30–32); diatrizoate occurs in hospital wastewater and is an iodinated X-ray contrast reagent (33). Azo dyes were chosen as the cocontaminants of interest because in initial studies we found that they enhanced catalytic reduction rates of oxyanion pollutants. Some azo dyes, along with some azo dye products after water treatment (amines and other derivatives), have carcinogenic and mutagenic properties (34–36). They are widely used in industrial processes such as textile, leather, printing, plastic, food, paint, cosmetics, and pharmaceutical industries (37). Their frequent occurrence in surface and ground waters is well-documented, especially in developing countries such as Brazil, China, and India; their occurrence in agricultural regions of developing countries where nitrate is present has also been observed (38–42).

The objectives of this study are to explore the effect of selected azo dyes on the enhancement of catalytic reduction rates for nitrate, nitrite, perchlorate, chlorate, bromate, NDMA, and diatrizoate, and to elucidate the mechanism of this enhancement. Methyl orange (MO) was initially selected as a probe azo dye to evaluate reaction rate enhancement of the selected contaminants. Next, nitrate was selected as a probe contaminant, and a suite of azo dyes were evaluated; these were MO, methyl red (MR), fast yellow AB (FYAB), metanil yellow (MY), acid orange 7 (AO7), congo red (CR), eriochrome black T (EBT), acid red 27 (AR27), acid yellow 11 (AY11), and acid yellow 17 (AY17) (dye structures are provided in Figure 1). Corresponding rates of reduction were compared to different dye properties to explore enhancement mechanisms, including hydrogenation energies calculated from density functional theory, and a kinetic model based on Brønsted–Evans–Polanyi (BEP) theory was developed for...
mechanistic interpretation. This is the first research that has identified the synergetic effects of some azo dyes on cocontaminant reduction in catalytic systems, and it provides new insights for developing novel catalysts with higher activity.

Materials and Methods

All chemicals except azo dyes were reagent grade and were purchased from Fisher (NaNO3 ≥99%, NaNO2 ≥99%, HCl 34%–37%, H3PO4 85%, NaOH ≥98%), Alfar-Aesar (methanol ≥99%, sulfuric acid ≥99%, dimethyl-p-phenylenediamine 96%) or Sigma-Aldrich (KBrO3 ≥99%, KClO3 ≥99%, NDMA, sodium diatrizoate dihydrate ≥99%, NaClO4 · H2O ≥99%, Na2HPO4 · 2H2O ≥99%, NaHIO4 ≥99%, triethylamine ≥99%, NH4Cl ≥99%, NH2ReO4 ≥99%, In(NO3)3 · 5H2O ≥99%). Azo dyes were technical grade (percent purity is reported as available) and were purchased from Sigma-Aldrich (fast yellow AB 95% purity, congo red 99% purity), Alfar-Aesar (methanol 99%, sulfanilic acid 99%, NaH2PO4 · 7H2O 99%, triethylamine ≥99%, In(NO3)3 · 5H2O ≥99%). The Pd was used for nitrate, nitrite, bromate, and chlorate reduction. The incipient wetness method was used to prepare a 5 wt % Pd–Cu catalyst (referred to as Pd–Cu) and a Pd–Cu colloidal catalyst (referred to as Pd–Cu C) on γ-Al2O3, which is referred to as Pd hereafter. The Pd was used for nitrite, bromate, and diatrizoate reduction. The incipient wetness method was used to prepare a 5 wt % Pd–Cu catalyst (referred to as Pd–In) and a Pd–In colloidal catalyst (referred to as Pd–In C) on γ-Al2O3 catalyst (referred to as Pd–Cu T) and Pd–Cu C were used for nitrate reduction. A Pd–Re/activated carbon catalyst (referred to as Pd–Re) was prepared by hydrogen reduction of perrhenate on 5 wt % Pd on activated carbon. The Pd on activated carbon was supplied from Sigma-Aldrich and was wet sieved to obtain particles less than 125 µm before use. It was then dispersed in an aqueous solution, adjusted to pH 2.68 with H3PO4, and ammonium perrhenate was added to the solution with hydrogen sparging for 5 h. The freshly prepared Pd–Re was used for chlorate and perchlorate reduction.

Catalytic reduction experiments were performed in a 500 mL five-neck reaction flask at 21 ± 0.3 °C with continuous H2 sparging (300 mL/min) and stirring at ca. 500 rpm. The same setup was used by Friedich (45) and Knitt (46). Control experiments demonstrated contaminant reduction kinetics were not limited by hydrogen supply or external mass transfer. The reaction flask was initially filled with 400 mL of nanopure water, and then amended with preweighed catalyst. The reactor was sealed with silicon rubber stoppers, and pressurized with H2 for 20 min at 300 mL/min to reduce the oxidized catalyst surface and remove dissolved oxygen. A target contaminant was added alone or with an azo dye. The pH of solution was maintained at either 5.00 or 2.68 (for perchlorate and chlorate) by adding small amounts of HCl or H3PO4 using a pH-stat (TIM 856, Radiometer Analytical). During reaction, 2–3 mL aqueous samples were taken at regular time intervals, filtered using 0.45 µm PTFE syringe filter (Cole-Parmer), and stored in a refrigerator at 4 °C before analysis. To evaluate the time scale over which azo dyes can enhance oxyanion reduction kinetics, an experiment was performed using the same reactor setup but nitrate was spiked into the system every 20 min to create the same initial concentration (2.35 mM) nine times. Catalytic reduction experiments for selected contaminants have been successfully performed at other pH values including neutral, and using buffers including CO2 (3, 14). The experimental conditions in this work were chosen to simplify interpretation of the mechanisms that affect reduction rate enhancement.

Nitrates, nitrites, bromates, and chlorates were analyzed using ion chromatography (Dionex ICS-2000; Dionex IonPac AS18 column; 36 mM KOH as eluent; 1 mL/min eluent flow rate;
FIGURE 2. Reduction kinetics of nitrate (NO$_3^-$), nitrite (NO$_2^-$), bromate (BrO$_3^-$), chloride (ClO$_3^-$), perchlorate (ClO$_4^-$), diatrizoate, and N-nitrosodimethyamine (NDMA) on Pd-based catalysts in the presence or absence of methyl orange (MO) addition. The different Pd-based catalysts (i.e., Pd, Pd–Cu, Pd–Cu T, and Pd–Re) are described in Materials and Methods. Data values above each pair of bars represent the rate constant enhancement factors, which are rate constants with MO addition divided by those without MO addition. Error bars represent 95% confidence intervals.

25 μL injection loop). Perchlorate was also analyzed by ion chromatography (Dionex ICS-2000; Dionex IonPac AS16 column; 36 mM KOH as eluent; 1 mL/min eluent flow rate; 1000 μL injection loop) (10). NDMA, diatrizoate, MO and its reduced product, sulfanilic acid (SA), were analyzed by high performance liquid chromatography (Shimadzu Prominance LC-20AT). Separation was achieved by a Dionex Acclaim 120 C18 (3 μm Analytical, 4.6 × 100 mm) column maintained at 40 °C. For NDMA analysis, the eluent was an 80/20 (V/V) water/methanol mixture at 1 mL/min (45). For diatrizoate analysis, the eluent was a mixture of 20 mM phosphate buffer (pH 7), 5 mM triethylamine and 5% (V%) methanol at 1 mL/min (46). The MO and SA were analyzed with the following eluents: a 10 mM phosphate buffer (pH 7) / nanopure water maintained for 2.5 min, a 0.5 min transition to a 60/40 methanol/nanopure water mixture maintained for 5 min, a 0.5 min transition back to the 10 mM phosphate buffer (pH 7) maintained for 3.5 min. NDMA, diatrizoate, MO, and SA were detected at 226 (45), 237 (46), 463, and 254 nm, respectively, with a photodiode array detector. Ammonia was measured with an ammonia gas sensitive probe (Orion 9512), after adjusting the pH of the samples to 13 by adding NaOH.

Contaminant concentrations during catalytic reduction followed pseudo-first-order behavior for degradation of at least half of initial concentrations, so first order rate constants were determined for all reaction experiments and used for comparison. First order rate constants were determined from linear regressions of relative concentrations on a natural log scale plotted versus time. Pseudo-first-order rate constants have been used to compare initial reaction rates for many different catalytic reduction experiments (4, 8, 10, 11, 46). Each reduction experiment (except for time scale evaluation of MO enhancement on nitrate) was repeated twice, and 95% confidence intervals were calculated for reduction rate constants.

Results and Discussion

Effects of Methyl Orange on Oxyanion, Diatrizoate, and NDMA Reduction. First order rate constants for catalytic reduction of the study pollutants in both the presence and absence of MO are illustrated in Figure 2. Rate constants for nitrate, nitrite, and perchlorate in the absence of MO are in the range of those reported in the literature (1, 3, 4, 10); however, reduction rates of diatrizoate and NDMA are slightly lower (55 and 66% lower, respectively) than reported (8, 46).

For diatrizoate, this may be due to the lack of catalyst activation by hydration (46). To the best of our knowledge, this is the first time that bromate reduction kinetics has been reported using Pd-based catalysts. Rapid bromate reduction on Pd-based catalysts was mentioned in an earlier study, but no data was provided (30). The reaction rates of bromate are comparable to those of nitrite under the same conditions. Reduction pathways of oxyanions were proposed to be successive oxygen atom transfers with deoxygenation (10, 14, 30) (e.g., nitrate/nitrite, bromate, and chloride/bromide were reduced to form nitrite, bromide, and chloride, respectively), whereas successive deiodination was proposed for diatrizoate reduction (46). The proposed reduction pathway for NDMA is N–N bond cleavage to form dimethylamine and N$_2$ or ammonia (45). First-order rate constants for all oxyanions (nitrate, nitrite, bromate, chloride, and perchlorate) and diatrizoate were enhanced in the presence of MO. Although the same concentration of MO (15.3 μM) was applied, it had a broad range of enhancement factors for oxyanions on Pd-based catalysts, ranging from 1.10 for perchlorate on Pd–Re to 5.24 for nitrate on Pd–In. However, rate constants for NDMA were less in the presence of MO.

The initial concentration of MO (15.3 μM) was small compared to initial oxyanion concentrations (2.35 mM), and many azo dyes are known to reduce on Pd-based catalysts in the presence of hydrogen (47). The first reduction step of MO is proposed to be hydrogination of the azo group to form reduced MO (dihydro MO); the second step is cleavage of MO at the azo group to form equimolar amounts of the two azoamines sulfanilic acid (SA) and dimethyl-p-sulfamlyldiamine (DMPPD); the third and subsequent steps include reduction of the SA, DMPPD, and their transformation products (48). We measured MO reduction and SA production on the Pd–In catalyst used for nitrate reduction. More than 99% of the MO was removed from solution after 5 min, and initial production of SA was almost stoichiometric (88% of transformed MO). At the same time, SA decayed slowly with a half-life of 3.23 h (see Figure S1 in the Supporting Information). Adsorption tests of MO and SA indicated their adsorption on the catalysts were negligible (≤3%). In contrast, 83% of nitrate remained after 5 min, and nitrate reduction enhancement occurred over the entire nitrate reduction period. This suggests that small amounts of MO (>12% of initial mass) and/or its reduction intermediates, either in bulk solution or even less amounts sorbed, cause enhancement of oxyanion reduction.

The presence of MO was shown to inhibit NDMA reduction. NDMA reduction is proposed to go through cleavage of the N–N bond (45), the mechanism of MO reduction to SA and DMPPD is similar (i.e., first the N–N double bond is reduced, and then the N–N single bond is cleaved). Similar reduction pathways may result in competition for the reactant (atomic hydrogen) and/or the same active locations on the catalyst (e.g., edge or terrace sites), and result in inhibition of NDMA reduction.

Oxyanion and halogenated contaminant reduction rate enhancement in the presence of MO was observed on all Pd-based catalysts tested (i.e., Pd, Pd–In, Pd–Cu T, Pd–Cu C, and Pd–Re). The mechanisms for contaminant reduction differ on each catalyst, and therefore suggest that the mechanism of enhancement is not metal specific and may be widely applicable to oxyanion and halogenated contaminant reduction on a variety of catalysts. For example, nitrate reduction is thought to occur on In or Cu, with hydrogen spillover from Pd; nitrite and bromate reduction is thought...
to occur on Pd, while chlorate and perchlorate reduction occurs on Re with hydrogen spillover from Pd. In or Cu is necessary for nitrate reduction, while Re is critical for chlorate and perchlorate reduction. No reaction occurs in the absence of Pd and H₂. The extent of rate enhancement, defined by the enhancement factors in Figure 2, varies widely for the same contaminant on different catalysts. For example, the enhancement factors for nitrate reduction on Pd–In was 2.74 times greater than that on Pd–Cu T. This indicates that catalysts properties (e.g., surface area, metal dispersion, and bimetallic distribution) affect reaction rate enhancement.

Mechanisms of Oxyanion and Diatrizoate Reduction Enhancement by Selected Azo Dyes. Mechanisms of azo dye-mediated reaction rate enhancement of oxyanions and diatrizoate are explored using nitrate as the probe contaminant and MO as the model azo dye. Several lines of evidence suggest that azo dye-mediated rate enhancement occurs by the adsorption of the azo dye to the catalyst surface. The MO transformation products SA and DMPPD were each combined with nitrate individually to evaluate if reaction rate enhancement occurred. Nitrate reduction rates are not enhanced in the presence of either SA or DMPPD, indicating that MO, and/or the reduced intermediate of MO, rather than amines is responsible for reduction enhancement of oxyanions and diatrizoate.

Nitrate reduction rates were evaluated at different MO initial concentrations. First order rate constants increase sharply between a MO concentration of zero and 0.546 mM; beyond the latter concentration (0.546 – 27.0 µM) they are relatively stable with enhancement factors between 4 and 6 (see Figure S2 of the Supporting Information). The initial nitrate concentration (2.35 mM) in all cases was much greater than the initial MO concentration (0.153 – 27.0 µM), the initial concentration ratios of nitrate to MO vary from 87.1 to 1.54 × 10⁴. First order rate enhancements are observed only at low levels of MO (relative to nitrate), and is insensitive to aqueous MO concentrations above some threshold. This observation suggests that only trace amounts of MO, and/or its reduced form are responsible for rate enhancement.

First-order rate constants were measured for nine sequential nitrate reduction experiments. Nitrate was spiked in the reactor in 20 min intervals with either MO addition at time zero only or without MO addition. First order rate constants decrease for each sequential experiment with and without MO; they decrease from 4.30 × 10⁻² min⁻¹ to 1.10 × 10⁻² min⁻¹ over nine sequential experiments with MO, and from 7.77 × 10⁻³ min⁻¹ to 2.49 × 10⁻³ min⁻¹ without MO (see Figure S3 in the Supporting Information). During nitrate reduction, OH⁻ is produced and HCl addition is necessary to control pH. Either increasing concentrations of these ions (3), or changes in catalyst morphology and configuration (2) negatively impact reactivity. Regardless of the reason, rate constants with MO are always greater than those without MO. This results in an enhancement factor for nitrate reduction that is relatively constant (varies from 4 to 7) over 180 min and nine sequential nitrate additions, even though MO in solution reached nondetect limits in less than 10 min. This result suggests that trace amounts of sorbed MO, and/or its reduced form, are stable over long periods, and result in reduction rate enhancement for nitrate.

Mechanisms of reaction rate enhancement are further explored using a suite of azo dyes (i.e., MO, MR, FYAB, MY, A07, CR, EBT, AR27, AY11, and AY17) and nitrate as the probe contaminant. All azo dyes except CR have one azo bond and were initially at 15.3 µM; CR has two azo bonds and was initially at 7.5 µM. As illustrated in Figure 3, reaction rate enhancement of nitrate was observed with MO, MR, FYAB, MY, A07, and CR, but not with EBT, AR27, AY11, and AY17.

Various azo dye physical and chemical properties were explored to search for correlations with nitrate reduction rate enhancement. Diffusion coefficient, logKow and average molecular charge estimated using the SPARC database (http://ibmlc2.chem.uga.edu/sparc/) were uncorrelated with nitrate reduction rate enhancement (see Table S4 in the Supporting Information). Mass-transfer limitations and overall dye polarity thus do not appreciably affect or contribute to the observed rate enhancement.

As noted above, the azo group (–N=N–) is readily reduced by hydrogen; to investigate the potential contributions of this redox process to nitrate reduction rate enhancement, we used first-principles density functional theory (DFT) methods to calculate azo dye hydrogenation energies (HE’s):
CR and MR are notable exceptions to the volcano trend. CR is a double-azo dye with first (−93 kJ/mol −N=N−) and second (−79 kJ/mol −N=N−) HE’s comparable to MO. However, it is larger than single-azo dyes and steric hindrance may restrict its reduction on or near the catalyst surface, thus diminishing its potential for enhancement of nitrate reduction kinetics. In contrast to CR, MR has a much greater observed enhancement than expected for its quite negative HE. MR has an ortho carboxylate group, and intramolecular hydrogen bonding contributes significantly to the stability of the hydrogenated product. This intramolecular effect is expected to be less significant in aqueous solution. Moving the carboxylate to the meta (HE = −107 kJ/mol −N=N−) or para (HE = −83 kJ/mol −N=N−) position eliminates this spurious effect and places MR closer to the volcano curve of Figure 3.

The volcano behavior can be explained in terms of a simple kinetic model that takes advantage of the Brønsted–Evans–Polanyi (BEP) relation between reaction energies and rate constants (50). All data except for CR and MR are applied to develop and fit the kinetic model. The overall reaction includes two steps: reduction of azo dyes with hydrogen oxidation, and oxidation of hydrazo dyes with nitrate reduction.

\[
\text{azo dye} + H_2 \xrightarrow{\text{Pd} - \ln} \text{hydrazo dye} \tag{1}
\]

\[
\text{hydrazo dye} + NO_3^- \xrightarrow{\text{Pd} - \ln} \text{azo dye} + NO_2 + H_2O \tag{2}
\]

We assume that the overall nitrate reduction rate is limited by either reaction 1 or reaction 2. However, because nitrate is still reduced at some background rate on the Pd−In catalyst in the absence of an azo dye, and because an azo dye can either enhance or have no effect on the reaction rate, the final expression for the overall nitrate reduction rate can be written as

\[
r = \max(r_{gb}, \min(r_1, r_2)) \tag{1}
\]

In this expression, \( r \) is the overall nitrate reduction rate (mol/(L min)), \( r_{gb} \) is the background nitrate reduction rate (mol/(L min)), and \( r_1 \) and \( r_2 \) are rates of reactions 1 and 2 (mol/(L min)).

We calculated the nitrate reduction rate constant rather than the reduction rate in our study, and nitrate reduction follows pseudo-first-order behavior for at least half of its decay. Consequently, nitrate reduction rate constant \( k_{NO_3} \) at time zero can represent the initial reduction rate constant, and it is derived as follows

\[
k_{NO_3} = \frac{r}{[NO_3^-]_0} = \begin{cases} \frac{r}{[NO_3^-]_0}, & \text{when } \min(r_1, r_2) \leq r_b \\ \frac{r_1 e^{-\alpha [H^+/H_2]/RT} [azo]_0}{[NO_3^-]_0}, & \text{when } r_b < r_1 \leq r_2 \\ \frac{r_2 e^{-\alpha [H^+/H_2]/RT} [azo]_0}{[NO_3^-]_0}, & \text{when } r_b < r_2 < r_1 \end{cases} \tag{2}
\]

In this equation, HE is the hydrogenation energy value of azo dyes (kJ/mol), \( \alpha \) is the transfer coefficient, \( \beta \) is the intrinsic activation barrier (kJ/mol), and \( \nu \) is the preexponential factor (L/(mol min)). [NO_3^-]_0 and [azo]_0 are nitrate and sorbed azo dye concentration at time zero (mol/L), respectively; [H_2]_0 is the saturated hydrogen concentration (0.773 mM) at 21 ± 0.3 °C, 1 atm. \( R \) is the gas constant (8.31 J/(K mol)), and \( T \) is the temperature in Kelvin (294 K). Full details of the model derivation are in the Supporting Information.

To fit the kinetic model to the data, we selected a value of \( \beta \) in the range of literature values (50 kJ/mol −N=N−, ca. 0.5 eV) (50), plotted natural log \( k_{NO_3} \) versus HE (equation S18 in the Supporting Information), adjusted \( \alpha \) to match the slope of the data, and adjusted \( \nu \) to match the intercept. We recognize that the range of \( \beta \) values in the literature are large, and other possible sets of parameter values will match the data. The model results are plotted as a dashed line in Figure 3. Model data inputs and fitting parameters are summarized in Table S6 of the Supporting Information. The kinetic model shows volcano behavior, and supports the hypothesis that azo dyes enhance contaminant reaction rates by reversibly shuttling hydrogen between catalyst and contaminants.

Enhancement factors observed for oxyanions and diatrizoate using MO but not SA or DMPPPD, the volcano relationship between azo dye hydrogenation energies and reduction rate enhancement factors for nitrate, and corresponding agreement of this relationship with the theoretical kinetic model, all support the reduction rate enhancement mechanism proposed in Figure 4. Here, Pd-based catalysts dissociate hydrogen and promote reduction of both the oxyanion or diatrizoate pollutants, and azo dyes to hydrazo dyes. The hydrazo dyes subsequently oxidize back to azo dyes, and in the process reduce oxyanions or diatrizoate. Experimental results with nitrate and the azo dye MO suggest that shuttling between the hydrazo dye and cocontaminant (i.e., oxyanion or diatrizoate) occurs in the presence of trace amounts of sorbed dye that persist on the catalyst surface after azo dyes are no longer detected in solution. This is the first time that azo dyes have been identified to promote the reduction rate enhancement of oxyanions and diatrizoate, or implicated in a hydrogen atom shuttling mechanism. NDMA does not appear to participate in this hydrogen shuttling mechanism, and this may be due to its shared reaction mechanism with azo dyes (N−N bond cleavage) that results in competition for hydrogen and/or shared locations on the catalyst surface where reaction occurs.

Environmental Implication. Capital costs and operational lifetime are two key factors that affect economic viability of Pd-based catalytic treatment technologies (13). In this work, selected azo dyes enhance reduction rate constants by up to a factor of 5.24 for a suite of oxyanions and for diatrizoate. This suggests that the amount of Pd-based catalyst required for catalytic treatment of these drinking water pollutants will be lower when azo dyes are present. As previously noted, azo dyes are common surface
water and groundwater pollutants in developing countries, and are found in agricultural watersheds where nitrate is also present. However, azo dyes are not commonly associated with the other contaminants evaluated in this study. Because many azo dyes, azo dye products (e.g., amines), and added dispersants are carcinogenic and/or mutagenic (34–36), adding them to water to enhance oxyanion or diatrizoate reduction kinetics is likely not prudent. An alternative approach to take advantage of reaction rate enhancement is to bind azo dyes or functional groups to catalyst supports. Azo dyes can be immobilized on activated carbon through a diazonium reaction (51, 52), and on silica or alumina by grafting with silane coupling (53) and a single stage Mannich reaction (54, 55). However, care must be taken to ensure that azo dyes are not mobilized into solution. Results from this study open up a new avenue of research that may lead to more active Pd-based catalysts for pollutant reduction and decreased capital costs for Pd-based treatment systems.

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Supporting Information Available
Data for oxyanion, diatrizoate, and NDMA reduction kinetics, the structures, physical properties, and hydrogenation energies for azo dyes, information for control experiments and kinetic model development, and schemes for immobilizing azo dyes on catalysts (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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