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OXIDATION OF METAL–DIETHYLENETRIAMINE-PENTAACETATE (DTPA)—COMPLEXES DURING DRINKING WATER OZONATION

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Abstract—This study investigates the oxidative transformation of diethylenetriaminepentaacetate (DTPA), a synthetic ligand, during drinking water ozonation. The rate coefficients for the reactions of CaDTPA^{3-} and ZnDTPA^{3-} with ozone were determined to be 6200 and $3500 \pm 150\,\mathrm{M^{-1}\,s^{-1}}$, respectively. The reactivity of Fe(III)DTPA^{2-} towards ozone was found to be much lower ($<10\ \mathrm{M^{-1}\,s^{-1}}$), but near neutral pH the reactivity of the Fe(III)-complexes is dominated by [Fe(III)(OH)]DTPA^{3-}. For the reaction of Fe[(III)(OH)]DTPA^{3-} with ozone a rate coefficient of $2.4 \pm 0.2 \times 10^5\,\mathrm{M^{-1}s^{-1}}$ was measured. The rate coefficients of the reactions of the ZnDTPA-and Fe(III)DTPA with OH radicals have been determined by a competitive method as $2.4 \pm 0.4 \times 10^9$ and $1.5 \pm 0.1 \times 10^9\,\mathrm{M^{-1}s^{-1}}$, respectively at $\mathrm{pH} = 7$. The degradation of low concentrations of DTPA complexes during ozonation was investigated in natural waters under drinking water relevant conditions. Based on our findings CaDTPA^{3-} and ZnDTPA^{3-} are judged as easily degradable. Fe(III)DTPA complexes showed a somewhat lower reactivity, but were still typically degraded by one order of magnitude at ozone dosages of $\sim 20\,\mu\mathrm{M}$ ($1\,\mathrm{mg\,L^{-1}}$) in the three natural waters tested. Molecular ozone was found to be the major oxidant for the metal–DTPA complexes during ozonation. © 2001 Elsevier Science Ltd. All rights reserved

Key words—ozonation, hydroxyl radical, drinking water, DTPA, EDTA, ligands, oxidation kinetics

INTRODUCTION

Diethylenetriaminepentaacetate (DTPA) is a synthetic ligand that forms stable complexes with most metals and is used in a variety of industrial applications, where free metal ions cause problems such as the formation of insoluble metal salt precipitations or the decomposition of additives or reagents. One of the major industries using DTPA is the paper industry. It has been shown that DTPA can be present in water resources relevant for drinking water production (Ternes *et al.*, 1996). In previous studies, the speciation of EDTA, a similar ligand, in river and ground water was estimated (Kari, 1994; Nowack, 1996). By taking naturally occurring ligands for copper and zinc into account, Fe(III)EDTA, ZnEDTA, Mn(II)EDTA and CaEDTA-complexes have been identified as important species. Based on these results we considered the Ca-, Zn- and Fe(III)DTPA-complexes as a representative selection of DTPA-species in drinking water resources and assessed their reactivity towards ozone. This was then tested for conventional drinking water ozonation processes with ozone dosage in the order of 1–3 $\mathrm{mg\,L^{-1}}$ (20–60 μM). A similar study has been previously carried out with atrazine, where both its disappearance and the formation of degradation products could be successfully predicted (Acero *et al.*, 2000). In the case of atrazine or other organic compounds which do not form metal complexes this seems to be possible with our approach. The present study will include the metal-dependent speciation of an organic compound (DTPA) and show the possibilities and limits of the prediction of its degradation during ozonation processes.

Ozonation can lead to oxidation of micro-pollutants either by the direct reaction of the compounds with molecular ozone or by radicals, mainly $^{\bullet}$OH, produced during the decay of ozone. To define and calibrate an ozonation process with respect to its oxidation capacity, it is necessary to estimate the oxidant concentrations. Whereas ozone can be readily measured, there are no fast and easy methods to determine the OH radical concentration during

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ozonation processes. In a previous study, an experimental approach to determine the concentrations of both ozone and OH radical during ozonation was developed (Elovitz and von Gunten, 1999). The method is based on the measurement of the decrease of a probe compound which reacts fast with OH radicals, but not with ozone and a simultaneous determination of the ozone concentration. The selected probe compound was *p*-chlorobenzoate (*p*CBA), which reacts with OH-radical with a second order rate coefficient $k(\mathrm{OH} + p\mathrm{CBA}) = 5 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and has a low reactivity with ozone $k(\mathrm{O}_3 + p\mathrm{CBA}) = 0.15\ \mathrm{M}^{-1}\mathrm{s}^{-1}$. The probe compound is used in low concentrations ($[p\mathrm{CBA}]_0 = 0.5\ \mu\mathrm{M}$) to minimise its influence on the behaviour of the natural water during ozonation. As described by Elovitz and von Gunten (1999), a R_{ct}-value can be defined as the ratio of the exposures of OH radicals and ozone (i.e. concentration of the oxidant integrated over the reaction time) and can be calculated from the decrease of *p*CBA:

$$\ln\left(\frac{[p\mathrm{CBA}]_t}{[p\mathrm{CBA}]_0}\right) = -k_{(\mathrm{OH}+p\mathrm{CBA})} \int_0^t [\cdot\mathrm{OH}]\,\mathrm{d}t = -k_{(\mathrm{OH}+p\mathrm{CBA})} R_{\mathrm{ct}} \int_0^t [\mathrm{O}_3]\,\mathrm{d}t \qquad (1)$$

The R_{ct}-value can be used to assess the importance of ozone and OH radical reactions during ozonation and was shown to be constant over a wide range of an ozonation process (Elovitz *et al.*, 2000). Therefore, it represents directly the ratio of the concentrations of OH radical and ozone. Hence, the concentration of OH radicals during an ozonation experiment can be easily calculated from the measured ozone concentration. The elimination of a compound (M), which reacts both with ozone and OH radicals, can then be calculated by second-order kinetics and expressed as a function of R_{ct}, k_{O_3}, k_{OH} and the ozone exposure ($\int [\mathrm{O}_3]\,\mathrm{d}t$):

$$\ln\left(\frac{[\mathrm{M}]_t}{[\mathrm{M}]_0}\right) = -\left(\int_0^t [\mathrm{O}_3]\,\mathrm{d}t\right)(k_{\mathrm{O}_3} + R_{\mathrm{ct}} k_{\mathrm{OH}}) \qquad (2)$$

k_{O_3} and k_{OH} are the second-order rate coefficients for the reactions of a micropollutant M with ozone and OH radicals, respectively.

MATERIALS AND METHODS

Natural water systems

Natural waters from three types of drinking water resources have been used to investigate the effect of different water quality parameters on the ozone-decay kinetics and the formation of hydroxyl radicals and its influence on the transformation kinetics of DTPA.

The following water types were investigated: (i) raw well water collected at the drinking water plant in Porrentruy, Switzerland (WP-water). It originates from a karstic area with a characteristic high alkalinity and a low DOC-content. (ii) raw lake water collected in a drinking water plant in Zürich, Switzerland (LZ-water). It was taken from a depth of 30 m in the hypolimnium of lake Zürich, a deep, oligotrophic, seasonally stratified lake with an alpine catchment area. This water is characterized by a low alkalinity and a low DOC-content. (iii) sand-filtered river water taken from river Seine in a drinking water plant in Paris, France (RSP-water). This water is characterized by a high alkalinity and a relatively high DOC-content. All waters have been filtered to remove bacteria (0.2 μm cellulose nitrate) to achieve a better conservation and stored at 4°C within 24 h after sampling. The test waters have been analysed for the water quality parameters of interest and for a selection of transition metals, which were thought to play a role in the speciation of DTPA in the natural waters. The results of these analyses are given in Table 1.

Analytical methods

The concentration of the in situ OH radical probe compound, *p*-chlorobenzoate (*p*CBA), was measured by HPLC as described previously (Elovitz and von Gunten, 1999).

The concentration of Fe(III)DTPA-complex was measured by ion pair chromatography on a RP-18, 5 μm, 250 × 0.4 mm LiChrospher 100 column (Merck), using an eluent mixture of 90% 20 mM sodium formate, 10 mM tetrabutylammonium hydrogen sulphate in water at pH 3.3 and of 10% methanol (Kari, 1994). Eluent flow was $1\ \mathrm{mL\,min}^{-1}$, UV-detection was set to 258 nm and injection volume was 500 μL.

To analyse Zn- and CaDTPA complexes, they were transformed into the Fe(III)DTPA complex by a procedure reported previously (Kari, 1994; Nowack, 1996) and analysed as above.

The dissolved ozone concentration in reaction solutions was determined by the indigo method (Bader and Hoigné, 1981).

Rate coefficients of OH radicals with DTPA-complexes

The rate coefficients of OH radicals with ZnDTPA and Fe(III)DTPA-complexes were measured in the pH range

Table 1. Physical–chemical water quality parameters of the waters used in this study

	Well water, Porrentruy (WP-water)	Lake water, Zürich (LZ-water)	River water, Seine, Paris (RSP-water)
Dissolved organic carbon (DOC) ($\mathrm{mg\,L}^{-1}$)	1.0	1.4	2.6
Conductivity ($\mu\mathrm{S\,cm}^{-1}$)	530	250	490
pH	7.5	7.9	7.8
Carbonate alkalinity (mM) HCO_3–	5.5	2.6	4.0
Total hardness (mM) [Ca] + [Mg]	3.3	1.5	2.7
Calcium (mM)	3.0	1.1	2.2
Copper ($\mu\mathrm{g\,L}^{-1}$)	19.3 (0.304 μM)	4.1 (0.064 μM)	4.8 (0.076 μM)
Iron ($\mu\mathrm{g\,L}^{-1}$)	2.2 (0.039 μM)	3.3 (0.059 μM)	4.1 (0.073 μM)
Manganese ($\mu\mathrm{g\,L}^{-1}$)	0.47 (0.0086 μM)	0.12 (0.0022 μM)	0.49 (0.0089 μM)
Nickel ($\mu\mathrm{g\,L}^{-1}$)	1.2 (0.020 μM)	0.88 (0.0015 μM)	1.7 (0.029 μM)
Zinc ($\mu\mathrm{gL}^{-1}$)	10.5 (0.161 μM)	12.0 (0.184 μM)	10.4 (0.159 μM)

of 6–8 relative to that of *p*-chlorobenzoate (*p*CBA; $k(\mathrm{OH} + p\mathrm{CBA}) = 5 \times 10^9 \mathrm{M}^{-1}\mathrm{s}^{-1}$).

OH radicals were produced by γ-irradiation of aqueous solutions saturated with a 1:4 O_2/N_2O-gas mixtures (^{60}Co source: GAMMACELL, Atomic Energy of Canada, radical flux 270 nM s^{-1}). Solutions of double-distilled water, buffered with 5 mM phosphate buffer and presaturated with the O_2/N_2O mixture, were spiked with the desired DTPA complex and with the reference compound *p*CBA to a concentration of 10 μM of both compounds and were then exposed for 10 different time periods between 0 and 180 s to the γ-radiation at room temperature.

Rate coefficients of ozone with DTPA-complexes

Ozone stock solutions of approximately 1 mM were produced by passing ozone-containing oxygen through bidistilled ice-cooled water (Bader and Hoigné, 1981). The rate coefficients of CaDTPA- and ZnDTPA-complexes with ozone have been determined by an absolute method involving the measurement of the ozone decay by its absorbance at 258 nm ($\varepsilon = 3150\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ (Hoigné, 1998)) in presence of an excess of the metal DTPA complexes (pseudo-first-order conditions). Buffered (5 mM phosphate) solutions of 50–200 μM of the DTPA ligand and a 10% excess of the respective metal-nitrate salt in double-distilled water were mixed with ozone solutions to mixtures with an initial ozone concentration of <10 μM. The reaction mixtures were prepared by a stopped-flow technique with a 370 μL flow-through-cell (5 cm). Two motor burettes (Metrohm 665 Dosimat) one filled with the buffered solution of the DTPA complex, the other filled with an ozone stock solution were connected over a mixing device with the UV-flow cell. Upon stopping the flow the decay of the ozone absorbance signal was monitored spectrophotometrically with a sampling rate of 10 Hz.

For Fe(III)-DTPA complexes the direct measurement of the ozone concentration is precluded by the strong absorbance of the iron-complexes at 258 nm. Therefore, an indirect method for the measurement of the ozone concentration was used. Reaction mixtures, containing 100 μM of the Fe(III)DTPA-complex (1% excess of $\mathrm{Fe(III)(NO_3)_3}$ over the DTPA ligand) and initially <10 μM of ozone, were prepared in a 1 L glass reactor and periodically samples were removed from the reactor by a dispenser system and injected in an acidified solution of indigo trisulphate in order to stop the reaction and to determine the ozone concentration.

Ionic strength of the reaction solutions was set to 0.1 M with $NaClO_4$, the pH was controlled with a 5 mM phosphate buffer and *t*-butanol (40 mM) was used as radical chain reaction inhibitor.

Ozonation of DTPA complexes in natural waters

The natural waters were buffered by 1 mM phosphate buffer to pH 6 or 7 or by 1 mM borate buffer to pH 8. The DTPA complexes were added in low concentrations (0.5 μM) to minimise its influences on the OH radical and O_3 budgets in the natural waters. To calibrate the system with respect to the OH radical exposure, *p*CBA was added as the probe compound (0.5 μM). After addition of ozone ($\approx 1\,\mathrm{mg\,L^{-1}}$), samples were withdrawn after certain time intervals with a dispenser for reaction times up to 10–25 min. The reaction was stopped by injecting the sample into an indigo trisulphate solution as described by Hoigné and Bader (1994).

Speciation calculations for metal–DTPA complexes

Calculations for the speciation of metals were performed with the ChemEQL code (Müller, 1996). The corresponding stability constants were taken from Martell and Smith, 1989, for an ionic strength of 0.1 M and a temperature of 25°C.

RESULTS AND DISCUSSION

Rate coefficients for the reactions of DTPA-complexes with OH radicals

The rate coefficient of ZnDTPA- and Fe(III)-DTPA-complexes derived by the competition kinetic method are given in Table 2. The rate coefficients do not exhibit a significant pH-dependence in the environmentally relevant pH range of 6–8.

Rate coefficients of DTPA-complexes with ozone

In Fig. 1(a) and 1(d) the observed bimolecular rate coefficients for the reaction of Zn- and Fe(III)DTPA complex with ozone are plotted as a function of pH. The data for the CaDTPA complex is not shown graphically. All the investigated complexes show strongly pH-dependent rate coefficients. The pH dependence can be explained by the changing speciation of the metal-complexes.

The rate coefficient of the ZnDTPA-complexes increases with increasing pH between 2 and 9. In Fig. 1(a) and 1(b) the observed rate coefficients are compared to the calculated speciation of the ZnDTPA-complexes under the experimental conditions. It is apparent that the partly protonated complexes $\mathrm{ZnH_2DTPA^-}$ and $\mathrm{ZnHDTPA^{2-}}$ have a relatively low reactivity towards ozone, their rate coefficient with molecular ozone are in the order of $100\,\mathrm{M^{-1}s^{-1}}$ at 25°C. The increasing reactivity towards the neutral pH region can be explained by the formation of the deprotonated complex, $\mathrm{ZnDTPA^{3-}}$ (dashed line), which appears to be much more reactive towards ozone. This relation is shown in Fig. 1(c). From the slope of this plot a rate coefficient for the reaction of ozone with $\mathrm{ZnDTPA^{3-}}$ of $3500 \pm 150\,\mathrm{M^{-1}s^{-1}}$ can be obtained. Other possible explanations as the formation of the binuclear complex $\mathrm{Zn_2DTPA^-}$ or of the free ligand present in solution can not explain the observed pH-dependence of the rate coefficients sufficiently.

For the Fe(III)DTPA-complexes a different pH-dependence was found. As shown in Fig. 1(d) the

Table 2. Rate coefficients of ZnDTPA- and Fe(III)DTPA-complexes with OH radicals ($T = 22 \pm 2$°C)

Reaction pH	$k_{\mathrm{OH}} (10^9 \mathrm{M^{-1}s^{-1}})$
OH + Fe(III)DTPA	
6.44	1.6 ± 0.1
7.22	1.5 ± 0.1
7.82	1.5 ± 0.1
OH + ZnDTPA	
6.35	2.8 ± 0.4
7.29	2.4 ± 0.4
7.68	2.2 ± 0.4

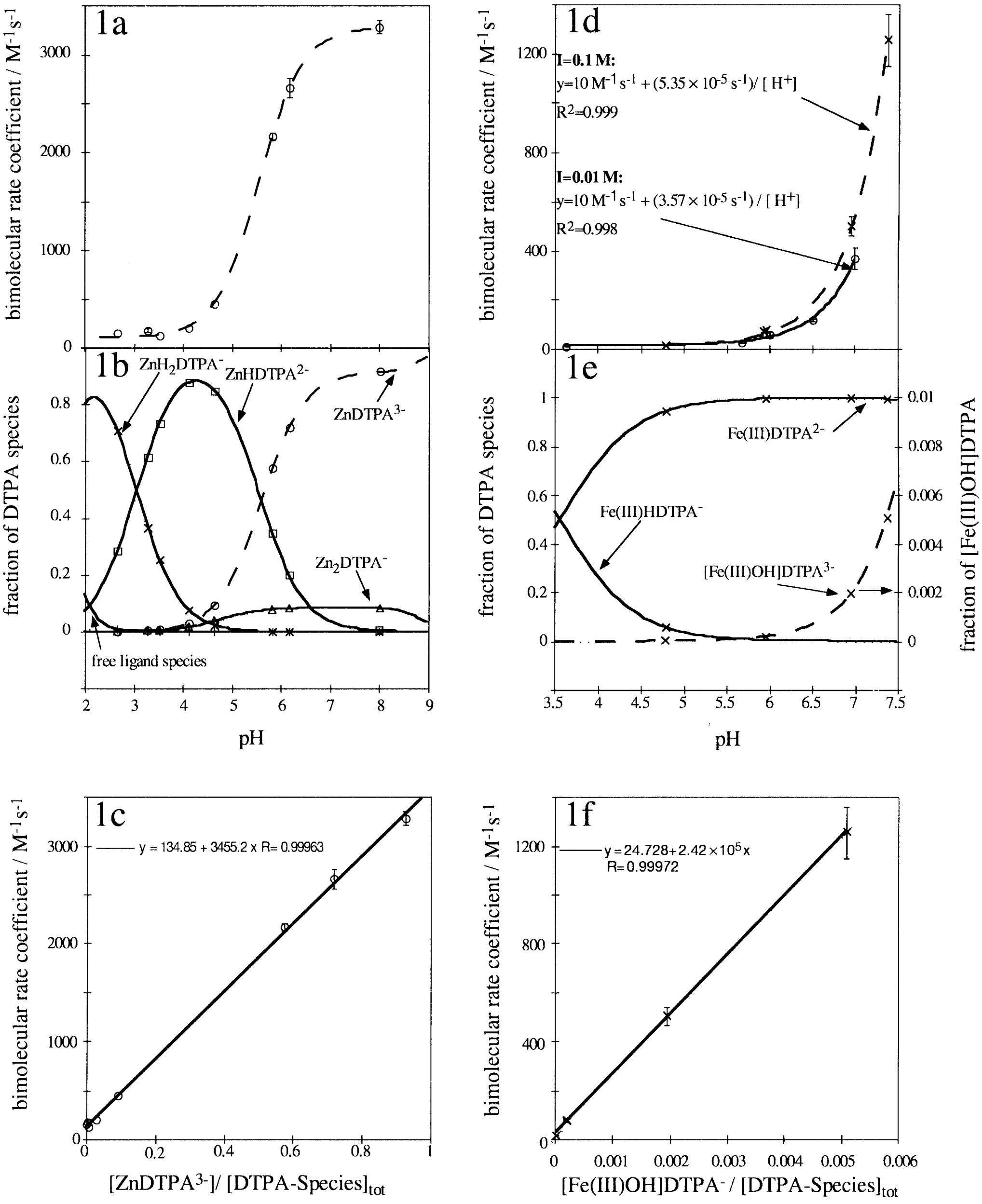
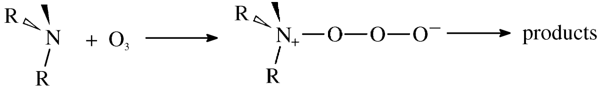


Fig. 1. (a): Plot of the observed bimolecular rate coefficient for the reaction of ozone with the ZnDTPA-complex versus the pH-value. Errors bars are 95% CI intervals. Ionic strength $I = 0.1$ M, $T = 25$°C. (b): Speciation calculation (Martell and Smith, 1989) for the DTPA species under the experimental conditions corresponding to panel 1(a). Symbols mark the actual speciation for which a rate coefficient determination was performed. (c): Relation of the observed rate coefficient of the reaction of ozone with the ZnDTPA-complex to the calculated fraction of the complex, which is present as the ZnDTPA^{3-}-species in the solutions. (d): Plot of the observed bimolecular rate coefficient for the reaction of ozone with the Fe(III)DTPA-complex versus the pH-value. (×) pH = 7.0, Ionic strength $I = 0.1$ M, $T = 25$°C, (○) pH = 7.0, Ionic strength $I = 0.01$M, $T = 25$°C. (e): Speciation calculation (Martell and Smith, 1989) for the DTPA species under the experimental condition corresponding to panel 1(d) at a ionic strength $I = 0.1$ M. (f): Relation of the observed rate coefficient of the reaction of ozone with the Fe(III)DTPA-complex to the calculated fraction of the complex which is present as the [Fe(III)(OH)]DTPA^{3-}-species in the solutions ($I = 0.1$ M).

observed rate coefficient of the Fe(III)DTPA-complexes increases in the pH range from 3.5 to 7.5 inversely proportional to the [H$^+$] concentration. A smaller pH range compared to zinc was chosen because the relevant iron complexes are accounted for between pH 3.5 and 7.5. Two sets of experiments with varying ionic strength were performed. An ionic strength I of 0.1 M (NaClO$_4$, 25°C) was chosen to allow a better comparison with the speciation calculation of the Fe(III)DTPA-complexes based on literature data ($I = 0.1$ M). The second data set was measured at $I \approx 0.01$ M to get closer to the conditions in natural waters, which often have a ionic strength in the order of 0.01M. Both data sets show a low reactivity of the Fe(III)DTPA-complexes in the pH range of 3.5–6. The major species in that pH-region are the Fe(III)DTPA^{2-}- and Fe(III)HDTPA^{-}-complexes. As an upper limit of their rate coefficient with ozone a value of $k \leq 10\,\mathrm{M^{-1}s^{-1}}$ was estimated. The observed increase of the reactivity of the Fe(III)DTPA-complexes at higher pH correlates with the formation of the [Fe(III)(OH)]DTPA^{3-} species. Although this complex is still a minor species with a fraction of less than 1% at neutral pH (see Fig. 1(e), right-hand scale), it appears to dominate the reactivity of the Fe(III)DTPA-complexes near neutral pH. The relation of the observed rate coefficients and the fraction of the [Fe(III)(OH)]DTPA^{3-} in the solution is shown in Fig. 1(f) for the data set measured at $I = 0.1$ M. From the slope of this plot a rate coefficient of $(2.4 \pm 0.2) \times 10^5\,\mathrm{M^{-1}s^{-1}}$ for the reaction of ozone with [Fe(III)(OH)]DTPA^{3-} was obtained. Because of the restrictions of our method with respect to time resolution no measurements in solutions containing high fractions of the [Fe(III)(OH)]DTPA^{3-} species were possible. However, this would have been necessary to thoroughly establish these kinetics.

For CaDTPA-complexes the pH-dependence of the rate coefficients for the reaction with ozone was again different. The reactivity of the Ca–DTPA mixtures was higher in the pH region 5–6 than at pH 7.5–8. Below pH 7 and under the experimental conditions a large fraction of DTPA is present as partly-protonated free DTPA-ligand. At pH 7.66 and 7.83, respectively, more than 99.7 and 99.8% of the DTPA was calculated to be present as a Ca-complex. The free ligand in these solutions was calculated to be mainly H$_2$DTPA^{3-} (0.26 and 0.13%, respectively, of the total DTPA content). Using the results obtained at these two pH-values a rate coefficient of ozone with CaDTPA^{3-} of $k = 6.2 \times 10^3\,\mathrm{M^{-1}s^{-1}}$ was estimated.



Simple organic amines react only fast with ozone when their amino group is deprotonated. This is a strong indication that the initial ozone attack occurs on the non bonding electron-pair of the nitrogen atom.

Similarly, in the case of ligands, such as DTPA, the nitrogen lone-pair is involved in the formation of metal complexes and may therefore be protected against ozone attack. As indicated in Table 3 the reactivity of the unprotonated metal–DTPA complexes is very variable. Fe(III)DTPA^{2-} reacts hardly with ozone and therefore this complex seems to coordinate the three nitrogen atoms of DTPA strongly. This is also confirmed by the low *p*K-value (3.6) of the Fe(III)HDTPA-complex (Fig. 1(e)) (Martell and Smith, 1989). Correspondingly, in solid samples of Ba[Fe(III)DTPA] •3H$_2$O it was found that Fe(III) and DTPA form a complex without coordinated H$_2$O and Fe(III) reaches heptacoordination, involving four carboxylate groups and all three N atoms (Anderegg, 1987). The [Fe(III)OH]DTPA^{3-} which is still a very strong complex, reacts very fast with ozone. A possible explanation for its high reactivity is that not all nitrogen atoms of DTPA can coordinate to the Fe(III)OH^{2-} centre anymore and therefore this complex may have a free amino group. The ZnDTPA^{3-} and CaDTPA^{3-} complexes are much more reactive towards ozone. Although also these complexes may involve all three nitrogen donors of DTPA (Anderegg *et al.*, 1998), they form strong hydrogen complexes (metal–HDTPA^{2-}) with pK$_a$-values of about 5.6 and 6.1 (Martell and Smith, 1989), indicating the protonation of one amino group, which is only weakly bond to the metal centre. This amino group may be responsible for the high reactivity with ozone. In the case of the ZnDTPA^{3-}-complex, the protonation of one of the amino groups reduces its reactivity with ozone drastically (Fig. 1(a) and 1(b)), showing that the two other amino groups are effectively protected by the metal-complexation.

Table 3. Rate coefficients some metal–DTPA complexes with ozone at 25°C

	$k(\mathrm{O_3} + \text{complex})(\mathrm{M^{-1}s^{-1}})$
CaDTPA^{3-}	6200
ZnH$_2$DTPA^{-}	≈ 100
ZnHDTPA^{2-}	≈ 100
ZnDTPA^{3-}	3500
Fe(III)HDTPA^{-}	≤ 10
Fe(III)DTPA^{2-}	≤ 10
[Fe(III)(OH)]DTPA^{3-}	240 000

Oxidation kinetics of DTPA complexes during ozonation of natural waters

Ozone is unstable in water. General mechanisms describing the ozone decay in natural waters have

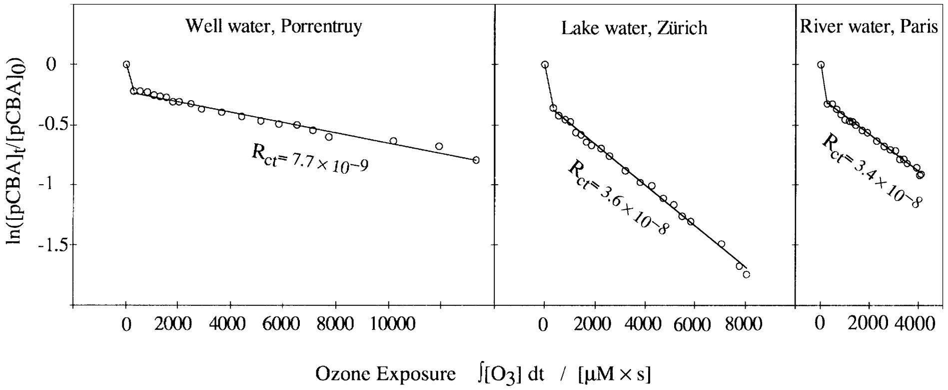


Fig. 2. R_{ct}-plots, according to equation (1), for the three natural test waters artificially set to pH = 7.0, $T = 25°C$, $[O_3]_0 = 23$–$24\,\mu M (1.1\,mg\,L^{-1})$.

been published previously (Hoigné, 1998). The influence of water quality parameters such as carbonate alkalinity, DOC-content, pH and of the temperature of natural waters on the ozone decay characteristics and on the R_{ct}-value has been discussed by Elovitz *et al.*, 2000. Figure 2 shows typical plots, according to equation (1), allowing the of calculation R_{ct}-values for the three natural test waters at pH = 7. As reported Elovitz and von Gunten (1999), the R_{ct}-plots of natural waters show two separate kinetic stages. In an initial phase (ca. 15 s at 25°C), a higher R_{ct} is observed, than during the rest of the reaction. This is due to an enhanced transformation of ozone into OH radicals during this initial stage of the ozonation. For the modelling of the degradation of the DTPA-complexes by ozonation in the three natural waters and at different conditions, for each situation a R_{ct} was derived as shown in Fig. 2 for both phases of the reaction. However for the initial phase only an approximate R_{ct}-ratio could be derived because of the short-time scale of this phase.

Figure 3 shows the measured (symbols) and modelled (lines) decrease of Fe(III)DTPA-complexes during batch ozonation experiments in the three natural waters at pH = 7. The waters were spiked with Fe(III)DTPA to a concentration of 0.5 µM and stored in the dark for 6–24 h before ozonation. In Fig. 3, the open circles represent measurements at the natural ionic strength ($I \approx 0.01\,M$) and were modelled with the rate coefficient $k(O_3 + Fe(III)DTPA,\ pH = 7,\ I = 0.01\,M) = 367\,M^{-1}s^{-1}$ according to Fig. 1(d). The filled circles represent measurements carried out at an ionic strength of $I = 0.1\,M$ artificially obtained by adding $NaClO_4$ and were modelled with the corresponding observed rate coefficient $k(O_3 + Fe(III)DTPA,\ pH = 7, I = 0.1 M) = 553\,M^{-1}\,s^{-1}$ (see Fig. 1(d)). For both ionic strengths a rate coefficient $k(OH + Fe(III)DTPA,\ pH = 7) = 1.5 \times 10^9\,M^{-1}s^{-1}$ (Table 2) was used to model the degradation via reaction with the OH radical. This reaction rate is less sensitive towards the speciation of the Fe(III)DTPA-complexes and therefore less dependent on the ionic strength. Figure 3 shows that the degradation of Fe(III)DTPA cannot be modelled with the same quality under all

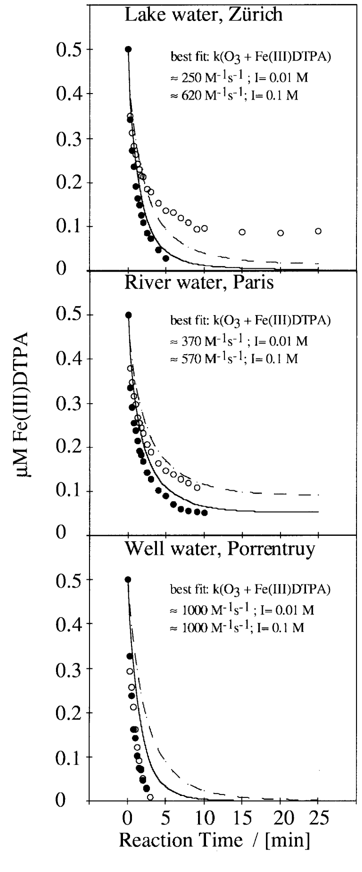


Fig. 3. Degradation of the Fe(III)DTPA-complex during ozonation in natural waters as a function of reaction time. $[O_3]_0 = 20$–$25\,\mu M(1$–$1.2\,mg\,L^{-1})$, pH = 7.0 (1 mM phosphate buffer), $T = 25°C$. (○) represent measurements at natural ionic strength, (●) at ionic strength $I = 0.1\,M(NaClO_4)$. The lines represent the modelled decay curves for both ionic strength conditions $I \approx 0.01\,M$ (dashed lines) and $I = 0.1\,M$ (full lines).

Table 4. Comparison of the observed and modelled degradations of Fe(III)DTPA-complexes under different conditions

Conditions	$k(O_3 + Fe(III)DTPA)$ predicted (Fig. 1(d)) ($M^{-1}\,s^{-1}$)	$k(O_3 + Fe(III)DTPA)$ best fit of data[a] ($M^{-1}\,s^{-1}$)	Predicted importance of OH-oxidation to O_3-oxidation[b]
Lake water, Zürich (LZ-water)			
pH = 7.0[c]	367	450–500 (3)	0.15
pH = 7.0[d] (see Fig. 3)	367	250–350 (2)	0.15
pH = 7.0; $I = 0.1$ M($NaClO_4$)[d,e] (Fig. 3)	553	620 (1)	0.10
pH = 7.0; spiked to 5.1 mM carbonate[c,e]	367	500 (1)	0.06
pH = 7.0; spiked to 7.6 mM carbonate[c,e]	367	500 (1)	0.03
Seine river water, Paris (RSP-water)			
pH = 7.0[c]	367	400–500 (4)	0.14
pH = 7.0[d] (Fig. 3)	367	250–370 (2)	0.14
pH = 7.0; $I = 0.1$ M($NaClO_4$)[d,e] (Fig. 3)	553	570 (1)	0.10
pH = 6.0[d]	47.5	48 (1)	0.62
pH = 7.9[d]	2963	1800 (1)	0.02
Well water, Porrentruy (WP-water)			
pH = 7.0[c]	367	1300 (2)	0.03
pH = 7.0[d] (Fig. 3)	367	900–1000 (2)	0.03
pH = 7.0; $I = 0.1$ M($NaClO_4$)[d,e] (Fig. 3)	553	1000 (1)	0.02

[a] In brackets: Number of experiments performed under the respective conditions.

[b] Predicted as $R_{ct} \times k(OH + Fe(III)DTPA)/k(O_3 + Fe(III)DTPA)$.

[c] Short-incubation time: Fe(III)DTPA was added 1 min prior to the experiment to the test water.

[d] Long-incubation time: Fe(III)DTPA was added 6–24 h prior to the experiment.

[e] When not specified the experiments, were performed in water with natural ionic strength and carbonate concentration.

conditions. Both, over- and under-prediction of the degradation rate was observed depending on the water source and conditions. Table 4 gives a more complete comparison of the observed and modelled degradations of Fe(III)DTPA-complexes under different conditions. As a measure of the quality of the model prediction the rate coefficient $k(O_3 + Fe(III)DTPA)$ determined experimentally in this study is compared with the rate coefficient of this reaction allowing the best fit of the experimental data in the natural waters. This comparison was chosen, because the degradation of the Fe(III)DTPA-complexes via ozone is in all conditions more important ($> 85\%$ at pH $= 7, > 60\%$ at pH $= 6$) than that via OH radical (see column 4 of Table 4).

The data obtained in LZ- and RSP-water (Table 4), show that the degradation of Fe(III)DTPA was faster, when Fe(III)DTPA was added immediately (1 min) before the experiment compared to mixtures prepared 6–24 h before addition of ozone. This indicates that during the incubation time a change in the speciation of the Fe(III)DTPA-complex occurs. In both waters (e.g. LZ- and RSP-water), the artificial increase of the ionic strength led, as predicted, to a higher elimination rate at pH = 7. In RSP-water the pH dependence of the elimination of Fe(III)DTPA was studied in the pH-range of pH 6–8. As predicted, the experiments showed an increased elimination rate towards higher pH-values. In general, the prediction of the degradation of Fe(III) DTPA agreed within 40% with the experimental data for these two natural waters.

The degradation of Fe(III)DTPA in WP-water was much less predictable. The elimination was 2–3.5 times faster in this water than predicted by our model indicating that additional processes need to be considered. The following sections focus on this special behaviour of WP-water with regard to its somewhat special composition (Table 1).

WP-water is characterized by high carbonate alkalinity and a low DOC-content leading to the reaction of a high fraction of the intermediary produced OH radicals with bicarbonate and production of carbonate radicals. To check if carbonate radicals are responsible for the faster elimination of Fe(III)DTPA in WP-water, LZ-water (similar DOC-content as WP-water) was spiked to total bicarbonate concentrations of 5.1 and 7.6 mM, respectively, by adding $NaHCO_3$. Table 4 shows that this did not lead to an enhanced elimination of Fe(III)DTPA compared to the experiment in unchanged LZ-water. Therefore carbonate radicals can be excluded as major oxidants for the Fe(III)DTPA-complex in WP-water.

As transition metals play an important role in the speciation of ligands as DTPA, they can have a strong influence on the oxidation kinetics of the ligands. By comparing the metal concentrations of the three waters in Table 1, it is apparent that copper is the most abundant transition metal in WP-water (0.30 μM) and its concentration exceeds the concentrations found in LZ-water (0.064 μM) and in RSP-water (0.076 μM) by a factor of 4. To check the influence of copper on the elimination rate of Fe(III)DTPA, ozonation experiments with different copper concentrations were performed in LZ-water containing 0.5 μM Fe(III)DTPA. Natural LZ-water was spiked with additional concentrations of 0.1, 0.25 and 0.5 μM $CuSO_4$, resulting in similar copper concentrations as observed in WP-water. Figure 4(a) shows the elimination rate of Fe(III)DTPA during the ozonation experiments in LZ-water containing different copper concentrations. It can be seen that trace concentrations of copper greatly enhance the

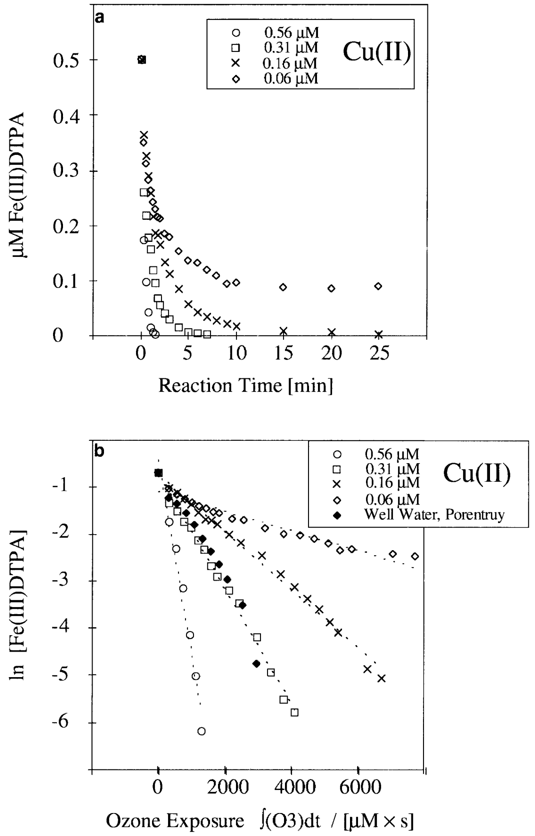


Fig. 4. (a): Degradation of the Fe(III)DTPA-complex during ozonation in LZ-waters. Influence of the copper concentration. $[O_3]_0 = 20$–$25\,\mu M$, pH = 7.0, $T = 25°C$, mixtures were prepared 6 h before the ozonation. (◇) natural LZ-water, [Cu] = 0.06 µM. (×, □, ○) LZ-water with artificially increased copper concentrations. (b): Comparison of the Fe(III)DTPA-decay in LZ-water (◇, ×, □, ○) with artificially increased copper concentrations, with the decay in WP-water (◆) with a natural copper concentration of 0.30 µM. Plot according to equation (2).

Table 5. Influence of transition metals on the degradation of Fe(III)DTPA during ozonation (pH = 7.0, $T = 25°C$, LZ-water)

Conditions (all LZ-water[a]) spiked amount of metal	$k(O_3 + \text{Fe(III)DTPA})$ best fit of data ($M^{-1}\,s^{-1}$)
Natural LZ-water[a]	250
0.1 µM Cu (II)	570
0.25 µM Cu (II)	1100
0.5 µM Cu (II)	4100
Natural LZ-water[b]	300
10 µM Zn (II)	2000
50 µM Zn (II)	2400
5 µM Ni (II)	350
10 µM Cd (II)	100

[a] First part of Table 6: experiments were carried out in LZ-water as characterized in Table 1.

[b] Second part of Table 6: experiments were carried out in uncharacterized LZ-water collected a month later.

elimination rate of Fe(III)DTPA. Figure 4(b) shows the data linearised according to equation (2). This plot, as it is normalised to the ozone exposure, allows to compare the elimination rate of Fe(III)DTPA in WP-water with that in LZ-water spiked with copper. It shows that, at similar copper concentration (0.3 µM), the elimination rate of Fe(III)DTPA is very similar. The acceleration of the reaction could be explained as an exchange reaction of copper with Fe(III)DTPA,

$$\text{Cu(II)} + \text{Fe(III)DTPA}^{2-} \xrightarrow[H_2O]{} \text{CuDTPA}^{3-} + \text{Fe(OH)}_3$$

However, such exchange reactions occur in much longer time scales, than required for the interpretation of our results (Margerum *et al.*, 1978). For example, Fe(III)EDTA$^-$ is known to exchange with Zn(II) with a half life of about 20 days at conditions found in river waters (Xue *et al.*, 1995). A possible effect of copper could be the formation of a binuclear complex (CuFe(III)DTPA). Such binuclear complexes can be formed, as DTPA is a octadentate ligand and Fe(III) prefers a lower coordination number (6–7). The formation of bimetalic DTPA-complexes and their stability constants are known for many metals (Anderegg *et al.*, 1959; Chaberek *et al.*, 1959), but no data for the coordination of a second metal to a Fe(III)DTPA-complex is reported in the literature. Hypothetically such bimetalic Cu-Fe(III)DTPA-complexes could have a higher reactivity towards ozone than the Fe(III)DTPA-complex, as the coordination of copper could distort the ideal N–Fe(III)-bonds in Fe(III)DTPA. Similar effects were observed for high concentrations of Zn(II) concentrations (second part of Table 5). Contrary to that, Ni(II) showed no and Cd(II) showed a reducing effect on the oxidation rate. The different effects of the different metals could not be attributed to any specific characteristics of the metals.

The degradation of the ZnDTPA-complex was investigated in LZ-water at pH = 7 (Fig. 5; open circles). As expected from the rate coefficient $k(O_3 + \text{ZnDTPA},\ \text{pH} = 7,\ I = 0.1) = 3200\,M^{-1}s^{-1}$ derived in this study, the decay of ZnDTPA is very fast. The half life of ZnDTPA was about 15 s under this conditions. The inset of Fig. 5 shows a plot of the data according to equation (2). It yields a straight line, where the slope equals $-k(O_3 + \text{ZnDTPA})$, when any contribution of OH radicals can be neglected. The rate coefficient obtained from the slope $k(O_3 + \text{ZnDTPA}) \approx 3200\,M^{-1}s^{-1}$ corresponds well to that measured in this study.

When 0.25 µM of free DTPA-ligand was equilibrated with LZ-water (see Table 1 for metal concentrations) for 24 h, a variety of metal–DTPA complexes may be formed. The degradation of DTPA in such a solution is shown in Fig. 5 as well (filled circles). An initial fast decrease (fitted as $k(O_3 + \text{DTPA}) \approx 3400\,M^{-1}s^{-1}$ in the inset of Fig. 5) is followed by a slower oxidation reaction (fitted as $k(O_3 + \text{DTPA}) \approx 700\,M^{-1}\,s^{-1}$). Such a behaviour can be expected when different DTPA-complexes

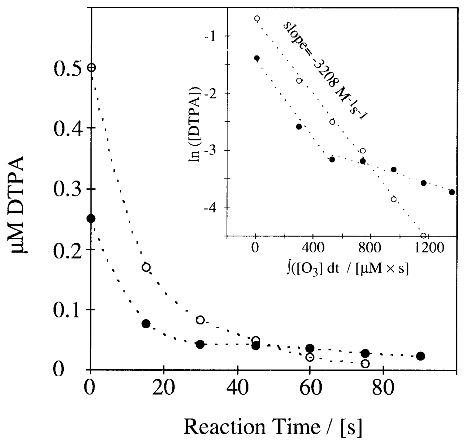


Fig. 5. Degradation of the DTPA-complexes during ozonation in LZ-waters. $[O_3]_0 = 23\,\mu M$ ($1.1\,mgL^{-1}$), pH = 7.0, $T = 25°C$. (○) ZnDTPA-complex, (●) DTPA-complexes obtained by equilibration of free DTPA-ligand (0.25 µM) in LZ-water for 24 h. Inset: Kinetic plots of the data according to equation (2).

with a different reactivity towards ozone are present. Although no exact speciation calculation can be performed for this solution. Table 1 suggests that a large fraction of the DTPA could be present as a ZnDTPA-complex, which would explain the fast decay of DTPA in the initial reaction phase.

CONCLUSIONS

Discussion of the behaviour of metal–DTPA complexes during drinking water treatment by ozonation

The approach followed in this study, the R_{ct}-concept, has been applied very successfully to predict the degradation of atrazine and its metabolites (Acero *et al.*, 2000) during ozonation and advanced oxidation processes. In the case of DTPA, the prediction is complicated by the variable speciation of this compound in natural waters.

Although the reactivity of these complexes towards ozone varies widely, all complexes react sufficiently fast with ozone in the pH range of drinking water (6.5–8) to allow a significant oxidation. The lowest reactivity was found for the Fe(III)DTPA complex at low pH values. But even in RSP-water (river Seine, France), which shows the lowest ozone stability, this compound was degraded by 80% at pH = 7 and by 60% at pH = 6 for an ozone dose of $1\,mg\,L^{-1}$ ($\sim 20\,\mu M$). The kinetic data for the more reactive Ca- and ZnDTPA complexes indicates that they are degraded by many orders of magnitude with an ozone dose of $1\,mg\,L^{-1}$ ($20\mu M$) in all the investigated natural waters. According to the kinetic data obtained in this study the degradation of DTPA is more effective at higher pH-values, where also the most persistent complex, Fe(III)DTPA, becomes readily degradable. Generally the DTPA-complexes can be judged as easily degradable by conventional ozonation.

As DTPA is a strong multidentate ligand, the question arises if the oxidative transformation by ozone destroys these complex forming properties. Therefore, the product formation during the ozonation has to be considered. During the ozonation of the DTPA complexes several strong Fe(III)-complexes where observed with the HPLC-analyses, but for some of the products we were not able to determine the identity. Among the products observed from ozonation of 0.5 µM Fe(III)DTPA or ZnDTPA in LZ-water, ethylenediaminetriacetate (ED3A) and the asymmetric isomer of diethylenetriaminetetraacetate (DTTA) were identified as described by Ternes *et al.* (1996, 1997) as major products. These compounds are both strong multidentate ligands. The chemical behaviour of these products was investigated in detail by Ternes *et al.* (1996, 1997). At least DTTA and another not identified multidentate ligand among the products were hardly degradable during ozonation (when present as a Fe(III) or Zn-complex) and will therefore be present in drinking water, when DTPA-containing raw waters are ozonated. This shows that although the reactivities of the DTPA-complexes towards ozone were found to be relatively high, this may not be the case for other polyaminocarboxylate ligands as the reactivity is very sensitive to the complex-geometry. More detailed informations on the product formation during ozonation are available for the polyaminocarboxylates EDTA (Gilbert and Hoffmann-Glewe, 1990) and NTA (Gilbert and Hoffmann-Glewe, 1984).

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