

***Critical review of literature for rate constants for
reaction of chemical oxidants with inorganic and
organic pollutants***

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Critical review of literature for rate constants for reaction of chemical oxidants with inorganic and organic pollutants

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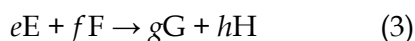
1 Reaction kinetics

The rate of a chemical reaction is defined as the change of the concentration of a reactant or product per time. The reaction rate depends on the concentration of the reactants and on the temperature. For an elementary reaction, i.e. a reaction directly caused by the collisions of atoms, ions, or molecules, the rate at a certain temperature can be derived from the known reaction stoichiometry. In the following example a bimolecular elementary reaction is given:



$$-\frac{\delta A}{\delta t} = -\frac{\delta B}{\delta t} = \frac{\delta C}{\delta t} = \frac{\delta D}{\delta t} = k[A][B] \quad (2)$$

where k is the rate constant which is concentration independent but not temperature independent. However, if only the stoichiometry (eq. 3) but not the mechanism of a reaction is known, one has to be aware that a combination of multiple elementary reactions, e.g. including unstable intermediate compounds, might lead to the observable reaction rate.

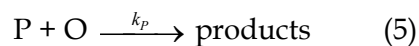


with e , f , g , and h being the stoichiometric coefficients. The corresponding rate expression can be written as follows:

$$-\frac{1}{e} \frac{\delta E}{\delta t} = -\frac{1}{f} \frac{\delta F}{\delta t} = \frac{1}{g} \frac{\delta G}{\delta t} = \frac{1}{h} \frac{\delta H}{\delta t} = k[E]^m [F]^n \quad (4)$$

The two new parameters, the powers m and n , give the order of the reaction: the reaction is m -th order in E , n -th order in F and the order of the overall reaction is $m+n$. In an elementary reaction (1) the order of the reaction can be derived from the stoichiometric coefficients. In eq. 1 the coefficients were 1 for A and B and accordingly the reaction was first-order in A , first-order in B , and overall it was a second-order reaction. In a non-elementary reaction the order cannot be derived from the balanced reaction equation. Therefore, m and n in eq. 4 remain unknown and can only be determined experimentally.

In the case of an oxidation reaction, equation (2) can be reformulated as the oxidation of a compound P by an oxidant O (eq. 5):



Since many reactions are experimentally found to be second-order reactions, first-order in both P and O, the rate for reaction 6 can be written according to eq. 4 and after multiplication with δt and division by [P] as given in eq. 6:

$$\frac{1}{P} \delta P = -k_p [O] \delta t \quad (6)$$

Since the concentration of P depends on the concentration of O and the concentration of O is dependant of the concentration of P, this equation system is not easy to be resolved for the concentrations. However, there are several methods for the determination of rate constants: direct measurement under pseudo first-order conditions of the decrease of the oxidant/P in excess of P/oxidants (depending on the reaction rate, sampling methods or stopped flow techniques are available) or by competition kinetics methods [1, 2].

2 The exposure concept

In real water matrices the concentration of the oxidant [O] often decreases due to reactions with matrix components. The concentration [O] cannot be considered constant any more, but if both concentrations [P] and [O] can be determined experimentally at a sufficient number of time points during the reaction of P with O and the decrease of O is independent of P, eq. 6 can be integrated and reformulated as eq. 7.

$$\ln\left(\frac{[P]}{[P]_0}\right) = -k_p \int [O] \delta t \quad (7)$$

The integral $\int [O] \delta t$ can be obtained from the measurement of the concentration [O] as a function of time. With O being an oxidant, this integral is named oxidant exposure [3]. If the oxidant exposure can be determined experimentally the reaction rate k_p can be derived from the slope of the linear plot of $\ln\left(\frac{[P]}{[P]_0}\right)$ versus the oxidant exposure.

In water treatment the oxidant or disinfectant exposure is crucial. Changes in water conditions (e.g. temperature, pH, water matrix) can change the decomposition rate of oxidants significantly. Therefore, the amount of oxidant added to the water (i.e. the oxidant dose) is not a suitable parameter to ensure a certain effect on pathogens or micropollutants. The oxidant exposure includes the oxidant decomposition/consumption by the water matrix over time and thus represents a measure of the transient oxidant concentration acting during a certain reaction time [3]. It has to be noted that within the engineering community the ct is often used instead of the oxidant exposure. Ct stands for "concentration x time" and has a slightly different meaning than exposure as illustrated by Figure 1. Since it is labor intensive for water utilities to determine the exposure $\int [O] \delta t$ - the oxidant concentration has to be determined at several time or reactor points - in water treatment a minimum estimated exposure for a reactor is calculated and referred to as ct . The ct is determined from multiplying the time it takes for

the water to flow through the reactor, with the remaining oxidant concentration measured at the reactor outflow.

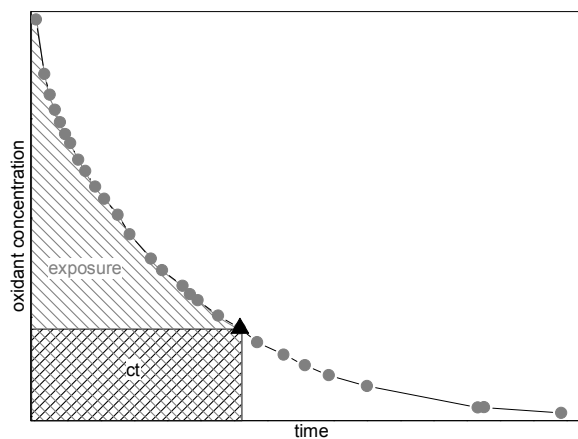


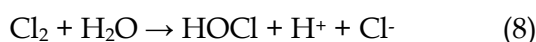
Figure 1. Illustration of the ct (marked with black lines) calculated from a one-point measurement of the oxidant concentration after a certain time and the exposure $\int [O] \delta t$ (marked with grey lines) after the same reaction time.

Equation 7 also illustrates that the relative elimination of a compound P is not necessarily high if k_P is high. If only a low oxidant exposure can be achieved as e.g., in the case of OH radicals, the degree of elimination might not be higher than for an oxidant with a low k_P but with a higher stability [4].

3 Reactivity of oxidants

Chlorine

Chlorine is the most common disinfectant and has been used for more than a century for drinking water treatment. It is relatively cheap and easy to handle. It can either be applied as hypochlorite salt (NaOCl) or as chlorine gas (Cl₂) [5]. Chlorine dissolved in water rapidly hydrolyses to hydrochloric acid and hypochlorous acid (eq. 8).

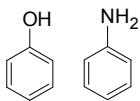
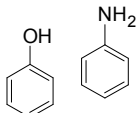
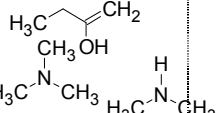
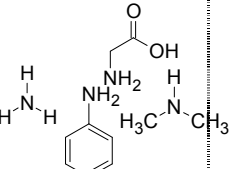
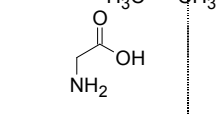
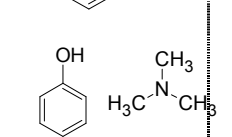
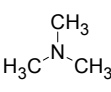
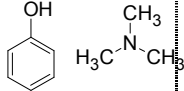
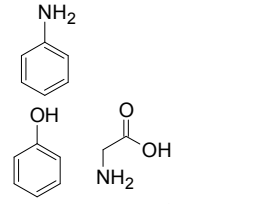

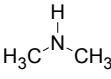
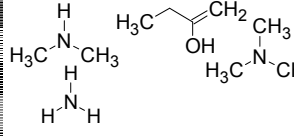
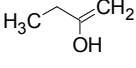
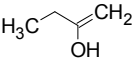




Hypochlorous acid undergoes acid base speciation (eq. 9) with a pK_a = 7.54. The hypochlorous acid is more reactive than the hypochlorite ion and acts as the actual disinfecting and oxidizing species. Therefore, the disinfection/oxidation power of chlorine is significantly pH-dependent.



In general, hypochlorous acid reacts fast with deprotonated amines and ammonia. Also its reaction with deprotonated dihydroxybenzenes and, to a lesser extent, phenolates is fast. However, the reaction with protonated phenols is much slower [6, 7]. Since chlorine is mainly present as hypochlorite ion at pH-values where (substituted) phenols are deprotonated (pK values roughly between 7 and 11), the overall reaction of phenolic compounds with chlorine is mediocre. Table 1 and Figure 2 give an overview over the reaction rate constants of selected oxidants at pH 8 and the pH range 5-10, respectively for several compounds with specific functional groups. A critical compilation of rate constants for the reaction of chlorine with inorganic and organic compounds is given in [4, 6]. Due to the relatively low reactivity of chlorine with organic compounds other than amines, chlorine is relatively stable in many water matrices.

Table 1. Reaction rate constants of oxidants with different compounds with distinctive functional groups at pH 8 (adapted from [4]).

| rate constant [M ⁻¹ s ⁻¹] | ozone | chlorine dioxide | chlorine | ferrate |
|--|---|---|--|---|
| 10 ⁹ | | | | |
| 10 ⁸ | | | | |
| 10 ⁷ |  | | | |
| 10 ⁶ | |  | | |
| 10 ⁵ |  | |  | |
| 10 ⁴ |  | |  | |
| 10 ³ | |  | | |
| 10 ² | | |  | |
| 10 ¹ | | | |  |
| 10 ⁰ |  |  | |  |
| 10 ⁻¹ | | | | |
| 10 ⁻² | | |  | |
| 10 ⁻³ | |  | | |
| 10 ⁻⁶ | |  | | |
| 10 ⁻⁷ | |  | | |

The fact that chlorine is relatively stable in water is an advantage that leads to the use of chlorine as residual disinfectant in water distribution system to avoid bacterial and biofilm growth in the pipes. However, the major drawbacks of chlorine are: (1) it is not very efficient in inactivating protozoa (e.g. *Cryptosporidium parvum* oocysts) and (2) it forms chlorinated, brominated, and iodinated disinfection by-products (DBP) of which some cause taste and odor problems and some are classified carcinogens (Table 2) [8-11].

To reduce the DBP formation, DOM has to be removed as far as possible prior to chlorination. A second strategy is to reduce the chlorine exposure to the minimum necessary for disinfection. To still maintain a disinfectant residual in the USA ammonia is often added to the chlorine containing water before release into the distribution system. The reaction of chlorine with ammonia is fast, as mentioned before, and leads to the formation of chloramines, which prohibit microbial growth, too. However, this practice is only used in exceptional cases in Europe.

The reactivity of monochloramine with inorganic and organic compounds is slow. One of the only fast reactions is the oxidation of iodide. The formation of iodinated organic compounds may result in natural waters [12], which might be even more toxic than brominated and chlorinated analogues [8, 13]. Another recent discovery is *N*-Nitrosodimethyl-amine (NDMA) which is formed from nitrogen-containing DOM, especially from dimethylamine (DMA). Hypochlorite also forms NDMA, however, the formation is approximately an order of magnitude slower than with monochloramine [14]. Fortunately, (pre-)oxidation with ozone and chlorine dioxide is able to transform significant parts of the NDMA precursors and hence reduce NDMA formation [15].

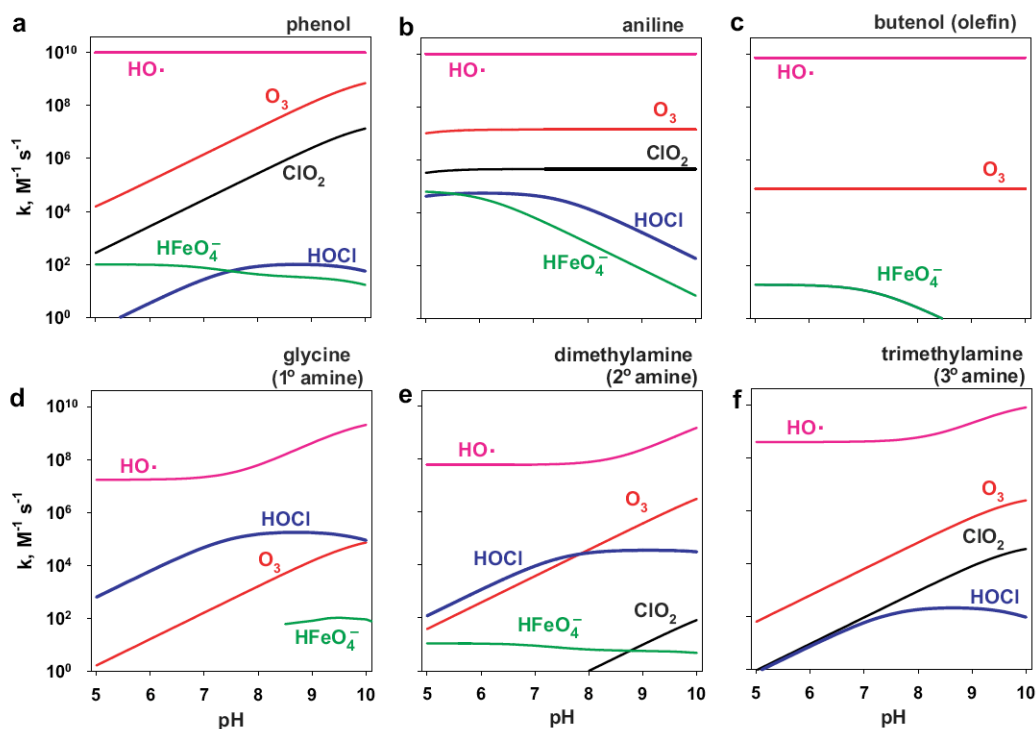


Figure 2. pH dependent second-order rate constants (k) for the reaction of the oxidants, chlorine (HOCl), chlorine dioxide (ClO₂), ferrateVI (HFeO₄L), hydroxyl radicals (HO%), and ozone (O₃) with (a) phenol, (b) aniline, (c) butenol, (d) glycine, (e) dimethylamine, and (f) trimethylamine. k values for chlorine: [6]; for chlorine dioxide and ozone: [16]; for ferrateVI: [17-19]; and for hydroxyl radicals: [20]. According to Lee and von Gunten 2010 [4], with permission.

Table 2. Today more than 600 DBPs are identified for commonly applied oxidants in drinking water [9]. A selection is given here (adapted from [5, 8, 10, 11]).

| Oxidant | DBPs |
|------------------|---|
| free chlorine | Trihalomethanes (THM), haloacetic acids, haloacetonitriles, haloketones, (halo-)aldehydes, chloral hydrates, trihalonitromethanes |
| chloramine | Nitrosamines, cyanogen halides, iodinated THMs, haloacetaldehyde |
| chlorine dioxide | Chlorite, chlorate, organic acids |
| ozone | Bromate, bromoform, aldehydes, aldoketoacids, carboxylic acids, <i>N</i> -nitrosodimethylamine |

Chlorine dioxide

Compared to chlorine, chlorine dioxide offers several advantages. Chlorine dioxide reacts generally as an electron acceptor and not by Cl-substitution. Therefore, fewer chlorinated organic DBPs and no THMs are formed [21]. Furthermore, it does not cause taste and odor problems, it is more effective in inactivating protozoa, its disinfection efficiency is not pH dependent, and

since it does not react with ammonia it is stable in water with low DOM content [22]. As a consequence in Europe it is often applied as residual disinfectant in the distribution system. However, chlorine dioxide is mainly transformed into chloride, chlorite, and chlorate, where chlorite can be formed to up to 75 % from chlorine dioxide (Table 2) [5, 22]. The formation of this regulated, blood poisonous by-product limits the chlorine dioxide dose in water treatment. Consequently, chlorine dioxide cannot be used for disinfection purposes in water with high DOM concentrations.

As an electron acceptor, chlorine dioxide reacts mainly through a one electron transfer reaction. Chlorine dioxide is a highly selective oxidant. It reacts fast with phenolates and neutral tertiary amines (Table 1 and Figure 2) [22]. Accordingly, a study showed that from a wide range of pharmaceuticals only those with these reactive moieties could be degraded in drinking water treated with chlorine dioxide [23].

Ozone

Ozone reacts selectively and fast with various compounds, e.g. phenolic and activated aromatic compounds, deprotonated amines, olefines, and sulfides [24], see Table 1 and Figure 2. A critical compilation of ozone rate constants is available at: <http://kinetics.nist.gov/solution>. Ozone is efficient in removing color and many micropollutants. Ozonation products are usually smaller, more polar and therefore less volatile than the parent compounds, e.g. aldehydes, ketones, and organic acids (Table 2). They can often be more easily degraded by microorganisms by a subsequent biological filtration step than non-oxidized DOM. This typically leads to a reduction of DOC concentration [25]. However, these easily bioavailable compounds can also enhance undesired biological growth in the distribution system. Unfortunately, oxidized biodegradable organic compounds are not the only products formed during ozonation. Bromate, which is potentially carcinogenic, is formed in bromide-containing waters [3]. Strategies to minimize bromate formation, e.g. pH depression, ammonia addition and the chlorine ammonia process, have been proposed [26, 27]. Additionally, NDMA that was discussed above, was recently found to be produced during ozonation [28, 29].

The high reactivity of ozone towards chemical functional groups present in DOM (phenolates, activated olefines, deprotonated amines) makes it unstable in water. Therefore, it cannot be applied as residual disinfectant in the distribution system. However, the stability of ozone in water is influenced not only by its reaction with DOM, but ozone also decomposes to form hydroxyl radicals ($\cdot\text{OH}$) in a chain reaction [24]. Depending on the composition of the water matrix (e.g. carbonate concentration, propagating or scavenging properties of DOM) more or less ozone is consumed due to $\cdot\text{OH}$ -catalyzed decomposition reaction.

Hydroxyl radicals

The hydroxyl radical is the strongest oxidant in water and reacts unselectively with high rate constants between 10^9 to $10^{10} \text{ M}^{-1}\text{s}^{-1}$, e.g. by hydrogen abstraction or addition to olefins (for rate constants see Figure 2 and for a critical compilation <http://kinetics.nist.gov/solution>). Therefore, during ozonation or advanced oxidation processes (AOPs) hydroxyl radicals are responsible for the oxidation of compounds that are resistant towards ozone. In this way these radicals add to the oxidative strength of the ozonation process despite their low steady state concentration. Oxidation with hydroxyl radicals is generally referred to as an AOP and can be enhanced by increasing the pH or adding H_2O_2 during ozonation. AOPs are also achieved by combinations of H_2O_2 with UV, titanium dioxide and UV, ozone and UV with or without H_2O_2 addition, and other processes. A comparison of ozonation with the AOPs $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{UV}/\text{H}_2\text{O}_2$ for the removal of various organic compounds was investigated within the Techneau project [30].

Ferrate

Ferrate (Fe(VI)) is not yet applied in water treatment, however, it has been proposed as novel process for wastewater treatment due to its ability to both oxidize micropollutants and precipitate phosphate by formation of ferric phosphates [19]. At low pH values ferrate undergoes self-decomposition reaction under formation of oxygen and hydrogen peroxide. Therefore, aqueous solutions need to be prepared directly prior to utilization.

Ferrate has been shown to react relatively fast with phenolic, anilinic, organosulfur compounds and to a certain extent with amines, olefines, and alcohols (Table 1, Figure 2). With phenol for example ferrate reacts by a one-electron transfer and produces phenoxy radicals through hydrogen abstraction [4, 17] and references therein). At pH values relevant for water treatment HFeO_4^- is the main reactive species ($\text{pK}(\text{HFeO}_4^-) = 7.2$, Figure 3). The ferrate species H_2FeO_4 and FeO_4^{2-} have been shown not to contribute significantly to the reaction with phenolic compounds [17]. The reactivity of ferrate is hence pH- dependent (see Figures 2 and 3). Ferrate has also been tested with regard to its disinfection efficiency and has been shown to achieve a 3-log removal of *E. coli* at exposures smaller than $10 \text{ mg}\cdot\text{min}/\text{L}$ at pH 5.6 - 8.2 [31]. In terms of *E. coli* inactivation H_2FeO_4 was clearly more effective than HFeO_4^- and FeO_4^{2-} . Not much information is available on disinfection by-products of ferrate reactions.

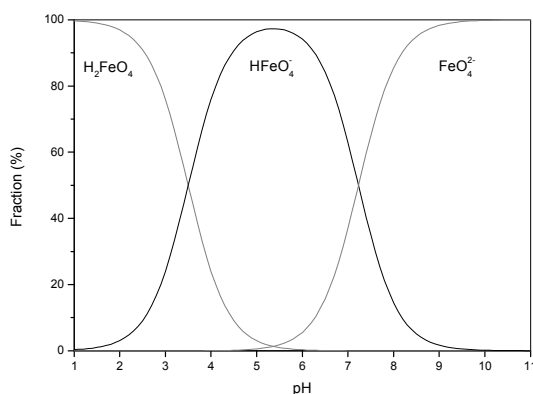


Figure 3. Distribution of Fe(VI) species as a function of the pH.

Permanganate

Permanganate is more expensive than chlorine and ozone, but it requires less equipment and is simple in application [5]. It is sometimes used to oxidize taste and odor compounds (e.g. fishy odors produced by methyl sulfides) and THM precursors and to control microorganisms. However, the reaction of permanganate with organic compounds is rather slow, with maybe the exception of olefins. It reacts with substituted phenols and olefins with rate constants between $10^{-1} - \approx 5 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$. For a compilation of second order rate

constants for the reaction of permanganate with various organic compounds including pharmaceuticals and cyanotoxins see [32-34].

4 Summary

Table 3 summarizes the most important characteristics of the selected oxidants related to oxidation processes. It can be concluded, whereas the reactivity (second order rate constant) of the oxidants generally increase in the order $\text{NH}_2\text{Cl} < \text{HOCl} \approx \text{Fe(VI)} < \text{ClO}_2^- < \text{O}_3 < \text{OH}$, the stability (oxidant exposure) typically decreases in the same order: $\text{NH}_2\text{Cl} > \text{HOCl} > \text{Fe(VI)} > \text{ClO}_2^- > \text{O}_3 > \text{OH}$. Based on eq. 6, the combination the oxidant exposure and the second order rate constants determine the overall efficiency of an oxidation process.

Table 3. Characteristics of selected oxidants with regard to the oxidation of inorganic and organic compounds. The main references for kinetic and mechanistic information are also given.

| Oxidant | Main reactivity with | Stability in water | Compilations for rate constants and mechanistic information |
|------------------|---|--------------------|---|
| Chlorine | Primary, secondary amines, anilines (phenols), Fe(II), NH_3 , NO_2^- , HS^- , I $^-$, Br $^-$, As(III) | Medium-high | [6] |
| Chlorine dioxide | Phenols, anilines, secondary, tertiary amines, Fe(II), Mn(II), I $^-$ | Medium | [22, 35] http://kinetics.nist.gov/solution/ |
| Ozone | Phenols, anilines, olefins, primary, | Medium-low | [1, 24, 36-39] http://kinetics.nist.gov/solution/ |

| | | | |
|--------------|--|--------|---|
| | secondary, tertiary amines, Fe(II), Mn(II), NO ₂ ⁻ , HS ⁻ , I ⁻ , Br ⁻ , As(III) | | |
| OH radicals | High reactivity with almost all organic and inorganic compounds | Low | http://kinetics.nist.gov/solution/ |
| Ferrate(VI) | Anilines, (phenols, olefins, primary, secondary amines), Fe(II), NO ₂ ⁻ , HS ⁻ , I ⁻ , As(III), | Medium | [17-19, 40-45] |
| Permanganate | Olefins, phenols, Fe(II), Mn(II), I ⁻ | High | [32, 33] |

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