Compilation of kinetics and mechanisms for the oxidative transformation of organic substances

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Summary

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1 Introduction

Oxidation processes are currently widely implemented for disinfection and decontamination of water and wastewater. Indeed, these processes can be applied to remove pathogenic agents (viruses, bacteria, protozoa) but also inorganic (iron, manganese, arsenic, etc.) and micropollutants (taste and odor compounds, fuel additives, pesticides, chlorinated solvents and algal toxins, etc.). Recently these processes have received a great interest to eliminate emerging substances, such as hormones, pharmaceuticals and personal care products, and sweeteners (Schwarzenbach et al., 2006). These organic micropollutants were demonstrated to be mainly discharged from wastewater effluents (Kolpin et al., 2002). Consequently, to achieve a decontamination of distributed and discharged water, oxidative treatment of water and wastewater have been discussed and investigated from bench- to full-scale (Snyder et al., 2006; Hollender et al., 2009; Rosario-Ortiz et al., 2010; Gerrity et al., 2011).

Ozonation is one of the most implemented oxidation processes for water and wastewater treatment. In this case, ozone (O_3) can oxidize easily compounds with electron-rich moieties (see item 3.1). However, ozone may also be self-decomposed, mostly by dissolved organic matter, to form hydroxyl radicals ($HO^{\bullet}$) which are known to react quickly and unselectively towards a very broad range of compounds (von Gunten, 2003). In water treatment plant, the formation of hydroxyl radicals can be also promoted by addition of hydrogen peroxide (H_2O_2) or UV irradiation.

UV irradiation has been used for disinfection purposes for decades already. However, some (organic) compounds also are sensitive towards UV irradiation, and can be decomposed upon UV absorption by means of photolysis. Photolysis of H_2O_2 results in the formation of hydroxyl radicals. By combining UV irradiation with H_2O_2 a very effective advanced oxidation process can be obtained, in which both photolysis and oxidation of compounds, like organic micropollutants, is combined. In general mercury UV lamps are used for this purpose. There are two types: low pressure (LP) UV lamps, which emit radiation with a wavelength of 253.7 nm, and medium pressure (MP) UV lamps, which emit a broader spectrum between 200 and 300 nm. During a UV/H2O2 process, also other reactions may take place. Examples are UV absorption by natural organic matter, nitrate and hydrogenocarbonate, which may be present in concentrations notably higher than the concentrations of organic micropollutants. Thus, these compounds may compete with the micropollutants for UV radiation. On the other hand, this may result in the formation of radicals, that may cause different reactions of micropollutants (e.g. radicals originating from nitrate photolysis) or may act as radical scavengers, thus hindering the reactions of hydroxyl radicals (hydrogenocarbonate is well known for this effect). Therefore, all such effects have to be taken into account to be able to understand the processes that occur.

Studying the reaction kinetics of the (advanced) oxidation process results in a better understanding of the process, and the factors which influence this process. Thus, insight into the parameters which can be used to control and optimize the process can be obtained. This gives valuable information to drinking water companies and wastewater treatment plants, which consider (advanced) oxidation processes for water treatment, and for companies who develop such technologies.

The aim of this manuscript is (i) to present the main mechanisms of the reactions involved during both oxidative water treatment investigated in the DEMEAU project, *i.e.* ozonation and photolysis, (ii) to describe the different methods for the determination of kinetics rate constants, and (iii) to compile from literature and recent lab studies the rate constants values of compounds relevant for the DEMEAU project.

2 Theory of oxidation kinetics

The efficiency of micropollutant elimination during oxidative water treatment depends on (i) the reactivity of the micropollutant toward the oxidant and (ii) the water quality, especially the water matrix components of water such as dissolved matter (Lee and von Gunten, 2010). The reactivity of a compound toward an oxidant is measured based on chemical kinetics, employing rate laws and rate constants. Indeed, the reaction between oxidants (Ox) and the substrate (M) typically follows second-order reaction kinetics, corresponding to the following equations (1) and (2):

$$M + \vartheta\, Ox \rightarrow M_{oxid} \quad (1)$$

$$-\frac{d[M]}{dt} = k\,[M][Ox] \quad (2)$$

Where k is the second-order rate constant for the elimination of M by the oxidant. Integration of eq. (2) over the reaction time for a closed system (e.g. batch or plug-flow system) yields equation (3) under the conditions [M] < [Ox] (pseudo first order kinetics). This condition is almost always valid during water treatment since the concentration of micropollutants is usually in the ng L^{-1} to the µg L^{-1} range while the concentration of the oxidant is in the mg L^{-1} range.

$$\ln\left(\frac{[M]}{[M_0]}\right) = -\,k \int [Ox]\, dt \quad (3)$$

In the case of ozonation where molecular ozone is partly decomposed to hydroxyl radicals, eq. (3) can be rewritten considering both oxidants as follows:

$$\ln\left(\frac{[M]}{[M_0]}\right) = -\,k_{M,O_3} \int [O_3]\, dt - k_{M,\bullet OH} \int [\bullet OH]\, dt \quad (4)$$

Where $k_{M,O3}$ and $k_{M,\bullet OH}$ are the respective second-order rate constants for the elimination of M by molecular ozone and hydroxyl radicals.
The rate constant $k_{M,O3}$ is typically measured by ozonation of the substrate in ultrapure water in presence of a radical scavenger so that eq. (4) can be simplified to yield:

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_{M,O_3} \int [O_3]\, dt \quad (5)$$

Due to its high water solubility and low reactivity with ozone (k_{O3} = 3 × 10^{-3} M^{-1} s^{-1}) (Hoigné and Bader, 1983a), tert-butanol is typically used to scavenge radicals. Conventional methods of determination of ozonation rate constants will be described hereafter in item 4.1.

UV/H_2O_2 processes can be divided into photolysis and oxidation reactions. The UV dose is the total amount of energy per surface unit (mJ/cm^2). In case of low pharmaceutical concentrations, the logarithm of degradation (ln $[M]_0/[M]$) can be regarded as linear with UV-dose H':

$$\ln\left(\frac{[M]_0}{[M]}\right) = -k_{M,UV}\, H' \tag{6}$$

In equation (6) $k_{M,UV}$ is the degradation rate constant (cm^2 mJ^{-1}) of a compound. This constant consists of the combination of the photolytic degradation rate constant ($k_{photo,UV}$; cm^2 mJ^{-1}), and oxidation rate constant (k_{ox}; cm^2 mJ^{-1}) (eq. (7)):

$$k_{M,UV} = k_{photo,UV} + k_{ox,UV} \tag{7}$$

For experiments without H_2O_2 $k_{ox,UV}$ will be zero. According to Bolton and Stefan, for a collimated beam equipped with LP lamps, assuming a constant water absorption, the photolytic degradation can be written as equation 8 (Bolton and Stefan, 2002):

$$k_{photo} = \ln(10)\frac{\Phi\varepsilon}{U_{254}} \tag{8}$$

"Φ" is the quantum yield, defined as ratio of the amount of absorbed photons resulting in a transformation of the molecule and the total amount of absorbed photons in a compound. "ε" is the molar absorption (L mol^{-1} cm^{-1}). Assuming a quasi-steady state OH radical concentration in the collimated beam, the photolysis of hydrogen peroxide can be written analogous to eq. (8), and the oxidation degradation rate constant becomes (for LP lamps):

$$k_{ox} = 2\ln(10)\frac{\Phi_H\varepsilon_H k_c[H_2O_2]}{U_{254}\sum(k_i[c_i]) + k_H[H_2O_2]} \tag{9}$$

In eq. (9) the subscript H stands for hydrogen peroxide, k_i is the reaction rate constant (L mol^{-1} s^{-1}) of compound c_i with hydroxyl radicals, whereas k_c represents the OH radical reaction rate constant with the target compound (Wols et al., 2013). This kinetic model was extended, taking into account reactions taking place in the water phase (Wols et al., 2014). In this model first and second order reactions were considered, as well as acid-base equilibrium interactions. In this way a system of differential equations was obtained, which can be mathematically written as a matrix consisting of vectors. In compact form this can be written as:

$$\frac{d[M]}{dt} = Nv \tag{10}$$

N represents a stoichiometric matrix with size (p,r), p is the number of reactions and r is the number of compounds. v is the reaction rate vector with length p and [M] is a vector of length r with all compounds. The reaction rate vector v consists of a part related to photolysis reactions and a part related to second-order reactions. A detailed description of this model can be found in Wols *et al.*, 2014.

The composition of the water matrix can play an important role in UV/H2O2 processes. Nitrate, e.g., can be photolyzed at relatively low wavelengths (<240 nm), resulting in the formation of radicals that may interfere with the reaction process. Other compounds, like e.g. (bi)carbonate may act as radical scavengers, hindering the oxidation by hydroxyl radicals. Depending on the circumstances, such reactions will have to be taken into account.

3 Reactivity of oxidants (ozone and hydroxyl radicals) with organic substrates

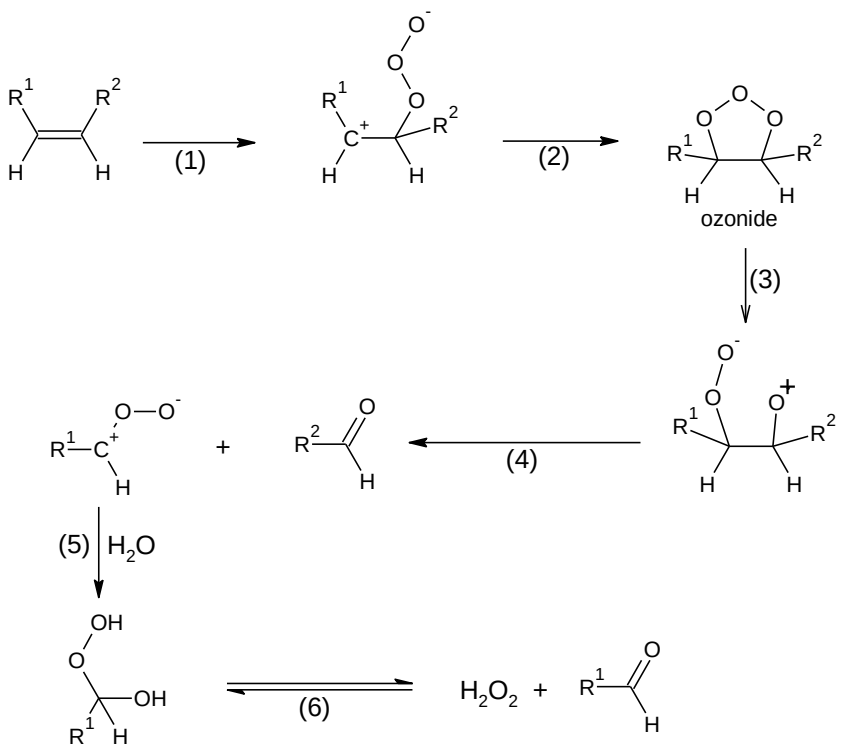
3.1 Reactivity of ozone

Ozone is an electrophilic molecule and may react fast with the electron-rich moieties like olefins, amines, anilines, phenols, among others. The mechanism of some ozonation reactions and the values of the ozonation rate constants will be presented and discussed hereafter. For a comprehensive compilation of reactions mechanisms, more information and examples can be found in the handbook written by von Sonntag and von Gunten (Sonntag and von Gunten, 2012).

3.1.1 Reactivity of ozone with olefins

Due to the high density of electrons in the carbon-carbon π-bond, olefins are usually very reactive with ozone unless they have electron-withdrawing substituents. A mechanism of alkene ozonolysis was first described by Rudolf Criegee [reactions (1)-(6)], and his name is now associated to this reaction (Criegee, 1975).

An intermediate, called ozonide, was demonstrated to be formed by (2+3)–cycloaddition of ozone on olefins [reaction (2)]. The ozonide is then successively transformed to zwitterrions and decomposed finally to carbonylated compounds.



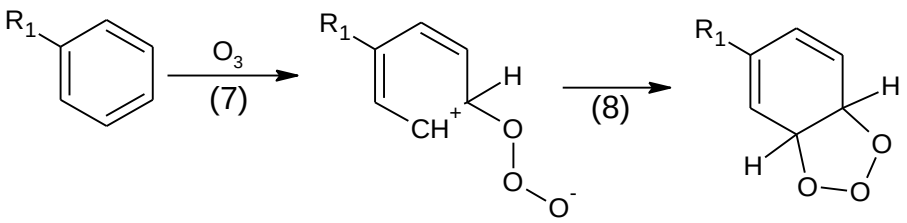
The high reactivity of olefins with ozone was confirmed by the determination of many rate constants (Dowideit and von Sonntag, 1998; Leitzke et al., 2001; Theruvathu et al., 2001; Leitzke et al., 2003; Leitzke and von Sonntag, 2009). The rate constants of alkene ozonolysis are usually superior to 10^4 M^{-1} s^{-1}. For instance, the rate constant of the most basic one, ethene, is 1.8×10^5 M^{-1} s^{-1} (Dowideit and von Sonntag, 1998). However the presence of electron-donating (*i.e.*, alkyl) or –withdrawing (*i.e.*, halide or carboxylic acid) functions can dramatically affect the reactivity of olefins by as much as 6 orders of magnitude, as shown in Table 1.

Table 1: Rate constants of the reaction of ozone with olefins.

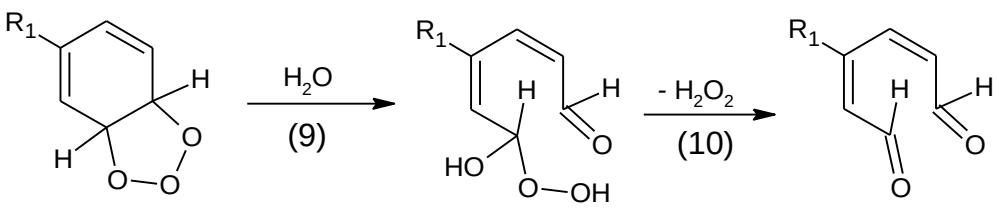
Compound	k (M^{-1} s^{-1})	Reference
Ethene	1.8×10^5	Dowideit and von Sonntag, 1998
Propene	8×10^5	Dowideit and von Sonntag, 1998
Tetramethylene	$> 1 \times 10^6$	Dowideit and von Sonntag, 1998
1,1-Dichloroethene	110	Dowideit and von Sonntag, 1998
cis-1,2-Dichloroethene	540	Dowideit and von Sonntag, 1998
trans-1,2-Dichloroethene	6.5×10^3	Dowideit and von Sonntag, 1998
Trichloroethene	14	Dowideit and von Sonntag, 1998
Tetrachloroethene	<0.1	Dowideit and von Sonntag, 1998
Acrylic acid	2.8×10^4	Leitzke and von Sonntag, 2009

3.1.2 Reactivity of ozone with aromatic compounds

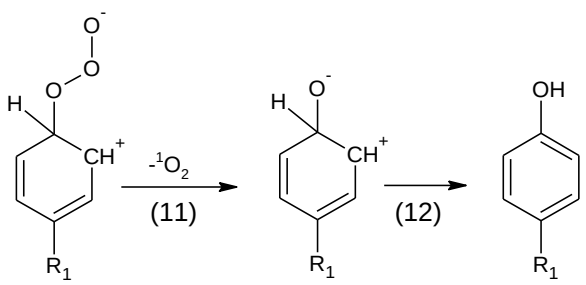
Similarly to olefins, the first step in the reaction of ozone with aromatic compounds is the formation of an ozone adduct *via* a zwitterion [reactions (7)-(8)].



Based on a mechanism similar to olefin ozonation, the initial carbon-carbon double bond where the ozone adduct is located is disrupted. The aromatic ring is consequently opened to produce a dialdehyde and H_2O_2 [reactions (9)-(10)].



The ozonation of aromatic compounds may also frequently lead to hydroxylation. This reaction occurs after the release of singlet oxygen from the zwitterionic adduct and the re-aromatization by proton loss [reactions (11)-(12)].



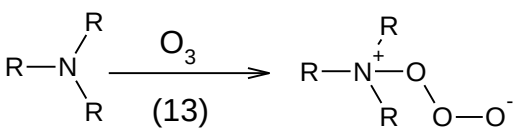
Benzene itself presents a low reactivity with ozone (2 M^{-1} s^{-1}, see Table 2). However, electron-donating substituents, such as hydroxyl, alkoxyl, alkyl or amine groups, activates the aromatic rings allowing an increasing reactivity with ozone (Table 2). On the contrary, electron-withdrawing groups, e.g. halide, deactivate benzene ring producing a significant decrease of reactivity. Obviously, increasing the number of activating (or deactivating) groups leads to a dramatic increase (respectively decrease) of the measured ozone rate constants. For example, the following compounds can be sorted by increasing rate constants as follows:
Trichlorobenzene < Dichlorobenzene < Chlorobenzene < Benzene < Methoxybenzene < Dimethoxybenzene < Trimethoxybenzene.

Table 2: Rate constants of the reaction of ozone with benzene and its derivatives.

Compound	k (M^{-1} s^{-1})	Reference
Benzene	2	(Hoigné and Bader, 1983a)
Aniline	9.0×10^7	(Hoigné and Bader, 1983b)
Dihydroxybenzene (catechol and hydroquinone)	$0.52 – 2.3 \times 10^6$	(Mvula and von Sonntag, 2003)
Phenol	1300	(Hoigné and Bader, 1983b)
anion	1.4×10^9	(Hoigné and Bader, 1983b)
Trimethoxybenzene (1,3,5-)	9.4×10^5	(Muñoz and von Sonntag, 2000)
Dimethoxybenzene (1,4-)	1.3×10^5	(Muñoz and von Sonntag, 2000)
Methoxybenzene	290	(Hoigné and Bader, 1983a)
Trimethylbenzene (1,2,4 and 1,3,5)	400-700	(Hoigné and Bader, 1983a)
Xylene (o-, m- and p-)	94-140	(Hoigné and Bader, 1983a)
Toluene	14	(Hoigné and Bader, 1983a)
Chlorobenzene	0.75	(Hoigné and Bader, 1983a)
Dichlorobenzene	0.57	(Yao and Haag, 1991)
Trichlorobenzene	< 0.06	(Yao and Haag, 1991)

3.1.3 Reactivity of ozone with amines

Ozone typically reacts with aliphatic amines by addition to the lone pair at nitrogen as shown in reaction (13).

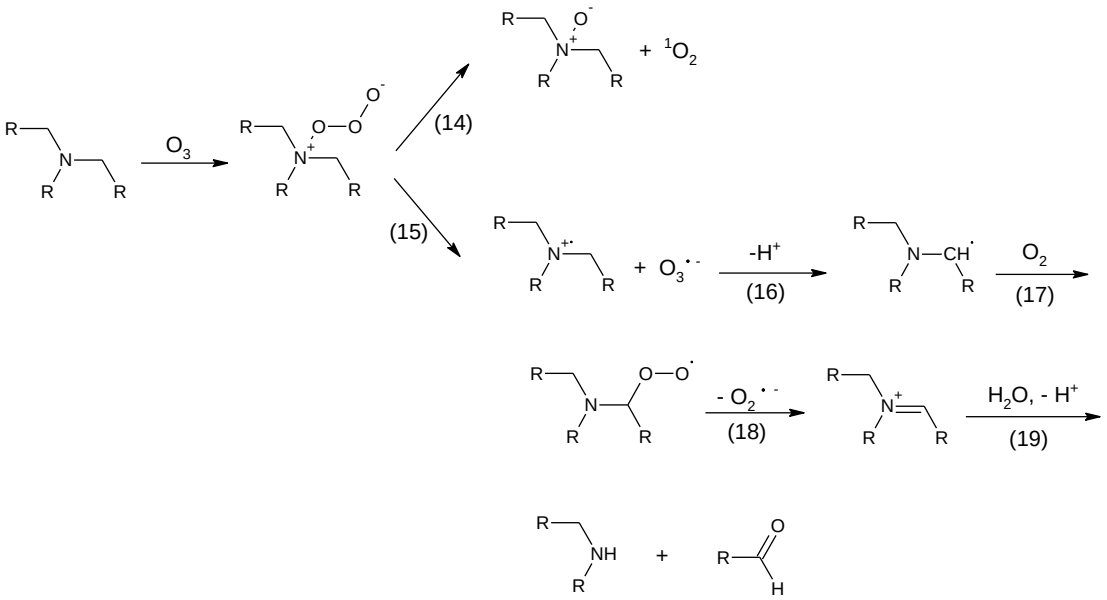


The presence of electron-donating alkyl groups increases the electron density at nitrogen atom and enhances the ozone addition reaction. The ozonation rate constants of alkylated amines are usually measured in the range 10^4-10^7 M^{-1} s^{-1}. However, the reactivity of amines increases with the number of alkyl substituents as shown in Table 3. In contrast, ammonia, not activated by alkyl group, has a very low reactivity with ozone (20 M^{-1} s^{-1}). While protonated (pKa ~ 9.5), amines present almost no reactivity. Thus, the kinetic of amine ozonation is greatly dependent to pH. This parameter, usually varying from 6.5 to 8.5 in drinking and wastewaters, can consequently influence greatly the efficiency of amine oxidation during water treatment.

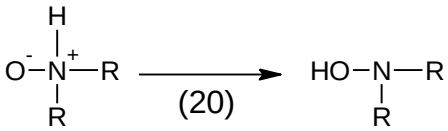
Table 3: Rate constants of the reactions of ozone with amine compounds.

Compound	pKa	k (M^{-1} s^{-1})	Reference
Triethylamine	11.0	4.1×10^6	Muñoz and von Sonntag, 2000
protonated		5 ± 4	(Pryor et al., 1984)
Diethylamine	10.5	9.1×10^5	Munoz and von Sonntag, 2000
protonated		11 ± 6	Pryor et al., 1984
Ethylamine	10.8	2.4×10^5	Munoz and von Sonntag, 2000
Ammonia	9.2	20	Hoigné and Bader, 1983
protonated		no reaction	Hoigné and Bader, 1983

The mechanism of amine ozonolysis is described hereafter.
In the case of tertiary amines, the formed ozone adduct can react in two different ways. On the one hand, the ozone adduct can lose O_2, resulting in the formation of an N-oxide and singlet oxygen $^1O_2$ [reaction (14)]. N-oxides have been already demonstrated to be formed during the ozonation of tramadol (Zimmermann et al., 2012), trialkylamine (Muñoz and von Sonntag, 2000) and clarithromycin (Lange et al., 2006), among others.

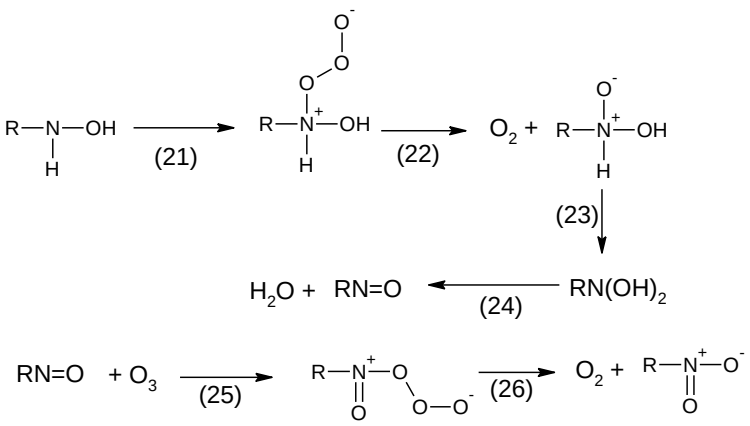


The second way of decomposition of the ozone adduct leads to the loss of an ozonide radical anion $O_3^{\bullet -}$ and the formation of an amine radical cation [reactions (15)-(19)]. After further reactions, this latter finally cleaves to give a secondary amine and an aldehyde. These products were identified after ozonation of tramadol (Zimmermann et al., 2012) and triethylamine (Muñoz and von Sonntag, 2000). Anyway, these studies showed that the N-oxide was the predominant ozonation products (about 90%).
Likewise, primary and secondary amines may form with ozone an N-oxide. However, this molecule is a short-lived intermediate and rearranges into hydroxylamine [reaction (20)].

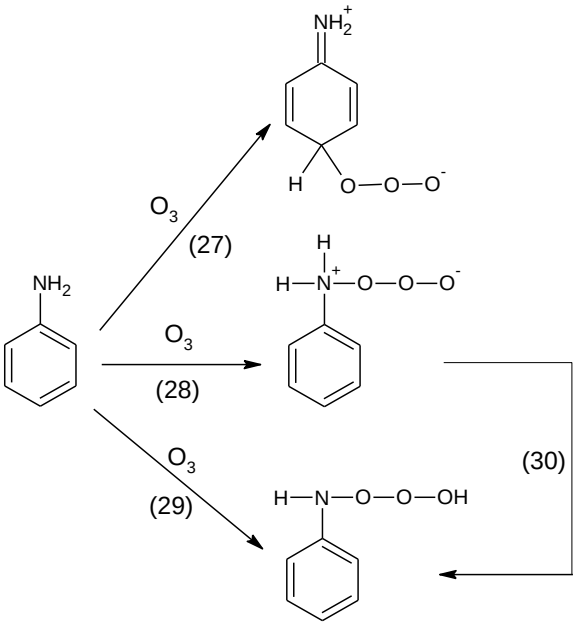


Hydroxylamine has been identified during the ozonation of β-blockers, metoprolol and propranolol (Benner and Ternes, 2009a; 2009b).

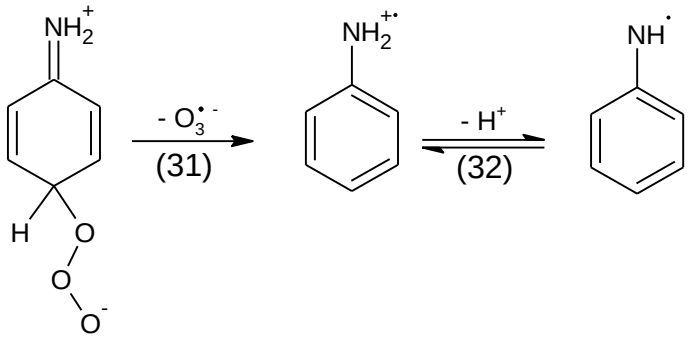
In the case of the primary amine, hydroxylamine can be further oxidized by ozone to form nitroso and nitro compounds [reactions (21)-(26)].



The reaction of aniline with ozone is very fast (9.0×10^7 M^{-1} s^{-1}, Table 2). For this reaction, addition of ozone to the strongly activated aromatic ring (as suggested in item 3.1.2, reaction (27)) as well as addition to nitrogen can be envisaged (reactions (28)-(30)).



Similarly to primary amine, aniline ozone adduct at nitrogen may be followed by the formation of nitroso and nitro compounds, *i.e.* nitrosobenzene and nitrobenzene.
Otherwise, ozone addition to the aromatic ring may lead to the release of $O_3^{\bullet -}$ and the subsequent formation of aniline radical cation [reactions (31)-(32)].



3.2 Reactivity of hydroxyl radicals

As mentioned before, hydroxyl radicals react very quickly and unselectively with a broad range of compounds. In order to be able to validate the kinetic model developed, reaction rate constants for a large set of pharmaceuticals were gathered, both from literature data as well as experimentally. An overview of literature data was presented here (Dorfman and Adams, 1973).

4 Determination of the second-order rate constants

4.1 Determination of the ozonation rate constants

Different protocols for the determination of the kinetic rate constants have been described before (Hoigné and Bader, 1983a, b; Yao and Haag, 1991). In our studies, only substrate monitoring and the competition kinetic methods were implemented with minor changes compared to methods described in the previous publications.

4.1.1 Substrate monitoring method

The substrate monitoring method is usually implemented for compounds with water solubility lower than 50 µM and lower rate constants, *i.e.* < 10^4 M^{-1} s^{-1} (Yao and Haag, 1991). In a 250-mL bottle equipped with a dispenser, a solution of an organic substrate S prepared in nanopure water in presence of a phosphate buffer (50 mM, pH 7) and the radical scavenger t-BuOH (20 mM) are oxidized by addition of an aliquot of an ozone stock solution. Under these conditions, the concentration of dissolved ozone is in excess compared to the substrate (usually ≥ 10-fold excess). At regular time intervals, a first aliquot (1.5 mL) is dispensed and placed in a vial containing sulfite in excess to quench the residual ozone and to stop the reaction. Right after, a second aliquot (1.5 mL) is dispensed and placed in a vial containing potassium indigo trisulfonate. The concentration of the organic substrate is monitored by HPLC by injecting the first aliquot (50-100 µL) into the HPLC system. The mobile phases ((A): 0.1% formic acid in ultrapure water and (B): 0.1% formic acid in methanol) are pumped at 300 µL min^{-1} using a binary pump. A diode-array detector was used for the detection of analytes at the wavelengths of 200, 221, 254, 271 and 310 nm. The dissolved ozone concentration in the reactor is monitored by measuring the bleaching in the second aliquot at the wavelength of 600 nm. The rate constant $k_{M,O3}$ of the substrate is determined with equation (11) already presented in the introduction.

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_{M,O_3} \int [O_3]\, dt \qquad (11)$$

The factor ∫[O_3] dt is calculated as the area under the curve representing the concentration of dissolved ozone [O_3] as a function of time.

4.1.2 Competition kinetic method

The competition kinetic method is generally used to measure rate constants of substrates reacting fast with ozone, i.e. > 10^4 M^{-1} s^{-1} ((Yao and Haag, 1991)). In batch reactors (8 mL), solutions containing a pair of compounds, the substrate M and a competitor C (here cinnamic acid), are ozonated in presence of a phosphate buffer (50 mM, pH 7) and the hydroxyl radical scavenger t-BuOH (20 mM) with different amounts of stock solution of ozone. The residual concentrations of the substrate and the competitor are measured with the HPLC-DAD system described above and the rate constant k_S of the substrate is calculated with the following equation:

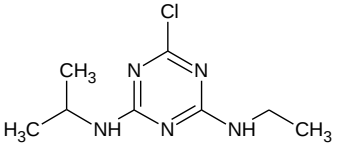
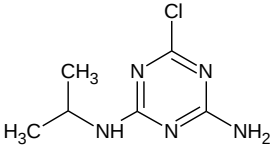
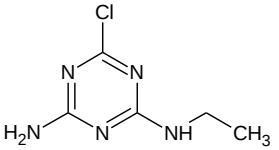
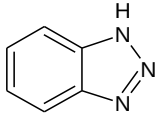
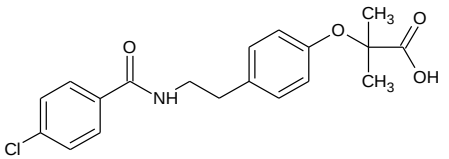
$$k_{M,O_3} = \frac{\ln\left(\frac{[M]_0}{[M]}\right)}{\ln\left(\frac{[C]_0}{[C]}\right)} k_{C,O_3} \qquad (12)$$

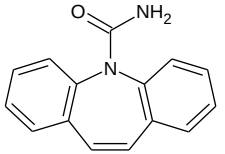
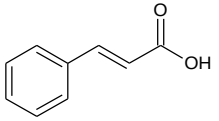
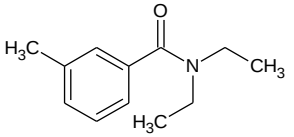
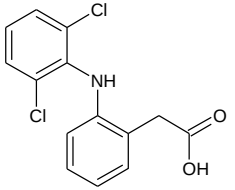
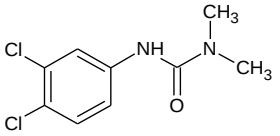
where $[M]_0$ and [M] are the initial concentration and the concentration at time t of the substrate M respectively; $[C]_0$ and [C] are the initial concentration and the concentration at time t of the competitor C, respectively, and k_C the rate constant of the competitor, here 3.8×10^5 M^{-1} s^{-1} for the anionic form of cinnamic acid (pKa = 4.4) (Leitzke et al., 2001).

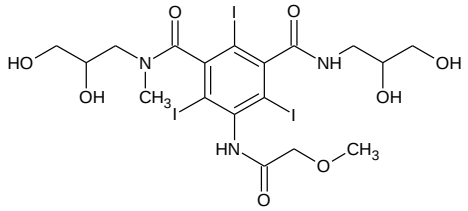
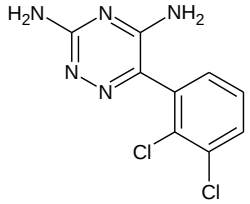
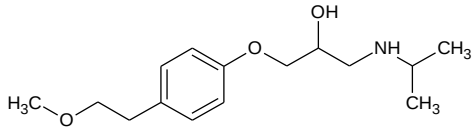
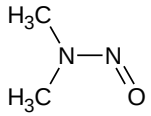
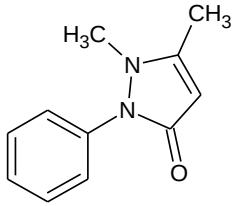
4.1.3 Compilation of rate constants of ozonation

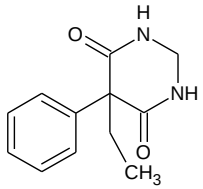
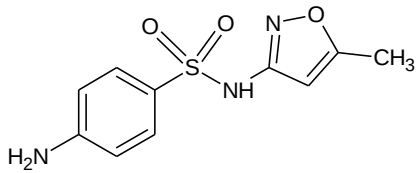
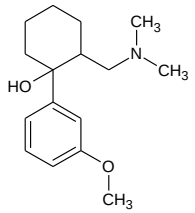
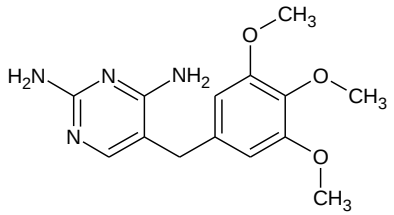
Based on the two methods previously described, second-order rate constants were determined and presented in Table 4.

Table 4: Rate constants of ozonation for the compounds of interest from the DEMEAU list.

Compound	Source/ Application	Structure	pKa	pH	k_{O3} (M^{-1} s^{-1})	Method	Reference
Atrazine	Pesticide			4 	5.65 6.0	SCR OM	(de Laat et al., 1996) (Acero et al., 2000)
Atrazine-Desethyl	OP (atrazine)			2	0.18	OM	(Acero et al., 2000)
Atrazine-Desisopropyl	OP (atrazine)			2	3.1	OM	(Acero et al., 2000)
Benzotriazole anion	Indus. Chem.		1.6, 8.2		20 36 2143	CK (metoprolol) CK (ibuprofen) CK (metoprolol)	(Benitez et al., 2014) (Vel Leitner and Roshani, 2010) (Benitez et al., 2014)
Bezafibrate	Pharm.			6	590	SM	(Huber et al., 2003)
Bromate	DBP	BrO_3^-			$< 1 \times 10^{-3}$	OM	(Hoigné et al., 1985)
Bromide	Inorganic	Br^-			160 258	OM OM	(Haag and Hoigne, 1983) (Liu et al., 2001)

Compound	Source/ Application	Structure	pKa	pH	k_{O3} (M^{-1} s^{-1})	Method	Reference
Carbamazepine	Pharm.			7	3×10^5	CK (nitrite or buten-3-ol)	(Huber et al., 2003)
Cinnamic acid anion	Chemical				5×10^4 3.8×10^5	CK (buten-3-ol)	(Leitzke et al., 2001) (Leitzke et al., 2001)
DEET	Pesticide				<10		(Lee and von Gunten, 2010)
Diclofenac	Pharm.			7	1.8×10^4 6.8×10^5 $\sim 10^6$	CK (phenol) CK (buten-3-ol) CK (phenol)	(Vogna et al., 2004) (Sein et al., 2008) (Huber et al., 2003)
Diuron	Pesticide			4	14.7 16.5	SCR CK (fenuron)	(de Laat et al., 1996) (Benitez et al., 2007)
Hydroperoxide ion protonated		HO_2^-/H_2O_2	11.6		5.5×10^6 <0.01	OM	(Staehelin and Hoigne, 1982) (Staehelin and Hoigne, 1982)
Hypobromous acid anion	DBP	$BrOH/BrO^-$			$< 1 \times 10^{-2}$ 330	OM	(Hoigné et al., 1985) (Haag and Hoigne, 1983)

Compound	Source/ Application	Structure	pKa	pH	k_{O3} (M^{-1} s^{-1})	Method	Reference
Iopromide	X-Ray CM			3.3-4.5	<0.8	OM	(Huber et al., 2003)
Lamotrigine	Pharm.			7	4	SM	(Keen et al., 2014)
Metoprolol unprotonated protonated	Pharm.		9.7	7	2.0×10^3 8.6×10^5 330	 CK (cinnam. ac.) SM	(Benner and Ternes, 2009a) (Benner and Ternes, 2009a) (Benner and Ternes, 2009a)
NDMA	DBP			2.5	0.052	OM	(Lee et al., 2007)
Phenazone	Pharm.			7	6.6×10^4	CK (carbamazepine)	(Favier et al., 2014)

Compound	Source/ Application	Structure	pKa	pH	k_{O3} (M^{-1} s^{-1})	Method	Reference
Primidone	Pharm.			7	1.0	CK (linuron)	(Real et al., 2009)
Sulfamethoxazole deprotonated	Pharm.		5.6		4.7×10^4 5.7×10^5	CK (cinnamic acid)	(Dodd et al., 2006) (Dodd et al., 2006)
Tramadol protonated	Pharm.		9.4		1.0×10^6 7.7×10^4	CK (cephalexin)	(Zimmermann et al., 2012) (Zimmermann et al., 2012)
Trimethoprim deprotonated monoprotonated diprotonated	Pharm.		3.2, 7.1	7	2.7×10^5 5.2×10^5 7.4×10^4 3.3×10^4	CK (cinnamic acid)	(Dodd et al., 2006)

Ind. Chem.: industrial chemical; Pharm.: pharmaceutical; X-Ray CM: X-Ray contrast medium; OP: oxidation product; SM: substrate monitoring; CK: competition kinetic; OM: ozone monitoring; SCR: semi-continuous reactor.

4.2 Determination of the photolysis reaction rate constants

4.2.1 Collimated beam method

Photolysis rate constants can be determined under well-defined laboratory conditions in an instrument using collimated beam of UV light:

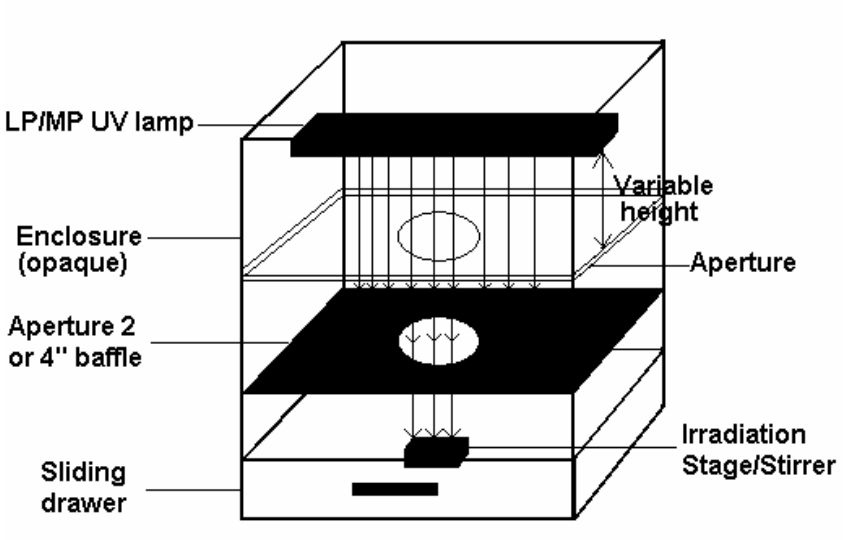


Figure 1: Schematic picture of a collimated beam installation.

The lamp ('beamer' in Figure 1) is placed in a box made of stainless steel. The irradiation enters a wooden box through a hole. By means of a collimator, formed by adjustable plates, a parallel UV bundle hits the water sample. As the plates are removed or adjusted, the bundle can be adjusted, obtaining an optimal uniform irradiation of the sample surface. Furthermore, the sample is stirred during the irradiation.
By means of an automatic shutter, the UV irradiation is interrupted after a certain irradiation time. The required irradiation time is calculated based on specific conditions (like UV_{254nm} (LP-lamp) or $UV_{200-300\ nm}$ (DBD- or MP-lamp), the UV-intensity of the lamp, sample volume, petri factor (the ratio of the average incident irradiance across the top cross section of the Petri dish divided by the irradiance at the center of the dish, correcting for the the fact that the UV beam is not uniform perpendicular to the axis of the beam) (Bolton and Linden, 2003). The petri factor accounts for the fact that the UV beam is never perpendicular to the axis of the beam, and is defined as the ratio of the average incident irradiance across the top cross section of the Petri dish, divided by the irradiance at the center of the disk. In order to determine the influence of radical scavengers, the k_{CO3} constants were measured using a collimated beam set up with Milli Q and HCO_3^-. Then pH was adjusted by adding NaOH or by blowing CO_2 through the solution. Experiments were carried out at pH 8.4 (HCO_3^-), 10.2 (with NaOH) and 6.5 (CO_2).
A model (Bolton, 2010) was used to determine the required irradiation time, depending on factors like the desired UV dose, the UV transmission of the water, the depth of the water sample, distance to the UV lamp, and the petri factor. The conversion of organic micropollutants can be determined as a function of the UV dose applied and the presence of H_2O_2, and from these data reaction rate constants can be determined (when the photolysis is known, oxidation constants can be derived from the combined data).

4.2.2 Compilation of photolysis reaction rate constants

By means of laboratory research, using a collimated beam set-up, kinetic parameters for UV/H_2O_2 processes were determined (Table 5). Furthermore, the total reaction rate constants of a selection of compounds for LP and MP UV/H_2O_2 processes were measured in different water matrices, as shown in Table 6.

Table 5: **Photolysis and oxidation rate constants for a set of pharmaceuticals, determined at KWR. When available, (average) literature data are shown in italics (Wols and Hofman-Caris, 2012b).**

Compound	**Φ_{254} (10^{-2})** (mol Einstein^{-1})	**E_{254} (10^{3})** (L mol^{-1} cm^{-1})	**k_{OH} (10^{9})** (L mol^{-1} s^{-1})	**k_{CO3} (10^{7})** (L mol^{-1} s^{-1})
Atenolol	6.5 (± 1.8)	0.35 (± 0.08)	7. (± 0.75)	0.52 (± 0.25)
Benzotriazole	n.a.	n.a.	n.a.	n.a.
Bezafibrate	0.24 (± 0.05)	14 (± 0.24)	8.7 (± 0.88)	n.a.
Carbamazepine	0.33 (± 0.1)	5.8 (± 0.09)	9.5 (± 1)	0.42 (± 0.35)
	0.060	*6.07*	*8.02 (± 1.90)*	
Clenbuterol	2 (± 0.37)	3.9 (± 0.007)	6.6 (± 0.89)	52 (± 14)
Clofibric acid	41 (± 2.7)	0.51 (± 0.03)	6.4 (± 0.44)	1 (± 0.44)
	27.5 (± 37.3)	*0.927 (± 0.93)*	*5.03 (± 2.38)*	
Cortisol	3.2 (± 0.31)	1.6 (± 0.34)	8 (± 0.91)	0.24 (± 0.56)
Cortisone	1.1 (± 0.17)	14 (± 0.075)	6.3 (± 0.41)	0.68 (± 0.54)
Cyclophosphamide	4.6 (± 2e2)	0.0031 (± 4.3e-5)	3.2 (± 0.19)	0.13 (± 0.26)
Diatrizoic acid	3.9 (± 0.36)	19 (± 0.82)	0.36 (± 0.13)	n.a.
	3.50	*31.2*	*0.54*	
Diclofenac	23 (± 1.6)	6.8(± 0.27)	8.2 (± 2.6)	7.8 (± 2)
	19.2 (± 8.6)	*4.77 (± 1.16)*	*8.38 (± 1.24)*	
Erythromycin A	n.a.	n.a.	3.8 (± 0.76)	8 (± 5.8)
Fluoxetine	41 (± 4.2)	0.79 (± 0.03)	9 (± 1.8)	n.a.
Furosemide	2.2 (± 0.28)	6.7 (± 1.2)	11 (± 1.89)	6.8 (± 0.96)
Gemfibrozil	9.2 (± 1.9)	0.37 (± 0.01)	9.1 (± 0.88)	0.41 (± 0.32)
Ifosfamide	n.a.	n.a.	3.6 (± 0.34)	n.a.
Iopromide	*3.90*	*21.0*	*3.30*	n.a.
Ketoprofen	22 (± 21)	38 (± 0.45)	15 (± 17)	39 (± 4.5)
	29.8 (± 8.7)	*15.3 (± 0.2)*	*6.89 (± 2.14)*	

Compound	Φ_{254} (10^{-2}) (mol Einstein^{-1})	E_{254} (10^{3}) (L mol^{-1} cm^{-1})	k_{OH} (10^{9}) (L mol^{-1} s^{-1})	k_{CO3} (10^{7}) (L mol^{-1} s^{-1})
Metformin	1.4 (± 0.64)	0.94 (± 0.01)	1.4 (± 0.12)	n.a.
Metoprolol	6.6 (± 4.7)	0.33 (± 0.001)	8.1 (± 0.98)	0.51 (± 0.41)
	3.47 (± 4.12)	*0.565 (± 0.33)*	*7.84 (± 0.77)*	
Metronidazole	1 (± 0.4)	2.2 (± 0.05)	5 (± 0.51)	n.a.
	0.340 (± 0.01)	*2.10*	*17.9 (± 22.6)*	
Naproxen	1.4 (± 0.16)	4.8 (± 0.12)	10 (± 1.6)	5.6 (± 1.1)
	2.78 (± 2.06)	*4.00 (± 0.70)*	*8.61*	
Niacin	n.a.	n.a.	1.7 (± 0.22)	0.55 (± 0.21)
Paracetamol	0.44 (± 0.1)	8.1 (± 0.13)	7.1 (± 0.58)	17 (± 3.9)
	0.180	*6.64 (± 2.14)*	*5.85 (± 4.51)*	
Paroxetine	21 (± 14)	0.25 (± 0.005)	9.6 (± 3.6)	42 (± 8.7)
Pentoxifylline	0.39 (± 0.12)	4.4 (± 0.15)	6.8 (± 0.41)	0.2 (± 0.3)
Phenazone	5.92 (± 0.35)	8.9 (± 0.071)	5.3 (± 0.35)	0.5 (± 0.18)
	3.37 (± 4.18)	*8.60 (± 0.43)*	*7.93 (± 4.34)*	
Prednisolone	13 (± 11)	71 (± 4)	16 (± 215)	25 (± 3.4)
Primidone	*8.20*	*0.220*	*6.70*	*n.a.*
Propranolol	3.2 (± 1.7)	1.3 (± 0.02)	11 (± 2.65)	25 (± 5)
Sotalol	39 (± 3.7)	0.37 (± 0.04)	7.9 (± 3.2)	22 (± 17)
Sulfachloropyridazine	0.58 (± 0.1)	22 (± 0.65)	11 (± 3.4)	30 (± 4.7)
Sulfadiazine	0.48 (± 0.08)	23 (± 0.27)	11 (± 1.8)	28 (± 3.2)
	0.581	20.1	4.50 (± 1.13)	
Sulfamethoxazole	8.4 (± 0.95)	13 (± 0.10)	6.3 (± 0.55)	12 (± 6.9)
	3.79 (± 1.15)	*13.2 (± 4.5)*	*5.82 (± 1.99)*	
Sulfaquinoxalin	0.26 (± 0.04)	39 (± 0.68)	11 (± 2.3)	26 (± 2.7)

Compound	**Φ_{254} (10^{-2})** **(mol Einstein^{-1})**	**E_{254} (10^{3})** **(L mol^{-1} cm^{-1})**	**k_{OH} (10^{9})** **(L mol^{-1} s^{-1})**	**k_{CO3} (10^{7})** **(L mol^{-1} s^{-1})**
Trimethoprim	0.09 (± 0.04) *0.118*	16 (± 0.12) *2.94*	8 (± 0.73) *6.30 (± 0.85)*	1.3 (± 0.41)
Venlafaxine	9.7 (± 5.7)	0.38 (± 0.02)	8.8 (± 1.5)	n.a.
Atrazine	*4.8 (± 1.4)*	*3.4 (± 0.66)*	*2.3 (± 0.14)*	0.4 (± 0.15) *0.4*
pCBA	*1.3*	*2.4*	*5.0*	1.3 (± 0.31)

n.a. : not analyzed

Problems were encountered to include 3 compounds (benzotriazole, iopromide and primidone) into the analytical method. Therefore, rate constants of these compounds could not be determined. For iopromide and primidone, literature values are available.

Table 6: Fluence based reaction rate constants for several pharmaceuticals in a LP and MP UV and UV/H_2O_2 processes with different types of water (*10^4) (cm^2 mJ^{-1}).

Lamp Type	**LP**	**LP**	**LP**	**MP**	**MP**	**MP**	**LP**	**LP**	**LP**	**MP**	**MP**	**MP**
Water Type	**MilliQ**	**NWG**	**Meuse**	**MilliQ**	**NWG**	**Meuse**	**MilliQ**	**NWG**	**Meuse**	**MilliQ**	**NWG**	**Meuse**
H_2O_2 (mg L^{-1})	**0**	**0**	**0**	**0**	**0**	**0**	**10**	**10**	**10**	**10**	**10**	**10**
Amph	1.6	0.5	6.6	54.2	73.6	392.5	212.2	85.1	78.3	301.9		338.1
Atenolol	1.1	0.3	0.8	29.5	10.0	20.4	191.7	25.7	20.6	308.8	49.9	37.1
Bezafibrate	1.8	1.2	1.2	42.1	17.9	25.7	237.3	31.8	25.3	363.7	62.1	46.1
Carbamazepine	0.9	0.1	0.7	30.6	8.2	26.2	256.8	34.5	26.0	390.4	59.4	46.0
Clenbuterol	4.0	3.0	5.2	61.9	51.1	348.0	175.5	56.1	50.4	254.6	189.6	307.8
Clindamycin	0.6	0.6	2.2	25.9	19.6	156.6	243.1	52.9	40.0	353.4	106.8	123.3
Clofibric Acid	10.5	10.0	10.3	122.1	88.2	79.8	183.5	32.1	27.6	372.5	125.1	90.3
Cortisol	26.8	27.4	24.9	34.2	17.5	34.4	244.4	60.4	54.0	328.5	60.0	47.8
Cortisone	7.9	7.7	7.4	24.2	7.9	17.2	184.0	32.9	25.5	264.8	37.8	29.8
Cyclophosphamide	0.1	-0.1	-0.2	10.8	2.0	6.5	89.8	11.2	9.4	125.8	16.5	13.9
Diatrizoic Acid	37.3	46.2	40.7	27.9	30.4	23.4	53.4	49.4	43.0	42.0	30.4	30.1
Diclofenac	78.8	79.3	81.8	270.0	179.6	444.7	281.4	127.3	152.9	441.7	309.9	426.2
Dimethylaminophenazone	151.2	143.7	392.3	414.0	426.7	414.5						
Erythromycin A	0.0	0.5	0.4	14.0	8.0	11.1	97.5	16.9	10.4	192.6	32.8	15.0
Fluoxetine	15.9	14.5	15.7	114.5	75.5	67.6	248.6	45.8	35.1	422.0	108.1	83.0
Furosemide	7.6	5.9	7.0	80.2	39.3	151.2	312.1	57.2	40.9	483.8	115.6	113.2

Lamp Type	LP	LP	LP	MP	MP	MP	LP	LP	LP	MP	MP	MP
Water Type	MilliQ	NWG	Meuse	MilliQ	NWG	Meuse	MilliQ	NWG	Meuse	MilliQ	NWG	Meuse
H_2O_2 (mg L^{-1})	0	0	0	0	0	0	10	10	10	10	10	10
Gemfibrozil	1.6	0.5	0.8	43.4	7.6	22.4	247.4	31.1	25.2	385.9	56.0	46.5
Guanylurea	3.9		-0.8	1.4			1.3		0.3	4.2		
Ifosfamide	0.2	-0.0	-0.3	12.8	3.0	7.8	101.1	12.0	10.3	150.4	20.6	15.3
Ketoprofen	422.8	428.1	444.5	430.0	432.1	446.3	832.7	823.1	808.6	870.9	635.9	621.4
Lincomycin	0.9	1.4	2.9	27.7	34.1	228.2		78.8	47.3	517.7		165.1
Metformin	0.8		-0.0	4.4			36.6		3.9	55.1		
Metoprolol	0.8	0.4	0.8	35.6	15.3	25.7	217.2	28.5	23.0	337.3	60.1	46.1
Metronidazole	1.4	0.9	1.8	17.6	5.3	12.8	133.6	19.2	14.5	201.7	27.9	23.9
Naproxen	3.3	2.5	3.8	79.8	56.4	133.1	276.5	47.8	37.8	449.5	147.6	114.4
Niacin	1.2	0.7	-2.3	5.9	2.1		42.8	9.6	7.2	60.9	14.2	6.6
Paracetamol	1.9	1.3	8.6	54.1	98.6	364.2	194.1	19.6	91.7	295.4		350.4
Paroxetine	2.4	2.6	3.8	72.9	20.2	113.7	233.6	33.7	28.4	383.9	79.5	92.7
Penicillin V	13.3		14.7	81.2		53.2						
Pentoxifylline	0.9	0.5	0.8	21.9	5.3	17.2	186.6	23.2	18.6	279.2	37.8	30.9
Phenazone	26.5	27.3	25.3	36.7	23.0	29.3	170.7	45.6	42.1	247.3	52.7	44.9
Pindolol	4.2	5.7	19.4	376.3	160.2	518.8		94.2	172.5	311.2	383.0	916.2
Prednisolone	454.4	451.8	508.8	391.3	408.0	460.8	888.0	889.8	722.6	722.4	439.8	452.5
Propranolol	1.6	2.3	4.5	53.5	68.0	300.7	286.1	94.5	56.3	445.4		222.7

Lamp Type	LP	LP	LP	MP	MP	MP	LP	LP	LP	MP	MP	MP
Water Type	**MilliQ**	**NWG**	**Meuse**	**MilliQ**	**NWG**	**Meuse**	**MilliQ**	**NWG**	**Meuse**	**MilliQ**	**NWG**	**Meuse**
H_2O_2 (mg L^{-1})	**0**	**0**	**0**	**0**	**0**	**0**	**10**	**10**	**10**	**10**	**10**	**10**
Salbutamol	1.3	2.4	3.7	38.4	41.9	343.0		22.3	29.5	260.2	116.5	190.4
Sotalol	7.3	43.8	51.2	79.6	83.3	307.9	177.2	91.0	71.0	300.8		155.5
Sulfachloropyridazine	6.2	4.2	5.8	85.1	37.9	342.3	278.9	51.5	37.7	401.2	166.6	199.3
Sulfadiazine	5.4	6.3	6.3	66.7	42.2	357.6	292.8	64.2	37.2	397.2	138.6	200.5
Sulfamethoxazole	56.9	25.9	24.0	109.5	51.1	302.1	228.2	58.3	46.7	361.9	85.3	169.4
Sulfaquinoxalin	4.9	1.0	1.8	79.0	27.9	309.0	288.3	31.9	28.1	431.8	83.7	163.1
Terbutaline	1.1	5.1	36.4	50.1	281.6	376.8						
Trimethoprim	0.9	0.3	0.5	25.0	6.9	23.9	219.9	29.0	22.8	334.6	49.0	41.6
Venlafaxine	1.5	0.6	1.1	37.7	16.4	40.6	232.3	31.5	25.4	371.1	67.3	55.6

Problems were encountered to include 3 compounds (benzotriazole, iopromide and primidone) into the analytical method. Therefore, rate constants of these compounds could not be determined.

4.3 Estimation of the second order rate constants using a quantitative structure-activity relationships (QSAR) approach

Water resources may be contaminated by an immense range of micropollutants presenting chemically structural diversity. To date, oxidation rate constants are far away to be available for all these compounds.
However, several models have been developed to correlate oxidation rate constants of compounds with their chemical structures using substituents descriptor variables (Canonica and Tratnyek, 2003). Oxidation rate constants and thus elimination of a micropollutant during an oxidative water treatment would be rapidly estimated.
Using the existing rate constants, models have been established to predict rate constants for chlorination (Gallard and von Gunten, 2002), ferrate^{VI} (Lee et al., 2005), ozonation and hydroxyl radical oxidation (Suarez et al., 2007; Lee et al., 2014).
Recently, Lee and von Gunten developed a general set of 18 QSARs based on 412 measured k-values for the oxidation of organic micropollutants with chlorine, chlorine dioxide, ferrate^{VI} and ozone (Lee and von Gunten, 2012). Developed QSARs enables to predict 303 of 412 (74%) rate constants within a factor of 3 compared to the measured values. Additionally, using models for the oxidation of selected micropollutants by hydroxyl radicals, 39 of 45 (87%) predicted k-values were obtained within a factor of 3 compared to the measured data.
Wols and Vries developed a QSAR model for OH reaction rate constants in UV/H_2O_2 processes (Wols and Vries, 2012).
Consequently, though there are still some uncertainties concerning the predicted rate constants, the QSAR models can be a useful tool for the estimation of rate constants and thus of the conversion of micropollutants in treated water.

5 Prediction of micropollutant elimination during oxidative water treatment

5.1 Prediction of micropollutant removal by ozonation in water

During a water treatment by ozonation, the elimination of a micropollutant can be predicted using a kinetic model based on the previously calculated rate constants $k_{M,O3}$ and $k_{M,OH}$ as well as the ozone and hydroxyl radicals exposures. Ozone exposure can be quantified by monitoring the evolution of its concentration over the time. On the other hand, the radical exposure is more complicated to estimate, since there is no direct method for the determination of hydroxyl radicals concentration in solution. Therefore, a water quality parameter has been introduced (Elovitz and von Gunten, 1999), the R_{ct} value defined as the ratio between the OH radicals and O_3 exposures:

$$R_{ct} = \frac{\int [\bullet OH] dt}{\int [O_3] dt} \quad (13)$$

The R_{ct} value can be measured by monitoring the decay of a probe compound, which is resistant toward ozone but reacts rapidly with OH radicals. In most cases, the used probe compound is pCBA, with a constant for the reaction with ozone and hydroxyl radical of $k_{pCBA,O3} = 0.15\ M^{-1}\ s^{-1}$ and $k_{pCBA,OH} = 5 \times 10^9\ M^{-1}\ s^{-1}$ respectively. Therefore, for pCBA, using eq. (4) and (13), the kinetic law can be expressed as equation (14):

$$\ln\left(\frac{[pCBA]_0}{[pCBA]}\right) = k_{pCBA,OH} \int [OH]\, dt = k_{pCBA,OH}\ R_{ct} \int [O_3]\, dt \quad (14)$$

Thus, the R_{ct} parameter can be experimentally estimated by plotting ln ([pCBA]0/[pCBA]) vs. ozone exposure, being the slope of the curve.

Finally, the concentration of the substrate during water treatment by ozonation can be modeled with equation (15):

$$[S] = [S]_0 \exp\left(-\left(k_{S,OH}.R_{ct} + k_{S,O_3}\right) \int [O_3]\, dt\right) \quad (15)$$

5.2 Prediction of micropollutant elimination by photolysis in water

In a collimated beam set-up, reaction conditions are very well defined and the UV dose applied can be determined. However, in pilot and full scale UV reactors flow conditions have to be taken into account, as these determine the UV dose distribution through the reactor. The kinetic model predicts the conversion of compounds as a function of UV dose, and computational fluid dynamics (CFD) can be used to calculate the UV dose distribution through the reactor, as a function of reactor geometry and flow (Wols and Hofman-Caris, 2012a). An example of CFD modeling of a reactor is shown in Figure 2.

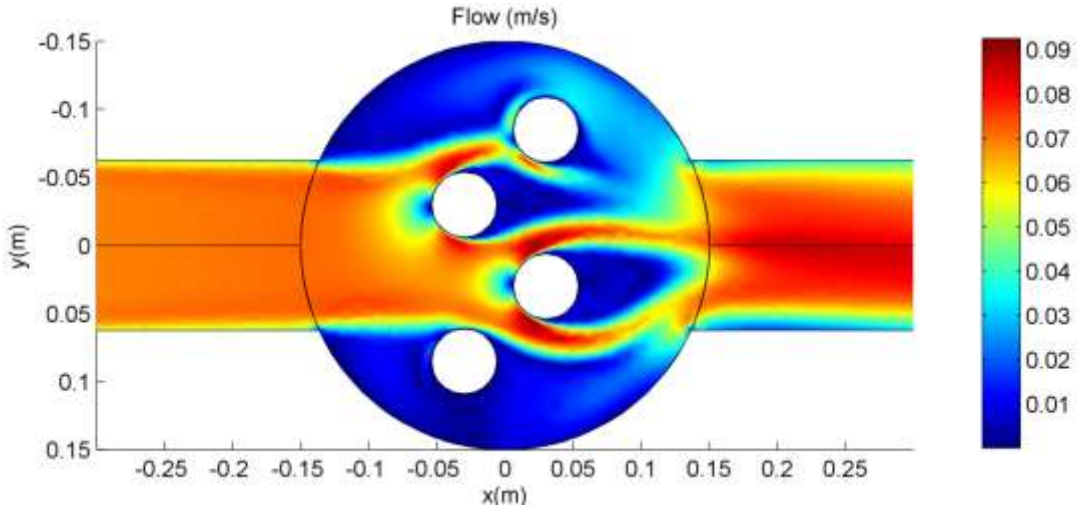


Figure 2: Flow through a UV reactor, calculated by means of CFD.

By combining both models, the conversion of organic micropollutants can be predicted for pilot or full scale UV reactors. This is shown in Figure 3.

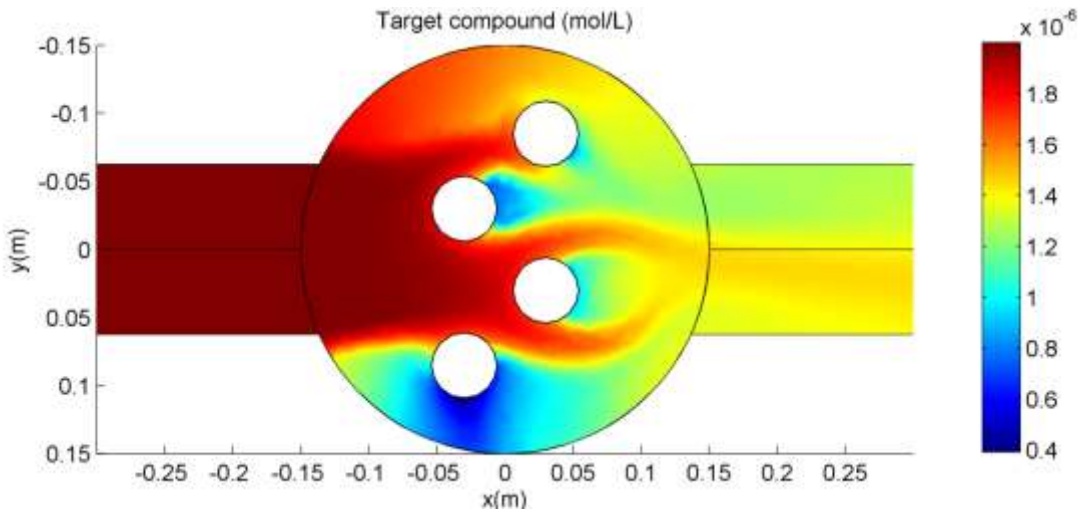


Figure 3: Compound degradation through the UV reactor.

Validation of the model in a pilot reactor showed good results. All modeling described in this paragraph was based on systems equipped with LP UV lamps. For MP lamps it is much more complicated to develop a kinetic model, as these lamps emit over a broad range of wavelengths instead of only one wavelength.

6 Conclusion

In this report it is presented how ozone and hydroxyl radicals can degrade efficiently most of the emerging substances including pharmaceuticals, pesticides and industrial chemicals during water treatment with a focus on the substances selected for the Demeau project.

The studies reviewed in this report show the different mechanisms involved in the oxidation of organic compounds. The knowledge of the mechanism of oxidation is certainly essential for the prediction and the identification of transformation products in the effluent of treated waters. Due to its higher selectivity compared to hydroxyl radicals, ozone can therefore lead to a more predictable list of transformation products.

On the other hand, rate constants of a selection of environmentally occurring emerging substances are also reviewed in this report. Though the rate constants have not been determined for many compounds yet, the implementation of existing data in QSAR models is very helpful for the prediction of unknown rate constants. Once rate constants are measured or predicted, elimination of the micropollutants in water treatment can therefore be forecasted considering different water quality parameters.

As a conclusion, this report aimed at giving the pertinent information for a better understanding of the reactions involved during (advanced) oxidation processes. Even though each situation needs a specific solution, this report will be certainly helpful for the selection of relevant parameters to scale up or optimize processes of water or wastewater treatment.

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