Reduction of 2,4,6-Trinitrotoluene by Iron Metal: Kinetic Controls on Product Distributions in Batch Experiments

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The reaction kinetics and product distributions for the reduction of 2,4,6-trinitrotoluene (TNT) by granular iron metal (Fe⁰) were studied in batch experiments under a variety of initial concentrations of TNT and Fe⁰. Although the kinetics of TNT disappearance were found to behave in accord with the standard theory for surface-mediated reactions, a complex relationship was found between the initial concentrations of TNT and Fe⁰ and the appearance of the expected nitro reduction product, 2,4,6-triaminotoluene (TAT). TNT was completely converted to TAT only when the initial concentration of TNT was low and/or the initial concentration of Fe⁰ was high. Mathematical analysis of a range of generic reaction schemes that produce stable end products in addition to TAT showed that (i) surface complexation of TAT is insufficient to describe all of our data and (ii) polymerization reactions involving TAT and/or various reaction intermediates are the likely source of the incomplete conversion of TNT to TAT at high initial TNT concentration and low Fe⁰ concentration. The relationship between TAT production and reaction conditions is shown to imply that passivation due to reaction products is more likely when the ratio of initial TNT concentration to Fe⁰ concentration is high and, therefore, that passivation rates observed at the laboratory scale are likely to be faster than those which would be observed at the field scale.

Introduction

A decade of intensive research into the kinetics and mechanisms of contaminant reduction by zero-valent iron metal (Fe⁰) has led to widespread consensus regarding the primary effects that influence this process. Many of these effects [e.g., contaminant disappearance rate constant (k_{obs}) versus concentration of Fe⁰ (ρ_m) or k_{obs} vs initial concentration of contaminant (C_0)] can be described with simple quantitative models. These models have been shown to apply over a wide range of contaminants, zero-valent metals, and experimental designs (1). However, as more high-quality data sets become available, evidence is accumulating for more complex effects that involve interactions among two or more primary effects.

One of the first interactions to be well-documented is between the effects of C_0 and mixing rate (e.g., rpm) for batch experiments done with azo dyes (2). In this case, it was shown that site saturation effects—which generally arise as C_0 becomes large—are apparent only at high rpm, where mass transport effects are small. Another interaction involving mixing rate is with molecular structure, where it has been shown that mass transport effects on contaminant disappearance kinetics—which generally become more significant at low rpm—are apparent only with contaminants for which reaction at the metal surface is comparatively fast (and therefore not rate limiting). Such highly reactive contaminants include nitrobenzene (relative to the carbon tetrachloride) (3) and 1,1,1-trichloroethane (relative to 1,1,2trichloroethane) (4).

In other cases, interactions arise from competition among parallel reaction pathways or mechanisms. This is likely to be the case for the chlorinated ethenes, which react with Fe⁰ by competing pathways (e.g., α - vs β -dechlorinations) and mechanisms (e.g., electron transfer vs hydrogen atom transfer). In fact, it has been argued that the relative rates of reduction for trichloroethene (TCE) and perchloroethene (PCE) vary with pH and C_0 in a manner that reflects the combined influence of these factors on the kinetics of hydrogen atom transfer (5). The nitro aromatics are a similar case, where competing parallel reaction pathways (e.g., nitro reduction vs coupling) and mechanisms (again, electron transfer vs hydrogen atom transfer) are likely to produce interactions among primary effects.

Nitro aromatic compounds in general, and 2,4,6-trinitrotoluene (TNT) in particular, have several properties that make them well-suited for probing process-level questions regarding the reactivity of Fe⁰. Among these properties is the well-characterized array of parallel and sequential reaction pathways-resulting in mixtures of characteristic productsthat occur under reducing conditions. The framework of this array involves the reduction of nitro groups, as shown in Scheme 1 for TNT. In Scheme 1, each set of three arrows represents the sequential reduction of a nitro group to an amino group via the corresponding nitroso and hydroxylamino intermediates (which are not shown). Some of these intermediates have been detected during reduction of TNT by Fe^{0} , but the yields have been small and transient (6, 7). Various combinations of the nitroso, hydroxylamino, or amino products can undergo coupling to form dimers or bound residues (8-12), but these products are difficult to extract or identify and have rarely been quantified. 2.4.6-Triaminotoluene (TAT) is the most quantifiable product of TNT reduction by Fe⁰, but the yield of this product varies widely, and this variability has not been explained.

The kinetics of the steps shown in Scheme 1 have been described for a variety of reducing systems, including some that contain Fe⁰ (6-8, 13-15). For the disappearance of nitro aromatic compounds, a number of standard primary effects have been noted, such as the linear dependence of k_{obs} on $\rho_{\rm m}$ and rpm^{1/2} (6, 8). The effect of rpm on the rate of nitrobenzene reduction has been shown to reflect a mixture of mass transport and surface reaction control (3), which leads to the interaction between effects of rpm and molecular structure that was noted above. Adsorption could also be rate limiting, although it is difficult to distinguish this from mass transport control with simple batch experiments (7). Under experimental conditions that minimize the role of mass transport, however, the kinetics of nitro reduction are strongly affected by the presence of competing adsorbates (16).

In contrast to the abundance of detailed analysis on the disappearance kinetics of nitro aromatic compounds under reducing conditions, very little quantitative information is available on the processes that determine the products of

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this reaction. The data reported by Oh et al. (7, 17) are suitable for quantitative kinetic analysis of products from nitro reduction, and their modeling of these data has provided evidence that the type of Fe⁰ affects the types of surface sites that are involved in nitro reduction (18). However, such effects may be coupled to other factors in a manner similar to the examples given above of interactions that reflect parallel and competing reaction pathways. In this study, we describe interactions between $\rho_{\rm m}$ and C_0 on the distribution of reaction products, using TNT as a model for an environmentally relevant nitro aromatic compound. The results show the rate of TAT appearance and limiting amount of TAT that appears in solution are dependent on $\rho_{\rm m}$ and C_0 in a manner that suggests a strong influence of polymerization reactions between reduction intermediates and/or TAT; which, in turn, are influenced by other variables such as pH of the solution or composition of the oxide film on the Fe⁰. Such complex interactions have implications for interpretation of data from controlled experiments in the laboratory and for the design and performance evaluation of full-scale remediation operations in the field.

Methods

2,4,6-Trinitrotoluene (TNT) was purchased from ChemService (West Chester, PA); 2-amino-4,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT) were purchased from Sigma/Supelco (Bellefonte, PA); 2-hydroxy-lamino-4,6-dinitrotoluene (2-HADNT), 4-hydroxylamino-2,6-dinitrotoluene (4-HADNT), 2,4-diamino-6-nitrotoluene (2,4-DANT), 2,6-diamino-4-nitrotoluene (2,6-DANT), and 2,4,6-triaminotoluene (TAT) were purchased from AccuStandard (New Haven, CT). All chemical standards were >99% purity and used as received.

Granular Fe⁰ was obtained from Peerless Powders and Abrasives (Detroit, MI, "PMP Traditional" Size 8/50, >90%). To remove fines, this material was sieved to the 18–35 mesh size fraction. When not in use, the Fe⁰ was stored in a vacuum desiccator. Only one batch of Fe⁰ was prepared, and all analyses were performed with subsamples from this preparation. The specific surface area, determined by BET N₂ gas adsorption, was 1.54 m² g⁻¹.

Batch experiments were conducted under anoxic conditions in 60-mL serum bottles containing 1, 2, 3, and 6 g of Fe⁰, which correspond to 17, 33, 50, and 100 g L⁻¹, respectively. The bottles were filled with N₂-sparged deionized water (no buffer, no headspace), sealed, and mixed by rotation at 20 rpm with the plane oriented 85° from horizontal. The Fe⁰

was preconditioned in this environment for 2 d to stabilize geochemical and Fe⁰ surface conditions (*15*, *19*). Then, the bottles were spiked with TNT stock solution to begin the reaction. Initial TNT concentrations were varied between 4 and 352 μ M. Measurements of pH in bottles containing the same Fe⁰ concentrations used in the kinetic experiments after 2 d pre-exposure gave a pH profile beginning at pH \approx 9.4 at 17 g L⁻¹ and increasing to pH \approx 9.9 at 100 g L⁻¹ (data not shown).

Periodically, $400-\mu$ L samples were withdrawn from the bottles, filtered through a 0.45- μ m nylon filter, and analyzed by HPLC using a platinum C-18 column (Alltech, Deerfield, IL). The mobile phase used for analysis of TNT and intermediates was 55:45 methanol/water at a flow rate of 0.9 mL min⁻¹, whereas TAT analysis was conducted with 5:95 methanol/ammonium acetate buffer (50 mM, pH 7) at a flow rate of 0.7 mL min⁻¹. In all cases, TNT and products were monitored at 254 nm.

Radiolabeled experiments were performed by replacing the TNT stock solution with a solution of ¹⁴C-labeled TNT (Perkin-Elmer Life Sciences, 1.48 GBq/mmol). Concentration data for ¹⁴C-labeled batch experiments were collected in the same manner as the unlabeled experiments. ¹⁴C activity was determined by mixing 0.3 mL of sample with 5 mL of ScintiVerse Scintillant (Fisher, Fairlawn, NJ) and measuring total decays with a liquid scintillation counter. In some of the cases where solution-phase radioactivity at the end of the experiment was substantially lower than at the beginning, the supernatant was adjusted to pH 5 by adding concentrated hydrochloric acid, and concentrations and radioactivity were re-analyzed as described above.

Sequential extractions were performed with ¹⁴C-labeled TNT under anoxic conditions in 53-mL centrifuge vials. A centrifuge vial containing 5 g of Peerless Fe⁰ was filled with deionized water and 0.2 mL of [¹⁴C]TNT stock solution resulting in an initial concentration of 264 μ M. After being mixed for 24 h, the supernatant was removed and the Fe⁰ was washed once with methanol. 5 mL of the respective solvent was then added to the Fe⁰, mixed for 24 h, and separated by centrifugation. The extraction solvents, in order of application, were acetonitrile, NaOH (pH 11), EDTA (pH 11), HCl (pH 4), and EDTA (pH 3).

Results

Kinetic Experiments and Data Fitting. Concentration time series collected from batch experiments (e.g., Figure 1) showed that TNT is reduced to TAT with some of the known



FIGURE 1. TNT disappearance, transient 2-HADNT, 2-ADNT, 2,4-DANT, and 2,6-DANT, and TAT appearance in batch reactors with TNT₀ = 176 μ M and ρ_m = 50 g L⁻¹. Data for radioactivity in solution from ¹⁴C-labeled TNT are plotted on the right axis (scaled so that the calculated initial radioactivity corresponds to TNT₀).

intermediates in this reaction sequence appearing briefly at low concentrations. These results are consistent with previous studies that have examined the reaction mechanism of nitroaromatic reduction (8) and the relative abundance of the intermediate species (7). Points that fell below the detection limit have been omitted from Figures 1–3 and from the fitting described below.

Analyses performed after 24 h of reaction indicate that TNT and all reactive intermediates were entirely consumed and that TAT was a stable end-product. In a number of cases (Figures 2 and 3), the final TAT concentration was significantly less than the initial TNT concentration. Experiments with radiolabeled TNT showed that the mass imbalance was not due to products in the solution phase (cf., ¹⁴C-labeled data in Figure 1). This is consistent with the finding that reduction products of nitro-aromatic compounds adsorb to the Fe⁰ surface (*16*). However, decreasing the pH to 5 by addition of HCl at the end of an experiment did not release a significant additional quantity of TAT, and serial extraction experiments yielded only a few percent of the missing radio-activity (data not shown). These results indicate that some of the reaction products were irreversibly bound to the Fe⁰ surface.

We found the kinetics of TNT disappearance to be accurately described with a first-order rate law:

$$\frac{\mathrm{d}[\mathrm{TNT}]}{\mathrm{d}t} = -k_{\mathrm{TNT}}[\mathrm{TNT}] \tag{1}$$

where k_{TNT} is the observed first-order rate constant. Preliminary experiments with low $\rho_{\rm m}$ (13 g of Fe⁰ L⁻¹, data not shown) exhibited a steep initial drop followed by slower firstorder disappearance of TNT. This bimodal behavior is consistent with mixed control of the kinetics by reversible formation of a reactive surface complex (i.e., by mass transport and/or adsorption) and irreversible surface transformations (7). To minimize complications due to this bimodal behavior and to achieve appreciable yields of TAT, we chose to focus on relatively high $\rho_{\rm m}$, which produced mass transport and/or sorption limited behavior.

The observed kinetics of TAT appearance could also be described with a first-order rate law:

$$\frac{\mathrm{d}[\mathrm{TAT}]}{\mathrm{d}t} = k_{\mathrm{TAT}} \mathrm{TAT}_{\infty} \exp(-k_{\mathrm{TAT}}t) \tag{2}$$

where k_{TAT} is a first-order rate constant, TAT_{∞} is the concentration of TAT at $t \rightarrow \infty$, and $\text{TAT}_{\infty} \exp(-k_{\text{TAT}}t)$ represents the disappearance of a parent compound from which TAT is produced. The TAT appearance data show only a small amount of the positive concavity that is expected during the early stages of a reaction that proceeds through intermediate compounds. This suggests that the rate-limiting process for TAT appearance is the disappearance of TNT.

We fit analytical solutions for the rate laws, obtained by direct integration of eqs 1 and 2, to the TNT and TAT data using Levenberg–Marquardt square error minimization (20). In all cases, the total concentration (TNT₀ or TAT_∞) and rate constant (k_{TNT} or k_{TAT}) where treated as fitting parameters. Since TAT_∞ did not always complete the mass balance, we fit the TNT disappearance and TAT appearance kinetics as independent processes so that TAT_∞ need not equal TNT₀ and k_{TAT} need not equal k_{TNT} . The results are tabulated as Supporting Information (Table S1), and some of the fitted time courses are shown in Figures 2 and 3.

Effect of Initial Conditions. By performing batch experiments with different Fe⁰ concentrations (ρ_m) and initial TNT concentrations (TNT₀), we explored the effects of reaction conditions on the kinetics of TNT reduction and on the appearance of reduction products. Given the likely presence of reduction products bound to the Fe⁰ surface (7, 16, 21) and the implications of this bound residue for long-term reactivity of the Fe⁰, we designed our experiments to highlight mass balance (i.e., TAT appearance).

Figure 2 shows the results of batch experiments at TNT₀ = 176 μ M with ρ_m = 17, 33, 50, and 100 g L⁻¹. Consistent with the surface mediated nature of the reaction, the rate of TNT disappearance increases with ρ_m . TAT appearance, however, responds to ρ_m in an unexpected fashion. TAT_∞ is close to zero for $\rho_m \leq 33$ g L⁻¹ (Figure 2A) but increases to give nearly complete mass balance at $\rho_m = 100$ g L⁻¹ (Figure 2D). This effect is inconsistent with simple partitioning of TAT onto the Fe⁰ surface because a larger surface area would sequester more TAT, not less.

Figure 3 shows experiments performed at $\rho_m = 50$ g L⁻¹ with TNT₀ = 3.5, 35, 176, and 352 μ M. The data in Figure 3 indicate that, in contrast to our previous findings (6), TNT disappearance rates decreased only slightly with increasing TNT₀. The difference between this result and our previous result is probably due to differences in the kinetic regime under which the experiments were performed. The current work was performed under mass transport or sorption limited conditions, so we do not expect to see the influence of accumulation of adsorbed products that we reported previously (6).

The data in Figure 3 indicate a nonlinear relationship between TAT appearance and TNT₀. TNT is mostly converted to solution-phase TAT when TNT₀ \leq 35 μ M (Figure 4A,B), but a significant portion of the TNT is unaccounted for when TNT₀ \geq 176 μ M (Figure 4C,D). The same trend was observed in batch data with $\rho_m = 17$ g L⁻¹, which gave TAT_∞ \approx TNT₀ only at TNT₀ = 3.5 μ M and in batch data with $\rho_m = 100$ g L⁻¹, which gave TAT_∞ \approx TNT₀ for all cases except TNT₀ = 352 μ M (time courses for these experiments not shown).

The trend of decreasing mass balance with increasing TNT_0 suggests that the capacity of Fe^0 to produce TAT can be overwhelmed by increasing TNT_0 . One explanation for this could be passivation of the Fe^0 surface by TNT reduction products, thereby preventing further reaction and causing the accumulation of undetected intermediate species. Respike experiments, however, indicated that, while some passivation occurred, the Fe^0 was still reactive toward TNT, both in the sense of TNT disappearance and in the sense of TAT appearance (data not shown). The processes that yield incomplete mass balance must, therefore, produce stable end-products and leave the Fe^0 at least partially reactive.



FIGURE 2. TNT disappearance (closed circles) and TAT appearance (open circles) in batch reactors with TNT₀ = 176 μ M and ρ_m = (A) 17, (B) 33, (C) 50, and (D) 100 g L⁻¹.



FIGURE 3. TNT disappearance (closed circles) and TAT appearance (open circles) in batch reactors with $\rho_m = 50$ g L⁻¹ and TNT₀ = (A) 3.5, (B) 35, (C) 176, and (D) 352 μ M.

Identification of processes that meet these criteria is the principal subject of the remainder of this work.

Quantitative Analysis. Figures 4 and 5 depict, in graphical form, the fitting results described above and tabulated in the Supporting Information. The plot of k_{TNT} against ρ_{m} (Figure 4A) shows a linear relationship, as has been reported previously for TNT (6) and many other contaminants (22, 23). The slope of this line gives the surface area normalized rate constant, $k_{\rm SA} = 2.03 \pm 0.10 \times 10^{-3} \, {\rm min^{-1}} \, {\rm m^{-2}}$ L. This value reflects the range of TNT₀ that were included in the calculation, even though-as noted above-high TNT₀ experiments produce slightly lower rate constants than low TNT₀ experiments (probably due to the increased influence of surface reaction kinetics for the high TNT₀ experiments). The value of k_{SA} reported here is about twice the value that we have reported previously for Peerless Fe⁰ (6, 15) but is well within the range of k_{SA} values that we reported previously for similar types of Fe^0 and the range of k_{SA} values for TNT and Fe^0 that have been reported by others (6, 15).

A plot of k_{TAT} versus ρ_{m} (Figure 4B) shows features that cannot be explained on the basis of the standard theory for surface mediated chemical kinetics. For each value of TNT₀, $k_{\text{TAT}} \approx 0$ at low ρ_{m} but increases linearly at high ρ_{m} . The slope of the increase appears to decrease with increasing TNT₀ and the ρ_{m} beyond which k_{TAT} increases linearly appears to be larger for higher values of TNT₀. A linear relationship between k_{TAT} and ρ_{m} could arise if the rate of TAT appearance is controlled by TNT disappearance. If this were the case, however, the linear relationship would hold even at low ρ_{m} and the slope would be independent of TNT₀.

Comparing k_{TAT} to our fitted values of TAT_∞ (Figure 4C) reveals a relationship between these parameters. This could either indicate that the processes causing TAT_∞ to be less than TNT₀ are occurring throughout the course of the reaction, or simply, that the fitting parameters k_{TAT} and TAT_∞ are covariant. Of the two parameters, TAT_∞ is more robust because it is largely independent of modeling details (e.g., order of reaction); in fact, nearly identical TAT_∞ values to those found by first-order fitting could be obtained by taking

the average value of the last few TAT points in the relevant time series. Therefore, we chose to analyze the variables controlling TAT appearance (and the behavior of k_{TAT} noted above) using TAT_∞ as the dependent variable rather than k_{TAT} .

Figure 5 shows TAT_{∞} plotted against ρ_m and TNT₀. TAT_{∞} increases with respect to each of these variables, but in most cases, TAT_w appears to approach a horizontal asymptote (which, if the slope is everywhere positive, is expected since TAT_{∞} \leq TNT₀). In the case of ρ_m (Figure 5A), the value of the asymptote is TNT₀, while for TNT₀ (Figure 5B) the asymptotic value appears to be a function of $\rho_{\rm m}$. In general, to approach a horizontal asymptote with positive slope, a function must have negative concavity (i.e., curved downward). This feature is apparent in the plot of TAT_w versus TNT₀ (Figure 5B) but is less apparent in the plot of TAT_{∞} versus $\rho_{\rm m}$ (Figure 5A) where the 176 and 352 μ M data display mostly positive concavity (i.e., curved upward), especially for $\rho_{\rm m} < 50$ g L⁻¹. Since we expect the TAT $_{\infty}$ versus ρ_{m} curve to approach TNT_{0} as $\rho_{\rm m} \rightarrow \infty$, the curve must have an inflection point (i.e., a $\rho_{\rm crit}$ below which little TAT is produced and above which nearly all TNT is converted to TAT).

Both the positive slope of TAT_{∞} with respect to $\rho_{\rm m}$ and the negative concavity with respect to TNT₀ are inconsistent with significant adsorption of nitro reduction products, in contrast to previous suggestions (16). As noted above, adsorption would be expected to produce $\partial TAT_{\infty}/\partial \rho_m < 0$, because increasing the adsorbent concentration (i.e., ρ_m) would increase the amount of TAT that is adsorbed. At constant $\rho_{\rm m}$, adsorption would be expected to produce $\partial TAT_{\infty} / \partial TNT_0 >$ 0 (as is observed) because increasing TNT₀ would increase the adsorbed concentration. Adsorption would, however, produce TAT_w versus TNT₀ profiles with zero concavity at both low TNT₀ where a linear isotherm would be expected and high TNT₀ where saturation of adsorption sites would occur. Since, under an adsorption mechanism, the slope of the low TNT_0 portion of the curve would be <1 while the slope of the high TNT₀ region would be equal to 1, the transition from linear adsorption to site saturation behavior



FIGURE 4. Rate constants obtained from fitting (A) TNT disappearance curves, (B) TAT disappearance curves plotted against ρ_{m} , and (C) fitted TAT... values plotted against k_{TAT} . A table of the fitting results is included in the Supporting Information.

would display positive concavity. This is in contrast to the data in Figure 5B, which appear to possess a slope equal to 1 at low TNT₀ and a concave down transition to slope ≈ 0 at high TNT₀.

Modeling

Scenarios Leading to Incomplete Mass Balance. To produce the partial mass balances that we observed, there must be reaction pathways that do not lead to TAT or reactions that involve the transformation of TAT to undetected products. These processes can be arranged into three scenarios: branching, partitioning, and coupling (Scheme 2). INT denotes a generic and/or lumped intermediate (which could include the various intermediates shown in Scheme 1 as well as TNT), and UNK represents undetected (unknown) products—most likely residing on the Fe⁰ surface—that are responsible for the incomplete mass balance that we often observed. In the following analysis we employ the subscripts



FIGURE 5. Fitted TAT_∞ plotted against (A) ρ_m and (B) TNT₀. The coarse dashed line in panel B represents complete conversion of TNT to TAT. Curves shown are the result of multi-variate fitting of eq 13 with $\kappa(\rho_m)$ given by eq 21.

SCHEME 2



"Branch", "Couple", and "Partition" to denote the source of a specific UNK species. No subscript is used when a statement applies to all three processes.

The branching scenario involves the formation of a product (or products) from the milieu of intermediates that (during the time course of our experiments) does not react further to form TAT. To produce incomplete mass balance, the branching reaction must be irreversible on the time scale of our experiments. Physically, a branching reaction might arise in this system due to coupling of nitroso intermediates with hydroxylamino intermediates, forming a polymeric substance that is likely to be sequestered on the Fe⁰ surface (24).

In the coupling scenario, TAT reacts with INT and, once all the INT is gone, the reaction stops, leaving the remaining TAT unreacted. This scenario could arise in a polymerization reaction similar to that leading to a branching scenario but with TAT as one of the reactants (*8*). The branching scenario is formally a subset of the coupling scenario. However, since the coupling scenario involves the added complexities associated with a feedback loop, we chose to analyze the two as separate cases.

In the partitioning scenario, TAT undergoes further reaction to form undetected species. The reaction, in this scenario, must be reversible, otherwise TAT would disappear entirely. Such a scenario could arise from the reversible sorption of TAT to the Fe^0 surface. Since we have already noted that adsorption cannot explain all aspects of our data, we have included the partitioning scenario mainly for completeness. However, we note that other reversible reactions involving TAT could exist, the character of which we address later.

To define models for TAT appearance based on the three scenarios represented in Scheme 2, we require that the models conform to the following criteria, which derive from our discussion of the trends represented in Figure 5:

$$\frac{\partial TAT_{\infty}}{\partial \rho_{\rm m}} \ge 0 \tag{3}$$

$$\frac{\partial^2 \text{TAT}_{\infty}}{\partial \rho_{\text{m}}^2} \begin{cases} \geq 0 & \rho_{\text{m}} < \rho_{\text{crit}} \\ = 0 & \rho_{\text{m}} = \rho_{\text{crit}} \\ \leq 0 & \rho_{\text{m}} > \rho_{\text{crit}} \end{cases}$$
(4)

$$\frac{\partial TAT_{\infty}}{\partial TNT_{0}} \ge 0 \tag{5}$$

$$\frac{\partial^2 \text{TAT}_{\infty}}{\partial \text{TNT}_0^2} \le 0 \tag{6}$$

Rate equations can be developed for each of the regimes shown in Scheme 2 by assuming reaction rates that are proportional to the concentrations of the reacting species (including, where appropriate, the reactive surface area). Owing to their linearity, the rate equations produced by this procedure do not meet the criteria of eqs 3–6. The goal of the modeling analysis that follows is to determine what modifications must be made to the standard rate equations in order to satisfy the above criteria and, in particular, to determine whether recourse must be made to factors that are not explicitly depicted in Scheme 2 (e.g., effects of pH or $[Fe^{2+}]$ in solution).

Branching. A model for the branching scenario can be written by assuming that the rates of TAT and UNK_{Branch} formation obey a power law in INT concentration with rate constants that depend on ρ_m (25–29):

$$\frac{\mathrm{d}[\mathrm{INT}]}{\mathrm{d}t} = f_{\mathrm{TNT}\to\mathrm{INT}}(t) - k_{\mathrm{TAT}}(\rho_{\mathrm{m}})[\mathrm{INT}]^{m_{\mathrm{TAT}}} - k_{\mathrm{UNK}}(\rho_{\mathrm{m}})[\mathrm{INT}]^{m_{\mathrm{UNK}}}$$
(7)

$$\frac{\mathrm{d}[\mathrm{TAT}]}{\mathrm{d}t} = k_{\mathrm{TAT}}(\rho_{\mathrm{m}})[\mathrm{INT}]^{m_{\mathrm{TAT}}}$$
(8)

$$\frac{d[\text{UNK}_{\text{Branch}}]}{dt} = k_{\text{UNK}}(\rho_{\text{m}})[\text{INT}]^{m_{\text{UNK}}}$$
(9)

where $f_{\text{TNT}\rightarrow\text{INT}}(t)$ is a generic function representing the production of INT, *k*'s are rate constants, *m*'s are the orders of reaction with respect to INT, and all concentrations are initially zero. The parameter subscripts in eqs 7–9 correspond to the product of the relevant reaction so that, for instance, m_{TAT} is the INT reaction order for the INT \rightarrow TAT reaction.

This notation is employed throughout the rest of the paper. If we assume that $m_{\text{TAT}} = m_{\text{UNK}}$, we can derive a formula for TAT_∞ by integrating the ratio of the rate of TAT production to the rate of UNK_{Branch} production from t = 0 to $t = \infty$ (details given in the Supporting Information):

$$TAT_{\infty} = TNT_0 \frac{\kappa(\rho_m)}{1 + \kappa(\rho_m)}$$
(10)

where $\kappa = k_{\text{TAT}}/k_{\text{UNK}}$. Equation 10 satisfies eq 3 if and only if $\partial \kappa / \partial \rho_{\text{m}} > 0$ (proof given in Supporting Information), implying that the rates of processes leading to TAT must increase with ρ_{m} faster than the rates of processes leading to UNK_{Branch}. Equation 10 satisfies eq 4 if and only if $\partial^2 \kappa / \partial \rho_{\text{m}}^2 > 0$ for $0 < \rho_{\text{m}} \le \rho_{\text{crit}}$, where ρ_{crit} is the inflection point in TAT_∞ versus ρ_{m} (Figure 5A). This implies that the concavity of k_{TAT} with respect to ρ_{m} must be large as compared to the concavity of k_{UNK} (proof given in Supporting Information).

Equation 10 is linear with respect to TNT₀ and, therefore, does not satisfy eq 6. This is a result of the assumption, used in deriving eq 10, that $m_{\text{TAT}} = m_{\text{INT}}$. To see this, we assume that $f_{\text{TNT}\rightarrow\text{INT}}(t)$ in eq 7 is a Dirac- δ style pulse (modulated by TNT₀) at t = 0 such that eq 7 becomes

$$\frac{\mathrm{d[INT]}}{\mathrm{d}t} = -k_{\mathrm{TAT}}(\rho_{\mathrm{m}})[\mathrm{INT}]^{m_{\mathrm{TAT}}} - k_{\mathrm{UNK}}(\rho_{\mathrm{m}})[\mathrm{INT}]^{m_{\mathrm{UNK}}}$$
(11)

with the initial condition

$$[INT]_{t=0} = TNT_0 \tag{12}$$

which is equivalent to assuming that the branching occurs at TNT rather than at INT. Integrating eq 6 from t = 0 to $t = \infty$ and substituting eq 11 on the right-hand side yields a relationship for TAT_{∞} (details given in the Supporting Information):

$$TAT_{\infty} = \int_0^{TNT_0} \frac{\kappa(\rho_m)}{\kappa(\rho_m) + w^{\Delta m}} \,\mathrm{d}w \tag{13}$$

where $\kappa = k_{\text{TAT}}/k_{\text{UNK}}$, $\Delta m = m_{\text{UNK}} - m_{\text{TAT}}$, and the dummy variable (*w*) has been substituted for [INT]. Equation 13 reduces to eq 10 when $m_{\text{UNK}} = m_{\text{TAT}}$ and satisfies eq 5 for all κ , m_{UNK} , and m_{TAT} . Equation 6 is satisfied if and only if $m_{\text{UNK}} > m_{\text{TAT}}$ (proof given in Supporting Information); therefore, the rates of processes leading to UNK_{Branch} must increase with INT concentration faster than the rates of processes leading to TAT.

Coupling. A model can be written for the coupling scenario in a fashion similar to the branching scenario with the addition of a TAT concentration dependence to the rate of $\text{UNK}_{\text{Couple}}$ formation:

$$\frac{\mathrm{d}[\mathrm{INT}]}{\mathrm{d}t} = f_{\mathrm{TNT}\to\mathrm{INT}}(t) - k_{\mathrm{TAT}}(\rho_{\mathrm{m}})[\mathrm{INT}]^{m_{\mathrm{TAT}}} - \nu_{\mathrm{INT}}k_{\mathrm{UNK}}(\rho_{\mathrm{m}})[\mathrm{TAT}]^{n_{\mathrm{TAT}}}[\mathrm{INT}]^{m_{\mathrm{UNK}}}$$
(14)

$$\frac{\mathrm{d}[\mathrm{TAT}]}{\mathrm{d}t} = k_{\mathrm{TAT}}(\rho_{\mathrm{m}})[\mathrm{INT}]^{m_{\mathrm{TAT}}} - \nu_{\mathrm{TAT}}k_{\mathrm{UNK}}(\rho_{\mathrm{m}})[\mathrm{TAT}]^{n_{\mathrm{TAT}}}[\mathrm{INT}]^{m_{\mathrm{UNK}}}$$
(15)

$$\frac{\mathrm{d}[\mathrm{UNK}_{\mathrm{Couple}}]}{\mathrm{d}t} = \nu_{\mathrm{UNK}} k_{\mathrm{UNK}} (\rho_{\mathrm{m}}) [\mathrm{TAT}]^{n_{\mathrm{TAT}}} [\mathrm{INT}]^{m_{\mathrm{UNK}}}$$
(16)

where $\nu_{\rm TAT},$ $\nu_{\rm INT},$ and $\nu_{\rm UNK}$ are stoichiometric factors such that

$$TNT_{0} = [TNT] + [TAT] + [INT] + \frac{\nu_{INT} + \nu_{TAT}}{\nu_{UNK}} [UNK_{Couple}]$$
(17)

and n_{TAT} is the order of the coupling reaction with respect to TAT. Setting $n_{\text{TAT}} = 0$ and $v_{\text{TAT}} = 0$ gives the branching model described above. In the case where $m_{\text{UNK}} = m_{\text{TAT}}$, an equation for TAT_{∞} can be found by dividing eq 15 by eq 16 and integrating the result (details given in Supporting Information):

$$\frac{\text{TNT}_0 - \text{TAT}_{\infty}}{\nu_{\text{INT}} - \nu_{\text{TAT}}} = \int_0^{\text{TAT}_{\infty}} \frac{w^{n_{\text{TAT}}}}{\kappa(\rho_{\text{m}}) - \nu_{\text{TAT}}} dw \quad (18)$$

where $\kappa = k_{\text{TAT}}/k_{\text{UNK}}$ and *w* has been substituted for [TAT]. Equation 18 satisfies eqs 3 and 4 if and only if $\partial \kappa / \partial \rho_{\text{m}} > 0$ and $\partial^2 \kappa / \partial \rho_{\text{m}}^2 > 0$ (proof given in Supporting Information). Equation 18 satisfies eqs 5 and 6 for any $n_{\text{TAT}} > 0$. The coupling model, therefore, has the same essential features with respect to ρ_{m} as the branching model but produces the observed behavior with respect to TNT_0 without need for nonlinearity in the INT reaction orders. The required nonlinearity is supplied by the TAT term in the UNK_{Couple} formation rate, indicating that both nonlinearity in the reaction order of reaction can give the behavior that we observed in Figure 5B.

Partitioning. We can derive a model for the partitioning scenario by assuming equilibrium conditions between TAT and UNK_{Partition} with a partitioning coefficient (κ^{-1}) that depends on $\rho_{\rm m}$:

$$\frac{1}{\kappa(\rho_{\rm m})} = \frac{\left(\frac{m_{\rm TAT}}{m_{\rm UNK}}\right)^{m_{\rm TAT}} ({\rm TNT}_0 - {\rm TAT}_{\infty})^{m_{\rm TAT}}}{{\rm TAT}_{\infty}^{m_{\rm UNK}}}$$
(19)

 m_{TAT} and m_{UNK} are stoichiometric factors, and a mass balance condition has been applied to obtain the right-hand side of eq 19. In the absence of nonlinearity (i.e., $m_{\text{TAT}} = m_{\text{UNK}}$), eq 19 reduces to the same form as eq 10:

$$TAT_{\infty} = TNT_0 \frac{\kappa(\rho_m)^{1/m}}{1 + \kappa(\rho_m)^{1/m}}$$
(20)

where $m = m_{\text{TAT}} = m_{\text{UNK}}$. As with the branching and coupling scenarios, κ can be interpreted as a ratio of rate constants, $\kappa = k_{\text{UNK} \rightarrow \text{TAT}} / k_{\text{TAT} \rightarrow \text{UNK}}$. Equation 19 satisfies eqs 3 and 4 if and only if $\partial \kappa / \partial \rho_{\text{m}} > 0$ and $\partial^2 \kappa / \partial \rho_{\text{m}}^2 > 0$ (proof given in the Supporting Information), indicating that the partitioning reaction must be shifted toward TAT with increasing ρ_{m} and that the shift must be stronger (i.e., higher order) than linear. Differentiation of eq 19 with respect to TNT₀ shows that the partitioning model will satisfy eq 5 for any values of m_{TAT} and m_{UNK} , but eq 6 will be satisfied if and only if $m_{\text{UNK}} > m_{\text{TAT}}$ (proof given in Supporting Information), indicating that nonlinearity plays the same role for the partitioning scenario as it does for the branching and coupling scenarios.

Fitting. We parametrized the models presented above by nonlinear square error minimization using both a single variable approach and a multivariate approach. In the single variable approach, the TAT_∞ versus ρ_m data with the same TNT₀ were fitted together, and in a separate exercise, the TAT_∞ vs TNT₀ data with the same ρ_m were fit together. In the multivariate approach, TAT_∞ is treated as a function of both ρ_m and TNT₀, and all TAT_∞ data were treated together.

The TAT_∞ versus TNT₀ data (Figure 5B) were fit by treating $\kappa(\rho_m)$ as an adjustable parameter. To fit the TAT_∞ versus ρ_m data, however, the functional form of $\kappa(\rho_m)$ must be assumed. One way to interpret the dependence of the rate constants

and partition coefficient on ρ_m is to treat Fe⁰ surface sites as reactants and, therefore, to assume that reaction rates obey a power law with respect ρ_m (28, 29):

$$\kappa(\rho_{\rm m}) = \kappa \; \rho_{\rm m}^{\ \Delta\lambda} \tag{21}$$

where $\kappa = k_{\text{TAT}}/k_{\text{UNK}}$ (as in eq 10 but with the ρ_{m} dependence factored out), $\Delta \lambda = \lambda_{\text{TAT}} - \lambda_{\text{UNK}}$, and λ is the order of each reaction with respect to reactive surface area. The conditions given above imply that, for each of the three models, $\Delta \lambda > 1$.

Under the power law assumption, a fitting equation can be derived for TAT_{∞} versus ρ_m (Figure 5A) from eq 10 for branching:

$$TAT_{\infty} = TNT_0 \frac{\kappa \rho_m^{\Delta \lambda}}{1 + \kappa \rho_m^{\Delta \lambda}}$$
(22)

To achieve the sharp increase in TAT_∞ that we observed in the data, it was necessary to set $\Delta\lambda$ to fairly large values (6.7 for 176 μ M, 3.6 for 352 μ M). Since $\lambda_{\text{UNK}} \ge 0$, this result indicates that λ_{TAT} must be significantly greater than 1. It is reasonable to expect the INT \rightarrow TAT reaction to depend on ρ_{m} , but values of $\lambda_{\text{TAT}} \gg 1$ are physically unrealistic. If we set $\lambda_{\text{TAT}} = 1$ and $\lambda_{\text{TAT}} = 0$, the model does not reproduce the positive concavity and inflection point that are shown in Figure 5A. Adding nonlinearity to the concentration dependence of the reaction rates (i.e., by employing eq 13 or eq 18) does not significantly decrease the value of $\Delta\lambda$ needed to replicate the TAT_∞ versus ρ_{m} data. This is not surprising because the conditions that were derived for $\kappa(\rho_{\text{m}})$ do not depend on the values of the INT or TAT reaction orders.

Although the application of a power law expression accurately reproduces the behavior of TAT_∞ versus ρ_m , the values of the fitted parameters indicate that additional chemical factors—factors indirectly influenced by ρ_m —must be involved in determining the distribution of material between TAT and UNK_{Branch} (or UNK_{Couple}). Since $\lambda_{TAT} = 1$ is consistent with our analysis, we hypothesize that, while the rate of the INT \rightarrow TAT reaction is adequately modeled with a power law expression, the rate of the INT \rightarrow UNK_{Branch} (or UNK_{Couple}) reaction depends on solution chemistry. Given the acid/base-catalyzed nature of many polymerization reactions (*24, 30*), it seems likely that pH may be influencing TAT appearance, though we cannot rule out other factors such as [Fe²⁺].

The character of the partitioning scenario can be investigated by deriving a fitting equation from eq 19 under a power law assumption for the partition coefficient κ^{-1} . In the case of $m_{\text{UNK}} = m_{\text{TAT}} = 1$, the fitting equation is identical to eq 22; therefore, the fitting results for the branching scenario also apply to the partitioning scenario. In this case, the large values obtained for $\Delta \lambda$ imply that the reaction order with respect to ρ_m for the UNK_{Partition} \rightarrow TAT reaction is significantly greater than that for the TAT \rightarrow UNK_{Partition} reaction, which is the opposite of what would be expected if adsorption of TAT to the Fe⁰ surface was controlling TAT... Modifying the $\rho_{\rm m}$ dependence to involve additional chemical factors (as we suggested for the branching scenario) could also be done for the adsorption model. Such a modification, however, would have to be strong enough to overcome the tendency for more material to adsorb to more adsorbent, making the success of such a modification unlikely

Equation 13 for branching, eq 18 for coupling, and eq 19 for partitioning can each be fit to the TAT_{∞} versus TNT_0 data by treating κ as an adjustable parameter. All three scenarios were capable of fitting the data equally well. In each case, the sharpness of the transition from $TAT_{\infty} = TNT_0$ to a horizontal asymptote increased with the degree of nonlin-

earity (i.e., $\Delta m = m_{\text{UNK}} - m_{\text{TAT}}$ in eqs 7–20 and/or n_{TAT} in eq 18). The fitting results indicate a sharp transition (e.g., Δm as large as 4.6 for eq 13), but the data are too sparse to produce definitive information about the nature of this transition. The existence of such a transition is, however, clearly indicated by these data, and nonlinearity in the TAT disappearance mechanism is sufficient for its description.

Since we expect that, for the branching and coupling models, $m_{\text{TAT}} = 1$, the nonlinearity in INT reaction orders indicates that the INT \rightarrow UNK reactions are multi-molecular. This is consistent with the interpretation of these reactions as polymerization of the intermediates and/or TAT. At high TNT₀, the concentrations of the intermediates become large and the rate of polymerization increases relative to the rate of TAT production, leading to an overloading of the capacity of the Fe⁰ to produce TAT without completely passivating the surface. In the context of the partitioning scenario, the interpretation of Figure 5B and the required nonlinearity is less clear. As noted above, the observed behavior is not consistent with simple adsorption of TAT to the Fe⁰ surface. The nonlinearity could be rationalized by assuming that the forward reaction (TAT \rightarrow UNK) is multi-molecular, which could arise if TAT undergoes a reversible coupling reaction with itself.

In total, these results indicate that the processes controlling TAT appearance are a combination of coupling and branching reactions with reaction rates that are sensitive to solution conditions. Lumping these processes into a single model would lead to eqs 14–17 for coupling, of which, eqs 7–9 for branching are a special case. Fitting eq 13 for branching (with eq 21 substituted for κ) to our TAT_∞ data with the multivariate approach shows that the branching scenario is sufficient to describe all of our data. The multivariate fitting results are shown in Figure 5. The fitted parameters from the multivariate approach are consistent with the results above that indicate significant nonlinearities in both $\Delta\lambda$ and Δm , which may be due to polymerization reactions involving TAT and/or various reaction intermediates.

Implications for Scaling Passivation Kinetics. Aromatic amines inhibit corrosion reactions both by competition for active sites (*31*) and by polymer film formation (*32*) and, therefore, the fate of TAT can be expected to effect the longevity of Fe⁰-based remediation technologies. To investigate the implications of our results for surface passivation, we can use our modeling results to show how the coverage of surface sites will vary with both TNT₀ and ρ_m . To do this, we assume that UNK precipitates onto active sites to form passive sites and that UNK precipitates onto passive sites with no effect on the reactivity of the site.

Scheme 3

$$S_{\rm A} + {\rm UNK} \rightarrow S_{\rm P}$$
$$S_{\rm P} + {\rm UNK} \rightarrow S_{\rm P}$$

where S_A and S_P represent active and passive sites, respectively. If the precipitation reactions are fast and occur with equal probability (details given in Supporting Information):

$$\frac{[S_{\rm P}]}{[S_{\rm Tot}]} = 1 - \exp\left(\alpha \frac{\rm TNT_0 - \rm TAT_{\infty}}{\rho_{\rm m}}\right)$$
(23)

where $[S_P]$ is the concentration of S_P (e.g., moles S_P per liter of solution), $[S_{Tot}]$ is the concentration of total sites (= $[S_A]$ + $[S_P]$), and α is a constant of proportionality between $[S_{Tot}]$ and ρ_m (set to 1 in this work). $[S_P]/[S_{Tot}]$ can be interpreted as the degree of reaction passivation, $k_{obs}|_t/k_{obs}|_{t=0}$. Figure 6 shows $[S_P]/[S_{Tot}]$ calculated from eq 23 with TAT_{∞} taken from the multivariate fitting of eq 13 to the data in Figure 5. The



FIGURE 6. Fraction of passivated surface based on Scheme 3 plotted as a function of ρ_m for each of the values of TNT₀ used in this study.

results indicate that significant passivation is likely when TNT₀/ ρ_m is large (i.e., the flat portion of the curves on the left side of Figure 6) as is the case in most laboratory investigations of passivation, while systems with small TNT₀/ ρ_m would passivate more slowly. The transition (with respect to both ρ_m and TNT₀) between the two regimes is sharp, implying that the rates of surface passivation found for respike batch experiments (*16*) and laboratory column experiments (*19*, *33*–*35*) will tend to overestimate the passivation rates that apply to most field conditions.

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Supporting Information Available

Fitting results, derivations, and proofs. This material is available free of charge via the Internet at http://pubs.acs.org.

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