



**KTH Chemistry**

# **Ozone chemistry in aqueous solution**

## **-Ozone decomposition and stabilisation**

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**Licentiate Thesis**

**Department of Chemistry  
Royal Institute of Technology  
Stockholm, Sweden, 2005**

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Hobbes: Do you have an idea for your story yet?

Calvin: No, I'm waiting for inspiration. You can't just turn on creativity like a faucet. You have to be in the right mood.

Hobbes: What mood is that?

Calvin: Last-minute panic.

---

Bill Watterson,  
*The Calvin and Hobbes Tenth Anniversary Book*



## **Abstract**

Ozone is used in many applications in the industry as an oxidising agent for example for bleaching and sterilisation. The decomposition of ozone in aqueous solutions is complex, and is affected by many properties such as, pH, temperature and substances present in the water. Additives can either accelerate the decomposition rate of ozone or have a stabilising effect of the ozone decay. By controlling the decomposition of ozone it is possible to increase the oxidative capacity of ozone.

In this work the chemistry of acidic aqueous ozone is studied and ways to stabilise the decomposition of ozone in such solutions. The main work emphasizes the possibility to use surfactants in order to develop a new type of cleaning systems for the sterilisation of medical equipment.



This thesis is based on the following papers:

- I M. Eriksson, R. Andersson, L. Kloo  
”*Reaction of SDS with ozone and HO radicals in aqueous solution*”,  
Submitted to Water Research, 2005
  
- II M. Eriksson, R. Östensson, L. Kloo  
”*Bacteriological study of an aqueous solution with ozone and SDS or SDS-peroxide*”  
Submitted to Applied and Environmental Microbiology, 2005
  
- III M. Eriksson, L. Kloo  
”*Ozone decomposition in acidic solutions*”  
Manuscript

The papers will be referred to by their Roman numerals.

The following patent application has resulted from this work, but it is not included in the thesis.

- IV Kloo, Lars; Eriksson, Margareta. (Otre AB, Swed.) *Cleaning compositions containing stabilized ozone solutions..* U.S. Pat. Appl. Publ. (2003), 13 pp.





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# 1 Introduction

## 1.1 Background

Ozone was first discovered by its very characteristic smell. The name ozone originates from Greek, “ozein”, to smell, and was coined by C. F Schönbein in 1840.<sup>1</sup> Today, ozone is a known powerful oxidant and is used in many industrial applications, for instance water treatment, odour control, chemical oxidant, bleaching and cleansing of semiconductors.<sup>2</sup> Most applications are connected to the antiseptic properties and ozone’s capability to oxidise and degenerate organic compounds. Advantages with ozone are its high and fast reactivity and non-selectivity towards microorganisms. However, since ozone is a reactive molecule it will also attack compounds in the surroundings, in particular organic materials such as plastics and rubbers. It is also toxic to human mucous membranes. Therefore, research is performed to enhance the reactivity to specific compounds by affecting the stability or the reactivity of ozone, for example by the use of porous materials or scavengers.

## 1.2 General properties of ozone

Ozone is an allotrope of oxygen, which at room temperature is a blue, explosive gas that absorbs UV-radiation in the range of 220-290 nm. It is a bent molecule with a bond angle of 116.8° and an interatomic distance of 1.278 Å. The melting point is -193°C and boiling point -112°C. The solubility of ozone in aqueous solutions is 14 mmol L<sup>-1</sup> at 20°C, but it is more soluble in organic solution. Thus, it can be regarded as a hydrophobic molecule.<sup>1,3-5</sup>

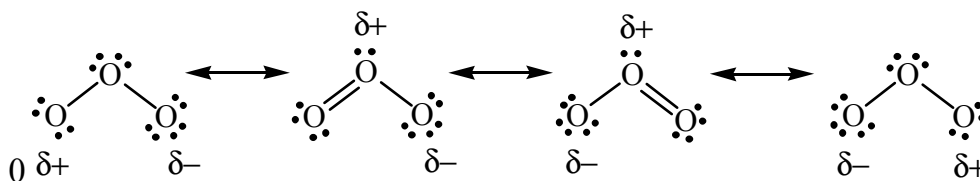


Figure 1.1. Resonance structures of ozone

Ozone is explosive at higher concentrations, but it is relatively stable at lower, which is attributed to delocalisation stabilisation illustrated by the resonance structures shown in figure 1.1.

Ozone is very reactive towards other substances. It is toxic to humans but can be detected by its smell long before it becomes dangerous.<sup>4</sup> Due to the reactivity and instability, ozone has to be generated *in situ*. This is generally done by an oxygen flow through an electrical field, so called silent corona discharge.<sup>6</sup> The gas flow from such an ozone generator outlet will therefore consist of a mixture of oxygen and ozone. Al/Si zeolites can be used to concentrate the gas mixture to higher concentrations.<sup>7</sup> It is still important to remember that oxygen always will be present when performing subsequent experiments. Ozone can also be produced using electrolysis or UV-radiation. However, these methods are normally less efficient, thus producing lower concentrations of ozone.

### 1.3 Properties of ozone in aqueous solution

In a pure aqueous solution ozone slowly decomposes in multiple steps involving radical formation. The depletion is a chain process and has been described by two different mechanisms, by Hoigné-Staehelin-Bader (HSB) and Gordon-Tomiyasu-Fukutomi (GTF).<sup>8</sup>

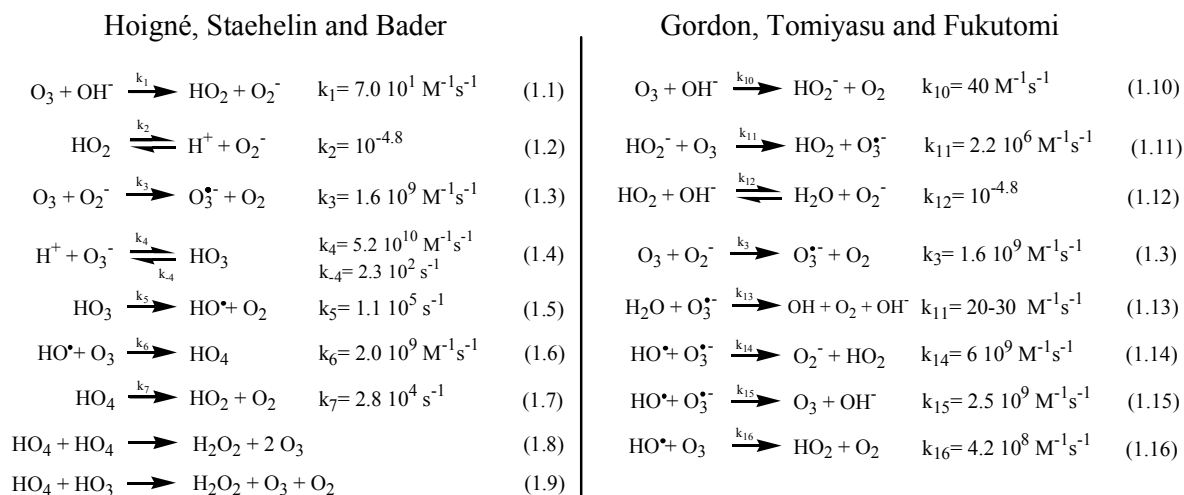
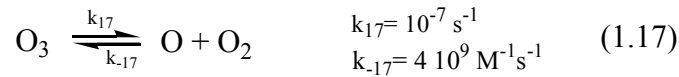


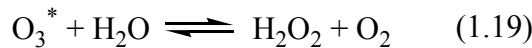
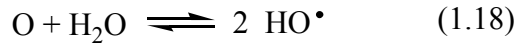
Figure 1.2. The decomposition of ozone in aqueous solution<sup>8</sup>

HSB state that the initial step is an oxygen-atom transfer from ozone to a hydroxide ion, followed by a reverse one-electron transfer. In contrast, GTF only state an oxygen-atom transfer. However, the fundamental reaction in both mechanisms is the initial step, where ozone reacts with OH<sup>-</sup>. Furthermore, removal of the superoxide anion radical, O<sub>2</sub><sup>-</sup>, and the HO-radical in the chain reaction reduces the speed of ozone decomposition.

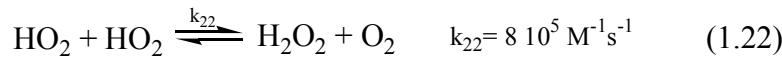
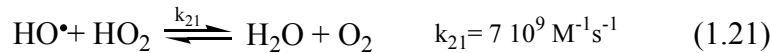
Since reaction with OH<sup>-</sup> is the initial decomposition step, the stability of an ozone solution is thus highly dependent on pH and decreases as alkalinity rises.<sup>9-12</sup> At pH above 8 the initiation rate has, in the presence of radical scavengers, been shown to be proportional to the concentrations of ozone and OH<sup>-</sup>.<sup>13,14</sup> However, in acidic solutions the reaction with OH<sup>-</sup> cannot be the only initiation step. Predicted reaction rates below pH 4 including a mechanism based only on reaction with OH<sup>-</sup> are much lower than those determined experimentally. According to Sehested *et al.*, the ozone equilibrium reaction (1.17) becomes significant and the initiation reaction is surface catalysed.<sup>15</sup>



The atomic O continues to react with H<sub>2</sub>O (1.18), or more likely forms an excited O<sub>3</sub><sup>\*</sup>, from recombination, that subsequently reacts with H<sub>2</sub>O (1.19). The reaction rate for this step has been simulated to k=5 M<sup>-1</sup>s<sup>-1</sup>.

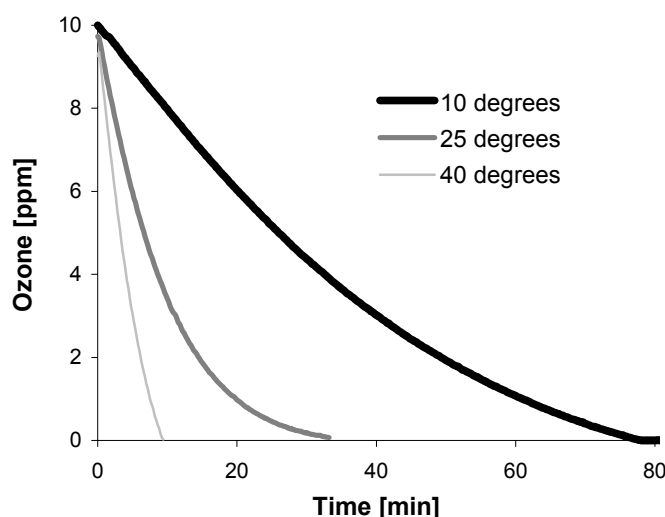


The species formed can then react further forming other radicals such as O<sub>2</sub><sup>-</sup>/HO<sub>2</sub>. The propagating products, HO<sup>•</sup> and HO<sub>2</sub>, diffuse and react with O<sub>3</sub> in the bulk continuing the chain reaction. Only low concentrations of the terminating species are present in the bulk, why the significant part of the termination reactions (1.20-1.22)<sup>16-18</sup> also takes place at the surfaces.



Contradictory to the behaviour in weakly alkaline solution, the depletion rate of ozone is reduced in strongly alkaline solutions. The half-life of ozone at room temperature is about 2 minutes in 1 M NaOH solutions, compared to 40 minutes in 5 M and 83 hours in 20 M solutions.<sup>4</sup> One reason for the observed decrease in overall decomposition rate can be the formation of ozonide,  $\text{O}_3^-$ , which reacts with  $\text{H}_2\text{O}_2$  or OH-radicals, that are produced in the ozone decomposition, reforming ozone.<sup>19</sup>

There are many other factors that affect the stability of aqueous ozone. For instance, higher temperature of the solution gives faster ozone depletion, see figure 1.3.



*Figure 1.3. When the temperature is increased, so is the rate of ozone decomposition. The experiments were performed in pure aqueous solution at controlled temperatures*

Furthermore, if the solution is stirred, higher speed of stirring can result in faster decomposition of ozone, which can be explained by desorption.<sup>20</sup> Also, higher ionic strength accelerates the depletion.<sup>21</sup>

In 1977 Hoigné and Bader described the reaction of ozone in aqueous solution towards other compounds in two ways, by direct reaction or by indirect reaction with radical species formed in ozone decomposition,<sup>8</sup> see figure 1.4.

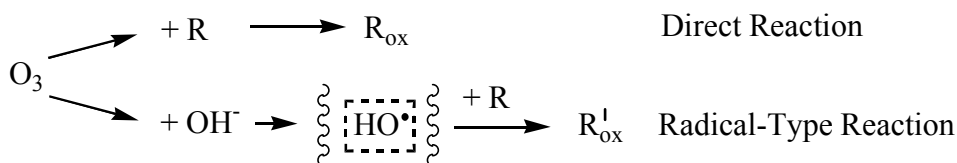


Figure 1.4. How ozone can act towards other compounds (R) in aqueous solution. Radical formation is represented by the hydroxyl radical<sup>8</sup>

The direct reaction of ozone is often selective towards specific compounds and functional groups. The dipolar structure of ozone gives rise to cyclo-addition to unsaturated bonds, Criegee mechanism, forming ozonides.<sup>1</sup> Ozone is also a strong electrophile and reacts fastly with both organic and inorganic compounds *via* an oxygen-atom transfer reaction.<sup>22</sup> The reactivity is enhanced by electron-donating groups and decreased by electron-withdrawing ones. In the case of electron-withdrawing groups ozone acts as a nucleophile.<sup>8</sup>

Regarding the radical-type reaction, chemicals or particles in the solution will affect the decomposition rate of ozone.<sup>23</sup> They can act in four different ways.

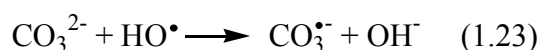
- Initiator
- Promotor
- Inhibitor
- Inhibitor with re-formation of ozone

Initiators are, in the free-radical reaction, compounds that form the superoxide anion  $\text{O}_2^-$  from an ozone molecule. Examples are  $\text{OH}^-$ ,  $\text{HO}_2^-$  and a number of organic compounds, such as formic acids and humic substances. Furthermore, UV-radiation at 254 nm can be used for activation of ozone chain reactions.<sup>24</sup> This is used in water treatment, since some organic compounds, for example saturated aliphatic molecules, are only degraded by HO-radicals.

Promoters are compounds that re-generate  $\text{O}_2^-$  from the hydroxyl radical. The reaction rate between ozone and the superoxide anion is high,  $k = 1.6 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , compared to many other ozone reactions. The presence of  $\text{O}_2^-$  will thus promote ozone decomposition. Examples of promoters are ozone itself, compounds with aryl groups, primary alcohols and humic acids.

Inhibitors are compounds, radical scavengers, which consume HO-radicals without re-generation of  $O_2^-$ , and thus retard ozone decomposition. Examples are tertiary alcohols, compounds with alkyl groups and acetic acid.

Bicarbonate/carbonate is an inhibitor that completely can inhibit the radical chain reaction and even re-form ozone (1.23,1.24).<sup>25-28</sup>



Bicarbonate is thus used in many ozone-selective reactions.<sup>29,30</sup> The decomposition of ozone is pH dependent, and increasing alkalinity acts in an accelerating way. Another positive effect is therefore the buffer capacity of carbonate. If other ions are present carbonate ions can somewhat prevent an increase of alkalinity, where  $OH^-$  ions are produced in the total reaction.

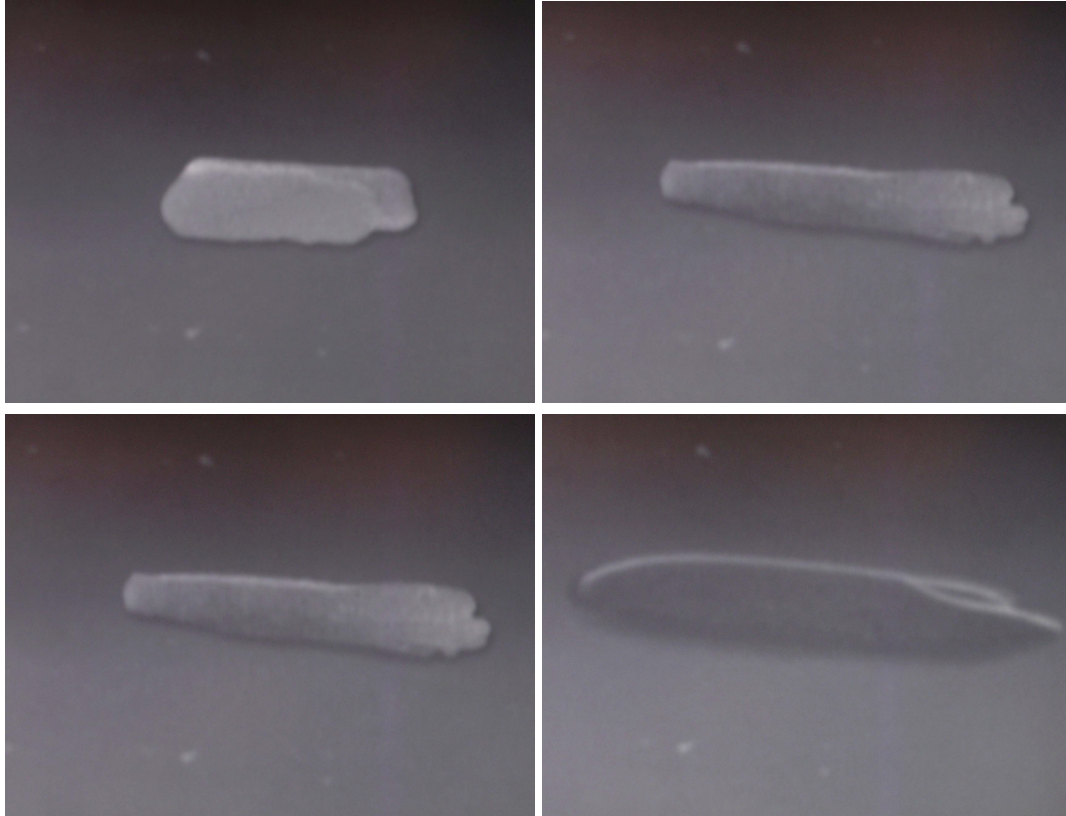
#### **1.4 Antiseptic properties**

When studying the literature, many articles about the reactivity of ozone with respect to different microorganisms can be found. Ozone has been shown to be a very effective antiseptic and is in many cases more efficient than other sterilizing agents, such as  $H_2O_2$ .<sup>31</sup>

Compared to chlorine, another frequently used antiseptic, ozone is in general much more efficient and powerful.<sup>32</sup> The time for sterilization can therefore be reduced and the concentration of ozone can be kept much lower. This can be explained by different mechanisms. Ozone oxidises the constituents in the cell wall or membrane, such as proteins and amino acids, followed by lyses reactions disrupting the cell wall,<sup>12,33</sup> see figure 1.5.

In contrast, chlorine is thought to first diffuse into the cell protoplasm through the cell wall and then to inactivate the bacterial enzymes. Furthermore, when chlorine is used halogenation will take place, and many different toxic chlorine-containing organic compounds will be formed, *e.g.* dioxins. Ozone itself does not form any toxic by-products. However, care has to be taken since ozone reacts with many compounds forming, for instance peroxides and bromates. Bromate formation during disinfection is a problem in wastewater treatment.<sup>34</sup>





*Figure 1.5. The action of ozone towards Bacillus subtilis. To the upper left: Bacillus subtilis before ozone treatment; Upper right beginning of ozonation; lower left: the cell membrane starts to collapse; lower right: the membrane has collapsed, lysis reaction*

In general, gram-positive bacteria show larger resistance towards ozone exposure than gram-negative ones. The difference between them is the property of the cell membrane. Gram-positive bacteria have much thicker walls that also are more hydrophilic than those of gram-negative bacteria. Furthermore, the cell membrane of the gram-positive bacteria is more resistant towards oxidation due to the chemical properties of the membrane constituents.<sup>35</sup> Comparing vegetative cells with spore forms, the latter is more resistant to ozone exposure.<sup>36</sup> Spores often display multi-layer, protein-based cell walls that can also include inorganic constituents.

## 1.5 Ozone “stabilisation”

There are different ways to approach the target of ozone solution stabilisation. In the choice of strategy, it has to be considered in what way ozone should be used and the degree of the stabilisation aimed at; long- or short-term.

Short-term solution stabilisation is mainly used to enhance a reaction path, where the direct reaction with ozone is significant. Some simple examples on how to achieve this were mentioned in the previous chapter, such as lowering pH, decreasing temperature, using highly alkaline solutions, or involving an inhibitor such as an HO-radical scavenger.

Both bicarbonate and t-butanol are frequently used scavengers. Another inhibitor is acetic acid, which reacts with HO-radicals forming  $\text{H}_2\text{O}_2$  and other products (“prod” in equation 1.27), such as formaldehyde, glyoxylic acid, glycolic acid and organic peroxides (1.25-27).<sup>37,38</sup> Furthermore, acetic acid will lower pH enhancing the stability of ozone solutions.



There are other ways than the use of scavengers to stabilise ozone in solution in order to enhance the ozone reactivity. The use of zeolites as catalysts in water treatment to enhance the efficiency of ozone towards impurities has been investigated with numerous types of zeolites, for example silica, silica/aluminium, titania or calcium.<sup>39-43</sup> IR spectroscopy shows that ozone adsorbs onto the surface and is thus stabilised. The amount of adsorbed ozone is higher than is soluble in aqueous solution.<sup>3</sup> The suggested mechanisms differ somewhat between the different zeolites, but ozone is mainly proposed to be adsorbed at weak Lewis-acidic sites by interaction with the  $\delta^-$ -terminal oxygen atoms. At the stronger Lewis-acidic sites ozone dissociation is claimed to occur. CaO surfaces differ from the others; here, the central oxygen is proposed to act as an electron acceptor interacting with basic sites, such as the oxygen atom of hydroxyl groups.

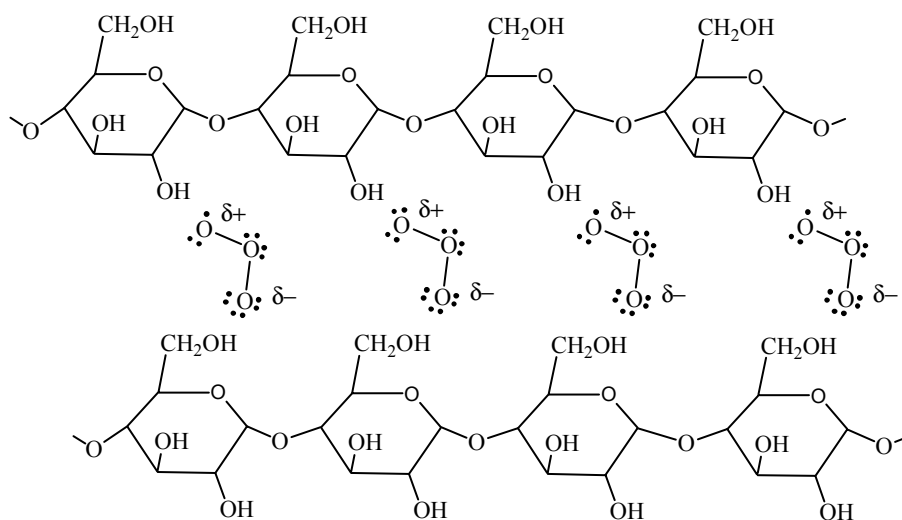


Figure 1.6. Ozone stabilised by a polysaccharide<sup>44</sup>

Aqueous solutions with starch or dextran form a complex that encloses ozone and both stabilises and increases the solubility of ozone.<sup>44</sup> The complex is proposed to form by enhanced electron density on the central oxygen atom corresponding to the resonance structure with one  $\delta^+$ -terminal and one  $\delta^-$ -terminal oxygen atom. The positive terminal oxygen can then interact with the OH-groups of one polysaccharide chain and the negative terminal oxygen with the  $\text{CH}_2\text{OH}$ -groups on another chain. Dextran is more effective, both regarding ozone stabilisation and solubility increase, than starch.

Clathrates formed by water occur naturally, and vast amount of methane gas are for instance stored in glaciers.<sup>45,46</sup> In clathrates the guest and host remains individualists and are therefore easy to separate. The stability of the clathrate is more dependent on the size of the guest molecule than its chemical properties. Smaller molecules lead to stronger complexation, thus more stable clathrates.<sup>47-49</sup> Ozone is a relatively small molecule and has also successfully been complexed in ice, so-called antiseptic ice.<sup>50-52</sup> The clathrates can, depending on the environment, be used for long-term stabilisation of ozone.

## **1.6 Scope of this work**

The aim of this project is to understand the fundamental ozone chemistry and to find ways to stabilise ozone or aqueous solutions thereof. The main work will be focused on the possibilities to stabilise ozone by micellar enclosure including kinetic studies. However, the aim is not to develop media for long-time storage of ozone, rather to find amphiphilic compounds that can co-exist with ozone in an aqueous solution allowing formulation of efficient cleaning agents. The ultimate application is to develop a new type of cleaning system suitable for medical devices that will remove hydrophobic particles (biofilm), dissolve calcium precipitates, and kill microbes in one step.

## 2 Experimental methods

### 2.1 General aspects

The rate of ozone decomposition in aqueous solution is very dependent on its constituents.<sup>8</sup> Therefore, when performing experiments it is important to use water of high purity. All kinetic experiments, and HO-radical treatment have been performed in deionised water, Millipore quality. Ozonisation experiments were performed in deionised water at ambient temperature.

Analysis of the concentration of ozone in aqueous solution can be done by many different methods, such as chemical titration, electrometric, optical or chemiluminescence techniques.

Chemical titration, often iodic titration, is a very commonly used method. However, care has to be taken, since it is not selective towards ozone. For instance, peroxides are formed in the decomposition of ozone and also in many reactions between organic compounds and ozone. The titrimetric method may thus overestimate the ozone concentration. In the experiments iodic titration was mainly used to obtain a rough estimate of ozone concentration.

Electrometric techniques can be used for continuous data collection and can be made relatively ozone selective. However, the commercially available ozone-specific electrodes have a relatively slow response time as compared to other method. In the experiments made, a membrane electrode, Fisher Rosemount 499A, has been used.

Ozone shows a broad and intense UV-absorption. UV spectrophotometry is therefore often used to determine ozone concentration. It is a very fast method and can be used for continuous data collection. The UV-spectrometers used in this work operates at 254 nm. However, care has to be taken since other compounds, such as peroxides, carbonyls and carboxylic acids often formed in ozone reactions with organic substances also absorb UV-radiation in the same region as ozone. Also the presence of particles and bubbles may cause an overestimation of ozone concentration due to UV-light scattering. Therefore, a UV-spectrum in the range of 190-350 nm was recorded intermittently during the experiments in order to ensure that only ozone causes absorption at 254 nm.

## 2.2 Kinetic experiments

The kinetics of a reaction is dependent on many different factors, such as mass transport, concentration, pH and temperature. It is therefore important to ensure controlled conditions. The temperature was thus regulated by using Julabo FP50 thermostat, see the system figure 2.1. Stable pH can be achieved by the use of a buffer, in the case of ozone generally a phosphate buffer. However, phosphate is not inert with respect to ozone and will affect the decomposition rate of ozone. A buffer was thus not used in the experiments, but instead pH was measured continuously using a glass electrode. The variation in pH between the different experiments was observed to be relatively small and should not have any significant effect on the results obtained or conclusions drawn.

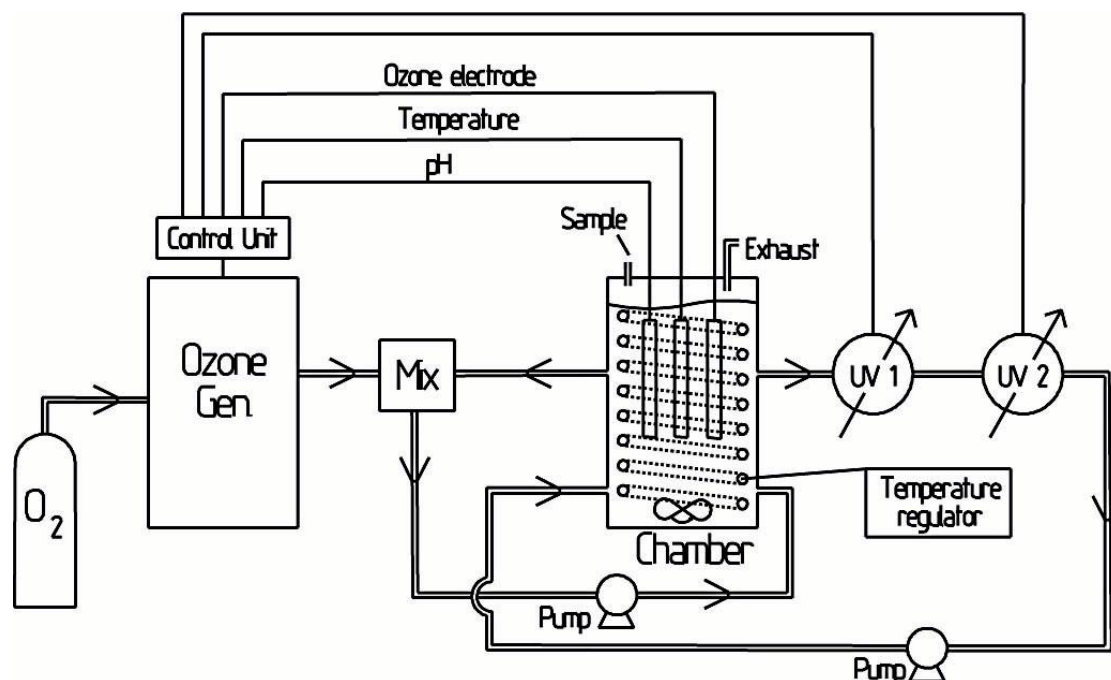


Figure 2.1. Equipment used for kinetic experiments

The kinetic experiments were performed in three different ways;

- Addition of an aqueous ozone solution to an aqueous surfactant or acidic solution. The data collection was initiated immediately after mixing.
- Addition of a concentrated aqueous surfactant or acidic solution to an aqueous ozone solution. Data collection was initiated directly after mixing.
- Addition of gaseous ozone to an aqueous surfactant or acidic solution until a set ozone concentration was obtained and data collection initiated.

The results obtained from the different methods were similar in spite of some complications caused by ozonisation of the surfactant when gaseous ozone was added.

In the kinetic experiments including surfactants another factor had to be taken into account, foam formation. Formation of foam affects the membrane electrode performance because of bubbles forming on the membrane surface. Additionally, bubbles also scatter UV-light, why the presence of bubbles can cause an overestimation of the ozone concentration. The concentration of ozone was thus recorded using both an ozone membrane electrode and two independent UV-analysers simultaneously. The formation of bubbles was kept to a minimum. Furthermore, in some experiments, samples were taken intermittently and analysed by UV-spectrophotometry (Varian Cary 300), or iodine titration.

### **2.3 Ozonisation**

In order to identify the predominant final products of ozonation it is necessary to ozonate over a longer period of time, this to ensure sufficient amount of product. In this case, the concentration of ozone becomes difficult to determine. Even in pure aqueous solution, due to ozone decomposition, hydrogen peroxide formed affects the analysis of ozone concentration. Furthermore, when organic compounds react with ozone carbonyl groups, carboxylic acids and peroxides can be formed. The concentration may become significant over a longer period of time and thus also cause overestimation of the concentration of ozone present in the aqueous solution. The amount of ozone added was therefore only monitored continuously in the gas phase and samples were taken intermittently for analysis by UV-spectroscopy. The ozone generator and the gas flow were monitored in order to give an ozone concentration above 10 ppm. The equipment used is showed in figure 2.2.

Foam formation is a general problem when a continuous gas flow is applied through an aqueous solution of surfactants. The gas flow was therefore kept as low as possible and a foam trap was added to the system.

For further details, see article I and II.

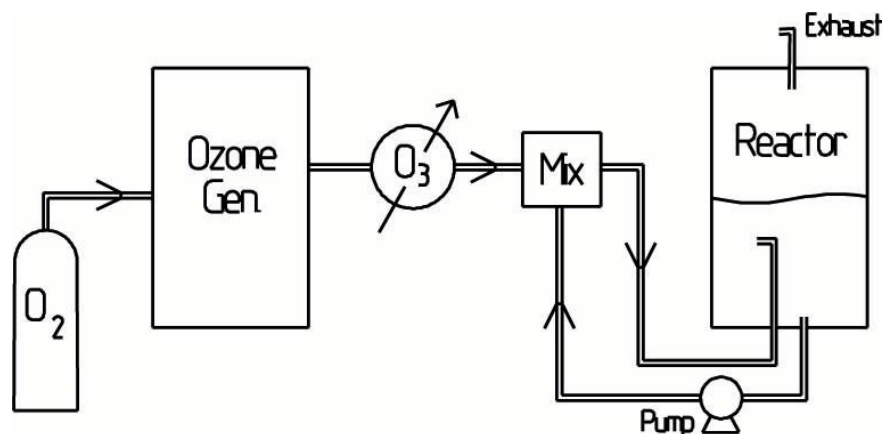


Figure 2.2. Equipment used for ozonation

## 2.4 NMR-spectroscopic analysis

NMR spectroscopy was found to be a useful tool for the product analysis after ozonisation. The analyses were performed using a Bruker DRX 400 MHz spectrometer. Since the experiments were performed using H<sub>2</sub>O, D<sub>2</sub>O was added to produce a signal for the frequency lock system. Furthermore, water as solvent gives rise to a large background peak. Therefore, an additional <sup>1</sup>H-NMR spectrum was recorded at 70°C in order to induce peak shifts for verification that no peaks were hidden by the large H<sub>2</sub>O peak. All other analyses were performed at ambient temperature.

When ozone reacts with organic compounds many different products are formed. It can therefore be difficult to determine and assign all peaks by use of only 1D-NMR spectroscopic techniques. By using 2D-NMR spectroscopy it is possible to reveal couplings between different atoms and thus to establish which atoms that are physically connected, consequently enabling identification and structure determination. <sup>1</sup>H-, <sup>13</sup>C-, COSY-, HSQC-, and HMBC-NMR spectra were recorded and analysed using standard Bruker programs. COSY pulse sequences highlight proton-proton correlation, HSQC the proton-carbon couplings of one-bond distance and HMBC the long-range proton-carbon couplings. For further details, see article I.



### 3 Decomposition rate in acidic aqueous solutions

#### 3.1 The effect of different buffer solutions

Since the decomposition rate of ozone in aqueous solution is base-catalysed, pH has to be controlled and monitored in kinetic experiments in order to avoid embedded effects of pH changes. In the acidic region mainly sulphuric, perchloric or phosphoric buffer solutions are used. The impact of these buffers on the decomposition rate was therefore studied.

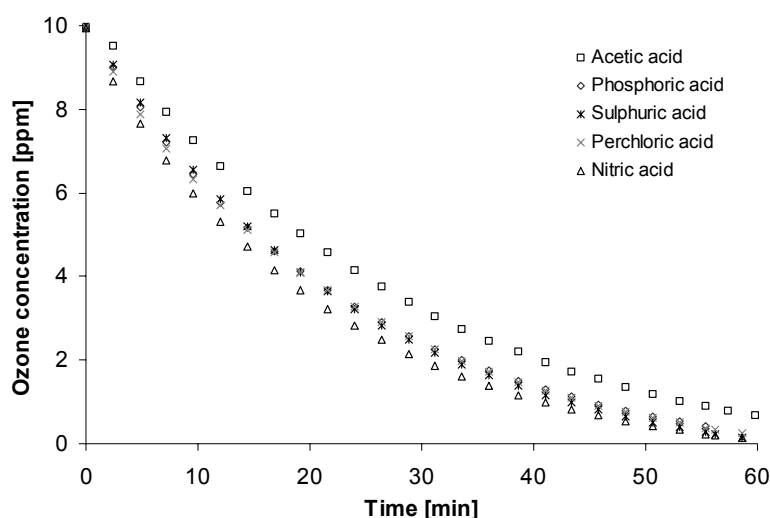


Figure 3.1. Decomposition of ozone at pH 3, in 1 mM acetic, phosphoric, sulphuric, perchloric and nitric acid, respectively

As can be seen in figure 3.1, the decomposition rate of ozone is similar for the three buffer systems, sulphuric, perchloric, and phosphoric acid, with overlapping curves. In the presence of acetic acid, a known radical scavenger, the decomposition rate is retarded whereas it is slightly increased in the presence of nitric acid.

The kinetic relation of ozone decomposition in acidic aqueous solution is complex. An analysis of the decay was therefore restricted to the initial decomposition, approximated with a first-order kinetic constant, see table 3.1 and figure 3.2.

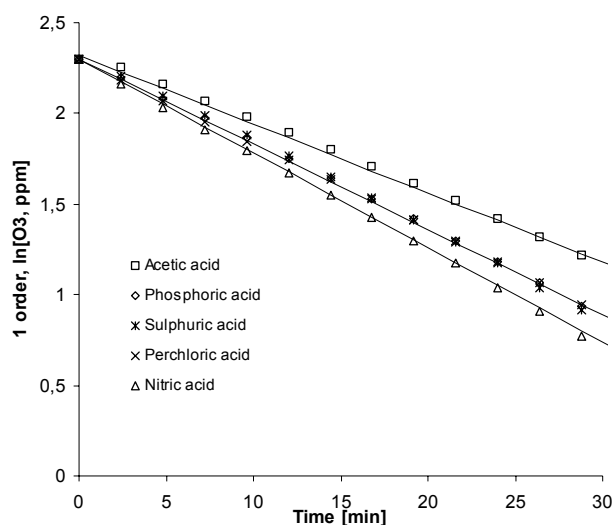


Figure. 3.2. First-order kinetics of the ozone decomposition at 25 °C and pH 3

Acid	$10^{-4} k [s^{-1}]$
Acetic acid	6.3
Phosphoric acid	7.8
Sulphuric acid	7.8
Perchloric acid	7.8
Nitric acid	8.6

Table. 3.1. Initial first-order rate constants of ozone decay at 25 °C and an initial ozone concentration of 10ppm

### 3.2 The effect of pre- and re-ozonated aqueous solutions

Some of the kinetic experiments were also performed in pre-ozonated aqueous solution. In these experiments the decomposition rate of ozone seemed to be higher, why kinetic measurements were made for re-ozonated samples. The result showed that the decay of ozone is accelerated after each re-ozonisation. The example in figure 3.2 shows the result for phosphoric acid. The other curves are presented in article III.

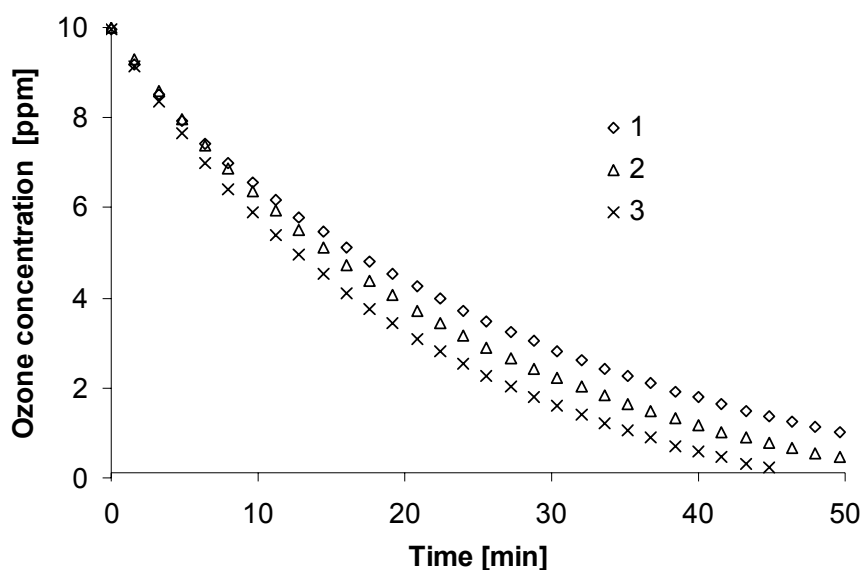


Figure. 3.3. Decomposition of ozone in phosphoric acid: The impact of repeated experiments performed with a re-ozonated sample: ◇ represents the initial run, △ the 2<sup>nd</sup> and × the 3<sup>rd</sup>

The sample after each re-ozonisation was after de-ozonisation analysed by UV-spectrophotometry showing an absorption peak below 190 nm, se figure 3.4. This is indicative of hydrogen peroxide, which is a known product in aqueous ozone solutions. Iodic titration was also performed on these samples showing a retained oxidative power in the absence of ozone.

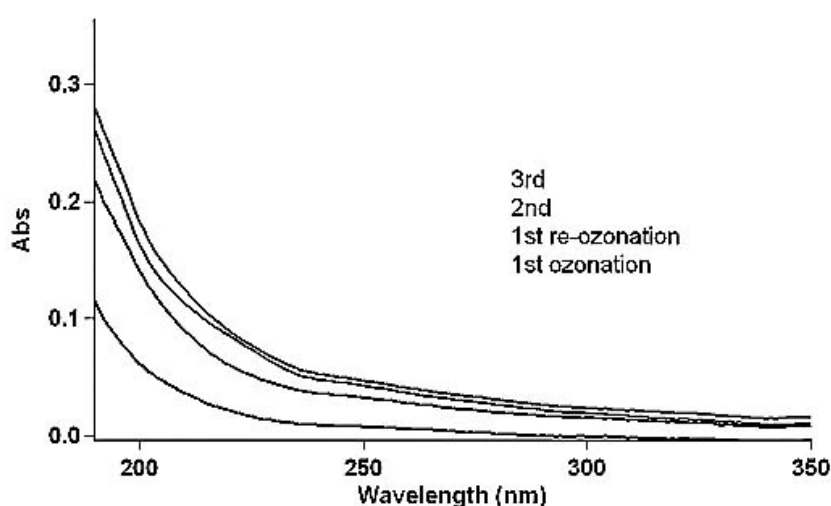


Figure. 3.4. UV-spectrophotometric analysis of re-ozonated phosphoric acid

The decay of the re-ozonisation was, as previously described, approximated to an initial first-order kinetics, see table 3.2 for k-values and article I for the obtained by least squares adaptation to experimental data curves.

Acid	$10^{-4} k [s^{-1}]$		
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
Acetic acid	6.3	7.0	7.5
Phosphoric acid	7.8	8.8	9.7
Sulphuric acid	7.8	8.7	9.8
Perchloric acid	7.8	8.8	9.8
Nitric acid	8.6	9.7	11.3

*Table. 3.2. Initial first-order rate constants of ozone decay at 25 °C.  
The acidic aqueous solutions were re-ozonated twice*

Hydrogen peroxide is known to initiate ozone decomposition. An explanation to the increase in decomposition rate of ozone after re-ozonisation is likely to be caused by sufficient amounts of hydrogen peroxide produced affecting the decay and thus the initial decomposition rate.

## 4 Micellar enclosure of ozone

### 4.1 Kinetics for different types of surfactants

The general idea behind using micellar enclosure is that ozone is a hydrophobic molecule, thus expected to be more soluble in hydrophobic solutions than in aqueous ones.

The effects on ozone decomposition rate of three different types of surfactants were examined, Dodecyl- $\beta$ -D-Maltoside, DDM; (neutral), Sodium dodecyl sulphate, SDS (anionic), and Dodecyl tri-methyl ammonium acetate, DAA, (cationic). The kinetics of ozone depletion was continuously recorded using an ozone-selective electrode, Fisher Rosemount 499A, at ambient temperature. The concentration of the surfactants used was 0.1 mM, thus below the critical micelle concentration (CMC) in all cases. The result of the kinetic experiments and surfactant structures are shown in figures 4.1 – 4.3.

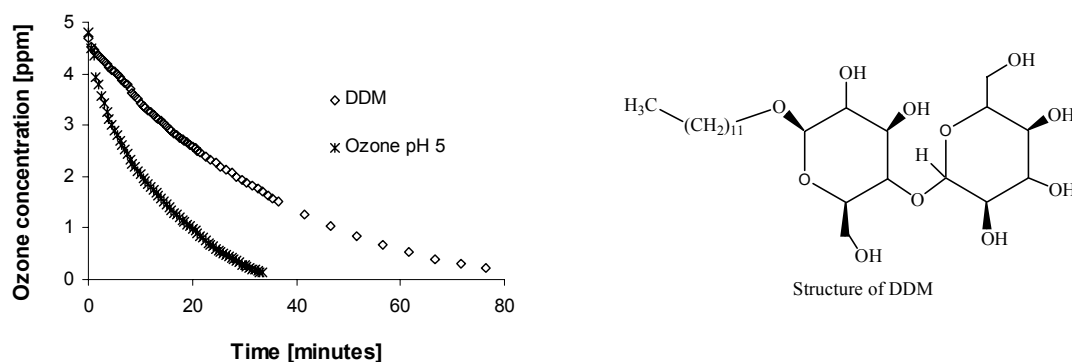


Figure 4.1. Ozone decomposition in an aqueous solution of 0.1 mM DDM

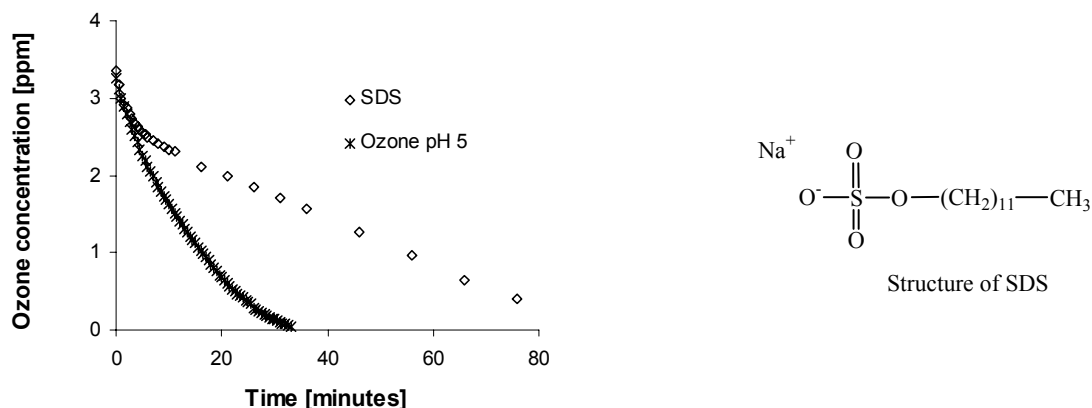


Figure 4.2. Ozone decomposition in an aqueous solution of 0.1 mM SDS

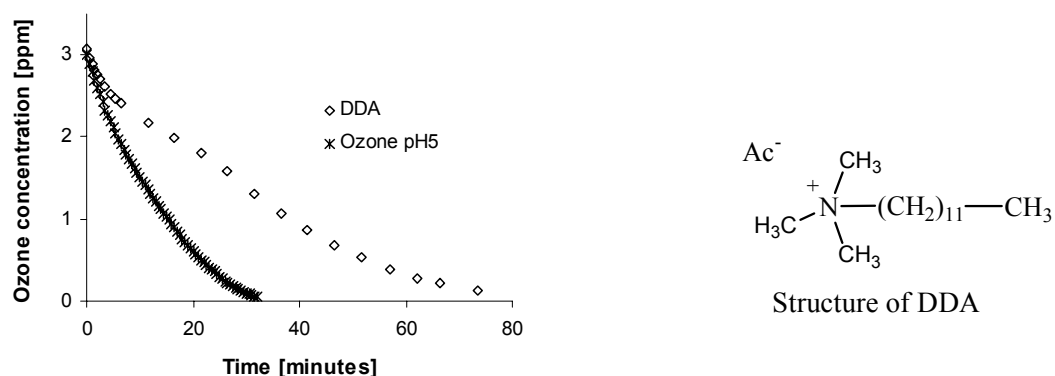


Figure 4.3. Ozone decomposition in an aqueous solution of 0.1 mM DDA

The kinetic experiments showed that all three types of surfactant have a stabilising effect on ozone as compared to a pure aqueous ozone solution at approximately the same pH. A comparison of the different surfactants shows that the retardation of the decomposition rate seems to be of similar magnitude for them all.

Since all three types of surfactants appeared to be relatively inert to ozone, and had a similar stabilising effect below CMC, one of the surfactants, SDS, was further investigated. The concentration was increased to levels above CMC, 200mM, figure 4.4.

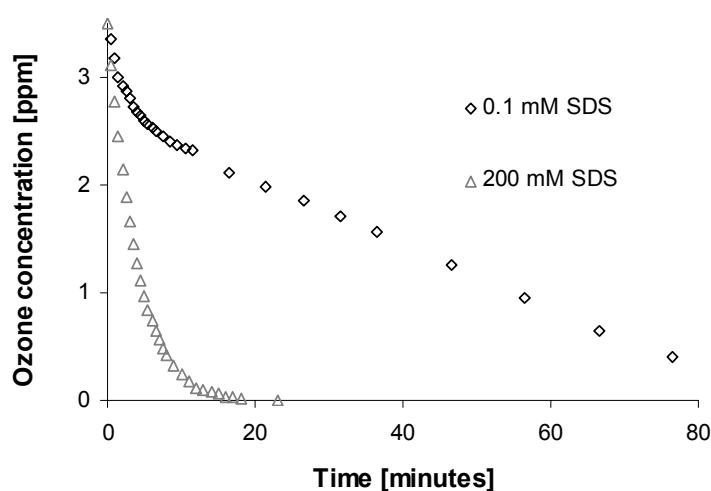


Figure 4.4. Ozone depletion at different SDS concentrations

When the concentration of SDS increases, the retardation of ozone decomposition is reversed and the reaction rate is in fact higher than observed in pure aqueous solution. An explanation to this behaviour can be that SDS is an HO-radical scavenger, thus stabilising ozone at low concentrations. However, at higher concentrations of SDS new reaction paths may dominate, involving direct oxidation.

## 4.2 The reaction between SDS and ozone

During the kinetic experiments, only small amounts of products are formed and direct detection is therefore difficult. For this reason a 10 mM SDS solution was ozonated for 8 hours, see chapter 2.2. Samples were removed intermittently, set aside and analysed the following day, in order to ensure ozone-free solution, by UV/Vis spectrophotometry. The UV-spectra show peaks emerging around 260 and below 190 nm, see figure 4.5.

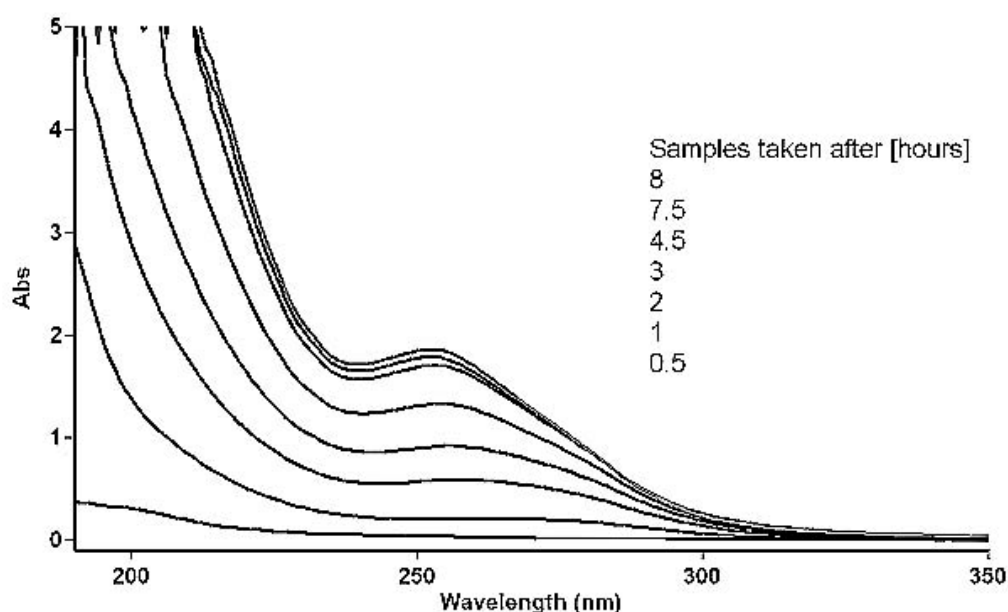


Figure 4.5. UV-spectra of ozonated, but ozone-free, 10 mM aqueous SDS solution

In order to determine which products are formed in the reaction between ozone and SDS NMR-spectroscopic measurements were made on a 0.1 M aqueous SDS solution before and after ozonisation. For comparison, the same type of analysis was made for a 0.1 M aqueous SDS solution that had been treated with HO-radicals formed by gamma radiation.

The NMR-spectroscopic measurements showed that both samples, exposed to ozone and HO-radicals, contained smaller carboxylic acids; mainly formic acid, acetic acid and propanoic acid. Furthermore, randomly positioned carbonyl groups were observed along the hydrocarbon chain. Typical values of UV-absorption for carboxylic acids are around 190 nm and for carbonyl groups around 190 nm and 250 nm, which is consistent with the UV-spectra of the ozonated sample. The presence of carbonyl groups in the hydrocarbon chain and the carboxylic acids was also confirmed by preliminary qualitative electrospray mass spectroscopy. These investigations also show that most SDS remains intact. Only smaller amounts of SDS have been cut in the terminal hydrocarbon tail end forming the carboxylic acids.

Carboxylic acids	Ozone	OH-radicals
Formic acid	-	0.0004
Acetic acid	0.032	0.005
Propanoic acid	0.038	-
<b>Carbonyl groups</b>		
2nd	0.083	0.003
3rd	0.095	0.016
<b>Other</b>		
Alpha-carbon affected	0.5	0
Alpha-carbon unaffected	0.5	1

Table 4.1. Integrated relative peak areas, where alpha protons are set to 1, of some important species in the  $^1\text{H}$ -NMR spectrum of ozonated and  $\text{HO}^\bullet$ -treated aqueous SDS solution, respectively

The predominant product in the ozonated sample is associated with a chemical change of the sulphate group. This was seen in the HMBC-spectra, where a new peak from  $\alpha$ -carbons, connected to the sulphate group, with a higher shift and with  $\beta$ -carbons unchanged emerged. This indicates that the sulphate group has been oxidised. The new peak was also clearly seen as a new triplet in the  $^1\text{H}$ -spectra, where the peak from  $\alpha$ -hydrogens with an oxidised sulphate group is shifted to a higher frequency, see figure 4.7.

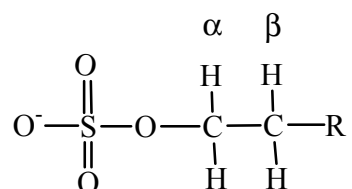


Figure. 4.6. Structure of unreacted SDS showing  $\alpha$ - and  $\beta$ - positions on the hydrocarbon chain



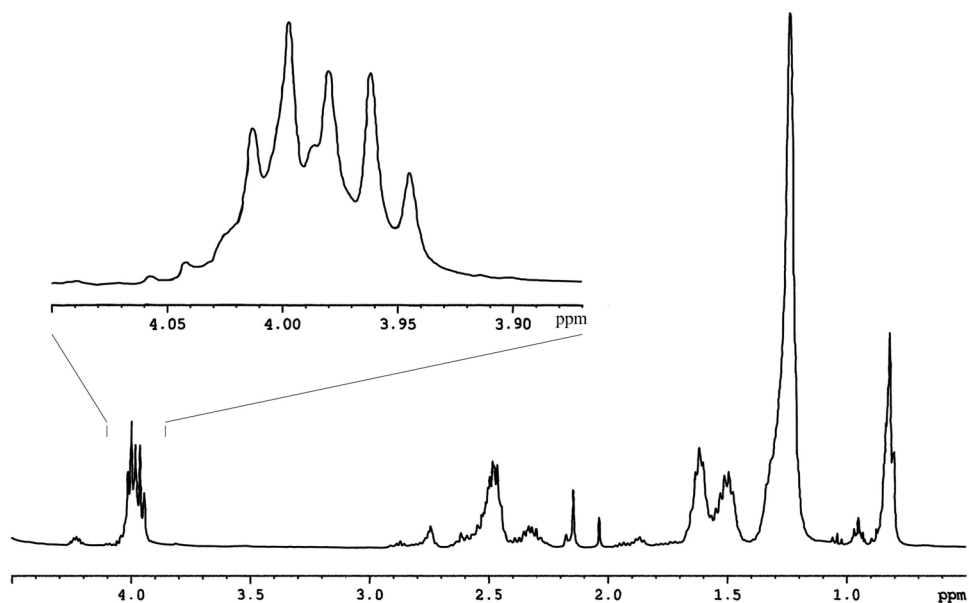


Figure 4.7.  $^1\text{H}$ -spectra of ozonated SDS with enlargement showing the two  $\alpha$ -hydrogen triplets

This change was not observed in the HO-radical-treated sample and seems to be a result of the direct reaction between ozone and the SDS-sulphate group. A comparison of the UV-spectra for the HO-radical-treated and the ozonated samples, figure 4.8, shows that the peak emerging below 190 nm is considerably stronger in the latter system. This may be attributed to the product from the direct sulphate-group reaction. Peaks below 190 nm are characteristic for compounds containing O-O groups, such as peroxides.

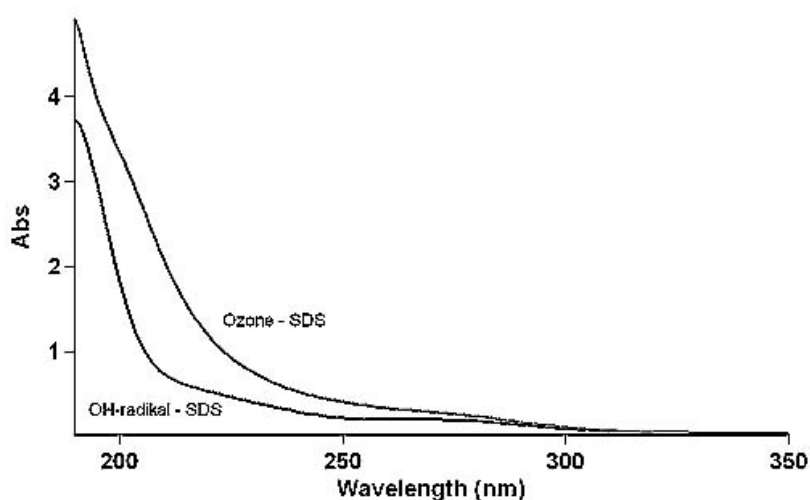


Figure 4.8. UV-spectra of the SDS sample treated with HO-radicals compared with a diluted ozonated sample

If a peroxide is formed, it is likely to exhibit oxidative properties as well, why iodine titration was performed. These showed that the ozonated SDS solution, as expected, was strongly oxidising, although no unreacted ozone remained in the solution. The oxidising power remains for a long period of time, and even after 8 months most of the oxidative product is retained, see table 4.2. However, during decomposition of ozone in aqueous solution hydrogen peroxide is formed and can form as well as by-product when ozone reacts with other compounds. The calculated concentration of the product will therefore be somewhat lower than stated in table 4.2, due to the potential hydrogen peroxide formation.

	SDS [mM]	Product [mM]
Freshly prepared	100	30
8 months old	100	20
8 months old	10	0.4

Table 4.2. The result of iodine titration of the ozonated SDS solution. For further details, see article I

Sulphate is not easily oxidised. However, when an organic group is attached to inorganic atoms, such as phosphorous, nitrogen and sulphate, ozone can transfer an oxygen atom. There are two possible ways for the sulphate group to be directly oxidised including O-O-group formation; either an oxygen transfer from ozone, forming an SDS-peroxide, or two SDS molecules merging to form an SDS-peroxodisulphate analogue, see figure 4.9.

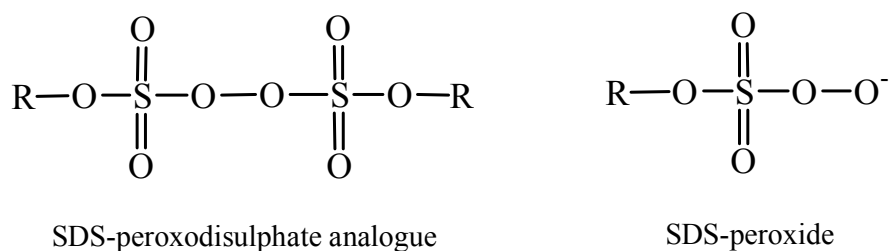


Figure 4.9. Possible products of the direct reaction between the SDS-sulphate group and ozone

The sulphate group could also be oxidised forming an ozonide, see figure 4.10. This is known for phosphorous. However, an ozonide is expected to absorb UV-radiation in the same range and with similar extinction coefficient as ozone. A peak was

observed in the UV-spectra around 250 nm, figure 4.5. The amplitude of this peak is lower than would be expected for significant amount of ozonide. This peak is instead, as previous mentioned, connected to the carbonyl groups in the hydrocarbon chain of SDS. The main products of ozonated SDS are therefore not likely to be ozonides.

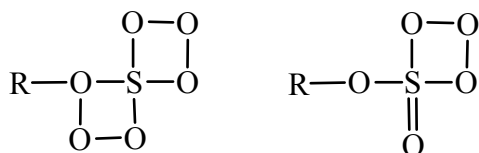


Figure 4.10. Structure of possible ozonides

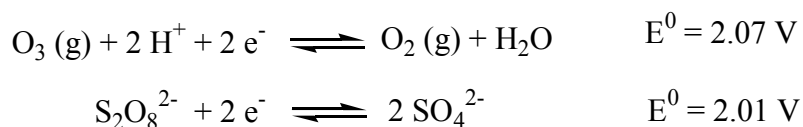
### 4.3 SDS-peroxodisulphate analogue or SDS-peroxide?

When the SDS solution is ozonated, the chemical and physical characteristics changes. The foaming capacity is reduced and it smells flat and sour. The foaming capacity of the SDS-peroxodisulphate analogue should be lower than that of SDS-peroxide. However, the dissociation constant for SDS-peroxide can be approximated to  $pK_a=10$ .<sup>53</sup> At pH 5 the SDS-peroxide will be protonated, thus neutral. Consequently, the SDS-peroxide will, just as the SDS-peroxodisulphate analogue, have a significantly lower foaming capacity than SDS, which is coherent with the physical changes of the solution.

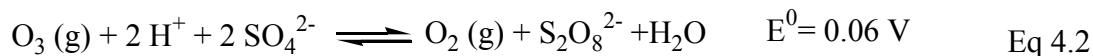
Furthermore, it is possible to estimate the thermodynamic driving force of a redox reaction by use of Nernst's equation:

$$E_0 = E^0 + \frac{RT}{nF} \ln \frac{[ox]}{[red]} \quad \text{Eq 4.1}$$

In the case of the SDS-peroxodisulphate analogue a rough estimate can be obtained by use of the known values for the reduction of peroxodisulphate to sulphate:



Giving the total reaction:

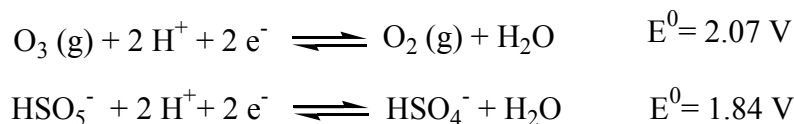


where  $n=2$ ,  $P_{\text{O}_2}=1$

$$E = 0.06 + \frac{T}{23210} \ln \frac{[\text{H}^+]^2 [\text{SO}_4^{2-}]^2 P_{\text{O}_3}}{[\text{S}_2\text{O}_8^{2-}]} \quad \text{Eq 4.3}$$

Nernst's equation shows that several factors, such as pH, temperature as well as ozone and sulphate concentration will affect the reaction. One interesting feature is that  $E$  is quite low with values close to zero. In fact, the conditions for the reaction in our experiments (pH 5, SDS = 0.1 M,  $P_{\text{O}_3} \sim 0.05$  atm,  $T=298$  K) gives negative values of  $E$ , thereby formally no driving force ( $\Delta G > 0$ ).

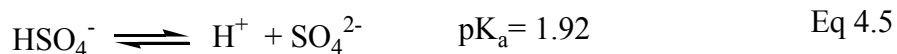
In the case of the SDS-peroxide, the reaction can be estimated using the values of peroxymonosulfate:<sup>54</sup>



Giving the reaction:



However the predominant species at pH 5 is  $\text{SO}_4^{2-}$ :



Giving the total reaction:



where  $n=2$ ,  $P_{O_2}=1$

$$E = 0.29 + \frac{T}{23210} \ln \frac{[SO_4^-][H^+] P_{O_3}}{[HSO_5^-]} \quad \text{Eq 4.7}$$

Again, the driving force depends on temperature, pH, ozone and sulphate concentration. In our experiments (SDS = 0.1 M,  $P_{O_3} \sim 0.05$  atm,  $T=298$  K) the driving force is positive ( $\Delta G < 0$ ) in the initial stages of reaction, and as the concentration of  $HSO_5^-$  increases the driving force  $E$  approaches zero.

From a thermodynamic point of view, the SDS-peroxide is the most likely product of oxidation. However, all estimations given above neglect the effect of the alkyl chain.

#### 4.4 Bacteriological experiments with SDS and ozone

In chapter 4 it was established that SDS reacts slowly with ozone, mainly involving the sulphate group. Furthermore, at low SDS concentrations, below CMC, stabilisation occurs due to radical scavenging effects of the hydrocarbon chain. Since a cleaning system may operate at SDS concentrations above CMC, around 10 mM, it is vital to investigate the antiseptic properties of ozone at higher SDS concentrations.

Two different species of bacteria were investigated the vegetative bacterium *Staphylococcus aureus* ATCC 6538,  $5 \times 10^7$ /ml, and spores of *Bacillus subtilis* ATCC 19659,  $5 \times 10^5$ /ml.

No	Sample	Exposure time		
		1 min	5 min	10 min
1	<i>St. aureus</i> and ozone	0	0	0
2	<i>St. aureus</i> , ozone and SDS	0	0	0
3	<i>B. subtilis</i> spores and ozone	10	0	0
4	<i>B. subtilis</i> spores, ozone and SDS	5	0	0

Table 4.3 The number of surviving CFU for different samples and exposure times. The concentration of ozone was 10 ppm, and in the samples containing SDS the concentration was 10 mM. For more details, see article II

The mixture of 10 mM SDS and ozone has the capacity to sterilise media of both bacteria by a minimum  $10^7$  reduction of *S. aureus* and  $10^5$  reduction of *B. subtilis* within 5 minutes. The same was achieved for the aqueous ozone solution. With an exposure time of 1 minute only the vegetative bacteria, *St. aureus*, was completely exterminated. The spores of *B. subtilis*, show, as would be expected, a higher resistance towards oxidation. Furthermore, the addition of SDS does not considerably affect the antiseptic properties of an aqueous ozone solution.

## 5 Conclusion

The decomposition rate of ozone in aqueous solution is affected by many factors such as temperature, impurities, and pH. In the acidic region sulphuric, perchloric and phosphoric buffers are used to control pH. With respect to the effect of ozone decomposition rate, kinetic experiments show that the buffers can be regarded as equal at low pH. However, in pre-ozonated and re-ozonated solutions hydrogen peroxide can form in sufficient amounts to influence the initial decomposition rate of ozone, why care should be taken in the interpretation of data from pre-ozonated solutions.

All three investigated surfactants retard ozone decomposition at low concentrations (below CMC), and the magnitude of the stabilisation is similar. For one of the surfactants, SDS, being more extensively studied the effects are reversed at higher concentrations and the decomposition rate of ozone is even accelerated. The explanation is that the direct reaction between surfactant and ozone becomes dominant. The stabilising effect on ozone solutions at lower concentration seems to relate to the radical scavenging effects of the hydrocarbon chain, forming carbonyl groups and carboxylic acids, rather than micellar stabilisation of ozone. Iodic titration, NMR- and UV-spectroscopic analyses indicate that the main product of the direct reaction between ozone and SDS involves an oxygen transfer to the sulphate group. The product formed is suggested to be an SDS-peroxide.

The bacteriological experiments performed show that the addition of SDS to an aqueous solution of ozone does not change the antiseptic properties of ozone noticeably, and the European standard for sterilisation prEN 137 27<sup>55</sup> can be met. A cleaning system with both ozone (antiseptic) and a surfactant (remove biofilm) should consequently be a realistic possibility, see paper IV.





## 6 Future work

The main product of the ozonisation of SDS, SDS-peroxodisulphate analogue or SDS-peroxide, is not fully characterised. A preliminary  $^{17}\text{O}$  NMR-spectroscopic analysis has been made without satisfactory results due to the low sensitivity of the technique. These experiments will therefore be refined, and new attempts be made. Furthermore, black, thin, threadlike crystals, typical for organic peroxides, have formed in the ozonated SDS solution, but the quality of them has so far unfortunately not allowed a full single crystal X-ray diffraction analysis.

Other ways to chemically or physically stabilise ozone will also be examined in the future using, cyclodextrin or glacial acetic acid.



## 7 Acknowledgments

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All present and previous **colleagues at Inorganic chemistry** sharing both good and bad times! But also all other colleagues at KTH especially at Nuclear chemistry: Welcome to us above the garbage room ☺

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