PERKIN 2

The reactions of ozone with tertiary amines including the complexing agents nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) in aqueous solution

Florinella Muñoz and Clemens von Sonntag *

Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34–36, PO Box 101365,
D-45470- Mülheim an der Ruhr, Germany. Tel: ++49-208-306-3529;
Fax: *++49-208-306-3951; E-mail: vonsonntag@mpi-muelheim.mpg.de*

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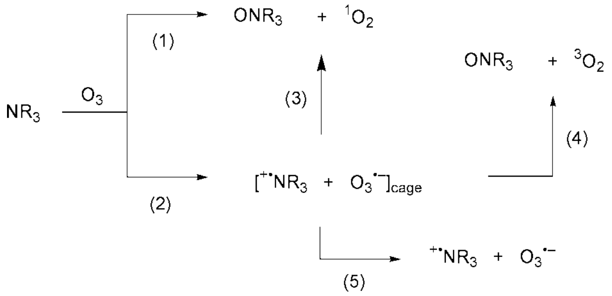
Using the stopped-flow technique, the rate constants of the reaction of ozone with a number of amines have been determined. While the protonated amines do not react with ozone, the free amines react with rate constants of around 10^6 dm^3 mol^{-1} s^{-1} in the case of tertiary and secondary amines, while primary amines react more slowly. Mono-protonated EDTA reacts only with $k = 1.6 \times 10^5$ and mono-protonated 1,4-diazabicyclo[2.2.2]octane (DABCO) with $k = 3.5 \times 10^3$ dm^3 mol^{-1} s^{-1}. In aqueous solution, tertiary amines react with ozone mainly by forming the aminoxide and singlet dioxygen [$O_2(^1\Delta_g)$] and to a lesser extent the secondary amine and the corresponding aldehyde, a reaction which can be partially suppressed by *tert*-butyl alcohol. These data suggest that O-transfer [aminoxide plus $O_2(^1\Delta_g)$] is in competition with an electron transfer which leads to the amine radical cation and an ozonide radical. In water, the latter gives rise to $^•$OH which further reacts with the amine (and ozone). The amine radical cation deprotonates at a neighbouring carbon. The resulting radical adds dioxygen. Subsequent elimination of $O_2^{•-}$ and hydrolysis of the Schiff-base thus formed leads to the secondary amine and the corresponding aldehyde. In its reaction with ozone, $O_2^{•-}$ yields further $^•$OH. Their reaction with the amines leads to the same intermediate as the free-radical pathway of ozone does, *i.e.* induces a chain reaction. This is interfered with by *tert*-butyl alcohol at the OH-radical stage. When complexed to Fe(III), EDTA reacts only very slowly with ozone ($k = 330$ dm^3 mol^{-1} s^{-1}). This explains why EDTA is not readily removed by ozonation in drinking-water processing.

The increasing use of ozone in drinking and waste water processing requires a better understanding of the underlying mechanisms for the prediction of the formation of potential by-products whenever such products are difficult to determine. In the present study, we report the kinetics and the products of the reaction of some simple aliphatic tertiary amines with ozone and extend these studies to the complexing agents nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). While NTA is readily biodegradable, EDTA is not and continues to be in certain cases a problem in drinking-water processing, although there seems to be a trend that EDTA contaminations are continuously decreasing (*cf.* ref. 1).

The reactions of ozone with tertiary amines have already been studied in organic solvents,[2–5] and it has been recognised that a major product is the corresponding aminoxide which in the case of secondary and primary amines rearranges into the corresponding hydroxylamine. These early studies suffered from the fact that high ozone to amine ratios were used, and hence a contribution of secondary reactions to the product spectrum was not excluded. In the present study, we have tried to minimise the problem by using a large excess of the amine.

The formation of the aminoxide may be written as an O-transfer [reaction (1)], and spin conservation rules require that the dioxygen formed in this reaction should be in its singlet state [$O_2(^1\Delta_g)$], *i.e.* should be electronically excited. Its formation can be quantified by measuring its emission at 1270 nm. We have recently increased the available[6] body of information on $O_2(^1\Delta_g)$ yields in ozone reactions and also reported $O_2(^1\Delta_g)$ yields of amines and their related compounds relevant to this study.[7]

Compared to olefins, amines have relatively low ionization potentials. Whereas with olefins there is no indication that electron transfer competes with the well-known 1,3-dipolar addition (Criegee mechanism),[8] electron transfer to ozone [reaction (2)] becomes noticeable with most of the amines studied here. As a consequence of this, free radicals, the amine radical cation and the ozonide radical are generated. They may recombine in the cage yielding the aminoxide and dioxygen, either in its excited singlet state or in its triplet ground state [reactions (3) and (4)]. Hence, the aminoxide yield might be somewhat higher than the singlet oxygen yield. In competition, the radicals formed in reaction (2) may diffuse out of the cage into the bulk solution [reaction (5)] and undergo further reactions which will be discussed below.



Experimental

Most compounds were commercially available and used without further purification. Solutions (typically 1×10^{-3} mol dm^{-3} in amine) were made up in Milli-Q-filtered (Millipore) water.

Aminoxides were prepared by treating the tertiary amine with 30% hydrogen peroxide.[9] The NTA-derived aminoxide was

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similarly synthesised.[10] ^{1}H NMR spectra were recorded (Bruker DRX: 500) in D_2O; trimethylamine *N*-oxide: δ/ppm 3.2 (s, 9H); triethylamine *N*-oxide: δ/ppm 1.2 (t, 9H, $J = 7.2$ Hz), 3.2 (q, 6H, $J = 7.5$ Hz); 1,4-diazabicyclo[2.2.2]octane (DABCO) *N*-oxide: δ/ppm 3.1 (t, 6H, $J = 7.5$ Hz), 3.2 (t, 6H, $J = 7.5$ Hz); DABCO *N,N′*-dioxide: δ/ppm 3.9 (s, 12H); NTA *N*-oxide: δ/ppm 4.4 (s, 6H).

The EDTA–Fe(III) complex was prepared by adding to an aqueous solution of 2×10^{-3} mol dm^{-3} EDTA an excess of $FeCl_3$ (3×10^{-3} mol dm^{-3}). This solution was brought to pH 6 with NaOH and kept in the dark overnight to let the precipitate of Fe(III) oxyhydrate settle. These solutions were filtered first with a 0.5 µm and then with a 0.2 µm microfilter in order to minimize the decomposition of ozone at small particles.

Ozone stock solutions were prepared with the help of a dioxygen-fed ozonator (WEDECO SWO-70), and their ozone content was determined spectrophotometrically taking[11] ε (260 nm) = 3314 dm^3 mol^{-1} cm^{-1}.

Rate constants were determined by stopped-flow (Biologic SFM-3) by following the ozone decay at 260 nm under the conditions of pseudo-first-order kinetics, *i.e.* with a large excess (typically 10-fold) of the substrate. For the determination of the rate constant of EDTA–Fe(III) with ozone with the help of the indigo method,[12] indigotrisulfonate solutions were made up at such concentrations that their absorption at 600 nm was nearly completely bleached upon the addition of the unreacted ozone solution. The progress of the reaction was followed by withdrawing aliquots at certain intervals and quenching the residual ozone with indigotrisulfonate. The (reduced) bleaching was then related to the remaining ozone concentration.

Secondary amines and glycolic acid yields were determined by ion chromatography (Dionex DX-100, CS14 column, using 1×10^{-2} mol dm^{-3} methanesulfonic acid as eluent for amines and an AS9 column with $NaHCO_3$–Na_2CO_3 buffer at about millimolar concentration for the acid). Acetaldehyde[13] was determined by HPLC as its 2,4-dinitrophenylhydrazone and formaldehyde[14] by the Hantzsch method. Iminodiacetic acid has been derivatized with fluoren-9-ylmethyl chloroformate (FMOC) and determined by HPLC with fluorescence detection.[15] The consumption of NTA and EDTA was followed by ion-pair chromatography.[16] Aminoxide yields were quantified in D_2O by NMR using *tert*-butyl alcohol or acetonitrile as internal standard and ozone stock solutions made-up in D_2O. Except for consumption measurements, the conversions were kept low (<20%), and in these cases linear yield dose relationships were obtained (data not shown). In experiments containing *tert*-butyl alcohol, this was added at a concentration of 0.1 mol dm^{-3}.

Results and discussion

Kinetics of ozone reactions with amines

The observed rate constant of the reaction of ozone with amines strongly depends on the pH of the solution, since only the free amine in equilibrium reacts with ozone, while the protonated amine is practically unreactive. Hence, a plot of the logarithm of the observed second-order rate constant is a linear function of pH as long as the pH is considerably below the pK_a value of the protonated amine. If the reaction of ozone with the free amine is the only reaction that determines the rate of reaction the slope of such a plot must be unity. This prerequisite is practically fulfilled for trimethylamine (p$K_a = 9.8$), triethylamine (p$K_a = 11.0$), diethylamine (p$K_a = 10.5$) and ethylamine (p$K_a = 10.8$) in the pH range of 4–9 as shown in Fig. 1. From these data and the known pK_a values, the rate constants of the reactions of the free amines were calculated. They are compiled in Table 1 together with the values reported in the literature. It may be worth mentioning that the higher reactivity of trimethylamine as compared to triethylamine (at a given pH, *cf.* Fig. 1) is only due to its lower pK_a value (*cf.* rate constants in Table 1).

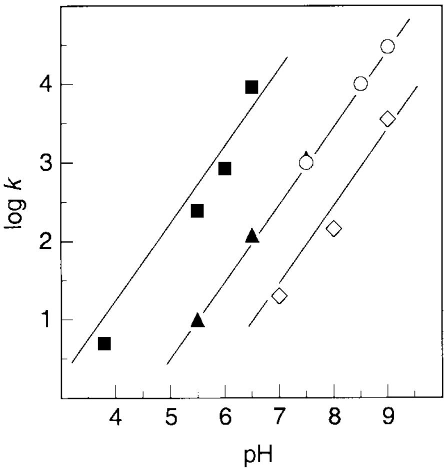

Fig. 1 Plot of the logarithm of the bimolecular rate constant of the reaction of ozone with trimethylamine (■), triethylamine (○), diethylamine (▲) and ethylamine (◇) *vs.* pH.

Table 1 Compilation of rate constants of some amines with ozone measured in this study

Amine	Rate constant/ dm^3 mol^{-1} s^{-1}	Reference
Trimethylamine	5.1×10^6	This work
	4.1×10^6	Ref.[17]
Triethylamine	4.1×10^6	This work
	2.1×10^6	Ref.[18]
DABCO–H$^+$	3.5×10^3	This work
	3.2×10^6	This work
EDTA–H$^+$	1.6×10^5	This work
EDTA	3.2×10^6	This work
EDTA[Ca(II)] pH 6	~10^5	This work
EDTA[Fe(III)] pH 6	3.3×10^2	This work
NTA	$9.8 \times 10^{5\,a}$	This work
Diethylamine	9.1×10^5	This work
	6.2×10^6	Ref.[18]
Iminodiacetic acid	$2.8 \times 10^{6\,a}$	This work
Ethylamine	2.4×10^5	This work
Glycine	$2.1 \times 10^{5\,a}$	This work
	1.3×10^5	Ref.[17]
	2.1×10^5	Ref.[18]
Alanine	$2.8 \times 10^{4\,a}$	This work
	6.4×10^4	Ref.[17]
	7.6×10^4	Ref.[18]

[a] In the presence of *tert*-butyl alcohol.

With compounds that have two amino groups, one observes markedly different rate constants for the mono-protonated and the free amine. A case in point is EDTA. Its reported pK_a values are 0.26, 0.96, 2.0, 2.7, 6.2 and 10.2.[19] As can be seen from Fig. 2, the logarithm of the observed bimolecular rate constant is linear with pH below pH 6. This linear part of the curve is followed by a short plateau and rises again at higher pH.

These data indicate that the last two pK_a values must be connected with a protonation at nitrogen, and all the lower pK_a values with protonations at the carboxylate groups. The data shown in Fig. 2 allow us to calculate the rate constant of the various protonation states of EDTA. As long as both nitrogens are protonated, EDTA is practically unreactive towards ozone, in agreement with the behaviour of the other amines. Based on the data at low pH and the known pK_a value at 6.2, the rate constant of the reaction of ozone with EDTA mono-protonated at nitrogen (EDTA–H$^+$) can be calculated ($k = 1.6 \times 10^5$ dm^3 mol^{-1} s^{-1}). The value for fully deprotonated EDTA is arrived at by using this value, the pK_a at 10.2 and all the other data points. The value of $k = 3.2 \times 10^6$ dm^3 mol^{-1} s^{-1}

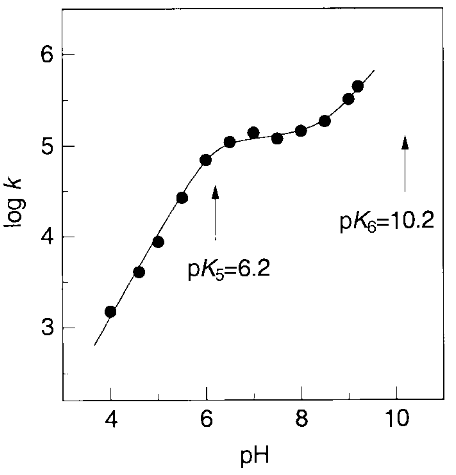

Fig. 2 Reaction of EDTA with ozone in aqueous solution. The logarithm of the observed bimolecular rate constant is plotted as a function of pH. The solid line is the best fit through all data points based on the known pK_a values and the rate constants given in Table 1.

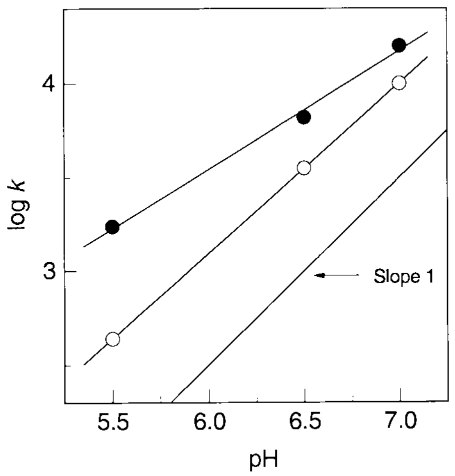

Fig. 3 Logarithm of the observed second-order rate constant of the reaction of ozone with iminodiacetic acid as a function of pH in the absence (●) and presence (○) of an excess of *tert*-butyl alcohol.

thus obtained is in good agreement with the rate constants observed for all the other tertiary amines studied here (*cf.* Table 2). These two species differ in their reaction towards ozone by a factor of about 20. In the case of 1,4-diazabicyclo[2.2.2]octane (DABCO) the corresponding ratio is *ca.* 10^3 (*cf.* Table 1). This noticeable difference is believed to be due to the enforced proximity of the neighbouring protonated amine function in the case of DABCO which reduces the reactivity of the other non-protonated amine more strongly than in the case of EDTA (for a graph of the kinetic data of DABCO as a function of pH see ref. 20).

In some cases, noticeable deviation of the slope from unity in the reaction of ozone with amino-group-containing compounds is observed. A case in point is iminodiacetic acid (Fig. 3).

As can be seen from this figure, a considerable improvement (*i.e.* reduction of the observed rate at lower pH) is obtained when the OH radical scavenger *tert*-butyl alcohol is added. This strongly points to the intermediacy of OH radicals which will be discussed below. It also suggests that the rate constant given in Table 1 might be on the high side.

Product yields

In the case of simple aliphatic amines, besides the aminoxide the corresponding secondary amines and aldehydes are formed (Table 2). An addition of *tert*-butyl alcohol reduces the yields of the free amine and, where its measurement makes sense, also that of the corresponding aldehyde. It is suggested that in aqueous solutions besides reaction (1), reaction (2) can also occur and some of the ensuing radicals diffuse into the bulk solution. The fate of the amine radical cation has been studied in the case of trimethylamine in some detail,[21] and it has been shown that it readily deprotonates at carbon yielding a carbon-centred radical [reaction (8)]. In contrast to the amine radical cation, this carbon-centred radical reacts with dioxygen at close to diffusion-controlled rates [reaction (9); $k \approx 2 \times 10^9$ dm^3 mol^{-1} s^{-1}].[22] The resulting peroxyl radical is too short-lived to be monitored ($k < 10^6$ s^{-1}) and yields the Schiff-base and a superoxide radical [reaction (10)]. The Schiff-base decomposes into the secondary amine and the aldehyde [reaction (11); for the kinetics see ref. 21].

The ozonide radical is only stable at high pH and decomposes when protonated (*e.g.* by water) into dioxygen and an OH radical [reaction (12)]. The OH radical reacts with the amine by producing the carbon-centred radical (also *via* a radical cation *cf.* refs. 23,24) [reactions (6) and (7)]. In any case, superoxide radicals are formed which react readily with ozone generating ozonide radicals [reaction (13); $k = 1.6 \times 10^9$ dm^3 mol^{-1} s^{-1}].[25] Moreover, the OH radical also reacts with ozone [reaction (14); $k = 1.1 \times 10^8$ dm^3 mol^{-1} s^{-1}].[25]

$$O_3^{\bullet -} + H_2O \longrightarrow \longrightarrow {}^{\bullet}OH + O_2 + OH^- \tag{12}$$

$$O_3 + O_2^{\bullet -} \longrightarrow O_3^{\bullet -} + O_2 \tag{13}$$

$$O_3 + {}^{\bullet}OH \longrightarrow O_2 + HO_2^{\bullet}/O_2^{\bullet -} + H^+ \quad [pK_a(HO_2^{\bullet}) = 4.8] \tag{14}$$

Thus, the free-radical pathway described in reactions (6)–(13) induces a chain reaction. Such a chain reaction will enhance the rate of ozone destruction, and its contribution will become noticeable whenever the rate of ozone reaction is slow, *i.e.* may become most noticeable at lower pH. It may partially be intercepted by *tert*-butyl alcohol at the stage of the OH radical intermediate [$k({}^{\bullet}OH$ + *tert*-butyl alcohol) $= 6 \times 10^8$ dm^3 mol^{-1} s^{-1}].[26] However, the *tert*-butyl alcohol-derived peroxyl radicals also release superoxide in 25–30% yield upon their bimolecular decay.[27] Thus, addition of *tert*-butyl alcohol does not fully suppress further ozone consumption. This may be one of the reasons why tertiary butanol does not fully restore the slope to unity in Fig. 3. In the simple aliphatic amines, the amine radical cation is very short-lived ($k > 10^6$ s^{-1}); in EDTA it complexes with the neighbouring nitrogen and thus the dimeric radical

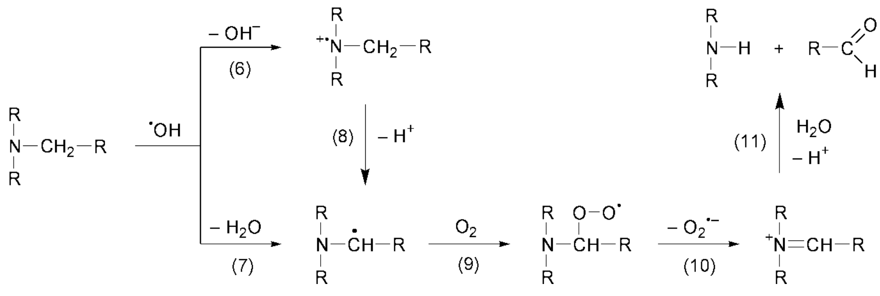

Table 2 Product yields in the reaction of some tertiary amines with ozone in aqueous solution

Product	Trimethylamine	Triethylamine	DABCO
Aminoxide	0.93	0.85	0.90
Singlet oxygen	0.69	0.85	0.92
Secondary amine	Not determined	0.15 (0.07)[a]	Not observed
Aldehyde	0.09	0.19	Not observed

[a] In the presence of *tert*-butyl alcohol.

Table 3 Products of the reaction of ozone with NTA and EDTA. Values in brackets are in the presence of *tert*-butyl alcohol

Product	NTA	EDTA
Substrate consumption	60% (70%)	60% (74%)
Singlet oxygen	19% (31%)	29% (50%)
Aminoxide	Not quantified	Not identified
Glyoxylic acid	25% (22%)	32% (18%)
Iminodiacetic acid	40% (30%)	20% (14%)
Formaldehyde	15%	15%

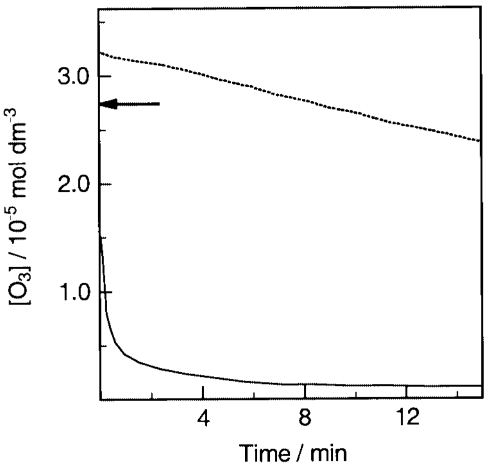

Fig. 4 Decay of ozone (3×10^{-5} mol dm^{-3}) in the absence (dotted line) and in the presence of 1.3×10^{-6} mol dm^{-3} EDTA at pH 7 as a function of time. The arrow indicates the starting ozone concentration in the reaction with EDTA.

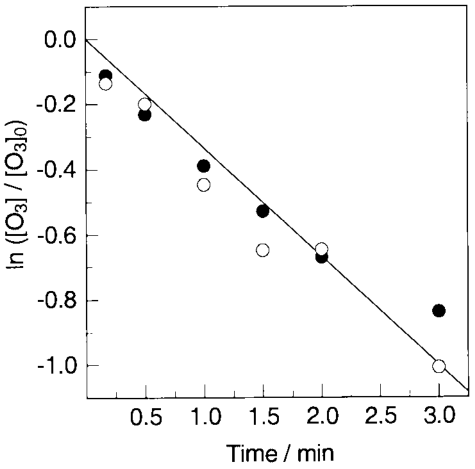

Fig. 5 First-order kinetics of the reaction of ozone (initial concentration *ca.* 1×10^{-4} mol dm^{-3}) with EDTA–Fe(III) (1×10^{-3} mol dm^{-3}) at pH 6. The residual ozone concentration was followed as a function of time by the addition of indigotrisulfonate whose bleaching at 600 nm was measured (●, ○ two different data sets).

cation (which absorbs at 480 nm) has a prolonged lifetime ($k = 10^4$ s^{-1})[24] (for the properties of the radical cations of more simple amino acids see refs. 28,29) and in DABCO its unimolecular decay (by deprotonation) has not yet been observed on the pulse radiolysis time scale ($k < 10^3$ s^{-1}).[30] The tendency of carbon-centred radicals to assume a planar conformation might exert such a high strain on the ring that in the case of the DABCO radical cation deprotonation no longer occurs at a reasonable rate.

From these data, it is concluded that the main process is the formation of the aminoxide according to reactions (1) and (4) as can be seen from the high yield of singlet oxygen. Reactions (4) and (5) must be minor and in particular the yield of the free radical ions [reaction (5)] must be low as can be seen from the yield of the secondary amine in the presence of *tert*-butyl alcohol.

Analytical problems which we had already encountered in our investigation of the reaction of the OH radical with EDTA[24] prevented complete material balance with respect to ozone consumption in the case of NTA and EDTA. Degradation yields are fraught with considerable errors because at higher conversions the products also react with ozone and OH radicals (for a study at elevated ozone to EDTA ratios see ref. 31). The importance of intermediate amine radical cations and ozonide (OH) radicals [*cf.* pathway (5)] in this system is evident from the formation of glyoxylic acid, iminodiacetic acid and formaldehyde (*cf.* ref. 24) as well as from their partial suppression by *tert*-butyl alcohol. It was not possible to identify the EDTA-aminoxide, but the high yields of $O_2(^1\Delta_g)$ point to its formation. With NTA, the aminoxide was indeed identified as a major product by NMR but not quantified. Other products are given in Table 3.

The fact that in the reaction of EDTA with ozone many products retain the amino function and hence react readily with ozone besides inducing a chain decomposition of ozone *via* the OH radical can lead to a remarkable destruction of ozone by trace amounts of EDTA (Fig. 4).

A similar situation has been reported before.[32] In drinking-water processing, however, EDTA seems to be quite ozone refractory. For example, in bank-filtered Rhine water EDTA is not degraded upon ozonation (Schick, personal communication). Under these conditions EDTA might, however, be present as the EDTA–Fe(III) complex which has a very high stability constant (p*K*~25)[33] and therefore EDTA preferentially complexes to Fe(III) rather than to any other ion, *e.g.* calcium (p*K* ~11),[33] which is much more abundant in natural waters. Evidence for this is the observation (Wenzel and Overath, personal communication) that EDTA contaminations from ground water are readily degraded by UV-photolysis while EDTA made-up in distilled water is not. Similarly to ferrioxalate,[34] EDTA–Fe(III) will undergo photoreductive decarboxylation, and Fe(III) is reformed by autoxidation (*cf.* ref. 35). While Ca^{2+} is bound by EDTA most likely only by the carboxylate functions, the nitrogens play a major role in the complexation of Fe(III). Thus, complexation to calcium does not affect noticeably the rate of reaction (Table 1). On the other hand, complexation of the EDTA nitrogens to Fe(III) should prevent its ready reaction with ozone.

The rate of reaction of ozone with EDTA–Fe(III) was not previously known. Its determination by stopped-flow was not possible because of the strong absorption of EDTA–Fe(III) at 260 nm. However, it turned out that the reaction of EDTA–Fe(III) with ozone is indeed slow. This allowed us to determine the rate constant by the indigo method.[12] In this assay indigotrisulfonate is added at intervals and its bleaching at 600 nm is measured. It reacts with ozone with a rate constant of 9.4×10^7 dm^3 mol^{-1} s^{-1},[20] and thus residual ozone is consumed practically immediately upon addition of indigotrisulfonate. From the data shown in Fig. 5 a rate constant of 330 dm^3 mol^{-1} s^{-1} is calculated.

This value has to be compared with the rate constant of ozone with uncomplexed EDTA which is 1.6×10^5 dm^3 mol^{-1} s^{-1} at this pH (see Table 1). Thus, complexation to Fe(III) reduces the reactivity of EDTA by a factor of about 500. This can explain why in drinking-water processing EDTA is not removed by ozonation, as in natural waters, EDTA may be mainly complexed to Fe(III) (note the ready photodegradation mentioned above) despite the fact that the steady-state concentration of free Fe(III) is very low, *i.e.* it is mainly bound at the surface of small particles (Schick, private communication).

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