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EXPERIMENTAL INVESTIGATIONS ON THE PROMOTED WET OXIDATION OF MODEL SUBSTANCES

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We and you too, you most of all, dear boy,
will have to pass through the bitter water before we reach the sweet.
But we must be brave of heart and unselfish, and do our duty,
and all will be well!

Bram Stoker (Dracula, 1897)

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Nomenclature

Latin letters

A	mg / L	Lumped initial compounds
A	-	Constant for Himmelblau correlation
B	mg / L	Lumped intermediates
B	-	Constant for Himmelblau correlation
BOD	mg-O_2 / L	Biological Oxygen Demand
C	mg / L, mol /L	Concentration Constant for Himmelblau correlation Carbon atom
C	mg / L	Lumped intermediates/products
COD	mg-O_2 / L	Chemical Oxygen Demand
D	-	Constant for Himmelblau correlation
D	mg / L	Lumped products
DC	mg-C / L	Dissolved Carbon
DOC	mg-C / L	Dissolved Organic Carbon
E	-	Constant for Himmelblau correlation
E_A	kJ / mol	Activation Energy (Arrhenius)
H	atm	Henry's coefficient
k	s	Constant of first-order reaction rate
k_0	s^{-1}	Frequency factor (Arrhenius)
K	L / mol, L / g	Equilibrium constant
p	atm, bar, Pa	Pressure, partial pressure
p	-	negative logarithm
pH	-	$-\log([H^+]\cdot 1\ \mathrm{mol}^{-1})$
R	8.31451 J/(mol·K)	Universal gas constant
T	K	Absolute temperature
TOC	mg-C /L	Total Organic Carbon
x	-	Mole fraction

X	-	Conversion

Greek letters

ϑ	°C	Temperature
$\tau_{1/2}$	s	Lifetime
ρ	kg / m^3	Density
x	-	Mole fraction

Subscripts and Superscripts

0	Initial
°	Standard
‘	Changed state, simplified, combined
A	Acid
Ani	Aniline
aq	dissolved in water
Dye	Azo dye Orange II
i	Initiator, compound
I	Promoter
NB	Nitrobenzene
m	Order of promoter
p	Propagation
tot	Total
t	Time, termination
Red	Reduction
x	mole fraction

Abbreviations

AOP/AOT	Advanced Oxidation Process/Technology
AU	Absorption Unit
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
CV	Coefficient of Variance
DIN	Deutsche Industrie-Norm
DOC	Dissolved Organic Carbon
EDTA	Ethylenediaminetetraacetic acid
ETH/ETHZ	Eidgenössische Technische Hochschule Zürich
FID	Flame Ionisation Detector
FTIR	Fourier Transformation-InfraRed (Spectroscopy)
GC	Gas-Chromatography
HPLC	High Performance (Pressure) Liquid Chromatography
IC	Inorganic Carbon, Ion Chromatography
LOPROX	Low Pressure Oxidation (Bayer AG)
M	Monomer
MOC	Mean Oxidation Number of Carbon
MS	Mass Spectrometer/Spectrometry
NaOH	Sodium hydroxide
NDOC	Non-dissolved organic carbon, TOC-DOC
NMR	Nuclear Magnetic Resonance
NTA	Nitrilotriacetic acid
OC	Organic Carbon, On Column
PANI	Polyaniline
Ph	Phenyl
ppm	parts per million
PTFE	PolyTetraFluoroEthylene
R	Hydrocarbon chain, rest
RI	Refractive Index
RP	Reversed Phase
RT	Retention Time
SC	Suspended Carbon
SCWO	Super Critical Water Oxidation
TC	Total carbon
TIC	Total Inorganic Carbon
TOC	Total organic carbon
TOD	Theoretical/Total Oxygen Demand
UV	Ultra Violet (Spectrum)
VC	Variance of coefficency
VIS	Visible (Spectrum)
WAO/WO	Wet (Air) Oxidation

Zusammenfassung

Die Nassoxidation mittels vorbehandelter Gallussäure (Promoter), Eisenionen und Sauerstoff wurde im Temperaturbereich 130°C...190°C und bei pH = 2 experimentell untersucht. Als Modell-Substanzen wurden drei organische, stickstofhaltige Verbindungen ausgewählt und untersucht. Die untersuchten Verbindungen waren Anilin, Nitrobenzol und der Azo-Farbstoff Orange II. Diese organischen Verbindungen unterscheiden sich aufgrund ihrer oxidativen Abbaubarkeit und Struktur.

Die Nassoxidiatonsversuche im sauren pH-Bereich ohne Promoterzugabe ergaben für die einzelnen Modell-Substanzen unterschiedliche Effekte. Der Azo-Farbstoff zersetzt sich ohne beobachtbare Verzögerung, während Anilin und Nitrobenzol keine Umsätze grösser als 10% innerhalb von 15 min Reaktionsdauer zeigten.

Die Versuche mittles Promoterzugabe ergaben für die untersuchten Modell-Substanzen eine Erhöhung des Umsatzes verglichen mit den erwähnten Experimenten ohne Promoter-Zugabe. Während der Sauerstoffpartialdruck über 10 bar keinen (im Fall des Farbstoffes) oder geringen (im Fall des Nitrobenzols) Einfluss auf die Umsatzgeschwindigkeit der Modell-Substanzen hat, bestimmt die Reaktionstemperatur die Umsatzrate und den Umsatzgrad deutlich.

Für den Azo-Farbstoff wurde der vollständige Abbau des Farbstoffes selbst bei einer Reaktionstemperatur von 130°C nach 60 min beobachtet. Durch Variation der Promotermenge wurde ein Einfluss der Promotermenge erster Ordnung auf die Abbaukinetik bestimmt und durch ein Geschwindigkeitsgesetz beschrieben. Nitrobenzol wird ebenfalls vollständig abgebaut, aber erst bei höherer Temperatur (160°C nach 45 min). Bei der Analyse der Nebenprodukte wurden Nitrophenole und Nitrobenzole nachgewiesen. Die Nitrophenole wurden erst bei Temperaturen höher als 130°C abgebaut. Anilin wurde erst bei 190°C nach 50 min vollständig abgebaut. Dabei wurde als Zwischenprodukt ein Feststoff festgestellt.

Bei allen Modellsubstanzen konnte Essigsäure und Ameisensäure als die wichtigsten, nachweisbaren Endprodukte nachgewiesen werden. Damit erreicht die Nassoxidation mittels Promoter keine vollständige Mineralisierung der organischen Substanzen. Die Untersuchungen der Nassoxidation mittels Promoter zeigen, dass die Menge des Promoters einen grossen Einfluss auf die Abbauleistung, ausgedrückt in Abbaugeschwindigkeit und -grad hat. Damit verfügt der Anwender neben Reaktionstemperatur und Sauerstoffpartialdruck über einen weiteren Parameter in der Nassoxidation, nämlich die Promotermenge. Der Promoter zerfällt bei der Anwendung in Carbonsäuren und Kohlendioxid. Die toxischen oder biologisch schwer abbaubaren Substanzen werden dabei umgesetzt. Dadurch wird die biologische Abbaubarkeit erhöht und das vorbehandelte Abwasser kann nach einer Neutralisierung der biologischen Stufe zugeführt werden. Das Verfahren zeigt eine deutliche Verbesserung der Nassoxidation bei den untersuchten Substanzen mit Hilfe des Promoters.

Summary

The wet oxidation using pre-treated gallic acid (promoter), Fe(II)-ions and oxygen was experimentally examined. The temperature range was between 130°C and 190°C; the experiments were performed with acidic solutions (pH=2). Three model substances were chosen in order to investigate the influence of the investigated process on different organic compounds. The organic compounds were aniline, nitrobenzene and the azo dye Orange II. These three model substances were chosen due to their different reactivities in reported oxidative treatments.

The experimental investigations with acidic solutions of the model substances without any addition of the promoter (wet oxidation) showed different effects. The wet oxidation of the azo dye lead to an immediate degradation and no delay (induction time) was observed. Aniline and nitrobenzene showed only small degradation rates and the conversion was not higher than 10% in the first 15 min of reaction time.

By addition of the promoter (promoted wet oxidation), all the examined model substances showed an increase in conversion compared with the mentioned experiments without addition of the promoter. The oxygen pressure higher then 10 bar showed no (azo dye) or small (nitrobenzene) influence on the conversion of compounds. The reaction temperature showed for the unpromoted and the promoted wet oxidation a significant influence indicated by increased conversion rates and lowered final effluent concentrations of the examined model substances.

The promoted wet oxidation of the azo dye Orange II revealed the complete degradation of the compound at 130°C after 60 min of reaction time. By variation of the promoter amount, a change in the degradation kinetic of the dye was observed. A description of the temperature and promoter influence was evaluated for the promoted wet oxidation of the azo dye. The treatment of nitrobenzene solutions showed also complete conversion of the examined compound after 45 min of reaction time and 160°C of reaction temperature. As intermediates, the three isomers of nitrophenol were identified by HPLC. The formed nitrophenols seem to be recalcitrant and only at reaction temperatures higher than 130°C, a conversion of the nitrophenols was observed. The promoted wet oxidation of aniline showed complete conversion at 190°C after 50 min of reaction time. The observed intermediates were mainly a black precipitate and phenol in small concentrations.

With all of the examined model substances, acetic acid and formic acid were identified as the main observable products. Therefore, the promoted wet oxidation leads not to a complete mineralisation of the examined organic compounds.

The important parameters in the promoted wet oxidation are the reaction temperature and the ratio between promoter amount and pollutant concentration. In addition, the behaviour of the first intermediates of the organic pollutant is important for the over-all performance of the intended process.

By the addition of the promoter, the classical wet oxidation may be enhanced. The conversion of toxic organic compounds to biodegradable products at moderate conditions is possible using the promoted wet oxidation. Especially recalcitrant compounds can be easily converted without using heterogeneous catalysts or dissolved toxic metal ions. Therefore, the effluent of the promoted wet oxidation can be biologically treated after pH-adjustment. The promoter itself decomposes to biodegradable carboxylic acids and carbon dioxide. These facts suggest that the promoted wet oxidation at moderate conditions is a favourable pre-treatment step for industrial wastewater disposal.

1 Introduction

This investigation focuses on the promoted wet oxidation. The objective of this work is to gain a deeper understanding of the promoted wet oxidation and to investigate model wastewater close to real industrial wastewaters. Therefore, special attention is given to the influence of the combination of Fe-ions and promoter to accelerate the wet oxidation at moderate conditions. As model substances for industrial wastewaters, three substances have been chosen: the azo dye Orange II, nitrobenzene and aniline.

First, we will present a general description of wet oxidation. We also focus on the range of conditions of the different wastewater treatments. The fundamentals of the promoted wet oxidation deal with the occurring phases in wet oxidation. An introduction in the autoxidation mechanism and the discussion of the used models gives the basis of the current knowledge in wet oxidation. The investigations of the three mentioned compounds will be presented and discussed in the corresponding chapters. The final remarks will compare the results of these investigations and give an outlook for the wet oxidation and for the presented system.

1.1 Oxidative Treatment of Wastewaters

Besides all the obvious and known advantages and disadvantages of industrialisation, a new kind of wastewater was created. The industrial wastewater may contain artificial compounds that are unknown in the biosphere, which are not easily degradable by biological or biochemical pathways in the environment. Therefore, the problems raised by poisoning or by accumulation in the environment had to be solved by the producing industries. We focus on the organic pollutants in the industrial effluents and discuss the known disposal methods.

The biological treatment is the most widely used method to treat wastewater. Especially in Switzerland, the biological purification plants are now treating over 98% of the municipal wastewater. The included biochemical and physical processes are well established and the requirements are also high. A modern wastewater treatment plant has to accomplish several duties, *i.e.* the reduction of the colour, the odour, the chemical oxygen demand (COD), the total organic carbon (TOC) and the nitrogen- and phosphorus-content. In order to treat the domestic, the activated sludge process has been the most commonly used process.

The activated sludge process is considered to be the most cost-effective way to remove the organic matter from wastewater. Besides that, it is very flexible and can be adapted to almost any type of biological wastewater treatment problem. The limits of biological treatment systems are mainly given by concentration and effluent volume. For industrial wastewaters, the biological treatment is the first choice, but non-biodegradable or toxic substances are not completely eliminated or are partially deposited in the sewage sludge.

To treat toxic or non-biodegradable compounds, different treatment processes are possible. We will distinguish between separation and destructive wastewater treatment processes.

The separation processes divide the wastewater into an aqueous phase with a given quality and into a phase containing the toxic or non-biodegradable pollutants. The pollutants may be deposed on a solid phase (*e.g.* filtration/ adsorption by activated carbon), in a liquid phase (*e.g.* liquid-liquid-extraction, distillation) or in a gaseous phase (*e.g.* stripping). These processes lead to purified effluents (*i.e.* water), but the pollutants are not chemically converted or mineralised. If the separated pollutants can not be recycled, the disposal problem is not solved.

The destructive processes solve the disposal problem. The regarded pollutants are treated by chemical reactions and these processes lead to mineralised products, *i.e.* carbon dioxide, nitrogen gas. For organic compounds, the oxidative treatment is a destructive process that converts the pollutants to substances with a higher oxidation number. Compared with the pollutant, the formed oxidation products have different solubilities, vapour pressures, biodegradabilities, molecular weights and so on. Among specialised processes, oxidation may be conducted by cheap air as oxidant source. The preferred system for oxidative treatment of toxic substances is incineration. Wet oxidation is also an oxidative treatment process. The formation of mineralisation products depends on the composition of the wastewater and on the treatment conditions. The promoted wet oxidation in a combination with a biological treatment step is a destructive wastewater treatment process for industrial wastewaters and leads to a complete mineralisation of the pollutants.

1.2 Wet Oxidation

The wet oxidation (WO) or Wet Air Oxidation (WAO) process is an aqueous-phase oxidation brought about when an organic and/or inorganic-containing liquid is mixed with a gaseous source of oxygen (usually air) at temperatures of 150 to 320°C. The temperature promotes the reaction. System pressures of 2 to 20 MPa are maintained to control evaporation [2].

The wet oxidation is an exothermal process like the combustion. The combination of waste disposal and energy recovery is the outstanding asset of this process. Combustion has also this advantage, but only at a high heating energy value (*i.e.* COD) of the wastewater. Wastewater with enough combustible organics releases an energy surplus by oxidative treating. Compared with combustion, calculations show the different energy consumption to reach reaction temperature. For that, we neglect the contribution of the pollutants to the specific enthalpy of a wastewater and start with water at 20°C and ambient pressure. The specific enthalpy $h'(20°C, 0.1\ MPa)$ is 84.01 kJ/kg. The heating of the wastewater up to 200°C and pressurising to 2.5 MPa leads to a specific enthalpy of $h'(200°C, 2.5\ MPa) = 857.77$ kJ/kg. The required energy for this change of state is $\Delta h = 768.76$ kJ/kg. The process needs a minimum combustion energy to work autothermally. This equivalence between the energy requirement for the heating and the released energy by combustion is called autogeneous point. The COD has to be higher than this autogeneous point to transform the combustion energy to a usable form *e.g.* as steam. By a given combustion energy of the wastewater (expressed in COD: $\Delta h_{COD} = 15$ kJ/g-O_2 [3]) at 20°C, the minimum COD values has to be of around 51 g-O_2/L. The pollution of a wastewater treated by combustion has to be higher for autothermal operation than by wet oxidation. This is expressed in Figure 1.1.

The break-even point in energy is the autogeneous point, *i.e.* no energy deficit or surplus, and depends on the energy recovery. With improved heat recovery, a lower COD or lower "external" energy input is necessary to run the process autothermally. This is true for the wet oxidation and the combustion. But the evaporation of the water is controlled by the system pressure. During the combustion at ambient pressure, the water evaporates. The system pressure above the vapour pressure prevents in WO-processes the evaporation of the water.

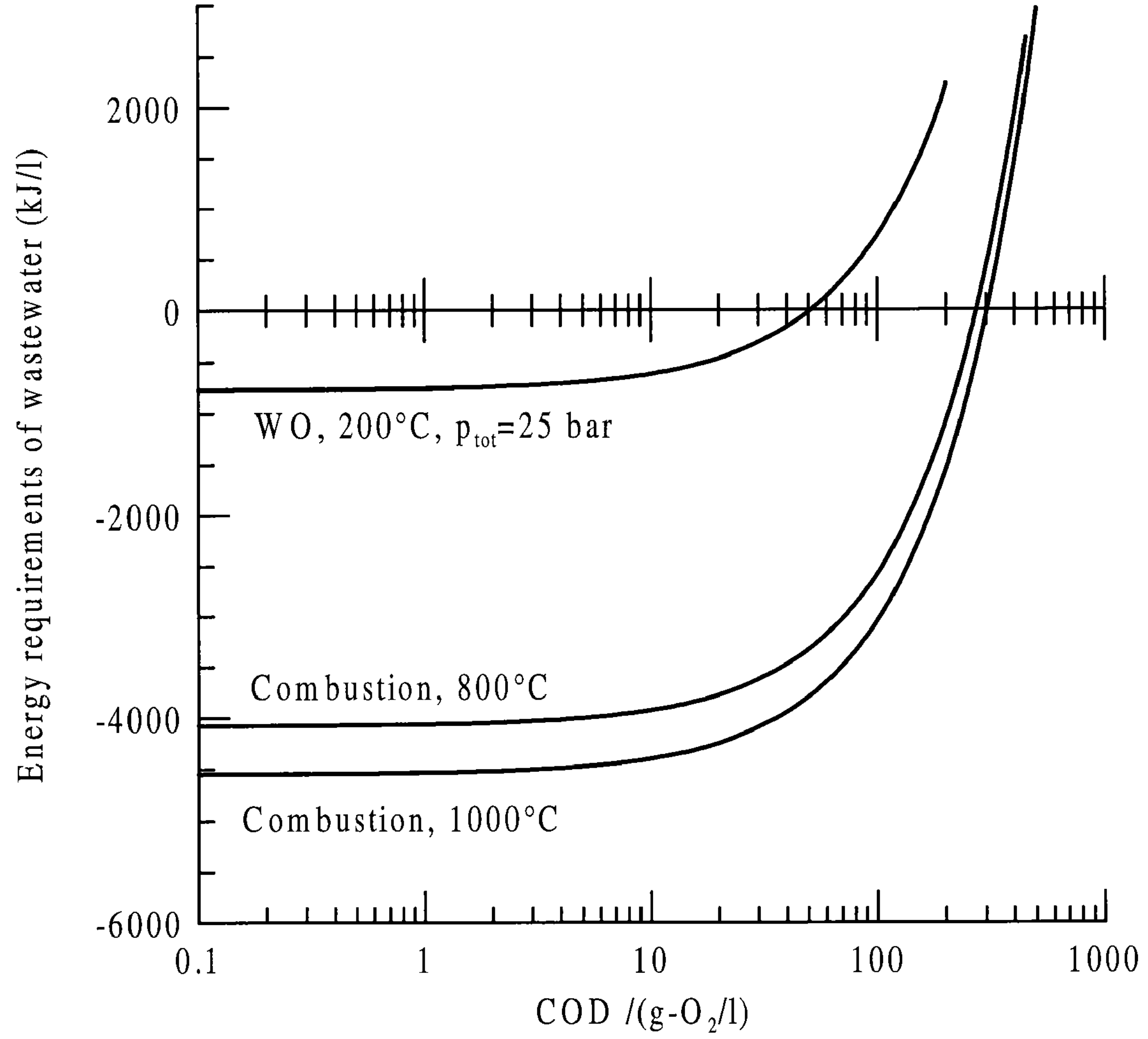

Fig. 1.1: Comparison of combustion and wet oxidation: heat-up energy. Without energy recovery, the autogeneous point for WO is around 51 g-O_2/L; for combustion, the autogeneous points are above 200 g-O_2/L

Therefore, the difference between combustion and wet oxidation in energy requirement is to a great extent due to the heat of vaporisation of the treated water.

The autogeneous points for combustion and WO (see Figure 1.1) are given by Harada [5] and Dietrich *et al.* [4]:

- Wet oxidation: 10 - 15 g-O_2/L
- Combustion (816°C): 300 - 400 g-O_2/L
- Combustion (1093°C): 400 - 500 g-O_2/L

Mishra *et al.* [11] mention that the treating of wastewater streams with COD-concentration higher than 20 g-O_2/L becomes energetically self-sustaining.

The wet oxidation as a disposal process is known for over 50 years and was commercially available since 1954. Since 1944, the wet oxidation process [14] is examined to treat paper mill effluents, sewage sludges, oil refinery streams, *etc.*

The removal of kaolin in wastewaters of paper industries is possible with wet oxidation and makes this process advantageous compared with the aerobic sewage sludge process. Because of the increasing use of the cheaper lime, the wet oxidation is not any more the first choice of disposal process for the paper industry effluents.

Under extreme temperature conditions (> 300°C) and sufficient oxygen pressure, organic matter removal exceeds 95%. But not all kinds of wastewaters require such increased conditions. Industrial effluents containing sulphides (*e.g.* spent caustic) may be treated at temperatures of about 100°C and at ambient air pressure [10]. A complete conversion toward sulphate is easily achieved at these moderate conditions.

The wet oxidation with a gaseous source of the oxidant is normally conducted in a bubble column. The industrial applications are based on this type of reactor.

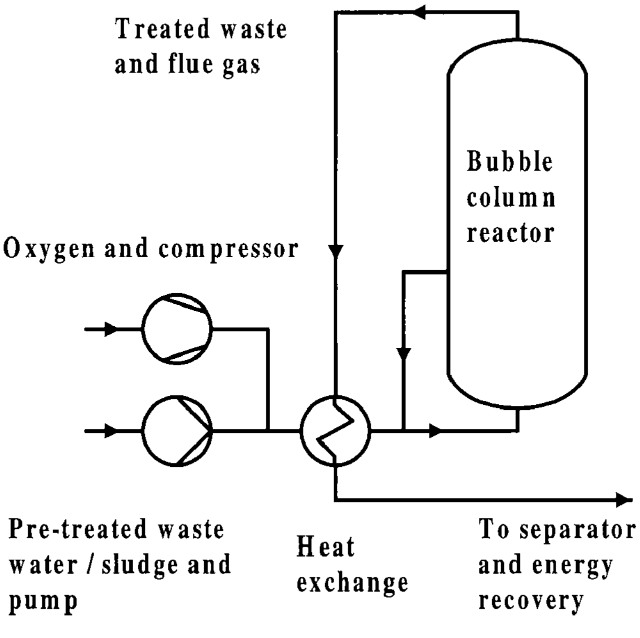

Fig. 1.2: Basic flow diagram of a wet oxidation treatment unit
The gaseous oxidant (air/oxygen) and the wastewater/sludge enter the reactor *via* a heat exchanger. The treated matter leaves the reactor and passes the heat exchanger. The loop increases the input stream into the reactor

The gaseous oxidant, *e.g.* oxygen gas, is introduced in the reactor by a compressor *via* a heat exchanger. The pressurised wastewater or sludge is also inserted in the reactor *via* this heat exchanger. The pre-heated mixture of oxidant and wastewater is mixed with the loop stream and enters the reactor through a nozzle. This loop increases the liquid stream in the nozzle and divides the reactor in a well-mixed lower part and in a bubble column (upper part). This approach is used in the sludge treatment. The optimal reactor and process design, *e.g.* number of reactor, is depending on the disposal problem and therefore on the chosen reaction conditions. Higher temperatures and appropriate catalysts lower the reaction time, but increase the building costs. Lower temperatures enable the use of cheaper materials (*e.g.* reactor material may be glass-lined steel instead of titanium). Without catalysts, lower reaction temperatures may lead to a larger reactor (higher residence time is needed for complete conversion) or to a number of sequentially connected reactors.

1.3 State of the art

Wastewater treatment has gone a long way from the deposition on the other side of the city wall in middle age (sometimes in the inside of the city walls!) to the modern, multi-step treatment systems. We will focus on the actually available non-biological oxidative processes and on their classification.

To describe the different commercial processes, we have to classify these systems. Several classifications are possible: One way is to distinguish the several sources of the oxidant, *e.g.* air, hydrogen peroxide, sulphide. Another way is to distinguish the method of activation, *e.g.* thermal, light induced, by sonication.

A general classification has been proposed by Hug [8]. It uses the system pressure, which is correlated with the system temperature by the vapour pressure of water:

Name	System pressure
Low Pressure	0.1...0.6 MPa
Medium pressure	0.6...6.0 MPa
High pressure	6.0...20.0 MPa

Table 1.1: Ranges of conditions of different WO processes

Not included in this table is the super-critical wet oxidation (SCWO). SCWO-systems have a system pressure higher than the critical pressure of water.

Compared with the most important component of the wastewater, *i.e.* water, Figure 1.3 shows the operation range of the different WO-processes:

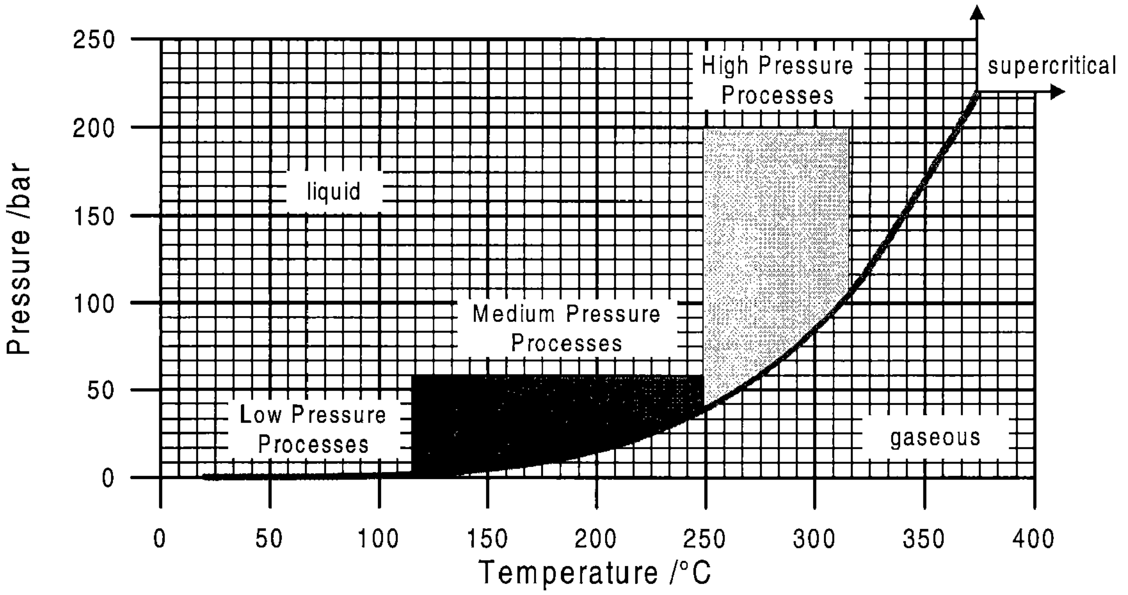

Fig. 1.3: Different wet oxidation processes and the phase diagram of water

In a general view, this classification distinguishes the scale of the plant or the flow-through of these systems. The high and medium wet oxidation processes have usually high throughput due to the high effluents of industrial production processes. The low-pressure processes or AOP's are located at smaller production plants and treat smaller wastewater streams. Of course, there are investigations to scale-down the high-pressure or supercritical systems to a scale suitable for a ship [1] or a space station. There are also on-going works to scale-up low-pressure systems, especially light-induced oxidation systems. But the AOP's are intended to treat small wastewater streams. Normally, the running costs of the AOP's are higher compared with the medium pressure systems, *e.g.* hydrogen peroxide as oxidant is more expensive than air.

Numerous publications are dealing with the topic "wet oxidation". For an overview about the experimental work on wet oxidation, refer to the publication of Mishra *et al.* [11]. The industrial applications are discussed by Luck [9].

This work is the continuation of three previous dissertations at our institute on the field of the medium pressure wet oxidation. These earlier works have focused on the phenol oxidation [12] and the wet oxidation of sewage sludge [6,8].

The works on the wet oxidation of sewage sludge resulted in the successful design and operation of medium scale bubble column [8]. The examination of sewage sludge enables the optimised conditions to operate this plant and resulted in the knowledge of the special sample treating, pre-treatment conditions and degradation of sewage sludge.

The discovery and formulation of a promoter for the wet oxidation by Vogel [12] is a specific improvement of the LOPROX system by Bayer AG, Leverkusen, Germany. The LOPROX system is a medium pressure wet oxidation system using a combination of Fe-ions and the so-called "quinones-generating substances". A source of these substances may be brown coal dust. For phenol or naphtol, reaction temperatures of 120 to 150°C are mentioned for complete removal. For other organic substances, increased reaction temperatures of about 180 to 200°C are necessary [7]. In most cases the bounded nitrogen is released as ammonia and may be recycled as purified distillate.

1.4 Scope and Project Objectives

As mentioned in the previous pages, a prescription to prepare a promoter has been established by previous works. Also some general remarks about the nature of the promoter and the function are made. But a more general investigation of the system has not been established yet. Only a few results are published ([7][13]), which are comparable with the assumed system. Therefore, the need for a wider result spectrum with other potential pollutants is obvious, and this leads to the objectives of this work:

- Investigations of chosen model substances with special focus on the use of the promoter: A number of model substances has to be evaluated to create artificial wastewaters including compounds occurring in industrial wastewaters. The chosen model substances are treated by wet oxidation and by promoted wet oxidation. Usually, the partial pressure of oxygen was set to 1 MPa and the pH of solution was 2.0.
- Comparison of reported results of other processes: In the intended temperature range (130...190°C) the wet oxidation without catalysts is usually not performed and therefore not examined. The subcritical wet (air) oxidation is usually performed at temperatures above 200°C. Oxidation technologies with hydrogen peroxide or ozone are performed below 150°C. At the chosen

temperature range, the conversion rate for COD and TOC will be lower compared with subcritical wet oxidation but higher compared with AOP's. For some pollutants, the AOP's and subcritical wet oxidation also differ in the observed intermediates. There is a given interest in comparing the actual results of the examined process with published results in intermediates and in conversion of other processes.

- Identification of the relevant parameters and of their influence: There are several parameters that control the process. It is obvious that a change in reaction temperature will have a great influence in the degradation rate. It is assumed that a raise in oxygen pressure increases the degradation rate. Also, the role of the promoter on the initial and further degradation has to be evaluated. The combination of the promoter precursor and Fe-ions yields further process parameters.
- Description of the degradation of the model substances: The description of coal and fuel conversion introduced several models for the global kinetic analysis in chemical engineering. The kinetic analysis in wet oxidation is usually focused on the arrangement of parallel- and consecutive pathways of lumped parameters. Therefore, several models and descriptions of the degradation of single substances and mixtures are published. Their availability in the investigated process has to be discussed.

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2 Fundamentals of the Promoted Wet Oxidation

2.1 Gases and Water

The important gases in promoted wet oxidation are oxygen and carbon dioxide. Oxygen gas is the used oxidant for the process; carbon dioxide is the most important gaseous product. In the case of air as the source of oxygen, nitrogen is also important for the process. We used in this work only pure oxygen as oxidant.

The solubility of gases in liquids depends on different parameters, *e.g.* salinity, temperature and pressure. At relatively low pressures of gases, Henry's Law can describe the solubility of the gas. For water and oxygen follows:

$$p_{Oxygen} = H_x \cdot x_{Oxygen} \tag{2-1}$$

The term p_{Oxygen} stands for the partial pressure of oxygen above the solution and x_{Oxygen} is the mole fraction of oxygen in the solution. The Henry coefficient H_x refers to the mole fraction and is of the dimension as the partial pressure (in this work: MPa).

The Henry coefficient, *i.e.* the solubility of oxygen, depends on the temperature. For the system water/oxygen, the correlation by Himmelblau [15] is used. This correlation is reliable in the used temperature range and also for partial pressures of oxygen up to 10 MPa. Based on four published sets of data, Himmelblau established a correlation in the following form:

$$A \cdot \log(H')^2 + B \cdot (1/T')^2 + C \cdot \log(H') \cdot (1/T') + D \cdot \log(H') + E \cdot (1/T') - 1 = 0 \tag{2-2}$$

A	-0.0005943
B	-0.1470
C	-0.05120
D	-0.1076
E	0.8447

Table 2.1: Constants for Himmelblau's correlation

The constants for the Himmelblau correlation are given in Table 2.1.

The temperature *T* (in Kelvin) is inserted as $(1/T') = (1/T)\cdot 10^3$. Henry's constant is extracted as $H = H'\cdot 10^4$ in bar. Himmelblau mentions an average deviation of 2.8% between this correlation and the experimental data.

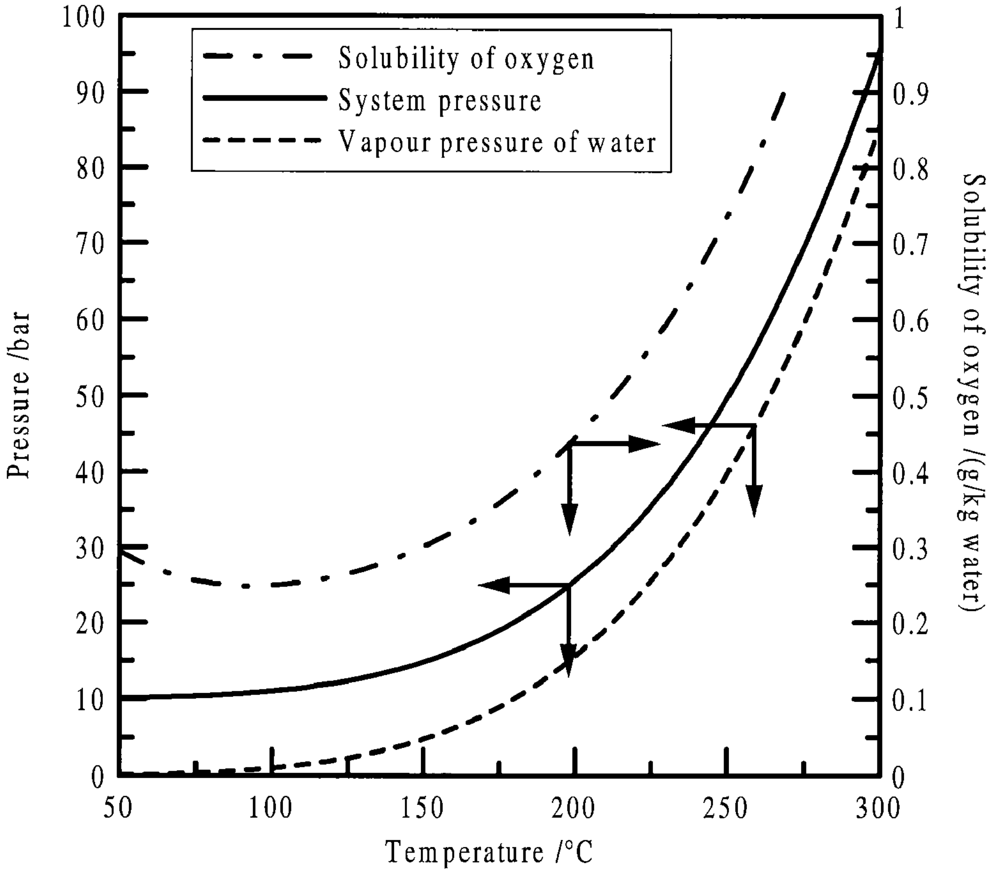

Fig. 2.1: Oxygen solubility at 1 MPa partial pressure: Vapour pressure is increasing with temperature; oxygen solubility shows a minimum at a temperature of 100°C

Figure 2.1 shows the amount of solved oxygen in function of temperature. The partial pressure of oxygen is $p_{Oxygen} = 1$ MPa. By practical experience a decrease in gas solubility by increasing the temperature is expected. This is true up to around 100°C. Above around 100°C, the oxygen solubility increases. If oxygen reacts in solution, Henry's law does not apply to the total concentration of dissolved gas, but may still apply to the concentration of unreacted gas.

Carbon dioxide is the final mineralisation product of any oxidised carbon source. Carbon dioxide may be released as gas or remain in solution as hydrogen carbonate (chemically solved) or as dissolved gas (physically solved). To determine the total amount of dissolved carbon dioxide, it is necessary to consider the effect of the pH on the dissociation. When carbon dioxide dissolves in water, it exists in ionic equilibrium with hydrogen atoms and bicarbonate ions.

$$CO_{2,\,aq} + H_2O \leftrightarrow H^+ + HCO_3^- \qquad [2\text{-}1]$$

The first ionisation constant varies from $K_1(25°C) = 3.47 \cdot 10^{-7}$ to $K_1(250°C) = 1.6 \cdot 10^{-8}$ [12]. The second dissociation can be ignored at the usual pH values. Only about 0.35% of CO_2 exists in the form of carbonic acid at 298.2 K and a partial pressure of CO_2 of 1.013 bar. Carbonic acid is a stronger acid than indicated by the above K values. The equilibrium constant for the reaction:

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad [2\text{-}2]$$

is $1.32 \cdot 10^{-4}$ at 298.2 K and the true pK_1 for carbonic acid is therefore 3.88 [10]. By increasing the temperature, the Henry coefficient is increasing while the solubility is decreasing. But as discussed with oxygen, the temperature dependence of carbon dioxide changes above a given temperature. Above about 180°C the mole fraction solubility for a partial pressure of 1.013 bar increases with temperature. In the case of wet oxidation at pH = 2, carbon dioxide can only be physically solved in water. Therefore carbon dioxide (and nitrogen) behaves as inert gases.

2.2 Oxidation and Degradation

Oxidation in the liquid phase is an important process in the production of chemicals on industrial scale. Well known processes are the production of phenol and acetone by the oxidation of cumene, the manufacturing of synthetic fatty acids by the oxidation of olefins and the epoxidation of olefins by organic hydroperoxides [9].

Water as the solvent in liquid phase oxidation is not important on industrial scale. In most cases, water does not have sufficient capabilities as solvent. An exception is two liquid phase oxidation, in which the aqueous phase contains the oxidant (*e.g.* hydrogen peroxide) and also bears the oxidised product.

A complete introduction in the field of oxidation by modelling and also by experimental work is given by Emanuel and Gal [9].

Oxidation of organics may result in addition of a hydroxyl- or a keto-group to the substance. This function changes the pK_{OW} and therefore increases the solubility in water. An example is the enzymatic P450 system in the liver, which increases the water solubility of hydrophobic substances and enables the organism to release toxic and hydrophobic substances.

Further oxidation of organics leads to carboxylic acids that may be released from the substance as carbon dioxide. The release of carbon dioxide is the final step in consecutive oxidation of hydrocarbons. Regarding a carbon atom of a hydrocarbon, the change in the oxidation state shows the release of carbon dioxide:

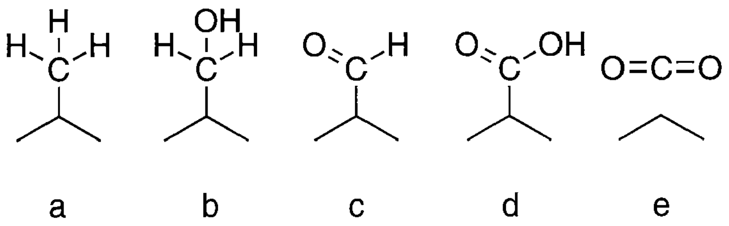

Fig. 2.2: Different oxidation states of carbon

The aliphatic carbon atom has the oxidation state -III (a). By increasing the oxidation number by adding oxygen, an alcohol (-I, b), an aldehyde (+I, c) and a carboxylic acid (+III, d) are formed. The final oxidation product is carbon dioxide (+IV, e). The possible release of carbon dioxide is mainly a thermal process and may be influenced by the constitution of the carboxylic acid.

An example for oxidation and degradation of an aromatic system is the ozonation. A double bond is attacked by an ozone molecule and over a primary ozonide, a carbonyl oxide and a secondary ozonide, carboxylic acids are formed and the aromatic core is broken [1].

The organic chemistry uses a whole series of oxidants with different oxidative strength. The oxidative strength is expressed by the reduction potential. A series of different oxidants and their standard reduction potential is given in Table 2.2. Keeping an oxidative disposal process in industrial scale in mind, fluorine is too expensive and it is difficult to handle safely. But the other mentioned oxidants have been used in (semi-) industrial scale. The hydroxyl radical is generated by the AOP's and is the dominant oxidant in these processes. Ozone is also an AOP and is mainly used in the drinking water sterilisation. Oxygen is the oxidant in wet oxidation. The liquid phase oxidation by nitric acid has found use in nitro-compounds treatment [2,14]. The redox-couple Fe(II)/Fe(III) is observed in the Fenton-like AOP's [7].

Oxidant	Reaction in acidic phase	E°_{Red} /V
Fluorine	$F_2 + 2H^+ + 2e^- \leftrightarrow 2HF$ [2-3]	3.07
Hydroxyl radical	$HO\cdot + H^+ + e^- \leftrightarrow H_2O$ [2-4]	2.85
Ozone	$O_3 + 2H^+ + 2e^- \leftrightarrow O_2 + H_2O$ [2-5]	1.90
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$ [2-6]	1.77
Oxygen	$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$ [2-7]	1.24
Nitric acid	$HNO_3 + 9H^+ + 8e^- \leftrightarrow NH_4^+ + 3H_2O$ [2-8]	0.87
Iron (III)	$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ [2-9]	0.77

Table 2.2: Different oxidants, see Christen [8]

2.3 Elementary Processes in Oxidation

The appearance of radicals in wet oxidation has been proved by different published works (summarised by Li *et al.* [17]). Radicals are atoms, molecules or ions with one or more non-paired electrons. The molecule in oxygen gas, *i.e.* O_2, is a natural biradical in triplet state and therefore not reactive. Radicals, as reactive intermediates, have a short lifetime of about $\tau_{½} = 10^{-10}$ s. A free-radical reaction mechanism appears to be accountable for wet oxidation of organic compounds in both subcritical and supercritical water [17]. A fundamental scheme of a radical mechanism may consist of the following elementary processes:

Initiation.

$$RH + O_2 \rightarrow R\cdot + HO_2\cdot \qquad [2\text{-}10]$$

$$In\cdot + RH \rightarrow R\cdot + InH \qquad [2\text{-}11]$$

Propagation.

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad [2\text{-}12]$$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot \qquad [2\text{-}13]$$

Branching.

$$ROOH \rightarrow RO\cdot + \cdot OH \qquad [2\text{-}14]$$

$$\cdot OH + RH \rightarrow R\cdot + H_2O \qquad [2\text{-}15]$$

Termination.

$$R\cdot + R\cdot \rightarrow R\text{-}R \qquad [2\text{-}16]$$

$$ROO\cdot + ROO\cdot \rightarrow ROH + RO + O_2 \qquad [2\text{-}17]$$

The elementary processes in the oxidation can be classified according to their different functions:

Initiation. The initiation processes [2-10] and [2-11] take place between molecules and lead to free radicals. Regarding the process temperature, thermal initiation below 100°C is not practically occurring and will therefore only be observed in medium pressure, high pressure and supercritical-systems. (Photo-) Catalysed (or chemical/photochemical) initiation is applied in the AOP's and in the proposed system. Examples of initiation are hydrogen abstraction [2-10] or the thermal decomposition of azo compounds.

The initiation may be performed by adding an initiator. The rate of the over-all reaction depends according to Eq. 2-3 (adapted from Zollinger [24]) on the square root of the concentration of the initiator as well as on that of its rate of decomposition:

$$r_{tot} = -\frac{d[M]}{dt} = k_p(fk_i/2k_t)^{0.5}[M][I]^{0.5} \tag{2-3}$$

where r_{tot} is the overall rate of reaction, *[M]* is the concentration of the compound, *[I]* is the concentration of initiator, k_i is the rate constant of the decomposition of the initiator in radicals, k_p is the rate constant of chain propagation, k_t is the sum rate of constants of the chain termination reactions and f denotes initiator efficiency. The formation of the radicals from the initiator is followed by addition to a species, *i.e.* a molecule of pollutant. But some of the radicals are lost through recombination. Hence not all the molecules of the initiator take part at the desired reaction with the pollutant. The initiator efficiency is fraction of formed radicals that successfully react with the pollutant.

Propagation. Two processes can be distinguished: Primary propagation is defined as the reaction between radicals and the substrate (target compound). An example is the oxygen addition [2-12]. The secondary propagation is the reaction of radicals with the more or less stable intermediates (*e.g.* hydrogen abstraction [2-13]). The product is a further radical and a stable intermediate or a product.

Branching. The decomposition of hydroperoxide, *e.g.* produced by reaction [2-13], leads to two radicals [2-14]. The produced radicals react further, *e.g.* attack of substrate [2-15]. The number of radicals is increasing and a new branch in the reaction chain may start. The over-all reaction rate is increased by the increasing number of reaction chains. This is the reason, why this type of oxidation is called auto-catalysed oxidation or autoxidation.

Termination. Termination processes occur between two radicals and produce stable molecules [2-16]. Reactions of radicals with the reactor wall also belong to the termination process. An example of radical termination is the radical recombination [2-17].

Other processes are known which are also observed as degradation of dissolved compounds:

Fission. Especially larger molecules can undergo fission by means of acid/base catalysis. This is also observed as degradation but the intermediates can recombine or remain as smaller compounds by adding hydrogen/hydroxyl. In both cases, the total carbon content remains the same as the initial value. The (bio-) chemical oxygen demand can significantly change. In the case of dyes, the colour will disappear, but the intermediates may be more toxic than the normally non-toxic dye. Fission is mainly dependent on the temperature and on the pH.

Polymerisation. During the autoxidation, formed radicals can recombine and will remain as compounds with a higher molecular weight than the initial compound. This polymer, especially known in phenol wet oxidation, will glue at the reactor walls or remain in solution as colloids or larger particles.

2.4 Co-Oxidation

The mentioned elementary processes show the possible formation of reactive hydroxyl radicals. These radicals may not only attack the initial pollutant or the produced intermediates, but also other solved compounds. If two compounds have different reactivity, the decomposition of one compound increases the decomposition of the second. The oxidative treatment of a mixture of two organic compounds generates two chains of reactions. These chains may overlap. This overlapping of reaction chains is called co-oxidation.

The simultaneous treatment of 1-propanol and methanol at near-critical water shows the effect of co-oxidation. The results of the single substance oxidation show, that 1-propanol is easier oxidised as methanol. Treating a mixture of both substances, the degradation of 1-propanol is slightly decreased, but methanol is significantly faster oxidised. Boock and Klein [6] were able to explain this behaviour by a mechanistic modelling.

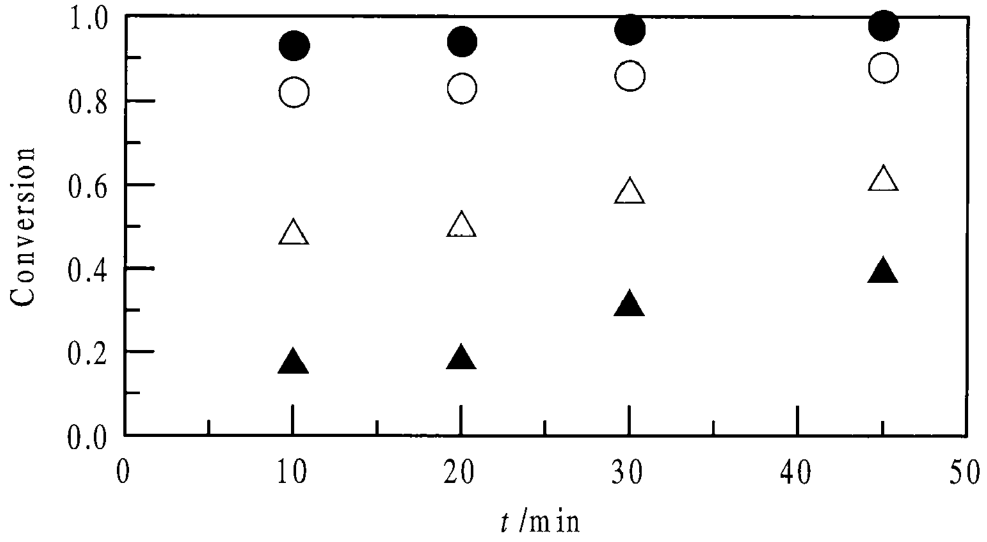

Fig. 2.3: Wet oxidation of 1-propanol (●), methanol (▲) and mixture of 1-propanol (○) and methanol (△) at $\vartheta = 300°C$, p_{Oxygen} = ca. 70 bar; initial concentrations for both compounds were 0.06 mol/L; data published by Boock and Klein [6]

The effect of co-oxidation was also observed at lower reaction temperatures. The treatment of morpholine and diethanolamine at ϑ = 160-240°C was examined by the observation of the single substances and of their mixture. The mixtures of diethanolamine and morpholine were found to oxidise faster than expected from the individual rates of oxidation [20]. Birchmeier and co-workers [4] examined the wet air oxidation of phenol, cellobiose and syringic acid (*i.e.* gallic acid 3,5-dimethylether) at ϑ = 155°C and $p_{Oxygen} \geq 1$ MPa. The reaction with oxygen was catalysed with water-soluble polyoxometalate anions. It is reported that the repeated injecting of the compound to the reacting solution of the same compound leads to an enhanced COD-removal. Birchmeier *et al.* concluded that formed recalcitrant intermediates are co-oxidised by the newly added compounds.

2.5 Reaction Schemes and Modelling

2.5.1. Temperature dependency

The temperature dependency of conversion leads to the derivation of activation energies and frequency factors. By varying the reaction temperature, the change in the reaction rate leads to the Arrhenius parameters:

$$k \propto \exp\left(-\frac{E_A}{RT}\right) \qquad (2\text{-}4)$$

Assuming the same behaviour of non-elementary reactions and after finding the concentration dependency of the reaction rate, an Arrhenius-type relationship may be established:

$$k = k_0 \cdot \exp\left(-\frac{E_A}{RT}\right) \tag{2-5}$$

By this approach, the influence of the system pressure on the density of the liquid and therefore on concentration may be neglected.

2.5.2. Kinetic of single substance

Regarding a pollutant A with the corresponding concentration in water [A], the reaction of A with oxygen O_2 is described by:

$$-d\frac{[A]}{dt} = k \cdot [A]^m \cdot [O_2]^n \tag{2-6}$$

The reaction order is not known *a priori* and has to be evaluated by experiments in a defined parameter range. The reaction order and the activation energy/frequency factor results from the experiments and lead to the model. The experimental conditions determine the range of prediction of the model. The reaction orders are not describing the real chemical behaviour of the pollutant and oxygen on a molecular scale. Therefore, the model describes the observed reactions, but gives only hints to the mechanism.

Assuming that gas-liquid phase transfer is fast, the oxygen concentration $[O_2]$ will remain nearly unchanged during the reaction and the Eq. 2-6 can be simplified to Eq. 2-8:

$$k' = k \cdot [O_2]^n \tag{2-7}$$

$$-\frac{d[A]}{dt} = k' \cdot [A]^m \tag{2-8}$$

The integration assuming an irreversible unimolecular first-order reaction and the initial concentration $[A]_0$ leads to the concentration decrease during the reaction

$$-\ln\frac{[A]}{[A]_0} = k' \cdot t \tag{2-9}$$

and to the conversion X_A:

$$-\ln(1 - X_A) = k' \cdot t \tag{2-10}$$

2.5.3. Kinetic lumping

Due to the huge number of possible reactions, the modelling in wet oxidation is performed by the use of lumped parameters, *e.g.* COD or TOC/TC. The usually published kinetic models are mainly mechanisms following a combination of series-parallel reactions.

Takamatsu [22] suggested a model for thermal decomposition of sludges. He divided the sludge in four parts of different behaviours in wet oxidation conditions: Solid matter, water and two parts of soluble matter. The soluble matter is separated into a non-evaporative (at 120°C) part and an evaporative part. In other kinetic studies of subcritical WO of sludges, the organic load is divided into three components of different reactivities [21] and is fitted using the overall COD value. Harf [13] used a model, which separated the TOC and COD into two classes of reactivity for description of sewage sludge treatment. This approach was used for fitting the TOC and COD values. Foussard [11] used the same approach to describe the COD decrease in biological sewage treatment.

For the wet oxidation treatment of grease and oil, Bernal *et al.* [3] have used the following approach: In the first step, partial oxidation of oil/grease (A) takes place very rapidly and the formed intermediates (B) are water- soluble. The further degradation reactions are described by two parallel reactions. In one reaction (with the reaction rate constant k_2), the intermediates are totally oxidised to the final products, carbon dioxide and water (C). In the other reaction (k_3), the intermediates are only partially oxidised to the so-called refractory compounds. The refractory compounds have a low reactivity in wet oxidation and are mainly short-chain organic acids (D).

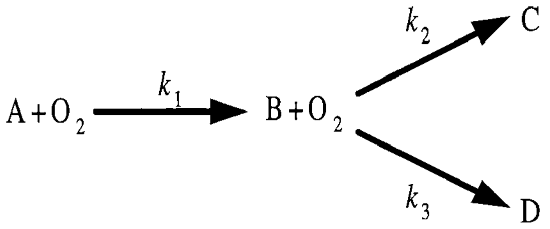

Fig. 2.4: Bernal's model [3]

Based on the mentioned and other works, a generalised kinetic model was evaluated by Li, Chen and Gloyna [17]. In this model, three parts of organic substances are lumped. The first part (A) includes the initial and unstable

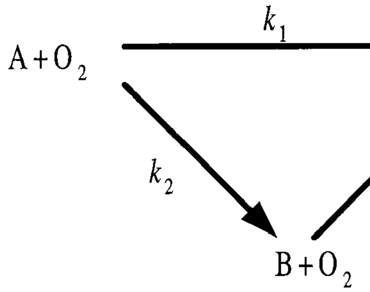

Fig. 2.5: Model by Li *et al.* [17]

intermediates except acetic acid. The second part (B) includes all the refractory compounds (represented by acetic acid) and the third part (C) is designated as the sum of the stable products. Li *et al.* proposed by evaluating a number of publications, that in most cases the reaction order of A and B is 1. The reaction order of oxygen is varying between 0 and 1. These assumptions are vague and the mentioned results are depending on the examined pollutant, oxygen pressure and reaction temperature.

The procedure of collecting all the unknown and supposed reactions in a group of reactions is called lumping. Two approaches are mentioned in literature to generate a lumped kinetic:

- To separate TOC or COD values in different classes of reactivity and to propose a generalised model. This approach is presented in the foregoing pages.
- To create a set of possible (elementary) reactions and to lump reactions or compounds to a smaller set of reactions by collecting reactions of equivalent reactions. This approach is discussed in the following chapter.

2.5.4. Detailed Reaction Schemes

In published works of Li *et al.* [18] and Boock and Klein [5,6], the use of mechanistic modelling or kinetic lumping is discussed. This attempt is based on the knowledge and application in petrochemical process engineering. The number of reactions in petroleum refining is extremely high as they are in wet oxidation (and in combustion). The wet air oxidation reactions are typically first-order with respect to the organic compounds and oxygen, respectively. It has been shown that first-order kinetic systems can be represented by linear differential equations involving lumps or pseudospecies.

The theoretical fundamentals of kinetic lumping in linear reaction systems were established more than three decades ago. More recently a structure-oriented lumping technique was developed. This concept uses incremental structural features to represent individual hydrocarbon molecules and mixtures. In another study, a lumping concept was used to group elementary steps of oxidation into eight controlling reaction families. These reaction families are comparable with the elementary steps in the autoxidation. This approach uses structure-reactivity relationships and detailed mechanistic models. Each reaction family has the same Arrhenius prefactor k_0 and the same function for the Arrhenius activation energy:

$$E_A = E_A{}^0 + \alpha \cdot \Delta_r H^0 \tag{2-11}$$

The constants in these Polanyi relationships are the same for all reactions in a reaction family and have to be evaluated by experiments with single compounds. Boock and Klein [6] established a model to describe the behaviour of up to four compounds. The behaviour of mixtures of low molecular alcohols and acetic acid (see “Co-Oxidation” on page 17) at oxidative conditions can be predicted by this approach. An interesting insight in these approaches and examples of them are given by Li *et al.* [18].

2.6 Promoted Wet Oxidation

The industrial process LOPROX (Bayer AG, Leverkusen) uses a combination of quinones and Fe-ions for wet oxidation at moderate temperatures [16]. This combination leads to an increased degradation of the TOC and COD of specific wastewaters compared with common wet oxidation. The wet oxidation and the heterogeneous catalysed wet oxidation have no need of additional chemicals (except oxidant). The homogeneous catalysts are usually converted during the reaction and will not be recycled (*e.g.* Ciba-process, see [19]).

On the basis of the LOPORX-process, Vogel [23] has evaluated the class of substances and the preparation, which are successful to promote the wet oxidation of phenol. The addition of easily oxidisable substances to a wastewater has a positive effect on the performance that is easily explained by co-oxidation and initiation.

2.7 References

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3 Experimental Set-up

Figure 3.1 shows a scheme of the bench scale system used for this work and all experiments reported here in. An autoclave HPM-P-4 (Premex Reactor AG, Lengnau, CH) is used as a batch reactor. The vessel is made of titanium; the cover is made of Hastelloy C-22. A hollow shaft impeller is used for mixing. All fittings and the piping are fixed at this cover and the vessel can be lowered or lifted by a hydraulic system for filling and cleaning. The stirrer and the baffles are also made of titanium. A circulating oil heating/cooling system is used to control the temperature in the autoclave. The used experimental set-up enables a heat-up time of around 50 min to reach a temperature of 190°C. The system is designed for a maximum pressure of 40 bar and a maximum temperature of 250°C. The reactor volume available is 4 liters. To inject small volumes of solution after heating-up, a container (V = 45 mL) is connected with the reactor. The content of the container can be pressurised with argon and transferred into the reactor. As oxidant, oxygen gas is directly taken from the bottle. The used system is described in detail in the dissertation of Vogel [8]. Sample collection is performed *via* a single water-cooled heat exchanger. The samples are cooled in ice-water and kept cool until the

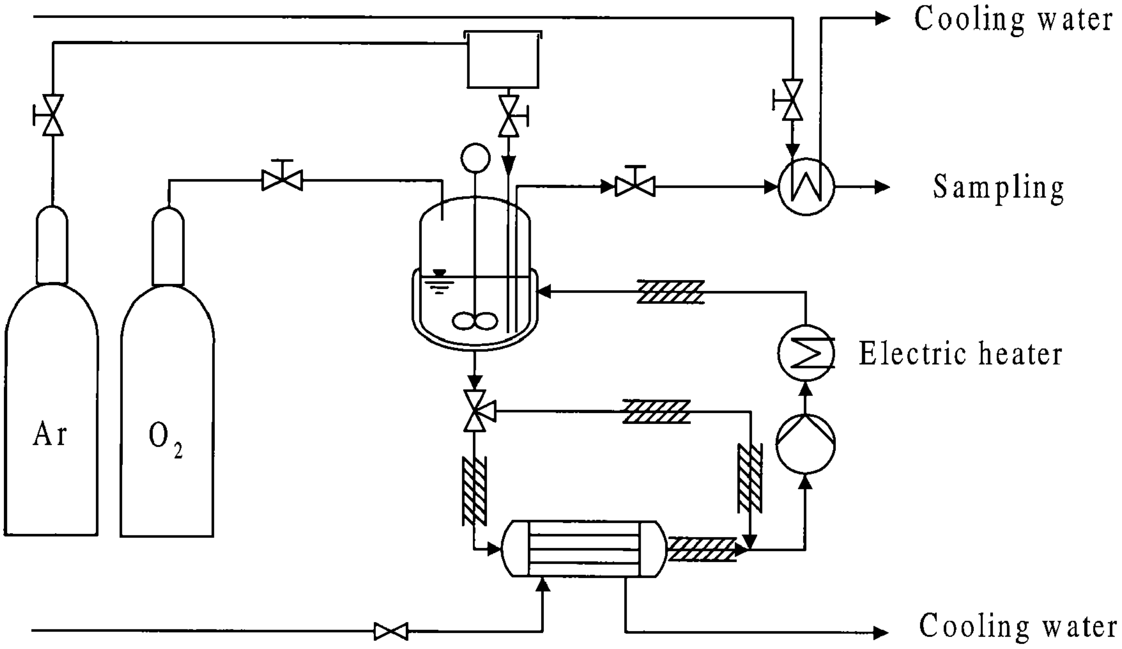

Fig. 3.1: Schematic drawing of the bench scale system used in this work

analysis performing. The filtering of the samples and analysis is performed with samples at ambient temperature.

3.1 Procedures

For wet oxidation experiments with temperature-sensitive substances, the model substance (usually 2 g) is solved in 40 mL of deionised water and inserted in the container. 1.96 L of water with pH = 2 is inserted in the reactor. After 2 min of degassing of the reactor content, the solution is heated up. After the desired temperature is reached, the content of the container is injected. After 2 min of mixing, a sample is drawn. The stirrer is shut down and the oxygen pressure is adapted. By starting the stirrer again, oxygen is forced through the solution and this time is taken as the start of reaction.

For the promoted wet oxidation experiments, the model substance and the promoter are mixed and inserted in the reactor. These experiments are carried out using Fe(II)-ions and pre-treated gallic acid as promoter. The promoter is chosen from a range of possible precursor substances. This range of precursor substances is based on a work by Vogel and is reported in a patent [9]. The various possible sources for the promoter are established by Vogel [8]. Gallic acid was chosen as the source compound for the promoter.

1.8 L of deionised water and the model substance (usually 2 g) are mixed and acidified with a few drops of sulphuric acid. 0.21 g of iron(II) sulphate heptahydrate is added. Gallic acid (0.8 g, 4.3 mmol) is suspended in 40 mL of purified water. NaOH (1 g, 250 mmol) is added. The solution is stirred under air atmosphere and after 12 min, the solution is black (under an inert gas atmosphere, the gallic acid solution shows no change in colour). The prepared precursor solution is then acidified by H_2SO_4 and transferred to the solution. The pH is now set to 2.0±0.1with H_2SO_4. A sample is taken and the rest of the prepared solution is poured in the vessel. After closing, the reactor is evacuated while stirring. After 2 min of degassing the solution is heated up without any oxygen gas flow and still stirred. When the required temperature is reached, a sample is drawn. The stirrer is shut off and the oxygen partial pressure is set.

To follow the reaction over the reaction time, samples are taken from the solution at specific time intervals (usually after 2, 5 10, 15, 20, 30, 45, 60 and 90 min). The samples are filtered (0.45 mm, PTFE syringe filters) and analysed.

3.2 Analytics and Reagents

The analysis of inorganic and organic matter in (waste-) water can be classified into two general types of measurements: those that seek to express either the total amount of the matter or some fraction of the total in general terms and those that are specific for individual compounds. Both types of analysis were used in this work and are presented below.

Methods for total organic carbon and chemical oxygen demand are used to assess the total amount of organics present. In the case of the chemical oxygen demand, the possible reaction of inorganic compounds can not be neglected.

3.2.1. COD

The chemical oxygen demand (COD) is used as a measure for the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong oxidant. Most types of organic substances are oxidised by a boiling mixture of chromic and sulphuric acid [6]. Different methods are described to assess the COD [2]:

- Open reflux method
- Closed reflux, titrimetric method
- Closed reflux, colorimetric method

The closed reflux methods are more economical than the open reflux method concerning the use of metallic salt reagents, but require homogenisation of samples containing suspended solids to obtain reproducible results. In this work the closed reflux, colorimetric method was used. The purchased test tube system (COD 1500, Nanocolor test 29, Macherey-Nagel AG, Oensingen, CH) contains sulphuric acid, mercury sulphate and potassium dichromate. The COD value is given by the photometric determination of the chromium (III) concentration after two hours of oxidation at 148°C in a heating block. The highest precision of this system is given by a COD value of 750 mg-O_2/L. Dilution of the samples was performed to reach COD values of 500 to 1000 mg-O_2/L.

The value of the measured COD value depends on the nature of the products. Gaseous products may not be completely oxidised and are therefore not correctly measured. Disturbances occur by the presence of nitrite and reduced inorganic species. High concentrations of chloride are disturbing the COD measurements. The TOD can not be set equal to the measures COD *a priori*. Besides the mentioned effects, a number of industrial pollutants are not measurable by COD-tests. Volatile straight chain aliphatic compounds are not oxidised and do not contribute to the observed COD. Also, many compounds lead to too high or low values.

Therefore, before interpreting COD values, a study which involves identification of critical effects has to be performed [3].

3.2.2. TOC/DOC/NDOC

Some of the solved carbon compounds do not respond to the COD. So, the COD-test (or also BOD-test) is unsuitable for the measurement of total organic content. Total Organic Carbon (TOC) is a more convenient and direct expression of total organic content than BOD or COD, but it does not provide the same kind of information. Unlike COD, TOC is independent of the oxidation state of the organic matter and does not measure other organically bonded elements, such as nitrogen and hydrogen and inorganics that can contribute to the oxygen demand.

To determine the quantity of organically bonded carbon, the organic molecules must be broken down to single carbon units and converted to a single molecular form that can be measured quantitatively. TOC methods utilise heat and oxygen, UV irradiation, chemical oxidants, or combinations of these oxidants to convert organic carbon to carbon dioxide (CO_2). The CO_2 may be measured directly by a nondispersive infrared analyser (NDIR), it may be reduced to methane and measured with a flame ionisation detector or CO_2 may be titrated chemically.

Analysis of the carbon content was carried out using a TOC-Analyser (Dohrmann, DC-190). A high temperature catalytic combustion (Pt on alumina) in an oxygen flow produces CO_2 which is detected by a NDIR (Rosemount Binos 1.1). The precision of the system is given by ±2% of the measured value [1]. The used combustion temperatures were 750°C or 800°C. Oxygen (200 bar, purity >99.99%) was purchased by PanGas, Lucerne, CH.

The methods used in measuring TOC analyse fractions of total carbon (TC). These fractions of total carbon are defined as:

- Inorganic carbon (IC): carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and dissolved CO_2, ev. CN^- or dissolved HCN
- Total organic carbon (TOC): all carbon atoms covalently bonded in organic molecules
- Dissolved organic carbon (DOC): the fraction of TOC that passes through a 0.45 μm-pore-diameter filter

- Non dissolved organic carbon (NDOC): also referred to as particulate organic carbon, the fraction of TOC retained by a 0.45 μm-pore-diameter filter or simply: NDOC=TOC-DOC
- Purgeable/non purgeable organic carbon (POC/NPOC): The POC, also referred to as volatile organic carbon, is the fraction of TOC removed from an aqueous solution by gas stripping under specified conditions, whereas the NPOC is the fraction of TOC that is not removed by gas stripping.

In most water samples, the IC fraction is many times greater than the TOC fraction. Eliminating or compensating for IC interferences requires multiple determination to measure true TOC. IC interference can be eliminated by acidifying samples to pH 2 or less to convert IC (not CN^-/HCN) species to CO_2. Subsequently, purging the sample with a purified gas removes the CO_2 and HCN by volatilisation. Sample purging also removes POC so that the organic carbon measurement made after eliminating IC interferences is actually a NPOC determination. Therefore, in practice, the NPOC determination is substituted for TOC.

The samples in the presented work have a pH = 2 and were well mixed with oxygen during the reaction. Therefore, the IC fraction and POC fraction can be neglected. The measured carbon content is equal to the TOC; the values of the filtered samples are equal to the DOC.

The procedure to measure TOC and DOC follows the standard methods [2]. The given precision of the so-called combustion-infrared method for samples with particulate matter is of about 5 to 10%. With clear samples or with filtered samples, precision approaches 1 to 2%. As external standard, dissolved anhydrous potassium biphtalate ($C_8H_5KO_4$) is used.

3.2.3. MOC

The mean oxidation state of carbon (MOC) is a value of the average oxidation state of the solved carbon. The wet oxidation process is intended to increase the oxidation number of the solved carbon and other atoms. Therefore, the MOC is a suitable tool to observe the fate of the carbon in solution [10].

For every carbon atom C of a molecule, the corresponding oxidation number OC can be given. The regarded molecule has a defined number n of carbon atoms $N(C)_i$ with the same OC_i. The MOC of this molecule is given by:

$$MOC = \frac{\sum\limits_{i=1}^{n} N(C)_i \cdot OC_i}{\sum\limits_{i=1}^{n} N(C)_i} \tag{3-1}$$

A solution of different substances has also an average value describing the oxidation state of the solved carbon. A solution with a number m of organic substances A_j with the corresponding concentrations $[A]_j$ and MOC_j has the following MOC:

$$MOC = \frac{\sum\limits_{j=1}^{m} [A]_j \cdot MOC_j \cdot N(C)_j}{\sum\limits_{i=1}^{m} [A]_j \cdot N_j} \tag{3-2}$$

To establish the MOC of a solution without knowing the concentration of the solved substances (or the existence), the following approach leads to the MOC using the COD and TOC:

$$MOC = 4 - \frac{4 \cdot M_m(C)}{M_m(O_2)} \cdot \frac{COD}{TOC} \approx 4 - 1.5 \cdot \frac{COD}{TOC} \tag{3-3}$$

For a complete discussion of the MOC, refer to the dissertation of Vogel [8] or Harf [5]. A general description of this concept is found by Stumm [7].

Several conditions and assumptions are made for organic substances:

- MOC, as the oxidation state of carbon, may only vary between -4 (*e.g.* methane) and +4 (*e.g.* carbon dioxide)
- The examined substances contains only C, H and O (*i.e.* every bonded hydrogen atom decreases the oxidation number of carbon by 1, every bond between oxygen and carbon increases the oxidation number of carbon by 1; H and O do not change their oxidation state)
- The measured COD is equal to the TOD.

The special nature in measuring MOC values lies in the combination of two different analytical methods. Despite the expected errors, the MOC gives insight in the over-all performance of a chemical system. Special attention has to be given in a proper practice in measuring. All the remarks for COD measurements are therefore true for the MOC calculations.

3.2.4. HPLC

The high performance (or pressure) liquid chromatography (HPLC) is used in this work to determine the presence and measure the concentration of specific water-soluble compounds.

The most common mode in HPLC is the reversed-phase chromatography. It uses hydrophobic packings such as octadecyl- or octylsilane phases bonded to silica or neutral polymeric beads. The mobile phase is normally water and a water-miscible organic solvent such as methanol (MeOH) or acetonitrile. An example for a reversed-phase HPLC-column is the used Nucleosil 100-5 C18 HD, 250x4 mm column (Macherey-Nagel AG, Oensingen, CH). A guard column having the same characteristics is used. This column is used for the determination of organic compounds. The measurement of carboxylic acids may be performed by using a reversed phase chromatography [4]. But the necessary pH value of the eluent is too low to guarantee a satisfying lifetime of the column ("bleeding" of the silica at low pH). For the conditions of measurement and for the retention times of the observed compounds, see Appendix 1.

The ion-exclusion chromatography makes use of the fact that ionic solutes can be separated from non-ionic or partially ionic solutes by an ion-exchange resin. The ionic solutes will move faster through the column than the non-ionic solutes. The ion-exclusion column Grom-Gel Acid 1, 300x7.8 mm column can be used in a pH range from 1 to 6. A guard column having the same characteristics is used. The determination of carboxylic acids is performed with this size-exclusion column. For the conditions of measurement, see Appendix 1.

The used HPLC-system is a Waters Alliance 2690 separations module, the detectors are a Waters 410, differential refractometer and a Waters 996, photodiode array detector (Wavelength range: 190 to 800 nm). The evaluation and storage of the data is done by the software Millennium 2010, Chromatography Manager, Waters AG. The HPLC system was supplied by Waters AG, Rupperswil, CH.

3.2.5. Other Tests and Analytical Equipment

Different tests were performed to establish the concentration of nitrate, ammonia and total nitrogen. These tests were purchased by Macherey-Nagel AG.

pH measurements are done by a Schott Handylab 2. A two-point calibration (pH 4 and 7) is performed before measuring.

GC/FID analysis is performed using a varian 3800 with flame ionisation detector (FID), equipped with a PERMABOND-FFAP-1.00 25m·0.53mm column (Macherey-Nagel AG).

GC/MS analysis is performed using a GC8000 with MD800 detector (FISIONS Instruments USA), equipped with a PTE TM-5 (Supelco) 30m·0.25mm column. The mass spectrometry is mainly done in the scan range 20-400 AMU, scan time 0.4s; interscan delay 0.1s; ionisation Mode EI+

3.2.6. Reagents

The chemicals are used as received from the manufacturers. Orange II, nitrobenzene, aniline and other organic substances are from Fluka Chemie AG, Buchs, CH. Iron(II) sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) is from Siegfried Handel AG, Zofingen, CH. Oxygen ($\geq$ 99.5 Vol.-%) is obtained from PanGas, Lucerne, CH. All reagents and HPLC-solvents are prepared in deionised water by a water purification system (Milli-RO 10 plus and Milli-Q 185 plus from Millipore AG, Volketswil, CH).

3.3 Reproducibility

To determine the influence of the different parameters of the process, three identical experiments were conducted. It is intended to establish the sum of error including errors by preparation of compounds, by experimental handling and by analytical measurement.

Three identical wet oxidation experiments with the azo dye Orange II were performed. They include all the relevant steps of procedure and handling: the starting material was purified by re-crystallisation and only the half of the promoter amount was inserted. The experiments were performed independently and the relevant standards and calibrations were freshly made for each set of samples. The analysis was always conducted on the same day when the experiment was performed.

Condition	Value
Temperature	160°C
Oxygen pressure	10 bar
Orange II	2 g, re-crystallised
Water	2 L, pH = 2
$FeSO_4 \cdot 7\ H_2O$	0.372±0.003 mM
Promoter precursor	0.4 g

Table 3.1: Conditions of the reproducibility experiments

The expected TOC at the beginning was 638 mg-C/L, the measured value was 620 mg-C/L (CV 1%). The concentration of the azo dye was measured by HPLC and for the first 15 min the average CV is 9%. The concentration measurements are showing growing variation coefficients during the reaction time. The TOC and COD measurements show CV of 4% over the whole range of measurements. Interesting is the high accuracy of the initial and final samples, this means: If the reaction rate is low, the accuracy of the measurements is high.

The presentation of the MOC as a function of TC and COD indicates the reliability of the measurements. Because of the possible zero value of the MOC,

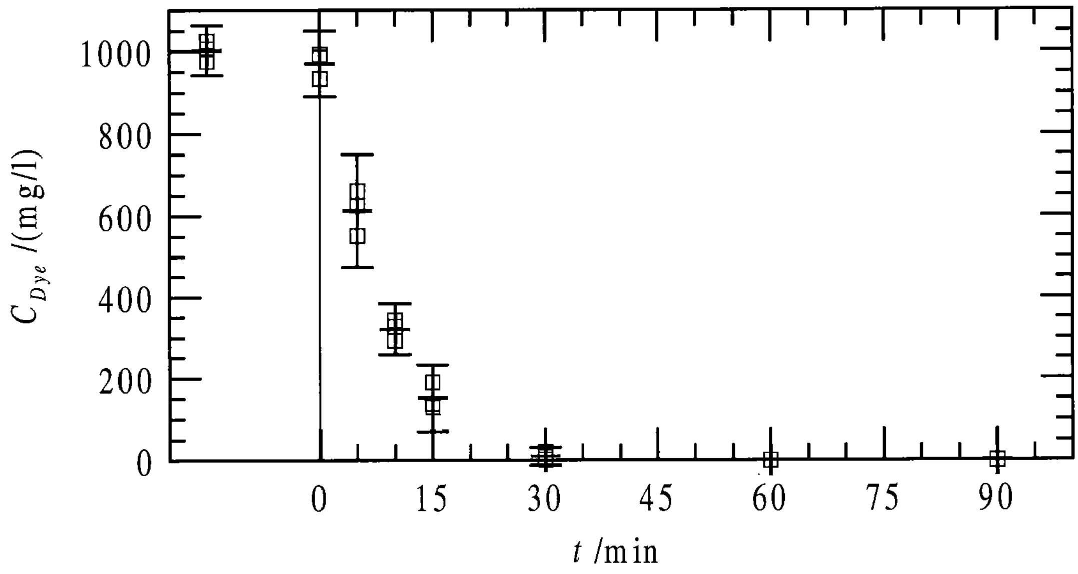

Fig. 3.2: Concentration measurements (□) of the reproducibility experiments; mean values (+) with 95% confidence interval

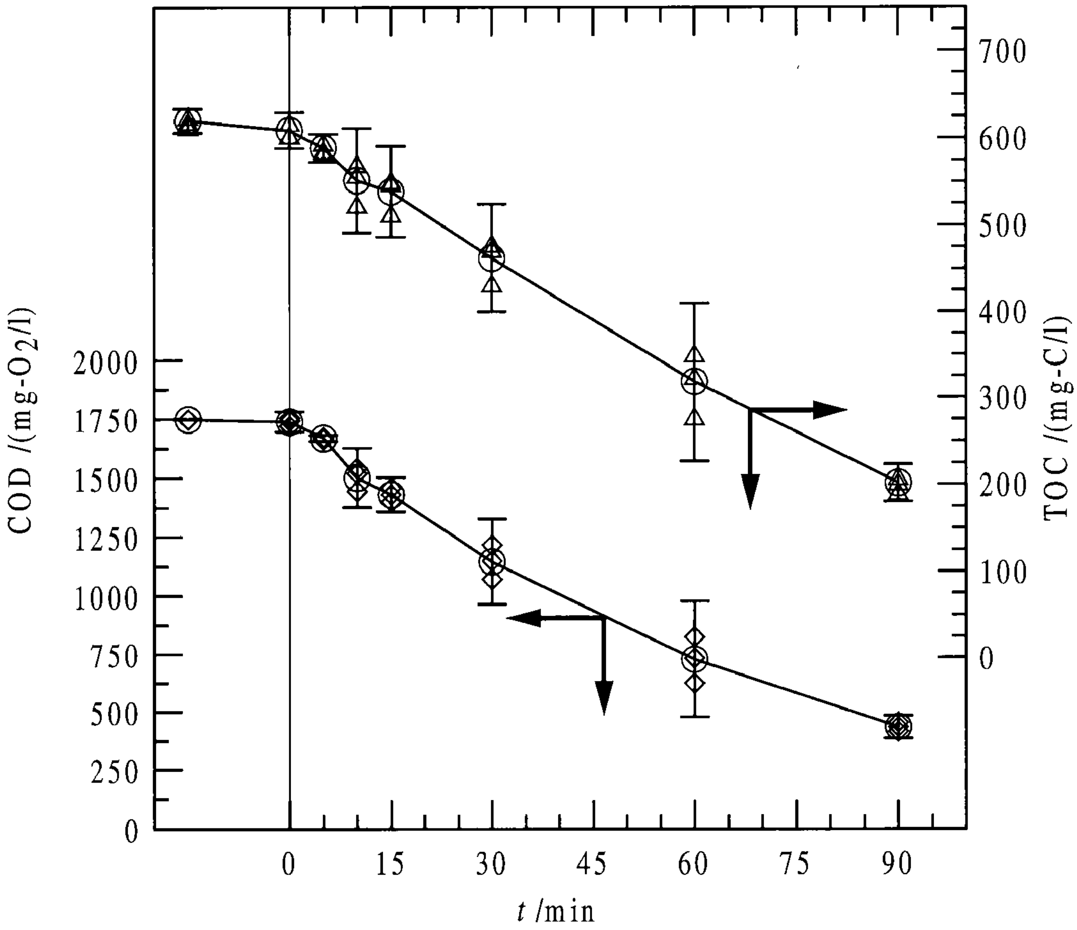

Fig. 3.3: COD (◇) and TOC (△)presentation; mean values (○) with 95% confidence interval

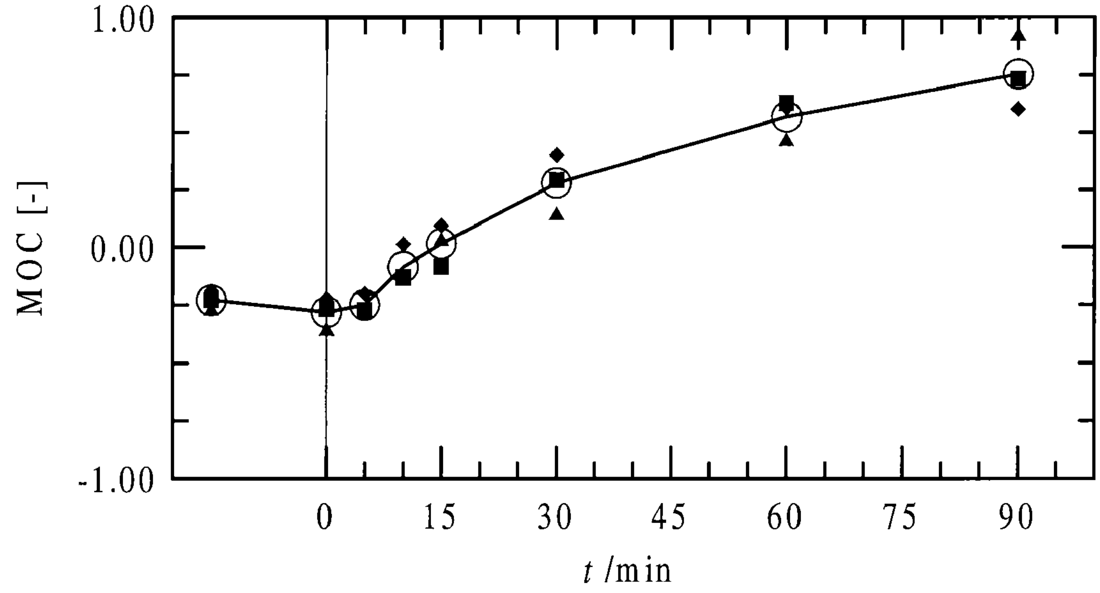

Fig. 3.4: MOC calculation of the reproducibility experiments with mean values (O)

the calculation of the standard deviation is not reasonable. The established mean values and the corresponding coefficients of variance are shown in Table 3.2.

Time / min	c_{Dye} /(mg/L)	CV /%	TOC /mg-C/L	CV /%	COD /(mg-O_2/L)	CV /%	MOC
Prep.	1002.3	2.5	620.3	0.9	1748.7	0.0	-0.23
0	970.5	3.3	609.4	1.4	1739.0	1.0	-0.28
5	612.2	9.1	589.1	1.1	1668.7	0.3	-0.25
10	321.1	7.9	551.8	4.4	1502.3	3.4	-0.09
15	152.0	21.6	538.8	3.9	1430.7	2.1	0.01
30	9.6	90.6	462.2	5.4	1146.0	6.4	0.28
60	0.0		318.3	11.6	729.3	13.8	0.57
90	0.0		201.7	4.3	436.0	4.6	0.75

Table 3.2: Mean values and CV of the different reproducibility measurements

3.4 References

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4 Promoted Wet Oxidation of an Azo Dye

4.1 Preface

The many studies on degradation, separation, environmental impact and health effects of dye-polluted effluents over the two last decades, clearly reveal the complexity of the subject, not only due to the structural variety of these compounds, but also as a result of the complex composition of effluents which they contaminate.

Some physical and (bio-) chemical techniques are available for the treatment of coloured effluents including coagulation and sedimentation, adsorption, bleaching, biological degradation by fungi or yeast, advanced oxidation technologies and wet air oxidation (with or without heterogeneous catalysts).

We will focus in this work on the promoted wet oxidation with an easily oxidisable adding to the dye-solution. It is expected, through a better understanding of the used system, to extent the available range of remediation tools. The azo dye Orange II (*i.e.* (E)-4-[(2-Hydroxy-1-naphthyl)diazenyl]benzenesulfonic acid) was chosen as a model substance due to the following criteria:

- The azo dye is not toxic and easy to handle. This criterion is important because the available laboratory is not equipped with special safety equipment, *e.g.* glove box.
- Orange II is a well examined model pollutant by different oxidative treatments, not only by wet (air) oxidation but also by advanced oxidation processes (AOP's). The first attempts for oxidative destruction of this azo dye are more than 100 years old.
- Solved Orange II is a model wastewater for the dye house effluents. The dye is a simple model substance for pollutants containing azo-linkage.

4.2 Chemistry of Azo Compounds

Azo dyes are a class of organic dyes characterised by the presence of the azo group. Although aromatic azo compounds have been prominent as dyestuff for some decades, their chemical reactions have not been investigated widely or systematically. But the reactions of aliphatic azo-compounds are well examined. Both chemically and technologically the most important reaction of these compounds is the thermolytic fission into molecular nitrogen and two radicals (see [4-1]). The produced radicals can undergo combination (see [4-2]) or transfer reactions, *e.g.* with the solvent (see [4-2] and [4-4]). The reaction can also occur photolytically.

$$\text{R-N=N-R}' \rightarrow N_2 + \text{R}\cdot + \text{R}'\cdot \qquad [4\text{-}1]$$

$$\text{R}\cdot + \text{R}'\cdot \rightarrow \text{R-R}' \qquad [4\text{-}2]$$

$$\text{R}\cdot + \text{X} \rightarrow \text{R-X}\cdot \rightarrow \text{Products} \qquad [4\text{-}3]$$

$$\text{R}\cdot' + \text{X} \rightarrow \text{R}'\text{-X}\cdot \rightarrow \text{Products} \qquad [4\text{-}4]$$

It was recognised how suitable different azo compounds, *e.g.* azodi-isobutyronitrile, are for the initiation of polymerisation. The experimental investigation of the decomposition of aliphatic azo compounds is relatively simple in comparison with other radical reactions. Fission is strictly first order [26], it is barely affected by the nature of the solvent, and substituents enable the reactivity to be varied within wide limits. Table 4.1 gives an overview of rates of decomposition of some aliphatic azo compounds. Azo compounds exhibit simultaneous homolytic fission of two bonds, two radicals being formed as well as a molecule of nitrogen. The rates of decomposition are determined principally by the stability of the products. In the case of azo compounds the rate of decomposition is determined by the enormous stability of one of the products, the nitrogen molecule. In aromatic azo derivatives, such as azobenzene, the C-N bond is so strongly stabilised by mesomerism that phenyl radicals are only formed far above 600°C.

Compound	Solvent	k /s^{-1}	ϑ /°C	E_A /(kJ/mol)
CH_3-N=N-CH_3	gas	$5.6\cdot10^{-4}$	300	210.2
C_6H_5-N=N-$CH(C_6H_5)_2$	decahydro-naphtalene	$2.7\cdot10^{-4}$	145	142.4
C_6H_5-N=N-$C(C_6H_5)_3$	toluene	$2.3\cdot10^{-4}$	54	112.2

Table 4.1: Rates of decomposition of some aliphatic azo compounds [26]

4.3 Degradation of Azo Dyes

The main environmental problem of azo dyes is their removal from wastewaters. Dyes are highly coloured and therefore a concentration of 1 ppm in water can still show the colour of the dye. However, it was reported that the concentration of azo dyes in municipal wastewater can reach the order of 2-5 mg/L. Untreated wastewaters from textile factories are usually coloured.

The decolouration methods that can be used for this purpose are adsorption, chemical degradation, photodegradation and biodegradation. For adsorption, activated charcoal, silica gel, cellulose derivatives and ion exchange resins can be used, but these processes are, in most cases, not economically feasible. We will briefly present the destructive disposal processes for dyes.

4.3.1. Biodegradation

Biodegradation would be an effective pathway for decolouration of coloured effluents and subsequently effective mineralisation. This process can be aerobic, anaerobic or a combined process. Synthetic (azo-) dyes are, by definition, xenobiotics and the natural environment does not contain enzymes, which are designed to degrade these compounds in the presence of air. So, dyes can only be degraded under anaerobic conditions. Sediments and effluents containing azo dyes under anaerobic conditions undergo changes in the ecosystem leading to hazardous nitroso and nitro amines which are toxic compounds [4].

The most effective way of bio-degradation of azo dyes in wastewater is a combined treatment that includes two processes. In the first step, the anaerobic degradation leads to the expected amine metabolites, which in the second stage are further degraded under aerobic conditions. The second aerobic stage promotes further mineralisation of substituted anilines that are stable under anaerobic conditions.

Provided that the proper micro-organisms and experimental conditions are used, biodegradation is always possible, by neglecting the time-scale. In general, and with the present means of wastewater treatment, most azo dyes degrade extremely slowly. They are thus considered to be non-biodegradable [13].

Of industrial importance are also the biochemical catalysts as mono-oxygenases or peroxidases from different organisms like soybean or horseradish [19]. These enzymes or porphyrin-based models of them use hydrogen peroxide as oxidant and they are intended for washing processes [11]. For a general discussion of azo dye degradation by biochemical means, see [10].

4.3.2. Photodegradation/Photocatalytic degradation

Photochemical degradation in aquatic environments or systems like rivers, lakes and oceans is a very slow process. It was found that the half-life of a wide range of commercial azo dyes in sunlight would be generally greater than 2000 hours.

Humic materials in natural water can strongly accelerate the photodecomposition of dyes, which is based on oxidation of singlet oxygen or oxyradicals that are formed by activation of the humic materials by solar radiation. For example, the protonated form of Acid Red IV has a half-life of 20 hours in irradiated humic acid solution (TOC of humic acid: 5 mg-C/L), the half-life of the non-protonated form is reported to be 2 hours [1]. The initial concentration of the dye was lower than 0.5 g/L. For the example of Solvent Red I, the mechanism of the degradation is proposed as follows: Azo-hydrazone tautomeric equilibrium promotes the oxidation through formation of the highly reactive intermediate, *i.e.* peroxide. This intermediate decomposes with C-N bond splitting, forming 1,2-naphtoquinone and a diazobenzene derivative that finally forms guaiacol (2-methoxyphenol) (see Figure 4.1).

Photocatalytic degradation of azo compounds by excited semiconductive materials, and especially titania and semiconducting iron compounds, seems to be very attractive. This process is relatively fast and leads to formation of phenols/ naphtols and benzenesulphonic acids in the first stage, but further mineralisation is slow. An overview about photodecomposition is given by Poon *et al.* [21].

4.3.3. Different degradation methods

It is known that the azo linkage in dyes is highly susceptible to reduction. This effect is proposed at electrochemical treatment and was examined with azo dyes by McClung *et al.* [18]. The interesting by-product of this process is aniline.

The degradation of azo dyes in acidic solutions is well examined. Especially the colour specialists have studied the durability of the different dyes. It is known that the dye is breaking in diazo-component, ammonia and the corresponding quinone. We will focus on the azo dye Orange II ((E)-4-[(2-Hydroxy-1-naphthyl)diazenyl]benzenesulfonic acid). During the formulation of different Orange II-salts, Sisley [24] observed that Orange II and Fe(II) sulphate easily form

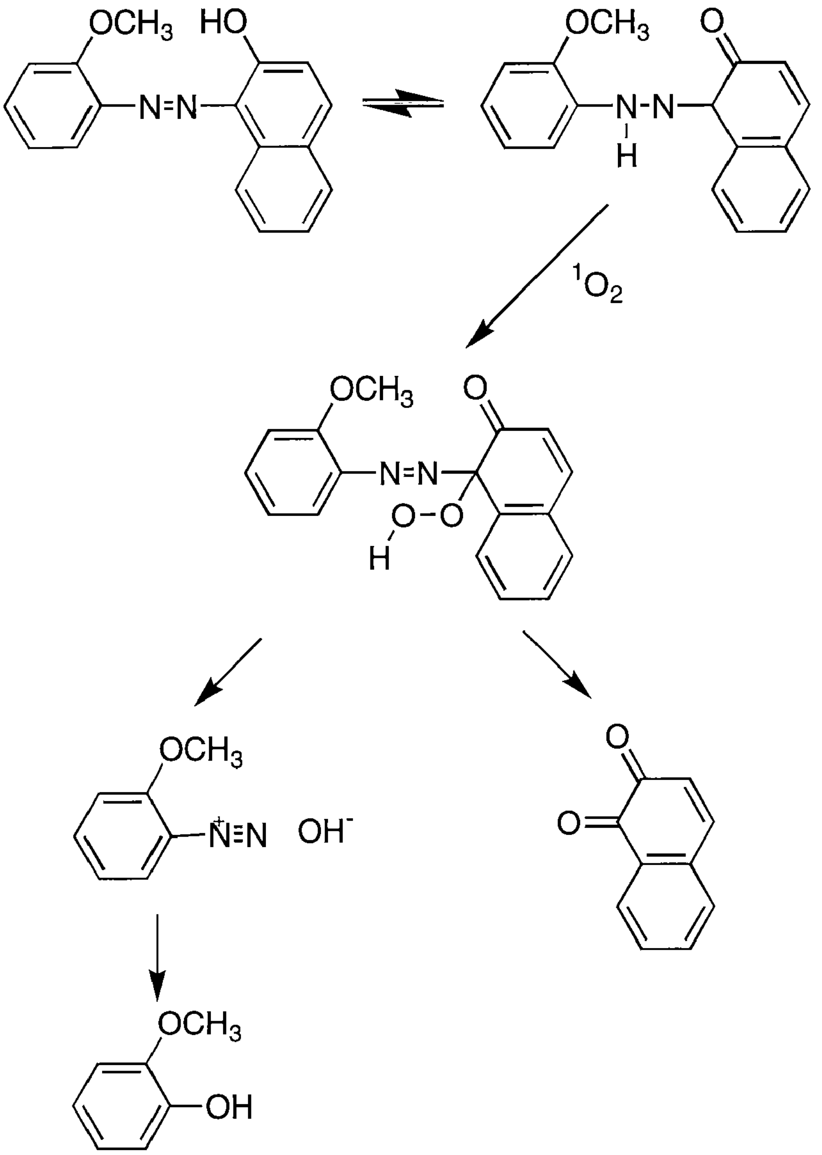

Fig. 4.1: Photo-oxidation of Solvent Red I by singlet oxygen [1]

a salt, but the trial to form the Fe(III)-salt by oxidation of the metal-dye salt led to the release of nitrogen and the smell of β-naphtoquinone. An early attempt [23] to decolourise dye house wastewater was performed with “eau de Labarraque” (solution of sodium hypochlorite, NaOCl) at low temperature. In acidic solution dihydroxy-β-naphtoquinone and the sulfonic acid according to the dye were observed.

4.3.4. Oxidative Degradation of Azo Dyes

To investigate the performance of oxidative disposal processes, several workers have chosen different dyes as model substances. From an industrial point of view, the publications about wet oxidation with high concentrations of dyes (around 0.5

g/L) [5] or combination of different processes are of interest [6,22]. For this work, we will focus on the azo dye as the main pollutant in the examined solutions. Several workers [15,16,22,25] examined the degradation of azo dyes by using ozone as the oxidant. Nitrogen gas was observed as the main product out of the azo-group. Traces of nitrate occurred, but no amines were detected.

4.3.5. Oxidative degradation of Orange II

There are several assumptions about how Orange II decomposes under oxidising conditions. As consequence it can be postulated that the catalyst and pH are important for the formation of different intermediates at low temperatures. After ozonation of Orange II Takahashi *et al.* [25] observed only little amounts of nitrate in the resulting solutions. They postulate the release of molecular nitrogen gas (see Figure 4.2) as the main pathway to remove the bonded nitrogen of the azo-group. Furthermore it is assumed that when a nitro group is produced or introduced in the system it will remain in solution as nitrate ion. Anyway the non-observable formation of nitrate or ammonia during the degradation of Orange II shows that the nitrogen either remains in solution as stable organic compound or it is released as gas (obviously as nitrogen gas, not as nitrous fumes). In the second case two cores without nitrogen-containing groups remain in the solution. It is not supposed that under more severe conditions the azo bridge is divided into two nitro or amino groups.

The Fenton-process also uses Fe-ions and the relevant publications are discussed. During the light induced Fenton reaction at pH of 2.8, Bandara *et al.* [3] observed almost equal amounts of nitrite (intermediate), nitrate and ammonia ions. They proposed that the breaking of the azo group leads to equal parts of nitrogen gas, nitrate and ammonia.

Wet oxidation at higher temperature [8] leads to intermediates as naphtol, 1,2-benzenedicarboxylic acid, 4-hydroxybenzene-sulfonic acid and phtalic acid (or anhydride) (see Figure 4.2). The observed final products are reported as glycolic, formic and acetic acids. The azo dye can decompose by the following steps, which will occur simultaneously:

- Thermal decomposition
- Oxidative degradation

Regarding the mentioned work of Donlagic, the fast thermal decomposition can be neglected below 190°C at neutral pH.

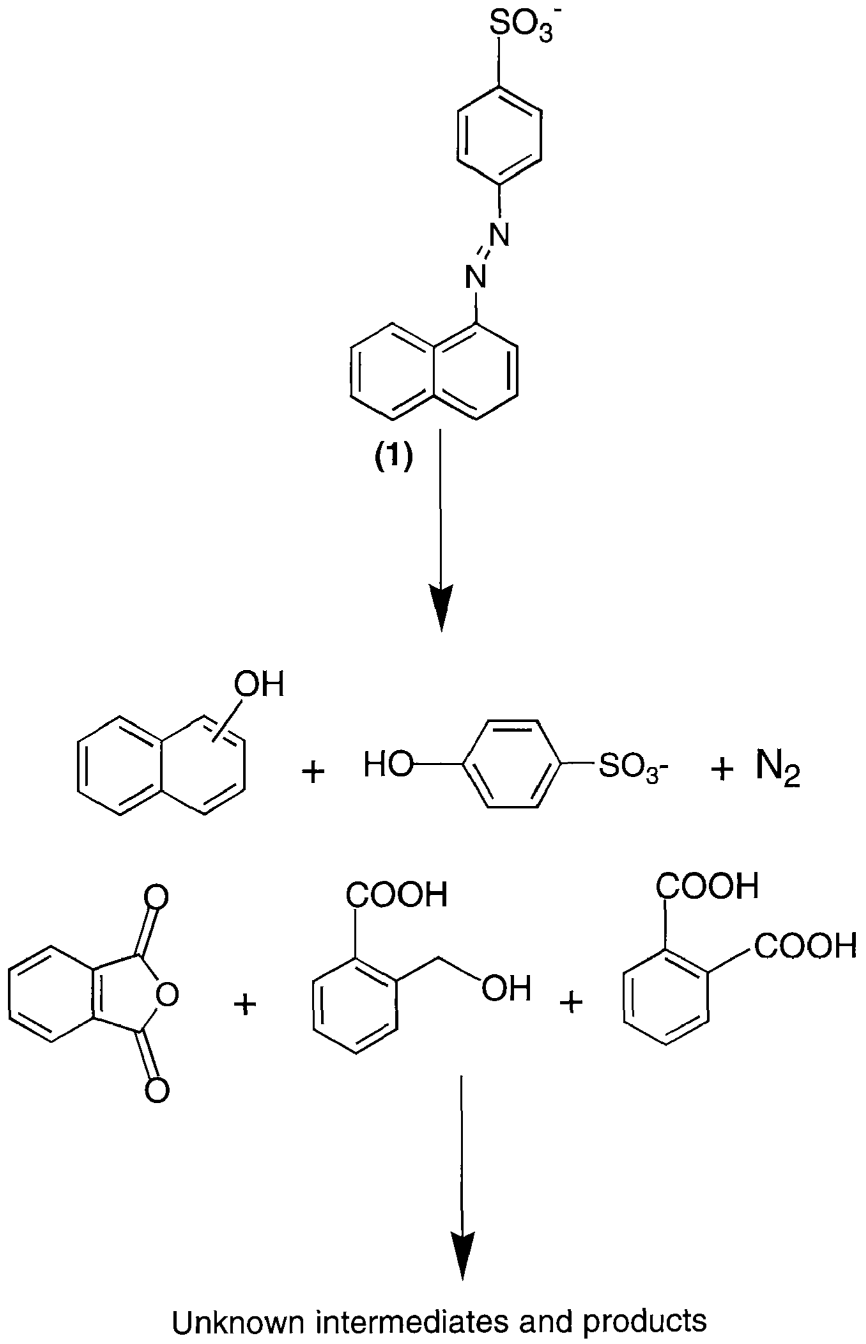

Fig. 4.2: Nitrogen release of Orange II (1), simplified reaction pathway by Donlagic and Levec [8]

In this work, the system can be described as a mixture of an easily oxidisable substance and the pollutant. The used substances are shown in Figure 4.3.

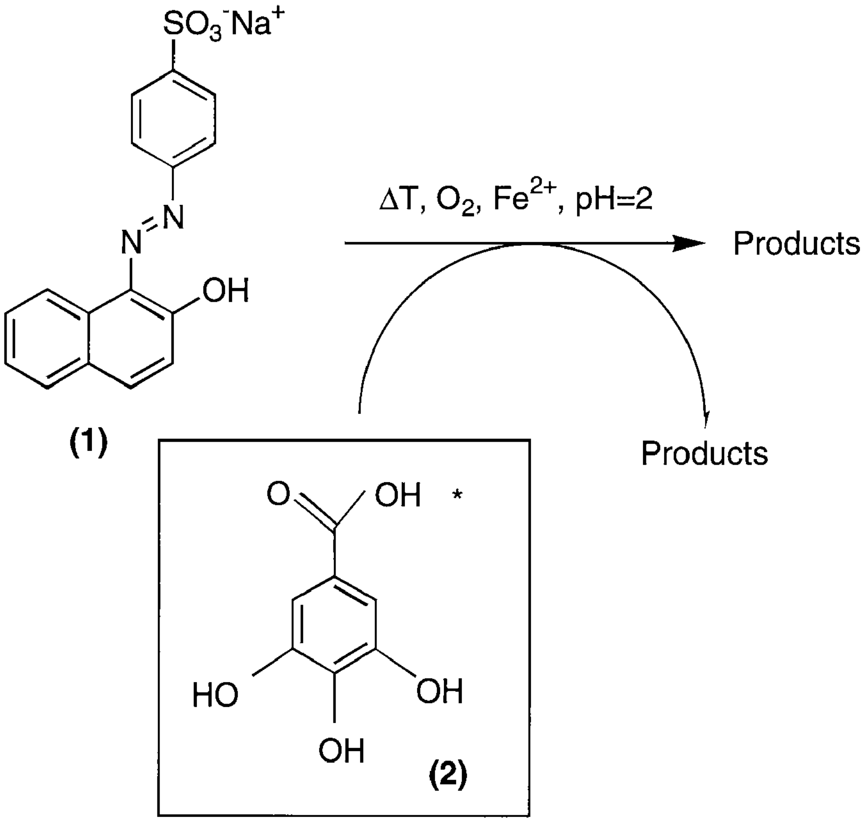

Fig. 4.3: Overview of the system: The azo dye Orange II (1) is converted at elevated temperature with oxygen. Pre-treated gallic acid (2) and Fe(II)-ions promote the wet oxidation at pH=2

4.4 Results

4.4.1. Preface

The used experimental equipment and analytical methods are described in chapter 3. Due to the chemical nature of the dye, some examinations were performed to evaluate the proper handling. The precipitation of the dye with Fe(II) ions needs special attention toward the concentration measurements. This leads to the use of complexing agents and is explained in “Precipitation” on page 48. The thermal instability of the dye was examined by preliminary tests. To avoid a partial decomposition of the dye during the heating-up, two possible solutions are presented in “Preliminary Experiments” on page 50. These discussions lead to the reliable measurements of the dye concentration. Other important analytical tools are TOC and COD measurements. TOC measurements will be reliable by proper use and are comparable between different TOC-analysers and therefore between published results. But some remarks have to be done to COD measurements. The compilation of Janicke [12] reveals the differences between the known instructions to measure COD.

In the case of azo dyes, concern is given to the fate of the azo bridge and the consequences on the COD-measurement. The theoretical oxygen demand (see Eq. [4-5]) of the azo dye is TOD = 1698.8 mg-O_2/g. This is evaluated by using the following reaction:

$$C_{16}H_{11}N_2O_4SNa + 18.5 \cdot O_2 \rightarrow 16 \cdot CO_2 + 5 \cdot H_2O + N_2 + Na^+ + HSO_4^- \qquad [4\text{-}5]$$

The TOD is therefore calculated with the estimated formation of gaseous nitrogen. By assuming other nitrogen-containing products formed out of the azo bridge, the calculated TOD would be different. It is obvious that the formed products influence the measured COD values. The COD values are therefore depending on how the COD was evaluated, *i.e.* used COD analyser or measurement instructions. This discussion is crucial for comparing published COD values or relative COD values (*i.e.* COD/COD_0). The published COD values are lower than the TOD (N_2-release) or the values in this work (see Table 4.2).

Oxygen Demand /(mg-O_2/g)	Remark/Publication
1553	TOD with ammonia formation
1699	TOD with nitrogen gas release
1964	TOD with nitrate formation
1706±31	COD measurement (this work)
1460	COD measurement [16],[7]
1418	COD measurement [9]

Table 4.2: Oxygen demand values: TOD values and observed dates.

Therefore, comparison of COD values was not performed in this work.

Some remarks have to be made to the nitrate- and ammonium-measurements: The nitrogen content of 1 g/L Orange II is 80.0 mg-N/L. For complete conversion of the nitrogen content either to ammonia or nitrate, two maximum concentrations can be calculated. For the complete conversion of the azo-bridge toward ammonia and assuming the complete remaining of the ammonia in the solution, the ammonia concentration would be 103.0 mg-NH_4^+/L. The maximum concentration of nitrate out of the degradation of the dye is 350 mg-NO_3^-/L. Due to the low pH, it is assumed that eventually formed nitrite (NO_2^-) is completely oxidised to nitrate.

To photometrically qualify the concentration of nitrate in the treated solution we used a relevant analytical system (Nanocontrol, Test 64, Macherey-Nagel). This determination with 2,6-dimethylphenol in sulphuric and phosphoric acid has been performed at a wavelength of 385 nm. We observed that the amount of nitrate is too high at the beginning and is decreasing during the treatment (see Table 4.3). The values for the untreated solution are also too high. The cause of these results seems to be the absorbance of the different dissolved compounds.

Another test to qualify the concentration nitrate is the photometrically determination using sulphanilic acid and 1-naphtylamine. This test uses a wavelength of 520 nm. Also in this case the dissolved compounds considerably absorb and the test is not useful.

With the mentioned tests it is not possible to trace the amount of nitrate during the treatment. But after the treatment - in this case after 90 min - nitrate may be observed due the degradation of the coloured substances (*i.e.* dye and intermediates). The total removal of the azo dye is no guarantee that the nitrate test gives reliable information due to the mentioned light-absorbing intermediates.

Sample	Observed values: $C_{Nitrate}$ / mg-NO_2^-/L
Pure water	8
Solved dye	> 100
Prepared solution	> 100
after 5 min treatment	> 100
after 30 min	21
after 90 min	15
estimated after treatment	350

Table 4.3: Measurements of nitrate; Conditions: ϑ = 160°C, $C_{Dye,0}$ = 1 g/L, p_{Oxygen} = 10 bar, pH = 2

Therefore, the chromatograms at the wavelength $\lambda = 385$ nm show only after 90 min of treatment time low absorbance and the nitrate test shows the smallest nitrate concentration of nitrate for these samples. The observed amount of nitrate is in the range of the error of the measurement and the formation of nitrate is not proved. The promoted wet oxidation produces no measurable amounts of nitrate from Orange II. Using the test for ammonia, no analytical problems raised. In the experiments, no ammonia in significant concentrations is found. It is concluded that the wet oxidation forms no or only marginal concentrations nitrate and ammonia from the azo bridge at the examined conditions.

4.4.2. Precipitation

By preparing an acid solution containing the azo dye and Fe-salt, we observed a partial precipitation of the dye. The colour of the solution remains unchanged, but red needles are formed. This precipitation of azo dyes and metal ions is also reported by other authors (*e.g.* [23], [20]) and it is a possible and used process to produce water-insoluble pigments ([26], p. 220). Bandara [2] mentions some experimental works in the field of Orange II precipitation and concludes that complexation is occurring by a bridge between sulphur and iron. The same group proposes the structure in Figure 4.4 [20]. The precipitation of the azo dye leads to a discrepancy between the COD/TOC values gained by unfiltered and filtered probes. Also the HPLC-measurements will result in the solved concentration and not in the true concentration of the dye. To establish an analytical way to gain the true concentration, two complexing agents for metal ions were examined. The mixing with EDTA (Ethlyenediaminetetraacetic acid) resolves the precipitate of a Fe(II)/dye-solution, while the addition of NTA shows no effect.

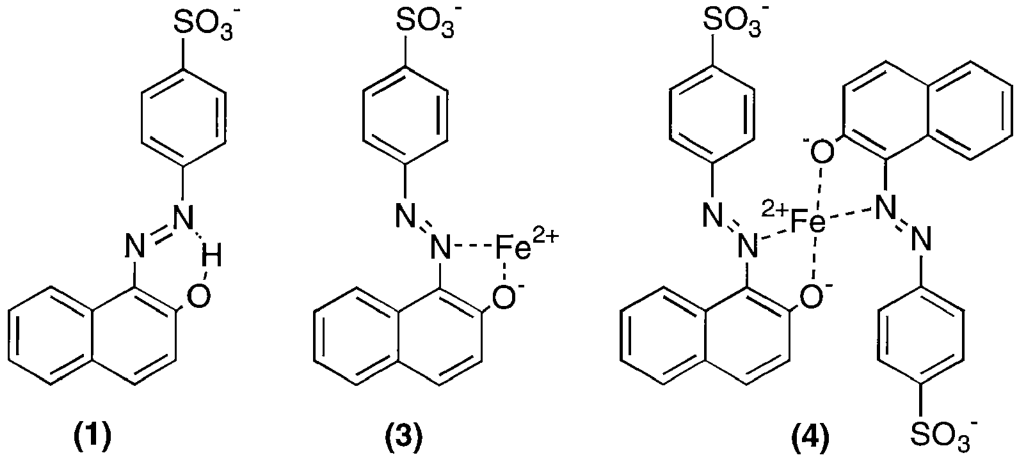
(1) (3) (4)

Fig. 4.4: The azo dye Orange II (1) and two assumed Fe(II)-complexes: 1:1-complex (2) and 1:2-complex (3), adapted from Nadtochenko [20]

After addition of EDTA and filtration, the concentration of the dye was analysed by using these prepared samples and only filtered samples. With $C_{Dye,0} = 1$ g/L and $C_{Fe(II),0} = 0.37$ mM, an average precipitation of 21% was observed. Over all, the precipitate is a complex containing 1.6 mol of azo dye per 1 mol of Fe(II)-ions. Therefore, the composition of the precipitate is assumed to be a mixture of 1:1- and 1:2-complexes. Purified Orange II (by re-crystallisation) showed no precipitation. It is assumed that the chloride ions in the purchased

Orange II are responsible for this effect. By re-crystallisation, the chloride ions are removed and the precipitate is not further observed.

By addition of gallic acid and Fe-ions ($C_{Gallic\ acid,0} = 0.4$ g/L, $C_{Fe(II),0} = 0.37$ mM) to a solution of the azo dye ($C_{Dye,0} = 1$ g/L, pH = 2), the precipitation is re-solved after a specific reaction time. At 160°C and after 10 min of reaction time, no significant differences for both after-treatment methods (*i.e.* with or without EDTA) are observed.

By adding the promoter and the Fe-ions ($C_{I,0} = 0.4$ g/L, $C_{Fe(II),0} = 0.37$ mM), the precipitate is re-solved during the heating-up in the observed temperature range (130...190°C). The first sample after the heating-up (but before the oxygen addition), shows no significant differences in *e.g.* TOC and DOC.

By lowering the amount of the promoter, the re-solving of the precipitate during the heating-up is not given. In the experimental work, the DOC and TOC were always compared and, if necessary, the samples were treated by EDTA before HPLC-measurement.

4.4.3. Preliminary Experiments

Neglecting the reported problems of the degradation of the azo dye during the heating up (see Donlagic and Levec [7]), an experiment at the temperature of 190°C was conducted as follows (pre-mixed procedure): After preparing an acidic solution of Orange II and taking the first sample, the solution was filled in the reactor, evacuated and heated up. After 50 min, the desired temperature (ϑ = 190°C) was attained and the second sample was taken. The stirrer was stopped and the oxygen pressure was adapted. The start time was set when the stirrer started. The analysis shows the decomposition of the azo dye during the heating up. Conversion of about 15% is observed during this period. Noteworthy are the nearly constant remaining values of TOC during the heating up.

To prevent the degradation of the dye, a solution of 1 g of the dye and 40 mL of water is inserted in a container. This container is connected to the reactor. 1960 mL of acidic water (pH=2) is inserted in the reactor, evacuated and heated. At the chosen reaction temperature, the content of the injector is pressurised with argon and injected in the reactor. Using this modified experimental set-up (post-mixed procedure), the decomposition of the dye during the heating-up is prevented.

The comparison of these two experiments shows, that the degradation at oxidative conditions of the dye itself is not infected by the partial decomposition during the heating up. The decay in concentration is comparable, see Figure 4.5. The curves for the TOC values are also comparable. In contrary to the work of Donlagic [8], we have not observed an induction time. The addition of Fe-ions does not change the behaviour of the degradation.

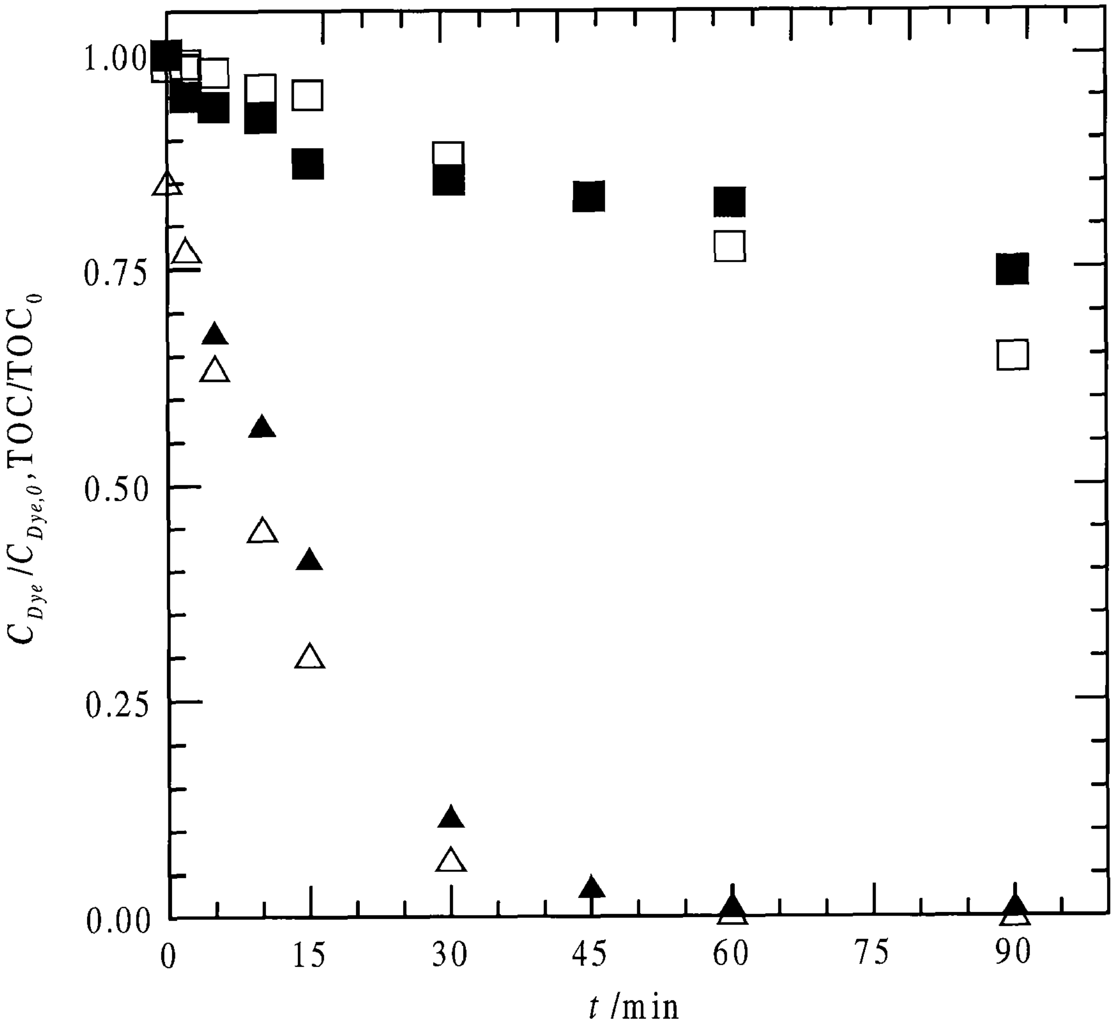

Fig. 4.5: Post- and pre-mixed results of wet oxidation experiments
The dye concentrations of the pre-mixed solution (△) show a low concentration at the reaction start ($t = 0$), but show a comparable decomposition of the dye compared with the post mixed solution (▲). TOC values of the pre-mixed (□) and post-mixed solutions (■) are comparable.
Conditions: $\vartheta = 190°C$, $C_{Dye,0} = 0.5$ g/L, $p_{Oxygen} = 10$ bar, pH = 2

4.4.4. Influence of Promoter Preparation

Two experiments at $\vartheta = 160°C$ and 10 bar of oxygen pressure were conducted in variation of the promoter preparation. The promoter precursor was once prepared with 0.805 g (4.28 mmol) gallic acid monohydrate and 1.00 g (25 mmol) sodium hydroxide. The same concentrations were used but no NaOH was added and gallic acid was solved in warm water under inert gas atmosphere. The initial azo dye concentration was 1.0 g/L (2.85 mM). The mixed solutions have comparable initial TOC values. The comparison of these experiments reveals no significant difference between the promoted wet oxidation and the co-oxidation with gallic acid.

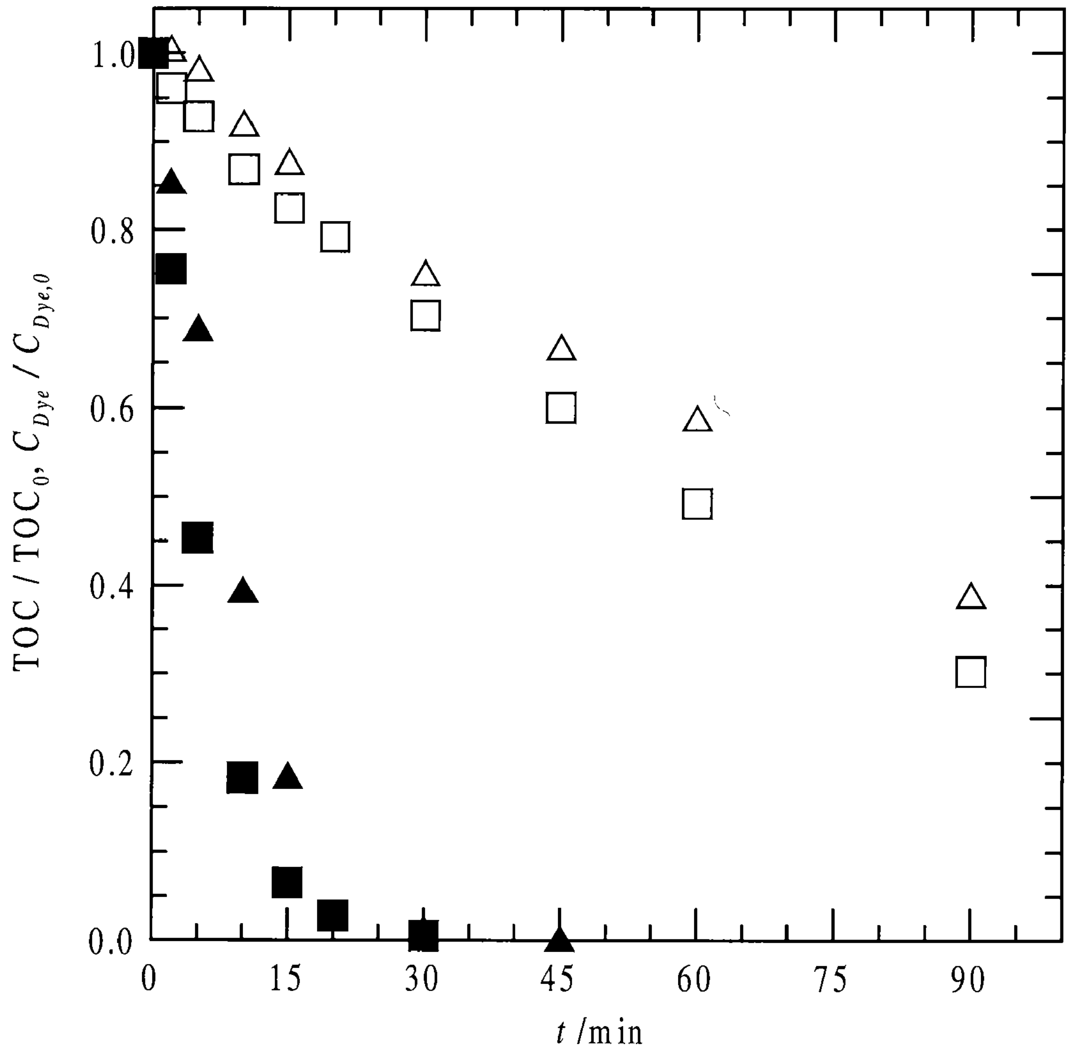

Fig. 4.6: Influence of promoter preparation; Experiments were performed with gallic acid (dye concentration (■) and TOC (□) and with promoter (dye concentration (▲) and TOC (△))
Conditions: $\vartheta = 160°C$, $C_{Dye,0} = 1$ g/L, $p_{Oxygen} = 10$ bar, pH = 2

4.4.5. Temperature and Oxygen Pressure

In wet oxidation, the influence of oxygen is depending on the substrate. Therefore, no universal dependency can be assumed. A variety of published results indicate a range of oxygen reaction order from 0 to 1, as mentioned by Li *et al.* [14]. The WO-treatment of Orange II, reported by Donlagic and Levec [7], led to a first-order kinetic in respect of oxygen for TOC and dye degradation.

Experiments were conducted by varying the partial pressure of oxygen. The oxygen pressure was set to $p_{Oxygen} = 5...10...15$ bar at $\vartheta = 160°C$. The ratio $C_{Dye,0} / C_{I,0}$ was set to 2.5. No significant differences in dye decomposition were obtained for the experiments at 10 and 15 bar. The experiment at 5 bar showed lower conversions in TOC, COD, and C_{Dye} than the experiments with higher p_{Oxygen} (see Figure 4.7). We assume therefore a mass transfer limitation below 10 bar oxygen pressure and only small influence of p_{Oxygen} on the degradation at the observed conditions.

The dependency in temperature was evaluated between 130 and 190°C. The initial concentration of the dye was varied. The amount of the added promoter was kept constant in experiments with promoter. Also experiments without addition of

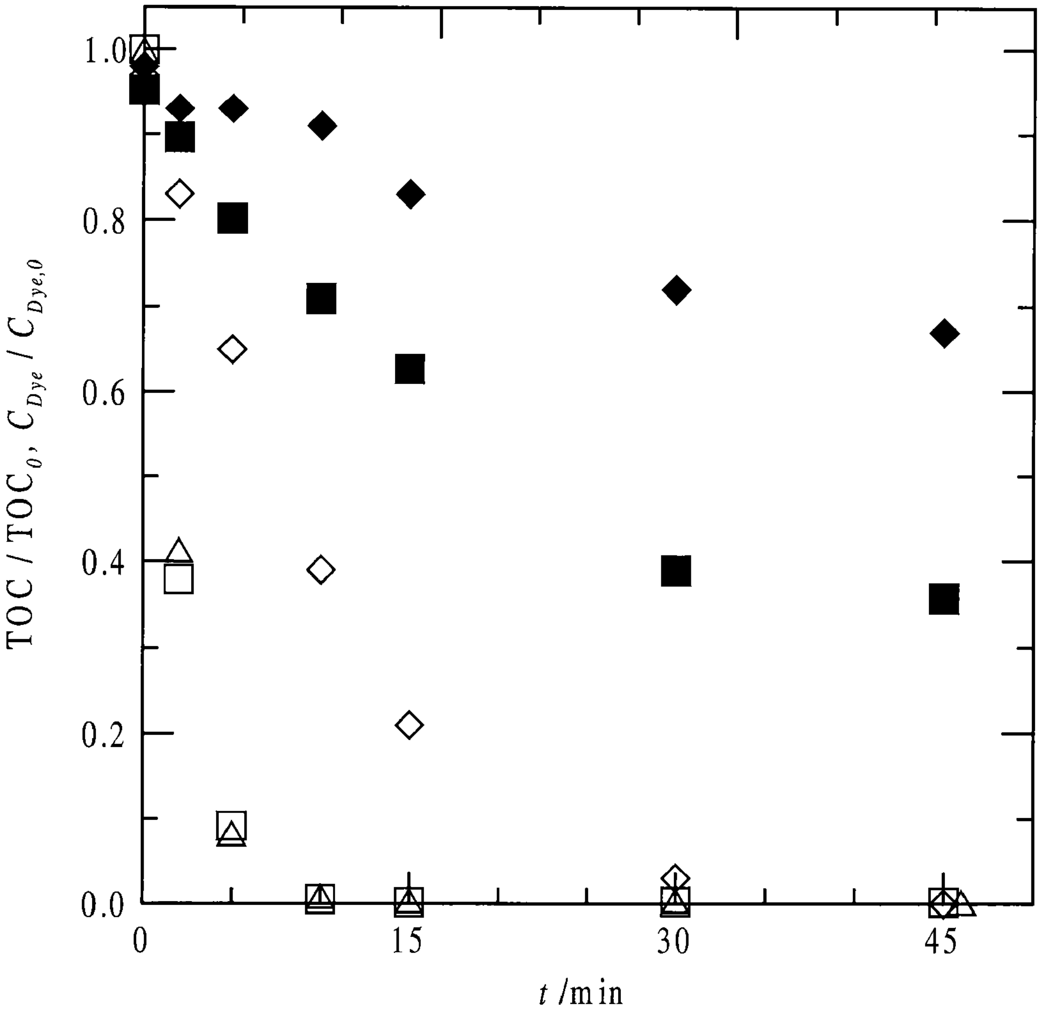

Fig. 4.7: Variation of p_{Oxygen} at $\vartheta = 160°C$ and $C_{Dye,0} = 0.8$ g/L
Dye degradation at 5 bar (◇), 10 bar (□) and 15 bar (△)
TOC degradation at 5 bar (◆) and 10 bar (■)

promoter were performed. Therefore two different ratios of $C_{Dye,0} / C_{I,0}$ were examined:

$C_{Dye,0} / C_{I,0}$	$C_{Dye,0}$ /(mg-C/L)	$C_{I,0}$ /(mg-C/L)
∞	520±20	0
3	520±20	180±2

Table 4.4:Promoter adding to evaluate temperature dependency

By treating the azo dye only at pH=2 (*i.e.* $C_{Dye,0} / C_{I,0} = \infty$), the experiments show for 160 and 130°C a zero-order kinetic. At 190°C, a first-order kinetic is adaptable to the non-promoted decay of the dye.

The experiments with the promoter (*i.e.* $C_{Dye,0}$ / $C_{I,0}$ = 3) were conducted with the same initial concentrations in dye, promoter and Fe-ions. The pH and p_{Oxygen} were equal as well. Using the promoter, the dye decomposition can be described as first-order decay within the chosen range of temperature. The parameters of the Arrhenius-like relationship (see Eq. (4-1)) were obtained by least-square evaluation of the obtained experimental results.

$$k(T) = k_0 \cdot \exp\left(-\frac{E_A}{R \cdot T}\right) \qquad (4\text{-}1)$$

By evaluating the experimental results, the following values for Eq. (4-1) were obtained:

ϑ /°C	Observed $k(T)$ /s^{-1}	Obtained $k(T)$ /s^{-1}
130	$1.7 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$
160	$3.2 \cdot 10^{-3}$	$3.9 \cdot 10^{-3}$
190	$10.2 \cdot 10^{-3}$	$8.9 \cdot 10^{-3}$

Table 4.5: Rate constants for $C_{Dye,0}$ / $C_{I,0}$ = 2.9 at p_{Oxygen} = 10 bar, Activation energy: E_A=46 kJ/mol (k_0=1370 s^{-1}), Average CV for rate constants: 0.2

Figure 4.8 shows the comparison between the WO- and PWO-experiments.

The fate of the intermediates is discussed by considering the decay of lumped parameters, *i.e.* of the COD and TOC values. As seen in Figure 4.9, the PWO experiment at 130°C shows only slow decay in both COD and TOC. At higher temperatures, the decay is more pronounced. At 190°C, a slower decay after 20 min is observable. At 160° reaction temperature, such a fast drop is not observed but is significantly higher than at 130°C.

To completely convert the azo dye, all three temperatures provide satisfying results as long as enough precursor is added. From an economical point of view, the addition of the precursor and the reaction temperature have to be minimised. The work of Donlagic and Levec [7] reveals that the TOC reduction achieves more than 80% at temperatures above 220°C. The promoted wet oxidation results in a TOC reduction of about 70% above 160°C. We decided to evaluate the influence

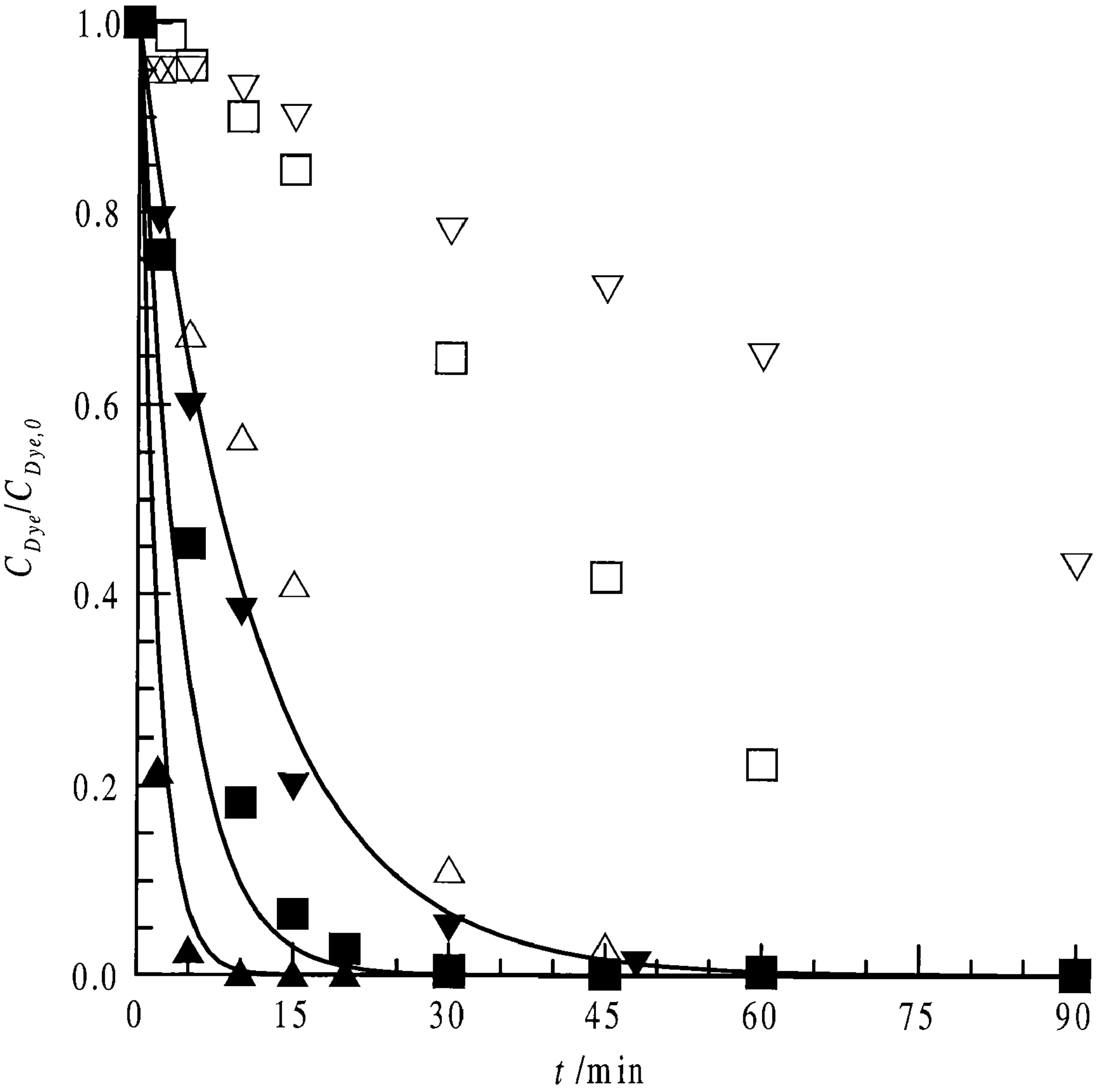

Fig. 4.8: Dye decay at different temperatures (130°C (▽,▼), 160°C (□,■) and 190°C (△,▲)): Comparison of WO (▽,□,△) and PWO (▼,■,▲). Lines are the corresponding curves of the Arrhenius relationship. p_{Oxygen} = 10 bar, pH = 2

of the promoter addition at 160°C due to the promising results in COD and TOC reduction at this reaction temperature.

4.4.6. Promoted Wet Oxidation: Variation of Promoter

The influence of the promoter addition was established at $\vartheta = 160°C$ and $p_{Oxygen} = 10$ bar (pH = 2.0). In addition, the amount of Fe(II)SO_4 was kept constant in the mentioned experiments. The only varied parameter is therefore the amount of the added precursor solution, expressed as $C_{I,0}$. The amount of $C_{I,0}$ was varied between 0 and 180 mg-C/L.

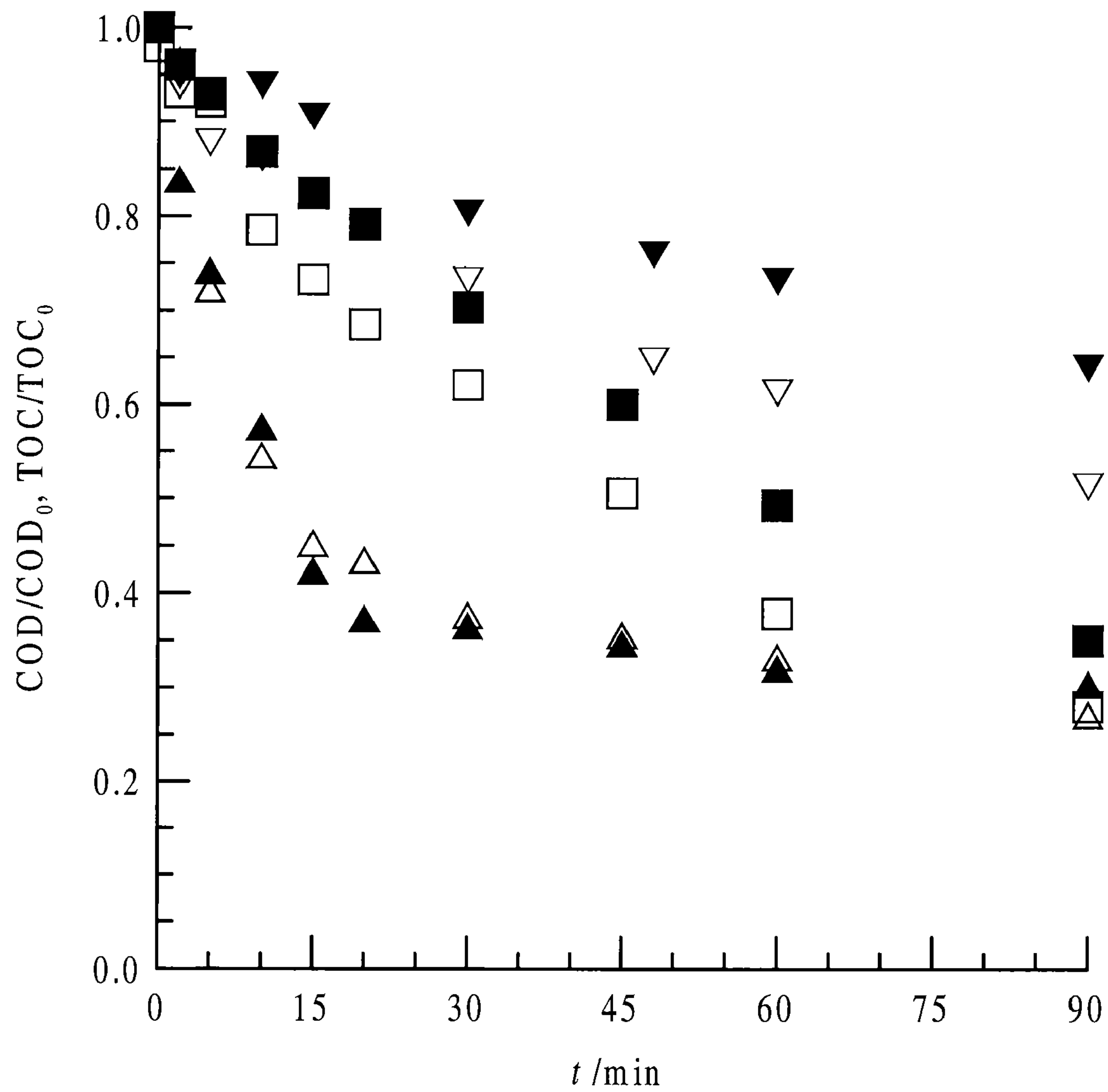

Fig. 4.9: Temperature dependency of COD (▽, □, △) and TOC (▼, ■, ▲) at 130°C (▽, ▼), 160°C (□, ■) and 190°C (△, ▲); p_{Oxygen} = 10 bar, $C_{Dye,0}$ / $C_{I,0}$ = 3, pH = 2

The amount of the precursor solution is given in Table 4.6. Also the symbols in following graphs are mentioned. It was observed that the dye decay seems to be zero order without the precursor. This behaviour was not influenced by added Fe-ions. With low content of the precursor, only marginal acceleration is observed. By high loading of the promoter, the azo dye decomposes rapidly. Therefore, the decay of the dye can be fitted by a first-order rate law. The overview of the azo decay in function of the precursor addition is shown in Figure 4.10.

Run	$C_{I,0}$/(mg-C/L)	$c_{\mathrm{Dye},0}/c_{\mathrm{CI},0}$	Symbol
a	0.0	∞	▽
b	4.5	122	△
c	22.3	25	□
d	89.4	6	○
e	178.8	3	●

Table 4.6:Variation of promoter amount, concentration of promoter and corresponding symbol

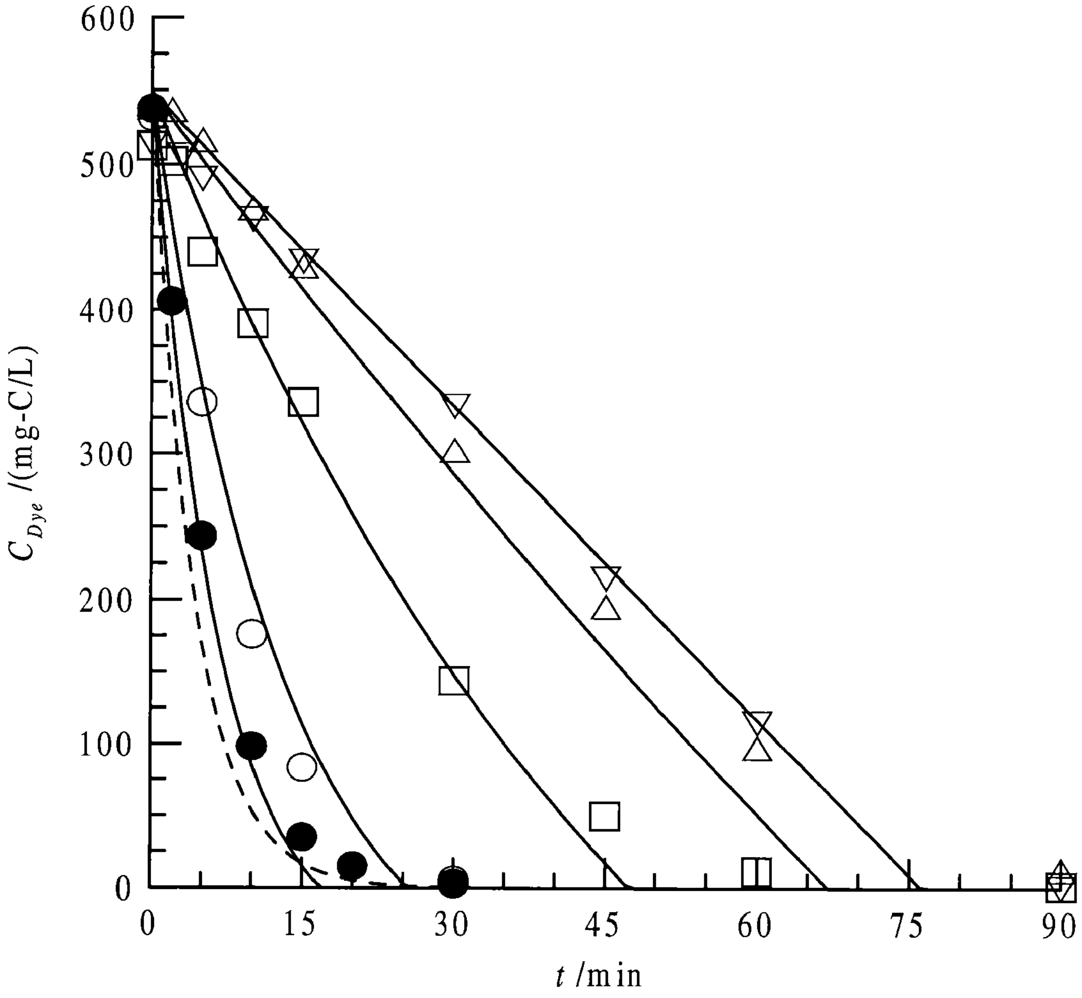

Fig. 4.10: Variation of precursor addition: Azo dye decay
Conditions: ϑ = 160°C, $C_{Dye,0}$ = 1.0 g/L (548 mg-C/L), p_{Oxygen} = 10 bar, pH = 2

To describe this behaviour, a combined kinetic was evaluated. This kinetic includes the mentioned zero-order decay without promoter and the first order decay with the promoter. The promoter is not analytical accessible and therefore, we assume, that *e.g.* by doubling the amount of the precursor solution, the promoter amount will be doubled. We used the initial TOC of the precursor addition as parameter $C_{I,0}$ to describe the influence of the promoter. For the description, the following model was adapted to the data. The combined kinetic consists of a zero order decay of the azo dye:

$$-\frac{dC_{Dye}}{dt} = k_1 \tag{4-2}$$

and a first order decay rate of the dye by a correction with the precursor addition:

$$-\frac{dC_{Dye}}{dt} = k_2 C_{I,0}^m C_{Dye} \tag{4-3}$$

The combined kinetic follows:

$$-\frac{dC_{Dye}}{dt} = k_1 + k_2 C_{I,0}^m C_{Dye} \tag{4-4}$$

By integrating, the C_{Dye} results as a function of time, of the initial concentration, of the dye and of the promoter:

$$C_{Dye} = \frac{k_1 + k_2 C_{I,0}^m C_{Dye}}{k_2 C_{I,0}^m C_{Dye}} \exp\{-t k_2 C_{I,0}^m\} - \frac{k_1}{k_2 C_{I,0}^m} \quad , C_{Dye} \geq 0 \tag{4-5}$$

This combined kinetic implies a change of the rate-determining step during the reaction. For high amount of the dye, the first order kinetic influences the overall kinetic. At low dye concentrations, the zero order kinetics will be rate determining. But the term $C_{I,0}$ controls this change of the determining reaction. Therefore, the change of determining rate is adapted to the range of experiments. At low concentration of the promoter, a zero order kinetic is proposed and at higher concentration of the promoter, a first order kinetic is proposed. These indications are consistent with the observed results.

This description, expressed in Eq. 4-4 and 4-5, is only true for low reaction temperature, *i.e.* zero-order decomposition for non-promoted WO. At 190°C, the azo dye decay is describable by first order kinetics for promoted and non-promoted WO. Therefore, the description has to be adapted for both first-order kinetics.

The results of adapting this description the experiments at ϑ = 160°C and p_{Oxygen} = 10 bar are summarised in Table 4.7 and Figure 4.10:

Parameter	Value
m	1.0
k_1	$0.12\ s^{-1}$
k_2	$1.4 \cdot 10^{-5}\ L \cdot s^{-1} \cdot mg\text{-}C^{-1}$

Table 4.7:Obtained values for Eq. 4-5 at ϑ = 160°C and p_{Oxygen} = 10 bar

Noteworthy is the comparison between the results of the Arrhenius relationship and the proposed model. For ϑ = 160°C and $C_{Dye,0} / C_{I,0} = 3$, the Arrhenius relationship results in $k = 3.9 \cdot 10^{-3}$ s-1 and the model yields in $k_2 \cdot C_{I,0} = 2.5 \cdot 10^{-3}\ s^{-1}$.

The addition of the promoter increases the initial TOC value of the solution. By keeping the concentration of the dye constant at $C_{Dye,0}$ = 1 g/L (548 mg-C/L), the prepared solutions have the following initial carbon content:

Run	$C_{I,0}$ /(mg-C/L)	TOC /(mg-C/L)
a	0.0	548
b	4.5	553
c	22.3	571
d	89.4	638
e	178.8	728

Table 4.8: Overview of experiments with varying precursor amount

The observation of the TOC, (see Figure 4.11) shows, for instance, the production of carbon dioxide in function of the precursor addition. By increasing the amount of the precursor, the TOC drop is becoming faster. The initially added carbon content (*i.e.* precursor) and the released carbon (*i.e.* CO_2) after 30 min treatment time are presented in Figure 4.12. The plot between the added and

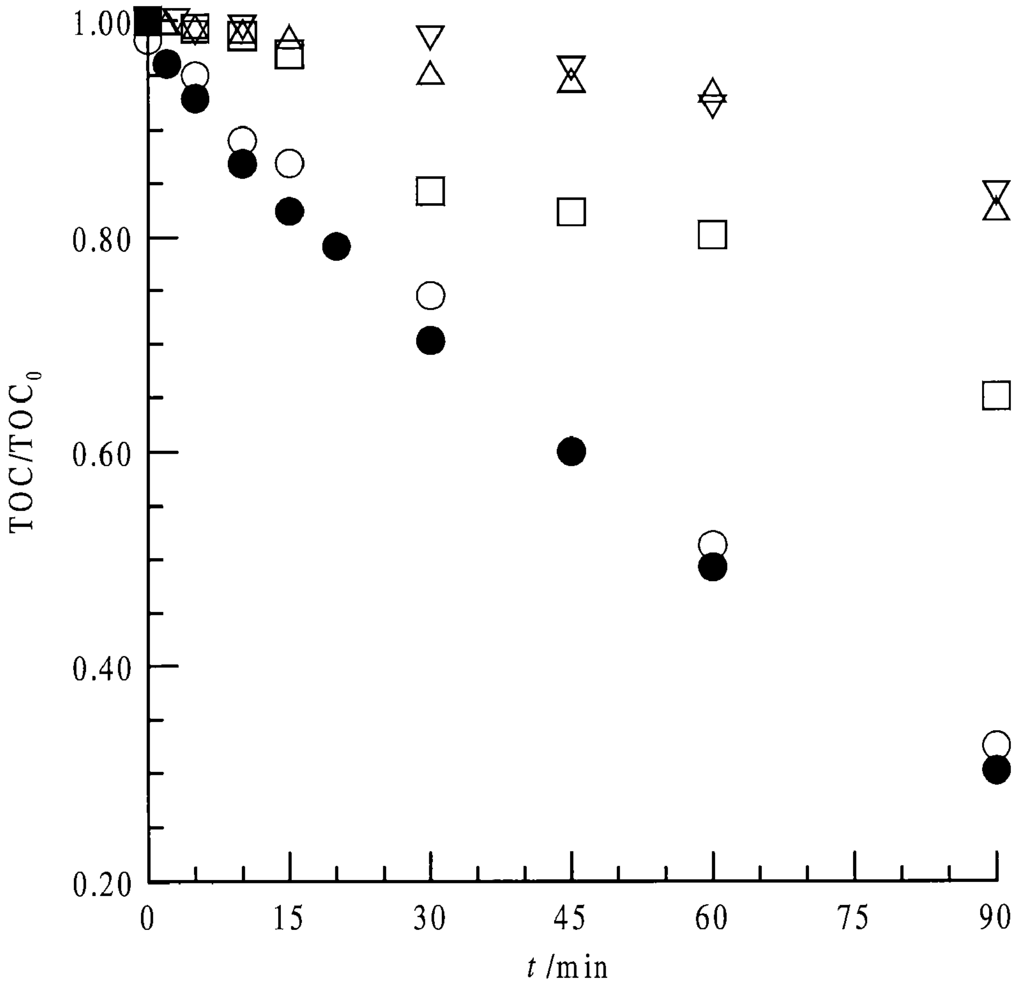

Fig. 4.11: Variation of precursor addition: TOC decay
Conditions: ϑ = 160°C, $C_{Dye,0}$ = 1.0 g/L (548 mg-C/L), p_{Oxygen} = 10 bar, pH = 2

released carbon content shows that more carbon is released than added. The promoter does not only decompose but also promotes the decay of the dye and of the intermediates, expressed as CO_2-release.

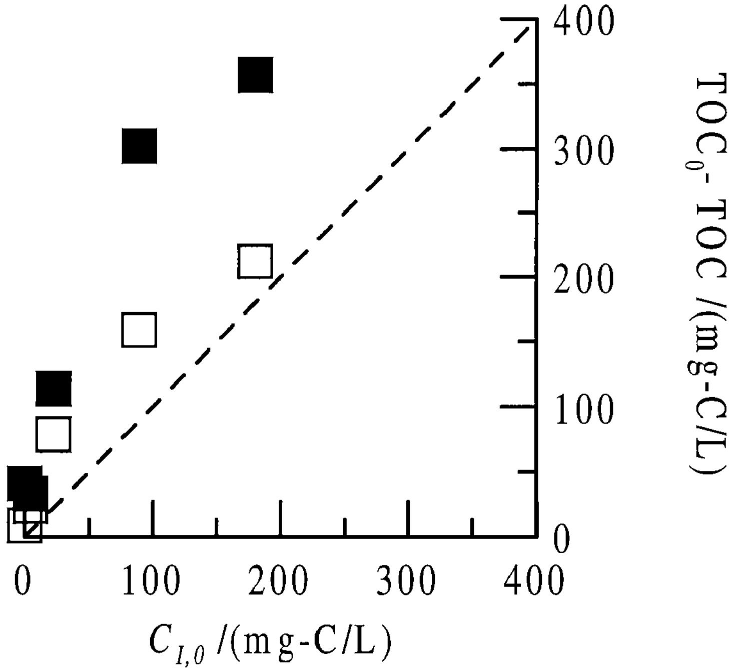

Fig. 4.12: Comparison of added carbon (*i.e.* $C_{I,0}$) and released carbon (TOC_0 - TOC) at ϑ = 160°C and p_{Oxygen} = 10 bar after t = 30 min (□) and t = 60 min (■)

4.4.7. Intermediates

The conversion of the azo dye and of the promoter leads indirectly to carbon dioxide, as the comparison between dye and TOC decay shows. The nature of the first intermediates of the dye is given by the assumed formation of nitrogen. The remaining initial intermediates have to contain a hydroxynaphthalene core and a benzenesulphonic acid. To measure the formation of the possible intermediates, a positive identification by retention time and UV/Vis-spectrum has to be performed. The examination of different samples by GC/MS did not give any insight in intermediates formation. The trial-and-error attempt in HPLC analysis revealed that sulfonic acids are not accessible by a C-18/RP column due to their low retention time. The possible naphthols and hydroxynaphthols were examined but not found in the experimental samples. The chromatograms in Figure 4.13 were

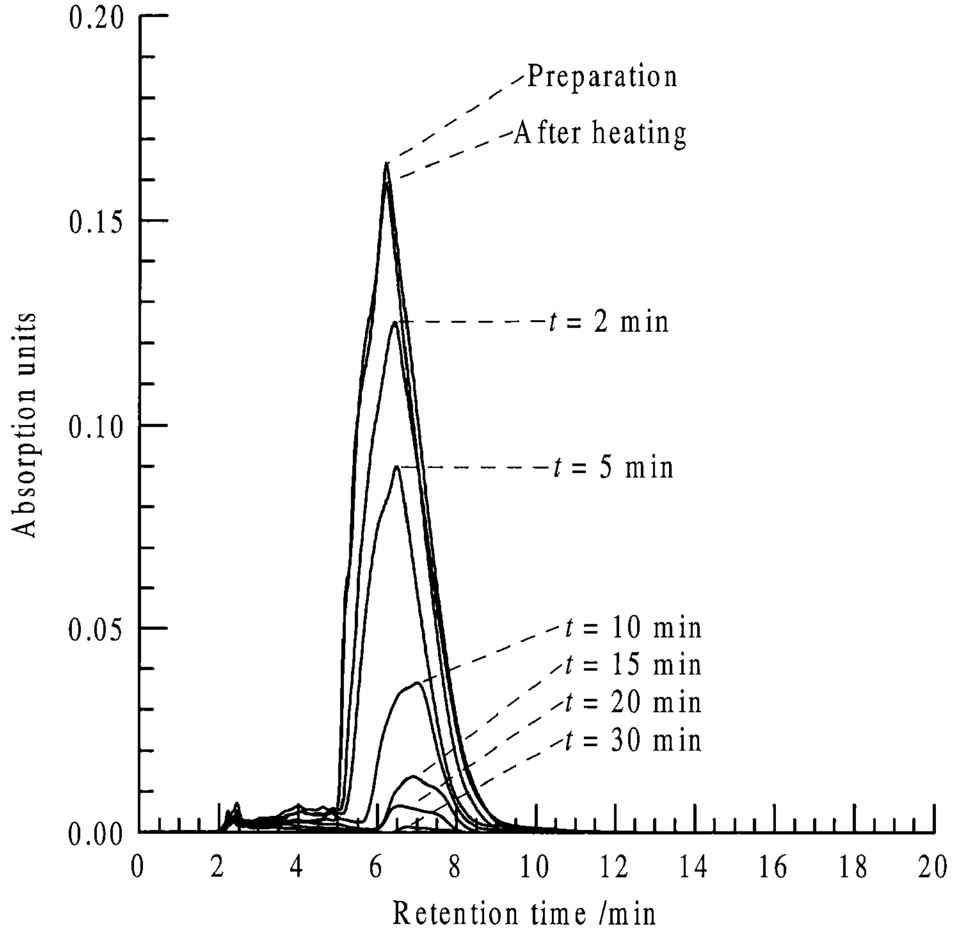

Fig. 4.13: Chromatograms at λ = 484 nm, RT(Dye) = 6.6 min
Reaction conditions: p_{Oxygen} = 10 bar, $C_{Dye,0} / C_{I,0}$ = 3, ϑ = 160°C

obtained at $\lambda = 484$ nm and show mainly the decay of the dye (RT = 6.6 min), while at 230 nm (see Figure 4.14), the formation of substances with lower retention time

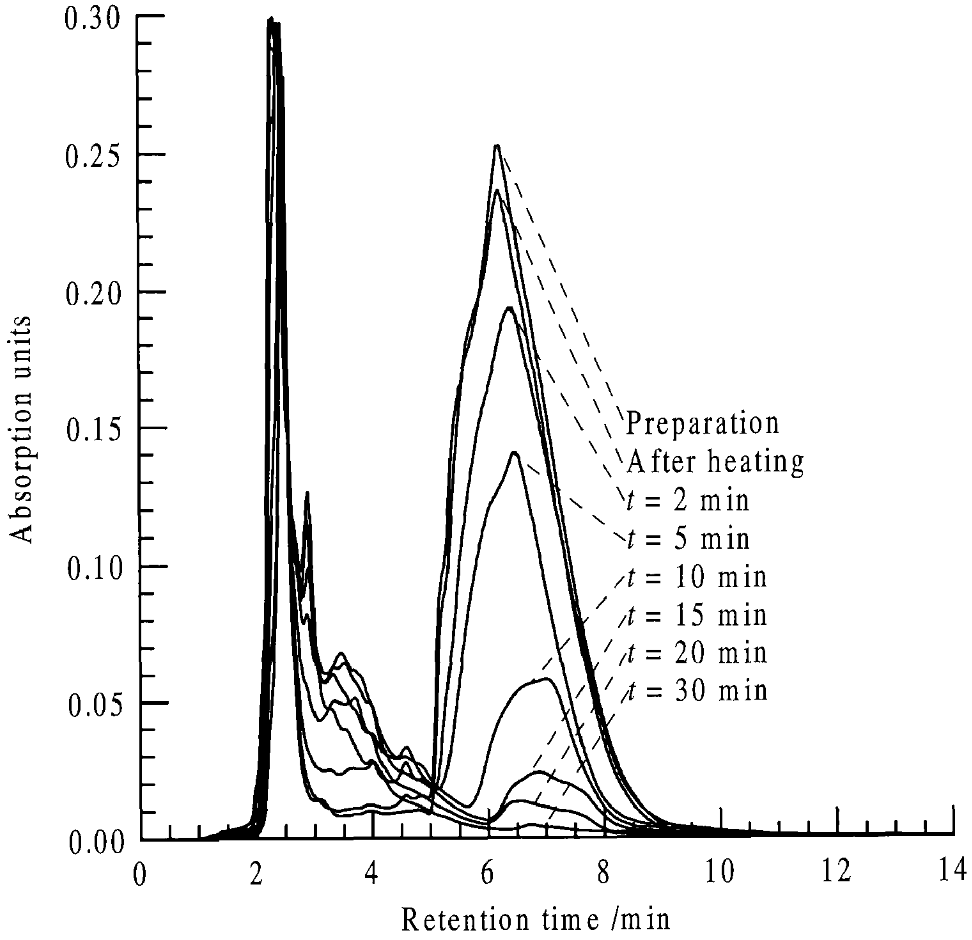

Fig. 4.14: Chromatograms at λ = 230 nm, RT(Dye) = 6.6 min
Reaction conditions: p_{Oxygen} **= 10 bar,** $C_{Dye,0} / C_{I,0}$ **= 3,** ϑ **= 160°C**

is also observable. For the carboxylic acids, fumaric, malenic, formic and acetic acid were found.

4.5 Discussion

The wet oxidation at pH = 2.0, p_{Oxygen} = 10 bar and ϑ = 190°C showed a fast decomposition compared with published results at unchanged pH (see Figure 4.15). This is explainable by the known instability of the azo bridge at low pH. By lowering the reaction temperature, the decay rate of the dye lowers and the reaction kinetics changes form first- to zero-order. By addition of Fe(II)-ions and the promoter, the decay is accelerated and can be described by first-order kinetics within the chosen temperature range. The acceleration of the dye decay by promoter addition is observed in the whole temperature range.

Oxygen pressure shows no observable influence on the decay, but increasing reaction temperature enhances the decay rate. This can be fairly well described by an Arrhenius relationship. By varying the amount of the promoter, the dye decay shifts from an observable zero-order rate law to a first-order decay. The promoter itself is not observable, but by using the initial concentration of promoter, the description of the influence by the promoter can be performed. The initial promoter concentration has a first order influence in the obtained combined kinetic. By using a defined preparation procedure and measuring the added carbon, a reproducible evaluation of industrial wastewater problems is given.

The experiments at the examined temperature range show only small conversion rates without the promoter. The increase of the promoter amount not only increases the decay of the dye but also changes the reaction kinetic. However, the treatment of the azo dye Orange II by promoted wet oxidation has shown that a further parameter influences the overall performance of the proposed system.

By addition of the promoter, the final TOC/COD and the rate of dye decay can be controlled. This allows to run an existing WO-plant at fixed reaction temperature and to influence the effluent quality by the addition of the promoter. The promoted wet oxidation allows also lower reaction temperatures in comparison with wet air oxidation.

To compare these results with a wet air oxidation process, the work of Donlagic [7] has to be discussed. In the mentioned work, the azo dye Orange II was treated at p_{Oxygen} = 10 bar and within the temperature range of ϑ = 200°C...240°C. The pH value of the solutions dropped within the first 40 min of oxidation (from 6.43 to 3.4-2.8) and then remained almost constant. It is reported that at lower temperature, *i.e.* 190°C, an induction period is observed. The same experimental set-up was used for catalysed wet oxidation at lower temperature. In this case, no pH drop was observed.

The comparison between the reported and the obtained results shows the great influence of the pH on the decay of the azo dye. The TOC removal is clearly lower at lower temperatures.

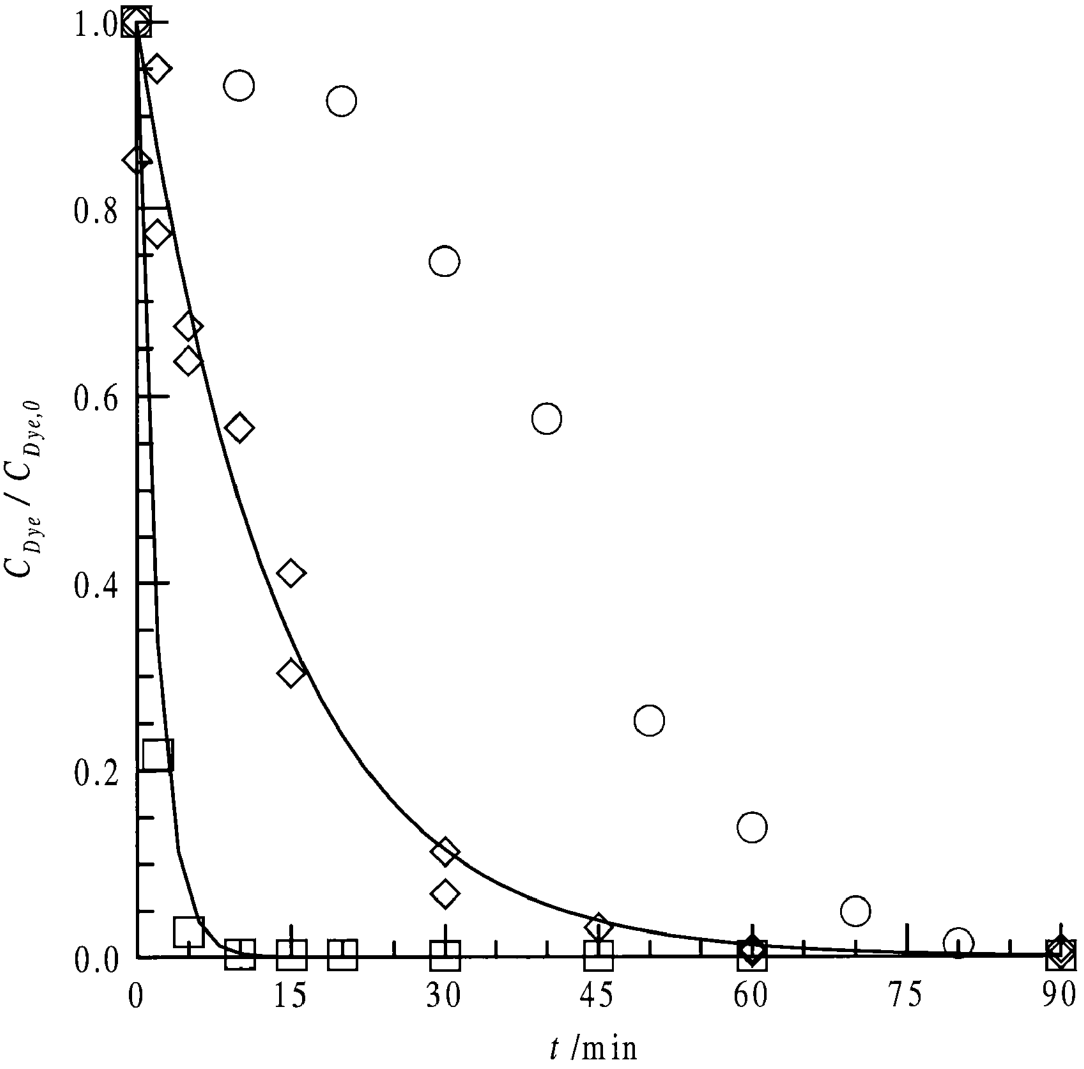

Fig. 4.15: Different wet oxidation results at $\vartheta = 190°C$ and $p_{Oxygen} = 10$ bar: Wet oxidation (○) [7], wet oxidation at pH = 2 (◇) and promoted wet oxidation (□). The curves corresponds to the evaluated kinetics

The promoter addition is a further parameter for the process. Not only temperature and pH but also the amount of the promoter has a strong influence on the decomposition of the dye and on the TOC removal. A low pH has also the great advantage to control the production of chloride-containing compounds [17]. The amount of the precursor suitable for an industrial application is controlled not only by chemical means but also by economical constraints. To successfully adapt the promoted wet oxidation, experiments on bench-scale have to be performed. The amount of promoter and the reaction conditions (*i.e.* temperature) have to be compared and optimised by suitable parameters (*i.e.* costs, effluent requirements). This means, the comparison between running costs (promoter addition) and investment costs (reaction temperature determines lining of the reactor) leads to an optimum.

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5 Promoted wet oxidation of Aniline

5.1 Introduction

Aniline is one of the most important industrially produced amines. It is most widely used for the manufacture of polyurethanes, rubber and pesticides. It is a useful intermediate in the production of many other products such as dyestuffs, drugs, photographic resins and varnishes. Thus, a variety of industrial effluents have aniline as a major wastewater constituent.

Aniline is highly toxic to aquatic life and it is also moderately toxic for humans. Workers exposed to small amounts of aniline in air over several years experience adverse blood effects. Limited evidence suggests that aniline may also cause adverse reproductive effects in humans. Other human health effects associated with exposure to aniline over long periods of time are not known. Laboratory studies with animals show that repeated exposure to large amounts of aniline over a lifetime causes cancer. Small amounts of aniline in air decreases the ability of blood to carry oxygen [7].

Aniline is a colourless, oily liquid with a weak amine odour. The substance is hygroscopic and light sensitive. The boiling point is $\vartheta_{boil} = 184°C$, the melting point is $\vartheta_{melt} = -6.2°C$. The vapour pressure was examined by Hatton *et al.* [10] in temperature range of 304...457 K and can be described by the following Antoine equation (p_{Ani} in bar, T in Kelvin):

$$\log(p_{Ani}) = 4.34541 - \frac{1661.858}{T - 74.048} \tag{5-1}$$

The relative low boiling temperature (compared with the proposed treatment temperatures of up to 190°C), the volatility of the compound has to be discussed. But the pK_A-value of 4.7 [4] and the moderate solubility of aniline in water (approx. 35 g/L at 20°C, [7]) leads to the assumption that the anilinium ion remains partially in solution at pH = 2.

Aniline shows a moderate biodegradability and is used as reference substance for the activity of the sewage sludge in wastewater treatment. In compounds such as aniline, the nitrogen component is also significant in wastewater treatment besides carbon. Biological conversion of aniline involves first, carbonaceous removal by heterotrophic bacteria releasing ammonia nitrogen as the end product [8].

There are several disadvantages in discharging effluents containing ammonia into water bodies. Biological conversion of ammonia to nitrite and nitrate consumes dissolved oxygen. Ammonia is also toxic to fish life. Likewise, it reacts with chlorine to form chloroamines, which are less effective disinfectants than free available chlorine. In treatment plants, a higher dose of chlorine will be required when ammonia is present. Thus, untreated ammonia can cause environmental damage [8].

Removal of ammonia can be accomplished by nitrifying bacteria that are autotrophic in nature. In industrial wastewater treatment, a basic evaporation leads to gaseous ammonia, which can be recirculated to the manufacturing plants.

Aniline was chosen due to the following reasons:

- Aniline is the simplest and the most important of the aromatic amines
- It is well examined in AOP-studies
- The fate of the amine group is interesting for industrial applications

5.1.1. Oxidation of amines

The amine group contains nitrogen in its lowest oxidation state. It is not surprising that primary amines are easily oxidised. Various products are obtained depending on the reaction condition used. As an example, primary amines react with peroxy acids to yield nitroso compounds via initially formed hydroxylamines. Nitroso compounds or their oxime tautomers can be oxidised further to nitro derivatives under more vigorous conditions. Oxidation of aniline with excess of cold peroxy acetic acid gives nitroso benzene in high yields [14]. The oxidation seems to have the PhNH-radical as precursor for the formed nitrosobenzene [9]. The reactions of hydroxyl radicals with aniline or the anilinium ion are summarised by Buxton [1].

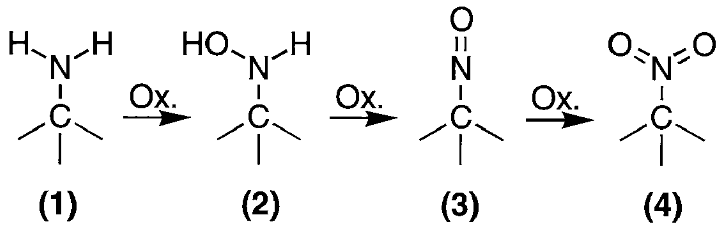

Fig. 5.1: The oxidation of an amine (1) yields to nitroso (3) *via* hydroxylamine (2), final product is a nitro-compound (4)

For the reaction with aniline, a σ-complex is reported. The anilinium ions react toward the radical cation and nitroaniline.

5.1.2. Polymerisation

A widespread use of the oxidative treatment of aniline is the production of polyaniline (PANI). PANI has been studied extensively and, as a conducting polymer, has found use in batteries, ion exchange, and corrosion control among other areas. Two possible ways of production are discussed:

- Electrochemical polymerisation
- Polymerisation by oxidants

Electrolytically, the polymer is readily prepared from aqueous solution (usually in acidic solution [11]) by anodic polymerisation onto the surface electrode. The electrochemical polymerisation mechanism leading to the insoluble polymeric state of aniline, particularly early in the polymerisation process, have been widely discussed and extensively studied over the last three decades using a variety of electrochemical and spectroscopic techniques. It is presumed that all of the aniline oligomers are formed *via* series of oxidation/addition reactions starting with the oxidation of aniline to a radical cation (see Figure 5.2).

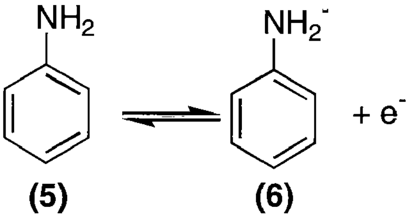

Fig. 5.2: Radical cation (6) formed by oxidation of aniline (5)

The radical-radical coupling by releasing two protons leads to three possible arrangements with three corresponding dimers:

- Head-to-tail dimer (N-phenyl-1,4-phenyldiamine, 4-aminodiphenylamine)
- Tail-to-tail dimer (benzidine)
- Head-to-head (hydrazobenzene, N,N-diphenylhydrazine)

These routes are shown in Figure 5.3. The first route is the head-to-tail arrangement with an amine-linkage. The second route leads to a phenyl-linkage and the third route leads to di-amine-linkage. By further oxidation and releasing of protons, the trimer or tetramer is produced. By further oxidation and coupling, polyaniline (PANI) is formed. PANI is insoluble in water and will deposit on the

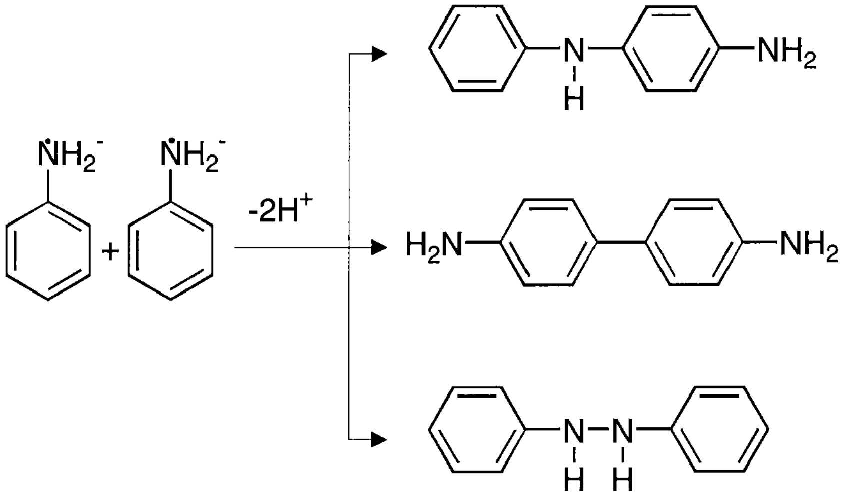

Fig. 5.3: Three routes for dimer formation by coupling of two cations, adapted from [6]

electrode (in the case of electrochemical polymerisation). It has a high conductivity and redox reversibility and it is air stable. The base PANI is thought to be of the general structure (Figure 5.4) that consists of alternating reduced (amine nitrogen) and oxidised (imine nitrogen) head-to-tail linked aniline dimeric subunits. The route of formation is well studied and recent results are reported by Deng and van Berkel [6]. The prove of the *para*-coupling was done by comparing different isomers of methyl aniline. By blocking the *para*-position, polymerisation is not occurring [5].

In solution chemistry, aniline is usually polymerised by the oxidation of the

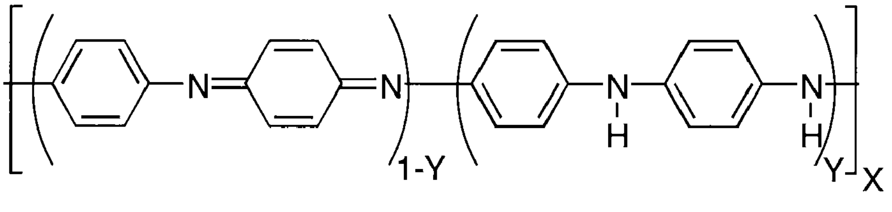

Fig. 5.4: Assumed structure of PANI, adapted from [6]

monomer with oxidants such as ammonium peroxydisulfate and potassium dichromate. Also in this case, three different routes are mentioned. It is stressed by Kloeppner and Duran [11], that the primary product is aminodiphenylamine at pH = 0-2 and oxidative conditions. This corresponds with the first route in Figure 5.3. Once polymerisation is initiated, it has been observed that the polymer formation rate undergoes an autoacceleration or autocatalytic effect. It is also observed that the increase in polymerisation rate is directly proportional to the amount of formed polymer [11]. A procedure for the synthesis of PANI is given by Wu et al. [15].

Interesting is the dominant role of the para-coupled oligomers in the cited references. An explanation for this effect is given by Larumbe *et al.*: The unpaired electron of the radical cation is mainly located at the carbon in the *para* position with respect to the amino group. This assertion is based on quantum-chemical calculations [13]. This may be the reason for the low reactivity in polymerisation of the *para*-substituted aromatic amines. Therefore, Figure 5.2 is not the "right" description for the predicted form or for the observed effects of the radical cation.

5.1.3. Oxidative Degradation

A comparative study of different AOP's in aniline degradation was performed by Brillas *et al.* The experiments were done with acidic solution (pH=3) of aniline. They found that electro-Fenton and photoelectro-Fenton-processes are suitable to completely convert aniline. The observed intermediates are benzoquinone, nitrobenzene and maleic acid. The corresponding mineralisation products are nitrate and ammonia (15.5 mg-NH_4^+/L, the complete conversion toward ammonia would lead to 19.4 mg-NH_4^+/L). The experiments with hydrogen peroxide addition reveals fast initial conversion and a slower second step. Therefore, no complete degradation was achieved by these Fenton-reaction or photocatalytic Fenton-process. Only the electrochemical-assisted Fenton-processes are suitable for aniline degradation.

The treatment of aniline with ozone results in the formation of nitrosobenzene, nitrobenzene and other mutagens, e.g. azobenzenes or benzidine [2,3]. Also the formation of nitroanilines is observed. This formation is explained by the reaction of pernitrous acid, hydroxyl radicals and nitrogen dioxide. The formation of mutagens using this process needs special attention to the degree of conversion during the reaction. Experimental works by using manganese dioxide as oxidant also revealed the formation of mainly azobenzene (oxidised N,N-diphenylhydrazine, third route in Figure 5.3) and 4-aminodiphenylamine (first route) in acidic solution [12].

5.2 Experiments

5.2.1. Preface

The experimental work consists of an analytical part, of the preliminary experiments, of the experiments toward the promoted wet oxidation with oxygen and of the description of the relevant phenomena. The preliminary experiments are to prove the reliability of the experimental set-up and of the preparation. The discussion will consider these different points and we will try to explain the promoted wet oxidation of aniline.

The different chemical and physical transformations of aniline are shown in Figure 5.5. The influence of the aniline volatility has to be examined by preliminary experiments. The initial aniline may be converted as anilinium ion or as solved aniline. The pK_A-value at ambient conditions indicates that 94% of the initial aniline is as anilinium ion in solution. A gas phase reaction is not assumed.

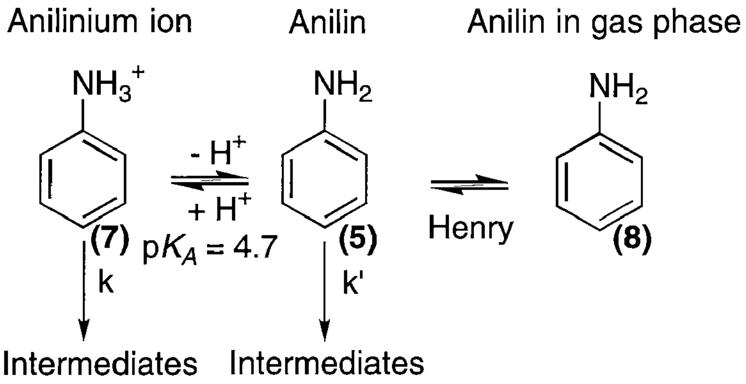

Fig. 5.5: The initial aniline may be found in the reactor as solved anilinium (7), as solved aniline (5) or as gaseous aniline (8), only the solved compounds are converted towards the intermediates

5.2.2. Analytics

The evaluation of the use of the size-exclusion column for the analysis of aniline was not successful. The C-18-column gained good results at the observed wavelength of 228 nm. The nitrate-test shows no interaction with the aniline, but the ammonium-test gives no reliable information as long as dissolved aniline/ anilinium is in the sample.

5.2.3. Preliminary experiments

To establish the solubility and stability of aniline, 0.5 g of aniline was dissolved in approx. 40 mL of acidic water (pH = 2). This solution was inserted in the container and approx. 1960 mL of acidic water (pH = 2) was inserted in the reactor. The content of the reactor was evacuated and heated up. After reaching 190°C, the content of the container was inserted in the reactor by argon-pressure. The reactor content was pressurised with 10 bar partial pressure of argon. The aniline concentration was measured by HPLC and TOC. After 20 min, an unidentified substance (λ_{max} = 308.8 nm) at low concentration is observed. The formation of this substance is increasing during the reaction time but at a low level. Therefore, the solved aniline shows no significant conversion and no observable evaporation.

Also the effect of the initial evacuation has to be evaluated. An aqueous solution of 2 L with pH = 2 with an aniline concentration of 0.5 g/L is inserted in the reactor. The solution has been evacuated (approx. 100 mbar) and then, without heating, pressurised with oxygen. A sample was drawn and analysed by HPLC and TOC. This procedure of evacuating and pressurising was done for three times. The lost aniline was determined to be lower than 1% per sample (*i.e.* not significant change in concentration or TOC). So, the influence of the initial evacuating can be neglected.

These results show that the anilinium remains solved in solution and will reduce neither by heating nor by evacuating. Therefore the experiments can be proceeded as follows:

The desired amounts of aniline, of the Fe-salt and of the initiator/gallic acid are mixed in water and the pH is adjusted to pH=2. The final volume of the solution is 2 L. The solution is transferred into the reactor, evacuated and heated up to the desired temperature. After reaching this temperature, the stirrer is shut down and the solution is pressurised with the desired partial pressure of oxygen. The start of the stirrer is taken as the start time of the reaction.

5.2.4. Wet Oxidation Experiments

Three experiments were performed to examine the wet air oxidation, *i.e.* the wet oxidation with only oxygen, at pH = 2.0. The observed temperature range was 130...160...190°C and the oxygen partial pressure was chosen to p_{Oxygen} = 10 bar. At 130°C, no significant loss in concentration of aniline or TOC was observed during the first 50 min. After 50 min of reaction time, a pink colour is observed and the aniline concentration is marginally reduced (about 1%). Regarding the HPLC-results, no intermediates could be detected. The TOC of the filtered samples shows no significant difference compared to the unfiltered analysis. At the experiment at $\vartheta = 160°C$, the pink colour is also observed and later, the colour changes to a light brown. The aniline concentration significantly decreases after 15 min. At 190°C, the pink colour is observed after 5 min and the colour darkens during the reaction time. After 60 min, a brown tarnishing occurs. The brown colour remains after filtering but also a brown precipitate is observed on the filter. After the reaction, a dark plaque is observed at the reactor wall. This plaque is removed by a HNO_3-solution at 160°C. The concentrations of aniline as a function of the temperature are shown in Figure 5.6.

The observation of TOC and NDOC (Non-dissolved organic carbon) shows interesting facts: The evaluation of TOC at the experiment at 130°C showed no significant difference to the aniline concentration (expressed in mg-C/L). Also the filtrated samples showed no significant difference in DOC compared to the TOC (*i.e.* $\text{NDOC} \approx 0$).

But at higher temperatures, the formation of NDOC is more pronounced while the TOC shows no significant change at 160°C. At 190°C, the TOC shows a loss of carbon from the solution. This fact may indicate a mineralisation of the inserted carbon toward CO_2. But the precipitation of the black material on the reactor wall also reduces the carbon content of the solution. The TOC and NDOC of the experiments at $\vartheta = 160°$ and $\vartheta = 190°C$ are shown in Figure 5.7.

The fate of the aniline is not obvious. The slow conversion at the beginning indicates an induction time. Then, a reaction diminishes the solved aniline. Two pathways of disappearance to describe the observed effects are possible:

- Oxidative polymerisation
- Oxidative decomposition and polymerisation

The possible answer would give an analysis of the nitrogen-containing ions. Assuming no formation of nitrogen gas, the mineralisation of aniline leads to nitrate or ammonia. The corresponding analysis did not indicate these ions in solution.

The analysis of the low molecular carbonic acids indicates the increasing amount of acetic acid (by GC and HPLC) and formic acid (HPLC). The concentrations of these acids reach around 40 mg/L (after 90 min at 190°C). Also

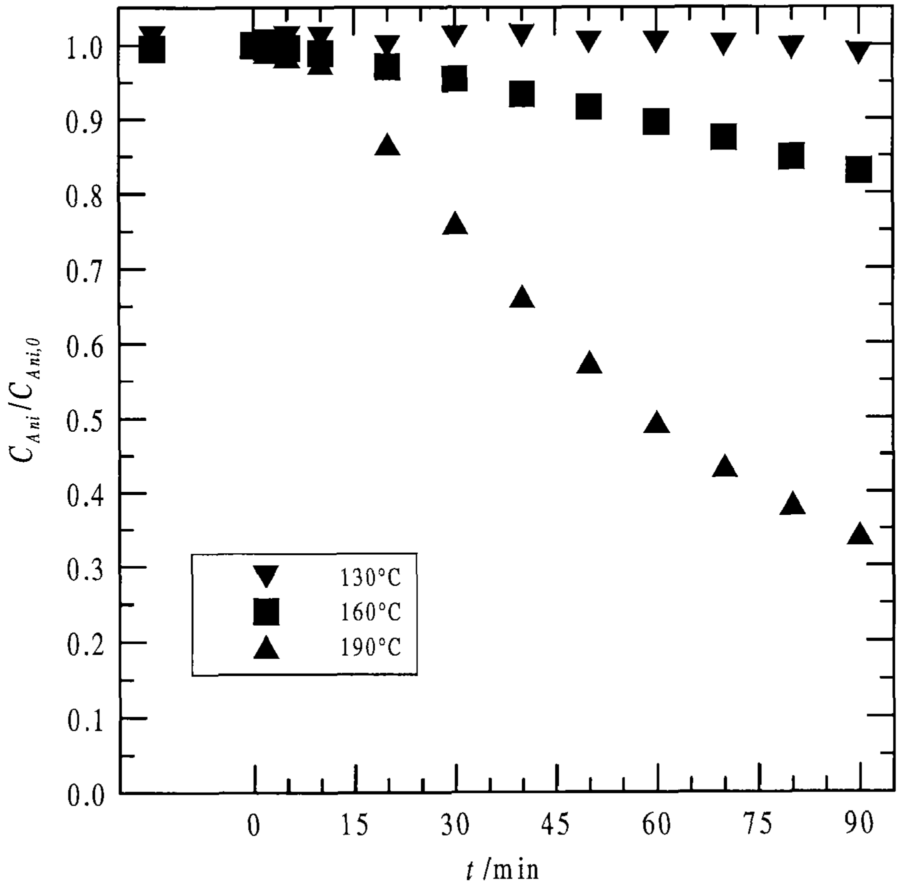

Fig. 5.6: Wet oxidation-experiments at different temperatures
p_{Oxygen} = 10 bar, pH=2, $C_{Ani,0}$ = 1.0 g/L

smaller amounts of fumaric and malenic acids (both by HPLC) were found. The GC-MS analysis gave no further information about the intermediates. Therefore, the wet oxidation of aniline leads mainly to a black precipitate and the observed reactivity is rather low. Aminophenols or nitrophenols were not observed.

5.2.5. Promoted Wet Oxidation

The experiments with addition of the promoter were performed at p_{Oxygen} = 10 bar, temperatures up to 190°C and by promoter addition of $C_{I,0}$ = 180 mg-C/L.

At ϑ = 160°C, the TOC decreases fast in the first 15 min and a slow rate is observable afterwards. Aniline shows the same behaviour: A fast initial period, afterwards a slower conversion. The NDOC shows also a two-phase formation: A fast initial period and after 10 min, only small growth. Only partial conversion of aniline was achieved. The experimental values of TOC, NDOC and aniline are shown in Figure 5.8. The effluent results after 90 min of reaction time at 160°C are:

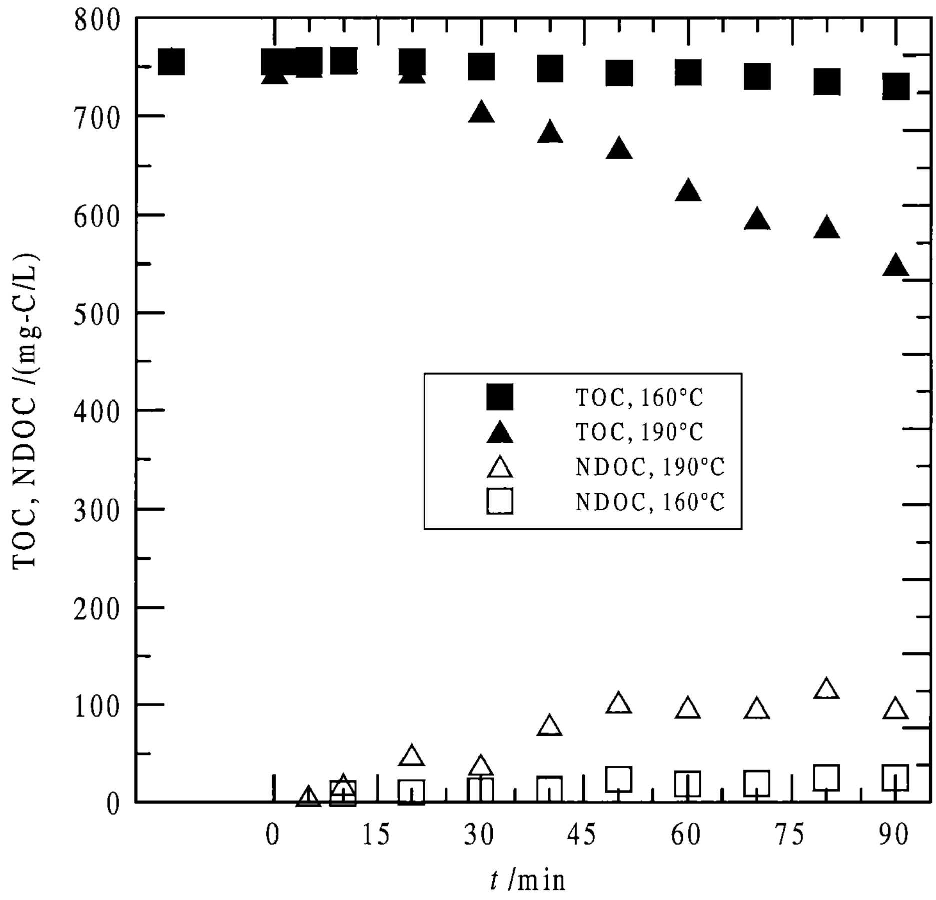

Fig. 5.7: Observation of TOC and NDOC for two WO-experiments p_{Oxygen} = 10 bar, pH=2, $C_{Ani,0}$ = 1.0 g/L, ϑ = 160°C and 190°C, for ϑ = 130°C (not included), no significant change in TOC or formation of NDOC was observed

- Reduction in TOC: 35.5%
- Reduction in COD: 47.3%
- Reduction in aniline: 89.4%

At ϑ = 190°C, the observations of the TOC, NDOC and aniline concentration show the immediate formation of the precipitate and the slow conversion of it (see Figure 5.9). The final values of the treatment at 190°C are:

- Reduction in TOC: 76.8%
- Reduction in COD: 81.5%
- Reduction in aniline: 100% (after 45 min)

The treatment at ϑ = 190°C shows the complete conversion of aniline and also the degradation of the formed precipitate. The fastest growth in the precipitate is observed in the initial phase of the treatment. Aniline is reduced by 180 mg-C/L and NDOC is increased by 110 mg-C/L in the first 2 min. The amount of the

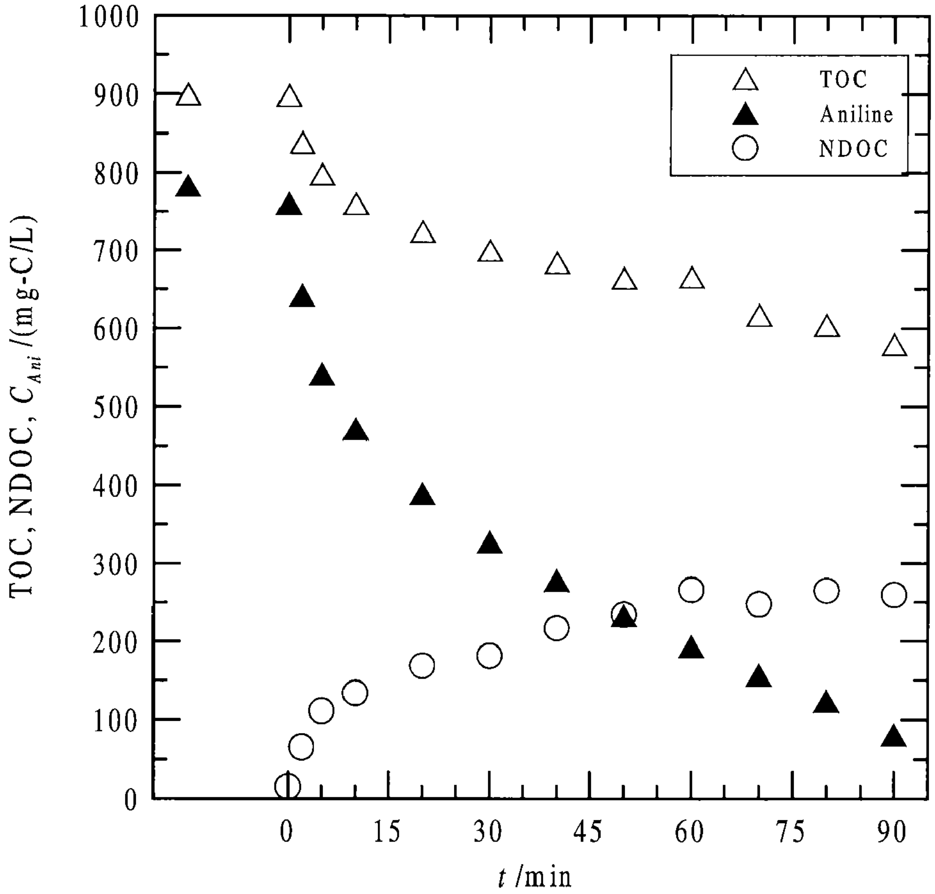

Fig. 5.8: Promoted wet oxidation of aniline at ϑ = 160°C and p_{Oxygen} = 10 bar

precipitate (*i.e.* NDOC) reaches its maximum at t = 15 min. Then, the precipitate disappears. The pH remains constant over the reaction time.

Aniline and gallic acid are the only observable compounds (HPLC) during the first 10 minutes of reaction time. Benzoquinone, nitrophenols or nitrobenzene are not observable, but hydroquinone and phenol are formed after 10 min of reaction time and are also decomposed afterwards. The sum of the observed carboxylic acids is not exceeding 50 mg-C/L after 90 min. Therefore, around 75% of the TOC is not identified. Also in these examinations, GC-MS measurements give no further information.

5.3 Discussion

The discussion of the published results of the different AOP's leads to the assumption that UV-light has a great influence on the effluent quality. The "dark" processes seem to produce aniline dimer as main intermediates, while photo-assisted processes lead to stable carboxylic acids and ammonia/nitrate. These facts may be explained by the structure of coupling products: Due to the increased

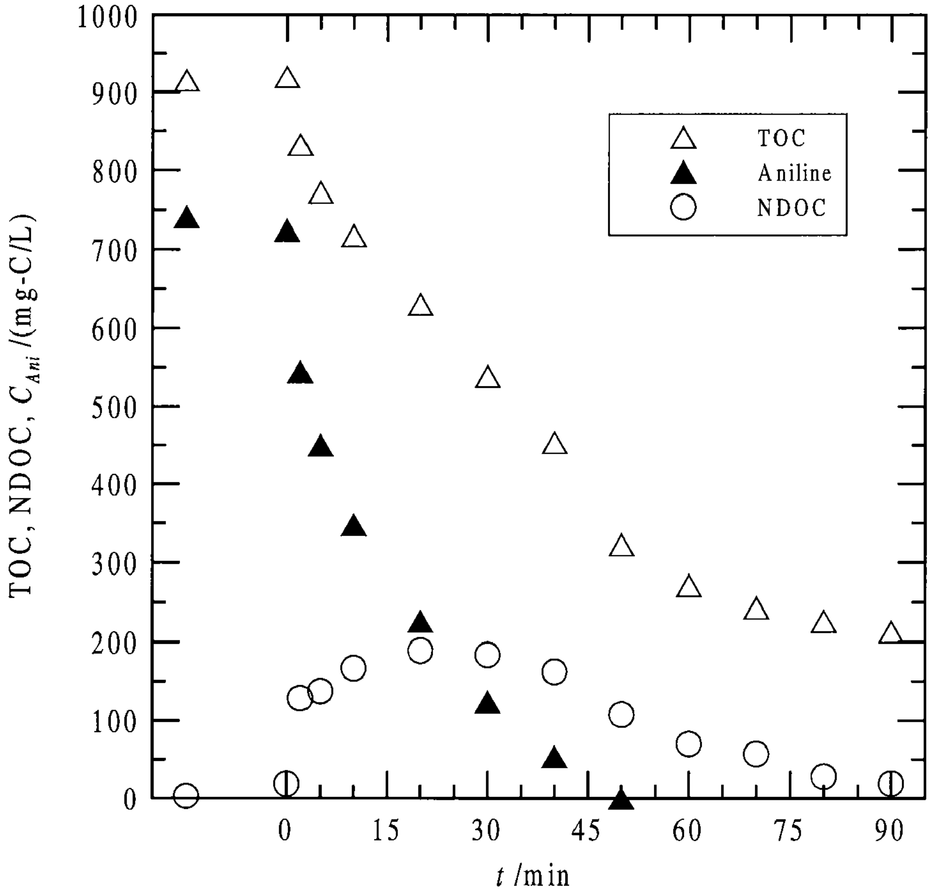

Fig. 5.9: Promoted wet oxidation of aniline at ϑ = 190°C, p_{Oxygen} = 10 bar and $C_{I,0}$ = 180 mg-C/L

mesomeric system by N- or N-N-coupling, the UV-absorption of these dimers is also increased compared with aniline. Therefore, the dimers are activated and show an increased conversion.

The preliminary experiments are showing the great influence of the pH to the solubility of aniline. Due to the boiling point of aniline (T_{boil} = 184°C), the remaining of the aniline in solution is not given. But the $pK_A = 4.7$ indicates the stability of the anilinium-ion in solution. This is also expressed by the low lost during the evacuating.

The precipitate was not further investigated, so the discussion of the nature of this precipitate (assumed as PANI) is based on literature data and assumptions. In wet oxidation, precipitation of organic material is known for the phenol treatment. Vogel assumes the formation of humic material from phenol. The question arises, whether the precipitate is formed *via* a phenolic compound or the mentioned PANI is formed. Also the difference of the observed solids in the promoted/unpromoted wet oxidation treatments are not examined.

The unsatisfying analytical observation of ammonia inhibits the prove of the conversion of the formed precipitate. Also the structure of this precipitate is not examined.

5.4 References

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6 Promoted Wet Oxidation of Nitrobenzene

6.1 Introduction

Nitroaromatic compounds are pollutants resulting from numerous industrial and agricultural activities. They are toxic to various organisms, often resistant to complete biodegradation and they tend to accumulate in the environment. To examine the behaviour of nitroaromatic compounds in the promoted wet oxidation, nitrobenzene as the simplest of these compounds was chosen as the model substance. Due to the use as hydroxyl probe and as model substance in the scientific examination of different oxidation processes, a number of publications is available to compare with the results of this examination.

Nitrobenzene is an intermediate in the synthesis of aniline (about 98% of the nitrobenzene production), azobenzene and m-/p-nitroaniline. The potential for nitrobenzene effects on the environment arises from the loss of nitrobenzene through emission or release during manufacture or use [4]. This causes contamination into the principal environmental systems - air, water and soil. Nitrobenzene is also an EPA-priority pollutant (cited in [7]). For general and toxicological aspects of the examined compound, see also relevant compilations, *e.g.* [3,4].

6.2 Chemistry of nitrobenzene

Nitrobenzene contains a single nitro group attached to a benzene nucleus. Presence of this electrophilic group results in the withdrawal of electrons and four possible resonance forms may be drawn:

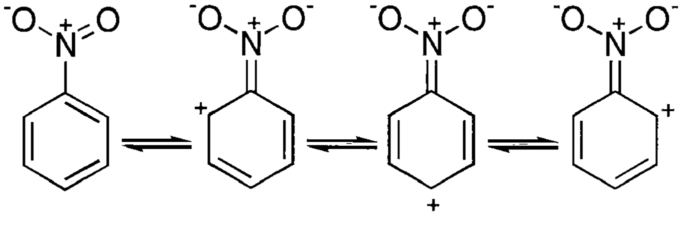

Fig. 6.1: Four possible resonance forms of nitrobenzene

The nitro group deactivates the ring system but substitution in meta-position is allowed under electrophilic conditions as occurring in sulfonation and nitration. Under nucleophilic conditions, the nitro-group is ortho/para-directing. The reduction and substitution reactions are of industrial importance.

It is known that the attacking agent in aromatic nitration is NO_2^+ occurring in the mixture of nitric and sulphuric acid. Compounds as nitric acid, nitrous acid and nitrogen oxides have two features as reagents for organic reactions: (a) use as nitrating or nitrosating agents and (b) use as oxidising agents. For substrates with π-electrons such as aromatic compounds and olefins, they mainly act as nitrating or nitrosating agents. For substrates which possess no π-electrons such as alkanes, they act as oxidising agents, especially in a dilute solution and in the presence of nitrogen oxides or nitrous acid [20].

6.2.1. Degradation of nitrobenzene

As a priority pollutant, nitrobenzene was examined in different studies concerning the environmental function and disposal attempts. We will focus on the disposal processes (*i.e.* AOP's, WO) and we will give only a short introduction in biochemical degradation. The degradation by micro-organisms *via* reduction is a two-step process, whereas the first step is the nitro reduction. The second step is the oxidative degradation of the amino compounds [24]. This two-step degradation by microorganisms can be adapted to create a three-reactor system, containing nitro reducing consortium and aniline-degrading consortium [22]. Saturated aqueous solutions of nitrobenzene (in water, 0.1 M nitric acid and 0.1 M potassium hydroxide) were irradiated with gamma-rays and the radiolytic products were found to be mainly isomeric nitrophenols, aminophenols and dinitrophenols [13].

6.2.2. Oxidation of nitrobenzene

Benzene and most other aromatic compounds (with the exception of phenols and aromatic amines) react slowly with ozone and hydrogen peroxide. They are largely refractory to these oxidants, at least at the short reaction times required for industrial processes.

On the other hand, OH-radicals react with aromatic compounds with rate constants which are close to the diffusion-controlled limit (for a review of rate constants, see Buxton *et al.* [6]). The OH-radical has electrophilic properties and hence adds preferentially to the position of the highest electron density within the benzene ring. Therefore the electron-donating or electron-withdrawing properties of a substituent will determine the ratio of ortho:meta:para:ipso addition reactions [28]. In the case of nitrobenzene as the oxidised compound, the possible sites of OH-radical attack are shown in Figure 6.2. By comparing the resonance structures

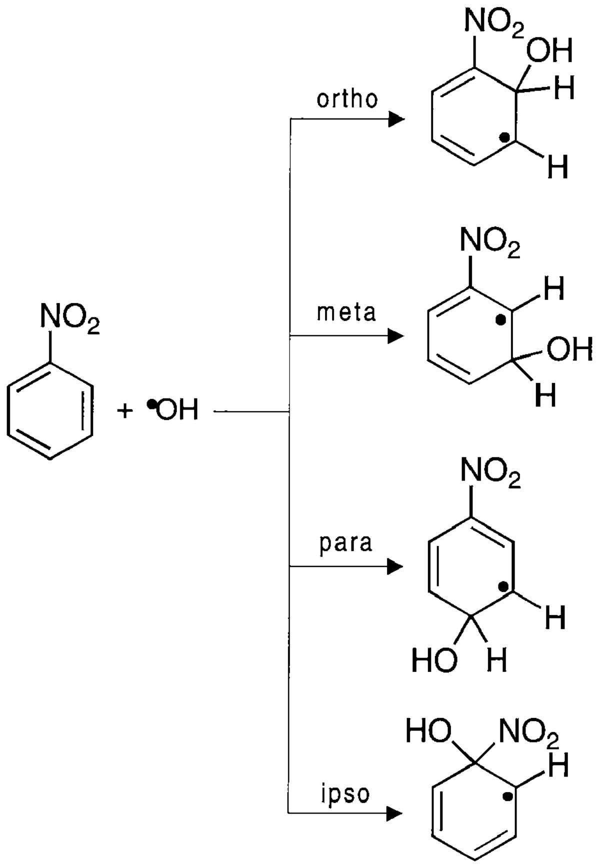

Fig. 6.2: Reaction of OH-radical with nitrobenzene: Four possible addition reactions (adapted from von Sonntag [28])

of nitrobenzene (see Figure 6.1) and the possible sites of OH-radical attacking, the *para*-route should be preferred. By oxidising the OH-adduct radicals (see Figure 6.2), the corresponding nitrophenols are formed. The *ipso*-route leads either to the initial nitrobenzene or to phenol. When a non-selective attack occurs, the following distribution of nitrophenols will appear: 2-NP:3-NP:4-NP = 1:2:2. If the nitro-group influences the reaction toward the nitrophenols, the following distribution of the intermediates will be observed:

2-NP:3-NP:4-NP = 2:0:1 (nucleophilic attack) or 0:1:0 (electrophilic attack).

The rate of conversion of nitrobenzene by the reaction with hydroxyl radicals is found in the compilation of Buxton [6]. The reaction rate of nitrobenzene with hydroxyl radical is in the same order of magnitude as the reaction of 4-nitrophenol.

Substance, Reaction	k /(L·mol^{-1}·s^{-1})	Remarks
Nitrobenzene $\cdot OH + C_6H_5NO_2 \rightarrow HOC_6H_5NO_2$	$3.9 \cdot 10^9$	Selected value
4-Nitrophenol $\cdot OH + 4\text{-}HOC_6H_4NO_2 \rightarrow 4\text{-}HOC_6H_4NO_3^- + H^+$	$3.8 \cdot 10^9$	pK_A=7.14, pH=7

Table 6.1: Rate constants for selected reactions of hydroxyl radicals at ambient conditions [6]

The degradation of nitrobenzene by wet (air) oxidation is known to be unsatisfying. Dietrich *et al.* [7] mention the 95% conversion of nitrobenzene ($C_{NB,0}$ = 5 g/L) at ϑ = 320°C after 2 h of treatment by using a not-specified catalyst. For dichloronitrobenzene at the same conditions, a conversion of 75% after t = 120 min is reported. Especially the chlorinated nitrobenzenes and nitrophenols were found to be relatively resistant to conventional wet air oxidation.

A rather simple attempt to convert nitrobenzene was made by Miura and co-workers [19]: They mixed nitrobenzene ($c_{NB,0}$ = 1 mM) and ferrous ions (41 mM) at pH 6.8 and 40°C. They found after three hours of oxygen bubbling all 3 nitrophenol isomers in the ratios 2-NP:3-NP:4-NP = 1:4:4, but the conversion of nitrobenzene toward these products is rather low.

Described in different papers, the degradation of nitrobenzene by ozonation leads mainly to the three nitrophenols. These nitrophenols are not only observed as intermediates but also used in experiments as the pollutant [25].

The examination of AOP's in nitrobenzene degradation also reveals the role of nitrophenols as intermediates [5]. Lipczynska-Kochany has found the lower reactivity of nitrobenzene in comparison with nitrophenols in Fenton-treatment [15,16]. This is an interesting fact by regarding Table 6.1. The Photo-Fenton-process seems to enhance the performance in nitrobenzene degradation [16,23].

Interesting is the influence of the photocatalysts on the nitrobenzene degradation. ZnO as photocatalyst (oxidant is hydrogen peroxide) shows only small conversion and leads mainly to 3-NP (*meta*-route, 2-NP:3-NP:4-NP = 1:6:1).

TiO_2 as photocatalyst shows faster conversion and leads to a nearly equal distribution of the three nitrophenols (2-NP:3-NP:4-NP = 1.1:1.1:1). For both photocatalysts, the formation of ammonia and nitrate is observed. Nitrite is observed as an intermediate that is occurring in the same molar concentration then the nitrophenols [18,21].

The treatment of nitrobenzene by supercritical water (without oxidant) shows benzene as the main intermediate. Due to the low reactivity of benzene at these conditions (ϑ = 500°C), the formation and slow degradation of this intermediate is observable. Also the formation of mainly nitrite, nitrate and ammonia is reported [14]. The SCWO-treatment (*i.e.* addition of oxygen) shows faster conversion of the nitrobenzene (compared with no oxygen addition) and shows also the formation of other intermediates. Observed intermediates include aniline, phenol and dibenzofuran. The formation of dibenzofuran and dibenzo-p-dioxin is also reported for SCWO-experiments with phenol [26]. The SCWO-experiments of nitrobenzene also indicates the formation of nitrogen gas from the nitro-group. The treatment of nitrophenols by SCWO leads mainly to CO and CO_2, the assumed pathway involves phenol as the main intermediate [17].

Finally, nitrobenzene is used as a hydroxyl radical probe in testing oxidation processes. A solution with a pollutant, *e.g.* polymers [1], is treated by an oxidative disposal system and the addition of nitrobenzene reveals some insight in the process (hydroxyl radical formation) by observing the formed nitrophenols [11,30].

6.3 Experiments

6.3.1. Preface

Performing the COD-test involves the comparison with published results. The experimental values in the observed literature reveals the large variety in COD-results, see Table 6.2. Therefore, the comparison with published results needs some precautions. Therefore, we do not perform comparisons on the basis of COD-measurements with other publications in nitrobenzene degradation.

Oxygen Demand /(mg-O_2/g)	Remark/Publication
1430	TOD with ammonia formation
1625	TOD with nitrogen gas release
1949	TOD with nitrate formation
2166±72	COD measurement (this work)
851...2009	Different publications, see [12]

Table 6.2: Oxygen demand values: TOD values and observed dates

To examine the wet oxidation of nitrobenzene, two important conditions have to be known. First, the solubility of nitrobenzene is known to be low. For sufficient observation of intermediates, enough initial nitrobenzene (at least 0.5 g/L) has to be solved. Of course is the handling of only partially solved compounds possible, but the accurate solubility in the observed reaction temperature range has to be known. Second, nitrobenzene is volatile. It is preferred, that the majority of the compound is solved at the reaction temperature. The intended temperature range goes up to 190°C, *i.e.* only 20 K below the boiling temperature of nitrobenzene at 1 bar. Partial vaporisation has to be expected at these conditions. In the studied literature, the system water-nitrobenzene is only examined up to 60°C and some preliminary experiments were performed to establish the influence of the volatility (and solubility) on the process.

Solubility. The solubility of nitrobenzene is rather low at ambient conditions but is increasing by increasing the temperature, as seen in Table 6.3. The published solubility of nitrobenzene is somewhat higher than 1 g/L. Therefore, the experiments were performed with $C_{NB,0}$ = 1 g/L. The visible dissolution of the nitrobenzene was only achieved after 1 h of mixing at ambient temperature.

ϑ	Value /(g/1 kg- water) and reference	Solubility /(g/L)
0°C	1.66 [27]	1.66
30°C	2.06 [27]	2.07
50°C	2.64 [27]	2.67
60°C	3.12 [2,27]	3.17

Table 6.3: Solubility of nitrobenzene in water

Volatility. Preliminary experiments were conducted to examine the thermal stability in the observed temperature range and the liquid-gas-distribution of nitrobenzene. In these experiments, argon was used as pressurising gas. Also experiments with oxygen only (wet oxidation experiments) were performed to establish the degradation of nitrobenzene without promoting. As mentioned, nitrobenzene is a volatile substance with ϑ_{boil}=210.9°C. An amount of the nitrobenzene may be in the gas phase at elevated temperature. The space above the liquid is a reservoir for the volatile compounds of the solution. In the discussed case these volatile compounds are water and nitrobenzene. At a given temperature and initial amounts of water and nitrobenzene, equilibrium will establish between the gas-liquid-phase. The initial amount of liquid water and solved nitrobenzene

ϑ /°C	p_{NB} /bar[a]
130	0.0946
160	0.2587
190	0.6061

Table 6.4: Vapour pressure of pure nitrobenzene [10]

a. Antoine-Eq, range: 407.2-483.78 K (134-210.63°C)
A=4.21553, B=1727.592, C=-73.438

will be decreased. By taking a liquid sample, the sample volume reduces the liquid volume and increases the gas volume. Assuming no reaction, the concentration of nitrobenzene in the liquid space reduces, due to the now larger gas space and the new gas-liquid-equilibrium. Therefore the next sample shows a reduced concentration (in C_{NB}, TOC, COD) and may be interpreted as a chemical reaction. Willms *et al.* [29] had described this effect on batch experiments in wet air oxidation.

To calculate the liquid-gas-distribution, a Henry coefficient or a similar function has to be known. A distribution function for water-nitrobenzene at the chosen temperature range was not found in the literature. This distribution was established by experiments at different temperatures.

To evaluate the gas-liquid distribution, the experimental procedure was changed: A nitrobenzene solution of 2 L (pH = 2, $C_{NB,0}$ = 1 g/L), was heated to the desired temperature. Oxygen or argon (p = 10 bar) were used to increase the pressure. The conditions were kept for 10 min and then the stirrer was stopped. After 2 min, a sample was taken and the TOC was measured. Neglecting the small formation of intermediates, the measured TOC was regarded as the equivalent of the amount of nitrobenzene. Experiments with only water (pH=2) and nitrobenzene showed no significant difference in the total pressure compared to pure water.

All of the performed experimental data were used to calculate the Henry's coefficients. The evaluated Henry's coefficients for three temperatures (ϑ = 130...160...190°C) are shown in Table 6.5.

ϑ /°C	H_x /bar
130	231
160	270
190	409

Table 6.5: Henry's coefficients, CV = 31%

The experimental Henry's coefficients are used to calculate the effect of sampling on the observed concentration. For the intended reaction temperatures (ϑ = 130°C, 160°C, 190°C), the observable concentrations of nitrobenzene are calculated. Assuming a fast vaporisation of the compound (immediate gas-liquid equilibrium after a sample), the "experiments" at different temperatures show an increasing "conversion", see Figure 6.3. This effect is temperature-dependent (*i.e.* gas-liquid-distribution) and is also depending on the number of sampling/sample volume (*i.e.* increasing of the gas space). A high number of samples at the initial phase of the experiment lead to a fast depletion of the observed compound in solution. Therefore, the decreasing of nitrobenzene (observed as liquid concentration) during an experiment does not indicate a chemical reaction. Only the comparison between the predicted and observed nitrobenzene decay and the observation of intermediates in solution reveals an insight in the wet oxidation of nitrobenzene.

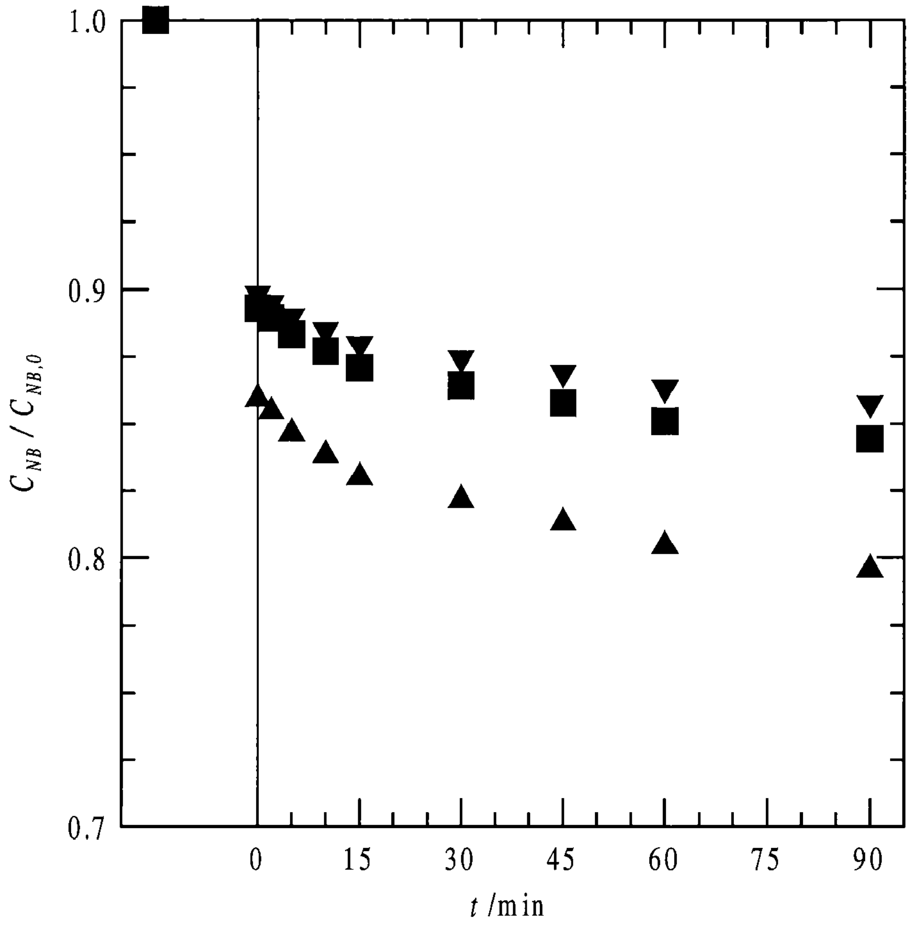

Fig. 6.3: Liquid concentration of nitrobenzene vs. time, showing the effect of liquid sampling (50 mL) on a 2 L-aqueous solution ($C_{NB,0}$ = 1 g/L) in a 4 L reactor at different temperatures: 130°C (▼), 160°C (■) and 190°C(▲)

6.3.2. Inert gas and oxygen atmosphere

Experiments with inert gas, p_{Argon} = 10 bar, ϑ = 190°C and pH = 2 showed small amounts of intermediates after 30 min of treatment time. The solution remains clear and colourless. These intermediates are not volatile and the whole amount of dissolved carbon was found at the end of the experiment, *i.e.* after cooling/ condensation to 20°C. The change of argon to oxygen did not increase the conversion of the nitrobenzene. Therefore, nitrobenzene thermally degrades slowly and the thermal decomposition will be neglected at the further discussions. Also the reactivity of nitrobenzene with oxygen is low and will also be neglected in the further discussions.

6.3.3. Oxygen and ferric ions

At ϑ = 190°C and 10 bar of oxygen pressure, a solution of 1 g/L of nitrobenzene and 0.36 mM Fe(II)-salt was treated for 90 min. The TOC is slowly decreasing for the first 60 min of reaction time. Nitrobenzene shows also the same slow decrease for the first 30 min, but afterwards, nitrobenzene decreases faster than the TOC. The observations of nitrobenzene and TOC show an induction time of the oxidative reaction. The same values of TOC and nitrobenzene (in mg-C/L) indicate the vaporisation of the nitrobenzene (and not a chemical reaction).

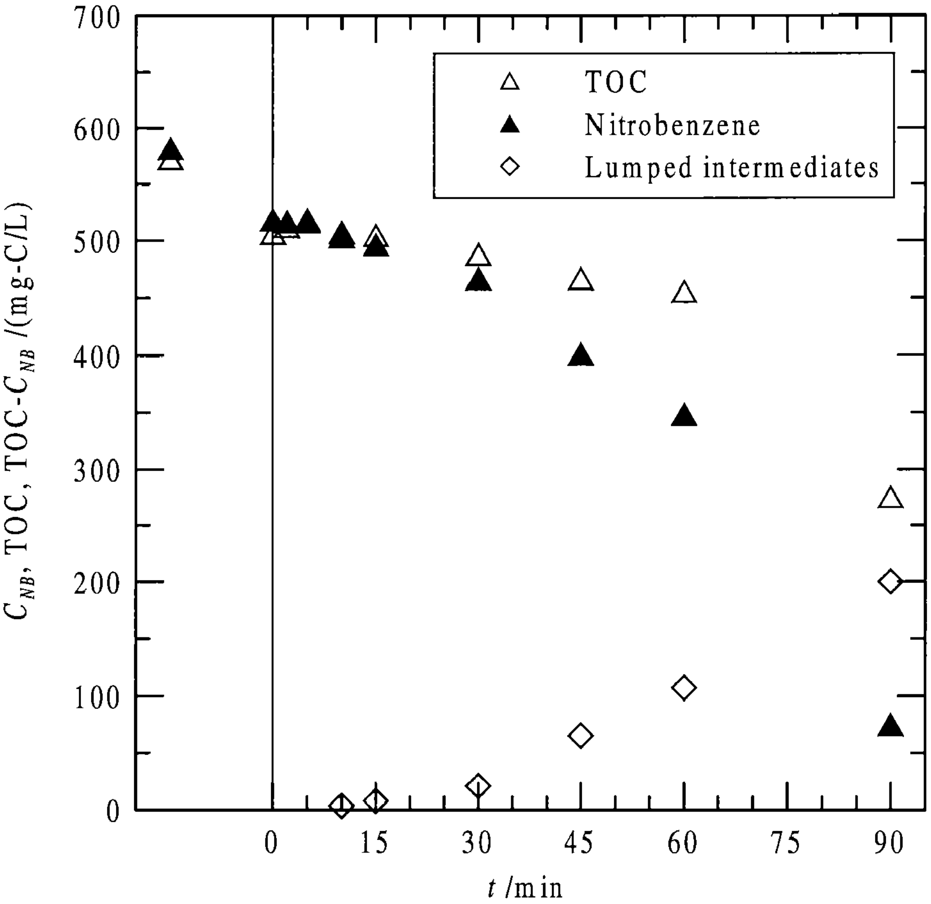

Fig. 6.4: Wet air oxidation of nitrobenzene, acidic solution, at ϑ=190°C and p_{Oxygen} = 10 bar, $C_{Fe(II),0}$=0.37 mmol/L, $C_{NB,0}$ = 1.0 g/L TOC (△) and C_{NB} (▲) are decreasing after an induction time and intermediates (◇) are formed

After 15 min the first by-products (mainly three compounds with the used HPLC-method) are observable. The probe after 30 min is yellow and clear. Between 60 and 90 min of reaction time, the TOC-amount drops 40% and the nitrobenzene concentration 78%. The TOC and nitrobenzene concentrations are shown in Figure 6.5.

The GC-MS-analysis indicates all mesomers of nitrophenols and mesomers of dinitrobenzene. By comparing retention times and UV/Vis-spectra [8], the three nitrophenols (but no dinitrophenol) were identified by HPLC. The three nitrophenols are therefore the observable intermediates. Phenol was not found. The corresponding HPLC-chromatograms (see Figure 6.5) show the formation of nitrophenols during the treatment. Compared with the experiments without Fe-

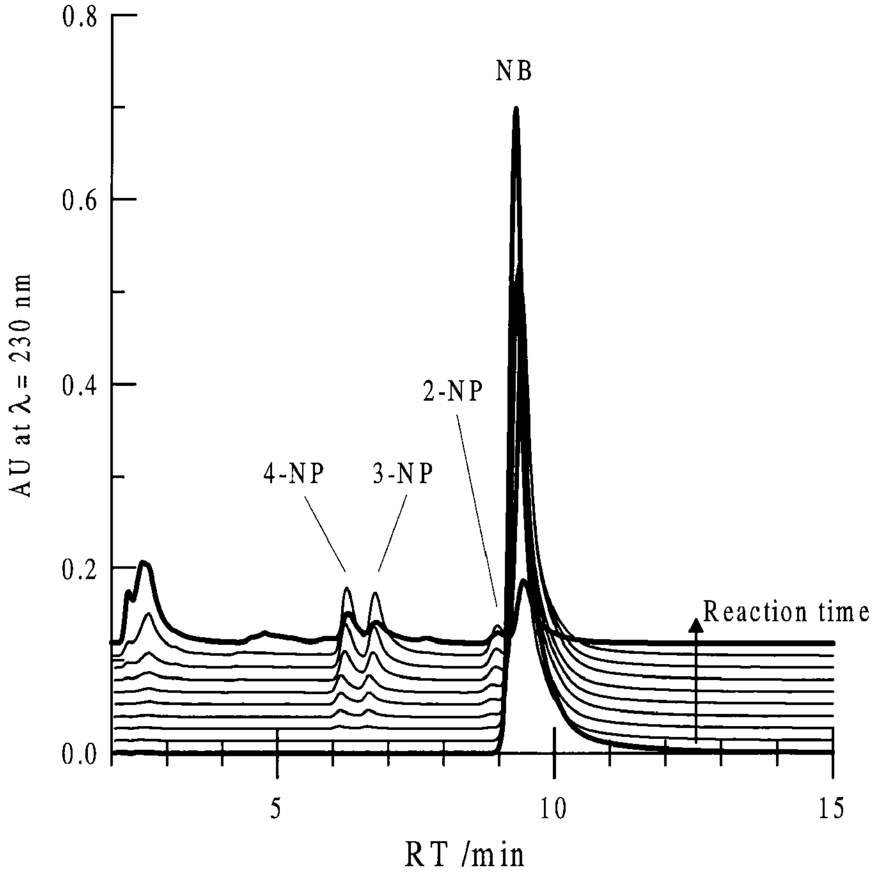

Fig. 6.5: HPLC chromatograms (see Figure 6.4), ϑ=190°C, p_{Oxygen} = 10 bar, $C_{Fe(II),0}$ = 0.37 mM, $C_{NB,0}$ = 1.0 g/,
NB: Nitrobenzene, x-NP: x-Nitrophenol

addition only a small enhancement in conversion is observed. The influence of Fe-ions is not excluded by these results due to the strong corrosion of the impeller ball bearing during the treatment.

6.3.4. Promoted Wet Oxidation

The experiments for the promoted wet oxidation were performed at three temperatures, different promoter addition and changing oxygen pressure.

Temperature dependency. The influence of the temperature was evaluated at $\vartheta = 130°C...160°C...190°C$. The further conditions are given in Table 6.6. The observation of the nitrobenzene shows the strong influence of the temperature. Surprisingly, the experiment at 160°C yields a higher final conversion of nitrobenzene compared with the experiments at lower or higher temperature. The temperature has also an influence on the formation and degradation of the intermediates. 3-Nitrophenol and 4-nitrophenol formation and degradation are shown in Figure 6.7 and Figure 6.8. First of all, the observed amounts for 3-nitrophenol are higher than for 4-nitrophenol. The increasing reaction temperature leads to higher amount and higher rates of formation of the first intermediates. The experiment at $\vartheta = 130°C$ shows the formation of the nitrophenols, a degradation is not observable. At higher temperatures, the nitrophenols are formed and, after a maximum in concentration, are decomposed. The decomposition seems to be a two-step process: a first, fast decomposition followed by a slow decomposition. At $\vartheta = 190°C$, the first step seems to be completed after 15 min and the slow decomposition controls the decay of the nitrophenols. At $\vartheta = 160°C$, the fast decomposition lasts until 30 min, afterwards the decomposition of nitrophenols is slow.

Parameter	Value
p_{Oxygen}	10 bar
$c_{Fe(II),0}$	0.37 mmol/L
pH	2
$c_{NB,0}$	1 g/L
$c_{I,0}$	79 mg-C/L

Table 6.6: Conditions of the experiments with temperature variation

The influence of the temperature is mainly expressed in the duration of the initial reactions (conversion of nitrobenzene, degradation of the nitrophenols). At

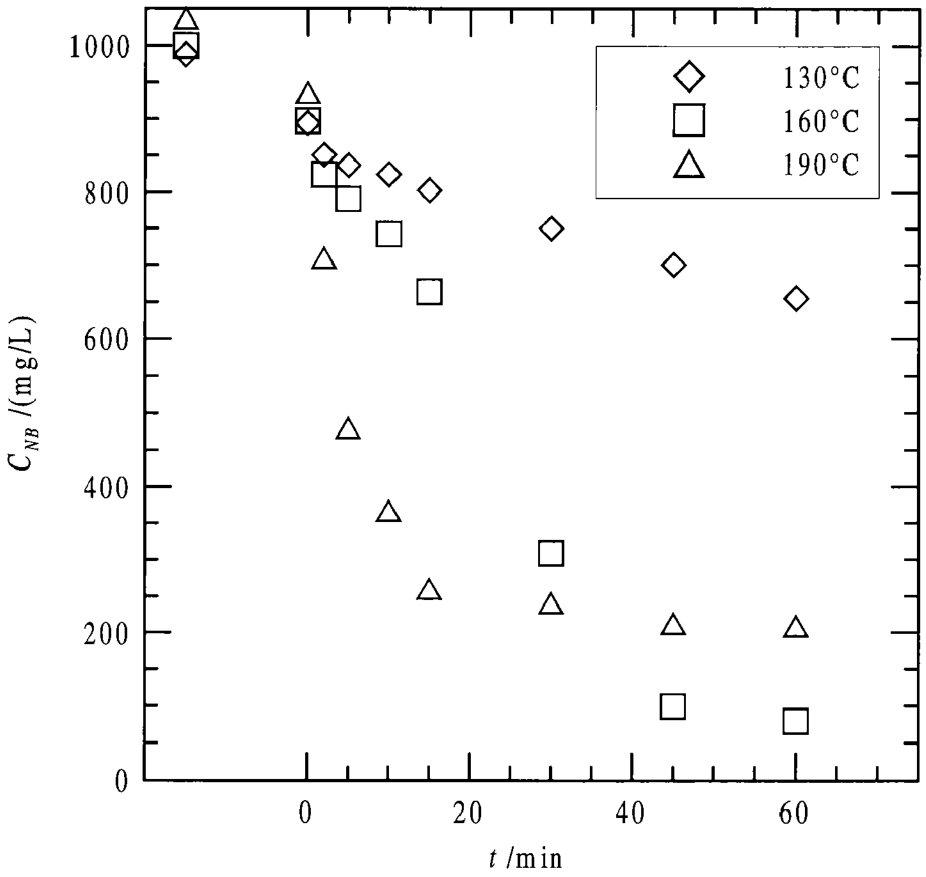

Fig. 6.6: Temperature dependency of the promoted wet oxidation of nitrobenzene

$\vartheta = 130°C$, only slow reactions are observed. At $\vartheta = 160°C$, the fast conversions of nitrobenzene and nitrophenols are accomplished between 30 min and 45 min. At $\vartheta = 190°C$, the fast reactions are finished after 15 min.

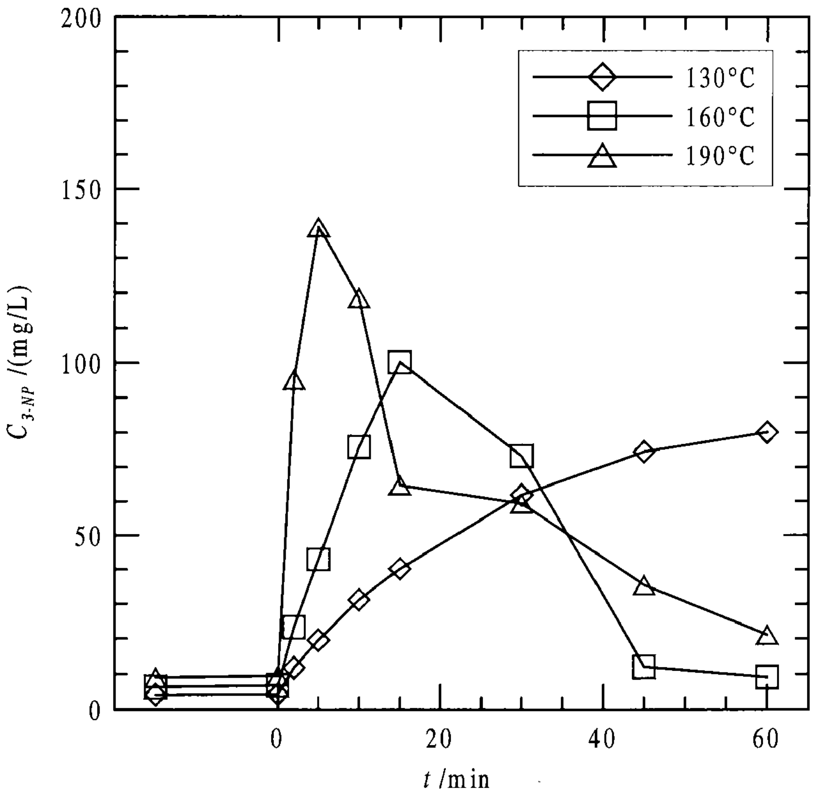

Fig. 6.7: Observation of 3-nitrophenol (3-NP)

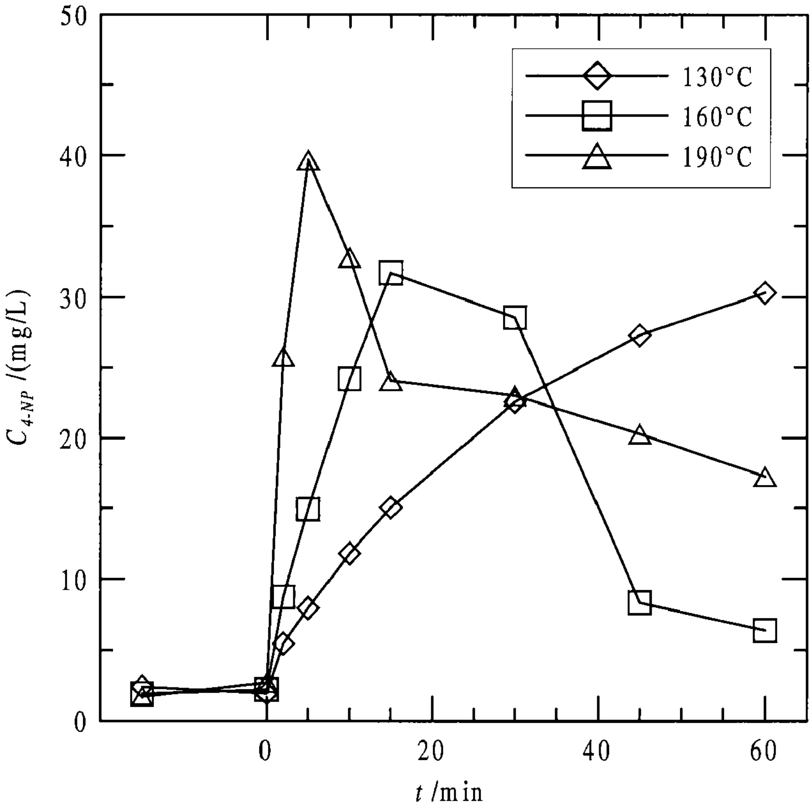

Fig. 6.8: Observation of 4-nitrophenol (4-NP) as a function of reaction temperature

Promoter influence. The influence of the promoter, *i.e.* $C_{I,0}$, was established at 160°C. The parameter for these experiments are given in Table 6.7. Figure 6.9 shows the comparison for the three different initial promoter addition $C_{I,0}$. Only a high amount of the promoter leads to a total conversion of the nitrobenzene at $\vartheta = 160°C$; the experiment at $C_{I,0} = 180$ mg-C/L shows after $t = 45$ min no nitrobenzene in the solution. By decreasing $C_{I,0}$, only partial conversion of nitrobenzene is observed. The lower the amount of the promoter, the lower is the conversion of nitrobenzene. Therefore, the conversion depends on the amount of

Parameter	Value
ϑ	160°C
p_{Oxygen}	10 bar
pH	2

Table 6.7: Parameters for experiments to establish promoter influence

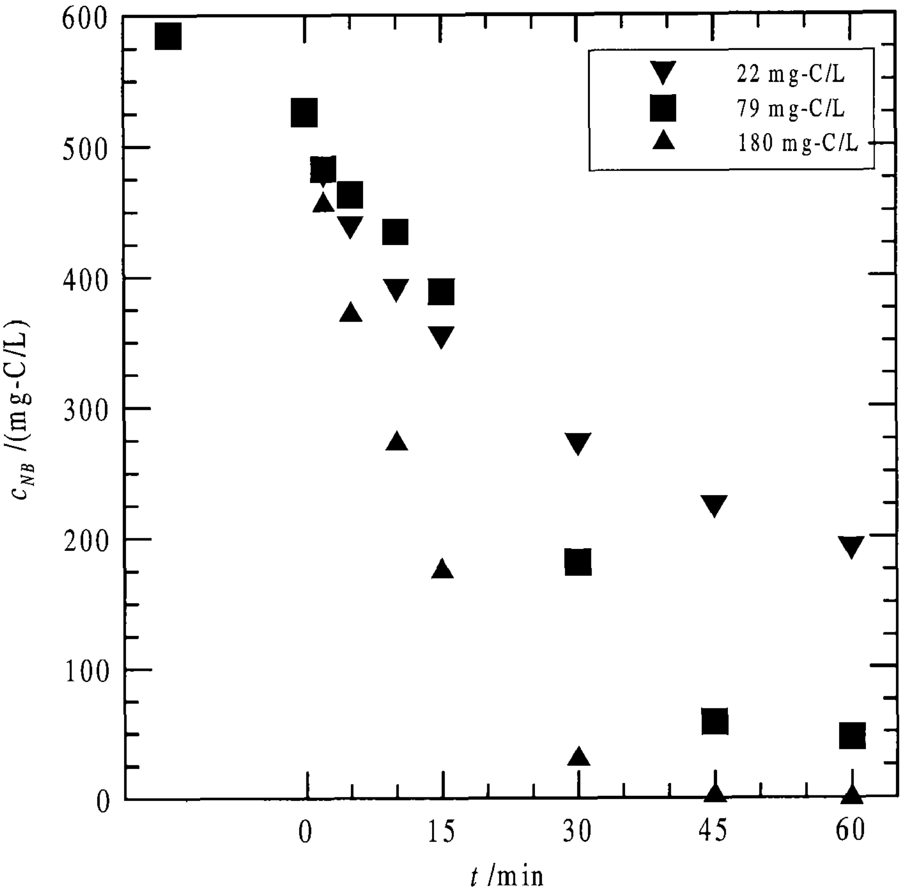

Fig. 6.9: Variation of promoter addition, ϑ = 160°C, p_{Oxygen} = 10 bar, pH = 2

the promoter. Also the rate of the conversion is positively influenced by the promoter addition.

The extinction of the reactions is influenced by the stability of the formed nitrophenols. The formation and the decay of 4-nitrophenol by variation of the initial promoter addition ($C_{I,0}$) are shown in Figure 6.10. The formation of 4-nitrophenol is fast and after 15-20 min reaction time, the concentration drops. Only the lowest addition of promoter leads to a slow decay. Other nitrophenols show a similar behaviour.

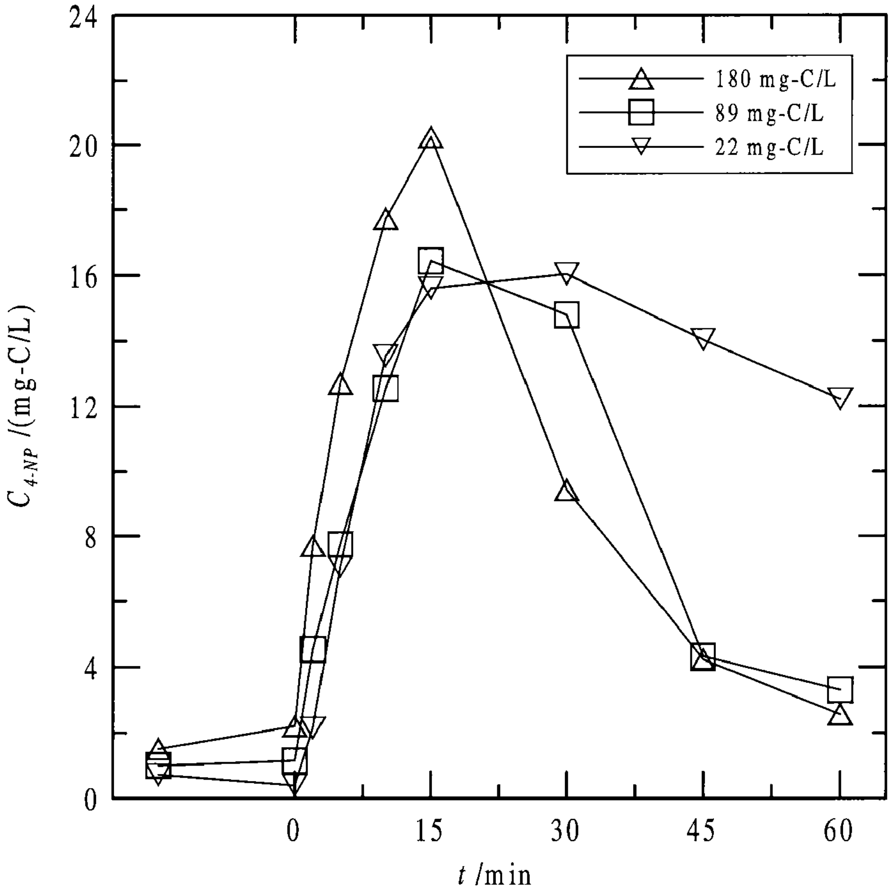

Fig. 6.10: 4-Nitrophenol: formation and degradation as a function of reaction time and initial promoter addition

Oxygen pressure. The variation of oxygen pressure was also performed with three experiments. The oxygen pressure was varied in the range 10 bar...15 bar...20 bar. The results for the nitrobenzene decay show the increasing decomposition rates

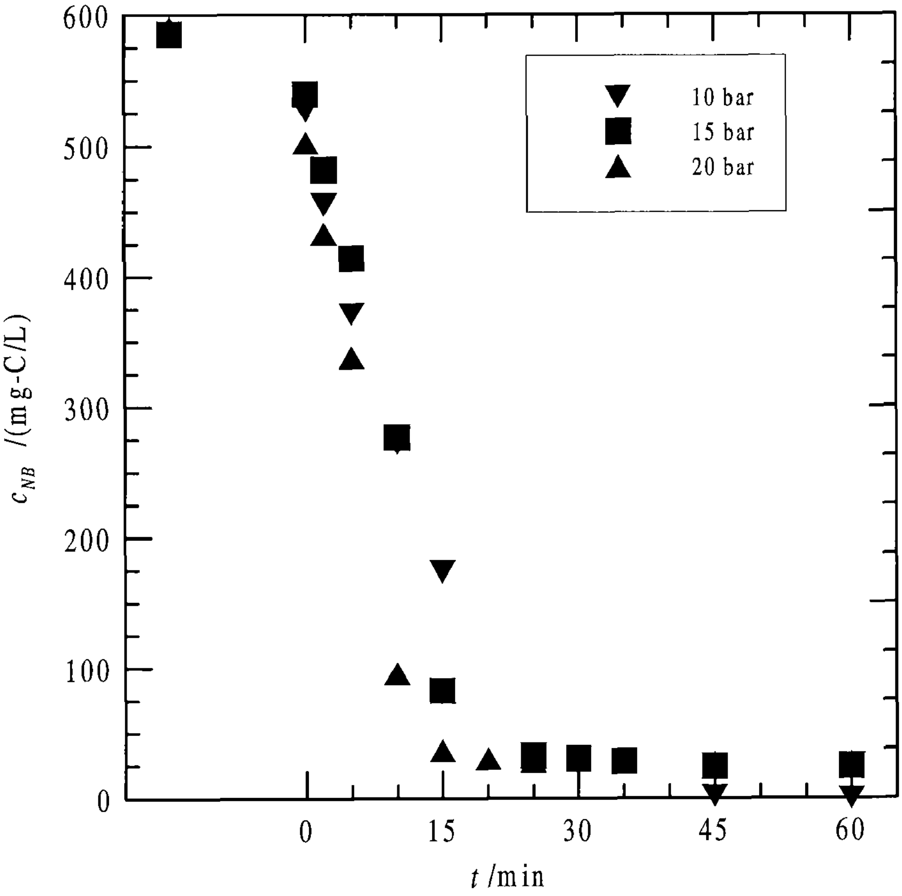

Fig. 6.11: Variation of the oxygen pressure: degradation of nitrobenzene

with increasing p_{Oxygen}. Also the observation of the TOC shows a similar behaviour. The final C_{NB} is 0-5% of the initial concentration. The TOC in solution shows a final reduction of 68% for all three experiments.

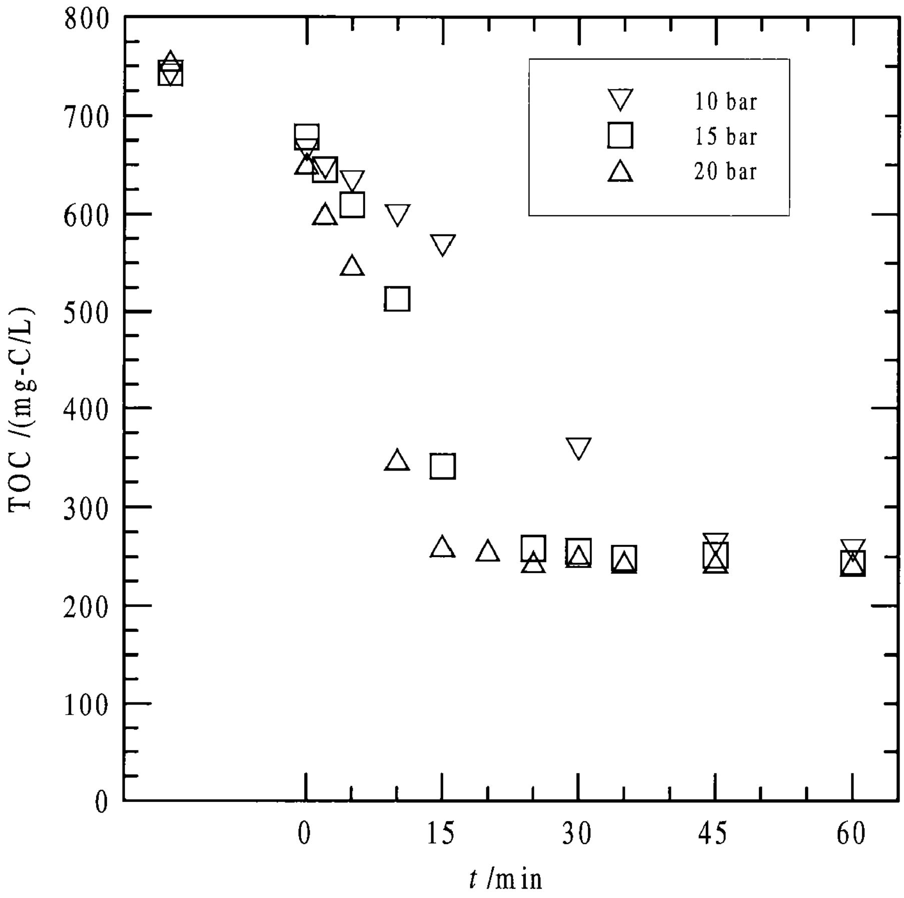

Fig. 6.12: Variation of the oxygen pressure in nitrobenzene treatment: TOC decay

6.3.5. Formation of Intermediates

To present the intermediates and products of promoted wet oxidation, we will discuss one of the experiments of the parameter variation. The conditions of the experiment are given as: ϑ=160°C, p_{Oxygen}=20 bar, $c_{Fe(II),0}$=0.37 mM, $C_{NB,0}$=1.0 g/L and $C_{I,0}$ = 89 mg-C/L. The observation of the formed nitrophenols indicates an unspecific attack of the hydroxyl-radicals. The formation of the nitrophenols is faster than the decomposition in the first 5 min of reaction time. Afterwards, the nitrophenols partially degrade within 10 min. The further treatment of the solution shows only marginal degradation of the nitrophenols after 15 min reaction time. Finally, after 15 min of reaction time, the nitroaromatics are not further converted.

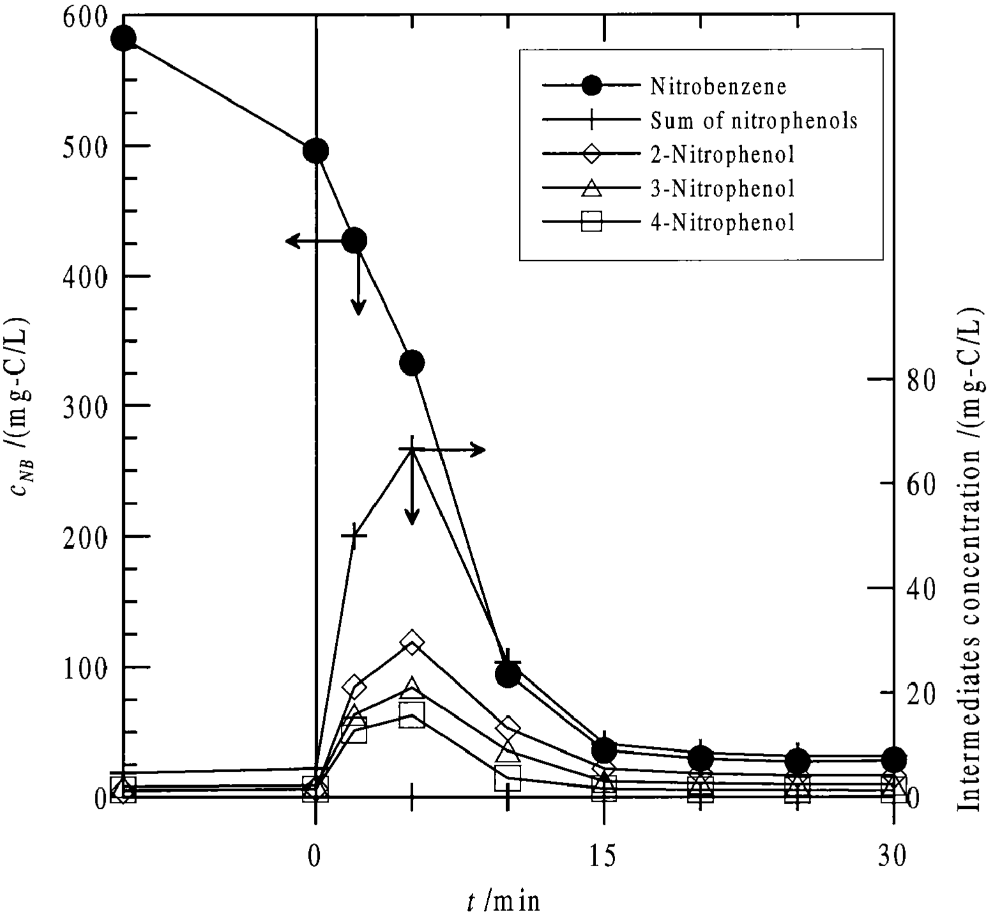

Fig. 6.13: Formation of nitrophenols during the promoted wet oxidation of nitrobenzene; ϑ = 160°C, p_{Oxygen} = 20 bar, $c_{Fe(II),0}$ = 0.37 mM, $C_{NB,0}$ = 1.0 g/L, $C_{I,0}$ = 180 mg-C/L

The analysis of some observed carbonic acids showed the degradation of the gallic acid during the first 10 minutes and the dominant generation of formic and acetic acid. Formic acid and acetic acid are quite stable at the examined conditions

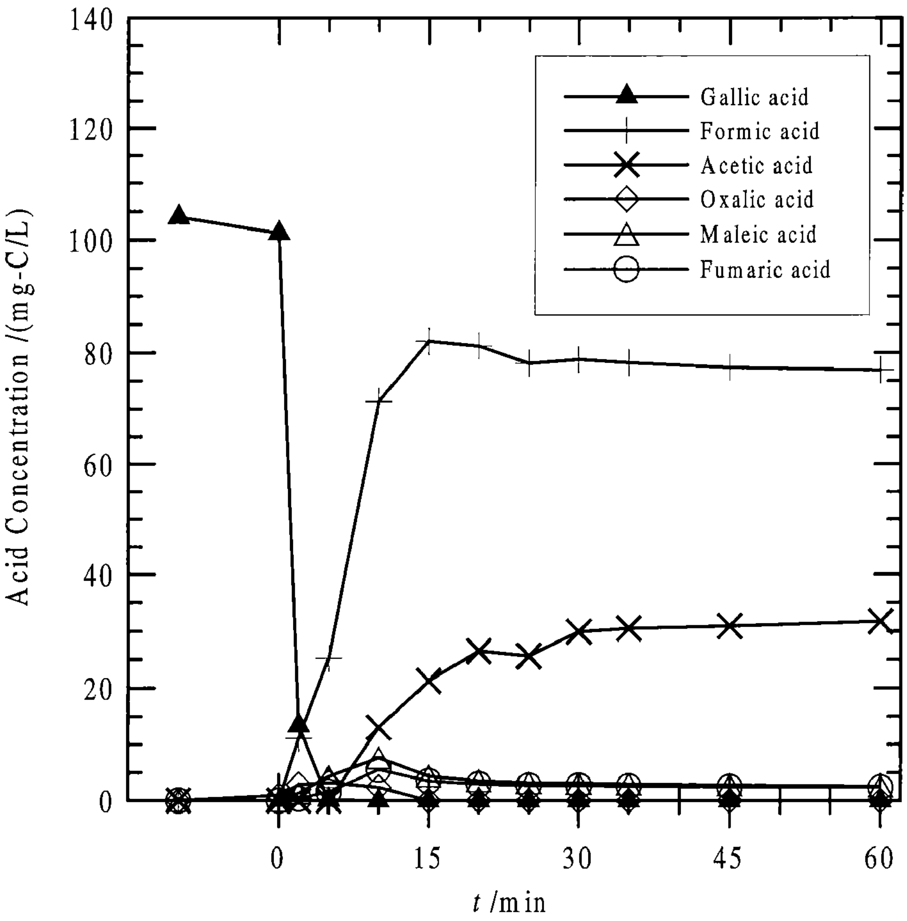

Fig. 6.14: Formation of carbonic acids; ϑ=160°C, p_{Oxygen}=20 bar, $c_{Fe(II),0}$=0.37 mM, $C_{NB,0}$=1.0 g/L, $C_{I,0}$ = 180 mg-C/L

and are regarded as products of the wet oxidation below 200°C. The carboxylic acids with higher molecular weight, like fumaric acid, maleic acid and oxalic acid are formed and also decomposed in the first 15 min and remain on the same level afterwards.

Overall, the TOC of the solution may be described during the initial phase of the reaction by the observed intermediates (and nitrobenzene) to 91%, after reaction to 61% by the observed carboxylic acids. The observed intermediates and products are shown in Figure 6.15. The first intermediates are the mentioned nitrophenols and also the observed dinitrobenzene (GC/MS). Fumaric and maleic acids are also intermediates that are not stable at the examined conditions. Finally we find the stable acetic and formic acids. Also, nitrate and ammonia were detected.

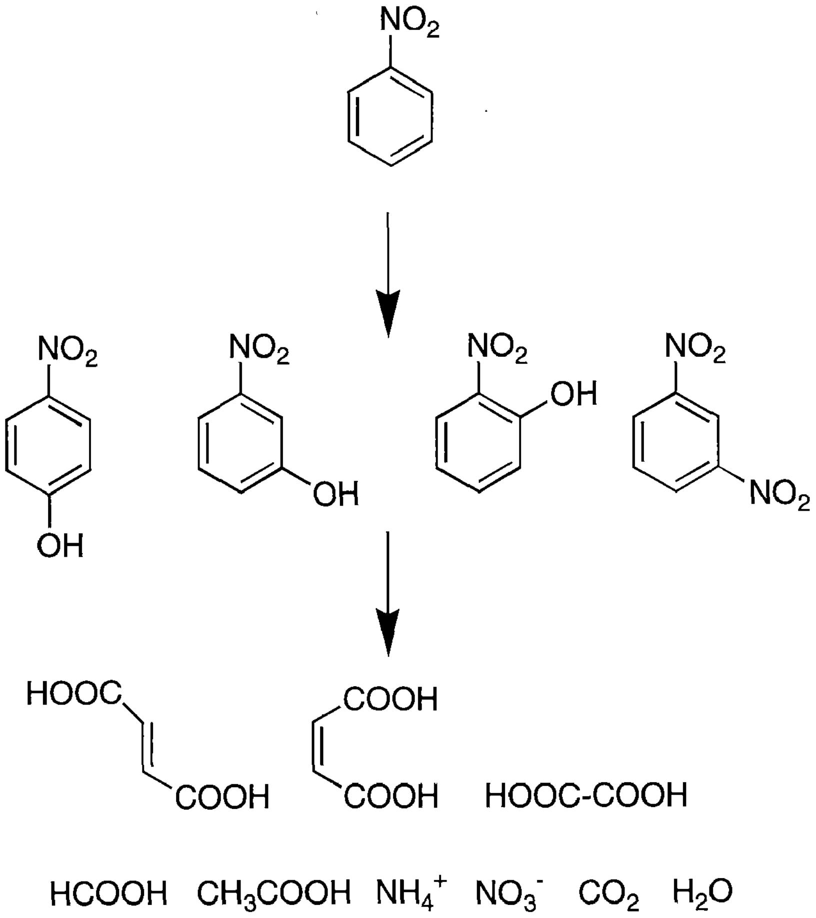

Fig. 6.15: Observed intermediates and products in the promoted wet oxidation of nitrobenzene

6.4 Discussion

To shortly summarise the results of the experiments, we mention the influences of the varied parameters on the nitrobenzene conversion:

- The temperature has a strong influence on the rate of conversion. Remarkably is the lower final conversion of nitrobenzene at 190°C and 130°C compared with the experiments at 160°C.
- The partial pressure of oxygen positively influences the rate of conversion, but not effluent quality.
- The amount of promoter influences the rate of conversion and the final conversion.

Discussing the influence of the first intermediates of the treatment, *i.e.* nitrophenols, we have to know the reactivity of the nitrophenols. Only the degradation of the nitrophenols (or the degradation of the compounds of the *ipso*-route) will lead to reactive intermediates. The thermal decomposition of nitrobenzene is too slow to influence the process. If the nitrophenols would have a slow decomposition compared with their formation, the auto-oxidative pathway would be slowed down by the decreasing number of reactive radicals. A fast formation of the nitrophenols and a slow degradation of them would be observed. This is exactly the fact observed by the experiments by variation of the promoter amount.

The addition of the promoter remarkably enhances the rate of conversion of nitrobenzene. This fast conversion does not lead to a higher amount of the first intermediates, which are also converted by the influence of the promoter. Also the final effluent quality, *i.e.* amount of nitroaromatics, is depending on the initial promoter addition.

As we have seen with the experiments by variation of the promoter, nitrobenzene as well as the formed nitrophenols are quite stable under the examined conditions. Only the promoter initiates the conversion of the nitroaromatics, therefore, it is assumed that a higher temperature increases the rate of decomposition of the promoter. The formed hydroxyl radicals are available for a decreasing time with increasing temperature. Therefore, all the substrate that is not converted in the "active" phase by promoter-generated hydroxyl radicals will remain unchanged in solution. These also implies an efficiency of the promoter, *i.e.* that number of "successful" attack of hydroxyl radicals compared with the total number of generated OH-radicals. This is true for the reaction of nitrobenzene toward the nitrophenols. The nitrophenols decompose slowly (not to dihydroxynitrobenzene) or also react with OH radicals of the promoter and will lead to further radicals.

The comparison of the chromatograms of the wet oxidation and with them of the promoted wet oxidation experiments shows the same formation of the intermediates. They only differ in the concentrations. Therefore, the promoted wet oxidation leads to the same observable intermediates as the wet oxidation. The observation of di-nitroaromatics is explainable by the reaction of NO_2-radicals with the σ-complex of the aromatic core. This formation of nitroaromatic compounds was also observed by photolysis and photocatalysis of aromatic compounds in a nitrate solution [9]. In this case, the nitrate is partially converted in NO_2-radicals by irradiation. The NO_2-radicals are then forming nitroaromatic compounds.

To treat nitrobenzene successfully, the fate of the nitrophenols is important. By using an insufficient promoter amount, the nitrobenzene is partially converted to the corresponding nitrophenols, but the molar amount of nitroaromatics remains unchanged. The promoter amount has to be chosen to convert nitrobenzene and nitrophenol.

The treatment of nitrobenzene with the promoter leads to several questions concerning the nature of the promoter. Due to the low reactivity of nitrobenzene without the promoter, the conversion of nitrobenzene indicates the amount of formed hydroxyl radicals during the conversion of the promoter. The formed nitrophenols seem to have also low reactivities.

6.5 References

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7 Discussion

7.1 Promoter

A promoter to lower the reaction temperature was invented by Bayer and introduced with the LOPROX-system. The system uses a combination of Fe(II)-ions and the so-called quinone-generating compounds. The promoted wet oxidation of phenol at $\vartheta = 140°C$ is reported by Horak [3], but it i also mentioned that phenol or naphthol compounds with an additional amine or hydroxyl group are easily converted below $\vartheta = 150°C$. For other aromatic compounds, reaction temperatures between 180°C and 190°C are necessary. The proposed mechanism for the promoter and the Fe(II)-ions follows the hydrogen peroxide formation by the quinone-generating substances and the formation of the hydroxyl radicals by the Fenton process (The combination of Fe(II)-ions and hydrogen peroxide is known as Fenton's reagent [7]). The hydrogen peroxide formation by organic substances and gaseous oxygen is well known in the anthraquinone-process [2]. The mentioned reactions for hydrogen peroxide formation are shown in Figure 7.1.

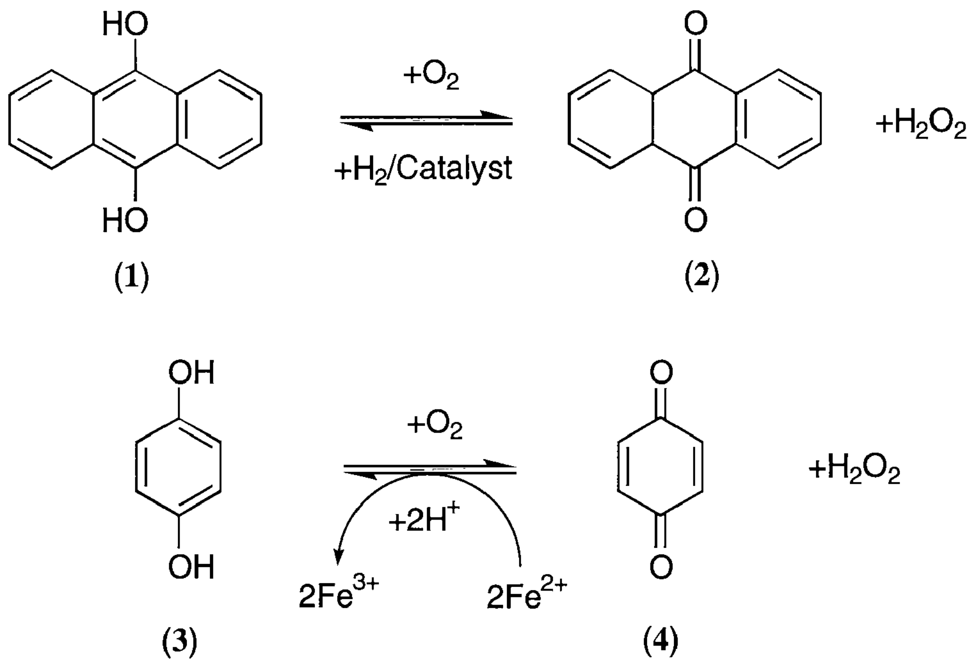


Fig. 7.1: Formation of hydrogen peroxide by reaction of organics and dissolved oxygen in solution, anthraquinone-process (1,2) and assumed reactions (3,4) in the LOPROX-process (promoter is hydroquinone (3)) [3]

The role of the Fe(II)-ions is to reduce the formed quinone (7-8) and to form hydroxyl radicals (7-4); Fe(II) is also consumed by the reaction with oxygen (7-1). Fe(III) is only reduced by hydrogen peroxide (7-3) in the scheme of Horak. Walling [7] proposes in his scheme the reduction of Fe(III) only by the reaction with $R\cdot$.

$$2Fe^{2+} + 1/2\cdot O_2 \rightarrow 2Fe^{3+} + O^{2-} \tag{7-1}$$

$$\mathbf{(3)} + O_2 \rightarrow \mathbf{(4)} + H_2O_2 \tag{7-2}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2\cdot + H^+ \tag{7-3}$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO\cdot + OH^- \tag{7-4}$$

$$RH + HO\cdot \rightarrow H_2O + R\cdot \tag{7-5}$$

$$RH + HO_2\cdot \rightarrow H_2O_2 + R\cdot \tag{7-6}$$

$$R\cdot + O_2 \rightarrow ROO\cdot \rightarrow \rightarrow \rightarrow R'\cdot + CO_2 \tag{7-7}$$

$$\mathbf{(4)} + 2Fe^{2+} + 2H^+ \rightarrow \mathbf{(3)} + 2Fe^{3+} \tag{7-8}$$

The role of the Fe(II)-ions in the mentioned scheme of Horak ((7-1)-(7-8)) is mainly as a reduction substance that is consumed by the different reactions. The formation of hydroxyl radicals is only due to the decomposition of the hydrogen peroxide. The decomposition of the promoter is included in the reactions with organics (*i.e.* (7-5)-(7-7)).

The investigations at our institute showed the important influence of the pre-treatment of the organic compounds (precursors) to form the promoter. The contact of the precursor at high pH with air leads to the promoter solution. This is expressed in the corresponding patent [6]. Based on patent, on an earlier work [5] and on the presented results, several observations concerning the promoter are important:

- Experiments without the promoter show no or slow conversion or long induction times
- For experiments with phenol, only the pre-treatment at high pH shows initial conversion
- There is no or only marginal conversion at ambient conditions of the investigated compounds with and without the promoter
- Only specific precursors (aromatic compounds) lead to the observed initial conversion [6]
- The precursor (*i.e.* gallic acid) shows fast conversion during the treatment at elevated temperature

It seems that only oxygen, Fe-ions and elevated temperatures initiate the conversion of the promoter and therefore, the reaction of the examined model substance. During the heating-up, the promoter seems not to form reactive species/ hydroxyl radicals. The experiments with the dye showed that the precursor/ promoter acts as an inhibiting substance in the solution. The observed inhibition is explainable by the known behaviour of gallic acid or gallic acid ester (gallate) as antioxidant [4]. The effect is due to H-abstraction and the stabilisation of the formed radical by the aromatic core of the antioxidant. As seen in the different experiments, gallic acid is easily converted with oxygen at elevated temperatures and therefore, the inhibiting effect is only observable during the heating-up phase. It seems that the Fe(II)-ions are removed of dye-complex by the promoter and that the gallic acid or the promoter reacts with the Fe-ions during the heating-up. Therefore it would be interesting to compare different precursors of the promoter on promoted wet oxidation of Orange II.

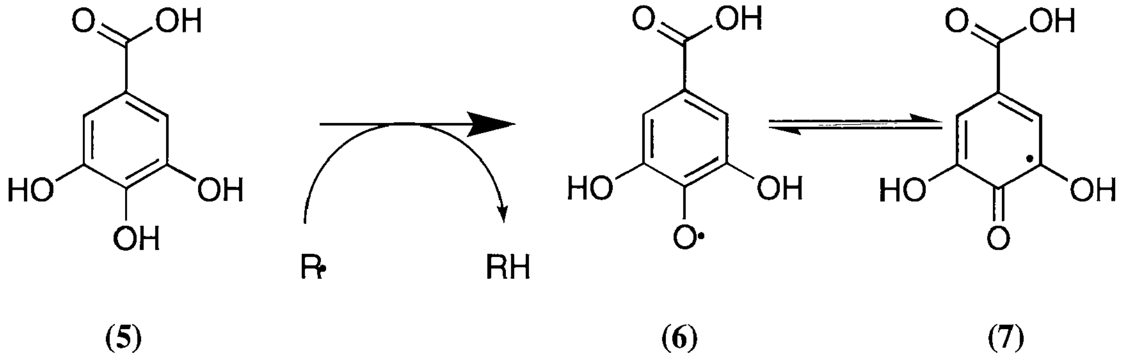
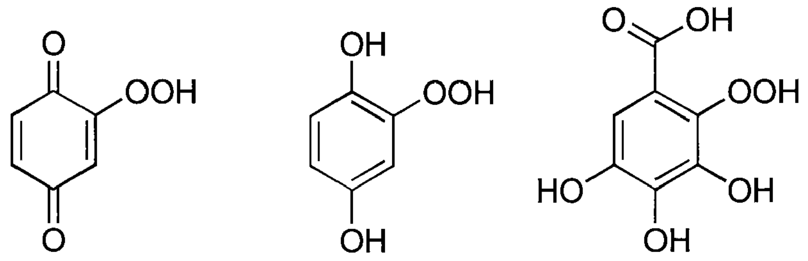


Fig. 7.2: Inhibiting effect on autoxidation by gallic acid (5), stabilisation of the formed radical (6) by delocalisation of the unpaired electron (*e.g.* (7))

Vogel [5] assumes the following peroxy-compounds as promoter (see Figure 7.3). The precursors for these structures are benzoquinone and hydroquinone.

Due to the fast reaction of gallic acid, the description of Horak seems to be too complicated and may only be adaptable for a short duration in the initial phase of the reaction. Stable peroxy radicals may also explain the fast conversion of the model substances in the initial phase. To propose a structure of the promoter with gallic acid as precursor, the corresponding peroxy compound seems to fit the observations. The role of the Fe(II)-ions seems therefore to catalyse the conversion of formed peroxy compounds. Radicals are formed by the decomposition of the peroxy compounds of the promoter.



(8) (9) (10)

Fig. 7.3: Hypothetical structures of the promoter, the corresponding precursors are benzoquinone (8) and hydroquinone (9), see [5], assumed structure of the promoter (10) with gallic acid as precursor

7.2 Simplified Mechanism

The treatment of aniline shows a product comparable with the treatment with peroxy acids and with OH-radical-generating processes. Nitrobenzene-treatment shows typical intermediates by OH-radical attack. These two facts are strong evidences that the promoted wet oxidation generates hydroxyl radicals.

Therefore, we propose a simple mechanism of the promoted wet oxidation that explains the observed effects. Three main reactions have to be included in this scheme. The first assumption is the formation of hydroxyl radicals by conversion of the promoter. This formation is the first main reaction in the scheme. The second main reaction is the reaction of the formed hydroxyl radicals with the model substance. This reaction implies a reaction rate of the hydroxyl radical and the model substance. In addition, only a part of the formed hydroxyl radical will react with the model substance. The third important reaction is the reaction (lumped by several reactions) of the formed intermediates which generates hydroxyl radicals. The formed hydroxyl radicals may react with the intermediates or with the model substances. These lumped reactions are comparable with the branching reactions in the autoxidation model. Therefore, we simplify the elementary reactions in the autoxidation scheme to a reaction that generates hydroxyl radicals by converting the intermediates.

We will discuss these steps with the example of the nitrobenzene treatment. The addition of the promoter/Fe(II) ions at $pH = 2$ (indicated by *) releases hydroxyl radicals by converting to products (indicated by k_1). This process only starts by addition of oxygen. This is proven with the observed stability of the model substances during the heating-up. The formed hydroxyl radicals attack the model substance (*i.e.* nitrobenzene) with a given efficiency (*f*) and an intermediate (*i.e.* σ-complex) is formed. This reaction is indicated by its reaction rate k_2. The intermediates may further convert to other intermediates (in this case: nitrophenol) which are further converted by reaction with oxygen. These reactions of the intermediates may also generate hydroxyl radicals that are attacking the model substance. This releasing of hydroxyl radicals out of the autoxidative loop is indicated by k_3. This simplified scheme is shown in Figure 7.4. We may distinguish between two cases: Either the intermediates are stable or inhibiting (low value of k_3) or the intermediates are easily oxidised without the promoter and generate further hydroxyl radicals/active species (high value of k_3). As we have observed with the treatment of the azo dye, the dye decomposes without observing a change of the kinetic during the treatment. However, aniline and nitrobenzene show a fast

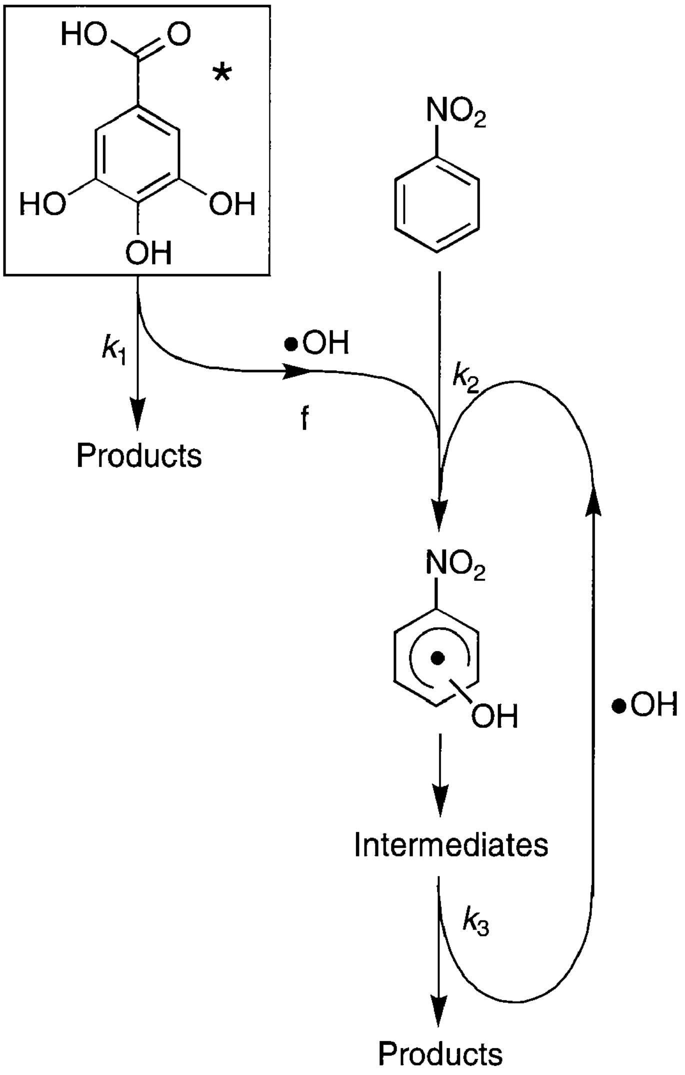


Fig. 7.4: Proposed mechanism of the promoted wet oxidation

initial conversion (especially in TOC) and a slower second reaction phase. Therefore we assume that the first intermediates of the dye treatment are easily oxidisable and enhance the performance of the process by releasing further active species (in our terms: high k_3). The formed nitrophenols observed in the nitrobenzene treatment seem to be rather stable and they are lowering the over-all performance. The precipitate in aniline treatment shows also only low conversion (lower k_3 for aniline and nitrobenzene treatment). Therefore, the azo dye on one hand and aniline/nitrobenzene on the other mainly show different behaviours due to the reactivity of the intermediates. This also indicates the influence of the promoter in the initial reaction phase but not during the whole reaction time. In addition, the compounds show different degradation rates due to the different reaction rates between the model substance and hydroxyl radicals. The only known parameter is the amount of the added promoter. This does not mean that k_1 and the amount of formed hydroxyl radicals/active species remain constant for the treatments of the different model substances. An influence of the model substance to the behaviour of the promoter may be possible. Nevertheless, for a first glance at the promoter, we neglect this influence. Therefore, the only differences in the initial phase of the treatment are the different rates of the reaction between the model substance and the hydroxyl radicals (*i.e.* k_2). Too few facts are available to prove this scheme. The promoter may also form a peroxy-compound that attacks the model substance directly and not *via* the hydroxyl radicals. This would also explain the observed accelerating of the initial phase. However, the rate constants of the reactions of hydroxyl radicals with the examined model substances are not available in the interesting temperature range. For the azo dye, a corresponding rate constant is even not known at ambient conditions. The number of formed hydroxyl radicals/active species by the conversion of the promoter is not known.

7.3 Comparison

In the presented experiments, the amounts of the model substances remained constant. To compare the different experimental series, we have to look at the initial concentrations of the investigated compounds. As seen in Table 7.1, the molar concentrations show larger differences than the initial carbon contents. To look further now at the observed results in the promoted wet oxidation experiments of the different model substances, the influence of the ratio between initial compound concentration and the initial promoter amount is obvious. For instance, by the initial promoter addition of 180 mg-C/L and initial concentrations of 1 g/L of the compounds, Aniline shows the highest conversion, of the examined model substances, the azo dye and nitrobenzene show nearly the same behaviour but at lower conversion. The corresponding curves are shown in Figure 7.5. When we now look at the reaction of the compounds with hydroxyl radicals at ambient conditions, aniline shows a higher reaction rate constant than nitrobenzene. (There is no relevant information available for the azo dye). The higher reaction rates for aniline compared with nitrobenzene are therefore observable in the promoted wet oxidation. To gain satisfying values for k_2, investigations with other sources of hydroxyl radicals have to be performed at the interesting temperature range.

Compound	$C_{i,0}$ /mM	$C_{i,0}$ /(mg-C/L)
Aniline	10.7	774
Azo dye	2.9	549
Nitrobenzene	8.1	585

Table 7.1: Initial concentrations of the investigated compounds for $C_{i,0} = 1$ g/L

Substance, Reaction	k /(L·mol^{-1}·s^{-1})	Remarks
Aniline $\cdot OH + C_6H_5NH_2 \rightarrow HOC_6H_5NH_2$	$1.4 \cdot 10^{10}$	Average of 5 values
Anilinium ion $\cdot OH + C_6H_5NH_3^+ \rightarrow ?$	$5.1 \cdot 10^{9}$	Average of 2 values
Nitrobenzene $\cdot OH + C_6H_5NO_2 \rightarrow HOC_6H_5NO_2$	$3.9 \cdot 10^{9}$	Selected value

Table 7.2: Rate constants for selected reactions of hydroxyl radicals at ambient conditions, no data were found for the azo dye, see also [1]

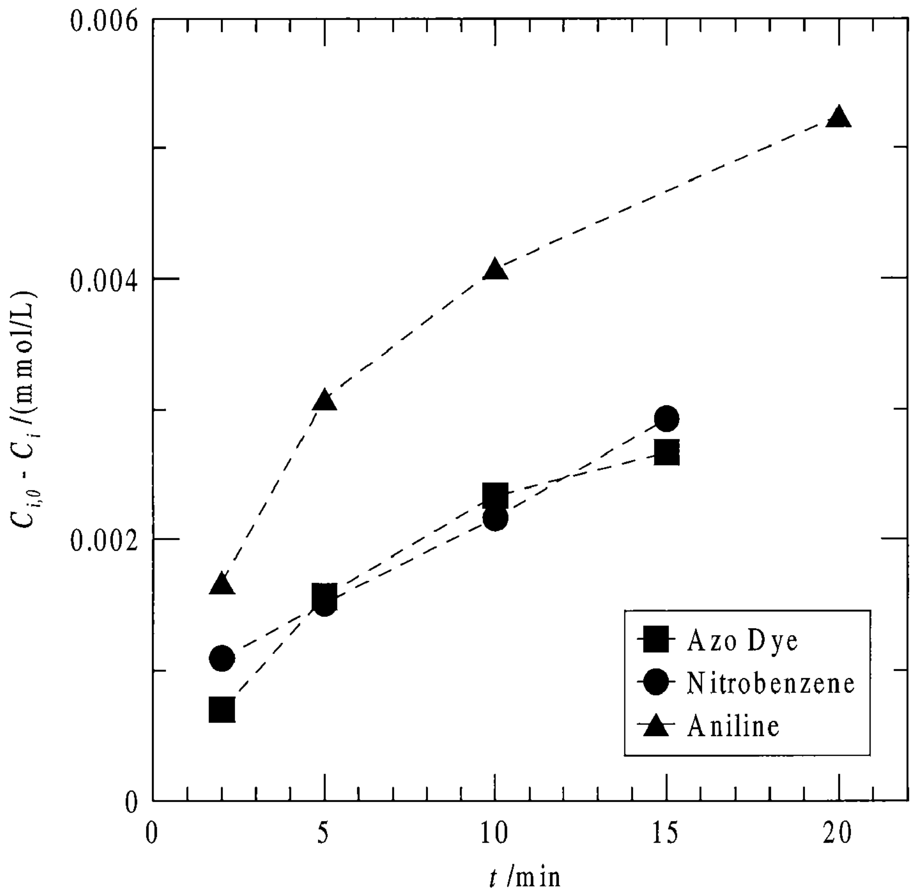


Fig. 7.5: Converted amounts of the different model substances at $\vartheta = 160°C$, pH = 2, $C_{I,0}$ = 180 mg-C/L and p_{Oxygen} = 10 bar, shown are molare concentration differences

7.4 References

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8 Conclusions and Recommendations

8.1 Conclusions

The wet oxidation of the three examined compounds (*i.e.* the azo dye Orange II, aniline and nitrobenzene) without the promoter leads to the expected low conversions. This is mainly due the moderate conditions, especially of the temperature range of $\vartheta = 130°C...190°C$. In all of the performed WO-series, the influence of the reaction temperature is obvious. However, only temperatures above 160°C lead to satisfying conversions of the compounds. To look closer at the process, the fate of the intermediates is important. Especially toxic intermediates may be formed and need longer reaction times than expected by the observation of the initial compound.

Wet oxidation is a highly competitive tool compared with the combustion as disposal process. But the examined temperature range is not favourable for the 'classic' wet oxidation. Nevertheless, the examined compounds are known to be only degradable under more rigid wet oxidation conditions than the chosen conditions.

The influence of the pH on the degradation was only remarkable for the dye-treatment. This may be easily explained by the pH-sensitivity of azo dyes. This may also indicate a possible use of the acidic thermolysis as a pre-treatment step for coloured wastewaters. In the case of the aniline as the model compound, the pH may influence the eventually formed polymer. However, this assumption has to be proven by a specific examination.

The influence of Fe-ions in the wet oxidation was not examined by a specific evaluation. Nevertheless, as observed by the preliminary experiments of the corresponding treatment series, the influence of the Fe-ions alone is not significant. This is also explained by the fast oxidation of the Fe(II)-ions by molecular oxygen. Therefore, the Fe(II)-ions have not the positive effect as the combination of the promoter and the Fe-ions. In fact, by using the actual equipment, the presence of iron oxide in the solution is given by the corrosion of the ball bearing. A remarkable effect is the precipitation of the dye with Fe(II)-ions. The precipitate is only occurring at the preparation. After heating-up, the precipitate is observable; the formed complex seems to be rather stable at the observed conditions.

The examinations of the promoted wet oxidation lead to different conclusions: The promoted wet oxidation has higher initial conversion rates in all of the examined compounds compared with the wet oxidation treatment. For example, by addition of a specific amount of the promoter, the dye decomposes at $\vartheta = 130°C$ as fast as observed at $\vartheta = 190°C$ without the promoter. In the case of aniline and nitrobenzene, the promoter starts the initial conversion. Without the promoter, the compounds do not convert after 15 min and $\vartheta = 190°C$ of treatment time. The promoter initiates the conversion of rather stable compounds. In the case of the azo dye-treatment, the promoter does not initiate the conversion. However, its addition enhances the observed degradation. Therefore, in all of the examined compounds, the addition of the promoter increases the observed degradation rate and increases the effluent quality (expressed as TOC). These improvements in effluent quality by promoter addition are shown in Table 8.1.

Compound	Aniline		Azo dye		Nitrobenzene	
	X_{Ani}	X(TOC)	X_{Dye}	X(TOC)	X_{NB}	X(TOC)
WO	5%	2%	34%	2%	10%*	10%*
PWO	57%	27%	99%	61%	83%*	52%*

Table 8.1: Comparison of wet oxidation (WO) and promoted wet oxidation (PWO) at moderate conditions: $\vartheta = 160°C$, $p_{Oxygen} = 10$ bar, pH = 2, t = 30 min, $C_{I,0} = 180$ mg-C/L, $C_{i,0} = 1$ g/L; star (*) indicates partial evaporation of nitrobenzene, X means conversion.

The question arises whether the promoted wet oxidation also influences the nature of the intermediates and products. First, the rate of formation for the first intermediates is enhanced by the promoter. The experiments with nitrobenzene as model substance show that the observed nitrophenols occur in the WO-treatment and also in the PWO-treatment. The formation of the different carboxylic acids is influenced by promoter addition. This is obvious by the formation of carboxylic acids by the conversion of the promoter.

The examination of nitrogen-containing pollutants needs special attention to the fate of nitrogen. While the evolution of nitrogen gas (*e.g.* by an azo-group) is not easily followed by analytical tools, the formation of nitrate and ammonia is accessible by analytical tools. The observation and quantification of these two mineralisation products is important. Therefore, an analytical tool has to be found that is able to analyse acidic samples with Fe-ions. Ion chromatography would be an interesting analytical tool, but so far, the samples are not suitable for the actually available systems. To describe the influence of the promoter on the investigated compounds, relevant data on the reaction of the compounds with hydroxyl radicals has to be measured.

8.2 Recommendations

As long as the zero by-product process technology is not fully implemented in the (chemical) industry, further investigations on the field of the wastewater treatment has to be performed. The necessary investigations on the promoted wet oxidation include experimental and theoretical aspects. The reported examinations clearly reveal the great role of the analytical equipment and of the right interpretation of the gained results. The used equipment gives valuable information about the phenomena of the examined process. The greatest disadvantage is the low sample-rate of the used bench-scale reactor.

The recommended further examinations are two-fold: On one hand, the evaluation of kinetical data in the interesting temperature range has to be accomplished and on the other hand, a theoretical description of the behaviour of the promoter has to be performed.

The evaluation of kinetical data is linked with equipment allowing fast sampling and fast handling. The fast sampling may be performed by on-line measurements by an UV-detector. This may be done by an optical probe. As we have seen with the experiments of aniline, this probe is not helpful by investigating polymerising compounds. Especially for the experiments with nitrobenzene and dye as model substance, the on-line measurement would give further insight for the initial phase of the reactions. To enhance the rate of samples, not only the analytical equipment is important. The handling is the main problem to collect kinetical data. Therefore, a smaller reactor-concept is needed. This reactor should be operable in the examined conditions ($\vartheta < 200°C$, $p_{tot} < 50$ bar, pH-range = 1-13) and should have good k_La-values (actual bench-scale system: $k_La = 101\ min^{-1}$ at 1500 revolution per min and $\vartheta = 150°C$). The reactor volume itself should be small and the filling/cleaning should be easy. The proposed system would be therefore designed like a stopped-flow set-up or a pipe, equipped with an optical window. Three fluids would be heated to the desired reaction temperature and mixed (static mixer) in the pipe. The reaction would be observed by UV/Vis-DAD through the optical window. One of the fluids would be water (pH = 2), saturated with oxygen.

The second fluid would be a solution with the model substance and the Fe(II)-ions (may also be saturated with oxygen if the compound shows only minor conversion with oxygen). The third fluid would be an aqueous solution at pH = 2 containing the pre-treated gallic acid (pressurised with argon). By mixing the three streams, any ratio between the relevant compounds would be possible. This system would allow observing the initial phase of the reaction with high accuracy. In addition, a high rate in samples would be possible. To observe the reactions over a longer time-scale, the existing system would be sufficient. In addition, experiments with several additions of promoter are possible with the existing system. Only minor changes would be necessary (*i.e.* a second container that can be pressurised with oxygen; adapted pressure control system). As model substance, nitrobenzene would be a promising probe for reactions with hydroxyl radicals.

From the chemical point of view, there are still some questions. Especially the experiments with aniline leave the reader and the writer without a full understanding of the formed precipitate. Its is interesting that the promoted wet oxidation may form the same product as the reported treatment with peroxy acids. These would be an interesting field for further examinations.

The further examinations on the promoter would lead to a description of the behaviour. This is important for industrial applications. A “real” wastewater has other parameters in salinity, concentrations of the main pollutant and other organic compounds or concentrations of inhibiting substances (scavengers). By knowing the rate and amount of formed hydroxyl radicals by the promoter, the prediction of experiments with several additions of the promoter are possible. For this purpose, the reaction rates of the model substances at the interesting conditions have to be known.

The influence of the matrix (*i.e.* the water without the model substance) on the performance of the system is not yet systematically examined. The pH should not be increased at higher temperatures due to the assumed formation chlorinated compounds in presence of chlorides. However, at lower temperatures, the fate of chloride is not examined in the WO-process. Therefore, a study in pH-variation at lower temperatures (*i.e.* lower then 160°C) by observation of the formation of chlorinated compounds should be a task of further studies. But the salinity of the solution and its influence on the performance (oxygen solubility, conversion) is not examined and may be an important point for industrial applications.

Important pollutants are the chloride-containing compounds. The observations of the model substances have revealed some phenomena. Now, the question arises whether the chlorinated compounds show the same behaviour.

The examination of nitrobenzene revealed the formation of nitrophenols as the first intermediates. Form the industrial point of view, the nitrophenols are important intermediates or starting compounds for different industrial products. The nitrophenols occur in wastewaters and are a scientific field with industrial background. Further examinations in nitrophenol treatment would result in important knowledge for industrial applications and would result in deeper insight in the nitrobenzene oxidation.

Appendix 1 Analytical Methods

To measure concentrations of the model substances, the corresponding HPLC-methods were established. The concentration measurements of the model substances and of the intermediates were performed by calibration. A specified concentration of the substances were analysed and these results were taken to calculate the corresponding calibration curve. The wavelength of the UV-detector was adjusted to minimise the influence of the matrix (*e.g.* intermediates) and to optimise the signal of the UV-detector. When the signal is too low, the sensitivity of the method is weak. When the signal is too strong (especially in the case of dyes), the linearity of the calibaration curve is not given.

The published, expected or identified (GC-MS) intermediates were identified in the HPLC-method by comparing the retention time (RT) and the UV-spectra. Due to the possible change in the spectra by pH-change or change of the eluent, the evaluation of the spectra for comparison were performed in the following way: All of the examined substances were dissolved in acidified water (pH = 2 by H_2SO_4) and the eluent was the same as used for the measuerement of the experiemental series. By using this procedure, the identification of intermediates by RT and UV-spectra is possible and reliable.

The measurement of aromatic compounds is mainly performed by using a RP-column, the measurement of carboxylic acids is performed by using a size-exclusion column.

Method Aniline (HPLC).

- Eluent: 90% H_2O, 10% MeOH, 0.9 mL/min
- Observed wavelength: 210 nm, 230 nm
- Column: EC 250/4 Nucleosil 5 C18 HD, Macherey-Nagel AG, Oensingen, CH
- Retention times

4-Aminophenol	Front/weak signal
Gallic Acid	4.9 min
Hydroquinone	5.6 min
3-Aminophenol	5.9 min
2-Aminophenol	9.6 min
Benzoquinone	9.9 min (4.6 min, 5.6 min)
Aniline	17.0 min
Phenol	27.8 min
Nitrobenzene	>45 min
Nitrophenols	>45 min

Method Nitrobenzene (HPLC).

- Eluent: 50% H_2O, 50% MeOH, 0.8 mL/min
- Observed wavelength: 210 nm
- Column: EC 250/4 Nucleosil 5 C18 HD, Macherey-Nagel AG, Oensingen, CH
- Retention times

Gallic Acid	Front
Hydroquinone	3.0 min
Benzoquinone	3.6 min
Aniline	2.6 min
Nitroaniline	4.7 min
Nitroaniline	4.9 min
Phenol	5.9 min
4-Nitrophenol	7.5 min
Nitroaniline	7.6 min
3-Nitrophenol	8.2 min
2-Nitrophenol	10.3 min
Nitrobenzene	10.8 min

Method Dye (HPLC).

- Eluent: 80% H_2O, 20% MeOH, 0.9 mL/min
- Observed wavelength: 230 nm
- Column: EC 250/4 Nucleosil 5 C18 HD, Macherey-Nagel AG, Oensingen, CH
- Retention times

Gallic Acid	5.1 min
Dye	16.5 min

Method Carbonic Acids (HPLC).

- Eluent: 100% H_2O, pH = 2 (H_2SO_4), 0.9 mL/min
- Observed wavelength: 230 nm, RI
- Column: GromGel Acid-1, STAGROMA AG, Wallisellen, CH
- Retention times

Formic acid	14.3 min
Acetic acid	15.5 min
Oxalic acid	7.6 min
Glyoxylic acid	10.2 min
Propionic acid	18.2 min
Maleic acid	9.5 min
Fumaric acid	15.5 min
Gallic acid	27.2 min

Appendix 2 Liquid-phase concentration of volatile substances

We use the following approach to model the behaviour of a volatile substance in a closed reactor (see also [1,3]):

- Vapour-liquid-distribution of water (concentration factor f_c)
- Estimation of the Henry-constant of the volatile substance
- Influence of the sampling on the gas-liquid-distribution
- Combination with the degradation rate

Concentration factor. The concentration factor is the quotient of the vaporized and the total water in a closed system.

The mass balance for water inside the reactor

$$m_{Water,\,tot} = m_{Water,\,L} + m_{Water,\,G}$$

and the volume of the different phases

$$V_{tot} = V_L + V_G$$

lead to the definition of the concentration factor f_c:

$$V_{tot} = \frac{m_{Water,\,L}}{\rho_L} + \frac{m_{Water,\,G}}{\rho_G}$$

$$= \frac{m_{Water,\,L}}{\rho_L} + \frac{(m_{Water,\,tot} - m_{Water,\,L})}{\rho_G}$$

$$m_L = \frac{m_{Water,\,tot} - V_{tot} \cdot \rho_G}{\left(1 - \frac{\rho_G}{\rho_L}\right)}$$

$$f_c = \frac{m_{Water,\,tot}}{m_{Water,\,L}} = \left(1 - \frac{\rho_G}{\rho_L}\right) \cdot \frac{m_{Water,\,tot}}{m_{Water,\,tot} - V_{tot} \cdot \rho_G}$$

The densities in this derivation are the densities of the corresponding water phase. The concentration factor is depending on the total pressure, *i.e.* the addition of a non-condensable gas. The density of the gas phase has to be corrected by the quotient of the saturated water pressure and the total pressure:

$$\hat{f}_c = \frac{m_{Water,\,tot}}{m_{Water,\,L}} = \left(1 - \frac{p_{Water} \cdot \rho_G}{p_{tot} \cdot \rho_L}\right) \cdot \frac{m_{Water,\,tot}}{m_{Water,\,tot} - V_{tot} \cdot \rho_G \cdot \frac{p_{Water}}{p_{tot}}}$$

The data for water in a chosen range are as follows:

T /°C	T /K	ρ_L /(kg/m^3)	ρ_G /(kg/m^3)	p_{Water} /Mpa
25	298.15	997.009	0.023	0.002
130	403.15	934.579	1.497	0.270
160	433.15	907.441	3.259	0.618
190	463.15	876.424	6.395	1.255

Tab App. 1: Properties of water [2]

Evaluating of the Henry constant. With the definition of Henry's law

$$x_i = \frac{p_i}{H_i}$$

and with the partial pressure of the organic compound

$$p_i = p_{tot} \cdot y_i$$

the vapour-liquid equilibrium can be approximated by

$$H_i = \frac{y_i}{x_i} p_{tot}$$

For evaluating the Henry constant H_i, we obtain the liquid phase mole fraction by

$$x_i = \frac{m_{i,L}}{M_i} \cdot \frac{M_{Water}}{m_{Water,L}}$$

and the gas phase mole fraction by

$$y_i = \frac{RT}{p_{tot} \cdot M_i} \cdot \frac{m_{i,tot} - m_{i,L}}{V_{tot} - V_L}$$

By neglecting the solved mass of the organic compound, the actual amount of water in the reactor can be determined by subtracting the purge and probe volumina of the initial amount of water:

$$m_{Water,tot} = \rho_{0,L} \cdot \left(V_{0,L} - \sum_{Probe,\,Purge=1}^{k} V_{Probe} + V_{Purge} \right)$$

The amount of water in the gas phase is therefore:

$$m_{Water,L} = \frac{m_{Water,tot}}{f_c}$$

$$= \frac{m_{Water,tot} - V_{tot} \cdot \rho_G}{\left(1 - \frac{\rho_G}{\rho_L}\right)}$$

And therefore, the volume of the liquid is known:

$$V_L = \frac{m_{Water, L}}{\rho_L}$$

The actual amount of the organic compound in the reactor, m_i, is determined subtracting the measured amounts of the probe/purge volumina and their concentration:

$$m_{i, tot} = m_{i, 0} - \sum_{Probe, Purge = 1}^{k} c_{Probe} \cdot (V_{Probe} + V_{Purge})$$

The amount of the organic compound in solution, $m_{i, L}$, can be determined by the measured concentration and by the calculated amount of liquid water, $m_{Water, L}$:

$$m_{i, L} = \frac{c_{Probe} \cdot m_{Water, L}}{\rho_{L, 0}}$$

All the necessary variables are available and the Henry constant can now be calculated.

Application of Henry's Law. Once an average H_i has been calculated, the liquid concentration of the organic compound can be determined at any given total mass of the compound and any given liquid volume. The mass in the vapour for an ideal gas in equilibrium with the liquid is given by:

$$m_{i, G} = c_{Probe} \cdot \frac{H_i M_{Water}}{RT\rho_{L, 0}} \cdot (V_{tot} - V_L)$$

The mass of the organic compound in the liquid phase is given by:

$$m_{i, L} = V_L \cdot \frac{\rho_L}{\rho_{L, 0}}$$

The total mass in function of the measured concentration and the liquid volume is now:

$$\begin{aligned} m_{i, tot} &= c_{Probe} \cdot \left(\frac{H_i M_{Water} V_{tot}}{RT\rho_{L, 0}} + V_L \cdot \left(\frac{\rho_L}{\rho_{L, 0}} - \frac{H_i M_{Water}}{RT\rho_{L, 0}}\right)\right) \\ &= c_{Probe} \cdot (\alpha + V_L \cdot \beta) \end{aligned}$$

The volume of the liquid remains constant between two probes and the gas/liquid volume changes only at the drawing of the probe. This equation can be simplified to

$$m_{i, tot} = c_{Probe} \cdot \phi_{Probe}$$

With no reaction of organic compound, this equation describes the behaviour of the concentration drop due to the sampling. To describe the degradation of the compound, the model has to be expanded with the kinetic.

Model. A general differential mass balance on organic compounds in the reactor is:

$$\frac{dm_{i,\,tot}}{dt} = -(q_{out} \cdot c_{i,\,L}) - (r_i \cdot V_L)$$

The flowrate q_{out} is zero between two probes and only non-zero during sampling. The integration of $q_{out}dt$ is the sum of the purge and probe volumina. Assuming first order kinetic and ignoring the sample term, the kinetic is

$$\begin{aligned}\frac{d(c_{i,L} \cdot \phi_{Probe})}{dt} &= -k \cdot C_{Oxygen} \cdot C_{i,L} \cdot V_L \\ &= -k' \cdot C_{i,L} \cdot V_L\end{aligned}$$

The liquid volume V_L, and therefore ϕ_{Probe}, is constant between two samples, the integration leads to

$$c_{i,L} = c_{i,L,0} \cdot \exp\left[\frac{-k' \cdot V_L}{\phi_{Probe}} \cdot (t - t_0)\right]$$

After taking the first sample and then pressurizing the solution with oxygen, $c_{i,L}$ is diminished continuously due to reaction and instantaneously due to sampling. The corresponding equations can be combined to predict $c_{i,L}$ at any time

$$c_{i,L} = \sum_{i=1}^{m} \frac{\phi_{i-1} - V_i}{\phi_i} \cdot c_{i,L} + \sum_{i=1}^{n} c_{i,L} \cdot \exp\frac{-k' \cdot V_L}{\phi_{Probe}} \cdot t - t_0 + \sum_{i=m+2,\,2}^{n} \frac{\phi_{i-1} - V_i}{\phi_i} \cdot c_{i,L}$$

The first term accounts for the first samples before the oxygen pressurization, the second and third summation terms alternately reduce $c_{i,L}$ due to reaction and due to sampling, respectively.

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Curriculum Vitae

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