

Homogeneous and Heterogeneous Oxidation of Nitrilotrismethylenephosphonic Acid (NTMP) in the Presence of Manganese(II, III) and Molecular Oxygen

Bernd Nowack*

*Institute of Terrestrial Ecology, Swiss Federal Institute of Technology,
Zürich (ETH), CH-8952 Schlieren, Switzerland*

Alan T. Stone

*Department of Geography and Environmental Engineering, The Johns Hopkins University,
Baltimore, Maryland 21218*

Received: November 20, 2001; In Final Form: April 5, 2002

In the absence of oxygen, NTMP (nitrilotrismethylenephosphonic acid) is oxidized by aqueous suspensions of the Mn^{III}-containing mineral manganite (MnOOH), yielding iminodimethylenephosphonic acid (IDMP) as the sole phosphonate-containing product, along with orthophosphate and two equivalents of Mn^{II}. Hence, both C–P and C–N bond cleavage take place. The reaction proceeds via formation of a Mn^{III}–NTMP surface complex and oxidation of NTMP by Mn^{III} via a carbon-centered methylene radical. Mn^{II} strongly inhibits the reaction, presumably by competition for available surface sites. Homogeneous NTMP oxidation in Mn^{II}– and O₂–containing solutions yields IDMP, formate, phosphate, and hydrogen peroxide. Interception of the methylene radical by O₂ leads to *N*-formyl-IDMP and a second not-identified product. The dual presence of MnOOH and O₂ yields autocatalytic NTMP oxidation, owing to the generation of dissolved Mn^{II}. Although the ultimate oxidants in the Mn^{II}–NTMP–O₂ and MnOOH–NTMP systems are different (O₂ versus Mn^{III}), both oxidation reactions begin with C–N bond cleavage. This finding supports the hypothesis that Mn^{III} is generated in the Mn^{II}–NTMP–O₂ system.

Introduction

Chelating agents are selected so that the corresponding metal ion complexes are stable during the technical operation under consideration. Breakdown typically requires longer time scales, more severe chemical conditions, or the presence of catalysts. The aminopolycarboxylate EDTA (ethylenediaminetetraacetic acid) is the most commonly used and most frequently studied synthetic chelating agent. Breakdown of free EDTA via hydrolytic C–N fission requires temperatures in excess of 175 °C.¹ Rates of EDTA hydrolytic breakdown in the presence of +II metal ions decrease in the order Mg^{II} > Ca^{II} > Zn^{II} > Fe^{II} > Ni^{II}, reflecting increasing percentages of total EDTA complexed by the added metal ion.² In a similar manner, rates of NTA (nitrilotriacetic acid) degradation at high temperatures decrease as the extent of complexation by +II metal ions is increased.³ Higher-valent metal ions, in contrast, may induce oxidation–reduction pathways for chelating agent breakdown. At 100 °C, Fe^{III} is able to oxidize EDTA.⁴ Mn^{III} is a far stronger oxidant than Fe^{III} in a thermodynamic sense, and indeed the Mn^{III}-containing mineral manganite (MnOOH) has been found to oxidize EDTA at room temperature with concomitant formation of Mn^{II}.^{5,6}

Aminopolymethosphonates are generally more resistant toward decomposition than the corresponding carboxylates. At pH 9.5 and temperatures above 200 °C, free NTMP (nitrilotrismethylenephosphonic acid) decomposes by hydrolysis and decarboxylation to various breakdown products.^{7,8} A number of studies pertain to moderate pH (pH 2 < pH < 10) and room-

temperature conditions.^{9,10} Steber and Wierich¹⁰ reported the loss of NTMP and the formation of breakdown products in unilluminated natural waters and a test medium containing a number of alkaline earth cations, transition metal cations, and inorganic anions, but did not identify which solute catalyzed the degradation reaction. Schowanek and Verstraete⁹ observed a slow loss of aminopolymethosphonates in nonilluminated, metal ion-free and H₂O₂-free solutions. Amending the solutions with Ca^{II}, Mg^{II}, and Fe^{II} increased the rates of degradation to discernible levels. Although they attributed the degradation to hydrolysis, it dropped to negligible levels in the absence of oxygen, indicating that redox reactions might play a role. Nowack and Stone¹¹ have recently shown that aminopolymethosphonates are rapidly degraded in the presence of Mn^{II} and molecular oxygen. Reactions of this kind have been explained by either an oxidation of Mn^{II} to Mn^{III} and subsequent oxidation of the coordinated ligand by Mn^{III}^{12–14} or by activation of O₂ by Mn^{II} bound to the coordinated ligand without any change in the oxidation state of manganese.^{15,16}

Phosphonate chelating agents are used more and more each year in a wide range of applications, including scale and corrosion inhibition, metal finishing, ore recovery, oil drilling, pulp, paper, and textile production, cleansing and laundry operations, and agriculture.¹⁷ Approximately 20 000 tons are used in the United States each year, corresponding to \$2.5 billion in revenues.¹⁸ Complete microbial mineralization of phosphonates has been observed in pure bacterial cultures.¹⁹ Low or negligible biodegradation takes place during activated sludge treatment.²⁰ Phosphonates are removed during water treatment by adsorption onto mineral surfaces.²¹ The metal-catalyzed

* Corresponding author. Fax: +41-1-633 11 23. E-mail: nowack@ito.umnw.ethz.ch.

degradation of phosphonates might therefore be an important process governing the fate of phosphonates in process, waste, and natural waters. Two oxidative breakdown products of NTMP have been detected in wastewater,²² indicating that oxidation reactions took place.

In this paper we present results concerning the degradation of NTMP in homogeneous solution and in heterogeneous solution with the Mn^{III} —mineral manganite (MnOOH). We have conducted experiments with (i) NTMP in MnOOH suspension in the absence of oxygen, (ii) with NTMP and Mn^{II} in the presence of oxygen, and finally (iii) a combination of (i) and (ii) with NTMP, MnOOH , Mn^{II} , and oxygen. The loss of parent compound and the formation of breakdown products are carefully monitored.

Experimental Section

Materials. All solutions and suspensions were prepared from distilled, deionized water (DDW, Millipore Corp. MA). All glassware was cleaned in a 10 g/L ascorbic acid solution for several hours to remove any manganese oxides and rinsed several times with DDW prior to use. Analytical grade chemicals were used without additional purification. A Mn^{II} stock solution was prepared by dissolving $\text{Mn}^{\text{II}}\text{Cl}_2 \cdot \text{H}_2\text{O}$, filtering the solution to remove any particulate (hydr)oxide contaminant, and acidifying to pH 3 with HNO_3 . The phosphonates NTMP (nitrilotris-methylenephosphonic acid) and IDMP (iminodimethylenephosphonic acid) were purchased from Fluka. FIDMP (*N*-formyl-iminodimethylenephosphonic acid) was prepared as described in Nowack and Stone.¹¹ MnOOH (manganite) was used from a stock solution stored at 4 °C, which was prepared and characterized as described in McArdeil et al.⁵

Experimental Setup. All experiments were conducted in brown glass bottles to minimize photodegradation reactions in a constant-temperature bath at 25 °C. All solutions were prepared from DDW water and contained 0.01 M NaNO_3 as background electrolyte. The experiments in the presence of oxygen were conducted under stirring and bubbling of air through the solution to maintain a constant O_2 -concentration. Oxygen-free experiments were performed in a controlled-atmosphere glovebag containing 96% N_2 , 4% H_2 , and a catalyst (Coy Laboratory Products); DDW and all stock solutions were degassed with N_2 prior to transfer to the glovebox and left in the glovebox overnight before the start of each experiment. During the experiment the suspensions were stirred open to the oxygen-free atmosphere inside the glovebag.

Adsorption isotherms of IDMP and Mn^{II} onto 0.85 mmol MnOOH per liter were measured at pH 7.0 in 1 mM MOPS buffer (3-morpholino-propanesulfonic acid) in batch reactors with additions between 10 and 70 μM IDMP and Mn^{II} . The suspensions were stirred for 2 h open to the atmosphere before samples were filtered through 0.2 μm polycarbonate filters (Nuclepore Corp.) and analyzed for dissolved IDMP or Mn.

Unless otherwise stated, degradation experiments involved bubbling of air through the solution during the whole experiments and for at least 30 min prior to NTMP addition and pH adjustment to the desired value using NaOH or HCl. The reaction was started by addition of MnOOH (0.85 mmol L^{-1}) or Mn^{II} . The reaction was stopped by removing 10 mL of the suspension, filtering through 0.2 μm polycarbonate filters (Nuclepore Corp.), and adding 5 mL to a vial with EDTA (4 mM final EDTA concentration) and increasing the pH to 8.5 with NaOH. EDTA is a stronger ligand²³ than the phosphonate NTMP and outcompetes NTMP for Mn^{II} . In this solution, IDMP, FIDMP, and formate were measured. Samples for total dissolved

manganese were acidified after filtering with HNO_3 (0.1%). Samples for residual NTMP concentration determinations were filtered and then diluted 100-fold into DDW containing 30 μM Fe^{III} at pH 3. Fe^{III} strongly complexes NTMP, and hence effectively quenches the Mn-catalyzed degradation reaction. Samples for UV/Vis measurements were filtered and the absorbance at 500 nm was measured immediately.

Analytical Methods. NTMP was analyzed by HPLC.²⁴ The phosphonates are complexed at low pH with Fe^{III} and separated on a polymer reversed-phase column (PLRP-S, Polymer Labs) with tetrabutylammonium bromide as counterion in a bicarbonate/acetonitrile eluent (76:24). Unlike the originally published method, no buffer/TBA-mixture was added prior to injection into the HPLC. This keeps the pH of the sample low, which (at the low phosphonate concentrations employed here) prevents further oxidation of the phosphonates.¹¹

Ion chromatography (IC) using a Dionex AG 11 column, 30 mM Na_2CO_3 -eluent, and conductivity detection after chemical suppression yields two peaks. Injecting IDMP yields a retention time comparable to the first peak, and IDMP is known not to degrade under IC conditions. Hence, this first peak corresponds to IDMP. Injecting FIDMP yields a retention time comparable to the second peak, but the peak is believed to be an unidentified product of FIDMP transformation within the IC column. Additional experiments using the derivative method for FIDMP detection²² have shown a rapid degradation of FIDMP at high pH values such as during the ion chromatographic separation. It was also established that FIDMP was rapidly degraded in the presence of Mn^{II} . Any reaction solution containing FIDMP and this unidentified product would therefore yield one merged peak. Hence, we will use the term R-IDMP throughout this paper to designate the sum of FIDMP and the unidentified transformation product.

Formate was measured by ion chromatography using the same column but with a 5 mM NaOH eluent. Phosphate was quantified by spectrophotometry using the molybdenum blue method.²⁵ Formaldehyde was measured by HPLC after derivatization with 2,4-dinitrophenylhydrazine.²⁶ Hydrogen peroxide was measured by the triiodide-method.²⁷ The pH was measured by a pH meter calibrated with standard buffers. Dissolved manganese was measured by flame atomic absorption spectroscopy.

Results and Discussion

Oxidation of NTMP by MnOOH in the Absence of Molecular Oxygen. A decrease in NTMP concentrations over time was observed in oxygen-free MnOOH -suspensions at pH 7 (Figure 1). The diphosphonate IDMP was the sole phosphonate-containing product. Scheme 1 presents an NTMP oxidation mechanism consistent with formation of this product. The first electron is transferred from the nitrogen to Mn^{III} and a nitrogen-centered radical is formed (reaction 1). Cleavage of this radical yields a carbon-centered methylene radical and phosphate (reaction 2). A similar carbon-centered radical has been proposed for the reaction of *N*-(phosphonomethyl)iminodiacetic acid oxidation catalyzed by $\text{V}^{\text{IV,V}}$ ²⁸ and $\text{Co}^{\text{II,III}}$,²⁹ for the photodegradation of $\text{Fe}^{\text{III}}\text{EDTA}$,³⁰ and for the reaction of EDTA with ozone.³¹ The methylene radical reacts with another Mn^{III} (reaction 3), forming an iminium cation, which rapidly hydrolyzes to IDMP and formaldehyde (reaction 4). This is similar to the degradation of EDTA, where iminodiacetic acid (IDA), the carboxylate-containing analogue to IDMP, has been identified.³⁰

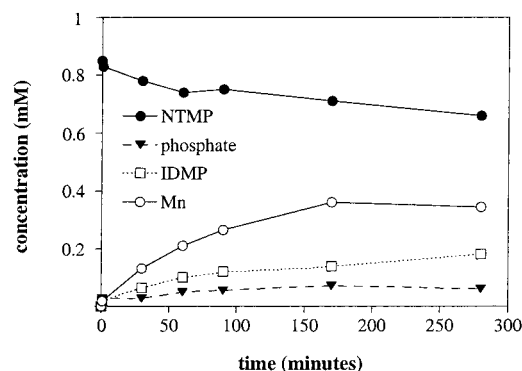
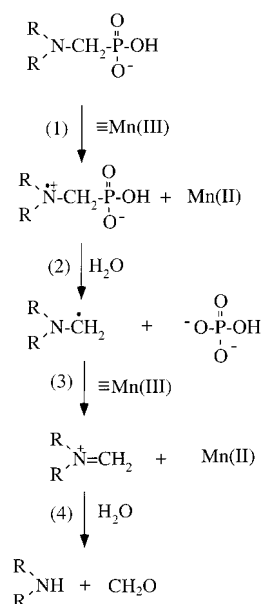


Figure 1. Degradation of NTMP with MnOOH in the absence of oxygen at pH 7.0. Conditions: 0.85 mM NTMP, 0.85 mmol MnOOH per liter, 2 mM MOPS buffer, 0.01 M NaNO₃.

SCHEME 1



Dissolved manganese was detected at about twice the concentration of IDMP. The dissolved manganese can be either Mn^{II} or a Mn^{III}-complex (Mn^{III}NTMP or Mn^{III}IDMP). Mn^{III}-EDTMP (ethylenediaminetetrakisphosphonic acid, a related aminopolysphosphonate) has a molar absorptivity of 271 cm⁻¹ molar⁻¹ at 500 nm.³² Mn^{III}NTMP or Mn^{III}IDMP should exhibit similar molar absorptivities. Absorbance at 500 nm was less than 0.005 in filtered reaction solutions, indicating that the concentration of dissolved Mn^{III}-containing species was less than 18 μM. At the end of the experiment, less than 5% of the dissolved manganese was therefore in the +III oxidation state. Hence, two moles of Mn^{II} are formed per mole of IDMP, in accordance with Scheme 1.

The reaction leveled off after a short time and 80% of NTMP remained unreacted. If 0.85 mM Mn^{II} is added to the MnOOH suspension prior to NTMP addition, the degradation reaction is completely inhibited; neither IDMP is formed nor NTMP degraded. One possibility is that Mn^{II} forms dissolved complexes with NTMP, which resist oxidation by the MnOOH surface. To evaluate this hypothesis, equilibrium calculations were made, based upon stability constants compiled by Martell et al.²³ The experiment shown in Figure 1 was terminated at the point where 0.18 mM IDMP has been produced and 0.66 mM NTMP remains. The equilibrium calculation indicates that 47% of this NTMP is in the free, uncomplexed form, while 53% is

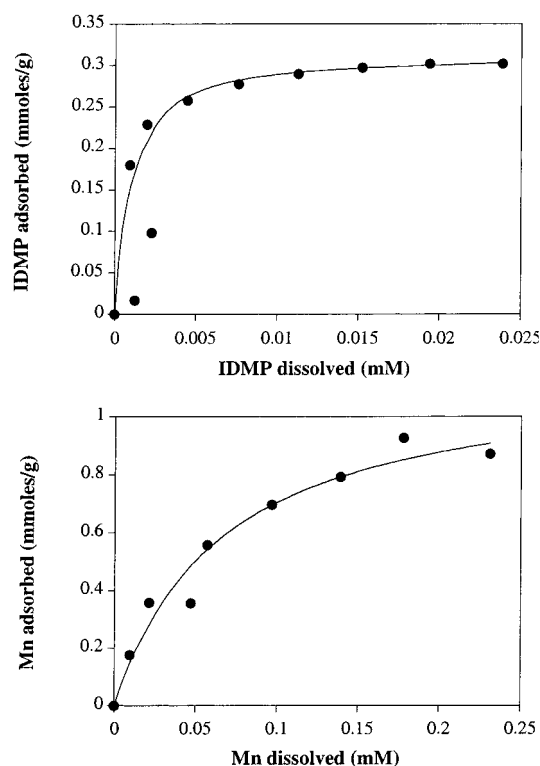


Figure 2. Adsorption of IDMP and Mn^{II} onto 0.85 mmol MnOOH per liter at pH 7.0. The lines are calculated with the constants from Table 1.

TABLE 1: Adsorption of IDMP and Mn^{II} onto MnOOH (at pH 7.0 and 0.075 g/L) Can Be Treated Using the Langmuir Adsorption Equation and the Adsorption Constants Provided Below.

$[X_{\text{ads}}] = (K \cdot X_{\text{ads,max}} [X_{\text{aq}}] / (1 + K \cdot [X_{\text{aq}}])),$ with X_{aq} in mol/L and $X_{\text{ads,max}}$ and X_{ads} in mol/g		
adsorbate	$X_{\text{ads,max}}$ [mol/g]	log K
Mn ^{II}	1.16×10^{-3}	4.19
IDMP	3.13×10^{-4}	6.09

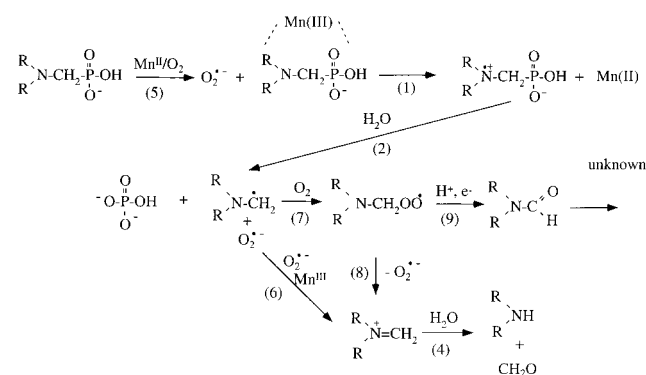
complexed with Mn^{II}. Hence, the fraction of NTMP complexed by Mn^{II} is not sufficient to explain the rapid drop-off in reaction rate.

An alternative hypothesis is that NTMP must compete with Mn^{II} and the oxidation products IDMP and phosphate for available surface sites on MnOOH. As far as competitive cation adsorption is concerned, it is known that adsorbed Cr^{III} effectively prevents the proton-promoted dissolution of iron^{III}-(hydr)oxides.³³ As far as competitive anion adsorption is concerned, it is known that phosphate³⁴ and pyrophosphate³⁵ inhibited the reduction of Mn^{III/IV}-(hydr)oxides by phenolic compounds and sulfide.

NTMP, like all aminophosphonates, adsorbs strongly onto a variety of oxide surfaces.^{36,37,38} Although we would like to determine the extent of NTMP adsorption onto MnOOH, the measurement is confounded by NTMP degradation. IDMP adsorbs onto the iron (hydr)oxide goethite in a manner quite similar to NTMP,³⁷ but unlike NTMP it is not subject to oxidation. Hence, IDMP was used as a surrogate for NTMP in adsorption studies.

Adsorption isotherm experiments of IDMP and Mn^{II} were measured at pH 7.0. Linear fits based upon the Langmuir equation (Table 1) were used and are shown in Figure 2, together with the experimental results. The maximum extents of adsorption (in mmol L⁻¹ g⁻¹) were found to be 1.16 for Mn^{II} and

SCHEME 2



0.31 for IDMP at this pH. $\log K$ was found to be 4.19 for Mn^{II} and 6.09 for IDMP. The MnOOH loading in our experiments was relatively low (0.85 mmol Mn per liter), yielding approximately 0.2% adsorption of 0.85 mM IDMP and 1.0% adsorption of 0.85 mM Mn^{II} . It can be concluded that the extent of adsorption of all phosphonate-containing reactants and products remains low as reactions progress at pH 7. It can also be concluded that during the time course of the experiments the surface concentration of the phosphonates remains constant because saturation of the sites is reached at low dissolved concentration (at approximately 0.01 mM).

Oxidation of NTMP in the Presence of Mn^{II} and Oxygen.

The homogeneous phase oxidation of NTMP in the presence of Mn^{II} (aq) and molecular oxygen has been reported.¹⁰ The reaction has been explained by a two-step mechanism. In a first step, Mn^{II} NTMP is oxidized to Mn^{III} NTMP by O_2 (reaction 5) which is followed by the oxidation of NTMP by Mn^{III} . This reaction is equivalent to the reaction described in Scheme 1 (reactions 1 and 2), except that now the reaction is homogeneous. In the presence of molecular oxygen, the methylene radical is rapidly intercepted by O_2 (Scheme 2, reaction 7, refs 30, 39) or by O_2^- (reaction 6, refs 40–42), which was generated by earlier one-electron O_2 reduction reactions. In reaction 7, a peroxy radical is formed that either decomposes to superoxide and the iminium cation (reaction 8)³¹ or to one of the substituted R-IDMP derivatives (reaction 9).²⁸

In our previous study that employed 10 μM Mn^{II} and NTMP, NTMP degradation was observed only when the pH was above 4.¹¹ The present study employs higher concentrations of both reactants (0.85 mM), and as a result rates of NTMP degradation at pH 3.4 were even faster than rates measured at pH 7 (Figure 3). This observation is quite interesting, since Mn^{2+} (aq) reacts at exceedingly low rates with O_2 . Mn^{II} oxygenation rates in simple aqueous media are proportional to $[\text{OH}^-]^2$, and only become appreciable above approximately pH 9.0, attributable to the formation of reactive hydroxo species such as $\text{Mn}^{\text{II}}(\text{OH})_2\text{O}(\text{aq})$.⁴³ The limited studies that have been conducted in the presence of organic chelating agents, e.g., EDTA,⁴⁴ oxalate ion,⁴³ or organic matter-rich natural waters,⁴³ have shown decreases, rather than increases, in Mn^{II} oxygenation rates. Klewicki and Morgan,⁴⁵ however, have reported a 10-fold increase in Mn^{II} oxidation kinetics at pH 7.5 in the presence of citrate. They propose a mechanism for the oxidation of Mn^{II} citrate that includes complexation of Mn^{II} , electron transfer to form Mn^{III} citrate, and concomitant formation of superoxide.

IDMP was the only phosphonate-containing NTMP breakdown product in O_2 -free MnOOH suspensions. In the presence of O_2 , *N*-formyl-IDMP (FIDMP) is also observed. In the absence of Mn^{II} , FIDMP is stable for at least 24 h. In the presence of Mn^{II} and at the pH values shown in Figure 3 (pH 3.4 and pH

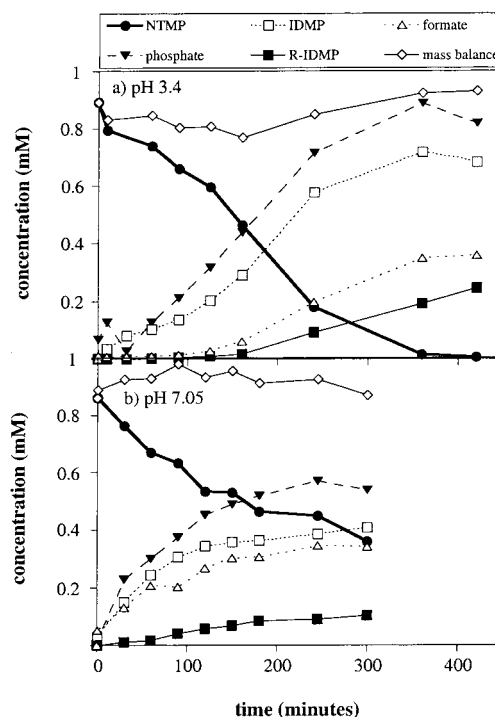


Figure 3. Degradation of NTMP in the presence of Mn^{II} and molecular oxygen at different pH values: reaction products at pH 3.4 (a) and 7.05 (b) as a function of time. The mass balance refers to $[\text{NTMP}] + [\text{IDMP}] + [\text{R-IDMP}]$. Conditions: 0.85 mM NTMP, 0.85 mM Mn^{II} , 250 μM oxygen, 0.01 M NaNO_3 .

7.05), FIDMP is rapidly degraded, indicating further oxidation of the aldehyde, presumably to a carboxylic acid. We can therefore hypothesize that the unknown product is bis(phosphonomethyl) carbamic acid. The mass balance for the sum $[\text{NTMP}] + [\text{IDMP}] + [\text{R-IDMP}]$ is nearly 100%, and the orthophosphate concentration equals the sum $[\text{IDMP}] + [\text{R-IDMP}]$. Hence, for the two pH values examined, no other phosphonate-containing breakdown products are formed. Riley and co-workers have reported rapid hydrolysis of a formyl-compound (*N*-formyl-phosphonomethylglycine), formed by oxidation of *N*-(phosphonomethyl)iminodiacetic acid by molecular oxygen.^{28,29,39} Hydrolysis of FIDMP to IDMP was, however, not observed in our experiments.

Hydrolysis of the iminium cation should yield formaldehyde and IDMP (reaction 4). Formaldehyde concentrations greater than our detection limit of 2 μM were not observed, however, either in the presence or absence of O_2 . Hence, any formaldehyde produced was less than 0.4% of the amount predicted from observed IDMP concentrations. Instead, formic acid was detected, an oxidation product of formaldehyde. Mn^{III} ⁴⁶ and hydrogen peroxide,⁴⁷ both present in the reaction suspensions, are known to oxidize formaldehyde to formic acid. At pH 3.4, the observed formate concentration was only 50% of the total amount of the carbon-containing breakdown product from the formation of IDMP. Presumably further oxidation of formic acid to carbon dioxide by hydrogen peroxide or Mn^{III} took place. This reaction has been found to proceed at pH 3 in the presence of iron as catalyst.⁴⁷

The product yield of IDMP and R-IDMP is pH dependent (Figure 4). In the homogeneous system R-IDMP shows decreasing yield with increasing pH, in the heterogeneous system R-IDMP shows a maximum around pH 6 with a decrease toward lower and higher pH. IDMP exhibits only a slight pH-dependence with a slight increase in the yield toward higher pH values. The disproportionation of superoxide at low pH⁴⁸

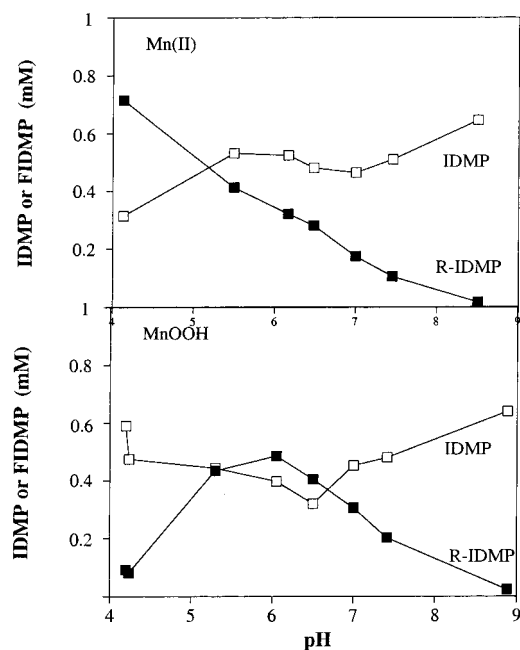


Figure 4. Product yield as a function of pH for the systems NTMP– Mn^{II} –oxygen and MnOOH –NTMP–oxygen.

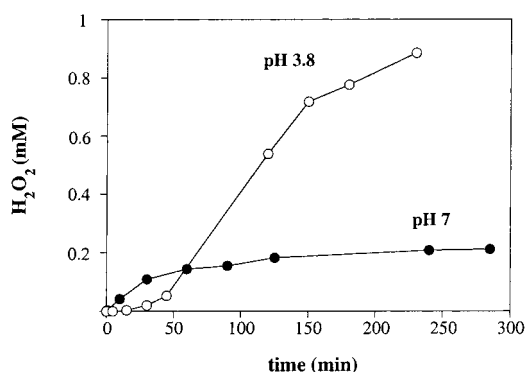


Figure 5. Formation of hydrogen peroxide during the oxidation of NTMP with Mn^{II} in the presence of oxygen at pH 7.0 and 3.8.

competes with the oxidation of the methylen radical^{40–42} (reaction 6) or Mn^{II} ⁴⁹ by superoxide, yielding IDMP. At low pH, the interception of the radical by molecular oxygen (reaction 7) therefore becomes more favorable due to the lower superoxide concentration and R-IDMP is preferably formed. This was found for the homogeneous system but not for the heterogeneous system where the yield of R-IDMP is very low at pH 4. The influence of the initial Mn^{II} /NTMP ratio on the product yield at pH 7 was also studied. It can be described by the following relationship ($R^2 = 0.997$):

$$\frac{\text{IDMP}_t}{\text{R-IDMP}_t} = 0.56 + 1.8 \frac{\text{Mn(II)}_0}{\text{NTMP}_0}$$

IDMP is preferably formed whenever the Mn^{II} /NTMP ratio is high.

Figure 5 shows the evolution of hydrogen peroxide during the oxidation of NTMP at pH 3.8 and 7.0. At low pH, H_2O_2 is formed at a rate similar to the formation of the breakdown products IDMP and R-IDMP. At pH 7.0, however, much less H_2O_2 was formed despite similar NTMP oxidation rates. Mn^{II} complexes with NTMP and other phosphonate chelating agents are known to catalyze hydrogen peroxide disproportionation, with rates of catalysis increasing with increasing pH.^{50,51} We

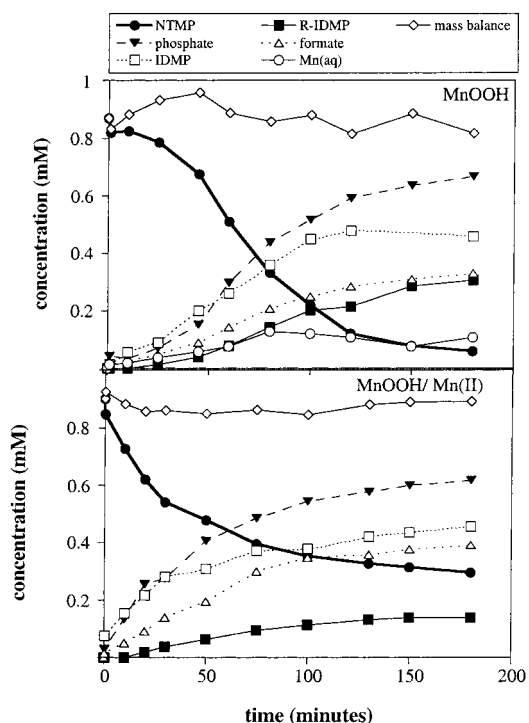


Figure 6. Degradation of NTMP in the presence of MnOOH and molecular oxygen: reaction products as a function of time at pH 7.0. (a) No Mn^{II} added (b) 0.85 mM Mn^{II} added. The mass balance refers to $[\text{NTMP}] + [\text{IDMP}] + [\text{R-IDMP}]$. Conditions: same as in Figure 3.

have conducted experiments at pH 3.8 and 7.0 and have found that at the low pH, no decomposition of H_2O_2 in the presence of Mn^{II} /NTMP takes place while at pH 7.0, a rapid decomposition of H_2O_2 is indeed observed. This reaction can explain the observed plateau in H_2O_2 concentration during oxidation of Mn^{II} -NTMP at pH 7 (Figure 5).

Oxidation of NTMP in the Presence of MnOOH and Oxygen. We have so far established that in the absence of oxygen, MnOOH is able to oxidize NTMP, yielding IDMP and Mn^{II} . Furthermore, NTMP is oxidized to IDMP and R-IDMP in the presence of Mn^{II} and molecular oxygen. Addition of NTMP to MnOOH in the presence of O_2 therefore yields a combination of the two processes. The reaction begins as outlined in Scheme 1, yielding IDMP and dissolved Mn^{II} without the involvement of O_2 . As soon as Mn^{II} appears in solution, the homogeneous reaction of Mn^{II} /NTMP with oxygen as discussed in the previous section also takes place.

As shown in Figure 6a, the reaction of NTMP with MnOOH in the presence of oxygen is autocatalytic. Adding Mn^{II} at the onset of the reaction increases the initial rate of NTMP loss and diminishes the magnitude of autocatalysis observed. This is different from the experiments in the absence of O_2 where the formation of Mn^{II} decreased the reaction rate.

The orthophosphate ion concentration matches the sum $[\text{IDMP}] + [\text{R-IDMP}]$ both in the absence and presence of added Mn^{II} . Orthophosphate ion and phosphonates adsorb in a very similar manner onto (hydr)oxides. We can therefore assume that the amount of adsorbed phosphate is in the same order of magnitude as adsorbed IDMP (less than 1%). The mass balance $[\text{NTMP}] + [\text{IDMP}] + [\text{R-IDMP}]$ is almost 100%, showing that no other major phosphonate containing breakdown products have been formed. Formate was again detected as carbon-containing breakdown product and the formaldehyde concentration was again less than $2 \mu\text{M}$. Hydrogen peroxide was measured with a maximum concentration of about 0.35 mM, again

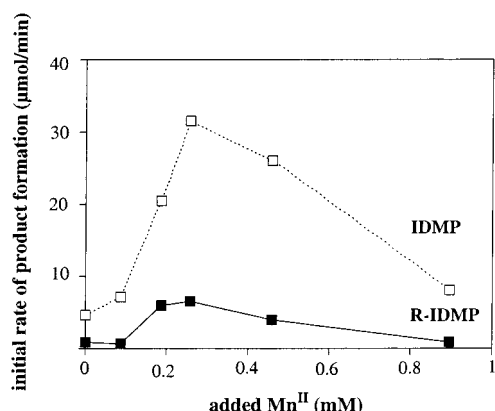


Figure 7. Initial rate of product formation (first half hour) at different initial Mn^{II} concentrations in the system NTMP– MnOOH – Mn^{II} –oxygen at pH 7.0. Conditions: same as in Figure 3.

indicating that reactions involving molecular oxygen took place.

To elucidate the effect of Mn^{II} on the reaction rate, we conducted experiments under various initial Mn^{II} concentrations. An example is shown in Figure 6b, with the addition of 0.85 mM Mn^{II} to the MnOOH suspension prior to the addition of NTMP. The initial rate of NTMP disappearance was greatly enhanced compared to the experiment with no addition of Mn^{II} . This clearly proves that Mn^{II} is responsible for the autocatalytic effect seen in Figure 6a. Experiments were conducted with different initial Mn^{II} additions and the initial rate of product formation (in $\mu\text{mol L}^{-1} \text{min}^{-1}$) is shown in Figure 7. Addition of Mn^{II} first increased the initial rate of product formation up to 0.3 mM and then decreased the rate at higher Mn^{II} concentrations. The relative yield of IDMP and R-IDMP did not change as the Mn^{II} concentration was increased. Both show the same increase in the reaction rate up to 0.3 mM Mn^{II} and a subsequent decrease at higher Mn^{II} . This indicates that IDMP and R-IDMP share a precursor, presumably the methylene radical. At higher concentrations, Mn^{II} had the same inhibitory effect on NTMP oxidation as was observed in the absence of oxygen, indicating that again competition for available surface sites took place.

The distribution of the two products IDMP and R-IDMP is pH-dependent as shown in Figure 4. Contrary to the homogeneous system, the yield of R-IDMP near pH 4 was low. Increasing the pH increased the R-IDMP product yield, but still higher pH values again decreased the yield. At a pH of 6 and above, MnOOH suspensions and homogeneous systems yielded a similar pH dependence.

IDMP exhibits no reactivity in the presence of MnOOH or Mn^{II} , either in the presence or in the absence of oxygen. The absence of absorption around 500 nm in filtered reaction suspensions also shows that it does not form significant concentrations of dissolved Mn^{III} complexes in the presence of MnOOH or Mn^{II} .

The oxidation of NTMP in the presence of Mn^{II} and oxygen is proportional to the concentration of the Mn^{II} NTMP complex.¹¹ The concentration of Mn^{II} NTMP was calculated for the different systems by equilibrium calculations using the log K values for the Mn^{II} complexes and the known total concentrations of Mn^{II} , NTMP, and IDMP. In the experiment shown in Figure 3a, the Mn^{II} NTMP concentration was between 90 and 95% of the total NTMP concentration. At the time of the maximum degradation rate at about 100 minutes, the Mn^{II} NTMP concentration is 0.65 mM. In the heterogeneous experiment shown in Figure 6, almost all Mn^{II} is complexed by NTMP. At the time of the maximum degradation rate at about 50 min, the concentration of Mn^{II} –

NTMP is only 0.06 mM, due to the low dissolved Mn^{II} concentration. The contribution of the homogeneous reaction to the overall degradation of NTMP is therefore small. These findings can be explained in two different ways:¹ A MnOOH – Mn^{II} –NTMP ternary complex may form on the surface that is more reactive toward O_2 than the Mn^{II} –NTMP solution complex; or² the oxidation of Mn^{II} (adsorbed) to Mn^{III} (adsorbed) by O_2 and rereduction by NTMP (or Mn^{II} NTMP(aq)) may set up a catalytic redox cycle on the surface that is faster than alternative oxidation pathways (e.g., direct reaction of NTMP with MnOOH surface sites, Mn^{II} -catalyzed NTMP autoxidation in solution). Distinctive redox pathways arising from the formation of metal ion–ligand complexes have been postulated in the past. The oxidation of Co^{II} EDTA by molecular oxygen is very slow in homogeneous solution.⁵² Co^{II} EDTA adsorbed to goethite ($\alpha\text{-FeOOH}$), however, is rapidly oxidized to Co^{III} EDTA by Fe^{III} in the presence and absence of oxygen.^{53,54} The difference to our work is that Co^{III} EDTA is stable while Mn^{III} –NTMP undergoes oxidative degradation. Co^{II} EDTA is also rapidly oxidized by MnO_2 to Mn^{III} EDTA, under reduction of the manganese oxide. Dissolved oxygen is then reoxidizing the active surface site.⁵⁵

The carbon–phosphorus bond has been considered to be very stable toward hydrolytic cleavage as well as oxidative and thermal decomposition.^{56,57} On the other hand, rapid radical-based dephosphorylation of organophosphonates has been observed during biodegradation by *Escherichia coli*.⁵⁸ The results reported here show that both C–N and C–P bonds of aminopolyposphonates are susceptible toward rapid oxidative cleavage in the presence of manganese. In O_2 -free MnOOH suspensions, C–N bond cleavage takes precedence over C–P bond cleavage, and IDMP is the sole phosphonate-containing product. When O_2 is present, however, C–N and C–P bond cleavage occur at more comparable rates, such that R-IDMP products can be found, as well as IDMP.

Acknowledgment. B.N. gratefully acknowledges financial support by the Swiss National Science Foundation and the Novartis Foundation, Basel, Switzerland. Additional funding was provided by Grant R82-6376, U.S. Environmental Protection Agency—National Center of Environmental Research and Quality Assurance (Office of Exploratory Research).

References and Notes

- (1) Motekaitis, R. J.; Hayes, D.; Martell, A. E. *Can. J. Chem.* **1979**, *57*, 99.
- (2) Motekaitis, R. J.; Cox, X. B.; Taylor, P.; Martell, A. E.; Miles, B.; Tvedt, T. J. *Can. J. Chem.* **1982**, *60*, 1207.
- (3) Booy, M.; Swaddle, T. W. *Can. J. Chem.* **1977**, *55*, 1770.
- (4) Motekaitis, R. J.; Martell, A. E.; Hayes, D.; Frenier, W. W. *Can. J. Chem.* **1980**, *58*, 1999.
- (5) McArdell, C. S.; Stone, A. T.; Tian, J. *Environ. Sci. Technol.* **1998**, *32*, 2923.
- (6) Klewicki, J. K.; Morgan, J. J. *Geochim. Cosmochim. Acta* **1999**, *63*, 3017.
- (7) Martell, A. E.; Motekaitis, R. J.; Fried, A. R.; Wilson, J. S.; MacMillan, D. T. *Can. J. Chem.* **1975**, *53*, 3471.
- (8) Kaslina, N. A.; Polyakova, I. A.; Kessenikh, A. V.; Zhadanov, B. V.; Rudomino, M. V.; Churilina, N. V.; Kabachnik, M. I. *J. Gen. Chem. USSR* **1985**, *55*, 472.
- (9) Schowaneck, D.; Verstraete, W. *J. Environ. Qual.* **1991**, *20*, 769.
- (10) Steber, J.; Wierich, P. *Chemosphere* **1987**, *16*, 1323.
- (11) Nowack, B.; Stone, A. T. *Environ. Sci. Technol.* **2000**, *34*, 4759.
- (12) Grinstead, R. R. *Biochemistry* **1964**, *3*, 1308.
- (13) Florence, T. M.; Stauber, J. L. *Sci. Total Environ.* **1989**, *78*, 233.
- (14) Lloyd, R. *Chem. Res. Toxicol.* **1995**, *8*, 111.
- (15) Tyson, C. A.; Martell, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 939.
- (16) Nishida, Y.; Tanaka, N.; Yamazaki, A.; Tokii, T.; Hashimoto, N.; Ide, K.; Iwasawa, K. *Inorg. Chem.* **1995**, *34*, 3616.

- (17) Gledhill, W. E.; Feijtel, T. C. J. In *The Handbook of Environmental Chemistry*; Hutzinger, O., Ed.; Springer-Verlag Berlin, Heidelberg, 1992; Vol. 3, Part F, pp 261–285.
- (18) Gerbino, A. J. Masters Thesis, Rice University, Houston, Texas, 1994.
- (19) Schowanek, D.; Verstraete, W. *Appl. Environ. Microbiol.* **1990**, 56, 895.
- (20) Horstmann, B.; Grohmann, A. *Vom Wasser* **1988**, 70, 163.
- (21) Nowack, B. *Water Res.* **1998**, 32, 1271.
- (22) Nowack, B. *J. Chromatogr., A* **2001**, 942, 185.
- (23) Martell, A. E.; Smith, R. M.; Motekaitis, R. J. *Critically selected stability constants of metals complexes database*, Version 4.0, NIST, 1997.
- (24) Nowack, B. *J. Chromatogr., A* **1997**, 773, 139.
- (25) American Public Health Association; American Water Works Association; Water Pollution Control Federation, *Standard methods for the examination of water and wastewater*, 17th ed.; 1989.
- (26) Tanner, R. L.; Meng, Z. *Environ. Sci. Technol.* **1984**, 18, 723.
- (27) Klassen, N. V.; Marchington, D.; McGowan, H. C. E. *Anal. Chem.* **1994**, 66, 2921.
- (28) Riley, D. P.; Fields, D. L.; Rivers, W. *Inorg. Chem.* **1991**, 30, 4191.
- (29) Riley, D. P.; Fields, D. L. *J. Am. Chem. Soc.* **1992**, 114, 1881.
- (30) Karametaxas, G.; Hug, S. J.; Sulzberger, B. *Environ. Sci. Technol.* **1995**, 29, 2992.
- (31) von Sonntag, C.; Munoz, F. J. *Chem. Soc. Perkin Trans. 2* **2000**, 2029.
- (32) Kurochkina, L. V.; Pechurova, N. I.; Snezhko, N. I.; Spitsyn, V. I. *Russ. J. Inorg. Chem.* **1978**, 23, 148.
- (33) Bondietti, G.; Sinniger, J.; Stumm, W. *Colloids Surf. A* **1993**, 79, 157.
- (34) Stone, A. T.; Morgan, J. J. *Environ. Sci. Technol.* **1984**, 18, 617.
- (35) Nico, P. S.; Zasoski, R. J. *Environ. Sci. Technol.* **2001**, 35, 3338.
- (36) Laiti, E.; Ohman, L. O.; Nordin, J.; Sjöberg, S. J. *Colloid Interface Sci.* **1995**, 175, 230.
- (37) Nowack, B.; Stone, A. T. *J. Colloid Interface Sci.* **1999**, 214, 20.
- (38) Nowack, B.; Stone, A. T. *Environ. Sci. Technol.* **1999**, 33, 3627.
- (39) Riley, D. P.; Fields, D. L.; Rivers, W. *J. Am. Chem. Soc.* **1991**, 113, 3371.
- (40) Archibald, F. S.; Fridovich, I. *Arch. Biochem. Biophys.* **1982**, 214, 452.
- (41) Howie, J. K.; Sawyer, D. T. *J. Am. Chem. Soc.* **1976**, 98, 6698.
- (42) Tyson, C. A.; Martell, A. E. *J. Am. Chem. Soc.* **1972**, 94, 939.
- (43) Morgan, J. J. In *Principles and applications of water chemistry*; Faust, S., Hunter, J., Eds.; Wiley: New York, 1967; p 561.
- (44) Bilinski, H.; Morgan, J. J. In *Abstracts for the Division of Water, Air, and Waste Chemistry*; American Chemical Society: Washington, DC, 1970; p 32.
- (45) Klewicki, J. K.; Morgan, J. J. *Environ. Sci. Technol.* **1998**, 32, 2916.
- (46) Mehta, M.; Nagori, R. R.; Mehrotra, R. N. *Ind. J. Chem.* **1998**, 37A, 234.
- (47) Ponce de Leon, C.; Pletcher, D. *J. Appl. Electrochem.* **1995**, 25, 307.
- (48) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *Chem. Phys. Lett.* **1981**, 77, 3371.
- (49) Pick-Kaplan, M.; Rabani, J. *J. Phys. Chem.* **1976**, 80, 1840.
- (50) Anis, S. S.; Mansour, M. A.; Khalil, L. H. *J. Chim. Phys.* **1991**, 88, 643.
- (51) Rizkalla, E. N.; Anis, S. S.; Khalil, L. H. *Polyhedron* **1987**, 6, 403.
- (52) Jardine, P. M.; Jacobs, G. K.; O'Dell, J. D. *Soil Sci. Soc. Am. J.* **1993**, 57, 954.
- (53) Xue, Y.; Traina, S. J. *Environ. Sci. Technol.* **1996**, 30, 1975.
- (54) Brooks, S. C.; Taylor, D. L.; Jardine, P. M. *Geochim. Cosmochim. Acta* **1996**, 60, 1899.
- (55) Fendorf, S.; Jardine, P. M.; Patterson, R. R.; Taylor, D. L.; Brooks, S. C. *Geochim. Cosmochim. Acta* **1999**, 63, 3049.
- (56) Blackburn, G. M. *Chem. Ind. (London)* **1981**, 7, 134.
- (57) Goldwhite, H. *Introduction to Phosphorus Chemistry*; Cambridge University Press: Cambridge, 1981.
- (58) Frost, J. W.; Loo, S.; Cordeiro, M. L.; Li, D. *J. Am. Chem. Soc.* **1987**, 109, 2166.