Ozone Bleaching of Cellulosic Chromophores

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Abstract

Chromophores, coloured substances of high stability that reduce brightness, are present in all kinds of cellulosic products, such as aged material and even highly bleached pulp. Thus, they are the targeted structures in industrial pulp and paper bleaching. In this study the chromophores 2,5-dihydroxy-1,4-benzoquinone (DHBQ), 5,8-dihydroxy-1,4-naphthoquinone (DHNQ), 2,5-dihydroxyacetophenone (2,5-HAP,), 2,6-dihydroxyacetophenone (2,6-HAP), tetrahydroxy-1,4-benzoquinone (THBQ) and the model compound 2-Hydroxy-1,4-naphthoquinone (2-OH-NQ) were bleached with ozone at pH 2 resembling industrial conditions and in organic solvents. Bleaching kinetics were followed via UV/Vis spectroscopy and the degradation products were analysed by NMR and GC-MS. Different carboxylic acids were determined as degradation products. Further, the influence of salts on the bleaching behaviour was investigated and reaction mechanisms of the ozone degradation of chromophores proposed.

Kurzfassung

Chromophore sind farbgebende Substanzen, welche in Zellstoff- und Papiermaterialien allgegenwärtig sind. Während der Zellstoffbleiche sollen diese Chromophore weitestgehend beseitigt werden. In dieser Studie wurden die Schlüsselchromophore 2,5-Dihydroxy-1,4-benzochinon (DHBQ), 5,8-Dihydroxy-1,4-naphthochinon (DHNQ), 2,5-Dihydroxyacetophenon (2,5-HAP) und 2,6-Dihydroxyacetophenon (2,6-HAP) mit Ozon bei pH 2 gebleicht. Aus wissenschaftlichem Interesse wurden auch die Chromophore Tetrahydroxy-1,4-benzochinon (THBQ) und die Modellsubstanz 2-Hydroxy-1,4-naphthochinon (2-OH-NQ) gebleicht. Diese Bedingungen spiegeln die industrielle Bleiche wider. Zusätzlich wurden die Chromophore in organischen Lösungsmitteln gebleicht. Die Entfärbung der Lösungen während der Bleiche wurde mittels UV/Vis Spektroskopie gemessen und es wurden entsprechende Reaktionskinetiken erstellt. Nach dem Bleichvorgang wurden die Abbauprodukte mittels NMR und GC-MS analysiert. Die Reaktionen zwischen Ozon und den Chromophoren brachte verschiede Carbonsäuren als Reaktionsprodukt hervor.

Weitere Untersuchungen über den Einfluss von Salzen bei der Bleiche, sowie über den Reaktionsmechanismus von Ozon wurden durchgeführt.

Contents

ACKNOWLEDGEMENT ..... **II**

ABSTRACT ..... **III**

KURZFASSUNG ..... **IV**

OBJECTIVE ..... **VII**

LIST OF ABBREVIATIONS ..... **VIII**

1 INTRODUCTION **1**

1.1 CHROMOPHORES IN CELLULOSICS 1
1.2 THE ELECTROMAGNETIC SPECTRUM AND COLOUR PERCEPTION 3
1.3 BLEACHING 6
1.4 TOTALLY CHLORINE FREE BLEACHING (TCF) BLEACHING 9
1.5 HYDROGEN PEROXIDE (P) BLEACHING 9
1.6 OXYGEN STAGE (O) 11
1.7 OZONE 11
1.7.1 Ozone generation *12*
1.7.2 Ozone (Z) Bleaching *13*
1.7.3 Criegee Mechanism *16*

2 MATERIAL AND METHODS **18**

2.1 MATERIALS 19
2.2 METHODS 19
2.3 SAMPLE PREPARATION 19
2.3.1 Chromophores dissolved in organic solution: *19*
2.3.2 Chromophores dissolved in aqueous solution: *19*
2.3.3 Chromophores dissolved in aqueous solution with various salts: *19*
2.4 BLEACHING PROCEDURE 20
2.5 SAMPLING 21
2.6 GC-MS ANALYSIS OF DEGRADATION PRODUCTS 21
2.7 NMR 22
2.7.1 NMR Codes for the relevant carboxylic acids *22*
2.8 UV/VIS SPECTROSCOPY 23
2.9 COMPOSITION OF THE SOLUTIONS 26

3 RESULTS AND DISCUSSION **31**

3.1 WORKFLOW 31
3.2 BLEACHING OF KEY CHROMOPHORES WITH OZONE 32
3.3 BLEACHING KINETICS CHROMOPHORES IN AQUEOUS SOLUTION 33
3.3.1 UV/Vis spectroscopy of 2,6-HAP and 2,5-HAP (aqueous) *34*
3.3.2 UV/Vis spectroscopy of DHNQ (aqueous) *36*
3.3.3 UV/Vis spectroscopy of DHBQ (aqueous) *38*
3.3.4 UV/Vis spectroscopy of 2-OH-NQ (aqueous) *39*
3.3.5 Effects of inorganic salts on DHBQ degradation with ozone *41*
3.3.6 Effects of pH 12 for DHBQ bleaching with ozone *42*
3.3.7 Analysis of the degradation products of chromophores obtained in the bleaching experiments in aqueous solution by GC-MS and NMR *43*
3.3.8 NMR results of the bleaching experiments in aqueous solution *47*
3.4 GC-MS RESULT 48
3.5 BLEACHING CHROMOPHORES IN ORGANIC SOLVENTS 49

3.5.1 UV/Vis spectroscopy of 2,6-HAP and 2,5-HAP (DCM) *50*
3.5.2 UV/Vis spectroscopy of DHNQ (acetone) *52*
3.5.3 UV/Vis spectroscopy of DHBQ (acetone) *53*
3.5.4 UV/Vis spectroscopy of 2-OH-NQ (acetone) *55*
3.5.5 Analysis of the degradation products of chromophores obtained in the bleaching experiments in organic solution by GC-MS and NMR *56*
3.6 COMPARISON BETWEEN BLEACHING CHROMOPHORES IN ORGANIC AND AQUEOUS SOLUTION 59
3.6.1 Bleaching times *59*
3.7 REACTION MECHANISM OF CHROMOPHORES AND OZONE 60
4 CONCLUSION 62
5 LIST OF FIGURES 64
6 LIST OF TABLES 65
7 REFERENCES 66
8 APPENDIX 73
8.1 NMR RESULTS OF DHNQ BLEACHED IN AQUEOUS SOLUTION 73
8.1.1 NMR results of DHBQ bleached in aqueous solution *74*
8.1.2 NMR results of 2,5-HAP bleached in aqueous solution *75*
8.1.3 NMR results of 2,6-HAP bleached in aqueous solution *76*
8.1.4 NMR results of 2OHNQ bleached in aqueous solution *77*
8.1.5 NMR results of THBQ bleached in aqueous solution *78*

Objective

The objective of the thesis was to bleach key chromophores from cellulosics with ozone in organic and aqueous solution to determine the formed degradation products. Bleaching on industrial level is carried out only in aqueous solution; still, in this study chromophores were also bleached in various organic solvents out of scientific interest and to learn about possible differences between aqueous and organic media regarding the chromophore bleaching behaviour.

To identify differences in bleaching behaviour bleaching kinetics of each chromophore were determined by sampling during the reaction and subsequent UV/VIS spectroscopy. Based on the bleaching behaviour conclusions can be drawn about the stability and reactivity of the different chromophores when bleached with ozone.

The chromophores used were: 2,5-dihydroxy-1,4-benzoquinone (DHBQ, 7), 5,8-dihydroxy-1,4-naphthoquinone (DHNQ, 8), 2,5-dihydroxyacetophenone (2,5-HAP, 10), 2,6-dihydroxyacetophenone (2,6-HAP, 11), tetrahydroxy-1,4-benzoquinone (THBQ, 12) and 2-hydroxy-1,4-naphthoquinone (2-OH-NQ, 9).

List of Abbreviations

^{13}C NMR	Carbon-13 nuclear magnetic resonance
^{1}H NMR	Proton nuclear magnetic resonance
2,5-HAP	2,5-Dihydroxyacetophenone
2,6-HAP	2,6-Dihydroxyacetophenone
2-OH-NQ	2-Hydroxy-1,4-naphthoquinone
A	Absorption
CRI	Chromophore release and identification
DCM	Dichloromethane
DHBQ	2,5-Dihydroxy-1,4-benzoquinone
DHNQ	5,8-Dihydroxy-1,4-naphthoquinone
DP	Degree of polymerisation
DTPA	Diethylenetriaminepentaacetic acid
ECF	Elemental chlorine free
EDTA	Ethylenediaminetetraacetic acid
GC	Gas chromatography
HEDTA	2-hydroxyethyl ethylenediamine tetraacetic acid
HMBC	Heteronuclear multiple bond correlation
HSQC	Heteronuclear single quantum coherence
MeOD	Deuterated methanol
min	Minute
ml	Millilitre
mM	Millimole
MS	Mass spectrometry
MW	Molar weight

nm	Nanometre (1 nm = 10^{-9} m)
NMR	Nuclear magnetic resonance
ppm	Parts per million
RT	Retention time
s	Seconds
TCF	Totally chlorine free
THBQ	Tetrahydroxy-1,4-benzoquinone
UV	Ultraviolet (light)
Vis	Visible (light)

1 Introduction

1.1 Chromophores in cellulosics

Chromophores in cellulosic products, such as pulp and paper, are responsible for yellowing and brightness revision. The literal translation of chromophore means “carrier of colour” which is descended from the Greek words chroma (colour) and pherein (carry) (Rosenau et al. 2014, 2011). In cellulosics, chromophores can be formed from residual lignin and from polysaccharides. The reason for chromophore formation from polysaccharides is the substantial number of process steps during pulping and bleaching that are necessary to separate the cellulose from lignin, hemicelluloses and minor compounds such as resins. Already in 1970ties studies of Theander et al. showed that carbohydrates form various aromatic compounds under acidic as well as under alkaline conditions. These products are also known as “Theander products” (Popoff and Theander 1976; Olsson et al. 1977; Popoff et al. 1976; Forsskahl et al.1976; Theander et al. 1987; Theander and Westerlund 1980).

During pulping and the processing of regenerated cellulose products (e.g. the Lyocell process) cellulose chains can be partly oxidized, cleaved and degraded. The low molecular weight degradation products of cellulose act as a precursor for the generation of chromophores. Further dehydration and condensation reactions lead to the formation of coloured molecules. Other influencing factors of chromophore formation are temperature and humidity, resulting in certain grades of ageing (Rosenau et al. 2005; Krainz et al. 2009).

The amounts of chromophores present in cellulosic materials is marginal and ranges from ppm to ppb (Rosenau et al. 2004, 2007, 2014, 2011). The human eye is very sensitive in the range of 500-600 nm, in which the colours green and yellow are visible, thus even the tiniest quantity of chromophores in cellulosic materials can be recognized as a yellow tint (Sharpe et al. 2011; Bowmaker and Dartnall 1980).

Due to the low quantity of chromophores present in cellulosic materials and their low solubility as well as low reactivity, for a long time it was not possible to isolate specific chromophores and determine their structures. Until a decade ago there were only assumptions regarding to the structure. The success of the chromophore release and identification (CRI) method made it possible for the first time to extract specific chromophores and gain information on their chemical structure (Rosenau et al. 2004). The CRI method was successfully applied to Lyocell and Viscose fibres, thermally aged pulp, cellulose triacetate as well as bleached pulps (Adorjan et al. 2005; Rosenau et al. 2005, 2004, 2007).

Introduction

The results of the structural analysis of the chromophores showed evidence that the chromophores are condensation products of (mono)saccharides, which originated from cellulose degradation. Two groups could be distinguished: primary chromophores that originate from the polysaccharide and are process independent, and secondary chromophores that are incorporate atoms from process chemical or bleaching agents in their structure. Primary chromophores shown in Figure 1 comprise hydroxyquinones (**1-3**), acetophenones (**4**) and naphthoquinones (**5**) (Rosenau et al. 2007). Carbon disulphide (CS_2) used in the viscose process can lead to the formation of sulfonated chromophores (**7**) and during the bleaching with chlorine dioxide (D-Stage) chlorinated hydroxyquinone (**6**) can be formed. The substances **6** and **7** are examples of secondary chromophores.

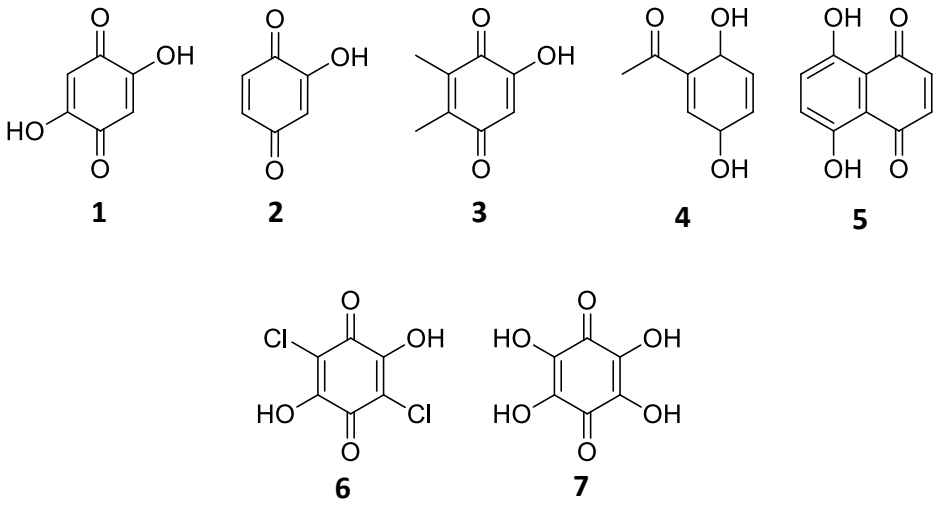

Figure 1: Primary chromophores identified by CRI in bleached pulps (top row) and the secondary chromophores **6**, a chlorinated hydroxyquinone and **7**, a sulfonated hydroxyquinone (bottom row).

Primary chromophores bare some interesting chemical characteristics. They exhibit change of colour in aqueous solution upon pH variation and show a high stability towards common bleaching agents due to resonance stabilization in alkaline media, H-bond and hyper conjugative effects in acidic media and solid state (Hosoya and Rosenau 2013; Krainz 2009).

In this study various Chromophores where selected for an ozone treatment in organic solvent and aqueous solution in acidic medium. The chromophores used are 2,5-dihydroxy-1,4-benzoquinone (DHBQ, **1**), 5,8-dihydroxy-1,4-naphthoquinone (DHNQ, **5**), 2,5-dihydroxyacetophenone (2,5-HAP, **4**), 2,6-dihydroxyacetophenone (2,6-HAP, **9**) which are known to be the key chromophores in pulp bleaching. Additionally, tetrahydroxy-1,4-benzoquinone (THBQ, **10**) and 2-hydroxy-1,4-naphthoquinone (2-OH-NQ, **8**), a model compound, were used in this bleaching

study. THBQ can form during chlorine dioxide bleaching of Kraft pulp (Zawadzki et. al 1998). 2-OH-NQ, also known as Lawsone can be used as a dye (hair, skin) (Mulholland 2008). The chemical structures of the substances are shown in Figure 2.

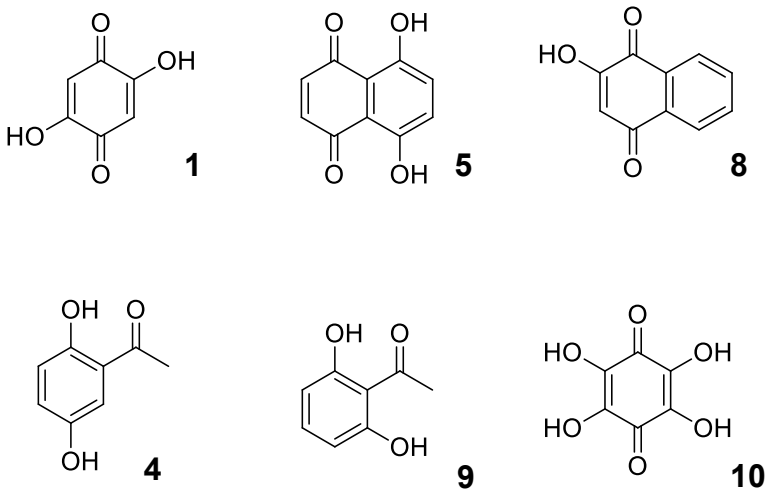

Figure 2: the key chromophores: 2,5-Dihydroxy-1,4-benzoquinone (DHBQ, **1**), 5,8-Dihydroxy-1,4-naphthoquinone (DHNQ, **5**), 2,5-Dihydroxyacetophenone (2,5-HAP, **4**), 2,6-Dihydroxyacetophenone (2,6-HAP, **9**); the chromophoreTetrahydroxy-1,4-benzoquinone (THBQ, **10**) and the model substance 2-Hydroxy-1,4-naphthoquinone (2-OH-NQ, **8**).

1.2 The electromagnetic spectrum and colour perception

Although the amount of chromophores in cellulosic material is only marginal, the human eye can easily recognize the yellow tint the chromophores cause as it is very sensitive towards yellow (Sharpe et al. 2011; Bowmaker & Dartnall 1980). The question arises what makes yellow different from other colours? By understanding how light and the human eye works this phenomenon can be well explained. All radiation can be arranged according to frequency and wavelength in the electromagnetic spectrum (Figure 3) (Albertz 2007).

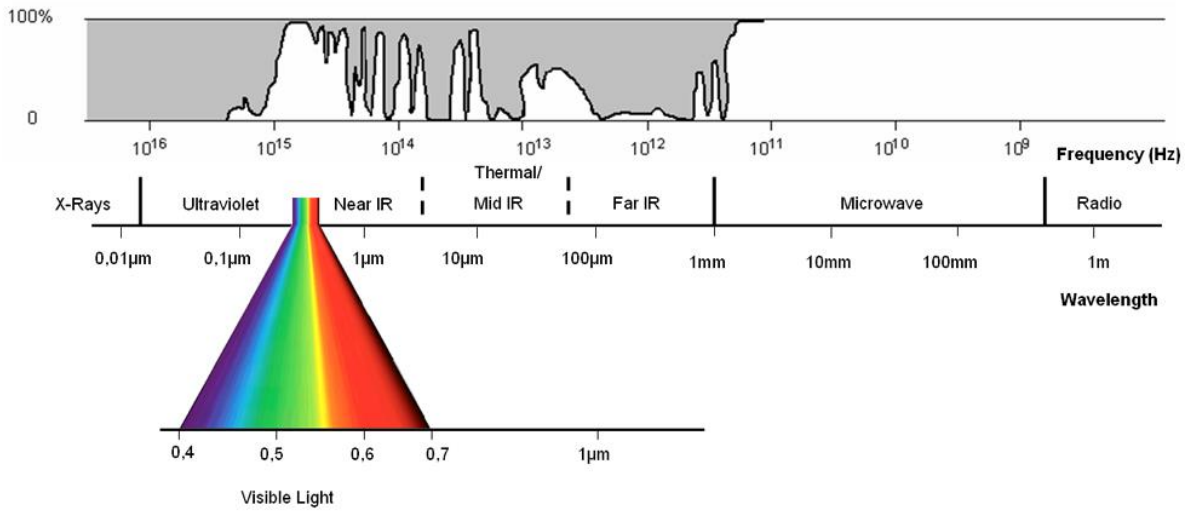

Figure 3: The electromagnetic spectrum of light with the corresponding wavelengths (Albertz 2007).

Within the electromagnetic spectrum, the coloured light spectrum ranges from 380 to 720 nm. This is also called the visible light because it can be detected by the human eye. In a vacuum, the colours one perceives have the following approximate wavelengths (Biermann 1996):

violet	380-430 nm
indigo	430-450 nm
blue	450-500 nm
green	500-560 nm
yellow	560-590 nm
orange	590-630 nm
red	630-720 nm

When electromagnetic radiation meets the retina of the eye a colour perception results in the brain through a neurological process (Ek et al. 2009c).

In the back of the retina there are two types of cells (neurons): cone-shaped cells and rod-shaped cells. These cells are the light sensitive components of the eye. Rods are sensitive to all light and are primarily used in low-light situations hence they are largely responsible for night vision and for the perception of black and white. Rods however do not allow colour vision. For colour vision cone cells are needed, they can be distinguished into three types: S-cones, for short wavelengths (responsible for blue); M-cones, for medium wavelengths (responsible for green); and L-cones, for long wavelengths (responsible for red). The three types of cones respond relative to the intensity of all shades of colour. Therefore, it is possible for every colour to be simulated in the brain (Biermann 1996). The eye's sensitivity peaks at a wavelength of

560-565 nm, which is a bright yellowish-green colour. This colour is perceived when both, red and green cones are stimulated (McGrath 1999; Serway et al. 2006). This specific colour that stimulates the eye the most is called “chartreuse”, it was named after a French liqueur and is also known as apple green. Two shades of chartreuse are shown in Figure 4. Because of its good recognisability chartreuse often finds use in traffic safety vests or as coating for emergency vehicles (Los Angeles Times 1995).

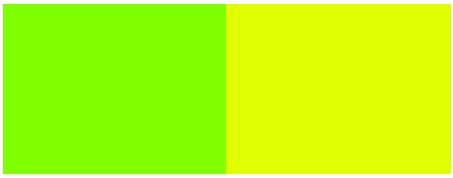

Figure 4: chartreuse green (left) and chartreuse yellow (right).

The distinct colour shades of the key chromophores are shown in Figure 5 and range from a bright (2,6-HAP) and greenish yellow (2,5-HAP) to orange (DHBQ) and a dark red (DHNQ), they are therefore also very recognizable to the human eye.

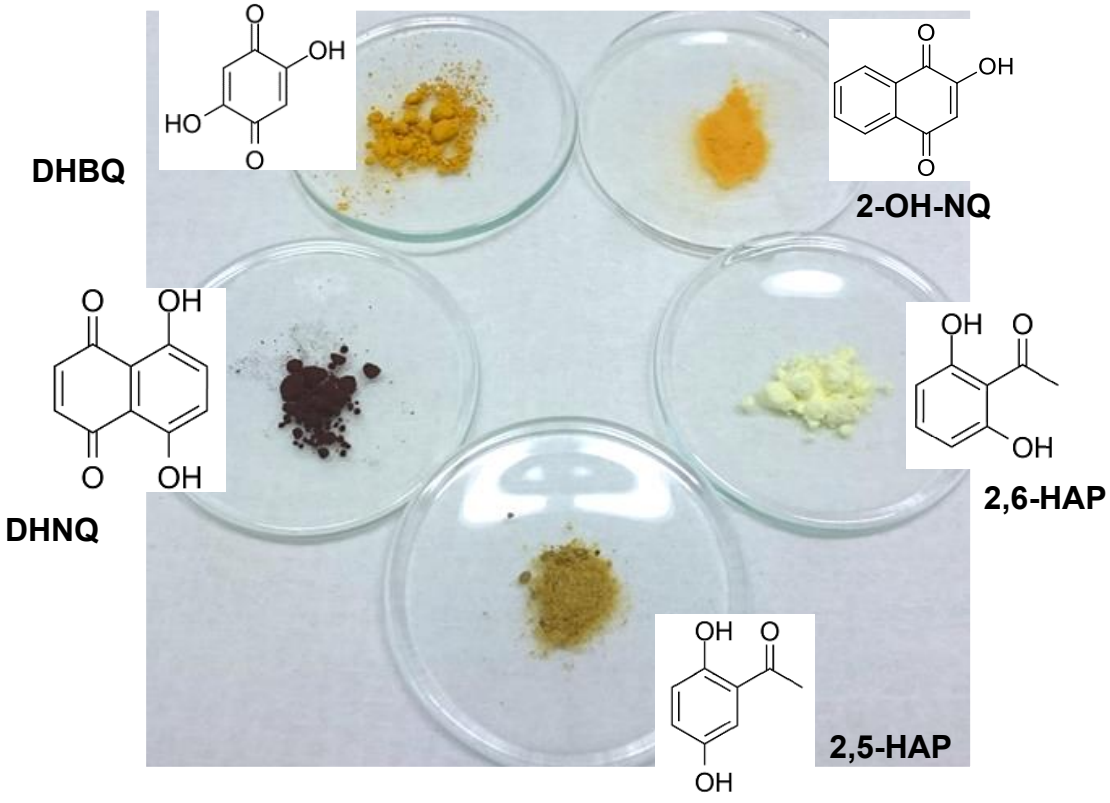

Figure 5: Chromophores in solid form.

1.3 Bleaching

Bleaching is a process were wood or other lignocellulosic pulp is treated with chemical agents to increase their brightness. The term brightness is used to describe the level of whiteness of pulp and paper and is defined by the reflectance of blue light (457nm) from paper. Brightness scales from 0% (absolute black) to 100% (relative to magnesium oxide standard which represents absolute white) Common brightness levels are given in Table 1 (Biermann 1996).

Table 1: Approximate brightness levels of lignocellulosic materials according to Biermann (1996).

Material	Brightness Level
Unbleached Kraft	20%
Unbleached sulphite	35%
Newsprint	60%
Groundwood	65%
White tablet paper	75%
High grade bond	85%
Dissolving pulp	90%

In the past, chemical pulp bleaching used to be a single stage treatment with chlorine or hypochlorite. Today single step bleaching is an exception and mostly applicable for already clean and bright materials such as in the case of textile bleaching or in the brightening of cotton. The state of the art is multistep bleaching. The advantage of multistep bleaching processes is that lower charges of chemicals can be used. Less chemicals cause fewer side reactions and therefore, the applied amount is consumed more economically (Suess 2010).

Unbleached Kraft pulp appears dark brown (20% brightness) and contains lots of chromophores originating mainly from residual lignin which makes it not suitable for printing and writing paper. Writing and printing paper requires a high level of brightness and a smooth surface to give a better contrast between the paper and the print (Ek et al. 2009b). Also, brightness stability and strength of paper are of high importance in a long-term perspective. It is crucial for paper to have a consistent cleanliness, otherwise impurities could turn up as dots that lower the paper quality and in the worst case could interfere with the printed letters (Ek et al. 2009b;

Ragnar 2000). This is especially crucial in countries like China where a dot can alter the meaning of a character. This example brought up by Ragnar (2000) is illustrated in Figure 6.

Wood 木 King 王

Method 术 Jade 玉

Figure 6: The meaning of a Chinese character is changed by a single dot (Ragnar 2000).

Bleaching is done in several stages containing also washings and extraction stages to remove heavy metals and wood extracts. However, the main target is the removal of rest lignin and chromophores. Stages are described in abbreviated sequences. Washings between the stages are not explicitly mentioned as it is assumed to be the common procedure. The abbreviation ODE for example represents the stages of oxygen, chlorine dioxide and an extraction stage. The use of brackets (ZD) indicates a sequence without intermediate washing (Suess 2010). A list of the bleaching stages and their abbreviations is given in Table 2.

Table 2: Bleaching stages, their effects and conditions according to Suess (2010).

Bleaching Stage and abbreviation	**Effects**	**Condition**
Oxygen stage: O	Oxidation of lignin	Alkaline conditions at 90-100°C
Acid stage: A	Removal of transition metals or hexeneuronic acid	40-60°C for transition metals, 90°C for hexeneuronic acid. Mostly, sulfuric acid is used
Acid stage: Q	Removal of transition metals	pH 5-6.5. Chelating agents (like EDTA, DTPA HEDTA) are used
Chlorine dioxide stage: D	Oxidation of lignin	Solution of ClO_2 at pH<5 in water is used
Extraction stage: E	Solubilization of oxidized lignin	pH 9.5-11. Caustic soda is used

Extraction with O_2: Eo	Improved lignin removal by oxidation	Oxygen gas is used
Extraction with O_2/H_2O_2: EOP	Improved lignin removal and brightening by oxidation	Oxygen and hydrogen peroxide is used
Alkaline stage: P	Bleaching	pH 10-11 at 60-90°C. Hydrogen peroxide is used
Pressurized peroxide stage: OP	Bleaching	T > 100°C at 0.3 MPa pressure. Hydrogen peroxide with additional oxygen is used
Ozone stage: Z	Oxidation of lignin	pH 2-3. Ozon gas is used
Weakly acidic stage: Paa	Oxidation of lignin and activation of a subsequent P stage	Weakly acidic, pH ~5. Peracetic acid is used
Enzyme treatment stage: X	Improves accessibility of lignin by the removal of precipitated carbohydrates	Xylase or hemicellulases are used
Reductive treatment: Y		Dithionite is used
Neutralization: N		

The first bleaching chemicals used were chlorine (Cl_2) and hypochlorite (OCl^-) in the 18th century. Simple bleaching sequences were enough to bleach sulphite pulps. Kraft pulps could not be bleached successfully due to the severe loss of strength. In the 1920s chlorine dioxide (ClO_2) was found to be an excellent bleaching agent for Kraft pulps with very little degradation of cellulose. This innovation enabled the industries to fully bleach Kraft pulps with small strength losses. Until today ClO_2 bleaching is important in pulp mills world-wide. The utilization of ClO_2 lead to the development of ECF (elemental chlorine free) bleaching sequences that no longer use elemental chlorine like chlorine gas or hypochlorite (Suess 2010).

Bleaching aims to achieve high brightness without damaging the fibre and its properties (fibre strength) in the process. From an economic point of view, requirements are the efficient use

of chemicals and inexpensive equipment. Further, a focus on an overall clean process for environmental protection should be ensured.

The environmental impact of certain bleaching methods (especially elemental chlorine) was openly discussed in the 80s due to the formation of chlorinated compounds and air pollution by evaporation plants and black liquor combustion plants which caused acid rain. Since then a shift towards environmental friendly bleaching methods of ECF (Elemental Chlorine Free) and TCF (Totally Chlorine Free) systems within the pulp mills began (Ragnar et al. 2000; Ragnar 2000).

1.4 Totally Chlorine Free Bleaching (TCF) Bleaching

Total chlorine-free bleaching (TCF) is performed without the use of any elemental chlorine or chlorinated compounds, using only bleaching agents with oxygen as the active, oxidizing species. Typically, oxygen (delignification) (O), hydrogen peroxide (P), and ozone (Z) are applied (Jafari et al. 2014; Ragauskas 1999; Sixta, 2006; Suess 2010). Particularly good results of full brightness were obtained with a combination of hydrogen peroxide and ozone. The first pilot plant utilizing ozone was built in 1986 in Baienfurt, Germany. Later in 1990 the first industrial scale installation was built in Lenzing, Austria (Ragnar et al. 2000; Ragnar 2000). Because of environmental issues and a demand for non-chlorine based chemical bleached pulp the importance and development of TCF increased over the past decades (Chirat and Lachenal 1997; Gierer 1997; Miri et al. 2015).

Initially, lower selectivity was observed in TCF bleaching as compared to ECF. This can result in a loss of DP (Degree of Polymerisation) due to chain scissoring, indicating the oxidation of the cellulose chains by the bleaching agent (Suess 2010; Sixta 2006; Sixta et al. 1994; Sixta and Borgards 1999). However, bleaching technologies were developed applying hydrogen peroxide, ozone, oxygen and peracetic acid in the bleaching sequence to increase efficiency. To avoid a loss in DP the removal of transition metal ions by treating the oxygen delignified pulp with chelating agents like DTPA or EDTA and washing stages is very important. Transition metal ions would otherwise rapidly decompose ozone and hydrogen peroxide to radicals (Ek et al. 2009b; Miri et al. 2015).

1.5 Hydrogen Peroxide (P) bleaching

Hydrogen peroxide (H_2O_2) is a compound with an oxygen-oxygen single bond. It is a clear liquid in its pure form and used as an oxidizer, antiseptic and bleaching agent (Hill 2001). It is

used in the bleaching of high yield mechanical pulps and is also a preferred bleaching agent in the case of chemical pulp for ECF and TCF bleaching (Jameel et al. 1996). The hydrogen peroxide (P) stage bleaching is carried out at a pH of 10.5 – 11.5 at a temperature of 70 -110°C and allows to achieve high brightness grades and brightness stability (Ek et al. 2009b; Kadla et al. 1999).

H_2O_2 can react with the hydroxyl ions (OH^-) in alkaline medium forming a perhydroxide ion (HO_2^-), the hydrogen peroxide's conjugate base is one of the reactive species in the peroxide bleaching process. HO_2^- reacts nucleophile and attacks chromophore groups within lignin (i.e. coniferaldehyde and quinoid structures) (Kadla et al. 1999). For the degradation of lignin into water soluble fragments hydroxyl radicals (OH•) and superoxide (O_2^-) are responsible. The degradation reactions of H_2O_2 into radicals is shown in Reaction 1 (Gierer, 1982 and Ek et al. 2009b). Due to the high reactivity of radicals, i.e. hydroxyl radicals, which react very unselectively and attack also carbohydrates (cellulose) the degradation of hydroxyl peroxide must happen in a controlled way to reach the optimum bleaching conditions. Metal ions of Mg, Cu or Fe accelerate the decomposition of hydroxyl peroxide as shown in Reaction 2. The degradation rate can be controlled by thorough metal ion management (use of chelating agents and acid wash) (Ek et al. 2009; Basta et al. 1991).

When bleaching chromophores with H_2O_2 the behaviour of the reaction depends in strongly on the pH of the solution. DHBQ and DHNQ forming highly resonance-stabilised anions at alkaline pH which makes them more resistant against bleaching with H_2O_2 (Zwirchmayr et al. 2017; Hosoya and Rosenau 2013).

$$H_2O_2 + HO^- \leftrightarrow H_2O + HO_2^-$$

$$H_2O_2 + HO_2^- \rightarrow HO\bullet + O_2^-\bullet + H_2O$$

$$HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$$

$$HO\bullet + HO_2^- \rightarrow O_2^-\bullet + H_2O$$

Reaction 1: Reactions of H_2O_2 and radical formation in aqueous and alkaline medium (Ek et al. 2009b).

$$H_2O_2 + Fe^{2+}\,(Mn^{2+}) \rightarrow HO\bullet + Fe^{3+}\,(Mn^{3+})$$

$$H_2O_2 + Fe^{3+}\,(Mn^{3+}) + 2HO^- \rightarrow O_2^-\bullet + Fe^{2+}\,(Mn^{2+}) + 2H_2O$$

Reaction 2: H_2O_2 reacts with metal ions and forms HO• and O_2^-• radicals (Ek et al. 2009).

1.6 Oxygen Stage (O)

The Oxygen stage (O) is used as a pre-treatment for delignification and is carried out under alkaline conditions (pH of 10-11) (Holik 2006; Ek et al. 2009b; Biermann 1996). The process was developed in the Soviet Union in the 1950s and 1960s as a method to continue the delignification in the cook before the actual bleaching stages (Ek et al. 2009b). As alkali source sodium hydroxide and oxidized white liquor are used which causes oxygen to attack also carbohydrates to a considerable extend. To avoid cellulose degradation French researchers in the 1960 found that small addition of magnesium salts (0.05-0.1% on pulp) protects the carbohydrates (Holik 2006; Ek et al. 2009b; Biermann 1996). The two main methods for the oxygen stage are medium and high consistency, while high consistency at 30% consistency and 90-110°C in is more common (Biermann 1996).

The environmental aspect when applying oxygen delignification is crucial as there is no chlorine used, the filtrates can be used in the brown stock washers or taken to the chemical recovery system for recycling. Also, corrosion caused by chloride ions can be avoided. As a result, the total effluent load of the bleaching plant can be reduced (Ek et al. 2009b; Biermann 1996). Further benefits from including an oxygen treatment into the delignification process are increased pulp strength (measured as pulp viscosity), reduced kappa number variation, reduction of the consumption of bleaching chemicals and in some cases reduced bleaching costs (Biermann 1996).

1.7 Ozone

Ozone is a highly active and allotropic form of oxygen and has been known since 1785 when Martinus Van Marum observed its formation in an electric discharge in oxygen. In 1840, Schönbein recognized ozone as a new substance. The molecule is bent and consists of three oxygen atoms. This triatomic composition (Figure 7) was shown by Jacques-Louis Soret in 1866 (Streng 1961; Ragnar 2000). At room temperature ozone is a slightly blue coloured gas with a pungent smell. For that reason its name was derived from the Greek word “ozein” which means “smell” (Streng 1961).

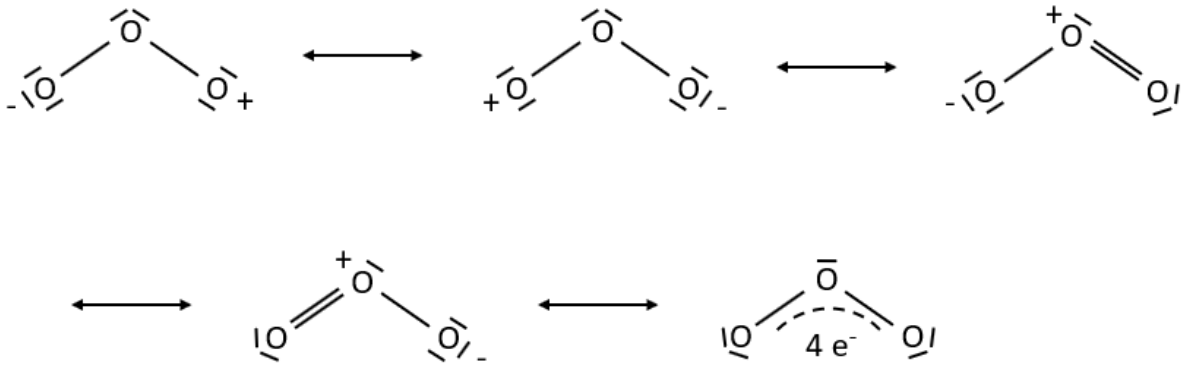

Figure 7: Mesomeric structures of ozone (Viebahn-Hänsler 2006).

The molecule is characterized by its low stability and strong oxidising power that makes it highly toxic. The stability of ozone in water is very low and is further influenced by the conditions as pH, organic matter and temperature (Von Gunten 2003). Especially at high temperatures and in alkaline medium ozone becomes more unstable and tends to decomposes quickly (Streng 1961). Depending on the conditions the half-life time of ozone ranges from seconds to hours.

Low temperatures improve the stability of ozone, at -183°C it becomes a blue liquid without noticeable decomposition. However, for industrial purposes, storing of the gas is not an option and ozone must be generated on site. For high efficiency, very dry initial gases for ozone generation must be used. Even low humidity contents can decrease the ozone generation significant. This should especially be considered if recycled oxygen gas is used (Ek et al. 2009b).

1.7.1 Ozone generation

The way ozone was discovered is the same as it is produced today by modern ozone generators - corona discharge - where an electric discharge transforms oxygen gas into ozone gas. One oxygen molecule (O_2) is cleaved into single oxygen atoms. These oxygen atoms are in an excited state and combine with other oxygen molecules (O_2) to form the ozone (O_3) molecule as shown in Reaction 3 (Sjöström 1993; Ek et al. 2009b; Viebahn-Hänsler, 2006).

Formation of ozone: $3\ O_2 + \text{power} \rightarrow 2\ O_3$

Decomposition of ozone: $2\ O_3 \rightarrow 3\ O_2$

Reaction 3: Formation of ozone according to Ek et al. (2009b).

The higher the ozone concentration (up to a maximum of 14%) of the produced gas the more power will be consumed (Ek et al. 2009b). As carrier gas oxygen or air can be used. If the latter is the case nitrogen oxides can be generated as impurities (Sjöström 1993). During the last 10 years the ozone generation technology experienced major developments making significant improvements considering the energy efficiency which resulted in cheaper ozone generation and made technical applications economical more competitive (Ek et al. 2009b).

Ozone is also generated by UV light, which happens naturally in the earth's atmosphere by solar UV radiation. The ozone layer in the atmosphere plays a significant role for the life on earth due to the absorption of harmful radiation that otherwise would strike the earth's surface (Cotton et al. 1999).

1.7.2 Ozone (Z) Bleaching

Ozone bleaching (Z-Stage) is a relative new bleaching method that makes use of the powerful oxidizing properties with an oxidation potential of 2.07 V (Volt). With the development of ozone bleaching techniques, it was first possible to achieve a TCF process of low molecular viscose and pulp (Nutt et al. 1992, Diller and Peter 1992; Sixta et al. 1994).

It is usually used as a replacement for the chlorine dioxide (Cl_2) stage which has an oxidation potential of 1.4 V (Sonnenberg 1997; Cotton et al. 1999; Ek et al. 2009b). Only a few other chemicals exceed in oxidizing power which are singlet oxygen (2.42 V), hydroxy radicals (2.86 V) and fluorine (2.87 V) (Cotton et al. 1999). Because ozone will react with most organic substances it is also widely used for the purification of drinking water (Ek et al. 2009b; Sjöström 1993). In bleaching, the brightness and stability of the final bleached pulp is particularly improved. In addition, the removal of wood extractives decreases odour in the pulp (Ek et al. 2009b). On the other hand, also cellulose can be attacked and degraded by cleavage of the glyosidic bond causing loss in DP and in viscosity (Katai and Schuerch 1966; Ek et al. 2009b; Sixta 2006). The reduction of viscosity can be a major drawback in the production of high viscosity pulp with high strength qualities (Claus 2007).

Introduction

Most commonly, ozone reacts as an electrophile at sites with high electron density like aromatic rings and carbon double bonds. At sites with low electron density, like C-H bonds, reactions run slower (Sonnenberg 1997). In some reactions ozone is also considered to behave like a nucleophile. The behaviour depends on conditions such as solvent, pH and the presence of either electron donating or withdrawing groups (Hoigné and Bader 1983; Bablon et al. 1991; Sjöström 1993). Under acetic conditions as applied in pulp bleaching, ozone reacts as electrophile (Sjöström 1993).

When ozone reacts with organic substrates it cleaves olefinic and activated aromatic bounds to give aldehydes, ketones and acids (Ragnar 2000; Criegee 1975; Epstein 2010; Hendrickx and Vinckier 2003; Sjöström1993; Reitberger et al. 1999; Bernatek and Frengen 1961). The reaction is called ozonolysis, where cyclic intermediates also known as ozonides are formed according to the Criegee-mechanism (Kuczkowski 1992; Criegee 1975; Bernatek and Straumsgsård 1959).

Nevertheless, model experiments confirmed that a reaction between ozone and aromatic rings - as they are present in lignin - can lead to both, the formation of radicals and to ionic species resulting in the formation of carboxylic acids (Ek et al. 2009b). Further, radicals can form during ozone reactions but also directly from ozone when it is decomposed (Sonnenberg 1997; Staehlin and Hoigne 1982; Ek, et al. 2009b; Musl 2017).

Radical formation depends strongly on the stability of ozone which is influenced by alkalinity and temperature. Depending on the conditions the half-life time of ozone ranges from seconds to hours. Consequently, the pH is of high importance in ozone bleaching, as hydroxyl ions (OH^-) initiate the decomposition of ozone to form •OH radicals as the major secondary oxidant. Additionally, superoxide radicals ($O_2^{\bullet -}$) can be formed which will accompany the bleaching process. Radicals react non-selective with any lignin and carbohydrate present which results in a loss of DP, lower viscosity and an overall weaker pulp. Therefore, pulp bleaching with ozone is generally performed at a low pH (2-3) (Chirat and Lachenal 1997; Gierer 1997; Reitberger et al., 1999; Von Gunten 2003; Musl 2017; Ek et al. 2009b).

Further radical formation is initiated by the presence of transitional metal ions like cobalt, iron, chrome and copper (Reitberger et al. 1999; Sonnenberg 1997; Sixta 2006). To reduce this effect chelating agents like ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) and 2-hydroxyethyl ethylenediamine tetraacetic acid (HEDTA) should be applied before bleaching to remove said transition metals at a pH of 5-6. For further elimination of transition metals acidic pre-washing (A Stage) of the pulp with sulfuric acid can be applied which causes the metals to turn into hydrated salts. Compared to H_2O_2 bleaching the influence

of metal ions is believed to be lower due to the short bleaching time (seconds to minutes) of the Z-Stage (Suess 2010; Ek et al. 2009b).

Nevertheless, even if precautions were taken it has been shown that a certain formation of •OH and O_2•$^-$ radicals will occur since the presence of O_2 will start a chain reaction that degrade O_3 into H_2O_2, •O_2^- and •OH radicals (Figure 8) (Sjöström 1993; Reitberger et al. 1999).

For pulp bleaching this means an inevitable oxidation of cellulose (Ek et al. 2009b). The Decomposition reactions of ozone is shown in Reaction 4.

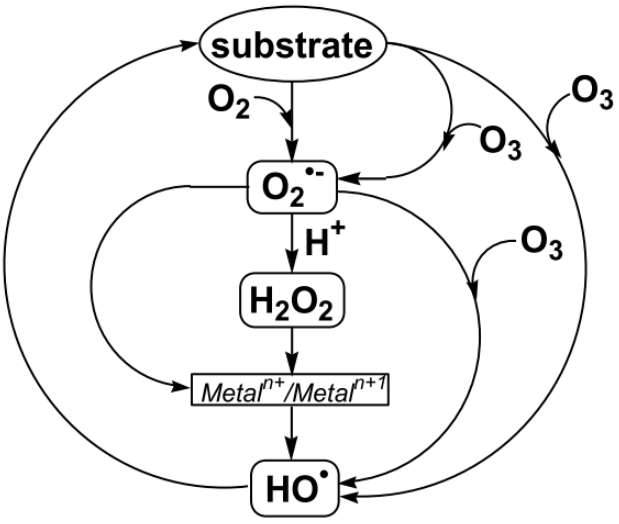

Figure 8: Chain reaction according to Reitberger et al. (1999) of ozone decomposition during the reaction with the substrate and O_2.

The Z stage is usually carried out at 30-60°C. At these temperatures ozone is less likely to decompose spontaneously (Ek et al. 2009b).

$$O_3 + HO^- \rightarrow O_2\bullet^- + HO_2\bullet$$
$$O_2\bullet^- + O_3 \rightarrow O_3\bullet^- + O_2$$
$$O_3\bullet^- + H^+ \rightarrow HO\bullet + O_2$$

$$2O_3 + H_2O \rightarrow HO_2^\bullet + 2O_2 + HO^\bullet$$

Reaction 4: Decomposition reaction of ozone in aqueous medium into hydroxyl and super oxide radicals according to Ek et al. (2009b).

The solubility of ozone in water is very low (494 mg/l at 0°C), in addition ozone tends to decompose quickly in the presence of water (Hollemann et al.1985). This makes the industrial application of ozone difficult to run effectively because the gas needs to be introduced to an adequate amount and in a consistent manner. Today, as described by Claus (2007), high or medium consistency mixers are used by pulp mills during ozone bleaching to enable the O_3 molecule to diffuse faster through the thin immobile hydrate film on the fibre, resulting in a quick reaction due to a short diffusion path. A steady reaction is achieved by well fluffed pulp from a refiner (Lindholm 1991; Sixta et al. 1991; Oltmann et al. 1992; Kappel et al. 1993). The amount applied can be relatively low. Depending on the type of pulp 6-7% ozone concentration for high consistency and 12-14% for medium consistency is sufficient (Ek et al. 2009b). The risk of DP loss increases with time, increasing amount of O_3 used and with decreasing content of rest lignin (Hruschka 1986; Patt et al 1991; Soteland 1978).

1.7.3 Criegee Mechanism

Ozonolysis according to Criegee is a three-step mechanism in which ozone reacts with olefins. The first step consists of the attack of the C double bond moiety by a 1,3-dipolar cycloaddition and followed by the formation of a 1,2,3-trioxolane, also called primary ozonide (Figure 9 top row). The primary ozonide is unstable and decomposes exothermically into a carbonyl compound (depending on the nature of the alkene either an aldehyde or ketone) and a highly reactive carbonyl-O-oxide – the Criegee intermediate with zwitterionic and biradical properties (Figure 9 middle row). In the last step (Figure 9 bottom row) the carbonyl-O-oxide and carbonyl compound react with each other to form 1,2,4-trioxolane the secondary ozonide (Criegee 1975; Kuczkowski 1992; Epstein 2010).

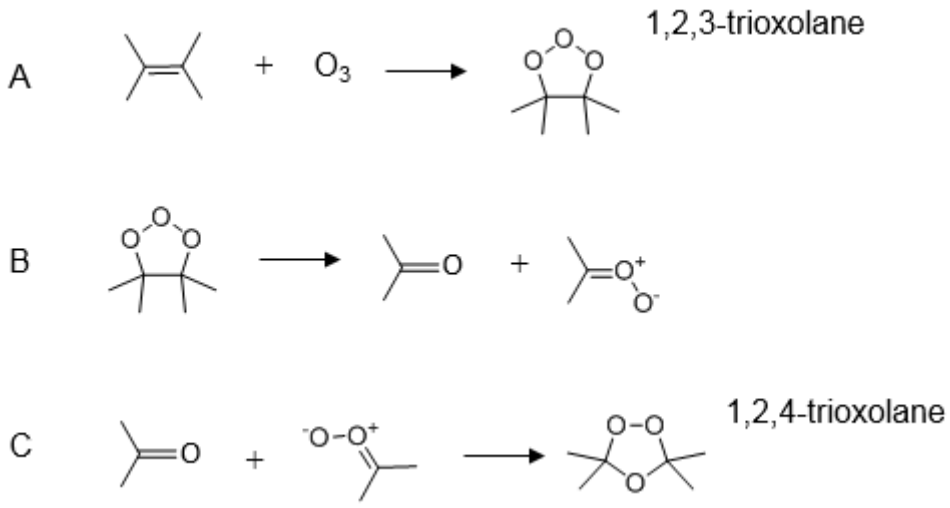

Figure 9: Three steps of the ozonolysis according to Criegee: A: formation of a primary ozonide (1,2,3-trioxolane); B: Decomposition into carbonyl compound and carbonyl oxide; C: Addition of the carbonyl oxide to the carbonyl compound to form the secondary ozonide (1,2,4-trioxolane) (Criegee 1975).

If the reaction takes place in aqueous medium, the secondary ozonide hydrolyses to form two carbonyl fragments and hydrogen peroxide. Alternatively, it can decompose into carboxylic acid and carbonyl compound (Sonnenberg 1997; Becker et al. 1999; March 1992; Vollhardt and Shore 2000). A full reaction of ozone with an alkene in aqueous medium is shown in Figure 10.

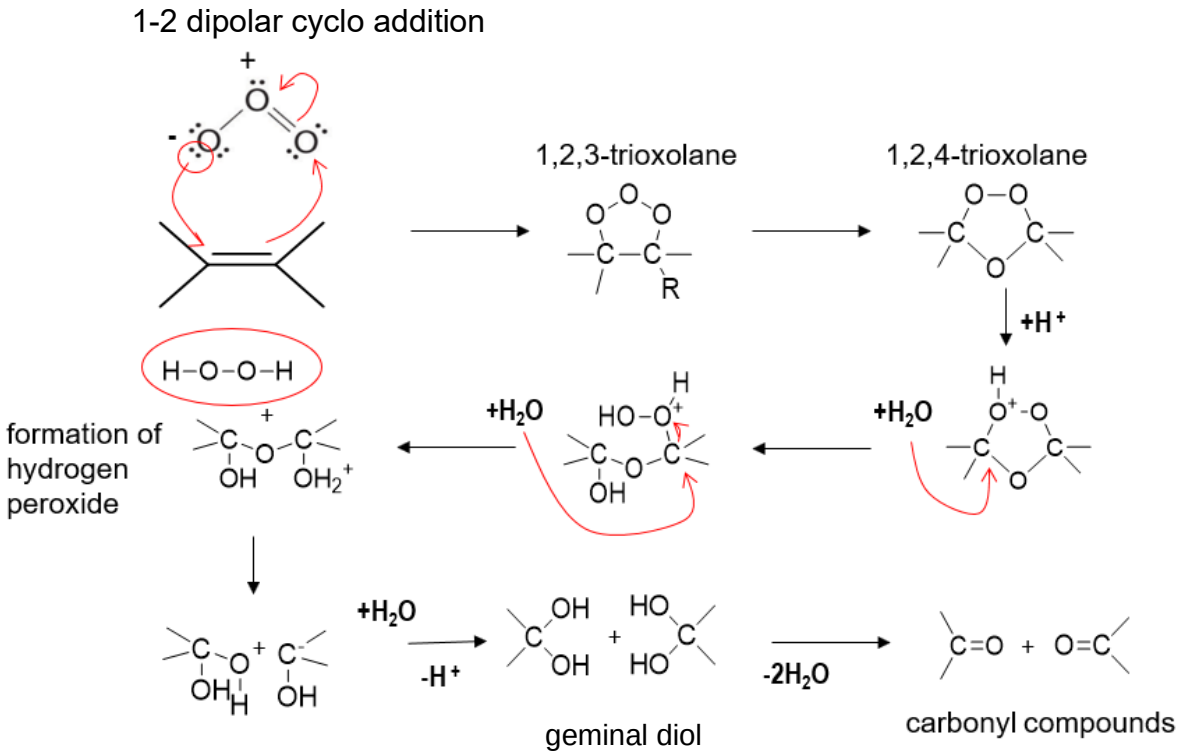

Figure 10: Ozonolysis of alkenes followed acid hydrolysis reduction reduction (Becker et al. 1999; March 1992; Vollhardt and Shore 2000; Sonnenberg 1997).

2 Material and Methods

General Experimental Methods. Commercial chemicals were of the highest grade available and were used without further purification. Reagent-grade solvents were used for all extractions and workup procedures. Distilled water was used for all aqueous solutions. GC-MS analysis was performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C triple axis mass selective detector (MSD; Agilent Technologies, Santa Clara, CA, USA). A DB5-MS column (30 × 0.25 mm i.d. × 0.25 µm film thickness; J&W Scientific, Folsom, CA, USA) was used. For NMR analysis, a Bruker Avance II 400 instrument (^{1}H resonance at 400.13 MHz, ^{13}C resonance at 100.61 MHz) with a 5 mm broadband probe head (BBFO) equipped with z-gradient with standard Bruker pulse programs was used. Data were collected with 32k data points and apodized with a Gaussian window function (GB = 0.3) prior to Fourier transformation. A 2.5 s acquisition time and a 1 s relaxation delay were used. Bruker TopSpin 3.5 was used for the acquisition and processing of the NMR data. For UV/Vis spectroscopy a LAMBDA 45 by PerkinElmer was used. For the measurement quartz glass cuvette were used. The speed of scanning was 480nm per minute in the range of 200 to 700 nm.

2.1 Materials

2,5-dihydroxy-1,4-benzoquinone (DHBQ, **1**), 5,8-dihydroxy-1,4-naphthoquinone (DHNQ, **5**), 2,5-dihydroxyacetophenone (2,5-HAP, **4**), 2,6-dihydroxyacetophenone (2,6-HAP, **9**), tetrahydroxy-1,4-benzoquinone (THBQ, **10**) and 2-hydroxy-1,4-naphthoquinone (2-OH-NQ, **8**) were commercially available and used as received.

2.2 Methods

2.3 Sample Preparation

The chromophores **1**, **4**, **5**, **9**, **8** and **10** were used in dissolved in organic solvents or water for ozone bleaching experiments. Details on solvent composition and concentrations can be found in Table 4,Table 5 and Table 6.

2.3.1 Chromophores dissolved in organic solution:

The pure chromophores were weighed (up to 600mg) and put in an Erlenmeyer flask (500 ml). Then 300 ml of organic solvent were added. If necessary, the solution was put into an ultrasonic bath for further dissolution of the chromophores for 10-15 minutes. To prevent overheating of the solution the ultrasonic bath was cooled using ice.

2.3.2 Chromophores dissolved in aqueous solution:

To improve chromophore solubility in water, a slurry of the chromophore (up to 200 mg) in methanol, acetonitrile, or acetone was prepared in an Erlenmeyer flask (500 ml). Then water (pH 2, H_2SO_4) was added. Full solubility in a volume of 300 ml could not always be achieved. To compensate this effect more organic solvent was added. In the most extreme case of DHNQ up to 50% of the solution consisted of organic solvent. In addition to bleaching experiments at pH 2, one experiment (bleaching of DHBQ) was carried out at pH 12 in aqueous NaOH.

2.3.3 Chromophores dissolved in aqueous solution with various salts:

Solutions with various salts as additives were produced as described above. Sodium sulfate (Na_2SO_4), potassium sulfate (K_2SO_4), magnesium sulfate ($MgSO_4$) or calcium chloride ($CaCl_2$) were added to the water (pH 2). The salt concentrations were 4.5 mM/l. DHBQ was bleached with all salts separately while DHNQ, THBQ, 2,5-HAP, 2,6-HAP and 2-OH-NQ were only bleached with Na_2SO_4 and $CaCl_2$ separately.

2.4 Bleaching Procedure

For the generation of the bleaching gas (O_3 with O_2 as carrier gas) the Anseros Ozone Generator COM-AD-02 was used. This generator has an ozone capacity of 1-10 g/h and a concentration capacity of 0.1-190 g O_3/m^3.

Before starting the bleaching experiment, the generator had a warmup time of one hour to achieve a constant ozone stream. After the warmup time the solutions with the dissolved chromophores were transferred into a sealable 500ml glass reactor (Schott). A schematic display of the reactor setup can be seen in Figure 11. A Teflon tube that carried the ozone gas was connected from the generator to the reactor. The gas stream was directly injected into the solution by a glass frit. Another two Teflon tubes were attached to the reactor, one acting as a gas outlet, the other one was used for sampling during the reaction. Further, a magnetic stirring bar was used for during the whole reaction.

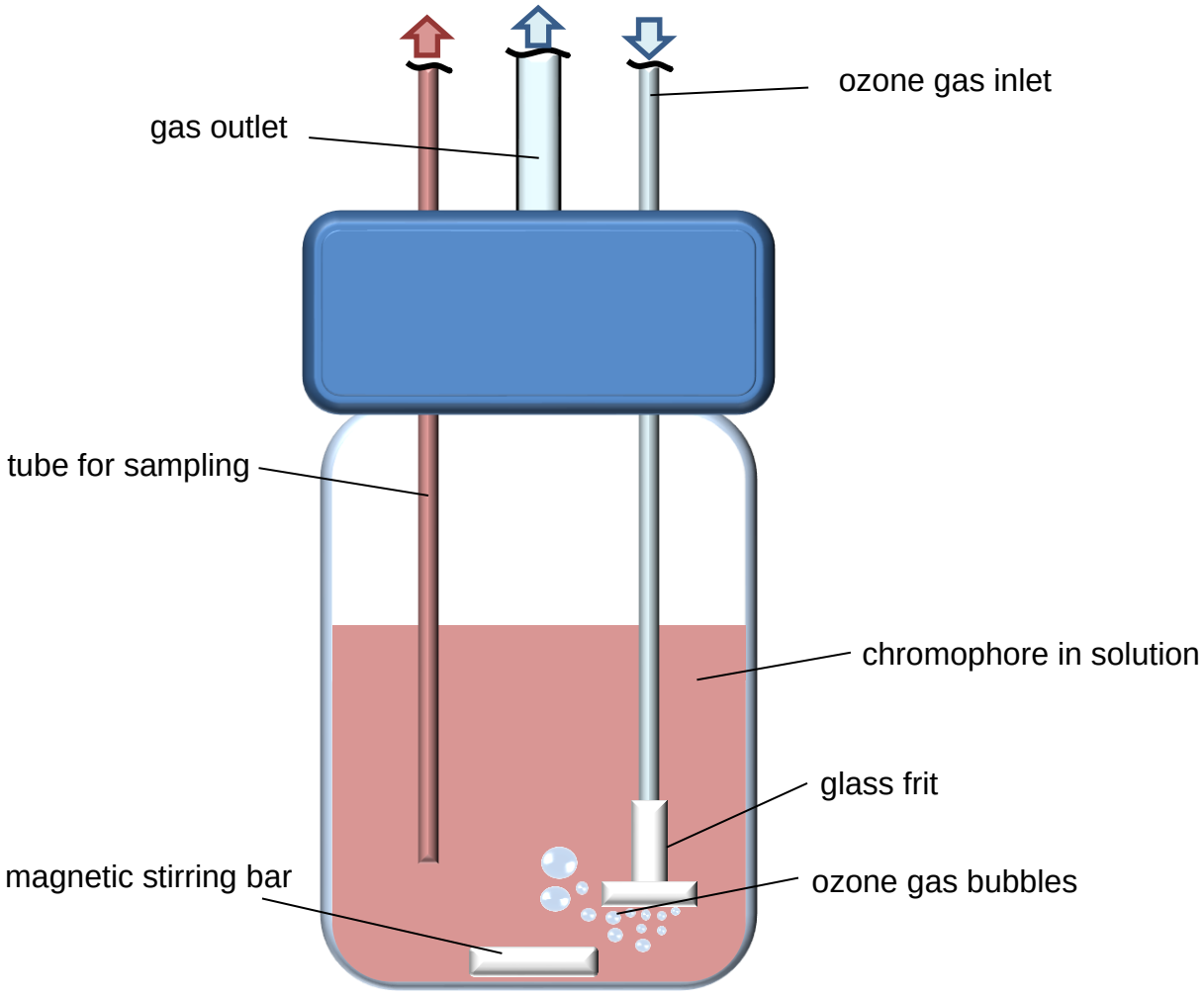

Figure 11: Setup of the reactor for the bleaching of the chromophores.

Experiments at different generator settings (generator level and gas flow), temperature, pH and with different solvents and additives (salts) were carried out. For bleaching an ozone concentration of 0.021 g O_3/l was used except in the first six experiments Z1 - Z6. This ozone concentration was achieved with a gas flow of 50 l/h and a generator level of 50% with the used ozone generator which led to an output of 1.05 g O_3/h. The amount of ozone which was produced at the selected generator adjustments was determined by iodometric titration and verified by the generator's datasheet.

Ozone reactions were carried at out room temperature, two reactions with 2-OH-NQ (Z2) and DHBQ (Z3) were carried out at 10°C.

In all experiments, ozone was bubbled through the solution until it was decolourized.

After bleaching of the chromophores in organic solvent the residual solutions were evaporated. Chromophores in aqueous solution at pH 2 were neutralized after the bleaching process. The aqueous solutions were evaporated and additionally the remaining decomposition products were dried by lyophilisation.

The dry residues of the bleached substances were further analysed via NMR and GC-MS.

2.5 Sampling

For sampling for UV/Vis spectroscopy, a syringe was attached to the sampling tube. The first (unbleached) sample was taken before starting the bleaching process. After that, every 1 or 2 minutes during the experiment samples with a volume of 4-6 ml were taken from the ongoing reaction. The samples were transferred into air tight test tubes and analysed by UV/Vis spectroscopy. If not subjected to UV/Vis spectroscopy right after bleaching, samples were stored in a freezer at -80°C.

2.6 GC-MS analysis of degradation products

The degradation products formed during the ozone treatment were derivatised by oximation and silylation (Liftinger et al. 2015). For this derivatization, between 8 and 10 mg of dry samples were put into 1.5 ml GC vials. Then 200 µl pyridine (containing 40 mg ethoxyamine HCL/ml pyridine, and 1 mg methyl-α-D-galactopyranoside/ml pyridine) was added. All suctions were mixed well and the vials put into an oven at 70°C for 1 hour. After letting the solution cool down another 200 µl pyridine (containing 1.5 mg 4-Dimethylaminopyridine/ml pyridine) and 200 µl

N,O-bis(trimethylsilyl)trifluoroacetamide (containing 10% trimethylchlorosilane) were added to each vial. All solutions were mixed well, closed tightly and the vials were put into an oven at 70°C for 2 hours. When the solutions were cooled to r.t., they were diluted with 600 µl ethyl acetate and mixed. If some undissolved residue was still present in the sample, the supernatant was put into a new vial and the precipitate discarded (Liftinger et al. 2015).

2.7 NMR

For NMR spectroscopy, the residual bleached solutions were evaporated and dried by lyophilisation. The NMR spectra were recorded in MeOD, D_2O, or $CDCl_3$ as solvents. The ^{1}H and ^{13}C chemical shifts are given in ppm, coupling constants in Hz. Peaks were assigned by means of ^{1}H. ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC) if possible. The multiplicity of the signals was abbreviated as the following: singlet (s), doublet (d), quartet (q).

2.7.1 NMR Codes for the relevant carboxylic acids

Acetic acid: ^{1}H NMR (MeOD): δ [ppm] 1.90 (s, 3H, CH_3), ^{13}C NMR (MeOD): 23.9 (CH_3), 178.1 (CO)

Ethylen glycol: ^{1}H NMR (MeOD): δ [ppm] 3.60 (s, 2H, CH_2), ^{13}C NMR (MeOD): 63.8 (CH_2)

Formic acid: ^{1}H NMR (MeOD): δ [ppm] 8.55 (s, 1H, CH), ^{13}C NMR (MeOD): 170.2 (CO)

Glycolic acid: ^{1}H NMR (MeOD): δ [ppm] 4.08 (s, 2H, CH_2), ^{13}C NMR (MeOD): 60.5 (CH_2), 176 (CO)

Lactic acid: ^{1}H NMR (MeOD): δ [ppm] 1.31 (d, 3H, *J*=6,85 Hz, CH_3), 4.01 (q, 1H, *J*=6,85 Hz, CH), ^{13}C NMR (MeOD): 21.5 (CH_3), 69.3 (CH), 182.2 (CO)

Maleic acid: ^{1}H NMR (MeOD): δ [ppm] 6.24 (s, 1H, CH), ^{13}C NMR (MeOD): 136.3 (CH), 166.5 (CO)

Malonic acid: ^{1}H NMR (MeOD): δ [ppm] 3.34 (s, 2H, CH_2), ^{13}C NMR (MeOD): 49.1 (CH_2), 179.9 (CO)

Tartronic acid: ^{1}H NMR (MeOD): δ [ppm] 4.68 (s, 1H, CH), ^{13}C NMR (MeOD): 72.3 (CH), 170.5 (CO)

2, 3-Oxiranedicarboxylic acid: ^{1}H NMR (MeOD): δ [ppm] 3.76 (s, 1H, CH), ^{13}C NMR (MeOD): 52.3 (CH), 165.9 (CO)

2.8 UV/Vis Spectroscopy

The samples obtained during the bleaching experiments were used for UV/Vis kinetic analysis. In the case of Z12 (bleaching of DHNQ) samples were diluted with 4ml acetone due to their intense Vis absorption. In Table 3 all samples taken from the bleaching experiments and analysed by UV/Vis spectrometer are listed.

Table 3: Overview of UV/Vis measurements carried out.

Label	Substance	Solvent	Number of samples taken during bleaching
Z4	DHBQ	Dichloromethane	7
Z5	DHBQ	Dichloromethane	5
Z6	DHBQ	Acetone	7
Z12	DHNQ	Acetone	10
Z13	2,6-HAP	Dichloromethane	10
Z14	2OHNQ	Dichloromethane	6
Z15	2,6-HAP	Dichloromethane	7
Z16	2,5-HAP	Aceton	6
Z17	2,5-HAP	Dichloromethane	5
Z18	DHBQ	Water/Acetone, pH2	4
Z19	2OHNQ	Water/Acetone, pH2	4
Z20	2,6-HAP	Water/Acetone, pH2	8
Z21	2,5-HAP	Water/Acetone, pH2	7
Z22	DHNQ	Water/Acetone, pH2	9
Z23	DHBQ	Water/Methanol, pH2	5
Z24	DHBQ, MgSO4	Water/Methanol, pH2	4

Z25	DHBQ, $CaCl_2$	Water/Methanol, pH2	4
Z26	DHBQ, NaSO4	Water/Methanol, pH2	4
Z27	DHBQ, $K2SO_4$	Water/Methanol, pH2	4
Z36	THBQ, $NaSO_4$	Water/Methanol, pH2	5
Z37	2OHNQ, $NaSO_4$	Water/Methanol, pH2	5
Z38	DHNQ, $NaSO_4$	Water/Methanol, pH2	8
Z39	2,6-HAP, $NaSO_4$	Water/Methanol, pH2	7
Z40	2,5-HAP, $NaSO_4$	Water/Methanol, pH2	8
Z41	2,6-HAP, $CaCl_2$	Water/Methanol, pH2	10
Z42	2,5-HAP, $CaCl_2$	Water/Methanol, pH2	8
Z43	THBQ, $CaCl_2$	Water/Methanol, pH2	5
Z44	DHNQ, $CaCl_2$	Water/Methanol, pH2	10
Z45	2OHNQ, $CaCl_2$	Water/Methanol, pH2	6
Z46	2,6-HAP	Water/Methanol, pH2	9

Z47	2,5-HAP,	Water/Methanol, pH2	7
Z48	2OHNQ	Water/Methanol, pH2	9
Z49	DHNQ	Water/Methanol, pH2	10
Z50	THBQ	Water/Methanol, pH2	5
Z51	DHBQ	Water/Methanol, pH12	/

2.9 Composition of the Solutions

The experiments are labelled chronology beginning with the first bleaching experiment “Z1”. The compositions of the solutions are presented in: Table 4 showing solutions in organic solvents, Table 5 showing aqueous solutions, and Table 6 showing solutions with salt additives.

Table 4: Composition of solutions in organic solvents. The concentration c is given in mM/l, the volume of the solvent in ml, the time of bleaching in seconds.

Label	**Sub-stance**	**c [mM/l]**	**Solvent**	**Solvent [ml]**	**Bleaching time [s]**
Z1	2-OH-NQ	4.33	DCM	300	240
Z2	2-OH-NQ	4.33	DCM	300	120
Z3	DHBQ	1.61	DCM	300	240
Z4	DHBQ	1.61	DCM	300	240
Z5	DHBQ	1.61	DCM	300	240
Z6	DHBQ	6.60	Acetone	300	480
Z7	DHBQ	6.41	Acetone	300	300
Z8	DHBQ	6.41	Acetone	300	300
Z9	DHBQ	6.41	Acetone	300	360

Z10F	2,5-HAP	6.57	DCM	300	900
Z11	2,6-HAP	57.97	DCM	300	/
Z12	DHNQ	2.09	Acetone	300	1200
Z13	2,6-HAP	6.66	DCM	300	540
Z14	2-OH-NQ	5.07	DCM	300	300
Z15	2,6-HAP	3.31	DCM	300	360
Z16	2,5-HAP	3.31	DCM	300	780
Z17	2,5-HAP	6.57	DCM	200	480

Table 5: Compositions of aqueous solution. The concentration c is given in mM/l, the volume of the solvents in ml, the time of bleaching in seconds.

Label	**Sub-stance**	**c [mM/l]**	**Solvent 1**	**Solvent 1 [ml]**	**Solvent 2**	**Solvent 2 [ml]**	**Bleaching time [s]**
Z18	DHBQ	3.73	Water pH 2	200	Acetone	150	480
Z19	2-OH-NQ	3.54	Water pH 2	150	Acetone	150	180
Z20	2,6-HAP	3.92	Water pH 2	150	Acetone	150	360
Z21	2,5-HAP	4.10	Water pH 2	200	Acetone	100	360
Z22	DHNQ	0.91	Water pH 2	200	Acetone	100	900
Z23	DHBQ	4.38	Water pH 2	290	Metha-nol	10	480
Z30	DHBQ	11.35	Water pH 2	300	Metha-nol	100	/

Z31	2,5-HAP	12.17	Water pH 2	250		Metha-nol	80	/
Z32	2,6-HAP	9.96	Water pH 2	300		Metha-nol	100	/
Z33	2-OH-NQ	9.19	Water pH 2	250		Metha-nol	130	/
Z35	DHNQ	2.27	Water pH 2	250		Acetoni-trile	100	/
Z46	2,6-HAP	4.05	Water pH 2	250		Metha-nol	50	480
Z47	2,5-HAP	3.47	Water pH 2	300		Metha-nol	50	300
Z48	2-OH-NQ	3.30	Water pH 2	300		Metha-nol	50	600
Z49	DHNQ	0.58	Water pH 2	290		Acetoni-trile	180	780
Z50	THBQ	3.52	Water pH 2	250		Metha-nol	55	240
Z51	DHBQ	4.40	Water pH 12	300	/		/	540

Table 6: Compositions of aqueous solution with salts as additive. The concentration c is given in mM/l, the volume of the solvents in ml, the time of bleaching in seconds.

La-bel	**Sub-stance**	**c [mM/l]**	**Salt**	**c Salt [mM/l]**	**Sol-vent 1**	**Sol-vent 1 [ml]**	**Solvent 2**	**Sol-vent 2 [ml]**	**Bleach-ing time [s]**
Z24	DHBQ	4.38	$MgSO_4$	4.5	Water pH 2	290	Metha-nol	10	240
Z25	DHBQ	4.38	$CaCl_2$	4.5	Water pH 2	290	Metha-nol	10	270
Z26	DHBQ	4.38	$NaSO_4$	4.5	Water pH 2	290	Metha-nol	10	240
Z27	DHBQ	4.38	K_2SO_4	4.5	Water pH 2	290	Metha-nol	10	300
Z36	THBQ	3.52	$NaSO_4$	4.5	Water pH 2	250	Metha-nol	55	180
Z37	2-OH-NQ	3.85	$NaSO_4$	4.5	Water pH 2	250	Metha-nol	50	300
Z38	DHNQ	0.91	$NaSO_4$	4.5	Water pH 2	250	Metha-nol	50	600
Z39	2,6-HAP	3.47	$NaSO_4$	4.5	Water pH 2	300	Metha-nol	50	360
Z40	2,5-HAP	3.46	$NaSO_4$	4.5	Water pH 2	300	Metha-nol	50	540
Z41	2,6-HAP	3.47	$CaCl_2$	4.5	Water pH 2	300	Metha-nol	50	540
Z42	2,5-HAP	3.07	$CaCl_2$	4.5	Water pH 2	300	Metha-nol	50	480
Z43	THBQ	3.07	$CaCl_2$	4.5	Water pH 2	300	Metha-nol	50	240

Z44	DHNQ	0.59	$CaCl_2$	4.5	Water pH 2	290	Acetoni-trile	170	780
Z45	2-OH-NQ	3.85	$CaCl_2$	4.5	Water pH 2	250	Metha-nol	50	360

3 Results and Discussion

3.1 Workflow

Since several steps were carried out before and after the actual bleaching experiments a workflow of the main steps was created (Figure 12), it should help to comprehend the course of the work.

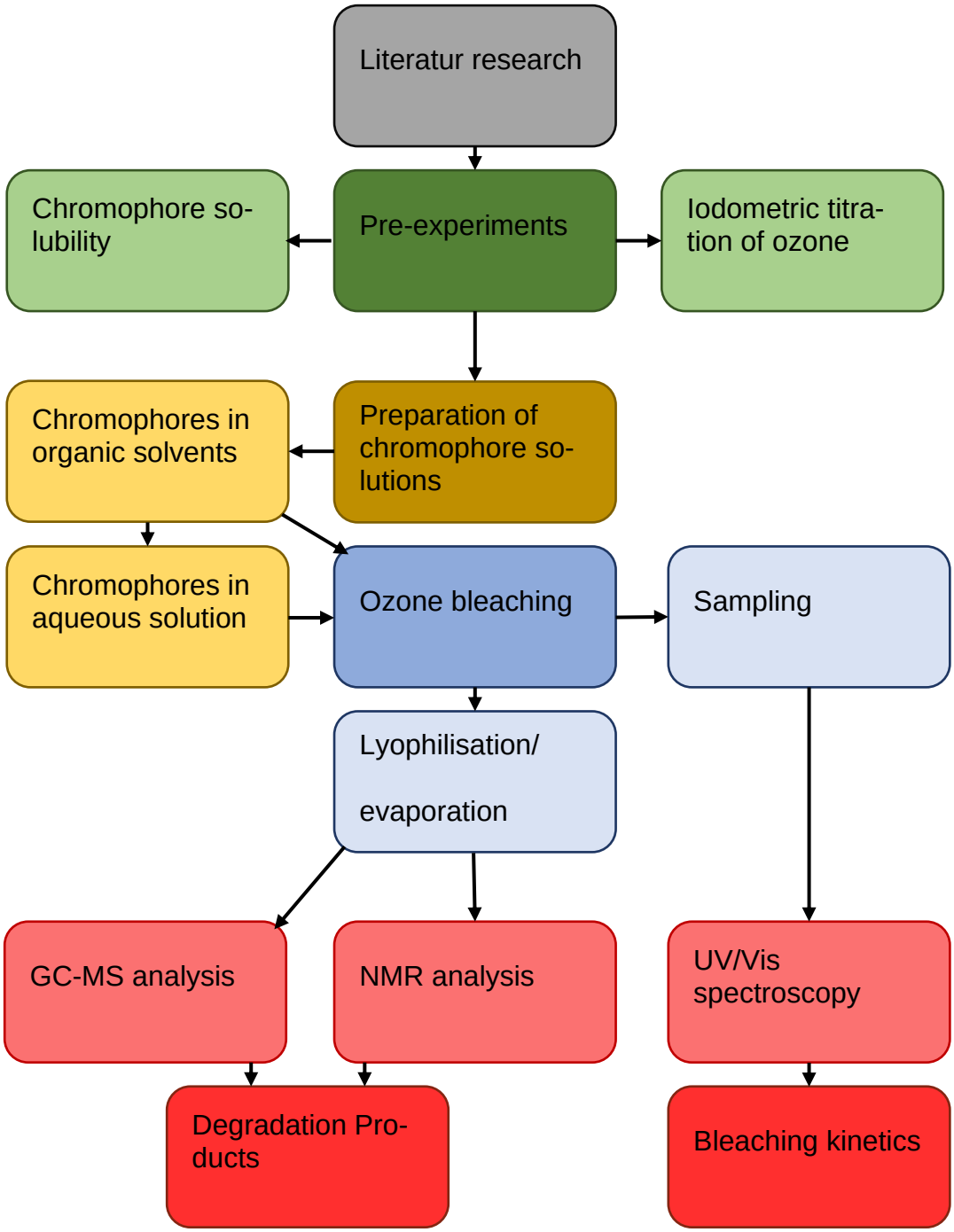

Figure 12: Overview of the project's workflow.

3.2 Bleaching of Key Chromophores with ozone

Chromophores solutions between 50 and 600 mg/ml (see Table 4, Table 5 and Table 6) were prepared and subjected to ozone treatment, with an ozone concentration of 0.021 gO_3/l. This concentration was chosen because it resulted in a bleaching reaction that lasted for about 6-15 minutes, depending on the chromophore treated. This bleaching time allowed to take samples for the UV/Vis analysis. The reaction speed varied for the different chromophores, so the target of 6 samples per bleaching reaction could not always be achieved.

To get a general idea of the reactivity of ozone, the chromophores were first dissolved in organic solvents (dichloromethane (DCM) and acetone) and bleached. After these preliminary experiments, aqueous solutions of chromophores at pH 2 were used. This pH value was chosen because acidic pH values lower decomposition of ozone into hydroxyl radicals (•OH) that can cause damages in the polysaccharide backbone. Consequently, industrial bleaching with ozone is also carried out at a pH of 2-3 (Ek et al. 2009b; Hruschka 1986; Patt et al. 1991). One sample (DHBQ) was bleached at pH 12 to determine the influence of the pH on the reaction mechanism and degradation products. At alkaline pH, the concentration of •OH is higher due to the decomposition of ozone, and the radicals' reactivity is fundamentally different than ozone's. (Musl 2017; Wang et al. 2004; Bablon et al. 1991; Horváth et al. 1985). In all cases, the bleaching was carried out until a complete decolouration was observed.

In the bleaching of DHNQ, an initial shift of colour from dark red to yellow was observed before the solution ultimately turned colourless. This effect indicates the formation of coloured (quinone) intermediates during the ozone treatment. The colour change of DHNQ in organic solution was more intense which resulted in a peak change from 515 nm to 400 nm in the UV/Vis measurement. This can be attributed to increased stability of the quinoid intermediates formed in organic solvents.

During the bleaching of 2,6-HAP a strong increase of colour from a light yellow to dark yellow could be observed. Similarly, to DHNQ, coloured intermediates were formed. Remarkably, the formation of coloured intermediates was not observed in 2,5-HAP, a constitutional isomer of 2,6-HAP. Instead 2,5-HAP, DHBQ and 2-OH-NQ resulted in a neat bleaching reaction with straight decolouration of the initially yellow solution.

After the bleaching, the solution was neutralized using NaOH. When neutralizing the bleached and colourless chromophore solutions of DHNQ and 2-OH-NQ they darkened into yellow. Colour change of chromophores depending on the pH value are already described by Krainz

(2009) were a significant difference in absorbance and wavelength in the visible spectrum between acidic and alkaline conditions was observed. The colour change in bleached solutions during neutralization indicates that chromophoric structures were still present after the bleaching procedure, even though the solution at pH 2 appeared to be colourless after the ozone treatment. Small amounts of undissolved chromophore, dissolving with increasing pH, can be another reason for the darkening of the solution, so this observation does not necessarily indicate an incomplete bleaching. Indeed, the NMR spectrum (Figure 13) of bleached 2-OH-NQ, shows peaks at 7.57 ppm, representing the starting material 2-OH-NQ.

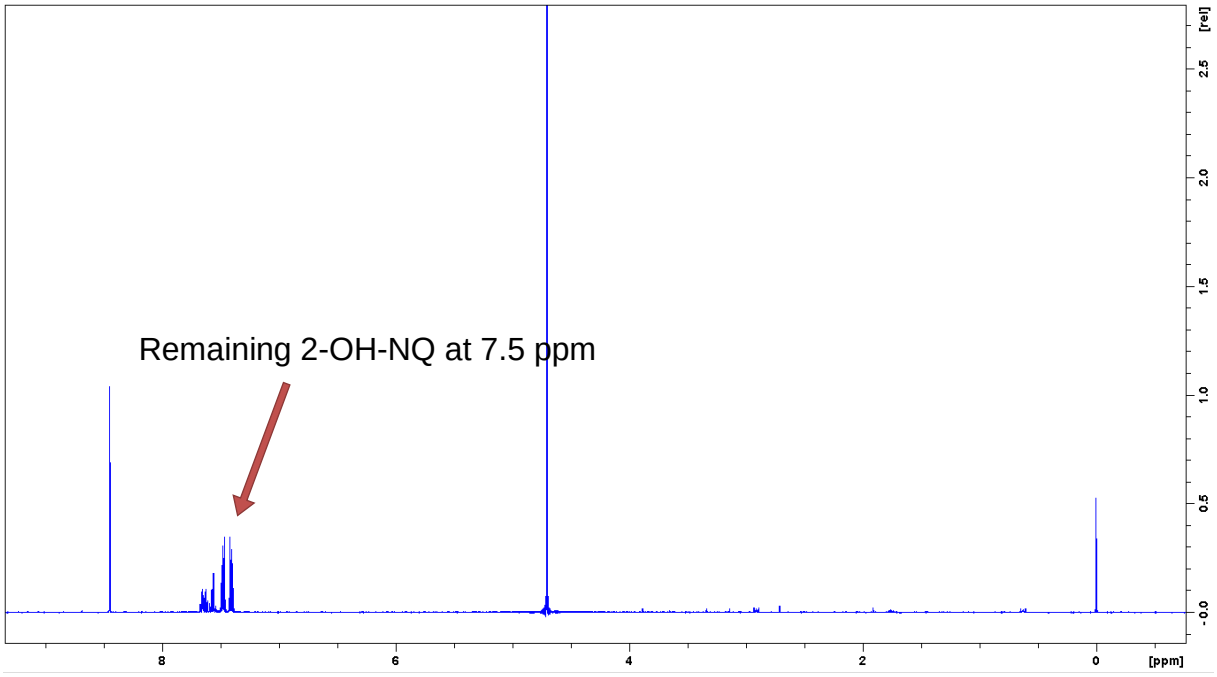

Figure 13: NMR Spectrum of bleached 2-OH-NQ (Z48) in aqueous solution with remaining 2-OH-NQ at 7.57 ppm.

3.3 Bleaching kinetics chromophores in aqueous solution

The UV/Vis experiments were performed to analyse the kinetics of the key chromophores when bleached with ozone. Additionally, experiments with different salts as additive were carried out to asses if salts influence the bleaching process in any way. Previous studies revealed that degradation of DHBQ (**1**) is influenced by salts during hydrogen peroxide bleaching (Hosoya et al. 2015). To assess differences in the bleaching behaviour samples were taken during the bleaching process and analysed by a UV/Vis spectrometer. Conclusions about the chromophores specific bleaching kinetics can be drawn from the kinet-

ics obtained. Generally, the visible light spectrum, 400-700 nm was analysed, as the degradation products – containing C=O bonds – would contribute to the solutions UV absorption. In some spectra no peaks are showing up in the range of 400-700 nm. The reason for this is believed to be the intense signals in the UV range caused by high amount of aromatic compounds in the sample (Musl 2017). This effect was especially strong the case for 2,6-HAP as seen in Figure 14. In these cases, the wavelength of 400 nm was chosen as a reference point. It lies still in the Vis range of the spectrum and coincides with the yellow color of the chromophore solutions.

3.3.1 UV/Vis spectroscopy of 2,6-HAP and 2,5-HAP (aqueous)

2,6-HAP has a light-yellow colour in aqueous solution at pH 2 and in organic solvent. The UV/Vis spectrum (Figure 14) of the chromophore shows no peak in the visible range. For kinetic evaluation (Figure 15) the highest absorption at the end of the visible range (400 nm) was chosen.

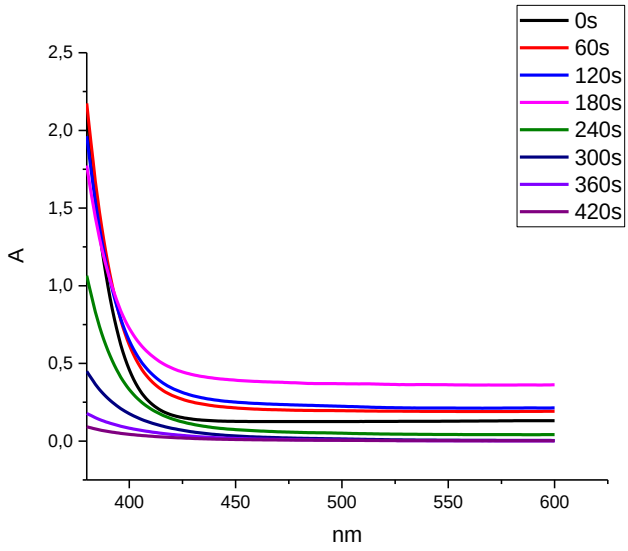

Figure 14: UV/Vis spectrum of Z20, 2,6-HAP in aqueous solution (pH 2).

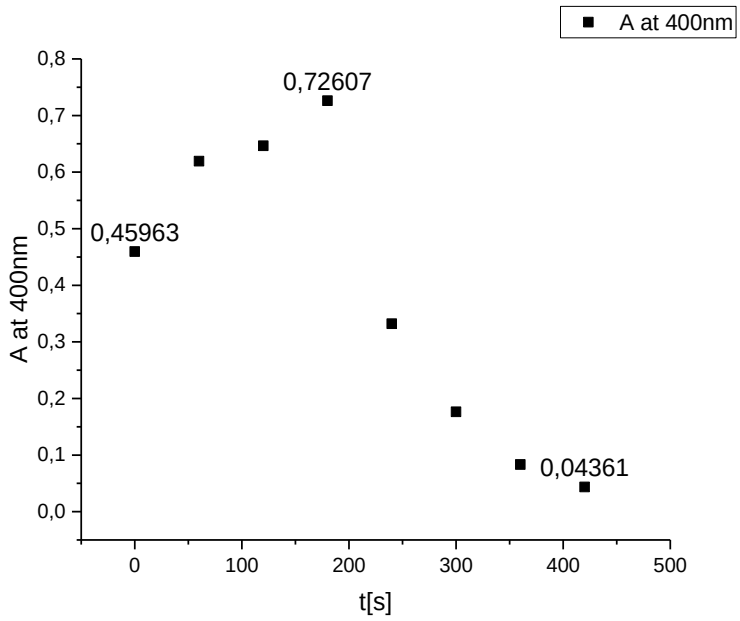

Figure 15: Absorption versus time at A=400nm of Z20, 2,6-HAP in aqueous solution (pH 2).

The first sample of starts at 0.46 A (400 nm). The rise in absorption seen in Figure 15 over the first three minutes in indicates coloured intermediates that were formed during the bleaching. The colour was a light yellow at the beginning and darkened during the experiment. The gain in colour was also visible to the naked eye during the bleaching process. After the colour reached its peak at 0.73 A the solution was decolourized within 4 minutes. The decrease in absorption suggest that the coloured intermediates are degraded into non- coloured products (various carbon acids seen in Table 10). The formation of coloured intermediates could be observed also in the bleaching of 2,6-HAP in organic solution.

The colour of 2,5-HAP in aqueous solution at pH 2 was yellow-greenish. Unlike the constitutional isomer 2,6-HAP, 2,5-HAP a did not undergo a colour change or a shift in colour during bleaching. Instead the reaction followed a straight decolouration that lasted 360 s until the solution was colourless. Signals below 380 nm (UV range) were cut out of the spectrum (Figure 16) due to their strong nature, like in 2,6-HAP. Although these strong signals appeared as well in 2,5-HAP it was possible to determine a peak at 400 nm. The decrease of colour over time can be seen in Figure 17.

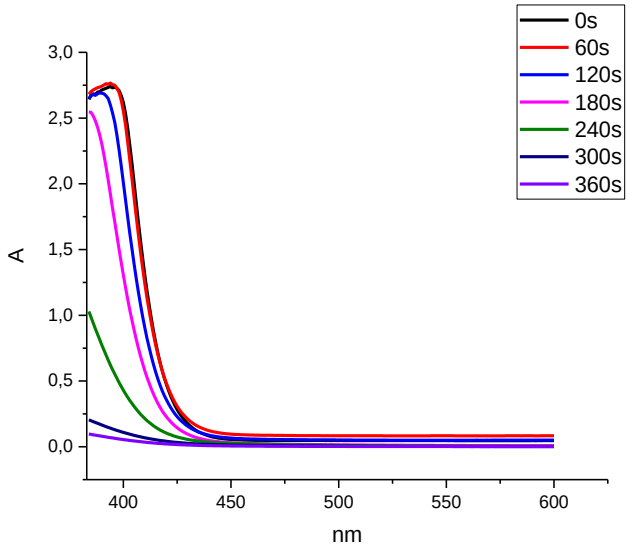

Figure 16: UV/Vis spectrum of Z21, 2,5-HAP in aqueous solution (pH 2).

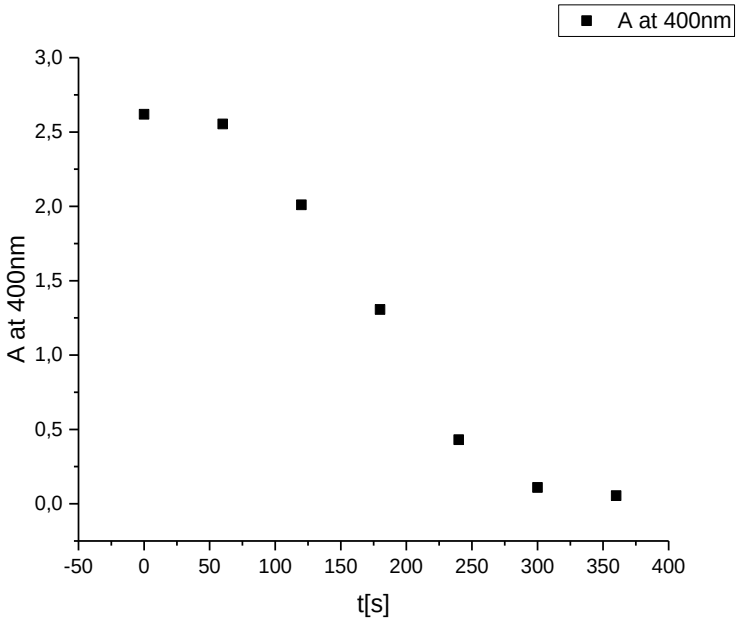

Figure 17: Absorption versus time at A=400nm of Z21, 2,5-HAP in aqueous solution (pH 2).

3.3.2 UV/Vis spectroscopy of DHNQ (aqueous)

The colour of DHNQ in aqueous solution at pH 2 and organic solvent can be described as dark red, similar to red wine. The first unbleached sample has an intense peak at 515 nm as shown in Figure 18.

The reaction started quickly, after 180 s a significant shift of the curves can be observed in the visible spectrum. The dark red colour of DHNQ changed into a light-yellow forming coloured intermediates during the ozone treatment. This effect was especially strong in the bleaching of DHNQ in organic solvent as discussed in 3.5.3. The peak shifted from 515 nm (red) to 400 nm (yellow) as shown Figure 19. It can be assumed that the new formed chromophoric intermediates are more stable than the original chromophore since the reaction drastically slows down after their formation.

Secondly the formation of intermediates indicate that the ozone-chromophore reaction happens in more than one stage as the molecule of DHNQ provides more than one possible site for ozone to react (Bernatek and Straumsgård 1959).

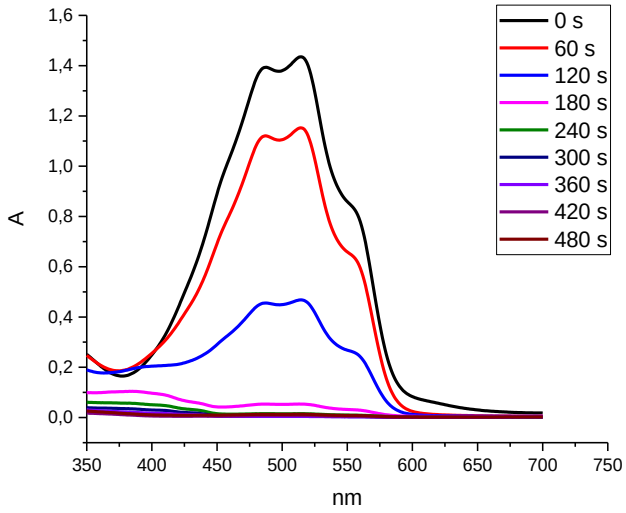

Figure 18: UV/Vis spectrum of Z22, DHNQ in aqueous solution (pH 2).

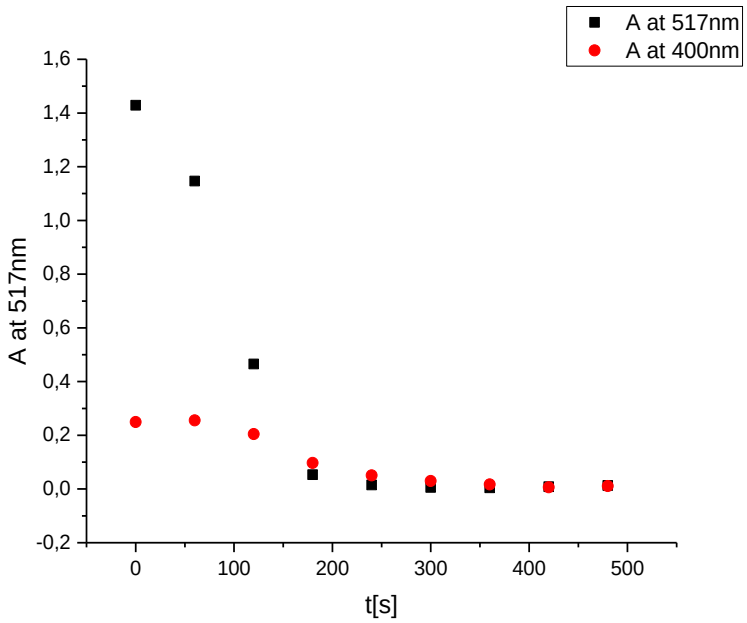

Figure 19: Absorption versus time: comparison between the absorption of 517nm and 400nm of Z22, DHNQ in aqueous solution (pH 2).

3.3.3 UV/Vis spectroscopy of DHBQ (aqueous)

The colour of the solution of DHBQ was orange which resulted in a peak at 400 nm in the visible spectrum shown in Figure 20. In the beginning the bleaching made quick progress in terms of decolouration. In the first 120 seconds the solution lost 50% of its intensity. After that the decolouration slowed down. The bleaching procedure lasted for a total 480 s and was carried out until the solution was colourless. In Figure 21 the progress of the decolouration is shown in absorption versus the bleaching time.

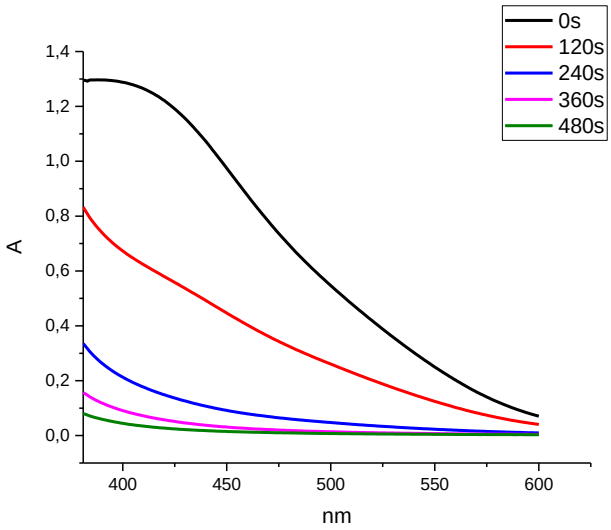

Figure 20: UV/Vis spectrum of Z23, DHBQ in aqueous solution at pH 2.

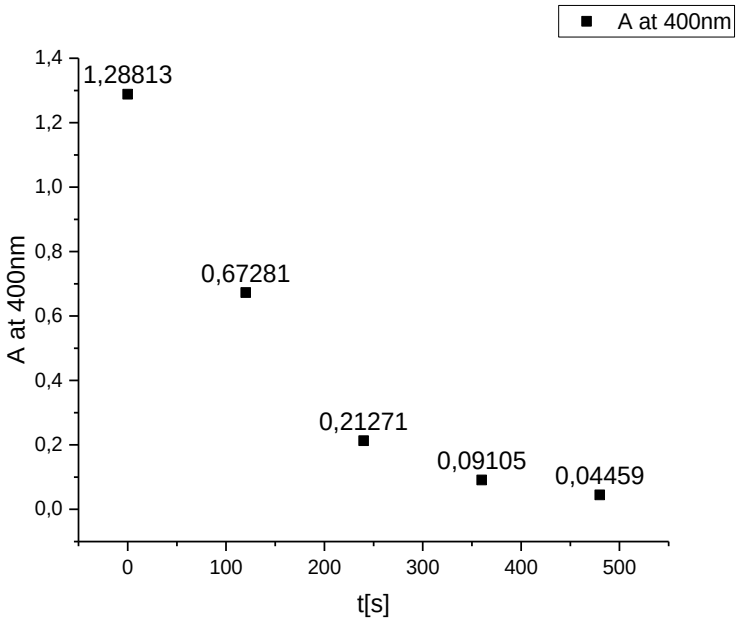

Figure 21: Absorption versus time at A=400nm of Z23, DHBQ in aqueous solution at pH 2.

3.3.4 UV/Vis spectroscopy of 2-OH-NQ (aqueous)

Figure 22 and Figure 23 are showing the visible spectrum of 2-OH-NQ. No peak could be determined, for further evaluation the highest absorption at 400 nm was chosen. 2-OH-NQ reacted quick compared to the other chromophores leading to a fast decolouration.

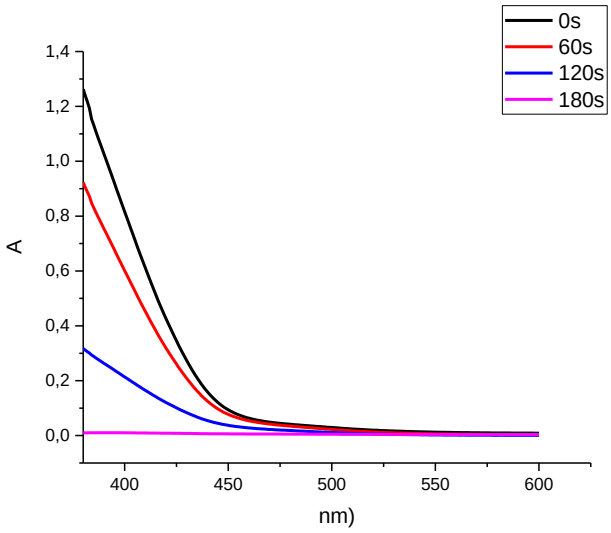

Figure 22: UV/VIS spectrum of Z19, 2OHNQ in aqueous solution (pH 2).

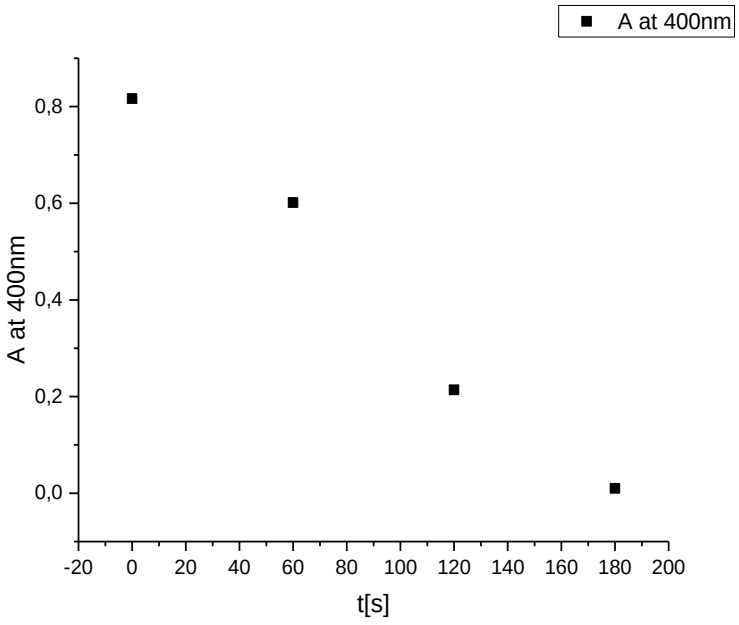

Figure 23: Absorption versus time at A=400nm of Z19, 2OHNQ in aqueous solution (pH 2).

Looking at the structure of 2-OH-NQ (Figure 2) its lesser stability can be explained by the following: the molecule has one OH group. This OH group can form a resonance stabilized bond with the adjacent oxygen atom. Since there is only one OH group in 2-OH-NQ this resonance stabilization is less strong as for example in DHNQ or DHBQ where two resonance bonds are possible (Hosoya et al. 2015).

3.3.5 Effects of inorganic salts on DHBQ degradation with ozone

When bleaching with hydroxyl peroxide (H_2O_2) at alkaline pH alkaline earth metal salts (Mg^{2+} and Cl^{2+}) can slow down the degradation of DHBQ due to stabilisation by complex formation which makes DHBQ more resistant to bleaching. On the contrary alkaline metal salts (Na^+ and K^+) can enhance the degradation of the chromophore.

In acidic medium DHBQ does not form stabilizing complexes with the salts because hydroxylhydrogens are placed in equal distance to the vicinal oxygens. Only the loss of hydrogens at alkaline condition would lead to the formation of the stabilized complex structure (Hosoya et al. 2015).

Nevertheless, experiments in acidic medium with salt additives were carried out to determine if the ozone degradation of DHBQ is influenced by metal salts similarly to what was observed in H_2O_2 bleaching (Hosoya et al. 2015). Magnesium sulfate ($MgSO_4$), calcium chloride ($CaCl_2$), sodium sulfate ($NaSO_4$) and potassium sulfate (K_2SO_4) were each added to an aqueous solution of DHBQ and bleached with ozone.

The added salts had no influence on the bleaching which is shown by the result of the UV/Vis analysis – DHBQ in aqueous solution resulted in a peak at 400 nm (pH 2) as already shown before.

Figure 24 shows absorption versus time from the UV/Vis analyses of DHBQ with 4.5 mM of the metal cations: Na_2SO_4, K_2SO_4, $MgSO_4$ and $CaCl_2$. The samples show minor differences in absorption intensity. In the first samples the difference of absorption amounts 0.18 A between the highest absorption value (control, 1.288 A) and the lowest value ($NaSO_4$, 1.107 A). These samples were taken before the bleaching process started (at 0 s). Because in all five experiments the same concentration of DHBQ was used, the difference can be caused by the salts added and their interaction with DHBQ. For example, variations in color can be caused by lower solubility of DHBQ due certain salt additives. Especially in the case of $CaCl_2$ solubility problems and slight precipitation occurred. Generally, the experiments proceed in a similar way as seen in 3.3.3. The salts added did not influence the bleaching behaviour of DHBQ.

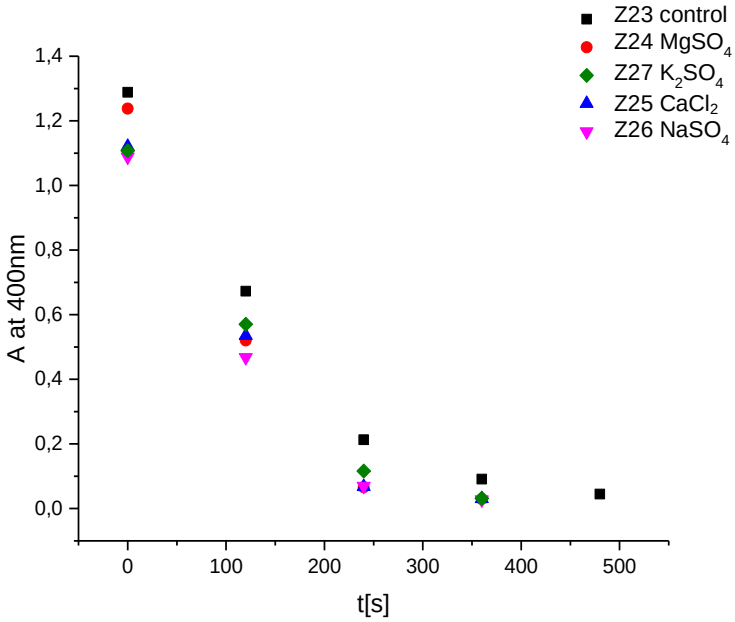

Figure 24: Absorption versus time at A=400nm of Z23 (control), Z24 ($MgSO_4$), Z25 ($CaCl_2$), Z26 ($NaSO_4$), Z27 (K_2SO_4), DHBQ in aqueous solution (pH 2).

Further the bleaching behaviours of DHNQ, 2,5-HAP, 2,6-HAP, THBQ and 2-OH-NQ with the addition of the salts $NaSO_4$ and $CaCl_2$ were investigated. Like in the case of DHBQ no significant effect on the bleaching kinetics could be determined for these two salts.

3.3.6 Effects of pH 12 for DHBQ bleaching with ozone

Bleaching at pH 12 causes the ozone molecule to quickly decompose due to the present OH^- ions and radical (•OH, O_2^- and HO_2^-) formation follows. Because of the high reactivity of the unselective radicals, i.e. the •OH radical, DHBQ can also be bleached until full decolouration in alkaline conditions (Ek et al. 2009b; Hruschka 1986; Patt et al. 1991). The bleaching at pH 12 was done out of scientific interest and to evaluate the different bleaching behaviour of ozone compared to acidic conditions.

After analysing of the residual products, the ^{1}H NMR spectrum shows different results than the spectrum from the bleaching at pH 2. In alkaline medium the main reactant is the •OH radical, resulting in different reaction paths and different reaction products than the acidic bleaching (Musl 2017). In the spectrum of DHBQ bleached at pH 12 but identical conditions regarding ozone concentration and gas flow, viewer degradation products are found – only two of which occur in both, the spectrum of DHBQ bleached at pH 2 and the spectrum of DHBQ bleached at pH 12: acetic acid (**13**) (singlet at 1.92 ppm) and formic acid (**14**) (singlet at 8.46 ppm)

(Figure 25). The other peaks of DHBQ bleached at pH 12 could not be identified since GC-MS also gave no further indications.

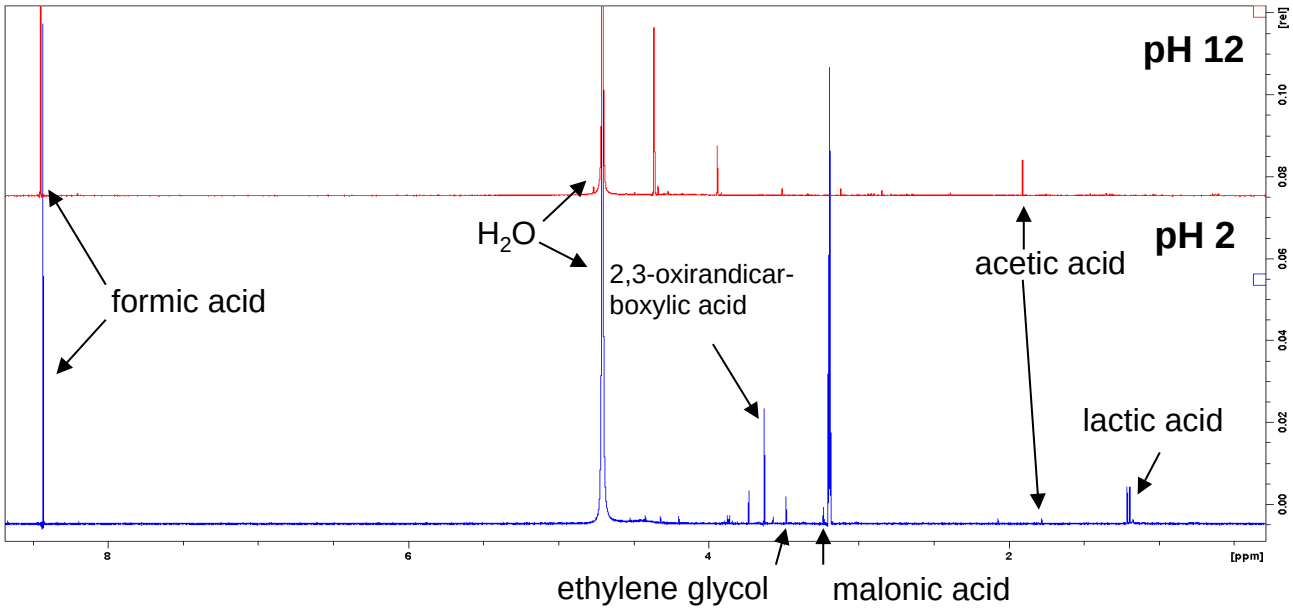

Figure 25: NMR spectrum of DHBQ bleached at pH 12 (top) compared to DHBQ bleached at pH 2 (bottom).

3.3.7 Analysis of the degradation products of chromophores obtained in the bleaching experiments in aqueous solution by GC-MS and NMR

The chromophores (**1**, **4**, **5**, **8**, **9**, **10**) were dissolved in aqueous solution and treated with O_3 upon complete decolouration of the initial intense coloured solution. After ozone treatment the remaining solutions were neutralized and further evaporated and freeze-dried. The solid dry residuals from each bleached chromophore were then subjected to ^{1}H NMR, 2D NMR (HSQC/HMBC), and GC−MS analyses to determine the degradation products formed during the reaction between O_3 and chromophore. Based on the interpretation of the NMR and GC-MS result different hydroxycarboxylic acids were identified as the main reaction products (Figure 26). Products detected by NMR were. acetic acid (**11**), formic acid (**12**), glycolic acid (**13**), malonic acid (**15**), 2,3-oxirandicarboxylic acid (**16**), lactic acid (**17**), ethylene glycol (**18**), malic acid (**19**) and tartronic acid (**20**). Except for compound **21** and **22** all chromophores share the same reaction products. By means of GC-MS analysis compound **12**, **15**, **17**, **19** and **20** could be confirmed and further oxalic acid (**14**) was detected. Due to missing of nonexchangeable protons of product **14**, it cannot be detected by ^{1}H NMR in D_2O (Zwirchmayr et al. 2017).

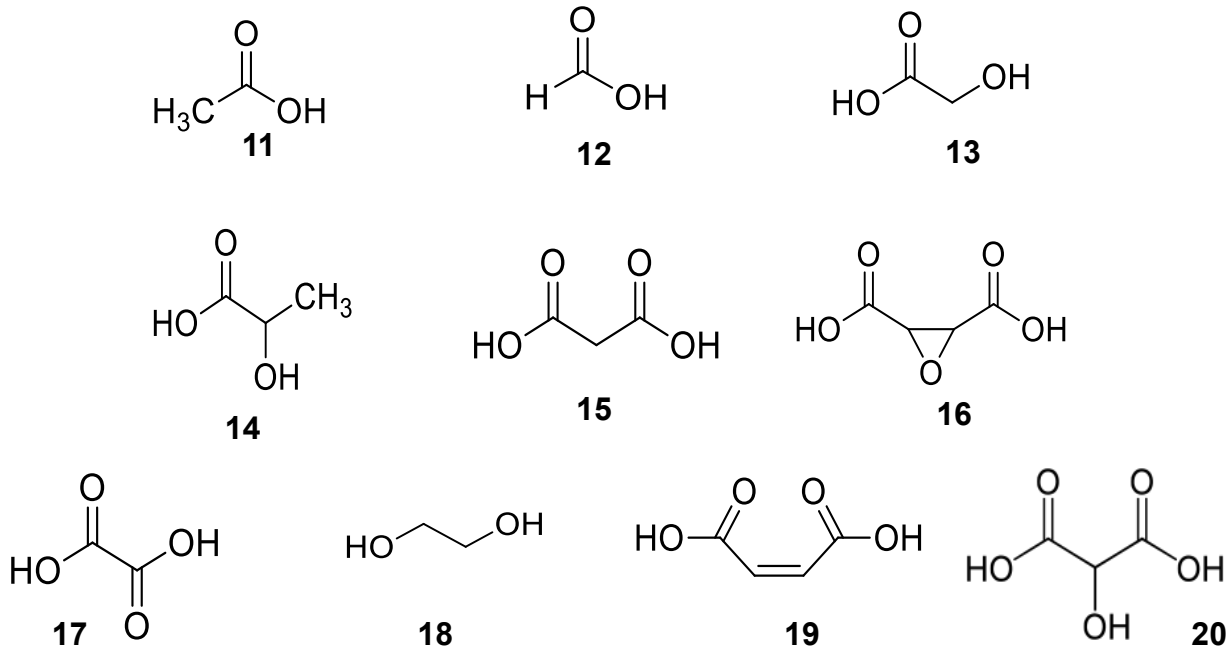

Figure 26: Degradation products identified by NMR and GC-MS analysis. acetic acid **11**, formic acid **12**, glycolic acid **13**, oxalic acid **14**, malonic acid **15**, 2,3-Oxirandicarboxylic acid **16**, lactic acid **17**, ethylene glycol **18**, malic acid **19** and tartronic acid **20**.

Glycolic acid (**13**) usually results in a signal at 4.08 ppm (^{1}H NMR). Nevertheless, the recurring peak at 3.85 ppm was assigned to **13** due to the corresponding ^{13}C shifts and the GC-MS results. The results of **13** from bleaching in organic solvents however show shifts at 4.08. This variation could be due to pH variations that can influence the NMR chemical shifts of carboxylic acids. The determined carboxylic acids for each chromophore are shown in Table 7, 8, 9 and 12. In Table 13 an overview of the GC-MS results is given.

Table 7: Degradation products of DHBQ (1). The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

DHBQ (1) degradation products	**^{1}H chemical shift [ppm]**	**^{13}C chemical shift [ppm]**	**GC-MS retention time [min]**	**MW [g/mol]**
Formic acid	s, 8.55	170.2	/	46.03
Acetic acid	s, 1.89	* ; *	/	60.05

Ethylen glycol	s, 3.60	64.3	/	62.07
Glycolic acid	s, 3.85	62.6; 180	11.22	76.05
Oxalic acid	/	/	13.06	90.04
Lactic acid	d, 1.31; q, 4.01	21.5, 69.3, 182.2	10.75	90.08
Malonic acid	s, 3.34	49.1; *	14.6	104.06
2,3-Oxirandicarbox-ylic acid	s, 3.75	52.1; 166.5	/	132.07

***signal not detected**

Table 8: Degradation products of DHNQ (2). The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

DHNQ (2) degradation products	**^{1}H chemical shift [ppm]**	**^{13}C chemical shift [ppm]**	**GC-MS retention time [min]**	**MW [g/mol]**
Formic acid	s, 8.55	170.2	/	46.03
Acetic acid	s, 1.89	23.86; 180	/	60.05
Ethylen glycol	s, 3.60	64.3	/	62.07
Glycolic acid	s, 3.85	62.6; 180	11.22	76.05
Oxalic acid	/	/	13.06	90.04
Lactic acid	d, 1.31; q, 4.01	21.5, 69.3, 182.2	10.75	90.08
Tartronic acid	s, 4.67	62.4; *	/	120.06
2,3-Oxirandicarbox-ylic acid	s, 3.75	52.1; *	/	132.07

***signal not detected**

Table 9: Degradation products of 2,5-HAP (3). The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

2,5-HAP (3) degradation products	**^{1}H chemical shift [ppm]**	**^{13}C chemical shift [ppm]**	**GC-MS retention time [min]**	**MW [g/mol]**

Formic acid	s, 8.55	170.2	/	46.03
Acetic acid	S, 1.90	23.7; 180	/	60.05
Ethylen glycol	s, 3.60	63.9	/	62.07
Glycolic acid	s, 3.87	52.2; 180	11.22	76.05
Oxalic acid	/	/	13.06	90.04
Lactic acid	d, 1.32; q, 4.00	21.5; 69.3; 182.1	10.75	90.08
Malonic acid	s, 3.35	46.1; 176	14.6	104.06
Maleic acid	s, 6.24	136.3; 171	18.04	116.07
Tartronic acid	s, 4.64	*; *	20.6	120.06
2,3-Oxirandicarboxylic acid	s, 3.76	52.1; 166.5	/	132.07

***signal not detected**

Table 10: Degradation products of 2,6-HAP (4). The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

2,6-HAP (4) degradation products	**^{1}H chemical shift [ppm]**	**^{13}C chemical shift [ppm]**	**GC-MS retention time [min]**	**MW [g/mol]**
Formic acid	s, 8.55	170.2	/	46.03
Acetic acid	s, 1.90	23.7; 180	/	60.05
Ethylen glycol	s, 3.60	63.9	/	62.07
Glycolic acid	s, 3.87	52.2; 179.5	11.22	76.05
Oxalic acid	/	/	13.06	90.04
Lactic acid	d, 1.32; q, 4.00	21.5; 69.3; 182.3	10.75	90.08
Malonic acid	s, 3.35	*; *	14.6	104.06
Maleic acid	s, 6.24	136.3; 171.2	18.04	116.07
Tartronic acid	s, 4.64	*; *	20.6	120.06
2,3-Oxirandicarboxylic acid	s, 3.76	52.1; 166.6	/	132.07

***signal not detected**

Table 11: Degradation products of 2-OH-NQ (5). The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

2-OH-NQ (5) degradation products	^{1}H chemical shift [ppm]	^{13}C chemical shift [ppm]	GC-MS retention time [min]	MW [g/mol]
Formic acid	s, 8.50	169.7	/	46.03
Acetic acid	S, 1.96	21.5; *	/	60.05
Ethylen glycol	s, 3.60	64.1	/	62.07
Glycolic acid	s, 3.85	52.5; 170.5	11.22	76.05
Oxalic acid	/	/	13.06	90.04
Lactic acid	d, 1.34	21.3; 69.0; 181.3	10.75	90.08
Malonic acid	s, 3.34	50.5; *	14.6	104.06
2,3-Oxirandicarboxylic acid	s, 3.77	52.8; 164.3	/	132.07

***signal not detected**

Table 12: Degradation products of THBQ (6). The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

THBQ (6) degradation products	^{1}H chemical shift [ppm]	GC-MS retention time [min]	MW [g/mol]
Formic acid	s, 8.45	/	46.03
Acetic acid	s, 1.90	/	60.05
Glycolic acid	/	11.22	76.05
Oxalic acid	/	13.06	90.04
Lactic acid	/	10.8	90.08
Malonic acid	s, 3.34	14.6	104.06

3.3.8 NMR results of the bleaching experiments in aqueous solution

After bleaching and drying by lyophilisation as described in 2.4 the residual material was subjected to NMR analysis. The ^{1}H NMR spectra showed that the chromophores, except for 2-

OH-NQ, were fully oxidized by the ozone treatment. Several reaction products have formed and are shown in different peaks in the spectra. In the case of 2-OH-NQ aromatic structures were still present after the ozone treatment, indicated by the peaks in the range of 7-8 ppm. A comparison of all five ^{1}H NMR spectra of the key chromophores can be seen in Figure 27.

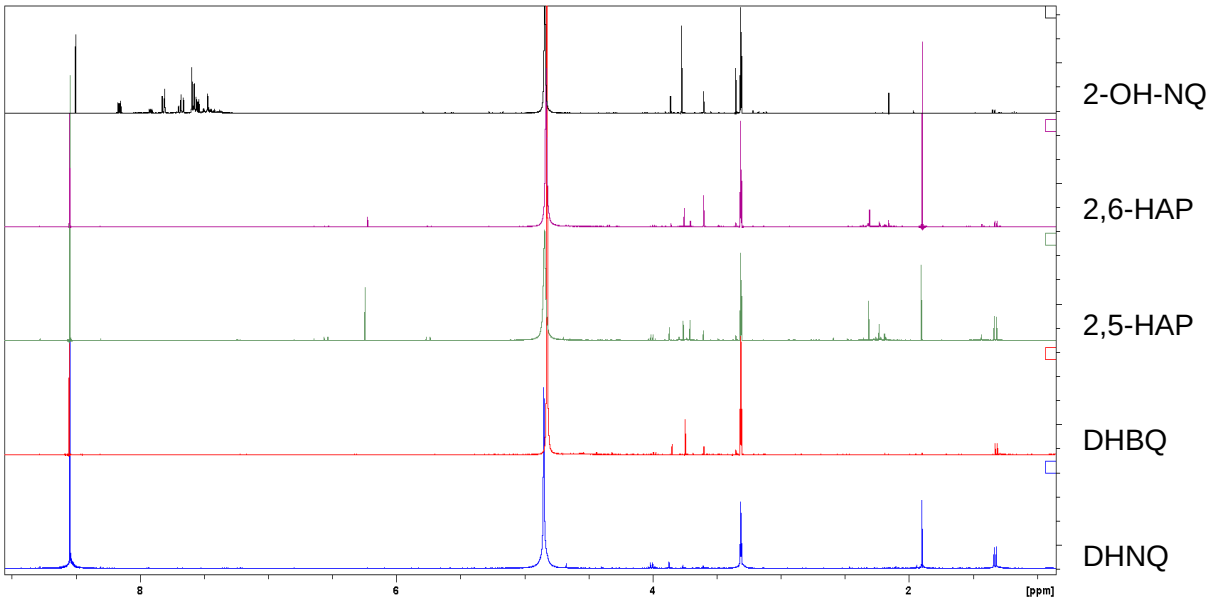

Figure 27: Comparison of the ^{1}H NMR spectra of the key chromophores and 2-OH-NQ, which were bleached in aqueous solution.

With the help of the GC-MS results, the use of online databases (predicted and experimental ^{1}H NMR spectra from various substances) and the evaluation of HSQC, HMBC spectra, the different signals from each spectrum were determined. It was possible to identify most of the mayor signals for each chromophore. As described before carboxylic acids were the main degradation products found in the bleached residual materials. In general, the spectra show minor differences between the peaks which can be also observed in Figure 27.

The solvent used for these ^{1}H NMR measurements was MeOD with a signal at 3.31 ppm, the signal at 4.85 ppm was determined as water which could not fully be removed from the samples.

3.4 GC-MS result

The results from GC-MS analyses were used to confirm the interpretation of the NMR spectra and visa-versa. In Table 13 the reaction products with corresponding retention time and chromophore are shown.

Table 13: Overview of the by GCMS determination of the degradation products obtained by bleaching of the five chromophores. The retention time is given in minutes.

RT [min]	Analyte	Found in
10.75	Lactic acid	DHBQ, 2,5-HAP, 2,6-HAP, 2OHNQ, DHNQ
11.22	Glycolic acid	DHBQ, 2,5-HAP, 2,6-HAP, 2OHNQ, DHNQ
13.06	Oxalic acid	DHBQ, 2,5-HAP, 2,6-HAP, 2OHNQ, DHNQ
14.6	Malonic acid	DHBQ, 2,5-HAP, 2,6-HAP, 2OHNQ, DHNQ
18.04	Maleic acid	2,5-HAP, 2,6-HAP
20.6	Tartronic acid	2,5-HAP, 2,6-HAP
28	Phthalic acid	2-OH-NQ

3.5 Bleaching chromophores in organic solvents

Chromophores were bleached in organic solvents to identify possible differences between aqueous and organic media regarding the chromophore bleaching behaviour.

To spot differences in bleaching behaviour kinetics of each chromophore were determined by sampling during the reaction and subsequent UV/Vis spectroscopy. Based in the obtained reaction order or bleaching behaviour, conclusions can be drawn about the stability and reactivity of the different chromophores when bleached with ozone.

3.5.1 UV/Vis spectroscopy of 2,6-HAP and 2,5-HAP (DCM)

The starting solution had a slightly yellow colour with low absorption at the end of the visible spectrum (0.26 A at 400 nm) and was rather difficult to detect with the bare eye. The UV/Vis spectrum of the chromophore shows no peak in the visible range as seen in Figure 28.

During the bleaching experiment with ozone 2,6-HAP reacted quickly and formed intense yellow coloured intermediates which was also the case in aqueous solution. Figure 29 shows that the maximum of absorption was reached after 240 seconds, followed by the bleaching of the solution until only a rest of colour (0.18 A at 400 nm) was remaining.

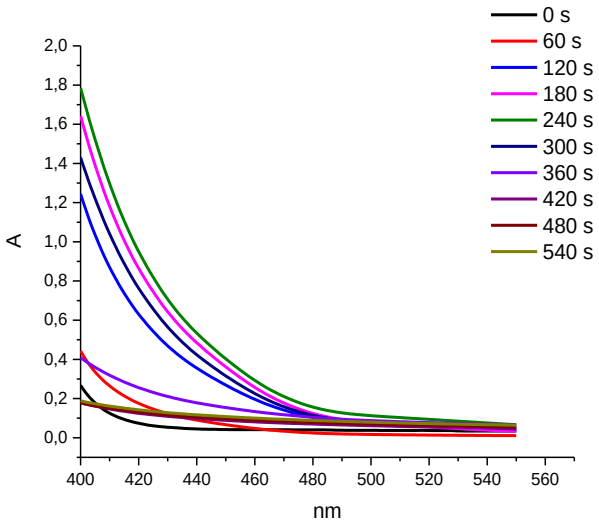

Figure 28: UV/Vis spectrum of 2,6-HAP in DCM. (Z13)

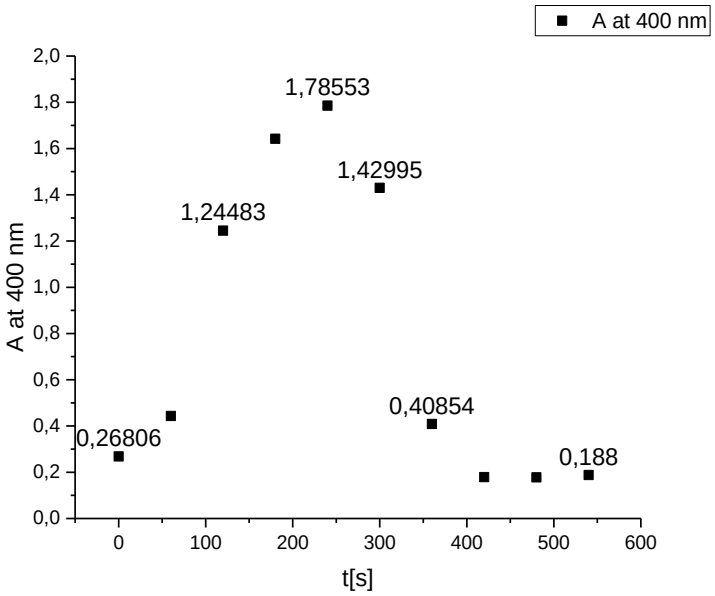

Figure 29: Absorption versus time at A=400nm 2,6-HAP in DCM. (Z13)

The colour of the solution with the unbleached 2,5-HAP can be described as slight yellow with an olive-green tint. Even though 2,5-HAP is a constitutional isomer of 2,6-HAP the two chromophores show major differences regarding their bleaching behaviour. The starting absorption from 2,5-HAP at 0s was exceptional high (2.59 A at 400 nm), although only half of the concentration (3.31 mM) of the chromophore was applied to the solution compared to 2,6-HAP.The chromophore 2,5-HAP does not show any signs of the formation of coloured intermediates instead the decolouration follows a neat curve until full decolouration as shown in Figure 31. Shared characteristics are that no peaks in the visible range are shown, instead very the strong signals in the UV range were detected which were cut out from the spectrum in Figure 30, as they would not contribute to the solutions visible color.

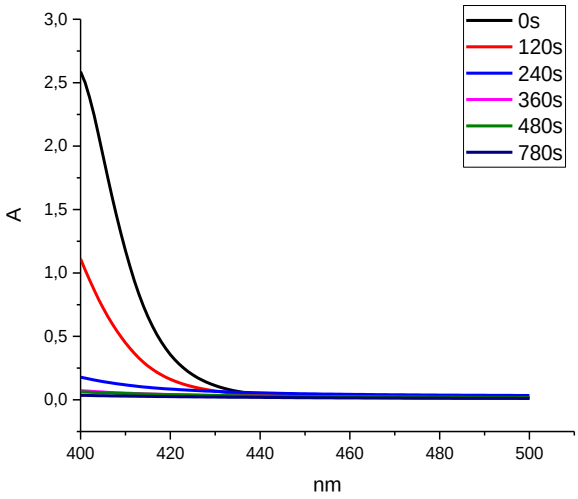

Figure 30: UV/VIS spectrum of 2,5-HAP in DCM. (Z16)

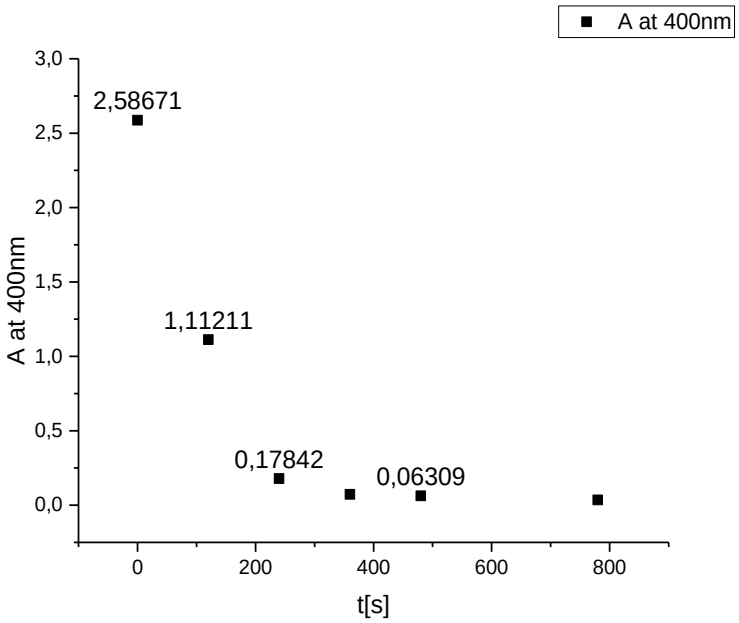

Figure 31: Absorption versus time at A=400nm 2,5-HAP in DCM. (Z16)

3.5.2 UV/Vis spectroscopy of DHNQ (acetone)

The concentration of the samples was diluted to 1.05 mM/l resulting in an absorption of 3.34.

The colour of the solution was dark red, similar to the colour in aqueous solution discussed in 3.3.2 with a peak at 517 nm. During the bleaching process the red colour disappeared quickly and turned into a bright yellow within 180 s. This behaviour indicates the formation of coloured intermediates and was also observed – albeit less intense – in aqueous solution. In organic solvent it seems that the intermediates formed are more stable as they withstand the bleaching

procedure much longer compared to aqueous solution. However, the comparison of the relative bleaching times, which are discussed in 3.6.1, show only a minor difference in bleaching time.

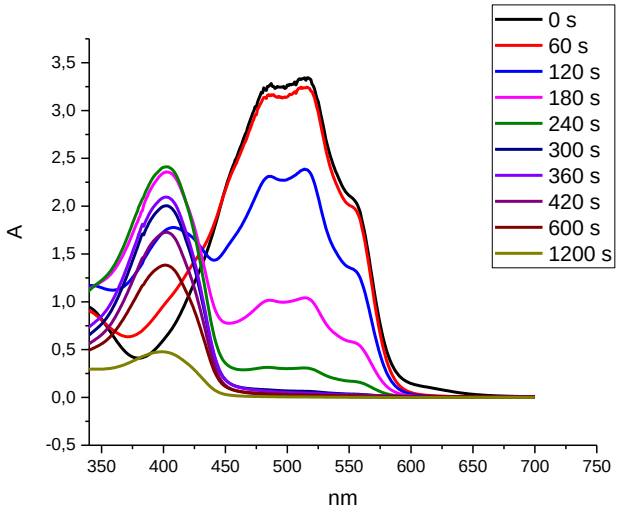

Figure 32: UV/VIS spectrum of DHNQ in acetone. (Z12)

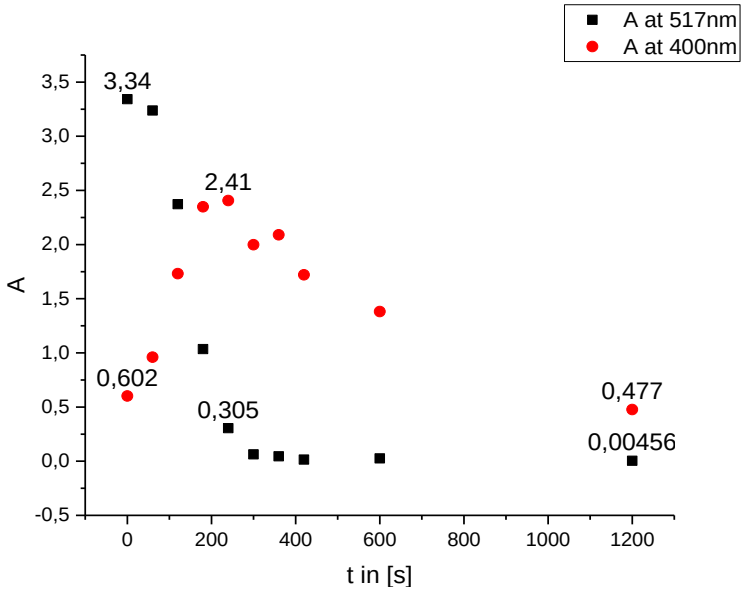

Figure 33: Absorption versus time at A=400nm DHNQ in acetone. (Z12)

3.5.3 UV/Vis spectroscopy of DHBQ (acetone)

The colour of the solution of DHBQ was orange as which resulted in a peak at 400 nm in the visible spectrum shown in Figure 34. The first sample started at 1.58 A at 400 nm and was

bleached for 600 s until full decolouration. Compared to the relative bleaching times discussed in 3.6.1 DHBQ in organic solution reacted 57% faster. In aqueous solution the bleaching time amounts 88 s, in organic solution 50 s. During the reaction no formation of coloured intermediates was observed. In Figure 35 the progress of the decolouration is shown in absorption versus the bleaching time.

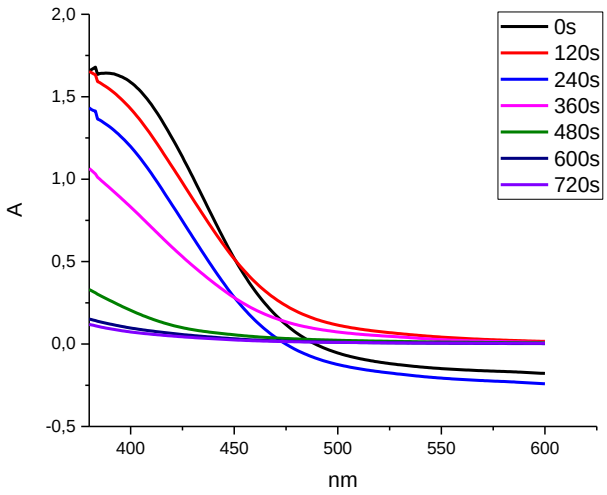

Figure 34: UV/VIS spectrum of DHBQ in acetone. (Z6)

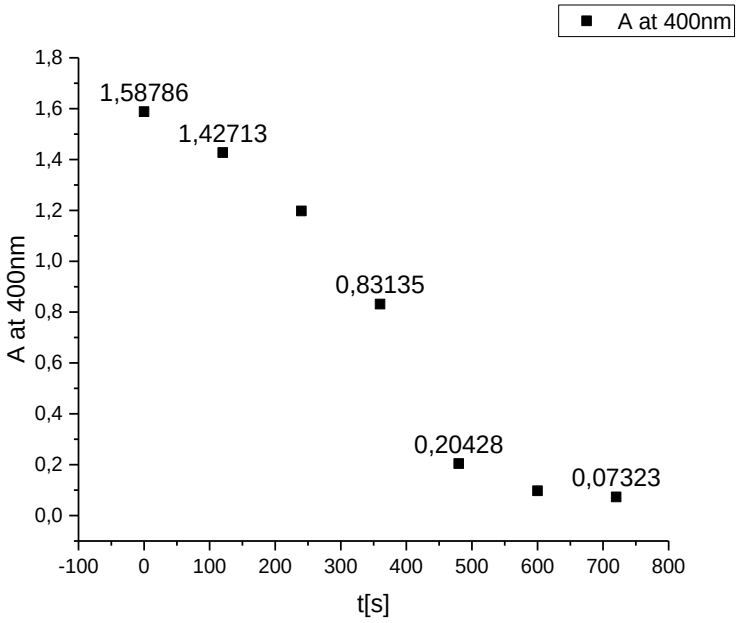

Figure 35: Absorption versus time at A=400nm DHBQ in acetone. (Z6)

3.5.4 UV/Vis spectroscopy of 2-OH-NQ (acetone)

The colour of 2-OH-NQ in acetone was an intense bright orange. As seen in Figure 36 no peak was detected in the visible range of the spectrum. For further evaluation the highest point of absorption (1.56 A) was chosen which was at 400 nm. 2-OH-NQ showed minor resistance against bleaching against ozone with resulted in a fast decolouration which can be seen in Figure 37.

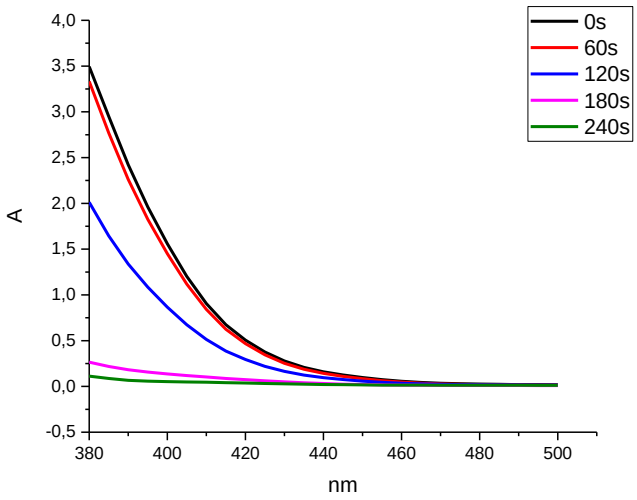

Figure 36: UV/VIS spectrum of 2-OH-NQ in acetone. (Z14)

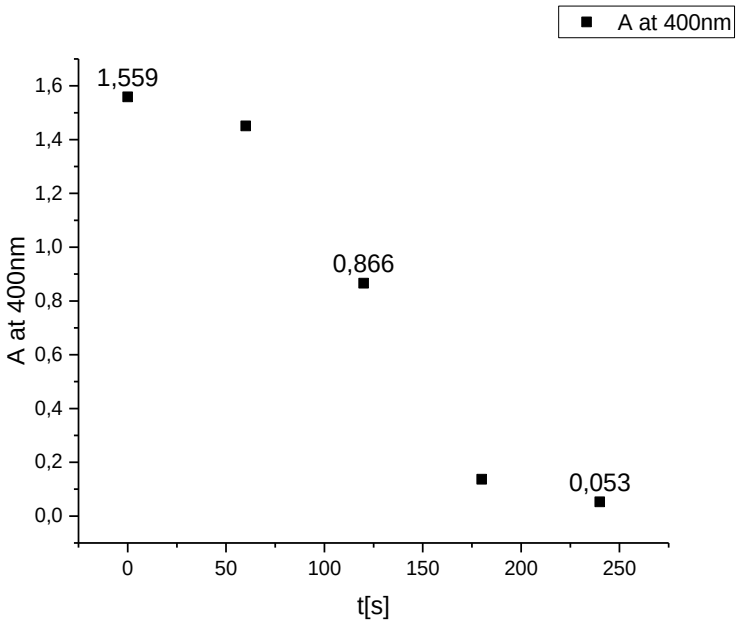

Figure 37: Absorption versus time at A=400nm 2-OH-NQ in acetone. (Z14)

3.5.5 Analysis of the degradation products of chromophores obtained in the bleaching experiments in organic solution by GC-MS and NMR

The chromophores **1**, **4**, **5**, **8**, **9**, and **10** were dissolved in organic solvents (DCM or Acetone) and treated with O_3 upon complete decolouration of the initial intense coloured solution. After ozone treatment the remaining solutions were evaporated. The solid dry residuals from each bleached chromophore were then subjected to ^{1}H NMR, 2D NMR (HSQC/HMBC), and GC−MS analyses to determine the degradation products formed during the reaction between O_3 and chromophore.

Products obtained from bleaching in organic solution were the same as in aqueous solution. Only one exception occurred which was phathalic acid, found in the GC-MS spectrum of 2-OH-NQ. Its structure is derived from 2-OH-NQ and is most likely one of the first products formed after ozonolysis of the chromophore. Further reactions with ozone will degrade phthalic acid in smaller carboxylic acids. The determined carboxylic acids for each chromophore are shown in Table 14, 15, 16, 17 and 18.

Table 14: Degradation products of DHBQ (1). The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

DHBQ (1) degradation products	1H chemical shift [ppm]	13C chemical shift [ppm]	GC-MS retention time [min]	MW [g/mol]
Acetic acid	S, 1.99	19.22; 172.7	/	60.05
Ethylene glycol	s, 3.61	62.78	/	62.07
Glycolic acid	s, 4.08	59.35; 175.0	11.22	76.05
Oxalic acid	/	/	13.06	90.04
Malonic acid	s, 3.35	49.57; 169.6	14.6	104.06
Tartronic acid	s, 4.68	72.3; 170.5	/	120.06
Maleic acid	s, 6.17	123.68; *	/	116.1
2,3-Oxirandicarboxylic acid	s, 3.75	52.47; 169.7	/	132.07

***signal not detected**

Table 15: Degradation products of DHNQ (2) in organic solvent. The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

DHNQ (2) degradation products	1H chemical shift [ppm]	13C chemical shift [ppm]	GC-MS retention time [min]	MW [g/mol]
Acetic acid	S, 1.99	20.4, 175.2	/	60.05
Ethylene glycol	s, 3.58	54.33	/	62.07
Glycolic acid	s, 4.08	60.5, 176.0	11.22	76.05
Oxalic acid	/	/	13.06	90.04
Malonic acid	s, 3.34	41.81, 169.6	14.5	104.06
Tartronic acid	s, 4.66	72.5, 171.7	/	120.06
2,3-Oxirandicarboxylic acid	s, 3.78	53.29, 169.2	/	132.07

Table 16: Degradation products of 2,5-HAP (3) in organic solvent. The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

2,5-HAP (3) degradation products	1H chemical shift [ppm]	13C chemical shift [ppm]	GC-MS retention time [min]	MW [g/mol]
Formic acid	s, 8.53	*	/	46.03
Acetic acid	S, 1.99	20.6, 175.0	/	60.05
Ethylen glycol	s, 3.60	47.36	/	62.07
Glycolic acid	s, 4.08	60.4, 176.0	11.22	76.05
Oxalic acid	/	/	13.06	90.04
Lactic acid	d, 1.38; q, 4.23	20.3; *; 178.0	10.75	90.08
Malonic acid	s, 3.35	46.9; *	/	104.06
Maleic acid	s, 6.27	118.5, *	/	116.07
Tartronic acid	s, 4.66	72.5, 171.6	/	120.06
2,3-Oxirandicarboxylic acid	s, 3.77	53.15, 169.2	/	132.07

***signal not detected**

Table 17: Degradation products of 2,6-HAP (4) in organic solvent. The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

2,6-HAP (4) degradation products	1H chemical shift [ppm]	13C chemical shift [ppm]	GC-MS retention time [min]	MW [g/mol]
Formic acid	s, 8.55	*	/	46.03
Acetic acid	S, 1.99	20.4; 167.1	/	60.05
Glycolic acid	s, 4.08	60.6; 174.5	11.22	76.05
Oxalic acid	/	/	13.06	90.04
Lactic acid	/	/	10.75	90.08
Malonic acid	s, 3.33	41.6; *	14.6	104.06
Maleic acid	s, 6.28	*; *	18.04	116.07
Tartronic acid	s, 4.65	72.3, 172.4	20.66	120.06
2,3-Oxirandicarboxylic acid	s, 3.75	48.9; *	/	132.07

***signal not detected**

Table 18: Degradation products of 2-OH-NQ (5) in organic solvent. The ^{1}H and ^{13}C chemical shifts are given in ppm. If possible, ^{13}C shifts were derived from 2D NMR spectra (HSQC, HMBC). Retention time from GC-MS analysis is given in minutes. The data is referring to the trimethylsilyl ester derivates of the substances. Molecular weights are given in g/mol for the underivatized, protonated reaction products.

2-OH-NQ (5) degradation products	1H chemical shift [ppm]	GC-MS retention time [min]	MW [g/mol]
Glycolic acid	/	11.22	76.05
Oxalic acid	/	13.06	90.04
Lactic acid	/	10.75	90.08
Malonic acid	s, 6.24	14.6	104.06
1,2-Benzenedicarboxylic acid	/	28	166.13

3.6 Comparison between bleaching chromophores in organic and aqueous solution

The determination of the reaction products which formed upon ozonisation of chromophores in aqueous solution was the one goal of this study. As reference experiments were also performed in organic solvents, even though industrial bleaching is only carried out in aqueous solution. Due to the absence of water and therefore the absence of OH^- ions, radical formation by O_3 degradation is reduced in organic solvent (Chirat and Lachenal 1997; Gierer 1997; Reitberger et al. 1999).

Various carboxylic acids were determined as reaction products formed both in aqueous and organic solution, as described in 3.3.7 and 3.5.5. Since the formed acids from the different chromophores were similar, it can be assumed that the reaction mechanism between ozone and the chromophore proceeds in a similar way in both solvents. The presumed degradation mechanism is the Criegee mechanism in which O_3 attacks and cleaved C double bonds as described in 1.7.3 (Criegee 1975).

3.6.1 Bleaching times

Chromophores samples taken during bleaching were analysed with UV/Vis spectroscopy to evaluate the reaction kinetics.

It was attempted to maximize the amount of chromophore dissolved in the solvent to facilitate degradation product analyses. Due to the different solubility of the chromophores in aqueous solution at pH 2 and in organic solvents it was not always possible to dissolve comparable amounts of the chromophores. To compare the bleaching times, they were calculated for a concentration of 1mM and arithmetically averaged for each chromophore to get the relative bleaching time. To get a bigger pool of data for the chromophores in aqueous solution the experiments with salt additives were taken into the calculation. This was legitimate because UV/Vis spectroscopy showed that the salts added had no effect on the bleaching behaviour. The different bleaching times for chromophores at pH 2 and DHBQ at pH 12 as well as for chromophores bleached in organic solvents are shown in Table 19 sorted by relative time until full decolouration.

Table 19: Calculated and averaged bleaching times for each chromophore for experiments carried out in aqueous solution and in organic solvents to evaluate the stability relative to each other chromophore. The bleaching time is calculated for a chromophore concentration of 1mM, bleached with an ozone flow of 1.05 g O_3/h or 0.021 g O_3/l. The ratio between volume [l] of solvent and mass of ozone [g O_3/h] added amounts 1:3.5.

Stability	**Chromophore**	**Rel. time aqueous [s]**	**Rel. time organic [s]**
Low	THBQ	66	/
	2OHNQ	87	47
	DHBQ	88	50
	2,6-HAP	121	86
	2,5-HAP	126	106
High	DHNQ	557	574
	DHBQ, pH 12	123	/

With the help of the bleaching times the “resistance” against ozone bleaching can be evaluated between the different chromophores. The times of bleaching at pH 2 and bleaching in organic solvents match well regarding the order of the chromophores. DHNQ turned out to be the chromophore with the highest stability against ozone in both solvents followed by 2,5-HAP, 2,6-HAP, DHBQ and at last 2-OH-NQ. THBQ was only bleached in aqueous solution at pH 2 and showed the lowest stability against bleaching at these conditions. The bleaching of DHBQ at pH 12 lasted longer compared to DHBQ at pH 2 even though the alkaline conditions promoted the degradation of ozone forming very reactive •OH radicals. (Gierer 1997; Chirat and Lachenal 1997; Lachenal et al. 2009)

3.7 Reaction mechanism of chromophores and ozone

When ozone reacts with phenolic compounds, alkenes or other unsaturated compounds, such as quinones, various carboxylic acids are formed as reaction product (Krainz 2009; Musl 2017; Pillar et al. 2017; Bernatek and Frengen 1961; Bernatek and Straumsgård 1959; Bernatek et al. 1961; Bernatek and Soteland 1962).

Most of the key chromophores bleached in aqueous solution share the same hydroxyl carboxylic acids as degradation product: formic acid (**14**), acetic acid (**13**), ethylene glycol (**20**), glycolic acid (**15**), lactic acid (**19**), malonic acid (**17**), maleic acid (**21**), tartronic acid (**20**) and 2,3-oxirandicarboxylic acid (**18**) as discussed in 3.3.7. Also, the reaction products from the bleaching in organic solvent were similar to those bleached in aqueous solution. This indicates that the degradation reactions of the chromophores follow the same paths in both organic and aqueous solution at pH 2-3.

Ozone cleaves olefinic and activated aromatic bonds to give aldehydes, ketones and acids. The oxidation can also take place at the double blond moiety of a quinone, forming the primary and secondary ozonide according to the Criegee mechanism. The ozonide degrades by three distinct types of ring fragmentation: anomalous ozonolysis, acid rearrangement and hydrolysis of ozonide. As a result, muconic acids and their derivatives form and decompose into small organic acids (Ragnar 2000; Kuczkowski 1992; Criegee 1975; Epstein 2010; Hendrickx and Vinckier 2003; Bernatek and Straumsgsård 1959). Comparing the NMR spectrum of the bleaching experiment of DHBQ at pH 12 with the spectra of DHBQ bleached at pH 2 supports the assumption that ozone is the main active species, and that competing reactions, such as the formation of •OH, O_2^- or HO_2^-, is minimized at the applied bleaching conditions (pH 2-3) that contribute to ozone's stability (Chirat and Lachenal 1997). In the spectrum of DHBQ bleached at pH 12 (Figure 25), viewer degradation products are found – in fact, only acetic acid (singlet at 1.92 ppm) and formic acid (singlet at 8.46 ppm) could be determined which were also present in the bleaching of DHBQ at pH 2. Bleaching at alkaline conditions causes the ozone molecule to disintegrate rapidly forming hydroxy radicals as a result (Ek et al. 2009b; Hruschka 1986; Patt et al. 1991). Hydroxyl radicals lead to unselective reactions that involve the formation of other radical species, such as (•OH, O_2^-). Naturally, ozone bleaching on an industrial scale would also work at alkaline pH, however the major drawback is the degradation of the cellulose itself, resulting in low molecular weight products (Chirat and Lachenal 1997; Lachenal et al. 2009).

In organic solvents the stability of ozone is increased because water and radical forming OH^- ions are absent which makes ozone the main active species (Biń 2006; Musl 2017). The formation of coloured intermediates during the ozone treatment of DHNQ and 2,6-HAP as described in chapter 3.3 and 3.5 indicates that the ozone-chromophore degradation happens in several oxidation steps. Furthermore, it should be considered that the molecules provide more than one possible site for ozone to react. Also in the case of benzoquinone ozone can attack on both sites of the C=C double bond forming monozonides and diozonides as shown by studies of Bernatek and Straumsgård (1959) in Figure 38. Further the studies of Bernatek and

Straumsgård (1959) show that the cleavage of these ozonides give carboxylic acids as reaction products of which formic acid is one of the main degradation products.

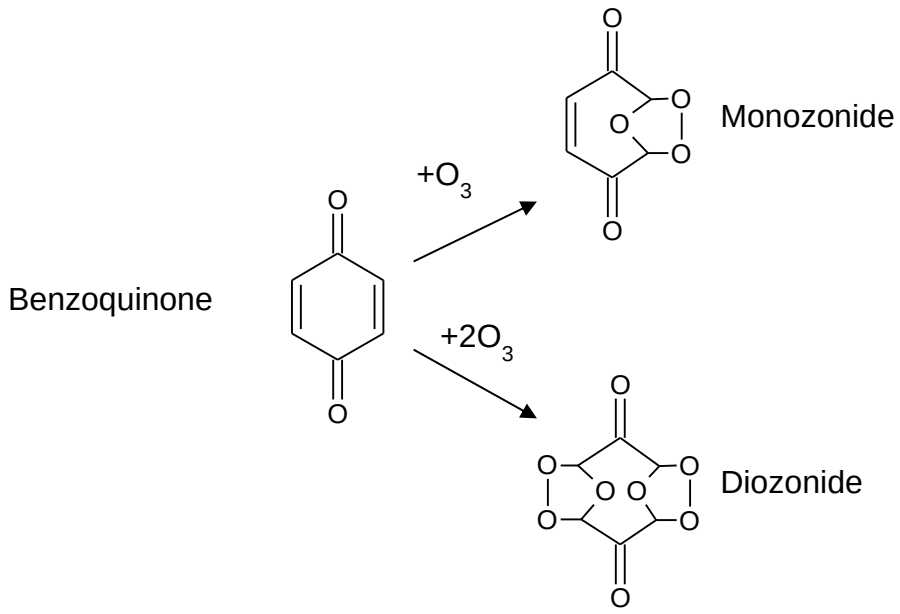

Figure 38: Ozonolysis of benzoquinone forming of monozonide and diozonide (Bernatek and Straumsgård 1959).

4 Conclusion

The key chromophores 2,5-dihydroxy-1,4-benzoquinone (DHBQ), 5,8-dihydroxy-1,4-naphthoquinone (DHNQ), 2,5-dihydroxyacetophenone (2,5-HAP,), 2,6-dihydroxyacetophenone (2,6-HAP) as well as the chromophore tetrahydroxy-1,4-benzoquinone (THBQ) and the model compound 2-Hydroxy-1,4-naphthoquinone (2-OH-NQ) could be bleached until full decolouration with ozone in aqueous solution at pH 2 and in organic solvents at room temperature. Even though bleaching in organic solvents is not crucial for industrial bleaching it gave reference data for comparison.

Different carboxylic acids could be identified as reaction products by NMR and GC-MS analysis: acetic acid (**11**), formic acid (**12**), glycolic acid (**13**), oxalic acid (**14**), malonic acid (**15**), 2,3-oxirandicarboxylic acid (**16**), lactic acid (**17**), ethylene glycol (**18**), malic acid (**19**) and tartronic acid (**20**).

The same reaction products were found when bleaching in aqueous solution (pH 2) as well as in organic solvents. A comparison of the bleaching kinetics showed comparable bleaching behaviour in both solvents. With these results it can be concluded that the reaction mechanism

proceeds the same way in aqueous and organic solution, i.e. according to the Criegee mechanism (Criegee 1975).

Ozone decomposition and the following radical formation is minimized by acidic conditions at pH 2. In organic solvent ozone is stabilized by the absents of water and OH^- (Biń 2006; Von Gunten 2003; Gierer 1997; Reitberger et al. 1999; Chirat and Lachenal 1997). A comparison of the relative bleaching times shows that bleaching chromophores in organic solvents proceeds faster with the only exception of DHNQ (nearly same time in both solvents). In the case of DHBQ the solution was 57% faster to be colorless when bleached in organic solvent.

However, bleaching in alkaline conditions supports radical formation by ozone decomposition, which resulted in slightly different degradation products. This was observed in the bleaching of DHBQ at pH 12 and room temperature (Horváth et al. 1985). Only acetic acid and formic acid were found in both, pH 2 and pH 12 bleaching experiments. The bleaching of DHBQ in alkaline media took ~40% longer until full decolouration compared to the bleaching in acidic media probably due to resonance stabilisation in alkaline media (Hosoya et al. 2015; Zwirchmayr et al. 2017).

Further, the effect of different salt additives (Na_2SO_4, K_2SO_4, $MgSO_4$ and $CaCl_2$) on the bleaching behaviour of DHBQ were examined. Salts have considerable influence in the bleaching with H_2O_2, as they promote stabilizing complex formation. Because these stabilizing complexes are mostly formed in alkaline media, the salts had no significant influence on the bleaching behaviour of DHBQ (Hosoya et al. 2015). Further the effects of $NaSO_4$ and $CaCl_2$ on the bleaching of DHNQ, 2,5-HAP, 2,6-HAP, THBQ and 2-OH-NQ were investigated. Also, in this case no effects on the bleaching behaviour caused by the salts were identified. This was confirmed by the results of the UV/Vis spectroscopy: the kinetics and shape of the degradation curves were largely similar between bleaching experiments with or without salts added.

5 List of Figures

FIGURE 1: PRIMARY CHROMOPHORES IDENTIFIED BY CRI IN BLEACHED PULPS (TOP ROW) AND THE SECONDARY CHROMOPHORES 6, A CHLORINATED HYDROXYQUINONE AND 7, A SULFONATED HYDROXYQUINONE (BOTTOM ROW). 2
FIGURE 2: THE KEY CHROMOPHORES: 2,5-DIHYDROXY-1,4-BENZOQUINONE (DHBQ, 1), 5,8-DIHYDROXY-1,4-NAPHTHOQUINONE (DHNQ, 5), 2,5-DIHYDROXYACETOPHENONE (2,5-HAP, 4), 2,6-DIHYDROXYACETOPHENONE (2,6-HAP, 9); THE CHROMOPHORETETRAHYDROXY-1,4-BENZOQUINONE (THBQ, 10) AND THE MODEL SUBSTANCE 2-HYDROXY-1,4-NAPHTHOQUINONE (2-OH-NQ, 8). 3
FIGURE 3: THE ELECTROMAGNETIC SPECTRUM OF LIGHT WITH THE CORRESPONDING WAVELENGTHS (ALBERTZ 2007). 4
FIGURE 4: CHARTREUSE GREEN (LEFT) AND CHARTREUSE YELLOW (RIGHT). 5
FIGURE 5: CHROMOPHORES IN SOLID FORM. 5
FIGURE 6: THE MEANING OF A CHINESE CHARACTER IS CHANGED BY A SINGLE DOT (RAGNAR 2000). 7
FIGURE 7: MESOMERIC STRUCTURES OF OZONE (VIEBAHN-HÄNSLER 2006). 12
FIGURE 8: CHAIN REACTION ACCORDING TO REITBERGER ET AL. (1999) OF OZONE DECOMPOSITION DURING THE REACTION WITH THE SUBSTRATE AND O_2. 15
FIGURE 9: THREE STEPS OF THE OZONOLYSIS ACCORDING TO CRIEGEE: A: FORMATION OF A PRIMARY OZONIDE (1,2,3-TRIOXOLANE); B: DECOMPOSITION INTO CARBONYL COMPOUND AND CARBONYL OXIDE; C: ADDITION OF THE CARBONYL OXIDE TO THE CARBONYL COMPOUND TO FORM THE SECONDARY OZONIDE (1,2,4-TRIOXOLANE) (CRIEGEE 1975). 17
FIGURE 10: OZONOLYSIS OF ALKENES FOLLOWED ACID HYDROLYSIS REDUCTION REDUCTION (BECKER ET AL. 1999; MARCH 1992; VOLLHARDT AND SHORE 2000; SONNENBERG 1997). 18
FIGURE 11: SETUP OF THE REACTOR FOR THE BLEACHING OF THE CHROMOPHORES. 20
FIGURE 12: OVERVIEW OF THE PROJECT'S WORKFLOW. 31
FIGURE 13: NMR SPECTRUM OF BLEACHED 2-OH-NQ (Z48) IN AQUEOUS SOLUTION WITH REMAINING 2-OH-NQ AT 7.57 PPM.. 33
FIGURE 14: UV/VIS SPECTRUM OF Z20, 2,6-HAP IN AQUEOUS SOLUTION (PH 2). 34
FIGURE 15: ABSORPTION VERSUS TIME AT A=400NM OF Z20, 2,6-HAP IN AQUEOUS SOLUTION (PH 2). 35
FIGURE 16: UV/VIS SPECTRUM OF Z21, 2,5-HAP IN AQUEOUS SOLUTION (PH 2). 36
FIGURE 17: ABSORPTION VERSUS TIME AT A=400NM OF Z21, 2,5-HAP IN AQUEOUS SOLUTION (PH 2). 36
FIGURE 18: UV/VIS SPECTRUM OF Z22, DHNQ IN AQUEOUS SOLUTION (PH 2). 37
FIGURE 19: ABSORPTION VERSUS TIME: COMPARISON BETWEEN THE ABSORPTION OF 517NM AND 400NM OF Z22, DHNQ IN AQUEOUS SOLUTION (PH 2). 38
FIGURE 20: UV/VIS SPECTRUM OF Z23, DHBQ IN AQUEOUS SOLUTION AT PH 2. 39
FIGURE 21: ABSORPTION VERSUS TIME AT A=400NM OF Z23, DHBQ IN AQUEOUS SOLUTION AT PH 2. 39
FIGURE 22: UV/VIS SPECTRUM OF Z19, 2OHNQ IN AQUEOUS SOLUTION (PH 2). 40
FIGURE 23: ABSORPTION VERSUS TIME AT A=400NM OF Z19, 2OHNQ IN AQUEOUS SOLUTION (PH 2). 40
FIGURE 24: ABSORPTION VERSUS TIME AT A=400NM OF Z23 (CONTROL), Z24 ($MgSO_4$), Z25 ($CaCl_2$), Z26 ($NaSO_4$), Z27 (K_2SO_4), DHBQ IN AQUEOUS SOLUTION (PH 2). 42
FIGURE 25: NMR SPECTRUM OF DHBQ BLEACHED AT PH 12 (TOP) COMPARED TO DHBQ BLEACHED AT PH 2 (BOTTOM). 43
FIGURE 26: DEGRADATION PRODUCTS IDENTIFIED BY NMR AND GC-MS ANALYSIS. ACETIC ACID 11, FORMIC ACID 12, GLYCOLIC ACID 13, OXALIC ACID 14, MALONIC ACID 15, 2,3-OXIRANDICARBOXYLIC ACID 16, LACTIC ACID 17, ETHYLENE GLYCOL 18, MALIC ACID 19 AND TARTRONIC ACID 20. 44
FIGURE 27: COMPARISON OF THE ^1H NMR SPECTRA OF THE KEY CHROMOPHORES AND 2-OH-NQ, WHICH WERE BLEACHED IN AQUEOUS SOLUTION. 48
FIGURE 28: UV/VIS SPECTRUM OF 2,6-HAP IN DCM. (Z13) 50
FIGURE 29: ABSORPTION VERSUS TIME AT A=400NM 2,6-HAP IN DCM. (Z13) 51
FIGURE 30: UV/VIS SPECTRUM OF 2,5-HAP IN DCM. (Z16) 52
FIGURE 31: ABSORPTION VERSUS TIME AT A=400NM 2,5-HAP IN DCM. (Z16) 52
FIGURE 32: UV/VIS SPECTRUM OF DHNQ IN ACETONE. (Z12) 53
FIGURE 33: ABSORPTION VERSUS TIME AT A=400NM DHNQ IN ACETONE. (Z12) 53
FIGURE 34: UV/VIS SPECTRUM OF DHBQ IN ACETONE. (Z6) 54
FIGURE 35: ABSORPTION VERSUS TIME AT A=400NM DHBQ IN ACETONE. (Z6) 54
FIGURE 36: UV/VIS SPECTRUM OF 2-OH-NQ IN ACETONE. (Z14) 55
FIGURE 37: ABSORPTION VERSUS TIME AT A=400NM 2-OH-NQ IN ACETONE. (Z14) 55

FIGURE 38: OZONOLYSIS OF BENZOQUINONE FORMING OF MONOZONIDE AND DIOZONIDE (BERNATEK AND STRAUMSGÅRD 1959). 62
FIGURE 44: ^{1}H NMR SPECTRUM OF DHNQ (Z35), BLEACHED WITH OZONE IN AQUEOUS SOLUTION. THE RESIDUAL MATERIAL COULD NOT FULLY DISSOLVE IN THE USED SOLVENT MEOD (PEAKS AT 3,31 PPM). IDENTIFIED SUBSTANCES ARE MARKED IN RED. 73
FIGURE 45: ^{1}H NMR SPECTRUM OF DHBQ (Z30), BLEACHED WITH OZONE IN AQUEOUS SOLUTION. THE RESIDUAL MATERIAL COULD NOT FULLY DISSOLVE IN THE USED SOLVENT MEOD (PEAKS AT 3,31 PPM). IDENTIFIED SUBSTANCES ARE MARKED IN RED. 74
FIGURE 46: ^{1}H NMR SPECTRUM OF 2,5-HAP (Z31), BLEACHED WITH OZONE IN AQUEOUS SOLUTION. THE RESIDUAL MATERIAL COULD NOT FULLY DISSOLVE IN THE USED SOLVENT MEOD (PEAKS AT 3,31 PPM). IDENTIFIED SUBSTANCES ARE MARKED IN RED. 75
FIGURE 47: ^{1}H NMR SPECTRUM OF 2,6-HAP (Z32), BLEACHED WITH OZONE IN AQUEOUS SOLUTION. THE RESIDUAL MATERIAL COULD NOT FULLY DISSOLVE IN THE USED SOLVENT MEOD (PEAKS AT 3,31 PPM). IDENTIFIED SUBSTANCES ARE MARKED IN RED. 76
FIGURE 48: ^{1}H NMR SPECTRUM OF 2-OH-NQ (Z33), BLEACHED WITH OZONE IN AQUEOUS SOLUTION. THE RESIDUAL MATERIAL COULD NOT FULLY DISSOLVE IN THE USED SOLVENT MEOD (PEAKS AT 3,31 PPM). IDENTIFIED SUBSTANCES ARE MARKED IN RED. 78
FIGURE 49: 1H NMR SPECTRUM OF THBQ (Z36), BLEACHED WITH OZONE IN AQUEOUS SOLUTION. THE USED SOLVENT WAS D2O (PEAKS AT 4.70 PPM). IDENTIFIED SUBSTANCES ARE MARKED IN RED. 78

6 List of Tables

TABLE 1: APPROXIMATE BRIGHTNESS LEVELS OF LIGNOCELLULOSIC MATERIALS ACCORDING TO BIERMANN (1996). 6
TABLE 2: BLEACHING STAGES, THEIR EFFECTS AND CONDITIONS ACCORDING TO SUESS (2010). 7
TABLE 3: OVERVIEW OF UV/VIS MEASUREMENTS CARRIED OUT. 24
TABLE 4: COMPOSITION OF SOLUTIONS IN ORGANIC SOLVENTS. THE CONCENTRATION C IS GIVEN IN MM/L, THE VOLUME OF THE SOLVENT IN ML, THE TIME OF BLEACHING IN SECONDS. 26
TABLE 5: COMPOSITIONS OF AQUEOUS SOLUTION. THE CONCENTRATION C IS GIVEN IN MM/L, THE VOLUME OF THE SOLVENTS IN ML, THE TIME OF BLEACHING IN SECONDS. 27
TABLE 6: COMPOSITIONS OF AQUEOUS SOLUTION WITH SALTS AS ADDITIVE. THE CONCENTRATION C IS GIVEN IN MM/L, THE VOLUME OF THE SOLVENTS IN ML, THE TIME OF BLEACHING IN SECONDS. 29
TABLE 7: DEGRADATION PRODUCTS OF DHBQ (1). THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS. 44
TABLE 8: DEGRADATION PRODUCTS OF DHNQ (2). THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS. 45
TABLE 9: DEGRADATION PRODUCTS OF 2,5-HAP (3). THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS. 45
TABLE 10: DEGRADATION PRODUCTS OF 2,6-HAP (4). THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS. 46
TABLE 11: DEGRADATION PRODUCTS OF 2-OH-NQ (5). THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS. 47
TABLE 12: DEGRADATION PRODUCTS OF THBQ (6). THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES.

THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS. 47
TABLE 13: OVERVIEW OF THE BY GCMS DETERMINATION OF THE DEGRADATION PRODUCTS OBTAINED BY BLEACHING OF THE FIVE CHROMOPHORES. THE RETENTION TIME IS GIVEN IN MINUTES. 49
TABLE 14: DEGRADATION PRODUCTS OF DHBQ (1). THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS. 56
TABLE 15: DEGRADATION PRODUCTS OF DHNQ (2) IN ORGANIC SOLVENT. THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS 57
TABLE 16: DEGRADATION PRODUCTS OF 2,5-HAP (3) IN ORGANIC SOLVENT. THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS 57
TABLE 17: DEGRADATION PRODUCTS OF 2,6-HAP (4) IN ORGANIC SOLVENT. THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS 58
TABLE 18: DEGRADATION PRODUCTS OF 2-OH-NQ (5) IN ORGANIC SOLVENT. THE ^{1}H AND ^{13}C CHEMICAL SHIFTS ARE GIVEN IN PPM. IF POSSIBLE, ^{13}C SHIFTS WERE DERIVED FROM 2D NMR SPECTRA (HSQC, HMBC). RETENTION TIME FROM GC-MS ANALYSIS IS GIVEN IN MINUTES. THE DATA IS REFERRING TO THE TRIMETHYLSILYL ESTER DERIVATES OF THE SUBSTANCES. MOLECULAR WEIGHTS ARE GIVEN IN G/MOL FOR THE UNDERIVATIZED, PROTONATED REACTION PRODUCTS 58
TABLE 19: CALCULATED AND AVERAGED BLEACHING TIMES FOR EACH CHROMOPHORE FOR EXPERIMENTS CARRIED OUT IN AQUEOUS SOLUTION AND IN ORGANIC SOLVENTS TO EVALUATE THE STABILITY RELATIVE TO EACH OTHER CHROMOPHORE. THE BLEACHING TIME IS CALCULATED FOR A CHROMOPHORE CONCENTRATION OF 1MM, BLEACHED WITH AN OZONE FLOW OF 1.05 G O_3/H OR 0.021 G O_3/L. THE RATIO BETWEEN VOLUME [L] OF SOLVENT AND MASS OF OZONE [G O_3/H] ADDED AMOUNTS 1:3.5. 60

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8 Appendix

8.1 NMR results of DHNQ bleached in aqueous solution

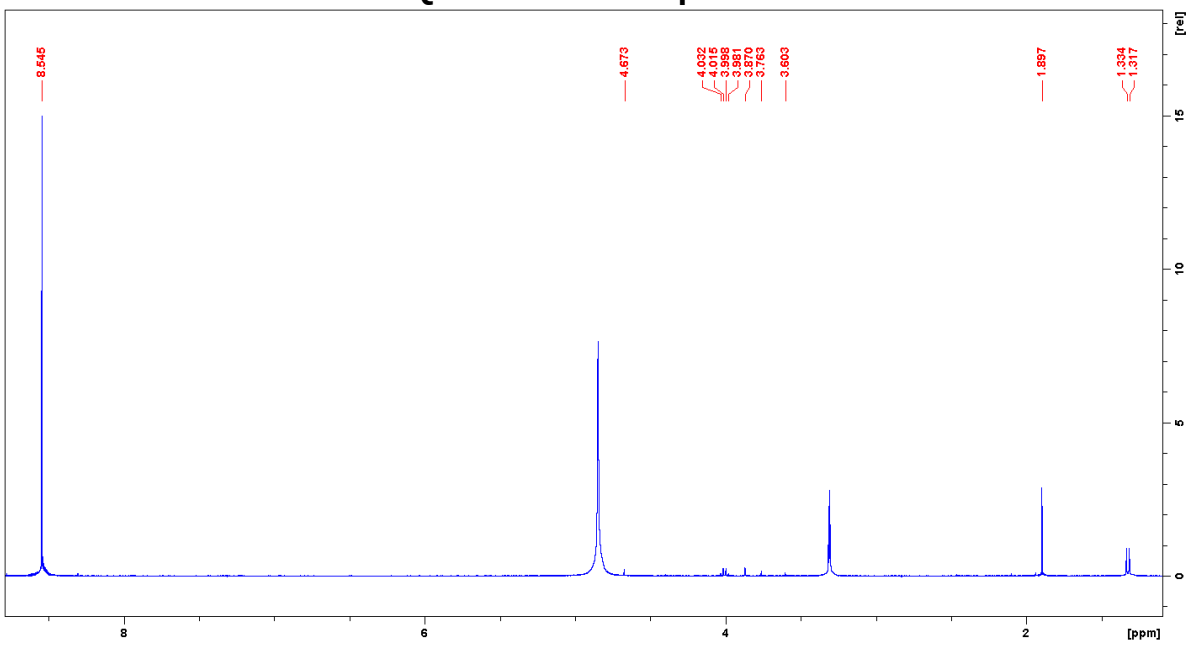

Figure 39: ^{1}H NMR spectrum of DHNQ (Z35), bleached with ozone in aqueous solution. The residual material could not fully dissolve in the used solvent MeOD (peaks at 3,31 ppm). Identified substances are marked in red.

NMR Identified substances from bleached DHNQ in aqueous solution:

Acetic acid: ^{1}H NMR (MeOD): δ [ppm] 1.90 (s, 3H, CH_3) ^{13}C NMR (MeOD): 23,9 (CH_3)

Ethylen glycol: ^{1}H NMR (MeOD): δ [ppm] 3.60 (s, 2H, CH_2), ^{13}C NMR (MeOD): 63.8 (CH_2)

Formic acid: ^{1}H NMR (MeOD): δ [ppm] 8.55 (s, 1H, CH), ^{13}C NMR (MeOD): 170.2 (CH)

Glycolic acid: ^{1}H NMR (MeOD): δ [ppm] 3,85 (s, 2H, CH_2), ^{13}C NMR (MeOD): 60.5 (CH_2), 176 (CO)

Lactic acid: ^{1}H NMR (MeOD): δ [ppm] 1.31 (d, 3H, *J*=6,85 Hz, CH_3) 4.01 (q, 1H, *J*=6,85 Hz, CH) ^{13}C NMR (, MeOD): 21.5 (CH_3) 69.3 (CH), 182.2 (CO)

2,3-Oxiranedicarboxylic acid: ^{1}H NMR (MeOD): δ [ppm] 3.76 (s, 1H, CH) ^{13}C NMR (MeOD): 52.3 (CH)

Tatronic acid: ^{1}H NMR (MeOD): δ [ppm] 4.67 (s, 1H, CH) ^{13}C NMR (MeOD): 62.4 (CH)

8.1.1 NMR results of DHBQ bleached in aqueous solution

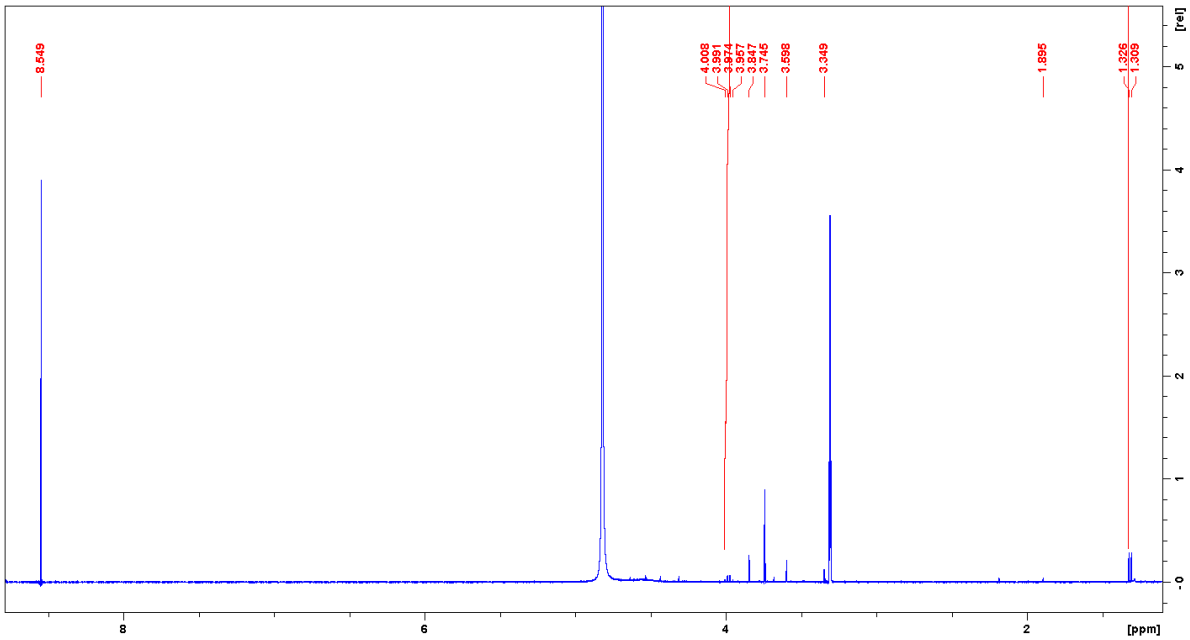

Figure 40: ^{1}H NMR spectrum of DHBQ (Z30), bleached with ozone in aqueous solution. The residual material could not fully dissolve in the used solvent MeOD (peaks at 3,31 ppm). Identified substances are marked in red.

NMR Identified substances from bleached DHBQ in aqueous solution:

Acetic acid: ^{1}H NMR (MeOD): δ [ppm] 1.90 (s, 3H, CH_3), ^{13}C NMR (MeOD): 23.9 (CH_3), 178.1 (CO)

Ethylen glycol: ^{1}H NMR (MeOD): δ [ppm] 3.60 (s, 2H, CH_2), ^{13}C NMR (MeOD): 63.8 (CH_2)

Formic acid: ^{1}H NMR (MeOD): δ [ppm] 8.55 (s, 1H, CH), ^{13}C NMR (MeOD): 170.2 (CO),

Glycolic acid: ^{1}H NMR (MeOD): δ [ppm] 3,85 (s, 2H, CH_2), ^{13}C NMR (MeOD): 60.5 (CH_2), 176 (CO)

Lactic acid: ^{1}H NMR (MeOD): δ [ppm] 1.31 (d, 3H, *J*=6,85 Hz, CH_3), 4.01 (q, 1H, *J*=6,85 Hz, CH), ^{13}C NMR (MeOD): 21.5 (CH_3), 69.3 (CH), 182.2 (CO)

Malonic acid: ^{1}H NMR (MeOD): δ [ppm] 3.34 (s, 2H, CH_2), ^{13}C NMR (MeOD): 49.1 (CH_2), 179.9 (CO)

2,3-Oxiranedicarboxylic acid: ^{1}H NMR (MeOD): δ [ppm] 3.76 (s, 1H, CH), ^{13}C NMR (MeOD): 52.3 (CH), 165.9 (CO)

8.1.2 NMR results of 2,5-HAP bleached in aqueous solution

Figure 41 shows 2,5-HAP. It was possible to identify some of the mayor signals in this spectrum which are marked by their ppm value in figure 6. Contrary to the previous two spectra of DHBQ and DHNQ, in the spectrum of 2,5-HAP a bigger variety of singlet signals can be observed. The peaks in the range of 2-2,5 ppm could not be identified.

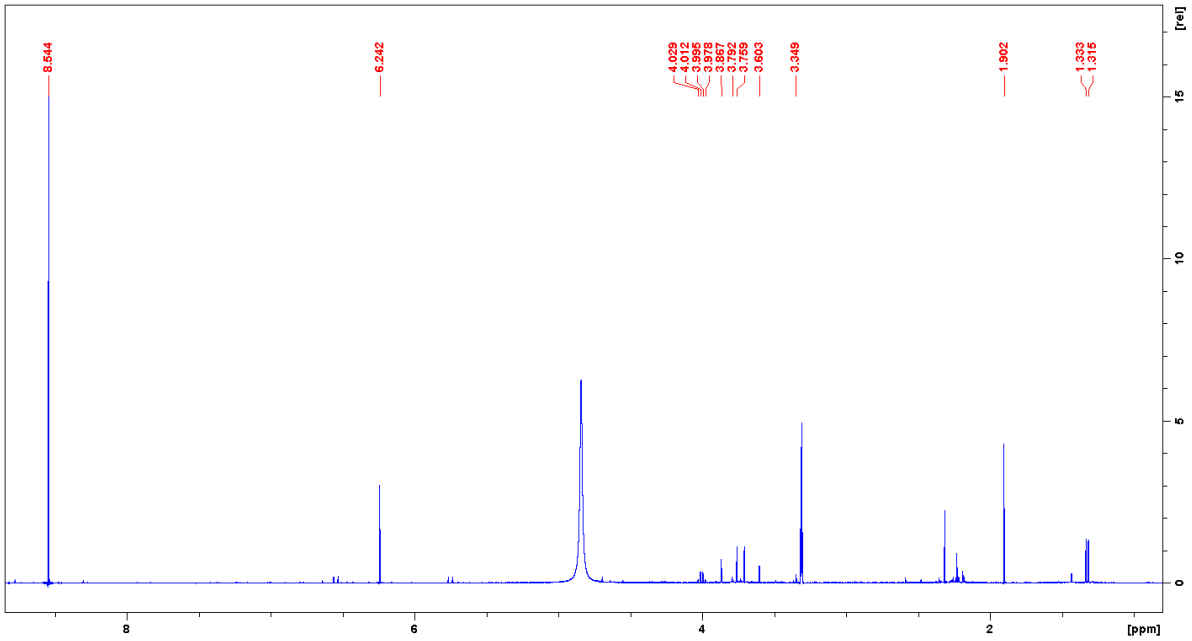

Figure 41: ^{1}H NMR spectrum of 2,5-HAP (Z31), bleached with ozone in aqueous solution. The residual material could not fully dissolve in the used solvent MeOD (peaks at 3,31 ppm). Identified substances are marked in red.

NMR Identified substances from bleached 2,5-HAP in aqueous solution:

Acetic acid: ^{1}H NMR (MeOD): δ [ppm] 1.90 (s, 3H, CH_3), ^{13}C NMR (MeOD): 23.9 (CH_3), 178.1 (CO)

Ethylen glycol: ^{1}H NMR (MeOD): δ [ppm] 3.60 (s, 2H, CH_2), ^{13}C NMR (MeOD): 63.9 (CH_2)

Formic acid: ^{1}H NMR (MeOD): δ [ppm] 8.54 (s, 1H, CH), ^{13}C NMR (MeOD): 170.2 (CO)

Glycolic acid: ^{1}H NMR (MeOD): δ [ppm] 3.86 (s, 2H, CH_2), ^{13}C NMR (MeOD): 60.5 (CH_2), 176 (CO)

Lactic acid: ^{1}H NMR (MeOD): δ [ppm] 1.31 (d, 3H, *J*=6,85 Hz, CH_3), 4.01 (q, 1H, *J*=6,85 Hz, CH), ^{13}C NMR (MeOD): 21.5 (CH_3), 69.3 (CH), 182.2 (CO)

Maleic acid: ^{1}H NMR (MeOD): δ [ppm] 6.24 (s, 1H, CH), ^{13}C NMR (MeOD): 136.3 (CH), 166.5 (CO)

Malonic acid: ^{1}H NMR (MeOD): δ [ppm] 3.35 (s, 2H, CH_2), ^{13}C NMR (MeOD): 46.1 (CH_2), 179.9 (CO)

2,3-Oxiranedicarboxylic acid: ^{1}H NMR (MeOD): δ [ppm] 3.76 (s, 1H, CH), ^{13}C NMR (MeOD): 52.2 (CH), 165.9 (CO)

8.1.3 NMR results of 2,6-HAP bleached in aqueous solution

Figure 42 shows the spectrum of 2,6-HAP which almost looks identical to the spectrum of 2,5-HAP. It is not surprising that 2,5-HAP and 2,6-HAP share the same composition of degradation products.

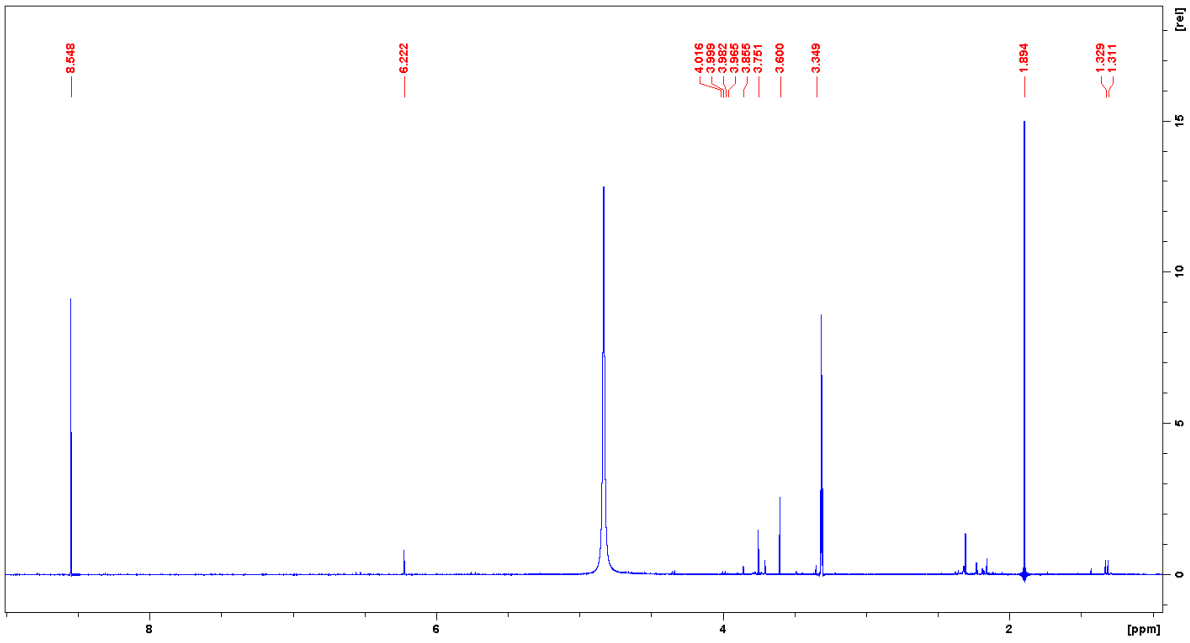

Figure 42: ^{1}H NMR spectrum of 2,6-HAP (Z32), bleached with ozone in aqueous solution. The residual material could not fully dissolve in the used solvent MeOD (peaks at 3,31 ppm). Identified substances are marked in red.

NMR Identified substances from bleached 2,6-HAP in aqueous solution:

Acetic acid: ^{1}H NMR (MeOD): δ [ppm] 1.90 (s, 3H, CH_3), ^{13}C NMR (MeOD): 23.9 (CH_3), 178.1 (CO)

Ethylen glycol: ^{1}H NMR (MeOD): δ [ppm] 3.60 (s, 2H, CH_2), ^{13}C NMR (MeOD): 63.8 (CH_2)

Formic acid: ^{1}H NMR (MeOD): δ [ppm] 8.55 (s, 1H, CH), ^{13}C NMR (MeOD): 170.2 (CO)

Glycolic acid: ^{1}H NMR (MeOD): δ [ppm] 3.86 (s, 2H, CH_2), ^{13}C NMR (MeOD): 60.5 (CH_2), 176 (CO)

Lactic acid: ^{1}H NMR (MeOD): δ [ppm] 1.31 (d, 3H, *J*=6,85 Hz, CH_3), 4.01 (q, 1H, *J*=6,85 Hz, CH), ^{13}C NMR (MeOD): 21.5 (CH_3), 69.3 (CH), 182.2 (CO)

Maleic acid: ^{1}H NMR (MeOD): δ [ppm] 6.24 (s, 1H, CH), ^{13}C NMR (MeOD): 136.3 (CH), 166.5 (CO)

Malonic acid: ^{1}H NMR (MeOD): δ [ppm] 3.34 (s, 2H, CH_2), ^{13}C NMR (MeOD): 49.1 (CH_2), 179.9 (CO)

2,3-Oxiranedicarboxylic acid: ^{1}H NMR (MeOD): δ [ppm] 3.76 (s, 1H, CH), ^{13}C NMR (MeOD): 52.3 (CH), 165.9 (CO)

8.1.4 NMR results of 2OHNQ bleached in aqueous solution

Figure 43 shows 2-OH-NQ, as described above, aromatic structures in the range of 7-8 ppm were remaining in the bleached residual material.

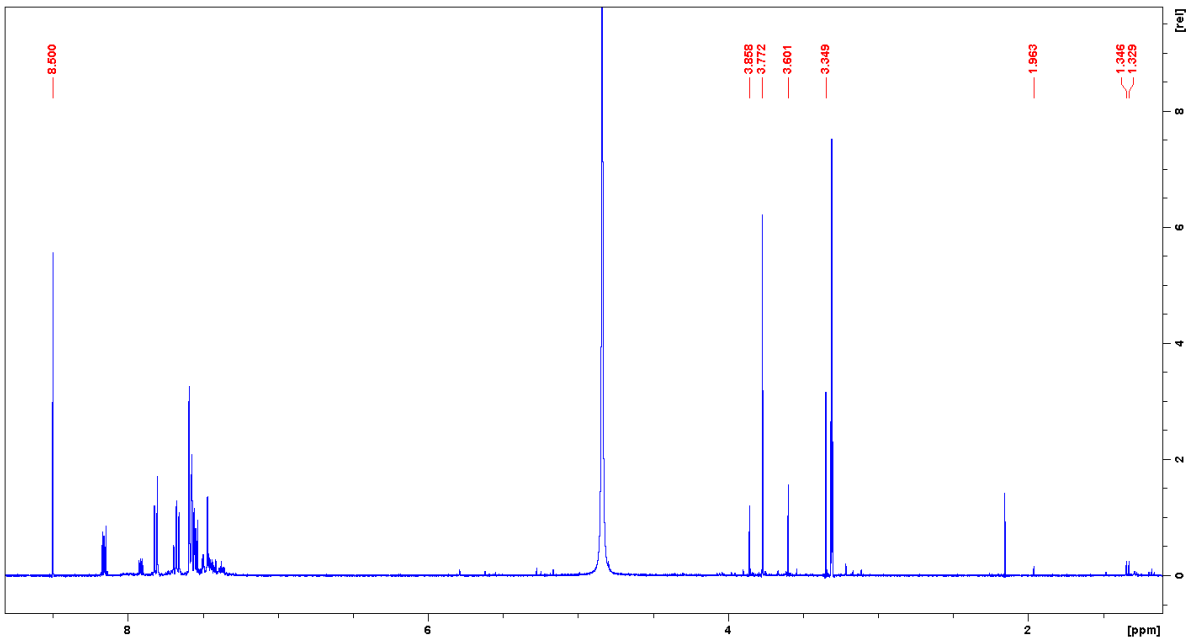

Figure 43: ^{1}H NMR spectrum of 2-OH-NQ (Z33), bleached with ozone in aqueous solution. The residual material could not fully dissolve in the used solvent MeOD (peaks at 3,31 ppm). Identified substances are marked in red.

NMR Identified substances from bleached 2OHNQ in aqueous solution:

Acetic acid: ^{1}H NMR (MeOD): δ [ppm] 1.90 (s, 3H, CH_3), ^{13}C NMR (MeOD): 23.9 (CH_3), 178.1 (CO)

Ethylen glycol: ^{1}H NMR (MeOD): δ [ppm] 3.60 (s, 2H, CH_2), ^{13}C NMR (MeOD): 63.8 (CH_2)

Formic acid: ^{1}H NMR (MeOD): δ [ppm] 8.55 (s, 1H, CH), ^{13}C NMR (MeOD): 170.2 (CO)

Glycolic acid: ^{1}H NMR MeOD): δ [ppm] 3.86 (s, 2H, CH_2), ^{13}C NMR (MeOD): 60.5 (CH_2), 176 (CO)

Lactic acid: ^{1}H NMR (MeOD): δ [ppm] 1.31 (d, 3H, *J*=6,85 Hz, CH_3), 4.01 (q, 1H, *J*=6,85 Hz, CH), ^{13}C NMR (MeOD): 21.5 (CH_3), 69.3 (CH), 182.2 (CO)

2,3-Oxiranedicarboxylic acid: ^{1}H NMR (MeOD): δ [ppm] 3.76 (s, 1H, CH), ^{13}C NMR (MeOD): 52.3 (CH), 165.9 (CO)

8.1.5 NMR results of THBQ bleached in aqueous solution

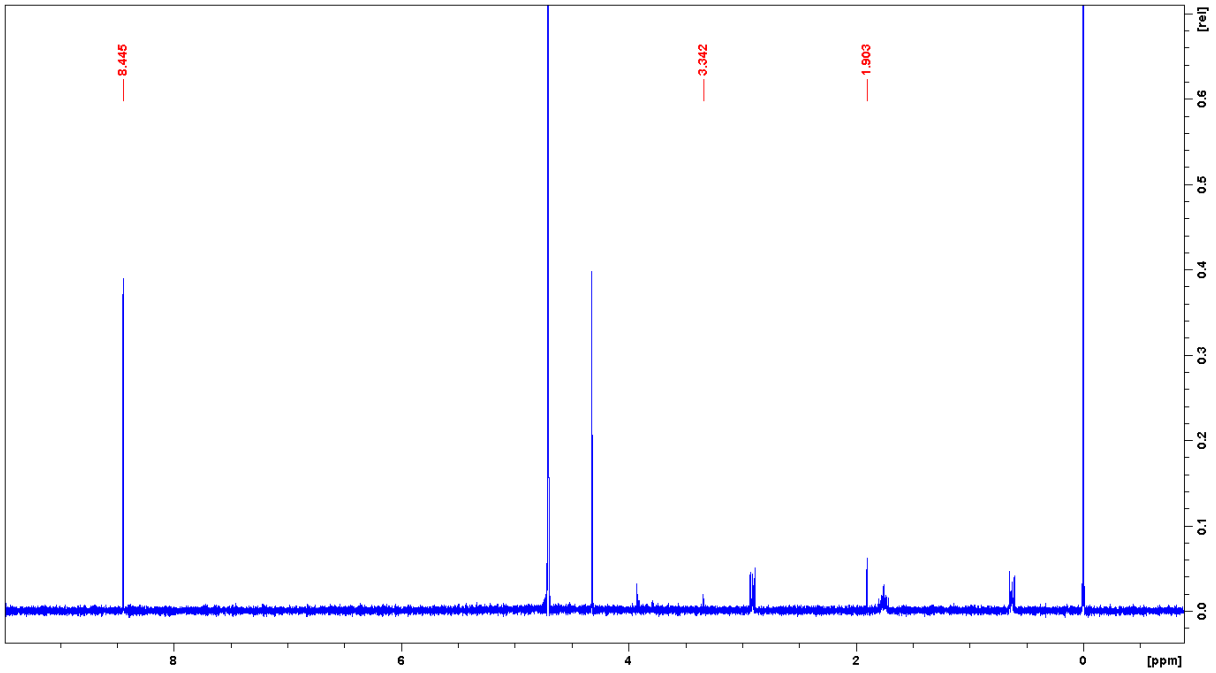

Figure 44: 1H NMR spectrum of THBQ (Z36), bleached with ozone in aqueous solution. The used solvent was D2O (peaks at 4.70 ppm). Identified substances are marked in red.

Appendix

NMR Identified substances from bleached THBQ in aqueous solution:

Acetic acid: ^{1}H NMR (MeOD): δ [ppm] 1.90 (s, 3H, CH_3), ^{13}C NMR (MeOD): 23.9 (CH_3), 178.1 (CO)

Formic acid: ^{1}H NMR (MeOD): δ [ppm] 8.55 (s, 1H, CH), ^{13}C NMR (MeOD): 170.2 (CO)

Malonic acid: ^{1}H NMR (MeOD): δ [ppm] 3.34 (s, 2H, CH_2), ^{13}C NMR (MeOD): 49.1 (CH_2), 179.9 (CO)

Lebenslauf

BSc Holz – und Naturfasertechnologie

David Budischowsky

AUSBILDUNG

Feb. 2016 – Sep. 2019	**Universität für Bodenkultur Wien** Masterstudium stoffliche und energetische Nutzung nachwachsender Rohstoffe. Masterarbeit im Department für Chemie zum Thema *Ozone Bleaching of Cellulosic Chromophores*, Prof. Thomas Rosenau, Prof. Ute Henniges.
Jan. 2018 – Jun. 2018	**Norwegian University of Life Sciences (NMBU)**, Auslandssemester in Ås, Norwegen – im Rahmen des Erasmus+ Programmes.
Sep. 2011– Feb. 2016	**Universität für Bodenkultur Wien** Bachelorstudium Holz- und Naturfasertechnologie. Bachelorarbeit im Department für Holztechnologie und Nachwachsende Rohstoffe zum Thema *Verbundwerkstoffe aus Abfällen*, Prof. Wimmer.
2005 – 2010	**Realgymnasium Diefenbachgasse** Laptopklasse, Matura mit schulautonomer Schwerpunktsetzung in Informations- und Kommunikationstechnologie.
2002 – 2005	**Evangelisches Gymnasium und Werkschulheim**

BERUFSERFAHRUNG

Jul.– Okt. 2018	**Praktikum bei Mondi Group im zentralen Qualitätsmanagement für Konsumgüterverpackungen** (Wien): Recherche zu verschiedenen Dokumentenmanagementsystemen, Analyse und Aufbereitung von KPI's, Dokumentenablage und Dokumentenverwaltung, Werkbesuch Korneuburg (QS Bereich).
Feb. – Jul. 2017	**Studentischer Mitarbeiter an der Universität für Bodenkultur** am Chemieinstitut für nachwachsende Rohstoffe (Tulln): Mitwirken am Projekt *Chromophore II* in Kombination mit der Masterarbeit. Laborversuche, Präsentation der Ergebnisse bei Austropapier und Lenzing AG, Werkbesuch Lenzing.

Lebenslauf

Sep.– Nov. 2015	**Praktikum bei HolzREC Recycling & Verwertung GmbH** (Herzogenburg): Qualitative Beurteilung des Abfalls „Rechengut“ für die Verwertung als Ersatzbrennstoffprodukt: Probenahme und Laboruntersuchungen (Feinanteil und Aschegehalt), Recherche der Rechtslage (AWG) und Berichterstattung.
Jun. – Jul. 2015	**Praktikum bei Kollwig Holz Handels GmbH** (Böheimkirchen): Qualitätskontrolle der Ware und Abfertigung für den Versandt.
Jul.-Aug. 2008	**Sommerjob bei Brandtner GmbH** (Traiskirchen und Hohenruppersdorf)

TÄTIGKEITEN NEBEN DEM STUDIUM

Okt. 2015 – Jan. 2017	**Kunstforum Wien** (geringfügige Beschäftigung).
2016-2017	**Mathematik Nachhilfe**
Mär. 2019	**Programmierprojekt, automatisierter Twitter-Bot:** veröffentlicht Day-Ahead-Preise des österr. Energiemarktes über Twitter. https://twitter.com/DavidB23152707

ZIVILDIENST

Nov. 2010 – Jul. 2011	**Kuratorium Wiener Pensionisten-Wohnhäuser** (Wien):

SPRACHEN UND EDV KENNTNISSE

Deutsch	Muttersprache
Englisch	Fortgeschritten
Norwegisch	Grundkenntnisse
PC	Experte: MS Office (Word, Excel, Power Point) Fortgeschritten: Python Grundkenntnisse: Matlab, R, OriginPro, AutoCAD