DEGRADATION OF CHLOROPICRIN IN THE PRESENCE OF ZERO-VALENT IRON

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Abstract—Halonitromethanes (HNMs) are a class of halogenated disinfection byproducts formed upon the addition of chlorine to water containing organic matter. Batch experiments were performed to investigate the reaction pathways and kinetics of three HNMs (chloropicrin or trichloronitromethane [TCNM], dichloronitromethane [DCNM], and chloronitromethane [CNM]) with zero-valent iron (Fe⁰). All three compounds reacted rapidly in the presence of Fe⁰ (1.8–4.4 g/L) with methylamine (MA) as the final product. The geometric surface area–normalized rate constants decreased with decreasing halogenation: TCNM (301 L/(h-m²)) > DCNM (153 L/(h-m²)) > CNM (45.9 L/(h-m²)). Nitromethane, an intermediate species, rapidly reacted to form MA (302 L/(h-m²)). These reactions all experienced some degree of mass transfer limitation (9–73%). The average carbon and chlorine mass balances for TCNM were >85%, indicating that the major reaction products were recovered. The degradation of TCNM and DCNM proceeded via the parallel reaction pathways of hydrogenolysis and α-elimination. For TCNM, 60.7 ± 8.7% of reaction proceeded via hydrogenolysis and 39.3 ± 6.4% via α-elimination. Knowledge of HNM reaction pathways and kinetics in the presence of Fe⁰ may be useful for predicting the fate of these compounds in drinking water distribution systems containing cast or ductile iron pipe and for developing treatment systems for HNM removal from water.

Keywords—Zero-valent iron Chloropicrin Hydrogenolysis α-Elimination Disinfection byproducts

INTRODUCTION

Chloropicrin (trichloronitromethane [TCNM]) is used as a soil fumigant because of its broad biocidal and fungicidal properties, and TCNM served as a chemical warfare agent because it is a powerful irritant or lachrymator. This compound also is a disinfection byproduct (DBP) that is formed upon the addition of chlorine to water containing organic matter. According to the results of a survey of 35 U.S. water-treatment facilities, TCNM concentrations in finished water ranged from nondetect to 0.59 μg/L, with a median value of 0.12 μg/L [1]. It also was detected in 73% of finished water samples collected at 53 Canadian water-treatment facilities with concentrations ranging from 0.1 to 2.5 μg/L [2]. Trichloronitromethane and other halonitromethanes (HNMs) currently are not regulated by the U.S. Environmental Protection Agency [3]. Nevertheless, some HNMs may present an equivalent or even greater public health risk than those halogenated organic DBPs that are currently regulated (i.e., trihalomethanes and haloacetic acids [HAAs]) [4].

Zero-valent iron (Fe⁰) is a potent reductant that is capable of reductively transforming a wide variety of compounds including halogenated methanes [5–9], halogenated ethanes [10–14], and halogenated propanes [15]. Compounds with more than one halogen on the same carbon atom can react via hydrogenolysis, α-elimination, or a combination of the two pathways [16]. With respect to DBPs, HAAs [17,18] and trihalomethanes [8] react with Fe⁰. The HAAs have been shown to react via sequential hydrogenolysis with acetic acid as the end product of the reaction [17]. Completely halogenated methanes, such as carbon tetrachloride, react rapidly with Fe⁰ via sequential hydrogenolysis [6–9] or competing pathways (hydrogenolysis and α-elimination) [16], but the trihalomethanes trichloromethane reacts more slowly, primarily via hydrogenolysis [8].

Reduction of TCNM has been demonstrated under environmental conditions. Biodegradation of TCNM by Pseudomonas putida via sequential hydrogenolysis with nitromethane (NM) as the end product has been observed [19]. Sodium sulfite, which commonly is used in wastewater treatment to remove residual chlorine before discharge, reacted with TCNM to form dichloronitromethane (DCNM) [20]. The overall reaction rate of TCNM with sulfite increased by nearly one order of magnitude as the pH was increased from 6.1 to 8.5 [20]. The compound also reacted with ammonium thiosulfate (t₁/₂ = 30 h). No chlorinated compounds were detected, but 2 mol of chloride formed for each mole of TCNM that was degraded, suggesting that DCNM and chloronitromethane (CNM) were the main degradation products [21]. Cervini-Silva et al. [22] studied the degradation of chloropicrin in the presence of ferrous iron-bearing clay. Simultaneous formation of DCNM and CNM was observed, which suggests that the reaction proceeded through competing pathways. Iron(II) porphyrins also degrade TCNM, but no products were reported [23]. We are unaware of any reports of TCNM transformation in the presence of Fe⁰ in the peer-reviewed literature.

Iron surfaces and reduced iron minerals often are present in drinking water distribution systems. A 1996 survey of 819 U.S. drinking water utilities reported that approximately 30% of distribution system mains were comprised of unlined cast or ductile iron pipe [24]. Over time, the surface of the iron pipe becomes corroded, and iron oxides such as goethite, lepidocrocite, magnetite [25–27], and green rust [27] accumulate on the pipe surface. These iron surfaces also may reduce DBPs such as TCNM as the DBPs travel through the drinking water distribution system. Knowledge of the reaction kinetics and pathways of HNMs in the presence of Fe⁰ and other reactive iron surfaces may be useful for predicting the fate of these compounds in water distribution systems and resulting human exposures. Such information also may be used for developing new treatment systems for HNM removal. Thus, batch experiments were performed to investigate the kinetics and pathways of the degradation of three chlorinated HNMs (TCNM, DCNM, and CNM) in the presence of Fe⁰.
MATERIALS AND METHODS

Chemicals

The following chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA) and used as received: TCNM (99.6%), NM (99.34%), methylyamine ([MA]; 39.9% wt in water), 2,4-dinitrofluorobenzene (99.7%), 3-[(N-morpholino)propanesulfonic acid ([MOPS]; 99.5%), 2,3-dimethyl-2-butene ([DMB]; 99.0%), and acetonitrile (99.9%). The DCNM (95.13%) and CNM (92.89%) were obtained from CanSyn Chemical Corporation (New Westminster, BC, Canada) and used as received. Reagent-grade methanol, reagent-grade pentane, and electrolytic iron (100-mesh, average diameter 150 μm, 99+%) were obtained from Fisher (Pittsburgh, PA, USA). Sulfuric acid (96.1%) and acetic acid (100%) were obtained from Mallinckrodt (Hazelwood, MO, USA). Ultra-high purity argon was obtained from TriState Airgas (LaCrosse, WI, USA). Diluted stock solutions of TCNM, DCNM, and CNM were prepared in methanol before addition to batch reactors. All aqueous solutions were prepared with deoxygenated (argon-sparged) ultrapure deionized water (Millipore, Billerica, MA, USA).

Batch experiments

Batch experiments were performed in 123-ml serum bottles prepared in an anaerobic chamber (93% N2/7% H2, Coy Laboratory Products, Grass Lake, MI, USA). Iron loadings ranged from 1.8 to 4.4 g/L of buffer. Experiments were performed under anaerobic conditions to prevent oxidation of the iron surface by competing oxidants. The Fe0 was washed with 1 M of sulfuric acid to remove any oxidation products from the iron surface, rinsed twice with deoxygenated water and once with acetone, and then dried under an argon atmosphere. Sulfuric acid was used instead of the commonly used hydrochloric acid to prevent contamination of the reaction system with residual chloride, which would preclude quantification of the chloride produced during the reactions. The Brunauer, Emmet, Teller (BET) surface area (as determined via the method of Brunauer et al.) of the acid-washed Fe0 was 0.061 m2/g and the geometric surface area, assuming spherical particles with a diameter of 150 μm, was 0.005 m2/g. Serum bottles containing acid-washed Fe0 were filled completely with deoxygenated 25-mM MOPS buffer (pH 7.5) and capped with a polytetrafluoroethylene-lined septum and aluminum crimp cap. The headspace-free serum bottles then were removed from the anaerobic chamber, and the parent compound in methanol was injected into the serum bottles (5–10 μl of methanol solution resulting in initial compound concentrations of 1.5 × 10−6–1.5 × 10−2 M in the batch reactors). The bottles were incubated on a rotator (Glas-Col, Terre Haute, IN, USA) at 40 rpm (longitudinal mixing) in the dark (foil-wrapped bottles) at room temperature (21°C). Control experiments were conducted in deoxygenated MOPS buffer without iron to monitor compound hydrolysis. Samples (~2 ml) were removed periodically from the serum bottles while simultaneously injecting an equal volume of deoxygenated MOPS buffer to maintain headspace-free conditions. A 0.5-ml subsample was extracted with 1.0 ml of n-pentane for analysis of halogenated compounds. The remaining 1.5-ml subsample was filtered (0.2 μm polytetrafluoroethylene Gelman Acrodisk syringe tip filter) and derivatized by the addition of 25 μl of 25-MOPS buffer (pH 7.5) and 10 mM TCNM. In addition, two control bottles were prepared. One was spiked only with 100 mM DMB, and the other was spiked only with 10 mM TCNM. The bottles were incubated and sampled in a similar manner to that described above (see Batch experiments section). The 0.5-ml samples were extracted with 1.0 ml n-pentane and analyzed for the presence of parent, degradation, and trapping products as described below (see Analytical procedures section).

Analytical procedures

Chlorinated organic compounds (TCNM, DCNM, and CNM) were analyzed by gas chromatography ([GC]; Trace GC, ThermoQuest, Austin, TX, USA) with electron capture detection. A 1-μl sample was introduced onto a DB-1 column (30 m × 0.32 mm i.d. × 5 μm film thickness; J&W Scientific, Folsom, CA, USA) via an on-column injector by an AS2000 liquid autosampler (ThermoQuest). The oven temperature initially was held at 40°C for 5 min, followed by a 10°C/min temperature increase to 180°C and then a 20°C/min temperature increase to 240°C. The temperature then was maintained at 240°C for 0.5 min.

Gas chromatography with flame-ionization detection was used for analysis of NM. A 0.5-ml aqueous sample was added to a 2.5-ml vial and capped with a polytetrafluoroethylene-lined septum and aluminum crimp cap. A 100-μl sample of the vial headspace was injected (splitless mode) onto a GS-GasPro Column (30 m × 0.32 mm i.d.; J&W Scientific) by an HS2000 headspace autosampler (ThermoQuest) after equilibration at room temperature (20°C) for a minimum of 1 h. The oven temperature initially was held at 90°C for 1 min, followed by a temperature increase of 25°C/min to 228°C. The temperature was held at 228°C for 5 min and then increased at 10°C/min to 240°C, at which it was held for 2 min.

Using a method adapted from Gui et al. [30], high-pressure liquid chromatography (Waters LC Module 1 Plus, Milford, MA, USA) was used to analyze MA. A 325-μl aqueous sample was filtered (0.2 μm polytetrafluoroethylene Gelman Acrodisk syringe tip filter) and then derivatized by the addition of 25 μl of 2,4-dinitrofluorobenzene and 100 μl of acetonitrile. The pH was adjusted to 10 by the addition of 50 μl of 0.1 M sodium hydroxide. A 20-μl sample of the mixture was injected onto a Discovery® RP Amide C16 column (15 cm × 4.6 mm i.d.; 5 μm particle diameter; Supelco, St. Louis, MO, USA) and detection was performed at a wavelength of 380 nm. The mobile phase consisted of 40:60 0.2% acetic acid (pH 4): methanol at a flow rate of 1 ml/min. Chloride was analyzed by capillary electrophoresis (Hewlett-Packard model HP10 CE; Palo Alto, CA, USA) using the method of Hozalski et al. [17].

Extracted samples from the trapping experiments were analyzed by GC (Agilent 6890 Series Plus+, Palo Alto, CA, USA) with mass selective detection (MS); Agilent 5973 Network mass selective detector) in selective ion monitoring mode. A 5-μl sample was injected (splitless) at 200°C onto a Rtx-1 column (30 m × 0.32 mm i.d. × 5 μm film thickness; Restek; State College, PA, USA).
Kinetic modeling

Pseudo–first-order reaction rate constants were determined using Scientist for Windows (Ver 2.01, MicroMath Research, St. Louis, MO, USA). The overall rate constants were calculated via a least-squares fit of the experimental data to the relevant numerically integrated differential equations. Mass-transfer limited reaction rate constants were determined for particles in suspension [31] with geometric surface area calculated assuming a particle diameter of 150 μm. The mass-transfer limited reaction rate coefficient was estimated based on a correlation including terms for the terminal settling velocity of the iron particles, the diffusivity of the organic contaminant, and the surface area of iron per volume of solution via the following equation [11,31]:

\[ k_{MT} = k_a^*a \]  

(1)

where \( a \) was the ratio of external surface area to solution volume calculated using the geometric surface area. The following equation was used to determine \( k_a^* \):

\[ k_a^* = \frac{D}{d_p} \left( 2 + 0.6Re^{1/3}Sc^{1/3} \right) \]  

(2)

where \( D \) is the molecular diffusivity estimated via the method of Hayduk and Laudie [32], \( d_p \) is the particle diameter, \( Re \) is the Reynolds number, and \( Sc \) is the Schmidt number. The technique has been applied successfully to zero-valent metal particles [11,18]. The reaction rate constant (\( k_r \)) was determined using the following equation:

\[ k_r = k_{MT} \left( 1 + \frac{1}{k_{MT}} \right) \]  

(3)

where \( k_{obs} \) was the observed, overall reaction rate constant and \( k_{MT} \) was the calculated mass-transfer limited reaction rate constant.

RESULTS

TCNM degradation

The degradation of TCNM (initial concentration 15 mM) with Fe⁰ was rapid (\( k_{obs} = 2.75 \pm 0.42 \) 1/h; 1.8 g Fe⁰/L buffer), for little TCNM remained after 60 min (Fig. 1A). Hydrolysis of TCNM was insignificant over the time frame of the experiment (half-life or \( t_{1/2} \) > 30 d). The pseudo–first-order reaction rate constant is compared to the calculated mass-transfer limited reaction rate constant (\( k_a^*a \)) in Table 1. The surface-area normalized rate constants for HNM degradation also were computed (Table 1) because the iron loading was not the same for all experiments. The reaction of TCNM with Fe⁰ was in the mixed control regime (73.3% mass-transfer limited), as determined by comparison of the observed and calculated reaction rate constants. The degradation of TCNM resulted in the simultaneous formation of two major products: DCNM and MA (Fig. 1A). Small amounts of CNM and NM also were formed (Fig. 1A inset). The total carbon mass recovery ranged from 74.7 to 118.2% and was 74.7% at the end of the experiment, indicating that the majority of the degradation products have been detected (Fig. 1A). Analytical errors (95% confidence limits) associated with individual data points were less than 15% of the reported values.

A separate experiment was performed to track the fate of the chlorine atoms originally present on the TCNM molecules (Fig. 1B). Because we were not concerned about detecting NM or MA in this experiment, a lower initial TCNM concentration (1.1 mM) was used. The iron loading was 2.5 g Fe⁰/L buffer. Total chloride mass recovery ranged from 83.1 to 97.0% and was 89.1% at the end of the experiment (317 min), with 99.2% of the recovered chlorine present in solution as chloride, indicating that complete dechlorination of TCNM occurred.

NM, CNM, and DCNM degradation

The reaction of NM with Fe⁰ was rapid (\( k_{obs} = 4.46 \pm 0.46 \) 1/h; 2.9 g Fe⁰/L buffer) with methyamine as the end product.
Fe<sub>0</sub> was slower than the rates observed for TCNM and NM. The bon mass balance was complete (102.9±111.1%) throughout the experiment. The reaction rate constant was within a factor of two of the calculated mass-transfer limited rate constant (Table 1). The reaction rate constant was within a factor of two of the calculated mass-transfer limited rate constant (Table 1). The reaction rate constant was within a factor of two of the calculated mass-transfer limited rate constant (Table 1). The reaction rate constant was within a factor of two of the calculated mass-transfer limited rate constant (Table 1).

The reaction of DCNM in the presence of Fe<sub>0</sub> proceeded rapidly, at a nearly mass-transfer–limited rate. The rapid formation of DCNM, CNM, NM, and MA suggests that TCNM was degraded via parallel reaction pathways. Thorough kinetic modeling was not possible (due to the partially mass-transfer–limited reaction rates of TCNM and NM), but data fitting coupled with simulation confirmed that the observed product formation cannot be explained by the sequential hydrogenolysis pathway (TCNM → DCNM → CNM → NM → MA) alone. A likely second pathway for TCNM degradation is reductive α-elimination, which has been observed for structurally related compounds such as carbon tetrachloride [28,29] and 1,1,1-trichloroethane [13]. Further evidence for the existence of a parallel pathway is provided below. Interestingly, the degradation of trihalogenated HAAs in the presence of Fe<sub>0</sub> did not proceed via α-elimination [17,18], indicating that the identity of the fourth substituent on the triply-halogen-substituted carbon atom plays an important role in determining the reaction pathway.

Thus, the simultaneous formation of DCNM and MA as primary products suggests that TCNM reacted with Fe<sub>0</sub> via both sequential hydrogenolysis and α-elimination. The overall pseudo–first-order TCNM degradation rate constant was 2.75 ± 0.42 l/h (Table 1). Using a kinetic model that allowed partitioning of the overall reaction into two pathways, it was determined that hydrogenolysis accounted for 60.7% (±8.7%, 95% confidence interval) of the overall reaction (k = 1.63 ±

### Table 1. Reaction rate constants for halonitromethane reduction by Fe<sub>0</sub>

<table>
<thead>
<tr>
<th>Compound</th>
<th>C&lt;sub&gt;i&lt;/sub&gt; (M)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>(g/L)</th>
<th>(m&lt;sup&gt;2&lt;/sup&gt;/L)&lt;sub&gt;b&lt;/sub&gt;</th>
<th>(m&lt;sup&gt;2&lt;/sup&gt;/L)&lt;sub&gt;geom&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>k&lt;sub&gt;a&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; (1/h)</th>
<th>k&lt;sub&gt;a,BET&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt; (L/(h-m&lt;sup&gt;2&lt;/sup&gt;))</th>
<th>k&lt;sub&gt;a,geom&lt;/sub&gt;&lt;sup&gt;f&lt;/sup&gt; (L/(h-m&lt;sup&gt;2&lt;/sup&gt;))</th>
<th>k&lt;sub&gt;b&lt;/sub&gt;&lt;sup&gt;g&lt;/sup&gt; (1/h)</th>
<th>k&lt;sub&gt;i&lt;/sub&gt;&lt;sup&gt;h&lt;/sup&gt; % RXN&lt;sup&gt;i&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloronitromethane</td>
<td>1.5E-02</td>
<td>1.8</td>
<td>0.0110</td>
<td>9.15E-03</td>
<td>2.75 ± 0.42</td>
<td>25.05</td>
<td>300.61</td>
<td>3.75</td>
<td>10.3</td>
</tr>
<tr>
<td>Dichloronitromethane</td>
<td>1.5E-06</td>
<td>2.9</td>
<td>0.177</td>
<td>1.47E-02</td>
<td>2.25 ± 0.34</td>
<td>12.72</td>
<td>153.19</td>
<td>6.69</td>
<td>3.39</td>
</tr>
<tr>
<td>Chloronitromethane</td>
<td>4.6E-05</td>
<td>4.4</td>
<td>0.268</td>
<td>2.22E-02</td>
<td>1.02 ± 0.29</td>
<td>3.80</td>
<td>45.93</td>
<td>11.31</td>
<td>1.12</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>4.6E-02</td>
<td>2.9</td>
<td>0.177</td>
<td>1.48E-02</td>
<td>4.46 ± 0.46</td>
<td>25.21</td>
<td>301.56</td>
<td>8.75</td>
<td>9.07</td>
</tr>
</tbody>
</table>

<sup>a</sup> Initial concentration.
<sup>b</sup> Iron loading determined using BET (method of Brunauer, Emmet, Teller) surface area (0.061 m<sup>2</sup>/g).
<sup>c</sup> Iron loading determined using geometric surface area assuming 150-μm particles.
<sup>d</sup> Observed pseudo–first-order reaction rate constant.
<sup>e</sup> Brunauer, Emmet, Teller surface area–normalized rate constant.
<sup>f</sup> Geometric surface area–normalized rate constant.
<sup>g</sup> Calculated mass transfer–limited rate constant.
<sup>h</sup> Calculated reaction-limited rate constant.
<sup>i</sup> % Reaction limited.
<sup>j</sup> Sum of reaction rate constants for hydrogenolysis and α-elimination.

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of the reaction (Fig. 2). The kinetics of the NM reaction with Fe<sub>0</sub> were in the mixed control regime, because the observed reaction rate constant was within a factor of two of the calculated mass-transfer limited rate constant (Table 1). The carbon mass balance was complete (102.9–111.1%) throughout the experiment.

For DCNM (Fig. 3A) and CNM (Fig. 3B), reaction with Fe<sub>0</sub> was slower than the rates observed for TCNM and NM. The reaction of DCNM also appears to be partially mass-transfer–limited, and CNM was reaction-limited (Table 1). Hydrolysis was insignificant for DCNM (t<sub>1/2</sub> > 3 d) and CNM (t<sub>1/2</sub> > 9 d) relative to the reduction reactions. No products were observed during the degradation of CNM, as any NM that formed would have reacted rapidly to form MA, and the expected MA concentrations were well below the detection limit (0.1 mM).

**Trapping experiments**

Attempts were made to trap the carbene(oid) intermediate species believed to be formed during the degradation of TCNM via reductive α-elimination (Fig. 4). The reaction was conducted in acetonitrile (with 4 M H<sub>2</sub>O) to increase the lifetime/ stability of the carbene(oid) intermediate [28,29]. The proposed carbene(oid) species should react with the trapping compound DMB to form a substituted cyclopropane [28]. In all three treatments (TCNM + DMB, DMB only, TCNM only), the concentrations of TCNM and/or DMB decreased. The appearance of DMB was more rapid in the presence of TCNM, suggesting that a trapping reaction occurred. We were unable, however, to detect the expected trapping product using GC–mass spectrometry (data not shown).

### DISCUSSION

**Degradation pathway**

The proposed degradation pathway for TCNM and its degradation products in the presence of Fe<sub>0</sub> is shown in Figure 4. The reaction of TCNM in the presence of Fe<sub>0</sub> proceeded rapidly, at a nearly mass-transfer–limited rate. The rapid formation of DCNM, CNM, NM, and MA suggests that TCNM was degraded via parallel reaction pathways. Thorough kinetic modeling was not possible (due to the partially mass-transfer–limited reaction rates of TCNM and NM), but data fitting coupled with simulation confirmed that the observed product formation cannot be explained by the sequential hydrogenolysis pathway (TCNM → DCNM → CNM → NM → MA) alone. A likely second pathway for TCNM degradation is reductive α-elimination, which has been observed for structurally related compounds such as carbon tetrachloride [28,29] and 1,1,1-trichloroethane [13]. Further evidence for the existence of a parallel pathway is provided below. Interestingly, the degradation of trihalogenated HAAs in the presence of Fe<sub>0</sub> did not proceed via α-elimination [17,18], indicating that the identity of the fourth substituent on the triply-halogen-substituted carbon atom plays an important role in determining the reaction pathway.

Thus, the simultaneous formation of DCNM and MA as primary products suggests that TCNM reacted with Fe<sub>0</sub> via both sequential hydrogenolysis and α-elimination.
Chloropicrin degradation by Fe<sup>0</sup>

Based on the relatively slow reduction rate of CNM, accumulation of CNM during the degradation of DCNM was expected if the reaction proceeded via sequential hydrogenolysis. Very little CNM was detected, however, and the small amount of CNM in the batch bottle at the start of the DCNM experiment was due to its presence as a contaminant in the DCNM stock. The poor fit of the sequential hydrogenolysis model to the experimental data (Fig. 3A) suggests that hydrogenolysis was not the dominant pathway. Thus, it appears that DCNM reacted via α-elimination alone or via a combination of α-elimination and hydrogenolysis. The ratio of hydrogenolysis to α-elimination, however, could not be quantified because NM and MA were not observed during the DCNM degradation experiment. If NM was formed, it would have reacted rapidly to form MA, and the expected MA concentrations were below the detection limit. We were unable to run the DCNM experiment at a sufficiently high concentration so as to be able to detect MA because of the high cost of the DCNM.

The reduction of a halogenated methane via α-elimination should give rise to a carbene(oid) intermediate [33]. A carbene(oid) intermediate was detected during the degradation of carbon tetrachloride in the presence of titanium dioxide [28] and magnetite [29] via trapping with DMB in acetonitrile. Attempts to isolate the chloronitrocarbene proposed herein were unsuccessful. Several potential explanations exist for the inability to trap the chloronitrocarbene intermediate. The GC–mass spectrometer in selective ion monitoring mode was used for trapping product detection, with m/z values selected based on interpretation of previous results described above. Though several m/z combinations were examined, none resulted in the detection of a degradation product of the TCNM/Fe<sup>0</sup>/DMB reaction. The expected initial products of the trapping reaction still would contain nitro and chloro substituents and, thus, may have reacted with Fe<sup>0</sup> to form products of unknown m/z.

Furthermore, it is possible that the chloronitrocarbene never leaves the iron surface until MA is formed, or, if it does leave the surface, it is too short-lived, even in acetonitrile, to be trapped by the DMB. The nearly complete carbon mass recoveries in the aqueous experiments support the hypothesis that the carbene(oid) never leaves the iron surface, because the free carbene would have been hydrolyzed rapidly to form products that would not have been detected by our analytical methods.

The reaction of TCNM with Fe<sup>0</sup> in the presence of DMB as a trapping agent was conducted in acetonitrile containing 4 mol/L water. The absence of buffer during this reaction may have resulted in a rapid pH increase and, thus, increased oxide formation on the iron surface. This may have altered the reaction pathway so that the carbene was not formed or was formed in low concentrations that were not detectable via GC–mass spectrometry. Finally, delocalization of the lone pair of electrons from the carbon to the nitro group also may have limited the trapping efficiency of the DMB. Nevertheless, failure to trap the proposed chloronitrocarbene intermediate does not preclude the pathway shown in Figure 4. The kinetic evidence discussed above (see this section) and the rapid release of chloride (Fig. 1B) strongly support the proposed pathway.
Environmental significance

The reaction of chlorine with dissolved organic matter during the disinfection process results in the formation of DBPs that are likely to come in contact with iron surfaces in the drinking water distribution system. This interaction could lead to the reduction of these compounds. In the case of TCNM, the end product of the reaction, MA, has low toxicity (lethal dose killing 50% of the test subjects in mice = 2.5 g/kg) [34] but is known to have an odor threshold concentration of 20 ppb in water [35]. Brominated HNMs, which are more toxic than their chlorinated analogues, also have been observed in drinking water [4]. The brominated compounds are expected to react with Fe⁰ at a faster rate based on trends observed for HAAs by Zhang et al. [18]. Knowledge of DBP degradation rates and pathways in the drinking water distribution system is important for developing treatment systems for the removal of DBPs such as HNMs, for predicting their fate in water distribution systems, and for predicting potential human exposure to these toxic compounds. The results of this research suggest that HNMs may undergo reduction reactions at the iron pipe wall in drinking water distribution systems. Nevertheless, in distribution systems, the reactions of competing oxidants such as oxygen and residual chlorine may have an effect on the HNM degradation kinetics [18]. In addition, the buildup of corrosion products on the pipe wall will limit the availability of Fe⁰-reactive sites, but iron minerals also may mediate the reduction of HNMs. To fully assess the ultimate fate of HNMs in distribution systems, these complicating factors also should be considered.

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