Environ. Sci. Technol. **2000**, *34,* 4759−4765

Degradation of Nitrilotris(methylenephosphonic Acid) and Related (Amino)Phosphonate Chelating Agents in the Presence of Manganese and Molecular Oxygen

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Phosphonates are used in an increasing variety of industrial and household applications including cooling waters systems, oil production, textile industry, and detergents. Phosphonates are not biodegraded during wastewater treatment but instead are removed by adsorption onto sludge. This study investigates the degradation of phosphonates in the presence of Mn^{II} and molecular oxygen. The half-life for the reaction of nitrilotris(methylene)phosphonic acid (NTMP) in the presence of equimolar Mn^{II} and in equilibrium with 0.21 atm O_2 is 10 min at pH 6.5, with the reaction occurring more slowly under more alkaline or acidic pH values. The presence of other cations such as Ca^{II}, Zn^{II}, and Cu^{II} can considerably slow the reaction by competing with Mn^{II} for NTMP. Catalytic Mn^{II} is regenerated in cyclic fashion as the reaction takes place. Although generation of a Mn^{III}-containing intermediate appears likely, electron transfer within the ternary complex $O_2-Mn^{II}-$NTMP cannot be completely ruled out. Formate ion, orthophosphate ion, imino(dimethylene)phosphonic acid and *N*-formyl imino-(dimethylene)phosphonic acid breakdown products have been identified. This work indicates that manganese-catalyzed thermal autoxidation of commercial (amino)-phosphonate chelating agents is likely to be an important degradation mechanism in natural waters.

Introduction

Metal ions are relevant to the environmental chemistry of all chelating agents. The presence (and identity) of a coordinated metal ion can substantially affect chelating agent adsorption (*1*−*3*), precipitation (*4*), ligand-assisted dissolution (*5*), thermal degradation (*6*), photodegradation (*7*), and biodegradation (*8*). Ecotoxicological effects of chelating agents arise from their ability to solubilize toxic metal ions from sediments (*9*) and sequester nutrient metal ions (*10*).

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. U.S. use of the industrial scale control reagent and co-builder nitrilotris(methylene)-phosphonic acid (NTMP) (Table 1), for example, exceeds 4 × 10^6 kg/yr (*11*). Phosphonates are not biodegraded during conventional wastewater treatment (*12*−*14*) but are removed by adsorption onto biosolids (*13*, *14*) and onto ferric flocs used in tertiary treatment (*15*, *16*). Hence, the speciation, transformations, and ecotoxicology of phosphonates in a wide range of environmental media are important. Like carboxylates (*7*), phosphonates resist photodegradation in the absence of metal ion coordination but readily photodegrade when complexed to Fe^{III} (*17*). Radical-generating solutions (H_2O_2 plus Mn^{II}, Fe^{II}, or Cu^{II}; riboflavin plus 450 nm light) also degrade phosphonates (*18*).

TABLE 1: Names, Abbreviations, and Log *K* Values of the Mn^{II} Complexes of the Phosphonates Used in This Study

abbreviation	name	log K^a
NTMP	nitrilotris(methylene)phosphonate	11.9*
IDMP	iminodi(methylene)phosphonate	7.3*
FIDMP	*N*-formyl iminodi(methylene)-phosphonate	
HEDP	1-hydroxyethane-1,1-diphosphonate	6.9**
EDTMP	ethylenediaminetetra(methylene)-phosphonate	14.7**
DTPMP	diethylenetriaminepenta(methylene)-phosphonate	13.6*

[a] Log *K*: $Mn^{2+} + L^{n-} = MnL^{(2-n)}$. Log *K* values from ref *31* denoted by * and from ref *35* denoted by **; calculated for $I = 0.01$ M.

Schowanek and Verstraete (*18*) observed a 1% loss of ethylenediaminetetra(methylene)phosphonate (EDTMP) and diethylenetriaminepenta(methylene)phosphonate (DTPMP) per day in nonilluminated, metal ion-free and H_2O_2-free solutions. Amending solutions with a 810 μM Ca^{II}, 170 μM Mg^{II}, and 71 μM Fe^{II} mixture slightly increased EDTMP and DTPMP degradation rates and increased rates of 1-hydroxyethane-1,1,-diphosphonate (HEDP) and NTMP degradation to discernible levels. Steber and Wierich (*14*) observed substantial loss of NTMP in nonilluminated solutions amended with a Mg^{II}, Ca^{II}, Mn^{II}, Fe^{III}, Co^{II}, Cu^{II}, and Zn^{II} mixture and in groundwater, river water, reservoir water, and tap water samples. Degradation was relatively fast (e.g., complete loss within 48 h) in some solutions. The degradation products hydroxymethylphosphonic acid (HMP), aminomethylphosphonic acid (AMP), imino(dimethylene)phosphonic acid (IDMP), and CO_2 were monitored over time in river water samples using HPLC.

At room temperature in the presence of 0.21 atm O_2, $Fe^{II}-$aminocarboxylate complexes (e.g., with NTA or EDTA) are oxidized far more rapidly than free Fe^{2+}(aq) (*19*, *20*). Once the corresponding $Fe^{III}-$aminocarboxylate complex has formed, no intramolecular ligand oxidation takes place. Under more stringent conditions (800 psig O_2 at 85 °C, Mn^{II} or Co^{II} catalyst, pH ∼ 1), oxidative degradation of the mixed carboxylate−phosphonate ligand *N*-(phosphonomethyl)-iminodiacetic acid has been observed (*21*). Nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and bis(phosphonomethyl)glycine, in contrast, are not subject to oxidative degradation under the conditions just described. Under hydrothermal conditions (125−300 °C), direct and metal ion-catalyzed decarboxylation and C−N bond cleavage reactions have been observed with NTA, EDTA, and NTMP (*22*−*25*). Progressive loss of ligand-donor groups eventually generates products that do not effectively coordinate metal ions and hence do not further degrade via metal ion-catalyzed pathways (*24*).

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10.1021/es0000908 CCC: $19.00
Published on Web 10/21/2000

Using oxidants such as MnO_2 and MnO_4^-, Mn^{III} complexes with EDTA, EDTMP, and NTMP have been synthesized. All such Mn^{III} complexes undergo intramolecular electron transfer and degradation of the coordinated chelating agent, even under room temperature, near-neutral pH conditions (*6*, *26*−*28*). Additionally, EDTA and NTA brought into contact with $Mn^{III}OOH$(s) are rapidly oxidized (*29*, *30*).

Although prior work by Schowanek and Verstraete (*18*) and Steber and Wierich (*14*) indicated that phosphonate degradation occurs under nonilluminated conditions, the presence of multiple metal ions prevented the investigators from identifying the metal ion reactant or catalyst responsible. To rectify this situation, we have completed a series of single metal ion experiments involving NTMP and six commonly occurring metal ions (Mg^{II}, Ca^{II}, Mn^{II}, Fe^{II}, Cu^{II}, and Zn^{II}). The presence of both Mn^{II} and O_2 was found to be necessary in order for NTMP degradation to occur. Experiments performed across a wide pH range with other phosphonates (HEDP, EDTMP, and DTPMP) and in the presence of competitor metal ions highlight the importance of Mn^{II}−phosphonate complex formation in promoting degradation. We conclude that degradation arises from manganese-catalyzed autoxidation.

Materials and Methods

Reagents. Reagent grade water (DDW, 18 MΩ·cm resistivity) was generated using a glass distillation apparatus and a Milli-Q reagent-grade water system (Millipore Corp.) and was used to prepare all solutions and suspensions. All glassware was cleaned in a 10 g/L ascorbic acid solution for several hours to dissolve any manganese oxides and rinsed several times with double-distilled water (DDW) prior to use. $MgCl_2·2H_2O$, $CaCl_2$, $Mn^{II}Cl_2·H_2O$, $FeCl_3·6H_2O$, $CuCl_2·2H_2O$, and $ZnCl_2·2H_2O$ (Baker analytical grade) were used to prepare metal ion stock solutions (acidified to pH 3 with HCl). The Mn^{II} stock solution was filtered to remove particulate impurities. NTMP, IDMP, HEDP (Table 1), hydroxymethylphosphonic acid (HMP), aminomethylphosphonic acid (AMP), and methylphosphonic acid (MP), all in the acid form, were purchased from Fluka. EDTMP, DTPMP, and methyl-IDMP, all in the acid form, were provided by Monsanto. Na_2HPO_4 and sodium formate (Baker analytical-grade reagent) were used as phosphate and formate standards, respectively. The organic buffers MES [2-(*N*-morpholino)-ethanesulfonic acid], MOPS [3-(*N*-morpholino)propanesulfonic acid], and HEPES [4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid] were obtained from Fluka.

Preparation of an *N*-Formyl Imino(dimethylene)phosphonic Acid (FIDMP) Stock Solution. FIDMP-containing solution was prepared as follows: 5 g of NTMP, 0.8 g of $Mn^{II}Cl_2·H_2O$, and 5 g of NaOH were dissolved in 1000 mL of DDW (pH 5.5) and sparged with air for 2 days at room temperature. The solution was passed over 20 g of cation-exchange resin (Dowex 50W) to remove the manganese, and the volume was reduced to approximately 60 mL using a rotary evaporator (Buchi Corp.). The solution was neutralized to pH 7 using NaOH. Addition of 120 mL of ethanol induced phase separation. The lower layer was dense and syrupy and contained all the FIDMP. After discarding the upper layer, the lower layer was dissolved in 100 mL of DDW. Again, 120 mL of ethanol was used to induce phase separation. The upper layer was again discarded, and the lower layer was dissolved in 100 mL of water.

Experimental Design. All experiments were conducted in brown glass bottles (to minimize photodegradation) placed in a constant-temperature bath at 25 °C and stirred with Teflon-coated stir bars. Glass electrode/reference electrode combinations for pH determination were calibrated using buffer solutions prepared using NIST-standardized formulas (Fisher Corp.).

All solutions contained 10 mM $NaNO_3$ and HNO_3 (pH < 3.5), 4.0 mM acetate (4.0 < pH < 5.0), MES (4.9 < pH < 6.1), MOPS (6.5 < pH < 7.2), or HEPES (7.2 < pH < 8.0) buffer. On the basis of reported equilibrium constants (*31*), these buffer reagents should have a negligible effect on the speciation of metal ions in our experiments. Experiments performed in the presence and absence of each buffer confirmed this expectation.

Time Course Experiments. O_2 was introduced into the solutions used for the time course experiments by stirring in contact with laboratory air for at least 30 min prior to the addition of all stock solutions and during the entire course of the experiment. Saturation with respect to 0.21 atm O_2 [i.e., 290 μM O_2(aq)] was assumed since active sparging with laboratory air had no discernible effect on experimental results. O_2-free experiments were performed in a controlled-atmosphere glovebag containing 96% N_2, 4% H_2, and a catalyst (Coy Laboratory Products.)

$NaNO_3$ electrolyte and buffer were added first. Mg^{II} and Ca^{II} were added at 1 mM concentrations while Mn^{II}, Fe^{III}, Cu^{II}, and Zn^{II} were added at 10 μM concentrations. NTMP and other phosphonate parent compounds were added last, at 10 μM concentrations.

Degradation was only observed in solutions containing both O_2 and Mn^{II}. The Mn-catalyzed reaction could be effectively quenched by adding 3 mL of reaction solution to 60 μL of a 1 mM Fe^{III} solution and 80 μL of a 0.1 mM HNO_3 solution (resulting in 3.0 < pH < 3.5). Low pH and formation of Fe^{III}−phosphonate complexes are believed to interfere with Mn^{II}−phosphonate complex formation.

Product studies were conducted at millimolar levels of NTMP and Mn^{II}. The solutions were sparged constantly with air. No buffer was used because the buffering capacity of NTMP is sufficient at this concentration. For analysis by ion chromatography, the reaction was stopped by adding aliquots of the reaction mixture (3 mL) to a vial containing 0.12 mL of a 0.1 M EDTA solution and enough NaOH to raise the pH to 8.5. For HPLC analysis, the reaction was stopped as described above by diluting 100-fold into 3 mL of DDW containing 60 μL of 1 mM Fe^{III} and 80 μL of 0.1 mM HNO_3.

Plots of the logarithm of the NTMP concentration as a function of time were not always linear, indicating deviation from pseudo-first-order behavior. The half-life for each trial is therefore defined as the time when 50% of the initial NTMP concentration remains; the half-life does not relate in any consistent way to a reaction rate constant.

Analysis of Parent Compounds and Degradation Products. Parent compounds were analyzed using an ion-pair HPLC method (*32*). Sample solution (3 mL) and 1.0 mM $Fe(NO_3)_3$/10 mM HNO_3 solution (0.1 mL) were mixed and left for 2 h at room temperature, generating Fe^{III}−phosphonate complexes that absorb at 260 nm. Unlike the originally published method, no $NaHCO_3$/tetrabutylammonium bromide (TBA-Br) buffer solution was added prior to HPLC injection. (It was found that the higher pH resulting from buffer solution addition encouraged phosphonate oxidation.) The HPLC mobile phase consisted of 76% 20 mM $NaHCO_3$/1 mM TBA-Br and 24% acetonitrile. Detection limits were 0.5 μM for HEDP, 0.05 μM for NTMP and EDTMP, and 0.1 μM for DTPMP. Orthophosphate was determined using the molybdenum blue colorimetric method (*33*). Other degradation products were determined using a Dionex 2010i ion chromatograph, which employed conductivity detection after chemical suppression. IDMP, methyl-IDMP, and FIDMP were analyzed using an AG11 column (Dionex Corp.) and 30 mM Na_2CO_3 eluent solution. Formate was analyzed using the same column and 5 mM NaOH eluent solution.

Identification of FIDMP. The FIDMP stock solution was analyzed by ion chromatography. Using authentic standards, two quickly eluting anions (phosphate and formate) and one

TABLE 2. Mass Spectrum of an NTMP Degradation Product for Which an Authentic Standard Was Not Available[a]

m/z	relative intensity (%)	tentative assignment
93	19	$P(OCH_3)_2^+$
110	10	$P(OH)(OCH_3)_2^+$
124	79	$CH_2P(OH)(OCH_3)_2^+$
152	100	$HC(O)N{=}CHP(OH)_2(OCH_3)^+$
166	5	$HC(O)NCH_2P(O)(OCH_3)_2^+$
260	10	$N(CH_2P(O)(OCH_3)_2)_2^+$
289	44	$HC(O)N(CH_2P(O)(OCH_3)_2)_2^+$

[a] Based on assignments by Klinger et al. (*34*).

slowly eluting anion (IDMP) were quickly identified. An additional slowly eluting anion required identification by other means. It was established using standards that the unknown was neither methyl-IDMP nor a monophosphonate (HMP, AMP, or MP). The formate concentration in the sample equaled the IDMP concentration. It can be concluded that formate production (indicating C−N cleavage) accompanies IDMP production but does not accompany production of the unidentified anion. A sample was derivatized using diazomethane, which converts phosphonate groups into phosphonic acid methyl esters and carboxylates into carboxylic acid methyl esters (*34*). The derivatized sample was analyzed using GC/MS (*34*) on a Hewlett-Packard 5890 GC equipped with a HP5970 mass spectrometer detector under electron impact ionization. A peak corresponding to tetramethyl-IDMP was easily identified based upon its molecular ion *m*/*z* of 261 and fragments indicating a methylated phosphonic acid (*34*). A second unknown peak yielded a molecular ion at *m*/*z* 289, consistent with the tetramethyl ester of FIDMP. Other attributes of the GC/MS spectrum (Table 2) are consistent with this assignment.

Characterization of the FIDMP Stock Solution. Using the ion-pair HPLC method, it was determined that the amount of residual NTMP in the 100 mL FIDMP-containing solution was negligible. Ion chromatography revealed the presence of three anions: orthophosphate, which was quantified using the colorimetric technique described earlier (*33*); IDMP, which was quantified using the available authentic standard; and an anion corresponding to the peak described in the preceding section and assigned to the degradation product FIDMP. Total phosphorus was determined using persulfate digestion (*33*) followed by the orthophosphate colorimetric method (*33*). By subtracting the orthophosphate and IDMP concentrations from total phosphorus, the FIDMP concentration was determined. The standard solution was found to contain 0.13 M FIDMP with a purity of 90%.

Thermodynamic Speciation Modeling. All log *K* values for phosphonate and metal speciation were taken from the Critical Database (*31*) or from Rizkalla (*35*) and adjusted to 0.01 M ionic strength using the Davies equation. The formation constant of the unprotonated Mn^{II}−phosphonate complex is given in Table 1. All calculations have been performed using the program ChemEQL 2.0 (*36*).

Results

Degradation of NTMP in the Presence of Metals. Our first experiment examined the loss of NTMP in nonilluminated, Baltimore City tap water (pH 7.9). Using the ion-pair HPLC technique described earlier, a 70% loss was observed during a 7-day period, corresponding to a half-life of approximately 4 days. Although the pH of the tap water used by Steber and Wierich (*14*) is not known, their reported half-life of 5.7 days compares favorably with our result. Addition of 10 μM EDTA, a stronger chelating agent than NTMP (*31*), completely prevented NTMP degradation. It can be concluded that one

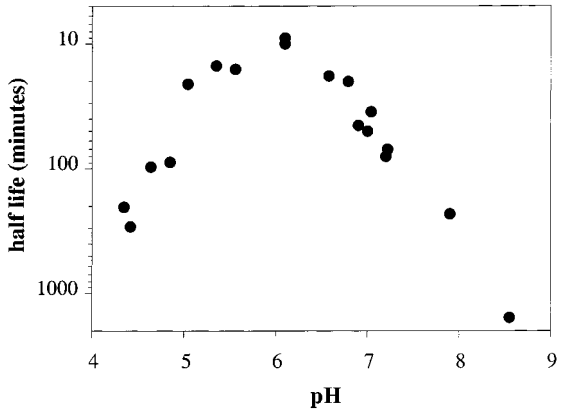

FIGURE 1. Effect of pH on the half-life of 10 μM NTMP degradation following addition of 10 μM Mn^{II}.

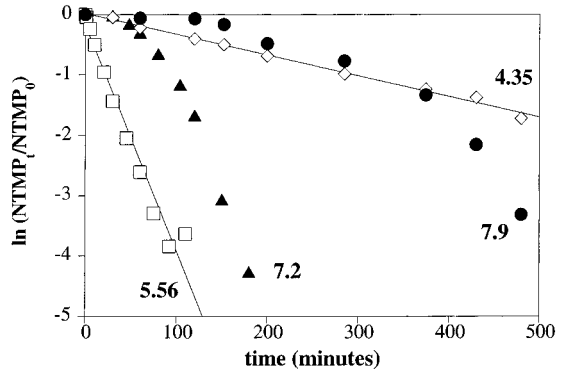

FIGURE 2. Loss of NTMP as a function of time in the presence of 10 μM Mn^{II} for 4 of the 18 runs shown in Figure 1.

or more trace metals at concentrations less than 10 μM are involved in the degradation reaction.

Steber and Wierich (*14*) had reported rapid NTMP degradation in a nonilluminated solution containing millimolar levels of Na, K, Ca, and Mg and less than 1 μM levels of Mn^{II}, Fe^{III}, Cu^{II}, Co^{II}, Zn^{II}, H_3BO_3, and $Na_2MoO_4{\cdot}2H_2O$. We attempted to replicate this experiment using our own reagent-grade water and a solution with the same composition as described in ref *13* and found no evidence for degradation during a 7-day period.

The degradation of 10 μM NTMP was investigated in a series of single metal ion experiments performed in 4 mM MES (pH 5.6)/10 mM $NaNO_3$ medium. During 10 days of investigation, no degradation was observed in metal ion-free solutions, in solutions containing Ca or Mg in 100-fold excess, or in solutions containing equimolar concentrations of Fe^{III}, Cu^{II}, or Zn^{II}. In contrast, rapid NTMP degradation was observed in solutions containing equimolar concentrations of Mn^{II}. We conclude that Mn^{II} is responsible for the degradation of NTMP in natural waters and have concentrated our further efforts to elucidate the kinetics, mechanism, and products of the reaction.

Degradation of NTMP in the Presence of Mn^{II}. The effect of pH on NTMP degradation is illustrated in Figure 1. Equimolar NTMP and Mn^{II} concentrations (10 μM) were employed, and contact with air (0.21 atm O_2) was maintained. Degradation is most rapid at pH 6.1, yielding a half-life of 9 min. Decreasing the pH to 4.4 increases the half-live to 5 h. Similarly, increasing the pH to 8.6 increases the half-life to 26 h. Results from 4 of the 18 time course experiments are presented in Figure 2 to illustrate the effects of pH. Between pH 4.5 and pH 6.5, the logarithm of the total NTMP concentration plotted against time is linear, indicating pseudo-first-order kinetics. Above pH 7, an initial lag period

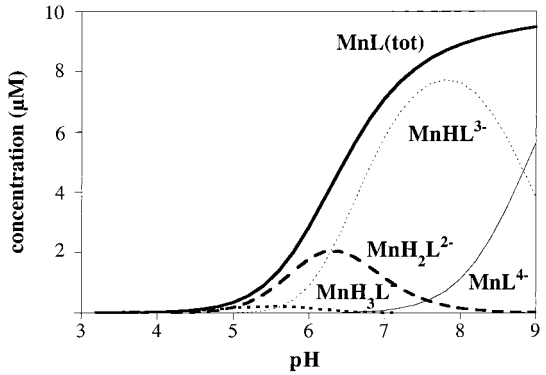

FIGURE 3. Speciation of 10 μM NTMP in the presence of 10 μM Mn^{II} calculated with the constants from ref *31* and adjusted to 0.01 M ionic strength.

is observed, indicating autocatalysis. The duration of the lag period increases with increasing pH. Figure 3 shows the calculated speciation of NTMP as a function of pH under the conditions of the experiments. Complexation of Mn^{II} by NTMP starts at pH 4. At pH 6, where the degradation rate is maximal, only about one-third of the Mn^{II} is complexed by NTMP.

As shown in Figure 3, complete NTMP degradation can be achieved when the added Mn^{II} concentration is two-fifths and even one-fifth of the NTMP concentration. At the pH employed in these experiments (pH 6.0), plots of ln[NTMP] versus time are linear at all Mn^{II} concentrations considered, indicating that the reaction is first-order with respect to [NTMP].

Equilibrium calculations have been applied to the experiments shown in Figure 4. As the total Mn^{II} concentration is increased from 1.9 to 3.7, 9.3, and finally 27 μM, the sum of four possible Mn^{II}–NTMP complexes ($Mn^{II}H_3$NTMP, $Mn^{II}H_2$NTMP, Mn^{II}HNTMP, and Mn^{II}NTMP) increases from 0.61 to 1.2, 2.3, and finally 5.1 μM. Despite the fact that the percentage of NTMP complexed with Mn^{II} continues to increase nearly linearly with increasing Mn^{II} concentration, the rate constant for loss of NTMP reaches a plateau when less than 25% of total NTMP is complexed.

Experiments presented in Figure 5(pH 7.0) provide important clues regarding the NTMP degradation mechanism. If O_2 is excluded from the reaction medium (using a controlled atmosphere glovebag), no NTMP degradation in the presence of Mn^{II} is observed (filled squares). All other experiments presented in Figure 5 were left open to laboratory air (0.21 atm O_2). 100, 200, and 500 μM Ca yield a slight decrease in the Mn^{II}-catalyzed degradation rate; 10 μM Zn^{II} causes a strong decrease in the degradation rate; and 10 μM Cu^{II} completely inhibits NTMP degradation in the presence of Mn^{II}. In all of these experiments, loss of NTMP as a function of time follows first-order kinetics.

Equilibrium calculations were again applied to the experimental data. As shown in the insert of Figure 5, the inhibitory effects of adding Ca, Zn^{II}, and Cu^{II} can be explained by decreases in the sum of the four possible Mn^{II}–NTMP complexes.

Degradation of Other Phosphonates. As shown in Figure 6, rates of phosphonate-containing ligand degradation in the presence of Mn^{II} and O_2 (at pH 5.6) decrease in the following order: NTMP (21 min half-life) > EDTMP (4 h half-life) > DTPMP (25 h half-life) ≫ HEDP. HEDP degradation was not discernible during the 3-day experiment. The degradation products IDMP and FIDMP also showed no change in concentration in the presence of Mn^{II} over a 2-day period at pH 7.

Product Identification. To obtain product concentrations within the working ranges of our analytical methods, a series

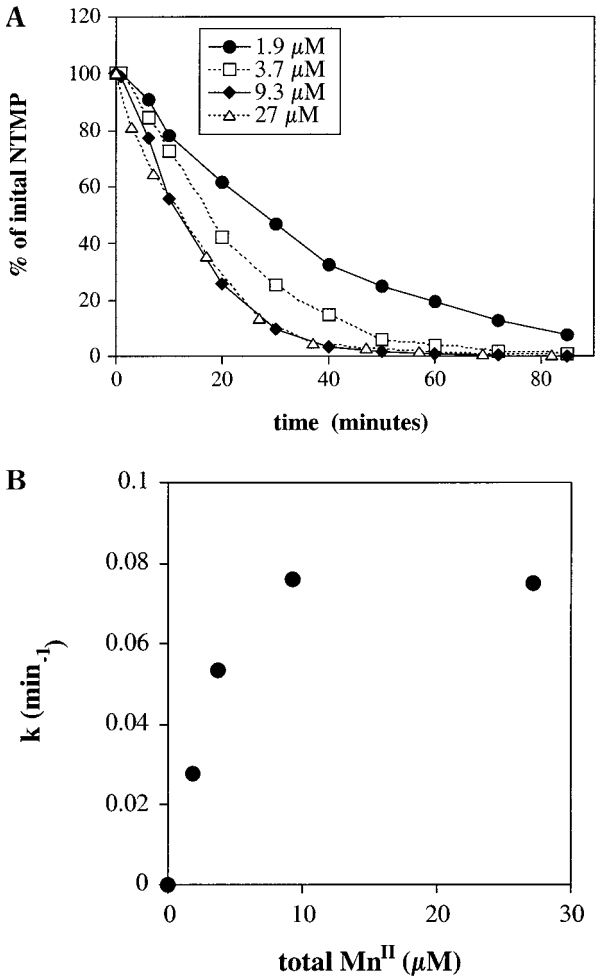

FIGURE 4. (A) Effect of Mn^{II} concentration on degradation of 10 μM NTMP as a function of time at pH 6.0. (B) First-order rate constant as a function of the total added Mn^{II}.

of experiments employing 0.85 mM concentrations of NTMP and Mn^{II} were performed. Figure 7 shows concentrations of NTMP and the four identified degradation products as a function of time at pH 7.0. Mass balance for the sum [NTMP] + [IDMP] + [FIDMP] is obtained, indicating that NTMP loss coincides with production of IDMP or FIDMP. IDMP appears as soon as the reaction begins, while FIDMP appears only after a slight lag period. Concentrations of IDMP are consistently higher than those of FIDMP by a factor of about 4.

The orthophosphate concentration matches the sum [IDMP] + [FIDMP], and the formate concentration nearly matches [IDMP]. Hence, product yields conform to the following two equations:

$$\text{NTMP} \xrightarrow{\text{oxidation}} \text{FIDMP} + \text{orthophosphate} \quad (1)$$

$$\text{NTMP} \xrightarrow{\text{oxidation}} \text{IDMP} + \text{formate} + \text{orthophosphate} \quad (2)$$

The higher Mn^{II} and NTMP concentrations employed in the product identification experiments provide the best opportunity for observing possible Mn^{III} intermediate species spectroscopically. Mn^{III}EDTMP at pH 4.5 has a λ_{max} value at 500 nm and a molar absorptivity of 271 cm^{-1} M^{-1} (*28*). If we assume that Mn^{III}NTMP has similar absorption characteristics, then we should be able to detect 20 μM concentrations (corresponding to approximately 0.005 absorbance unit). No absorbance at 500 nm was observed in our experiments, when 0.85 mM level concentrations were employed. It can therefore be concluded that less than 3% of the manganese

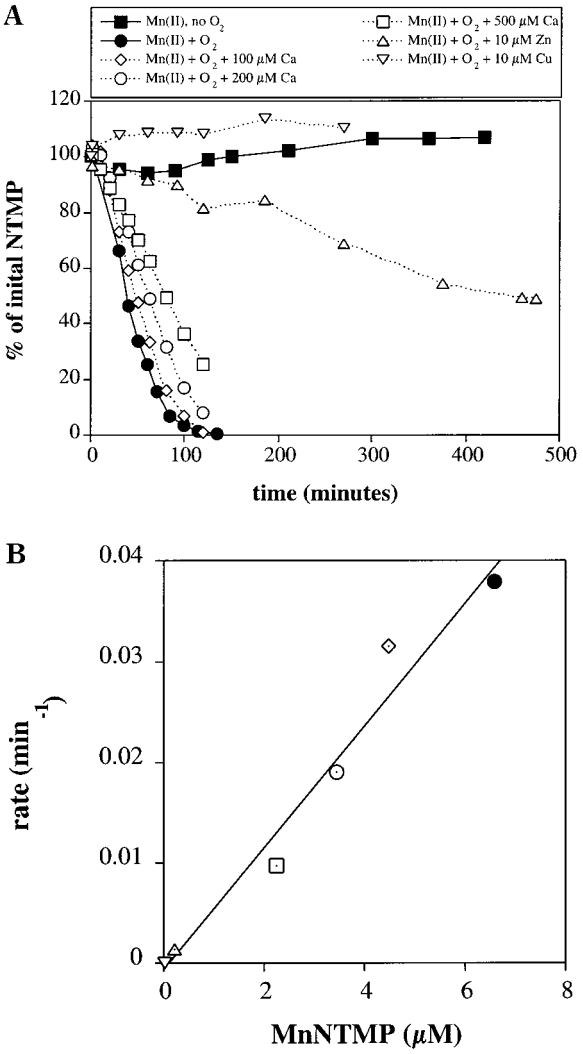

FIGURE 5. (A) Effect of O_2, Ca, Cu, and Zn addition on degradation of 10 μM NTMP as a function of time at pH 7.0. The first experiment was conducted in an O_2-free glovebox. All other experiments were left open to laboratory air (0.21 atm O_2). (B) First-order rate constants as a function of the sum concentrations of all possible Mn−NTMP complexes.

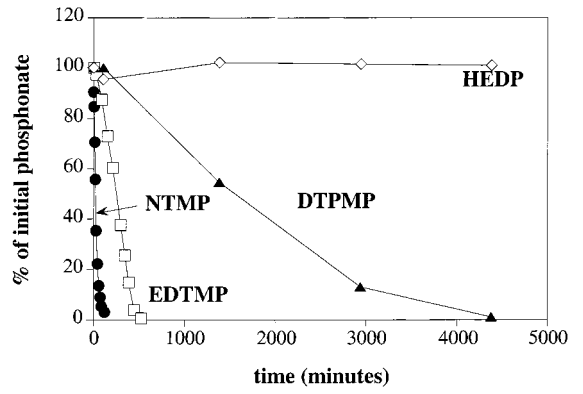

FIGURE 6. Loss of NTMP, EDTMP, DTPMP, and HEDP as a function of time in the presence of 10 μM Mn^{II} (10 μM ligand, pH 5.6).

added to the system is in the +III oxidation state at any given time.

Discussion

Aminopolyphosphonates are used in numerous technical applications due to their high stability against chemical

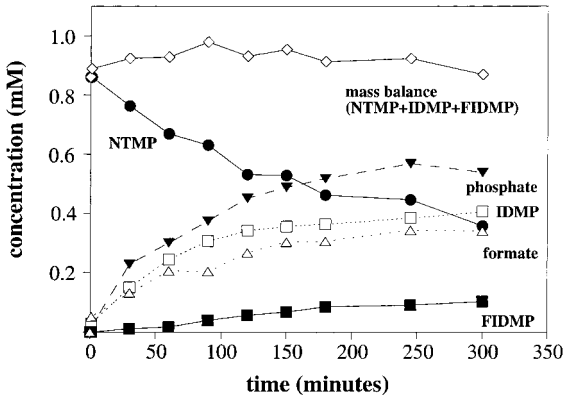

FIGURE 7. Loss of NTMP (0.85 mM) and appearance of four oxidation products as a function of time in the presence of 0.85 mM Mn^{II} (pH 7.1). To ensure constant [O_2(aq)], the solution was constantly bubbled with laboratory air.

degradation and hydrolysis (*11*). This study shows, however, that they are rapidly degraded in the presence of molecular oxygen and Mn^{II}. The reaction is fastest around pH 6.5 with a half-life of 9 min and decreases toward more acidic and alkaline pH values.

The degradation is initiated by a complex formation between Mn^{II} and the phosphonate. This was shown by competition experiments with NTMP and Mn^{II} in the presence of different metal cations with different log *K* values for complex formation with NTMP. Different extents of inhibition (Ca < Zn, Cu) (Figure 5) follow the increase in the stability constants for the respective NTMP complexes (*31*). Cu and Zn form stronger complexes with NTMP than Ca and Mn^{II} and are therefore able to displace more Mn^{II} than Ca. The concentration of Mn^{II}NTMP is rate limiting; hence, complexation of NTMP with metals other than Mn^{II} reduces the reaction rate.

The necessity of molecular oxygen for the reaction to proceed indicates that in fact a redox reaction takes place. In the absence of metals or with nonredox active metals (e.g., Ca, Zn) or metals in the oxidized form (Fe^{III}), no reaction takes place. Therefore, Mn^{II} has to be involved in the oxidation reaction. The experiments at Mn^{II} < NTMP (Figure 4) clearly prove that Mn^{II} has to act as a catalyst and not as a stoichiometric reagent. Complete degradation of NTMP is observed even when Mn^{II} is only 20% of NTMP.

Under the conditions employed in our experiments, Mn^{II} oxidation by molecular oxygen is thermodynamically favorable at pH values greater than 4.9 (*37*). Log *K* values for complexes of NTMP with Mn^{III} are not known, but based on available analogies (e.g., NTA, EDTA), log *K* values for Mn^{III}NTMP should be considerably larger than for Mn^{II}NTMP. Thus, the net effect of adding NTMP should be to (i) increase the thermodynamic driving force for Mn^{II} oxidation at pH values greater than 4.87 and (ii) expand the range of pH where oxidation is possible toward more acidic pH values. Despite favorable ΔG under neutral and slightly alkaline pH conditions, the autoxidation of Mn^{II} in the absence of added ligands is exceedingly slow. At the concentrations employed in most of our experiments (below 10 μM), the half-life for Mn^{II} autoxidation at pH 9.0 is 14.1 days and increases to 141 days at pH 8.5. Half-lives for Mn^{II} autoxidation in the absence of added ligands exceed 1000 days at pH values less than 8.0 (*38*, *39*).

The oxidation of organic compounds in the presence of Mn^{II} and O_2 has previously been observed. The reactions have been explained either by an oxidation of Mn^{II} to Mn^{III} and subsequent oxidation of the organic molecule by Mn^{III} (*40*−*42*) or by an activation of molecular oxygen by Mn^{II}

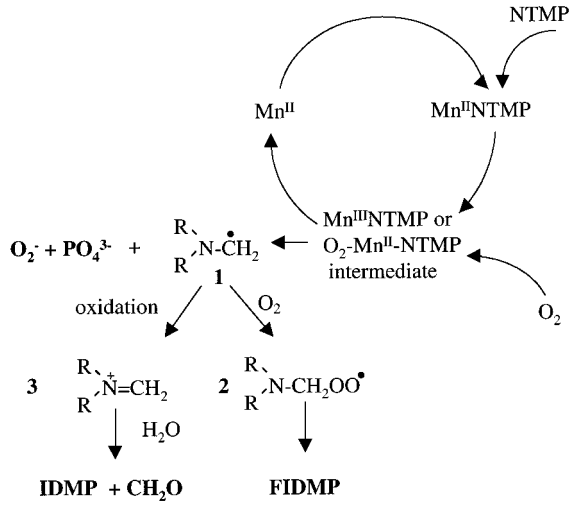

FIGURE 8. Tentative scheme of the degradation of NTMP in the presence of Mn^{II} and O_2.

bound to an organic molecule without involving any change in oxidation state of manganese (*43*, *44*). On one hand, the lack of UV absorption around 500 nm in our system indicates that dissolved Mn^{III} is either not formed or is rapidly reduced to Mn^{II} by oxidizing the phosphonate. On the other hand, the oxidation of NTMP and EDTMP by Mn^{III}−pyrophosphate complexes has been reported (*28*). Hence, additional studies are needed to confirm the existence of the postulated Mn^{III}-containing intermediate.

Table 1 includes available log *K* values for the reaction $Mn^{2+} + L^{n-} \Leftrightarrow MnL^{(2-n)}$. EDTMP and DTPMP, which possess log *K* values higher than for NTMP, are also subject to Mn^{II}-catalyzed autoxidation although at a slower rate. HEDP, IDMP, and presumably FIDMP have log *K* values lower than for NTMP and are not subject to autoxidation within the time scales considered in our experiments. NTMP, EDTMP, and DTPMP possess tertiary amine group(s); IDMP and FIDMP possess a secondary amine group; while HEDP possesses an alcohol group instead of an amine. HEDP was found to be much more stable against oxidation by ozone than NTMP or EDTMP (*34*), which suggests that the presence of an amine group might be important. Although a complete pH dependence has been determined for the Mn^{II}−NTMP−O_2 reaction, results with the other five phosphonates are limited to a single pH value. Hence, drawing conclusions regarding structure−reactivity relationships must wait for completion of pH dependence studies with a number of representative phosphonates.

As shown in the scheme presented in Figure 8, the first oxidation step may occur within a ternary complex involving molecular oxygen (O_2−Mn^{II}−NTMP) or more likely within a Mn^{III}−NTMP complex. Regardless of the nature of this intermediate, it breaks down via intramolecular electron transfer, yielding an NTMP-oxidized intermediate and Mn^{II}. Complexation of Mn^{II} by free NTMP substrate completes the catalytic cycle.

As far as the NTMP oxidation product is concerned, one-electron abstraction from the nitrogen followed by cleavage of a nitrogen−carbon bond yields the carbon-centered methylene radical **1** and orthophosphate ion. The methylene radical is rapidly intercepted by O_2, which is an extremely efficient trapping agent for carbon-centered radicals (*45*), yielding the peroxyl radical **2**. The peroxyl radical can accept a H atom and dehydrate to yield FIDMP. A similar reaction scheme has been proposed for the V^{IV} catalyzed oxidation of *N*-(phosphonomethyl)iminodiacetic acid (*46*). The methylene radical **1** can also be further oxidized to the iminium cation **3** (*21*, *46*), which rapidly hydrolyzes to yield IDMP and formaldehyde. Formaldehyde has been detected in studies of Fe^{III}EDTA photodegradation (*47*) and *N*-(phosphonomethyl)iminodiacetic acid oxidation (*21*). Instead of formaldehyde, we have detected formic acid in our system. A further oxidation of formaldehyde to formic acid may therefore have taken place. The hydrolysis of FIDMP could also produce formate (*21*), but monitoring formate concentration in a FIDMP solution at pH 3 revealed no hydrolysis within a few days. Superoxide ($O_2^{\bullet-}$) and H_2O_2 generated from the reduction of O_2 are likely to be consumed by reaction with Mn^{2+}(aq), Mn^{II}NTMP, or partially oxidized NTMP-derived intermediates. Oxidation of Mn^{II} complexes to Mn^{III} complexes by superoxide ion is known to be rapid (*43*) and may explain the autocatalysis observed at pH values greater than 6.5.

The oxidation products that we have identified are indicative of both C−N and C−P bond cleavage; IDMP, FIDMP, and orthophosphate were observed but not HMP or AMP. The Steber and Wierich study of NTMP-amended water samples (*14*), however, only observed products of C−N bond cleavage; NTMP was converted into HMP and IDMP, which subsequently degraded into HMP and AMP. A different mechanism may be responsible, but details are unclear. It is possible that other metal ions or natural organic matter may participate in the reaction in unanticipated ways.

Environmental Implications. It is well-known that manganese^{III,IV}oxides are facile oxidants for organic compounds (*48*). Our study reveals that Mn^{II}, regenerated in cyclic fashion, can serve as a powerful catalyst for the reactions of O_2. Any ligand that is able to chelate Mn^{II} and increase the rate of Mn^{II} autoxidation (or form a O_2−Mn^{II} ligand complex that activates molecular oxygen) can be degraded via this mechanism. Commercially relevant (amino)phosphonate chelating agents such as NTMP, EDTMP, and DTPMP are very likely to degrade via this mechanism in natural waters.

In environmental media, competitive complexation of chelating agents by other metal ions must definitely be accounted for, since Mn^{II} complexes are the only ones subject to breakdown. In one speciation study, 15% of EDTA in river water and 30% of EDTA in infiltrating groundwater was complexed to Mn^{II} (*49*). Log *K* values for EDTA and NTMP complexation with +II metal ions are comparable, and hence appreciable NTMP complexation and Mn^{II}-catalyzed oxidation should occur.

Although rapid degradation of NTMP was observed, two recalcitrant products were formed. EDTMP and DTPMP should also yield recalcitrant products since oxidation necessarily leads to fewer Lewis base functional groups, less effective chelation, and hence less complexation by Mn^{II}. To date, only one analytical method exists for the determination of phosphonates in natural waters (*32*). This method, however, is not able to measure the breakdown products IDMP and FIDMP. Measurements of phosphonates during wastewater treatment have been reported (*16*), but no other data for phosphonate concentrations in the environment are available. This study shows that not only the parent compounds but also recalcitrant breakdown products should be included in such a field study.

Acknowledgments

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). We thank M. Trehy from Monsanto (St. Louis, MO) for providing samples of EDTMP, DTPMP, and methyl-IDMP.

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Received for review May 2, 2000. Revised manuscript received August 7, 2000. Accepted August 11, 2000.

ES0000908