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Review

Ozonation of drinking water: Part I. Oxidation kinetics and product formation

Urs von Gunten*

Swiss Federal Institute for Environmental Science and Technology, EAWAG, Ueberlandstr 133, CH-8600 Dübendorf, Switzerland

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Abstract

The oxidation of organic and inorganic compounds during ozonation can occur via ozone or OH radicals or a combination thereof. The oxidation pathway is determined by the ratio of ozone and OH radical concentrations and the corresponding kinetics. A huge database with several hundred rate constants for ozone and a few thousand rate constants for OH radicals is available. Ozone is an electrophile with a high selectivity. The second-order rate constants for oxidation by ozone vary over 10 orders of magnitude, between $<0.1\,M^{-1}s^{-1}$ and about $7\times10^{9}\,M^{-1}s^{-1}$. The reactions of ozone with drinking-water relevant inorganic compounds are typically fast and occur by an oxygen atom transfer reaction. Organic micropollutants are oxidized with ozone selectively. Ozone reacts mainly with double bonds, activated aromatic systems and non-protonated amines. In general, electron-donating groups enhance the oxidation by ozone whereas electron-withdrawing groups reduce the reaction rates. Furthermore, the kinetics of direct ozone reactions depend strongly on the speciation (acid-base, metal complexation). The reaction of OH radicals with the majority of inorganic and organic compounds is nearly diffusion-controlled.

The degree of oxidation by ozone and OH radicals is given by the corresponding kinetics. Product formation from the ozonation of organic micropollutants in aqueous systems has only been established for a few compounds. It is discussed for olefines, amines and aromatic compounds.

Keywords: Ozone; Advanced oxidation; Water treatment; Kinetics; Micropollutants; Product formation

Contents

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*Tel.: +41-1-823-52-70; fax +41-1-823-52-10.
E-mail addresses: vongunten@eawag.ch (U. von Gunten).

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1. Introduction

The present article gives an overview over ozonation of drinking waters with an emphasis on oxidation kinetics and product formation. Disinfection and by-product formation will be discussed in a second article [1].

The application of ozone in drinking-water treatment is widespread throughout the world [2–8]. The main reasons for the use of ozone are disinfection and oxidation (e.g. taste and odor control, decoloration, elimination of micropollutants, etc.) or a combination of both [9–11]. Similar to other disinfectants for water treatment (e.g. chlorine or chlorine dioxide), ozone is unstable in water and undergoes reactions with some water matrix components. However, the unique feature of ozone is its decomposition into OH radicals ($^{\bullet}OH$) which are the strongest oxidants in water [12]. Therefore, the assessment of ozonation processes always involves the two species *ozone* and *OH radicals*. However, for different applications of ozone the two species are of differing importance. While disinfection occurs dominantly through ozone, oxidation processes may occur through both oxidants, ozone and OH radicals [13,10,14]. Ozone is a very selective oxidant; OH radicals react fast with many dissolved compounds and the water matrix. For ozone reactions more than 500 rate constants have been measured [15–19] for OH radical reactions the database is even larger and contains a few thousand rate constants [20,21]. In conjunction with the beneficial effects of disinfection and oxidation, undesired by-products can be formed from the reaction of ozone and OH radicals with water matrix components [22–24]. They include numerous organic and some inorganic species. Because ozonation is usually followed by biological filtration, partly oxidized organic compounds can be mineralized microbiologically. The only ozonation by-product regulated in drinking waters today is bromate, which is formed during ozonation of bromide-containing waters [25,26]. In contrast to organic oxidation/disinfection by-products (DBPs), bromate is not degraded in a biological filtration process.

Fig. 1 shows a schematic representation of the effects of ozone in drinking-water treatment. Disinfection and oxidation can be achieved simultaneously if ozone reactions are responsible for the oxidation. However, if ozone-resistant compounds have to be oxidized, ozone has to be transformed into OH radicals (see “advanced oxidation processes, AOPs”). This measure has the effect of decreasing the disinfection efficiency. Therefore, optimization of disinfection and oxidation requires careful evaluation of the overall process. If, in addition, by-product formation (e.g. bromate) has to be kept at a minimum, the corresponding formation mechanisms and oxidant concentrations have to be known.

In drinking water, the problem of by-product formation has become even more prominent since the recognition of the importance of microorganisms such as *Cryptosporidium parvum* oocysts (*C. parvum*), which are more resistant against disinfection [27]. This requires higher ozone exposures and in turn leads to more by-product formation.

The present paper gives an overview on ozone decomposition in water and its effects on oxidation

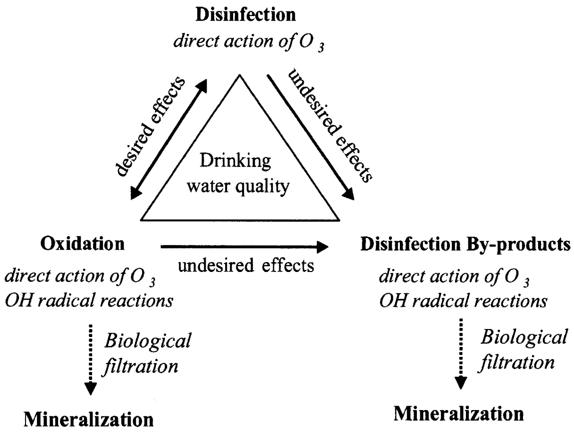

Fig. 1. Desired and undesired effects of ozonation processes. Disinfection and oxidation are the main goals for the application of ozone. Both processes are accompanied by the undesired formation of disinfection by-products.

processes with ozone and secondary oxidants (OH radicals) during drinking-water ozonation and AOPs, including methods of determining oxidant concentrations. A selection of drinking-water relevant micropollutants is presented together with a discussion of their oxidation kinetics and how this information can be used to assess the fate of these compounds during drinking-water ozonation. Furthermore, a state-of-the-art discussion on inorganic and organic oxidation products is provided.

2. Stability of ozone in water

Ozone is unstable in water. The decay of ozone in natural waters is characterized by a fast initial decrease of ozone, followed by a second phase in which ozone decreases with first-order kinetics. The mechanism and the kinetics of the elementary reactions involved in ozone decomposition have been investigated in numerous studies [12,28–36]. Depending on the water quality, the half-life of ozone is in the range of seconds to hours [10,37]. The major secondary oxidant formed from ozone decomposition in water is the OH radical. The stability of ozone largely depends on the water matrix, especially its pH, the type and content of natural organic matter (NOM) and its alkalinity [10].

The pH of the water is important because hydroxide ions initiate ozone decomposition which involves the following reactions [29,38,39]:

$$\mathrm{O_3 + OH^- \rightarrow HO_2^- + O_2}, \quad k = 70\ \mathrm{M^{-1}s^{-1}}, \tag{1}$$

$$\mathrm{O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2}, \quad k = 2.8 \times 10^6\ \mathrm{M^{-1}\ s^{-1}} \tag{2}$$

$$\mathrm{O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2} \quad k = 1.6 \times 10^9\ \mathrm{M^{-1}\ s^{-1}} \tag{3}$$

$$\begin{aligned} &\mathrm{pH} < \approx 8: \quad \mathrm{O_3^{\bullet -} + H^+ \rightleftharpoons HO_3^{\bullet}} \\ &k_+ = 5 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}} \\ &k_- = 3.3 \times 10^2\ \mathrm{s^{-1}} \end{aligned} \tag{4a}$$

$$\mathrm{HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2} \quad k = 1.4 \times 10^5\ \mathrm{s^{-1}} \tag{4b}$$

$$\begin{aligned} &\mathrm{pH} > \approx 8: \quad \mathrm{O_3^{\bullet -} \rightleftharpoons O^{\bullet -} + O_2} \\ &k_+ = 2.1 \times 10^3\ \mathrm{s^{-1}\ s^{-1}} \\ &k_- = 3.3 \times 10^9\ \mathrm{s^{-1}} \end{aligned} \tag{5}$$

$$\mathrm{O^{\bullet -} + \rightarrow {}^{\bullet}OH + OH^-} \quad k = 10^8\ \mathrm{s^{-1}} \tag{6}$$

$$\begin{aligned} &\mathrm{{}^{\bullet}OH + O_3 \rightarrow HO_2^{\bullet} + O_2} \\ &k = 1 \times 10^8\ \mathrm{M^{-1}s^{-1}} - 2 \times 10^9 \mathrm{M^{-1}\ s^{-1}} \end{aligned} \tag{7}$$

According to reactions (1) and (2) the initiation of ozone decomposition can be artificially accelerated by increasing the pH or by the addition of hydrogen peroxide. This leads to an AOP (see below). Reaction (7) is a fast process and is important for waters with low scavenger concentrations (low DOC, low alkalinity) — it leads to the consumption of ozone and OH radicals and lowers the oxidation capacity in the system. The rate constant is controversial in literature and varies between $k = 1 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$ and $2 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ [29,38].

NOM can affect the ozone stability in two ways: it can either (i) directly react with ozone (eqs. (8) and (9)) or (ii) indirectly affect its stability through scavenging of OH radicals (eqs. (10)–(13)):

$$\mathrm{O_3 + NOM1 \rightarrow NOM1_{ox}} \tag{8}$$

$$\mathrm{O_3 + NOM2 \rightarrow NOM2^{+\bullet} + O_3^{\bullet -}} \tag{9}$$

The direct reactions ((8) and (9)) with ozone are generally attributed to double bonds, activated aromatic systems, amines and sulfides (see below).

The reaction of OH radicals with NOM (scavenging) may have two effects on ozone stability. After reaction of NOM with OH radicals ($k \approx 2.5 \times 10^4\ (\mathrm{mg\,l^{-1}})^{-1}\,\mathrm{s^{-1}}$[10]), a fraction of the NOM leads to carbon centered radicals (Eq. (10)). A reaction of these carbon centered radicals with oxygen subsequently leads to the formation of superoxide radicals (eq. (11)), which react quickly with ozone to form OH radicals again (Eqs. (3–6)). This part of the reaction sequence is generally referred to as propagation:

$$\mathrm{{}^{\bullet}OH + NOM3 \rightarrow NOM3^{\bullet} + H_2O\ or\ NOM3^{\bullet} + OH^-} \tag{10}$$

$$\mathrm{NOM3^{\bullet} + O_2 \rightarrow NOM - O_2^{\bullet} \rightarrow NOM3^+ + O_2^{\bullet -}} \tag{11}$$

This chain reaction leads to an accelerated ozone decrease, which is only terminated by inhibitors. Inhibitors are entities that do not liberate superoxide after reaction with OH radicals. In natural waters they consist of a fraction of the NOM and carbonate/bicarbonate [20]:

$$\mathrm{{}^{\bullet}OH + NOM4 \rightarrow NOM4^{\bullet} + H_2O} \tag{12}$$

$$\mathrm{NOM4^{\bullet} + O_2 \rightarrow NOM4\text{-}O_2^{\bullet} \rightarrow no\ O_2^{\bullet -}\ formation} \tag{13}$$

$$\mathrm{{}^{\bullet}OH + CO_3^{2-} \rightarrow CO_3^{\bullet -} + OH^-} \quad k = 3.9 \times 10^8\ \mathrm{M^{-1}\ s^{-1}} \tag{14}$$

$$\mathrm{{}^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet -} + H_2O} \quad k = 8.5 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}. \tag{15}$$

The bicarbonate radical ($\mathrm{HCO_3^{\bullet}}$) is not important under typical drinking-water treatment conditions because it is quickly deprotonated ($\mathrm{pK_{HCO3}} < 0$, [40]). While the rate constants for the reactions of all the inorganic species (including carbonate) are known, it is difficult to assess the ozone stability in natural waters due to the unknown effect of NOM. In particular, it is impossible to estimate the fraction of the NOM which promotes or inhibits ozone decay. There have been various attempts to deduct both the kinetics of the direct ozone-NOM reaction and the promoting and inhibiting fraction of NOM from spectroscopic and structural information of the NOM. The rate constant for direct reaction of ozone with NOM showed the best correlation with the UV absorbance or the specific UV absorbance (SUVA) at 254 nm [41–43]. It is more difficult to estimate the fraction of promotion and inhibition of NOM. In one study an attempt was made by modeling the ozone decay [44]. However, without a calibration of the system with an OH radical probe this information is only of limited value.

To avoid the problems of curve fitting, several protocols with a minimum set of experiments have been developed to assess ozonation processes with respect to concentrations of ozone and OH radicals (see below) [43,45–48].

3. Characterization of ozonation processes

To assess ozonation processes with respect to oxidation by ozone and OH radicals, the concentrations or the exposures to both oxidants have to be known. Ozone concentrations can be easily measured by electrochemical, optical[1] or colorimetric methods ([13] and refs. therein). Standardized procedures for the characterization of ozonation processes with respect to ozone have been described for systems where ozone is added from a concentrated stock solution [46] or from the gaseous phase [49]. In contrast to the concentration of ozone, OH radicals are difficult to measure in aqueous solution. This is due to their high reactivity towards the water matrix and ozone, which leads to very low steady-state concentrations, typically below 10^{-12} M during ozonation. Basically, there are two ways of tackling this problem:

1. Modeling the ozone decay and thereby calculating the OH radical concentrations [44,50]. The application of these models in natural waters is difficult due to the varying reactivity of the natural organic matter (NOM) (see above). Usually, some rate constants have to be fitted to mimic the behavior of the real waters [50,44]. Therefore, model predictions of transient OH radical concentrations are quite arbitrary and generally do not agree well with experimental observation. Only in well defined laboratory systems using a probe compound for OH radicals has it been demonstrated that it is possible to simulate both ozone decay and formation of OH radicals [51].

2. Experimental calibration of natural waters by indirect measurement of OH radicals with an ozone-resistant probe compound [41,47,48]: In these methods, the decrease of an added probe compound (e.g. *para*-chlorobenzoic acid (*p*CBA)), which does not react with ozone but reacts quickly with OH radicals, is followed either as a function of the ozone dosage [41] or continuously during ozonation [47,48]. The first approach leads to the integral exposure by OH radicals (OH radical CT) and the corresponding ozone dose required to eliminate a micropollutant to a certain degree in a particular water. The latter methodology leads to information on the dynamics of the oxidation of a micropollutant during ozonation of natural waters. Haag and Yao [48] used continuous ozonation experiments to achieve steady-state concentrations of OH radicals. Part of the scavenging capacity of NOM was lost during these experiments and therefore the mean steady-state concentrations of OH radicals was overestimated. In another study, single ozone dosage experiments were used to simulate real reactor conditions [47]. The decrease of *p*CBA can be formulated as

$$\ln([p\mathrm{CBA}]/[p\mathrm{CBA}]_o) = -R_{ct}\, k_{\mathrm{OH,pCBA}} \int \mathrm{O_3}\, \mathrm{d}t \qquad (16)$$

A plot of the logarithmic decrease of pCBA (OH radical *ct*-value, OH radical exposure[2]) vs. the measured ozone exposure[3] showed two phases (initial and secondary) for which fairly good linear correlations of the two parameters could be established. The slope of this correlation corresponds to $R_{ct} \times k_{\mathrm{OH,pCBA}}$. Because $k_{\mathrm{OH,pCBA}}$ is constant, this means that the ratio R_{ct} of the exposures (*ct*-values) of OH radicals and ozone remains constant. For these conditions, the ratio R_c of the concentrations of OH radicals and ozone ($[^{\bullet}\mathrm{OH}]/[\mathrm{O_3}]$) can also be considered constant. This empirical concept is based on the fact that during an ozonation process, the pseudo first-order rate constant for transforming ozone and scavenging OH radicals remains constant. R_c was typically in the range of 10^{-7}–10^{-9} (M/M) for various waters with varying water quality parameters such as pH, alkalinity, DOC, and temperature [43]. During the initial fast decomposition of ozone the ratio is usually higher ($\leqslant$factor of 10) and varies as a function of the ozone concentration [52]. However, even during the initial phase of ozonation, the ratio R_c of the concentrations of OH radicals and ozone can be approached by just one value without significant

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[1] The molar extinction coefficient at 258 nm has been determined as 3150 $\mathrm{M^{-1}\,cm^{-1}}$ [10].

[2] The OH radical exposure ($\int[\mathrm{OH}]\,\mathrm{d}t$, OH-*ct*) can be measured by the decrease of an ozone-resistant probe compound such as *para*-chlorobenzoic acid (*p*CBA) according to: $\int[\mathrm{OH}]\mathrm{d}t = -\ln([p\mathrm{CBA}]/[p\mathrm{CBA}]_o)/k_{\mathrm{OH}}$

[3] The ozone exposure can be calculated by the integration of the ozone concentration over reaction time

deviations for the prediction of micropollutant oxidation [53,54]. In summary, three elements are required to predict the oxidation of a target compound during ozonation:

1. Ozone concentration by direct measurement.
2. OH radical concentration by measuring the oxidation of an ozone-resistant probe compound.
3. Second-order rate constants for the reaction of the target compound with ozone and OH radicals.

4. Oxidation of inorganic and organic compounds by ozone

The oxidation of inorganic and organic compounds with ozone occurs via several primary reactions which are discussed in detail below (Scheme 1). The kinetics of the reactions of ozone with inorganic and organic compounds is typically second order, i.e. first order in ozone and first order in the compound. This yields the following rate equation (16–19):

$$S + O_3 \rightarrow \text{products}, \tag{17}$$

$$-d[S]/dt = k[S][O_3] \tag{18}$$

For a batch-type or plug-flow reactor this yields:

$$\ln([S]/[S]_o) = -k\int [O_3]\,dt \tag{19}$$

And the ozonation time required to decrease the concentration of S to 50% of its initial value becomes

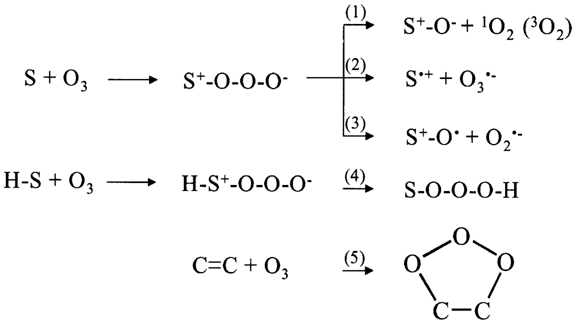
$$t_{1/2} = 0.69/(k[O_3]) \tag{20}$$

where S is the inorganic or organic compound, k the second-order rate constant, $\int[O_3]\,dt$ the ozone exposure, $t_{1/2}$ the half-life for S. The activation energies for ozone reactions usually lie in the range of 35–50 kJ mol^{-1} [15].

4.1. Oxidation of inorganic compounds

4.1.1. Kinetics of ozone reactions

The main mechanism for the oxidation of inorganic compounds is the apparent transfer of an oxygen atom from ozone to the inorganic compound, according to Scheme 1 (reaction (1)). The transfer of an oxygen atom from ozone to the oxidizable species is formally a two-electron oxidation of this compound. Fig. 2 shows a linear free energy relation (LFER) [55,56] for anionic species reacting according to reaction (1) in Scheme 1. The second-order rate constant for the reaction of inorganic anions with ozone and the two-electron-oxidation potential of these compounds is shown. The second-order rate constants were compiled from Hoigné et al. [17], whereas the standard oxidation potentials were calculated from [57].



Scheme 1. Primary reaction of ozone with a compound S: This electrophilic addition leads to an intermediate adduct (S–O_3) which then decomposes by formation of primary products: reactions (1): oxygen atom transfer to anionic, uncharged and cationic species; reaction (2): electron transfer (2); reaction (3): formation of an oxyl radical; reaction (4): ozone insertion; reaction (5): ring formation.

Fig. 2 shows that most of the investigated anionic inorganic species lie on a straight line, which spans a range of rate constants over 7 orders of magnitude. Between an oxidation potential of –0.76 V (Br^-) and –0.81 V (Cl^-) there is a sharp drop-off in the rate constants. Therefore, the corresponding two-electron reduction potential for ozone, which is connected to an oxygen transfer, can be assumed to be approximately 0.8 V. A two-electron reduction potential for ozone of 2.08 V [57] is usually given in literature. The significance of this is limited for these non-reversible oxygen transfer reactions. Fig. 2 also shows that protonation of a species decreases the rate of oxidation significantly (see e.g. H_2SO_3, HNO_2 or HOCl [16]). This is due to a decrease in nucleophilicity by protonation. Compared to the other anions, iodide reacts faster than would be expected from its oxidation potential (Fig. 2). This could be attributed to a different mechanism involving a one-electron transfer instead of an oxygen transfer. If this mechanism is relevant, an initiation of a chain reaction for ozone decomposition should be observed in the presence of iodide. However, no such effect could be measured [17,58]. One-electron transfer reactions of inorganic anions to ozone are rare and not well documented. The reaction of ozone with the superoxide radical (Eq. (3)) is frequently cited as a possible electron transfer reaction [10]. However, according to Eq. (3) an oxygen transfer from ozone to $O_2^{\bullet-}$ is also possible. It is indistinguishable from an electron transfer by simple kinetic measurements. It has been reported that ClO_2 is formed as an intermediate product from the reaction of chlorite with ozone [17,59,60]. This is a clear indication that an electron transfer reaction between chlorite and ozone occurs. For further discussion see also von Gunten [1].

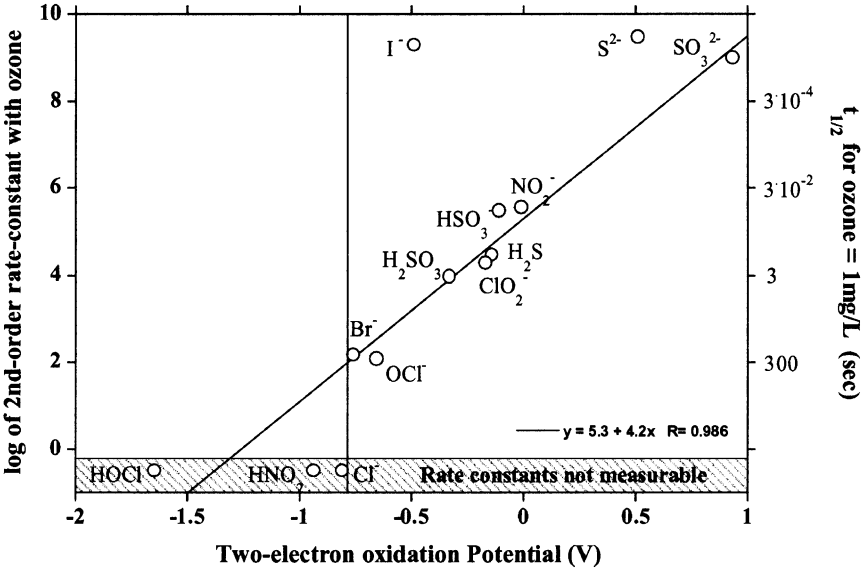


Fig. 2. Linear free energy relation between the pH-adjusted two-electron oxidation potential [57] (e.g. $Br^- + 2\ OH^- \rightarrow OBr^- + H_2O + 2e^-$) and the rate constant for the oxidation of various inorganic anions by ozone via an oxygen atom transfer.

Table 1
Kinetics of the oxidation of selected inorganic compounds with ozone and OH radicals at ambient temperature

Compound	k_{O_3} ($M^{-1}s^{-1}$)	$t_{1/2}$^{c}	Refs.	k_{OH} ($M^{-1}s^{-1}$)	Refs.
Nitrite (NO_2^-)	3.7×10^5	0.1 s	[17]	6×10^9	[136]
Ammonia (NH_3/NH_4^+)	20/0	96 h	[17]	$9.7 \times 10^{7\,d}$	[137]
Cyanide (CN^-)	10^3–$10^{5\,a}$	~1 s	[17]	8×10^9	[138]
Arsenite ($H_2AsO_3^-$)	$>7^b$	82 min	[134]	$8.5 \times 10^{9\,e}$	[139]
Bromide (Br^-)	160	215 s	[135]	1.1×10^9	[131]
Sulfide			[17]		[140]
H_2S	$\approx 3 \times 10^4$	~1 s		1.5×10^{10}	
S^{2-}	3×10^9	20 µs		9×10^9	
Manganese (Mn(II))	1.5×10^3	~23 s	[62]	2.6×10^7	[141]
Iron (Fe(II))	8.2×10^5	0.07 s	[61]	3.5×10^8	[142]

[a] Cyanide reacts with ozone via a radical chain reaction, rate constant given is a result of the overall process [133].
[b] estimated from ref. 2.
[c] Half-life time at pH 7 for $[O_3] = 1\ mg l^{-1}$ (ozone reaction only).
[d] Rate constant for NH_3.
[e] Rate constant for H_3AsO_3.

Oxygen atom transfer reactions also occur with cationic species such as Fe(II) and Mn(II) [61,62]. These reactions are also very fast; however, the database is not sufficient for a LFER.

Table 1 shows a selection of second-order rate constants for the oxidation of drinking-water relevant inorganic micropollutants with ozone and OH radicals. The second-order rate constants for ozone reactions span more than 9 orders of magnitude. Table 1 also shows the half-lives of the compounds at pH 7 for an ozone concentration of $1\ mg l^{-1}$ (ozone as only oxidant). They are in the range of a few µs to 100 h which exemplifies the selectivity of ozone. In the case of short half-lives ($t_{1/2} < 5$ min), ozonation is very efficient for the transformation of a compound because it occurs mainly via the direct ozone reaction. For slower processes, OH radicals play an important role. However, this indirect pathway leads to a substantial loss of oxidation capacity in the system due to the fast scavenging of OH radicals by many compounds of the matrix (see below).

4.1.2. Kinetics of OH-radical reactions

The rate constants for the oxidation of inorganic compounds with OH radicals are usually very high (Table 1). Only the rate constants for the oxidation of NH_3, Mn(II), Fe(II) and carbonate (not shown) are relatively low. Because the oxidation of NH_3 with ozone is a slow process, its removal during ozonation is also slow. The oxidation of Fe(II) and Mn(II) during ozonation occurs mainly by direct reaction with ozone.

4.2. Oxidation of organic micropollutants

4.2.1. Kinetics of ozone reactions

The kinetics of the reaction of organic compounds with ozone have been measured for several hundred compounds [15,16,18,19]. Table 2 shows second-order rate constants for the oxidation of selected natural and anthropogenic micropollutants with ozone and OH radicals. Similar to inorganic compounds, rate constants for ozone cover a range of more than 9 orders of magnitude. The half-lives of the compounds are given for the ozone reaction (at a concentration of $O_3 = 1\,\mathrm{mg\,l^{-1}}$) at pH 7.

4.2.1.1. Algal Products. Under certain circumstances, usually a combination of high nutrient loads and warm, stable conditions, algae and cyanobacteria can grow excessively and develop blooms. The resulting tastes, odors and toxins make additional treatment necessary [63].

Earthy–musty taste and odor compounds such as geosmin and 2-methylisoborneol (MIB), as produced by algae have an extremely low taste and odor threshold concentration in the order of a few $\mathrm{ng\,l^{-1}}$. Both compounds are difficult to oxidize with ozone (see Table 2) because they consist of saturated ring systems. Since these compounds have high rate constants for the oxidation by OH radicals (Table 2), advanced oxidation processes (e.g. O_3/H_2O_2) are well suited for their oxidation [64–67]. Only a partial oxidation of the compounds is necessary to eliminate taste and odor problems.

Cyanobacteria (blue–green algae) produce toxins that may present a hazard for drinking-water safety. These toxins (microcystins, nodularins, saxitoxins, anatoxins, cylindrospermopsin) lead to liver damage (including liver cancer) and may cause neurotoxicity. Based on the concerns about non-lethal and chronic effects of microcystin, the WHO has issued a provisional guideline for drinking water of $1\,\mathrm{\mu g\,l^{-1}}$ [68]. Microcystin-LR is investigated in most treatability studies, but information on other toxins is missing [69]. Because microcystin-LR contains several double bonds and amino groups, it is easily oxidized by ozone, with a high rate constant of $k = 3.4 \times 10^4\,\mathrm{M^{-1}\,s^{-1}}$ [70]. This is reflected in ozonation experiments in real waters, where only relatively small ozone doses and contact times were required to oxidize microcystin-LR [71]. Therefore, ozonation can be considered to be an efficient barrier against microcystin-LR-induced diseases. Based on their chemical structure (double bonds and/or amino groups) it can be expected that also nodularin, anatoxin-a, anatoxin-a(s) and saxitoxins react quickly with ozone.

4.2.1.2. Pesticides. The rate constants for the oxidation of pesticides with ozone cover a range of more than five orders of magnitude (for the chemical structure of the listed pesticides see e.g. [18]). The lowest reactivity is observed for endrin, a cyclic compound with a chloro-substituted double bond. These electron-withdrawing groups lead to the low reactivity (see below). The other pesticides shown in Table 2 contain aromatic entities with heteroatoms (atrazine) or various substituents. The rate constants for atrazine and alachlor are quite low, while the rate constant for carbofuran is much higher and dominated by the secondary amino group. The reactivity of dinoseb is given by its phenolic structure. Methoxychlor reacts with almost the same rate constant as methoxybenzene ($290\,\mathrm{M^{-1}\,s^{-1}}$ [16]).

4.2.1.3. Solvents. The second-order rate constant for the reaction of olefines with ozone (ethene: $k = 1.8 \times 10^5\,\mathrm{M^{-1}\,s^{-1}}$ [72]) decreases by a factor of $\geqslant 10$ for each additional chlorine substituent. Chloroethene (vinyl chloride) still reacts very quickly with ozone with a half-life time of about 2.5 s for an ozone concentration of $1\,\mathrm{mg\,l^{-1}}$. Vinyl chloride in drinking water is a concern because of its toxicity (EU drinking-water standard $0.5\,\mathrm{\mu g\,l^{-1}}$ [25]). The products of its oxidation by ozone will be discussed below. Dichloroethenes still have a relatively high reactivity with ozone. In conventional ozonation processes, this pathway is dominant. The reactivity of tri- and tetrachloroethene with ozone is substantially lower and especially in the case of tetrachloroethene, the oxidation is governed by OH radicals.

4.2.1.4. Fuel(additives). The reactivity of benzene, toluene, ethylbenzene and xylene (BTEX) with ozone increases with the degree of substitution with methyl groups. While benzene is relatively unreactive, xylenes have a higher reactivity depending on the position of the substitution [15]. For substituted benzene, a good LFER can be found for a plot of the log (k_{O_3}) vs the Hammett coefficient [15,55]. This correlation yields a Hammett slope $\rho = -3.1$ which means that the reaction of ozone with the aromatic ring system is highly electrophilic and also highly selective. Electron donor groups on the aromatic ring lead to an enhanced rate, whereas electron-withdrawing groups cause a slower rate. If benzene is assigned a relative rate constant of 1, methoxybenzene has 145 and nitrobenzene has only

Table 2
Kinetics of the oxidation of selected organic compounds with ozone and OH radicals at ambient temperature

Compound	$k_{\mathrm{O_3}}$ ($\mathrm{M^{-1}\,s^{-1}}$)	$t_{1/2}{}^{\mathrm{c}}$	Ref.	k_{OH} ($\mathrm{M^{-1}\,s^{-1}}$)	Ref.
Algal products					
Geosmin	$<10^{\mathrm{a}}$	>1 h	[66]	8.2×10^{9}	[66]
2-Methylisoborneol (MIB)	$<10^{\mathrm{a}}$	>1 h	[66]	$\approx3\times10^{9}$	[66]
Mycrocystin-LR	3.4×10^{4}	1 s	[70]		
Pesticides					
Atrazine	6	96 min	[53,18]	3×10^{9}	[53]
Alachlor	3.8	151 min	[18]	7×10^{9}	[21]
Carbofuran	620	56 s	[18]	7×10^{9}	[21]
Dinoseb	$1.5\times10^{5\,\mathrm{b}}$	0.23 s	[18]	4×10^{9}	[21]
Endrin	<0.02	>20 d	[18]	1×10^{9}	[21]
Methoxychlor	270	2 min	[18]	2×10^{10}	[21]
Solvents					
Chloroethene	1.4×10^{4}	2.5 s	[72]	1.2×10^{10}	[143]
Cis-1,2-dichloroethene	540	64 s	[72]	3.8×10^{9}	[144]
Trichloroethene	17	34 min	[15]	2.9×10^{9}	[144]
Tetrachloroethene	<0.1	>4 d	[15]	2×10^{9}	[144]
Chlorobenzene	0.75	13 h	[15]	5.6×10^{9}	[145]
p-Dichlorobenzene	$\leqslant3$	$\geqslant3$ h	[15]	5.4×10^{9}	[146]
Fuel (additives)					
Benzene	2	4.8 h	[15]	7.9×10^{9}	[145]
Toluene	14	41 min	[15]	5.1×10^{9}	[147]
o-Xylene	90	6.4 min	[15]	6.7×10^{9}	[148]
MTBE	0.14	2.8 d	[74]	1.9×10^{9}	[74]
t-BuOH	$\sim3\times10^{-3}$	133 d	[15]	6×10^{8}	[20]
Ethanol	0.37	26 h	[15]	1.9×10^{9}	[20]
Ligands					
NTA					
$\mathrm{NTA^{3-}}$	$9.8\cdot10^{5}$	$0.04\ \mathrm{s^{e}}$	[75]	2.5×10^{9}	[150]
$\mathrm{HNTA^{2-}}$				7.5×10^{8}	[150]
$\mathrm{H_2NTA^{-}}$	83^{d}	$7\ \mathrm{min^{e}}$	[149]		
Fe(III)NTA				1.6×10^{8}	[151]
EDTA					
$\mathrm{HEDTA^{3-}}$	1.6×10^{5}	$0.2\ \mathrm{s^{e}}$	[75]	2×10^{9}	[150]
$\mathrm{EDTA^{4-}}$	3.2×10^{6}	$0.01\ \mathrm{s^{e}}$	[75]	4×10^{8}	[150]
$\mathrm{CaEDTA^{2-}}$	$\approx10^{5}$	$0.35\ \mathrm{s^{e}}$	[75]	3.5×10^{9}	[150]
Fe(III)EDTA	3.3×10^{2}	$105\ \mathrm{s^{e}}$	[75]	5×10^{8}	[152]
DTPA					
$\mathrm{CaDTPA^{3-}}$	6200	$6\ \mathrm{s^{e}}$	[77]		
$\mathrm{Zn(HDTPA^{2-}/H_2DTPA)}$	≈100	$6\ \mathrm{min^{e}}$	[77]	2.3×10^{9}	[77]
$\mathrm{ZnDTPA^{3-}}$	3500	$10\ \mathrm{s^{e}}$	[77]		
$\mathrm{Fe(III)(DTPA^{2-}/HDTPA)}$	$\leqslant10$	$\geqslant60\ \mathrm{min^{e}}$	[77]	1.5×10^{9}	[77]
$\mathrm{Fe(III)(OH)DTPA^{3-}}$	2.4×10^{5}	$70\ \mathrm{s^{e}}$	[77]		
Disinfection by-products					
Chloroform	$\leqslant0.1$	$\geqslant100$ h	[15]	5×10^{7}	[21]
Bromoform	$\leqslant0.2$	$\geqslant50$ h	[15]	1.3×10^{8}	[21]
Iodoform	<2	>5 h	[153]	7×10^{9}	[153]
Trichloroacetate	$<3\times10^{-5}$	36 yr	[15]	6×10^{7}	[151]
Pharmaceuticals					
Diclofenac	$\sim1\times10^{6}$	$33\ \mathrm{ms^{f}}$	[79]	7.5×10^{9}	[79]
Carbamazepine	$\sim3\times10^{5}$	$0.1\ \mathrm{s^{f}}$	[79]	8.8×10^{9}	[79]

Table 2 (*continued*)

Compound	k_{O_3} (M^{-1} s^{-1})	$t_{1/2}$[c]	Ref.	k_{OH} (M^{-1} s^{-1})	Ref.
Sulfamethoxazole	$\sim 2.5 \times 10^6$	14 ms[f]	[79]	5.5×10^9	[79]
17α-Ethinylestradiol	$\sim 7 \times 10^9$	5 μs[f]	[79]	9.8×10^9	[79]

[a] Estimated from Glaze et al. [66].

[b] Rate constant for deprotonated form ($pK_a = 4.5$)

[c] Estimated for 1 mgl^{-1} ozone.

[d] Observed rate constant at pH 2. Estimated from Hoigné and Bader [16].

[e] Half-live calculated for indicated species.

[f] Most reactive form.

0.05 [15]. Increasing the number of aromatic rings (benzene → naphtalene → phenantrene) also leads to an enhanced reactivity, naphtalene reacts 1500 [15], phenantrene 10,000 [73] times faster than benzene. Additional information on kinetics of the oxidation of aromatic compounds with ozone can be found in [19].

Methyl-tertbutylether (MTBE) and (tertiary butanol) (*t*-BuOH) as fuel additives have a low reactivity with ozone [74]. This is typical for saturated hydrocarbons and in particular ethers and tert-butyl groups [15]. In many cases, ethanol is also used as an oxygenate (fuel additive). As would be expected, its reactivity with ozone is very low.

4.2.1.5. Ligands. The reactivity of the ligands nitrilotriacetate (NTA), ethylenediamintetraacetate (EDTA) and dethylenediamintetraacetate (DTPA) is dominated by the tertiary amine functions in these compounds. Both the degree of protonation and complexation of the amines leads to a decrease of their reactivity towards ozone [75]. In the case of NTA, a change of the reactivity over 4 orders of magnitude results from a protonation. At a pH of 7.8 an apparent second-order rate constant of 516 $M^{-1}s^{-1}$ has been determined, which is in agreement with the values shown in Table 2 [76]. Metal complexation can affect the rate constants mainly through the ability to bind to the nitrogen groups. While group IIA elements (e.g. Ca(II)) complex mostly to the carboxylic groups, transition metals have a stronger interaction with nitrogen groups ($CaDTPA^{3-}$ vs. $ZnDTPA^{3-}$ in Table 2). A protonation of the amino group in addition to metal complexation leads to even lower rate constants ($ZnDTPA^{3-}$ vs $ZnHDTPA^{2-}$). An increase in the valence of the metal ion leads to a stronger interaction with the nitrogen groups which, in turn results in lower rate constants (Zn(II) vs. Fe(III) complexes in Table 2). A partial substitution of the ligand by OH^- increases the rate constant substantially (Fe(III)DTPA vs. Fe(III)(OH)DTPA complexes, Table 2 [77]). This is due to a weakening of the metal-nitrogen bond.

4.2.1.6. DBPs. The oxidation of chlorination-derived DBPs by ozone is slow because of their high degree of halogenation. This leads to a low electron density at the carbon centers. Even with OH radicals, only iodinated trihalomethanes show a high reactivity. Hence, ozonation is not a suitable process for the removal of DBPs formed during chlorination.

4.2.1.7. Pharmaceuticals. In recent studies, it has been shown that traces of pharmaceuticals can be present in water resources used for drinking-water production [78]. Therefore, the behavior of these compounds during ozonation processes can be relevant. Second-order rate constants for the oxidation of pharmaceuticals were recently determined [79]. A selection of relevant compounds is shown in Table 2. Diclofenac (antiphlogistic) contains an amino group and carbamazepine (antiepileptic) a double bond. Both compounds showed high reactivity with ozone. The other two compounds shown in Table 2, sulfomethoxazole (antibitotic) and 17α-Ethinylestradiol (ovulation inhibitor) also contain structure elements that react quickly with ozone, an aniline entity and a phenol, respectively. The oxidation of all the pharmaceuticals in Table 2 with OH radicals is very fast with high rate constants.

From the data presented in Table 2 it can be concluded that the oxidation of micropollutants by ozone is only an efficient process for compounds that contain an amino group, an activated aromatic system or a double bond. In addition, sulfidic groups also react very fast with ozone. Protonated amino groups are almost non-reactive with ozone. Because of their high pK_a-values (≈ 10) the fraction of the unprotonated species is lower by 2–3 orders of magnitude for typical drinking-water treatment conditions. Therefore, the effective rate constants for the oxidation of amines by ozone under these conditions are also lower by 2–3 orders of magnitude. Electron withdrawing groups (e.g. –Cl, $–NO_2$) always lead to a decrease in the rate constants, whereas electron-donor groups (e. g. $–CH_3$, O^-, $–OCH_3$) increase the reactivity.

4.2.2. Kinetics of OH-radical reactions

Second-order rate constants for the reactions of organic compounds with OH radicals are also presented in Table 2. With a few exceptions (e.g. Fe(III)NTA, $CHCl_3$, $CHBr_3$), most of the second-order rate constants reflect near diffusion-controlled reactions. All the rate constants presented in Table 2 lie within 3 orders of magnitude. The high rate constants for the OH radical oxidation could lead to the conclusion that the elimination of organic compounds with OH radicals is very fast. However, a large fraction of the OH radicals is scavenged by the water matrix and not available for micropollutant elimination (for quantification see below).

4.3. Quantification of the oxidation by ozone and by OH radicals

To quantify the extent of oxidation during an ozonation process, it is necessary to combine the characterization of the ozonation process with the available kinetic information. The oxidation of a micropollutant S during an ozonation process can be formulated as follows:

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k_{\mathrm{O}_3}[\mathrm{S}][\mathrm{O}_3] + k_{\mathrm{OH}}[\mathrm{S}][{}^{\bullet}\mathrm{OH}] \tag{21}$$

As shown above, the ratio R_c of the concentrations of OH radicals and ozone can be measured by adding an ozone-resistant probe compound (e.g. *para*-chlorobenzoic acid):

$$R_\mathrm{c} = [{}^{\bullet}\mathrm{OH}]/[\mathrm{O}_3] \tag{22}$$

Substituting eq. (22) in eq. (21) yields

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t = (k_{\mathrm{O}_3} + k_{\mathrm{OH}}R_\mathrm{c})[\mathrm{S}][\mathrm{O}_3] \tag{23}$$

Integrated for a batch or plug-flow reactor this yields:

$$\ln([\mathrm{S}]/[\mathrm{S}]_\mathrm{o}) = -(k_{\mathrm{O}_3} + k_{\mathrm{OH}}R_\mathrm{c})\int[\mathrm{O}_3]\mathrm{d}t \tag{24}$$

where S is the micropollutant, k_{O_3} the second-order rate constant for the reaction of S with ozone, k_{OH}: second-order rate constant for the reaction of S with OH radicals.

The fraction f_{OH} of S reacting with OH radicals can be calculated as

$$f({}^{\bullet}\mathrm{OH}] = (k_{\mathrm{OH}}R_\mathrm{c}/(k_{\mathrm{O}_3} + k_{\mathrm{OH}}R_\mathrm{c}). \tag{25}$$

Fig. 3 shows the fraction of selected compounds from Table 1 and 2 that are oxidized by OH radicals for a typical range of R_c values in natural waters. The lower range of R_c values ($10^{-9} < R_\mathrm{c} < 10^{-7}$) represents typical conditions for the secondary phase of ozonation, whereas $R_\mathrm{c} > 10^{-7}$ can be observed during the initial phase of an ozonation or throughout an advanced oxidation process (e.g. combination of ozone with hydrogen peroxide, [54]).

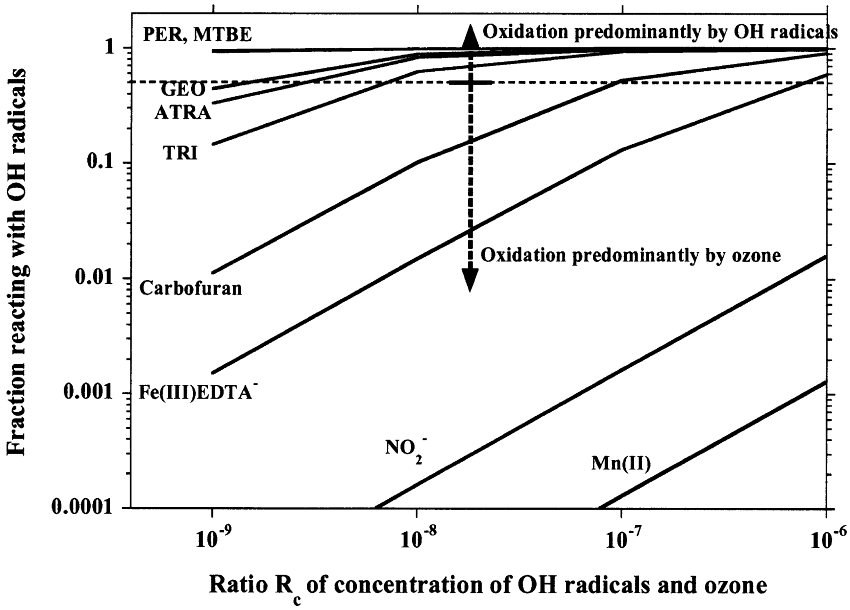


Fig. 3. Fraction of organic compounds reacting with OH radicals for a drinking-water relevant range of ratios R_c of the concentrations of OH radicals and ozone. PER: tetrachloro ethene; MTBE: methyl tert-butyl ether; GEO: geosmin; ATRA: atrazine; TRI: trichloro ethene.

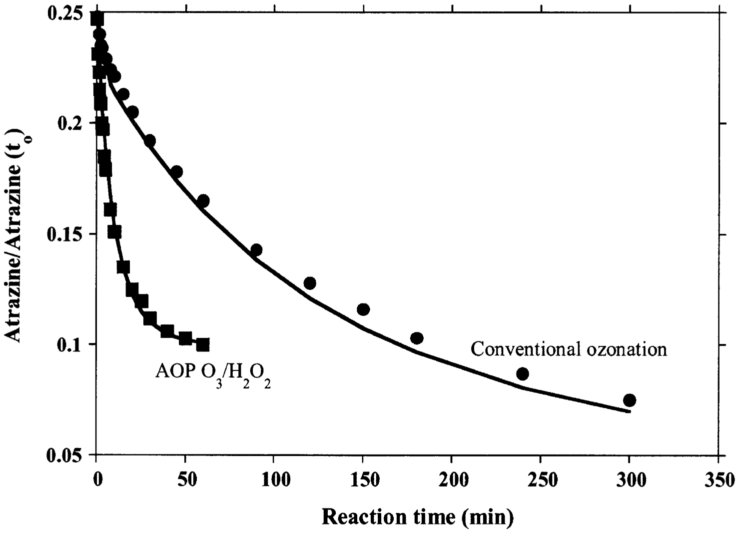


Fig. 4. Oxidation of atrazine during conventional ozonation and the advanced oxidation process (AOP) O_3/H_2O_2. Data are shown for groundwater (DOC $1\,mg\,l^{-1}$, alkalinity 5.2 mM). Symbols represent experimental data, lines stand for model calculations. Experimental conditions: pH = 7.2, T = 11°C, $[O_3]_o = 2.3\times10^{-5}$ M, $[H_2O_2] = 1.1\times10^{-5}$ M, $[p\text{CBA}]_o = 0.25\,\mu M$, $[\text{Atrazine}]_o = 0.25\,\mu M$. Adapted from Acero and von Gunten [54].

Fig. 3 also shows the two zones for which the oxidation occurs predominantly (>50%) by ozone or OH radicals. Many of the inorganic compounds of concern in drinking waters which are considered here (Table 1) will be below the line (predominantly oxidation by ozone) over the entire range of R_c values in ozonation processes. In contrast, many organic micropollutants (Table 2) are above the line (predominant oxidation by OH radicals).

Based on a system for which the R_c has been determined, Eq. (24) also permits calculating the evolution of any micropollutant if the corresponding rate constants for the reactions with ozone and OH radicals are known. Fig. 4 shows the measured (symbols) and calculated (lines) decrease of atrazine in a groundwater (for water quality data see figure caption) for conventional ozonation and for the AOP O_3/H_2O_2. The calculations are based on Eq. (24); R_c was determined with the ozone resistant probe compound *para*-chlorobenzoic acid. The good agreement between measured and calculated data shows that this approach is well suited to dynamically model the oxidation of a micropollutant. It has been successfully demonstrated for atrazine that the same approach can be used to predict the formation of degradation products [53]. For this purpose the fractions of rate constants leading from the original product to a particular degradation product has to be known. This approach may be necessary if information on degradant concentration is required due to the products' potential health hazards (see MTBE degradation, for example).

4.4. Reaction products from oxidation with ozone and OH radicals

There are numerous product studies for inorganic and organic compounds in literature. In many of the older product studies published prior to 1985, reactions with ozone and OH radicals were not carefully distinguished. Therefore, it is very difficult to derive mechanistic information from these studies [80]. Compounds can basically be divided into three categories with (i) high, (ii) intermediate and (iii) low reactivity towards ozone. For the first category (i), only ozone reactions and for the third category (iii), only OH radical reactions have to be considered. For compounds (ii), oxidation by both ozone and OH radicals has to be considered. The assessment of the importance of the oxidation pathway (OH radicals vs ozone) can be made by the approach shown above in Eq. (25) after the ratio R_c of the concentrations of OH radicals and ozone has been determined. Product formation from pure OH radical oxidations in oxygen-containing waters have been established in many previous studies ([81] and references therein). For this reason, they will be only discussed in this overview where they are necessary to understand and predict product formation in drinking waters.

A general reaction pathway of the reaction of ozone with inorganic and organic compounds is shown in Scheme 1. An electrophilic addition of ozone to the compound S leads to an intermediate adduct ($S–O_3$), which then decomposes by formation of primary products. It can be seen from Scheme 1 that there is a wide spectrum of reactions such as oxygen atom transfer (1), electron transfer (2), formation of an oxyl radical (3), ozone insertion (4) and ring formation (5). Depending on the investigated compound, these products are stable in water or react further with compounds that will eventually be detected in drinking waters after the ozonation step. Numerous degradation products are mineralized in the biological filtration step following ozonation.

4.4.1. *Inorganic compounds*

Inorganic anions (e.g. Br^-, I^-, NO_2^-, etc.) react mostly over an oxygen transfer reaction (Scheme 1, reaction (1)). The formation of singlet oxygen $[O_2(^1\Delta_g)]$ can be used as an indicator for these oxygen transfer reactions. For the oxidation of nitrite by ozone, a yield of singlet oxygen of 100% was found [82]. However, especially with heavy anions (Br^-, I^-) the yield of singlet oxygen of these reactions is substantially below 100%. This can be explained by the hypothesis that the $S–O_3$ adducts are sufficiently long-lived to reduce the $O_2(^1\Delta_g)$ yield by conversion due to heavy atom effect [82]. The oxidation of halogenides (Br^-, I^-) and sulfide by ozone is a succession of O-atom transfer reactions with the final products bromate, iodate (von Gunten, Part II) and sulfate.

Low valent transition metal ions (e.g. Fe(II) , Mn(II)) also react with an oxygen atom transfer reaction (Scheme 1 reaction (1)). In the case of iron, an intermediate $Fe–O^{2+}$ (Fe(IV)) is formed which reacts quickly with Fe(II) or with other constituents in the water to Fe(III) ([61]). In drinking-water treatment, this leads to the formation of iron(III)(hydr)oxides. It has been observed in manganese-containing drinking waters that permanganate (MnO_4^-) is formed upon ozonation [83]. However, if Mn(II) is oxidized in distilled water, MnO_4^- can only be observed under acidic conditions. In the circumneutral pH range only the formation of MnO_2 can be observed in excess of ozone [84]. This can be expected if an oxygen transfer (reaction (1) in Scheme 1) is suggested for this process and the hydrolysis of Mn(IV) is faster than its further oxidation:

$$Mn(H_2O)_6^{2+} + O_3 \rightarrow MnO(H_2O)_5^{2+} + O_2 + H_2O \qquad (26)$$

$$Mn(OH_2O)_5^{2+} \rightarrow MnO(OH)_2 + 2H^+ + 3H_2O \qquad (27)$$

$$MnO(OH)_2 \rightarrow MnO_2 + H_2O \qquad (28)$$

The formation of MnO_4^- in circumneutral pH can only be observed in distilled water if a ligand such as oxalate is added to retard the hydrolysis of Mn(IV) [84]. However, the necessary oxalate levels were substantially above expected levels of ligands in drinking waters. To oxidize Mn(II) to permanganate (Mn(VII)), the first step has to be an electron transfer reaction to Mn(III) followed by two oxygen-atom transfer reactions. Because Mn(II) is released through microbiologically mediated reductive processes into the water, it is usually found together with Fe(II) [85]. The concentrations of Fe(II) and Mn(II) are typically in the same order of magnitude. However, the rate constant for the reaction of Fe(II) with ozone is almost 2 orders of magnitude higher than for Mn(II) (see Table 1). It has therefore been suggested that the formation of permanganate during ozonation of manganese-containing waters can be initiated by the oxidation of Mn(II) with Fe(IV) ($Fe–O^{2+}$) [84]:

$$Fe\text{-}O^{2+} + Mn(II) + H_2O \rightarrow Fe(OH)_2^+ + Mn(III) \qquad (29)$$

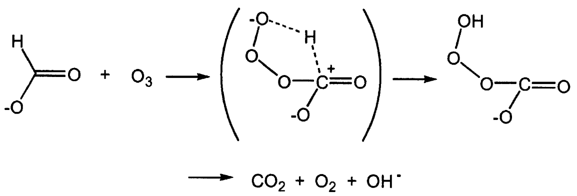
$$Mn(III) + 2O_3 + 2H_2O \rightarrow MnO_4^- + 2O_2 + 4H^+ \qquad (30)$$

The formation of permanganate in drinking-water treatment can thus be minimized if iron is removed in a pretreatment step.

4.4.2. *Organic compounds*

The growing toxicological concern about degradation products resulting from the oxidation of micropollutants calls for thorough product studies. Combined with kinetic information, this would allow the prediction of the dynamics of micropollutants during ozonation and AOPs and thus assessing the overall process. A compilation of reactions of ozone with organic compounds is given for non-aqueous solvents [86,87]. The reaction products from the reaction of ozone with organic compounds in aqueous solutions are often difficult to predict and establish. The information is scattered throughout the available literature and no comprehensive collection is available. Mechanistically, the primary products from the reaction of ozone with organic compounds are summarized in Scheme 1 by reactions (1)–(5). In the following, existing product studies for various types of organic compounds are summarized according to the reactions in Scheme 1.

4.4.2.1. Aldehydes, alcohols, ketones and carboxylic acids. The reactivity of saturated compounds with ozone is typically very low [15,16]. Many of these compounds are formed as oxidation products from the reaction of ozone with NOM. Even though they will be oxidized by OH radicals, their oxidation rate is usually lower than their formation rate. Therefore, they will accumulate during ozonation processes and subsequently need to be removed by biological filtration. The mechanisms of the oxidation of unsaturated compounds with OH radicals is well known ([81] and references therein). Formate is an exception with regard to reaction with ozone in that it reacts with ozone with a second-order rate constant of $140\,M^{-1}s^{-1}$. The



Scheme 2. Reaction of formate with ozone.

oxidation of formate with ozone occurs via reaction (4) in Scheme 1. As shown in Scheme 2, inserting O_3 leads to the formation of CO_2, molecular oxygen and hydroxide ions.

4.4.2.2. Ethers. Ethers are discussed in more detail because the widespread occurence of methyl tertiary butyl ether (MTBE, $(CH_3)_3C\text{-}O\text{-}CH_3$) has become a major concern in the drinking-water community [88]. The reactivity of methyl and other alkyl ethers with ozone is very low and can be neglected for the transformation of these compounds in ozonation processes [15,74]. The transformation of ethers with OH radicals has been studied in detail for 2-butoxyethanol in aqueous atmospheric systems [89] for diethyl and diisopropyl ether in aqueous solution [90,91] and for MTBE during drinking-water treatment [92,74]. Hydrogen abstraction occurs most easily in the position α to the ether function. In oxygenated solutions, the resulting carbon centered radicals add oxygen to form a peroxy radical which further reacts in a bimolecular reaction to a tetroxide which decomposes via various channels [81]:

$$2R_2CHO_2^{\bullet} \rightleftharpoons R_2CHO_4CH\,R_2 \tag{31}$$

$$\rightarrow R_2C{=}O + R_2CHOH + O_2 \tag{32}$$

$$\rightarrow 2R_2C{=}O + H_2O_2 \tag{33}$$

$$\rightarrow 2R_2CHO^{\bullet} + O_2 \tag{34}$$

Reactions (32) and (33) lead to the formation of carbonyl and hydroxyl-functionalized compounds. Reaction (34) is a non-terminating pathway with the formation of two oxyl radicals. They may further react by β-bond fragmentation to a carbonyl compound and a carbon centered radical (reaction (35) or isomerize by a H-atom shift to a hydroxyl-functionalized carbon centered radical (reaction (36) [81]):

$$RCH(O^{\bullet})R' \rightarrow RC^{\bullet}(O)H + R', \tag{35}$$

$$RCH(O^{\bullet})R' \rightarrow RC(OH)R'. \tag{36}$$

The mechanism of the oxidation of MTBE by OH radicals is shown in Scheme 3. It was estimated from the product distribution that 60% of the OH radical attack occurs on the methoxy side and 40% the tert-butyl side of MTBE [92,74]. The two main products found were tert-butyl formate (TBF, $(CH_3)_3COCHO$) and 2-methoxy-2-methyl propionaldehyde (MMP, $CH_3O(CH_3)_2C\text{-}CHO$) which result from reaction (33) through an attack of OH radicals at the methoxy and the tert-butyl group, respectively. An OH radical attack on the methoxy group also leads to tert-butanol (TBA, $(CH_3)_3COH$) and acetone (AC, $(CH_3)_2CO$) which cannot be directly explained by the above mechanism. For the attack of OH radicals on the tert-butyl group an additional important product is formed: methyl acetate (MA, $CH_3C(O)OCH_3$). The percent formation of each product was determined during the initial phase of the reaction with a good mass balance. It is shown in Scheme 3 [74]. Formaldehyde is formed in several reactions and therefore reaches high concentrations after the oxidation of MTBE. The further oxidation of the degradation products occurs once more by an OH radical pathway. The further oxidation of TBF and TBA is also shown in Scheme 3. The oxidation of TBA leads mainly to AC and HiBA [92,74]. In contrast to Acero et al., von Sonntag and Schuchmann [81] also found 2-methyl-2,3-propanediol and bis(2-hydroxy-2-methylpropyl)peroxide in lower yields for this oxidation process. Because of the lower reactivity of TBF and TBA with OH radicals ($k_{TBF} = 7 \times 10^8\,M^{-1}\,s^{-1}$, $k_{TBA} = 6 \times 10^8\,M^{-1}\,s^{-1}$, [74], degradation of these compounds is slow under typical ozonation conditions [74].

A combination of chemical kinetics with the product distribution as, e.g., shown in Scheme 3 allows quantitative modeling of the products during ozonation. For MTBE, the following kinetic model can be applied to predict degradant formation:

$$O_3 \xrightarrow{k_{O_3}} \tag{37}$$

$$O_3 \Leftrightarrow {}^{\bullet}OH \quad R_C = [{}^{\bullet}OH]/[O_3] \tag{38}$$

$$\text{MTBE} + {}^{\bullet}\text{OH} \xrightarrow{k_{\text{MTBE}}} \text{Prod.} \tag{39}$$

$$\text{MTBE} + {}^{\bullet}\text{OH} \xrightarrow{k_{\text{MA}}} \text{MA} \tag{40}$$

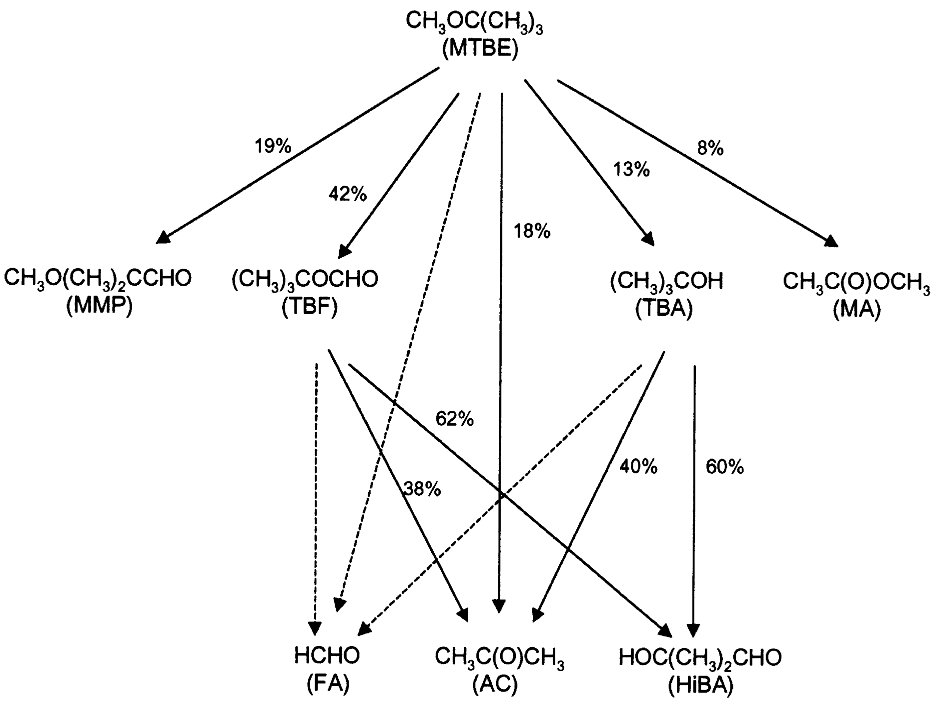
$$\text{MTBE} + {}^{\bullet}\text{OH} \xrightarrow{k_{\text{TBA}}} \text{TBA} \tag{41}$$

$$\text{MTBE} + {}^{\bullet}\text{OH} \xrightarrow{k_{\text{AC}}} \text{AC} \tag{42}$$

$$\text{MTBE} + {}^{\bullet}\text{OH} \xrightarrow{k\text{TBF}} \text{TBF} \tag{43}$$

$$\text{MTBE} + {}^{\bullet}\text{OH} \xrightarrow{k_{\text{MMP}}} \text{MMP} \tag{44}$$

where k_{O3} is the measured first-order rate constant for the decrease of ozone, R_c the Ratio of the concentrations of OH radicals and ozone, $k_{\text{MTBE}} = \Sigma\ k_n$ the



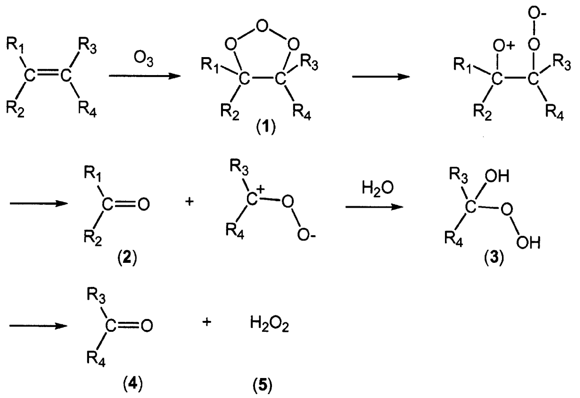
Scheme 3. Oxidation of methyl tert-butyl ether (MTBE) with OH radicals. Percentages indicate the relative importance of the corresponding reaction pathway to primary and secondary products. MMP: 2-methoxy-2-methyl propionaldehyde; TBF: tert-butyl formate; TBA: tert-butyl alcohol; MA: methyl acetate; AC: acetone; FA: formaldehyde; HiBA: hydroxyisobutyraldehyde.

Second-order rate constant for the reaction MTBE with OH radicals,

k_n the fraction of second-order rate constant leading to individual products ($k_{MA} = 0.08\,k_{MTBE}$, $k_{TBA} = 0.13\,k_{MTBE}$, $k_{AC} = 0.18\ k_{MTBE}$, $k_{TBF} = 0.42\ k_{MTBE}$, $k_{MMP} = 0.19\ k_{MTBE}$).

Reactions (37)–(44) can be extended by further reactions of the primary products with OH radicals. Several chemical kinetics programs are available to calculate product distribution. *ACUCHEM* [93] allows calculating the system in batch or plug-flow systems, *AQUASIM* [94] permits coupling the above reaction system with any reactor hydraulics to simulate reaction kinetics in real reactors [95].

4.4.2.3. Olefines. The oxidation of olefines with ozone strongly depends on substitution and the corresponding second-order rate constants vary over 8 orders of magnitude. The mechanism is well established and generally referred to as the Criegee mechanism (reaction (5), Scheme 1) [96,86,72]. The reaction of olefines with ozone is depicted in Scheme 4 and is initiated by the formation of an ozonide (**1**), an unstable cyclic trioxide. It decomposes into a carbonyl compound (**2**) and a hydroxyhydroperoxide (**3**). This hydroxyhydroperoxide then slowly decomposes into a carbonyl compound (**4**) and hydrogen peroxide (**5**) [72].



Scheme 4. Reaction of olefines with ozone.

The oxidation mechanism has also been established for substituted ethenes. In the case of acrylic acid ($H_2C{=}CHCOOH$) the attack of ozone leads to an ozonide intermediate which can loose CO_2 and form formic acid (HCOOH) and formaldehyde (H_2CO) or decompose into formaldehyde and glyoxylic acid (OHCCOOH). For the oxidation of cinnamic acid

($C_6H_6CH=CHCOOH$), the main oxidation products are benzaldehyde (C_6H_6CHO) and glyoxylic acid (OHCCOOH) [97]. Furthermore, the ozone oxidation mechanism has been established for chloro-substituted ethenes. For vinyl chloride and *trans*-1,2 dichloroethene, the major products are formaldehyde (HCHO), formyl chloride (ClCHO) and formic peracid (HCOOOH) [72]. Formyl chloride decomposes rapidly into CO and HCl [98]. For 1,1-dichloroethene, one of the suggested products is phosgene (Cl_2CO) which quickly hydrolyses to CO_2 and HCl at circumneutral conditions ($t_{1/2} \approx 0.1$ s at pH 7) [99,72]. For the reaction of higher chlorinated ethenes, it can be expected that oxidation by OH radicals will be the main pathway. It has been shown that the oxidation of tetrachloroethene by OH radicals in clean waters yields chloride, CO, CO_2 and trichloroacetic acid (Cl_3CCOOH, TCA) [81]. TCA is undesired due to its potential carcinogenicity [26]. The formation of TCA in clean waters is a result of the production of Cl radicals. However, in natural waters much lower TCA concentrations can be expected due to scavenging of Cl radicals by CO_3^{2-}/HCO_3^- ($k(CO_3^{2-}) = 5 \times 10^8\,M^{-1}\,s^{-1}$, $k(HCO_3^-) = 2.2 \times 10^8\,M^{-1}\,s^{-1}$, [100]).

4.4.2.4. Amines. Rate constants for the reaction of ozone with various amines have been determined [16,75,101]. Protonated amines show practically no reactivity toward ozone, while the deprotonated form reacts readily. The substitution of hydrogen atoms by alkyl groups at the amine-N typically increases the rate constant significantly [101]. Ammonia oxidation by ozone is a slow process with a second-order rate constant of $20\,M^{-1}\,s^{-1}$. Diethylamine and triethylamine react much faster with rate constants of 9.1×10^5 and $4.1 \times 10^6\,M^{-1}\,s^{-1}$, respectively [75]. The reactions of amines with ozone can be summarized by reactions (1) – (3) in Scheme 1. The primary products are an aminoxide and singlet oxygen (reaction (1)) or an amine radical cation and $O_3^{\bullet -}$ (reaction (2)). It is still unclear whether reaction (3) to an amin-oxyl radical and a superoxide radical can also occur. Reaction (2) in Scheme 1 leads to the formation of OH radicals whereas reaction (3) acts as a promotor for the ozone decomposition. Aminoxide is the only stable nitrogen-containing product. Both the amine radical and the amin-oxyl radical react to further products (see below).

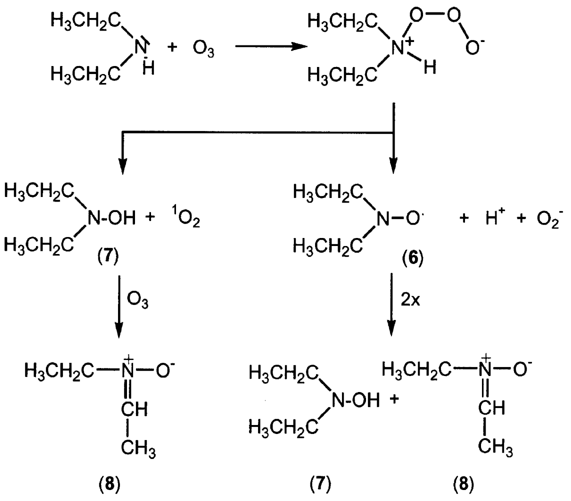
Some publications discuss the product formation resulting from the oxidation of amines with ozone. Reaction products of the oxidation of primary, secondary and tertiary amines with ozone are given in Elmghari-Tabib et al. [102]. However, this study presents product analyses for various degrees of oxidation and it is not clear to what extent OH radicals were involved. Therefore, the results of this study can only be regarded as a general qualitative guideline as to which products can be expected during oxidation of amines. Few product studies for the oxidation of *primary* (NH_3, amino acids) [103–105], *secondary* (atrazine) [106,53,107] and *tertiary* amines (EDTA, NTA) [108,75] have been performed so far.

Primary amines. Both the oxidation of *ammonia* with ozone and OH radicals yield NO_3^- [103]. For the oxidation with ozone a stoichiometry of ~ 5 O_3 per NH_3 was found. This is close to the expected theoretical stoichiometry of 4. Because the reaction of NH_3 with ozone is relatively slow, the oxidation by OH radicals was estimated to be more important at pH ≥ 9 [103].

The kinetics of the oxidation of *amino acids* with ozone has been investigated by Pryor et al. [101]. For amino acids which do not contain a sulfur group or an aromatic ring, the reactivity is quite low for a protonated amino group. The second-order rate constants for the deprotonated form are $> 2 \times 10^4\,M^{-1}\,s^{-1}$ for all amino acids.

Product studies for the oxidation by ozone have been performed for glycine (H_2NCH_2COOH) [105] and serine ($HOCH_2CH(NH_2)COOH$) [104]. For both compounds, the only inorganic nitrogen compound after excessive ozonation was nitrate. In the case of glycine, the major organic products are oxalic acid (HOOCCOOH) and oxamic acid ($H_2NCOCOOH$). In the case of serine, the main organic products are hydroxyacetaldehyde ($HOCH_2CHO$), formaldehyde (HCHO) and glycolic acid ($HOCH_2COOH$) [104]. The oxidation of amino acids by OH radicals has been investigated in depth [109,110]. The primary products for the reaction of glycine with OH radicals are an amino radical cation $^+H_2N^\bullet{-}CH_2{-}CO_2^-$ (63%) and an aminyl radical $HN^\bullet{-}CH_2{-}CO_2^-$ (37%). $^+H_2N^\bullet{-}CH_2{-}CO_2^-$ undergoes a fast fragmentation to CO_2 and a strongly reducing $^\bullet CH_2NH_2$ radical. $HN^\bullet$ -CH_2-CO_2^- also undergoes a fragmentation to CO_2^- and an imine ($HN=CH_2$).

Secondary and tertiary amines. The oxidation of secondary amines by ozone has been investigated for diethyl amine [108]. Preliminary results show that the reaction mainly proceeds through reaction (3) in Scheme 1, with the formation of an amine-oxyl radical, a superoxide radical and a proton. Part of the reaction (20%) also proceeds via pathway 1 in Scheme 1 by forming diethyl hydroxylamine. The entire mechanism is shown in Scheme 5. The amine oxyl radical (**6**) further reacts in a disproportionation reaction to hydroxyl amine (**7**) and a nitrone (**8**). This was demonstrated experimentally by the fact that both compounds increase simultaneously [108]. Ozone reacts quickly with diethyl hydroxylamine to nitrone (**8**) which hydrolyses to acetaldehyde and ethyl hydroxylamine. Ethyl hydroxylamine reacts analogously with ozone, leading to hydroxylamine which yields nitrate upon oxidation with ozone. Even though atrazine is not a typical secondary amine (partial reduction of electron density at the



Scheme 5. Reactions of secondary amines with ozone.

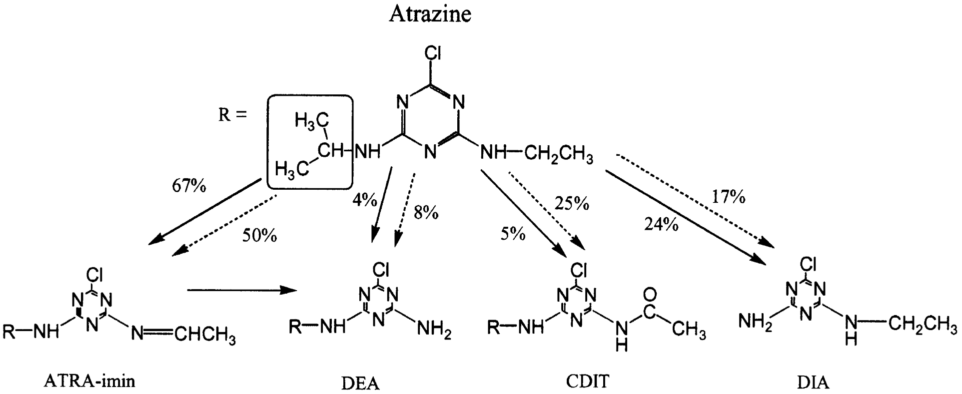
N-atom through triazine ring), it is discussed here because of its relevance for water treatment. The products of atrazine oxidation have been investigated in detail in several studies (for kinetic data see Table 2) [106,53,107]. Scheme 6 shows the product distribution for the reaction of ozone and OH radicals with atrazine.

The percentage numbers indicate the percentage formation of a particular product by reaction with ozone (solid lines) and OH radicals (dashed lines). The attack of ozone on atrazine occurs mainly at the nitrogen group in α-position to the ethyl group. This leads to an atrazine-imine (Atra-imin) which slowly hydrolyses to deethylatrazine (DEA) and acetaldehyde [53]. The attack of ozone on the nitrogen group in α-position to the isopropyl group is less effective and leads to deisopropyl atrazine (DIA). The same product is formed by OH radicals via a H-abstraction on the carbon in α-position to the (ethyl-)nitrogen. The formation of (DIA) occurs with the analogous mechanism by attack of an OH radical on the isopropyl side (nitrogen or CH bond). This leads to an imine which hydrolyses readily to (DIA) and acetone. One of the other major products is an amide (CDIT). Its formation is not well understood to date [53]. Under typical ozonation conditions, atrazine is not fully mineralized and the main products found are the daughter products. Because the triazine ring is still preserved in these molecules, the advantage of such oxidation is minor. In the European Union, this has important consequences because the first generation degradation products are also considered to be pesticides and are governed by the same drinking-water regulation [25].

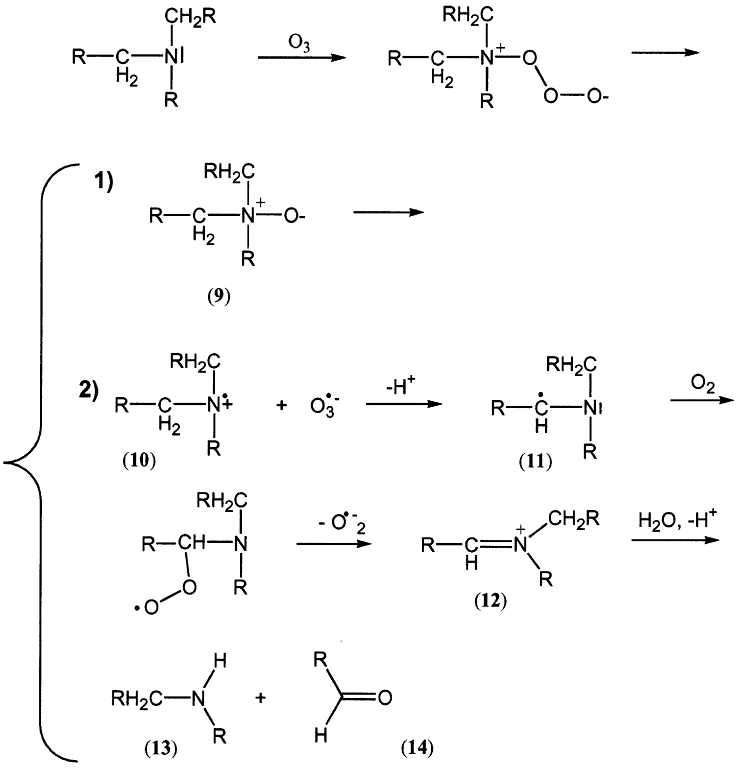
In terms of drinking-water quality, the most important tertiary amines are ligands such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Kinetic data for the oxidation of these ligands by ozone and OH radicals are given in Table 2. Metal complexation can affect the reactivity of these ligands significantly [75,77]. Product studies were performed for ozone and OH radical reactions only for free ligands (in the absence of metals) [111,75]. The reaction of ozone with tertiary amines occurs again at the nitrogen (Scheme 7). The two possible primary products are an aminoxide (**9**) (90%) or an amine radical cation ($^+NR_3$) (**10**) (10%) and the ozonide radical ($O_3^{\bullet -}$) [75]. The amine radical cation leads to an α-amino alkyl radical (**11**), which then forms a Schiff-base (**12**) and finally a secondary amine (**13**) and an aldehyde (**14**). This mechanism was confirmed by oxidation of NTA and EDTA with ozone. For both ligands, iminodiacetic acid (IDA, HO_2C-NH-CO_2H) and glyoxylic acid (OHC-CO_2H) were found as major degradation products [111,75]. The oxidation of tertiary amines with OH radicals occurs either at the amine-N or at a C–H bond in α-position to the amino group [112]. The intermediate product is an imine (**12**) which hydrolyses to a secondary amine (**13**) and an aldehyde (**14**) [75]. The oxidation of EDTA by OH radicals occurs at the two types of C–H bonds in α-position to the nitrogen (leading to two products, A and B) or at the nitrogen itself [113]. The N-centered radical cation converts mainly into carbon-centered radicals (same products A or B as for OH radical attack on C–H bonds) [113]. The addition of oxygen to the carbon-centered radicals and subsequent elimination of superoxide radicals leads to the Schiff-base which hydrolyses to the aldehyde and the secondary amine. The main primary products of the attack of OH radicals on EDTA are glyoxylic acid, IDA and ethylenediamintriacetic acid (ED3A) [113]. In addition, NTA can be expected if the solutions are further oxidized.

In the case of DTPA, a product study for the process UV/H_2O_2 showed that IDA, NTA and EDTA were some of the major identified degradation products [114]. The mechanism of their formation is expected to be similar to EDTA. Therefore, a partial degradation of ligands leads to new ligands with lower stability constants. However, ozonation and AOPs do not suppress metal complexation as long as the ligand skeleton is present.

4.4.2.5. Aromatic compounds: benzene, substituted benzenes, polyaromatic compounds. The reaction products of the oxidation of aromatic compounds with ozone are not well covered in literature. The oxidation of benzene by ozone is a relatively slow process $k_{O_3} = 2\,M^{-1}s^{-1}$, [15]. Therefore, under typical ozonation conditions or AOPs, the oxidation of benzene occurs with OH radicals. The major product of the oxidation of benzene with OH radicals is phenol (55% of OH radicals, [115]).



Scheme 6. Oxidation of atrazine with ozone (solid lines) and OH radicals (dashed lines). Percentage indicate the relative importance of corresponding reaction pathways to primary products. DEA: deethyl atrazine; DIA: deisopropyl atrazine; CDIT: 4-acetamido-2-chloro-6-isopropylamino-s-triazine. Adapted from Acero et al. [53].



Scheme 7. Reactions of tertiary amines with ozone.

It results from an OH and subsequent O_2 addition reaction followed by elimination of $HO_2^\bullet$ or $O_2^{\bullet -}$, respectively. The reaction of phenol with ozone is controlled by the phenolate species in the pH range of drinking waters [16]. The mechanism of this reaction was investigated recently and it was found that ozone is transformed into OH radicals in a first step, which subsequently led to the formation of hydroquinone and catechol. It is still unclear whether OH radicals are formed by direct electron transfer from phenol to ozone or if superoxide is formed as an intermediate [116]. Most product studies for the reaction of phenols with ozone were performed under ill-defined conditions where the role of OH radical reactions is unclear. Some of the primary reaction products were catechol, hydroquinone and muconic acid [117,118]. Especially, in wastewater applications, polymeric condensation products were also reported [119,120].

The reaction of naphtalene with ozone is faster than that of benzene and leads to products with an intact aromatic ring [121]. The products containing the original skeleton were *ortho*-phthaldialdehyde, phtalaldehydic acid, phthalic acid with oxalic acid, glyoxal and formaldehyde as simultaneous by-products.

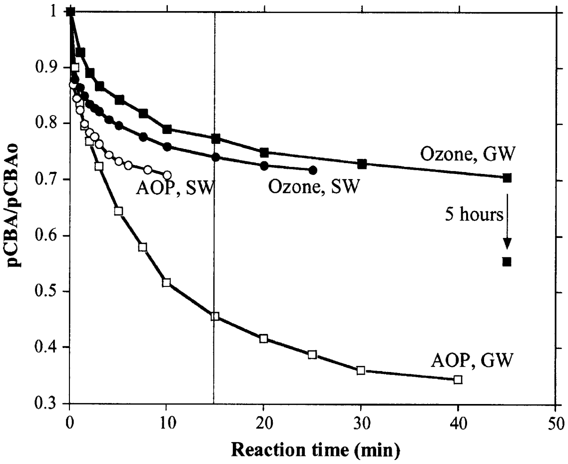


Fig. 5. Oxidation of *p*CBA (relative decrease) during ozonation and the accelerated AOP O_3/H_2O_2 for a groundwater (GW) and a surface water (SW). GW: DOC 1 mg l^{-1}, alkalinity 5.2 mM; SW: DOC 3.2 mg l^{-1}, alkalinity 3.8 mM. Experimental conditions: pH = 7, T = 11°C, $[O_3]_o = 2.1 \times 10^{-5}$ M, $[H_2O_2] = 1 \times 10^{-5}$ M, $[p\text{CBA}]_o = 0.25\,\mu$M. Adapted from Acero and von Gunten (2001) [54].

5. Advanced oxidation processes

Processes which involve the formation of highly reactive OH radicals as an oxidant are generally referred to as AOPs [122,10]. In drinking-water treatment, they are applied to oxidize ozone-resistant compounds such as pesticides [123–125], aromatic compounds and chlorinated solvents such as tri- and tetrachloroethene [126,127]. For complete ozone consumption of a water, the OH radical yield is almost independent of the rate of the ozone decomposition. Therefore, the main advantage of ozone-based AOPs is a shorter reaction time which allows the application of higher ozone dosages without causing excess ozone concentrations at the outlet of a reactor. Ozone-based AOPs are most commonly applied in drinking-water treatment because conventional treatment schemes including an ozonation step can be easily retrofitted for these processes. The easiest solution to convert a conventional ozonation process into an AOP is to increase reaction time after ozone addition, increase the pH, or add hydrogen peroxide. While the first two possibilities can be costly, the addition of hydrogen peroxide is a cheap solution, most commonly used in drinking-water treatment. Another alternative is the combination of ozone with UV irradiation [10]. In this process, the first step is a photolysis of ozone to oxygen and O (^{1}D and ^{3}P) atoms [128]. Whereas O(^{1}D) is very reactive and reacts with H_2O to hydrogen peroxide, O(^{3}P) reacts either with O_3 to 2 O_2 or under certain treatment conditions with organic solutes RH by H-atom abstraction from –CH_3 groups (Reisz et al. [128]). Therefore, part of the oxidation capacity of the system is lost through the reaction $O_3 \rightarrow\rightarrow H_2O_2$ but some additional effect can be gained from the direct reaction of organic compounds with O(^{3}P). Additional ozone-based AOPs include the combination of ozone with activated carbon [129] or with Mn(II) or Mn(IV) [130].

The following discussion will concentrate on the combination of ozone with hydrogen peroxide because it is the most commonly applied technical AOP. In this process, the ozone transformation is accelerated by hydrogen peroxide. The reaction of ozone with hydrogen peroxide proceeds through the deprotonated form of hydrogen peroxide according to Staehelin and Hoigné [29]. As shown in Eq. (2), hydrogen peroxide initiates the ozone decomposition by formation of an OH radical and superoxide which further reacts with ozone according to Eq. (3). The yield of this reaction sequence is one OH radical per decomposed ozone molecule. This is somewhat higher than the yield achieved in low DOC waters in conventional ozonation processes [54]. Because the initiation reaction is less important in high DOC waters compared to the promotion reaction, the AOP O_3/H_2O_2 does not lead to a better degradation of ozone-resistant micropollutants in such waters. However, the main advantage of the AOP O_3/H_2O_2 lies in the acceleration of the ozone transformation process. Fig. 5 shows an example of the oxidation of an ozone-resistant compound (*para*-chlorobenzoic acid, *p*CBA). Data for two waters are presented (water quality given in figure caption, GW: groundwater, SW: surface water) for a conventional ozonation and the AOP O_3/H_2O_2 with an ozone dose of 1 mg l^{-1} for a complete depletion of ozone.

The oxidation of *p*CBA is faster for both waters for the AOP. The degree of oxidation in the two waters is related to the concentration of scavengers in the water, i.e. higher in the surface water (see below). The extent of oxidation of *p*CBA is similar for conventional ozonation and the AOP in the case of the surface water, while it is somewhat higher for the AOP applied to the groundwater. This is due to the stronger effect of the initiation vs promotion in low DOC waters such as the groundwater. In Fig. 5, a line for a hypothetical hydraulic residence time (HRT) of 15 min in a reactor is also shown. Once again in the case of the surface water, there is no large difference between conventional ozonation and the AOP because ozone is readily transformed into OH radicals in both cases. However, for the groundwater, only about 20% of *p*CBA is oxidized in conventional ozonation whereas in the AOP it is more than 50%. This shows that the same degree of oxidation can be achieved in a much shorter contact time. Because the ozone residual concentration after a certain HRT is much lower in the AOP it is possible to increase the ozone dose without excessive ozone remaining at the outlet of a reactor. This increases the overall oxidation capacity in the system [131,74].

As discussed above, the efficiency of an AOP is largely given by the OH radical scavenging of the water matrix. Typically, the DOC and carbonate/bicarbonate are the most important scavengers in natural waters. The fraction f_{OH} of the OH radicals reacting with a micropollutant can be calculated by competition kinetics:

$$f_{OH} = k_S[S]/(k_{NOM}[DOC] + k_{HCO_3} - [HCO_3^-] + k_{CO_3^{2-}}[CO_3^{2-}] + k_S[S]), \qquad (45)$$

where $k_{NOM} = 2.5 \times 10^4\,l\,mg^{-1}\,s^{-1}$; [10], $k_{HCO_3^-} = 8 \times 10^6\,M^{-1}\,s^{-1}$ [20], $k_{CO_3^{2-}} = 4 \times 10^8\,M^{-1}\,s^{-1}$, [20] and k_S are the second-order rate constants for the reaction of natural organic matter, bicarbonate, carbonate and a micropollutant S with OH radicals, respectively. For a typical composition of a drinking water ([DOC] $= 2\,mg\,l^{-1}$, alkalinity $= 3$ mM, pH $= 8$), the fraction of OH radicals reacting with a micropollutant ([S] $= 10^{-8}$ M, 1 µgl^{-1} for a compound with an M_w of 100 g mol^{-1}) are 0.007%, 0.014% and 0.07% for $k_S = 5 \times 10^8\,M^{-1}\,s^{-1}$, $10^9\,M^{-1}\,s^{-1}$, $5 \times 10^9\,M^{-1}\,s^{-1}$, respectively. This shows that only a very small fraction of OH radicals actually reacts with a target micropollutant. Therefore, AOPs are quite inefficient processes and mineralization of micropollutants is very costly. Hence, AOPs should only be applied in cases where a partial oxidation of a molecule changes its undesired properties (e.g., toxicity, taste, odor, etc.) and the degradation by-products are not of similar toxicological concern as the original compound. The new drinking-water regulation of the European Union for pesticides also includes their *relevant metabolites, degradation and reaction products* [25]. Under these restrictions for ozone-resistant pesticides such as atrazine, AOPs are no longer a suitable treatment option. In a typical treatment scenario, the sum of the concentrations of the original compound (e.g. atrazine) and the degradation products remained constant in laboratory experiments with the AOP O_3/H_2O_2 [53]. Therefore, the application of AOPs requires a thorough analysis and quantification of the degradation products. However, in some cases, the degradation products are more easily biodegradable and are efficiently eliminated in biological filtration following ozonation. MTBE oxidation during the AOP O_3/H_2O_2 and the formation of the corresponding degradation products has recently been investigated [74]. Fig. 6 shows data for three different Swiss raw waters (△,▲:Lake Murten; □,■:Lake Zürich; ○,●:well water, Porrentruy; for water quality data see figure captions).

The data shown in Fig. 6 was gained from conventional ozonation experiments and the AOP O_3/H_2O_2 with ozone doses in the range 2 – 4 mgl^{-1} at pH 7 and 8. The MTBE degradation lies in the range of a few percent to >60%. On a molar basis, there is a linear correlation between the degraded MTBE and the formation of the primary degradation products with distinct slopes (Fig. 6). Within certain limits the slopes of the straight lines are independent of the investigated water types which span a wide range of concentrations of DOC and alkalinity. The slopes of the straight lines (moles product formed/moles MTBE oxidized) are 0.35 mol mol^{-1} for tert-butylformate (TBF), 0.23 mol mol^{-1} for acetone (AC), 0.11 mol mol^{-1} for tert-butanol (TBA) and 0.07 mol mol^{-1} for methylacetate (MA). Based on these correlations it is possible to

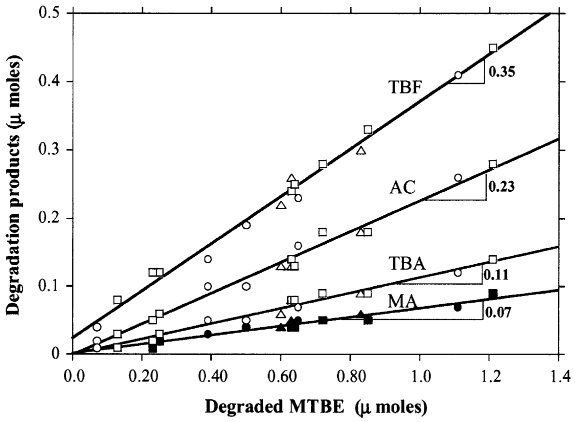


Fig. 6. Formation of some degradation products as a function of MTBE elimination for various waters treated with conventional ozonation and the AOP O_3/H_2O_2. TBF: tert-butyl formate, TBA: tert-butyl alcohol, AC: acetone, MA: methyl acetate. Water types: △,▲ Lake Murten: DOC 2.7 mgl^{-1}, alkalinity 3.8 mM, pH 7.8; □, ■ Lake Zürich: DOC 1.4 mgl^{-1}, alkalinity 2.5 mM, pH 7.8; ○, ● well water, Porrentruy: DOC 0.8 mgl^{-1}, alkalinity 5 mM, pH 7.2. Adapted from Acero et al. [74].

derive the extent of product formation from the decrease of MTBE [74]. Further studies are required to link the decrease of micropollutants during AOPs to the formation of degradation products to obtain an overall assessment of the merits of these processes and to avoid a tradeoff between the toxicity of original and secondary products.

So far, only ozone and OH radicals have been discussed as possible oxidants during conventional ozonation and the AOP O_3/H_2O_2. However, the reaction of OH radicals with NOM and carbonate causes the formation of secondary radicals (peroxy radicals, carbonate radicals). The reactivity of peroxy radicals with organic micropollutants is restricted to easily oxidizable compounds. However, these compounds are rapidly oxidized by ozone and therefore the contribution from the oxidation by peroxy radicals will be small. The second-order rate constants for the reaction of organic micropollutants with carbonate radicals are relatively high for amine- and sulfur-containing pesticides [132]. However, these compounds also react fast with ozone, with a concentration of at least 6 orders of magnitude higher than carbonate radicals. Therefore, carbonate radicals will only play a minor role in ozone-based oxidation processes.

6. Conclusions

It has been demonstrated that many of the oxidation reactions that occur during ozonation are beneficial to the overall drinking-water quality. These advantages include decoloration of the water, improvement of organoleptic properties and oxidation of micropollutants. During ozonation of drinking waters, the two major oxidants *ozone* and *OH radicals* govern the chemical processes. While ozone is a very selective oxidant which reacts quickly with double bonds, activated aromatic compounds and deprotonated amines, OH radicals react with most water constituents with nearly diffusion controlled rates. This high reactivity leads to low transient steady-state concentrations of OH radicals, which is manifested by a low remaining oxidation capacity. To assess oxidation processes during ozonation, empirical methods have to be applied to allow measuring the ozone and the OH radical exposure with a minimal set of experiments.

The oxidation of inorganic micropollutants (e.g. Fe(II), Mn(II), H_2S, NO_2^-) by ozone is usually fast and very efficient. The most prominent exception is ammonia which is only slowly oxidized by ozone and OH radicals. In turn, ammonia also does not affect disinfection efficiency.

The oxidation of organic micropollutants can be divided into compounds that can be directly oxidized by ozone and those which do not react with ozone. For the compounds that can be directly oxidized, ozonation is very efficient. For these compounds, their speciation (e.g. complexation of metals, state of protonation) is decisive for their oxidizability. For ozone-resistant compounds, ozone-based advanced oxidation processes (AOPs, O_3/H_2O_2 or O_3/UV) can be applied for their oxidation. However, in these processes, a large fraction of the oxidation capacity is lost to the matrix. Therefore, the aim of achieving a mineralisation of organic compounds is not realistic. A careful analysis of the degradation products must be performed to evaluate the overall gain of the process with respect to degradation of original compounds and the formation of potentially harmful products. Product studies have been performed for many compounds for the oxidation with OH radicals, and only in a few cases did they cover ozone. For the reaction with ozone, there is general information available on product formation from olefines, amines and some aromatic compounds. Because a mineralization of undesired compounds is not economical during ozonation or AOPs, the best candidates are compounds that change their undesired properties by only slightly altering the original product. In addition, beneficial effects can be achieved by enhancing the biodegradability of the degradation products. They can then be eliminated in a biofilter after ozonation.

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