IONISING RADIATION AND OZONE IN ENVIRONMENTAL STUDIES: INTERMEDIATES, STABLE PRODUCTS AND MECHANISTIC CONCEPTS

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ABSTRACT

This work is presenting some selected fundamental studies related to the environmental problems of toxicity of organic compounds and ozone treatment in drinking water and wastewater processing.

Radiation chemistry was chosen as a tool to induce and investigate free-radical degradation of widely-spread environmental pollutants such as halogenated organic compounds in both, oxygen-free and oxygenated aqueous solutions.

The new approach employed in this work allowed for the first time, via radiation chemical studies, a detailed investigation the reactive fates of the key intermediates, namely halogenated hydroperoxides, peroxyl and alkoxy radicals, independent of each other in well defined model systems. Special attention is paid to the improvement of the analytical methods for determination of unstable intermediates such as organic hydroperoxides. This led to a qualitative progress in the understanding of the degradation mechanisms of halogenated organic compounds. The results also helped to clarify the chemical basis of their toxic side effects. Radical-mediated processes often involve chain mechanisms. As far as peroxyl radicals are concerned, some selected examples have been investigated and are discussed in view of their environmental and biological significance.

Detailed knowledge of ozone reactions in aqueous solutions is a prerequisite for any further evaluation of a wider application of ozone in the remediation technology. In the present work experimental methods are proposed for the determination of the key intermediates of ozone reactions in aqueous solutions, namely, •OH, O₂•− and hydroperoxides. They allow to understand more deeply the mechanisms of ozonation reactions. A firm set of rate constants for ozone reactions with DNA constituents and related compounds have been established in order to reach a better understanding of its possible biological effects when applied as a disinfectant in drinking water treatment. Reinvestigation of the ozonation of pyrimidines revealed, in particular, the formation of highly reactive organic peroxides, whose characterization, together with detailed products analysis, provided a new concept regarding the mechanism of the underlying processes.
STRESZCZENIE

W niniejszej pracy przedstawiono badania podstawowe, dotyczące wybranych zagadnień środowiskowych związanych z toksycznością związków organicznych oraz obróbką ozonem wody pitnej oraz ścieków.

Chemia radiacyjna została wybrana jako narzędzie badawcze do inicjowania oraz badania wolno-rodnikowej degradacji szeroko rozpowszechnionych związków chemicznych powodujących zanieczyszczenie środowiska naturalnego, takich jak halogenowe związki organiczne w roztworach wodnych, w obecności lub nieobecności tlenu.


Dokładna wiedza o reakcjach ozonu w roztworach wodnych jest warunkiem koniecznym dla późniejszego określenia szerszego zastosowania ozonu w technologii remediacyjnej. W niniejszej pracy zaproponowano eksperymentalne metody służące do oznaczania głównych produktów przejściowych, takich jak •OH, O₃⁻ oraz wodoronadtlenki, powstających w reakcjach ozonu w roztworach wodnych. Pozwala to na głębsze zrozumienie mechanizmów ozonowania. Otrzymany zwarty zbiór stałych szybkości reakcji ozonu ze składnikami DNA i związków pochodnych jest potrzebny dla lepszego zrozumienia możliwych efektów w układach biologicznych spowodowanych obecnością ozonu, kiedy jest on wykorzystywany jako środek dezynfekcyjny podczas obróbki pitnej wody. Powtórzone badania, w szczególności procesów ozonowania związki pirymidynowych, wskazują na tworzenie się wysoko-reaktywnych organicznych nadtlenków, których charakterystyka wraz z dokładną analizą produktów dostarczyła nowych pomysłów związanych z mechanizmami wspomnianych wyżej procesów.
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<tr>
<td>AN</td>
<td>acrylonitrile</td>
</tr>
<tr>
<td>BF</td>
<td>bromoform</td>
</tr>
<tr>
<td>5ClUra</td>
<td>5-chlorouracil</td>
</tr>
<tr>
<td>CDFAA</td>
<td>chlorodifluoroacetic acid</td>
</tr>
<tr>
<td>CF</td>
<td>chloroform</td>
</tr>
<tr>
<td>CT</td>
<td>carbon tetrachloride</td>
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<tr>
<td>1,2-DBE</td>
<td>1,2-dibromoethane</td>
</tr>
<tr>
<td>DBFA</td>
<td>dibromofumaric acid</td>
</tr>
<tr>
<td>DBM</td>
<td>dibromomethane (methylene dibromide)</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane (methylene dichloride)</td>
</tr>
<tr>
<td>DMSe</td>
<td>dimethylselenide</td>
</tr>
<tr>
<td>DMSeO</td>
<td>dimethylselenoxide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protective Agency</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>FPA</td>
<td>formic peracid</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GCMS</td>
<td>Gas Chromatography/Mass-Spectroscopy</td>
</tr>
<tr>
<td>HMHP</td>
<td>hydroxymethylhydroperoxide, CH$_2$OH(OOH)</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
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<tr>
<td>IC</td>
<td>Ion Chromatography</td>
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<tr>
<td>2-ProOH</td>
<td>2-propanol</td>
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<tr>
<td>LCMS ESI</td>
<td>Liquid Chromatography/Mass-Spectroscopy with Electrospray Ionisation</td>
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<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>MetS</td>
<td>methionine</td>
</tr>
<tr>
<td>MetSO</td>
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</tr>
<tr>
<td>MSA</td>
<td>methanesulfinic acid/methanesulfinate anion</td>
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<td>1,3Me$_2$Ura</td>
<td>1,3-dimethyluracil</td>
</tr>
<tr>
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</tr>
<tr>
<td>NF</td>
<td>nitroform anion</td>
</tr>
<tr>
<td>RHal</td>
<td>halogenated hydrocarbon</td>
</tr>
<tr>
<td>RHalO*</td>
<td>halogenated alkoxyl radical</td>
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<td>alkoxyl radical</td>
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<td>peroxyl radical</td>
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<td>tertiary butanol</td>
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<tr>
<td>TCAA</td>
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<td>trifluoroacetaldehyde</td>
</tr>
<tr>
<td>TFSA</td>
<td>tetrafluorosuccinic acid</td>
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<tr>
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<td>Thy</td>
<td>thymine</td>
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<td>TNM</td>
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<tr>
<td>Ura</td>
<td>uracil</td>
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<tr>
<td>UV-Vis</td>
<td>Ultraviolet and Visible Spectroscopy</td>
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<tr>
<td>VA</td>
<td>vinyl acetate</td>
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<tr>
<td>VB</td>
<td>vinyl bromide</td>
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<tr>
<td>VC</td>
<td>vinylene carbonate</td>
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PREFACE

In my dissertation I would like to present the work done on radiation chemistry [1-9] and ozone chemistry [7, 10-15] of selected organic compounds in aqueous solutions. All investigated compounds belong to the class of environmentally important substances.

The great majority of the results have been published (see ref. [1-15]). Chapter 1 presents an overall concept of this work with a detailed argumentation why radiation and ozone chemistry have been chosen as the major tools to study degradation processes. Special attention has been paid to the fates of peroxy radicals which represent the major radical species of the degradation processes studied in this work. Chapter 1 introduces the readers to the basics of radiation and ozone chemistry in aqueous solutions.

Chapter 2 describes experimental methods and techniques employed in this work.

Chapter 3 describes results obtained on the mechanisms of radiation induced transformations of environmentally important organic compounds. These investigations have been done in aqueous solutions in the absence or presence of the molecular oxygen. The key molecular intermediates investigated through the whole work are organic hydroperoxides. Therefore, a short description of existing methods for hydroperoxide analysis, together with our recommendations for their determination, is given in Chapter 3. The model systems allowing to investigate the chemistry of halogenated oxyl radicals as well as hydroperoxides have been described. Based on this the detailed mechanisms of free-radical degradation of halogenated pollutants have been proposed. Some interesting examples of the chain processes have been discussed.

Chapter 4 is devoted to investigations done on the mechanisms of ozonolysis of environmentally and biologically important organic compounds in aqueous solutions. Essential part of Chapter 4 is focused on the methodological improvements regarding the determination of the key radical and molecular intermediates in ozonation processes in aqueous solutions. The new findings for the ozonation of pyrimidines have been described and a new mechanisms based on them are proposed.

Chapter 5 summarizes the whole work and contains general conclusions. Acknowledgments are given in Chapter 6 and the reference list in Chapter 7.
1. INTRODUCTION

1.1. Background

Ecological problems are one of the biggest concerns of mankind. They include questions of air, ground, ground- and drinking waters as well as food stuff quality.

Water is essential for life and plays a vital role in the proper functioning of the Earth's ecosystems. The pollution of water has a serious impact on all living creatures, and can negatively affect the use of water for drinking, household needs, recreation, fishing, transportation and commerce [16].

Degradation of environmentally relevant and hazardous chemicals typically involve homolytic breakage of bonds and/or redox processes. All these processes require an initiation through some kind of energy demanding first step such as an ionisation, excitation, thermal dissociation, chemical molecular initiators of high reactivity, or free radicals. The latter are, in fact, often the most efficient means. Suitable methods, generally known under the umbrella name of Advanced Oxidation Technologies (AOTs) include UV photolysis, photocatalysis, ozonation, sonolysis, Fenton systems, high-energy radiation including electron beams. All these techniques have, in the meantime, been well developed and successfully applied in laboratory as well as larger scale operations [17].

Among all methods radiation chemistry provides the best choice for generation of free radicals of defined structure in a wide range of temperatures. Secondly, in contrast to other methods, free radicals from substrates can be generated in both, reductive and oxidative ways, using the primary species from solvent radiolysis. If needed for purpose of higher selectivity, the latter species may be transformed into species of milder power. For example, •OH radicals (generated as primary species upon radiolysis of aqueous solutions) can be quantitatively substituted by radicals derived from alcohols, which possess reductive properties in a wide range of redox potentials. Similarly, primary species from water radiolysis of reductive nature (hydrogen atom and hydrated electrons) can be transformed into species of lower reductive power or redox neutral ones.

Halogenated organic compounds are known to be potentially very hazardous chemicals and potent toxins, and are, nevertheless, still in widespread use in various important fields of civilization. Their toxic action, e.g. in the liver of animals and humans, to a decisive extent, involves free radicals. To degrade these substrates to preferably harmless and easily disposable substrates is possible via an overall mechanism generally referred to as mineralization in which the halogenated organics end up as inorganic carbon dioxide and hydrogen halide. This has been demonstrated in many studies involving a variety of experimental approaches [2, 18-20]. Many of the original studies dealing with the mineralization process, while providing reliable product data and making some reasonable mechanistic suggestions, nevertheless often lacked a deep and detailed mechanistic insight due to the absence of material balance [20].
Practical uses of halogenated methanes and anaesthetics and vinyl compounds and their environmental aspects.

**Halogenated methanes.** For this study we have chosen the family of halogenated methanes as the most used halogenated solvents. Here belong dichloromethane, chloroform, carbon tetrachloride, dibromomethane and bromoform.

The largest consumers of dichloromethane (DCM) are companies that make paint strippers and removers. Foam makers use DCM as a blowing agent. Other companies employ it to clean metal surfaces. DCM is a process solvent in the manufacture of drugs, pharmaceuticals, and film coatings; as a metal cleaning and finishing solvent in electronics manufacturing; and as an agent in urethane foam blowing [21]. It is an extraction solvent for hops and for the removal of caffeine from coffee.

DCM does not occur naturally but is produced in large amounts (350 million pounds in 1992 in the USA) [21]. Approximately 80% of the world production of DCM is emitted into the atmosphere during its use as a solvent, and in paint removers, aerosols, solvent degreasers, and fumigants. The major sources of DCM emission (total $6.6 \times 10^7$ kg per year) are wood pulp and paper industry, together with drinking and other water treatment account for about $5.5 \times 10^7$ kg per year and the chemical and pharmaceutical industries account for the remainder [22].

DCM has been detected in both surface water and groundwater samples taken at hazardous waste sites, and even in drinking water at very low concentrations [21]. Humans acutely exposed to DCM experience adverse effects of the central nervous system and the heart.

Dibromomethane (DBM) finds limited use in chemical synthesis, as a solvent, and as a gage fluid [23]. Natural production by marine algae also adds to its environmental input. If released in water, DBM would be primarily lost by volatilization. In the atmosphere, DBM will be lost by reaction with photochemically produced hydroxyl radicals. The estimated half-life for this reaction is 213 days. In a survey of 14 treated drinking water supplies of varied sources in England, DBM was detected in seven supplies [23],[24]

Chloroform (CF) may be released to the air as a result of its formation in the chlorination of drinking water, wastewater and swimming pools [25]. Other sources include pulp and paper mills, hazardous waste sites etc. Chronic exposure to CF by inhalation in humans has resulted in effects on the liver, including hepatitis and jaundice, and central nervous system effects, such as depression and irritability. CF has been shown to be carcinogenic in animals after oral exposure, resulting in an increase in kidney and liver tumors. CF may also be found in some foods and beverages due to the use of tap water during production processes [25].

Bromoform (BF) is used as a fluid for mineral ore separation in geological tests, as a laboratory reagent, and in the electronics industry in quality assurance programs. BF was formerly used as a solvent for waxes, greases, and oils and as an ingredient in fire resistant chemicals. The principal route of human exposure to BF is from drinking water that has been disinfected with bromine or bromine compounds [26]. The acute (short-term) effects from inhalation or ingestion of high levels of BF in humans and animals consist of nervous system
effects such as the slowing down of brain functions, and injury to the liver and kidney. Chronic animal studies indicate effects on the liver, kidney, and central nervous system from oral exposure to BF, long-term oral exposure can cause liver and intestinal tumors [26].

BF is the most abundant form of biogenic reactive organic bromine with an atmospheric lifetime of 2-3 weeks to several months. BF is the largest single source of atmospheric organic bromine and therefore of importance as a source of reactive halogens to the troposphere and lower stratosphere. Estimated annual global flux of bromoform is $\sim 10 \text{ Gmol Br per year}$, whereas anthropogenic sources account for $\sim 0.3 \text{ Gmol Br per year only}$ [27].

Carbon tetrachloride (CT), was produced in large quantities to make refrigerants and propellants for aerosol cans, and has been used as a solvent for oils, fats, lacquers, varnishes, rubber waxes, and as a grain fumigant and a dry cleaning agent. Consumer and fumigant uses have been discontinued and only industrial uses remain [28].

U.S. Environmental Protective Agency (EPA) has classified all above mentioned halogenated solvents as a Group B2, probable human carcinogens [21, 23, 25, 26, 28].

**Halogenated anaesthetics.** Halothane and isoflurane, $\text{CF}_3\text{CHClBr}$ and $\text{CHF}_2\text{OCHClCF}_3$, have been used as anaesthetics for many years. Despite high efficiency of both substances as anaesthetic, several serious side effects are known, such as tachycardia, respiratory depression, nausea, vomiting, disturbance of liver function, icterus and liver damage, coughing, respiratory depression, hypotension and hypoxia etc.

It is estimated that the current emissions of halothane and isoflurane are 1500 and 750 tons/yr, respectively [29]. The atmospheric lifetimes of halothane (1 year) and isoflurane (5 years) are relatively short [30, 31] compared to the time scale over which they have been emitted into the atmosphere. Atmospheric oxidation of halothane [32] and isoflurane [31] gives $\text{CF}_3\text{C(O)Cl}$ resulting in a global deposition rate of 800 tons/year of $\text{CF}_3\text{C(O)OH}$. The main atmospheric fate of $\text{CF}_3\text{C(O)OH}$ is rain-out to the surface. Indeed, TFAA has been detected at low levels in surface water, rain and tropospheric air samples [33, 34].

Halothane belongs to the family of halons, compounds consisting of bromine, fluorine, and carbon. Halons are known to be the most powerful ozone depletion agents, since bromine is many times more effective at destroying ozone than chlorine.

**Vynil compounds.** Vynil compounds are another class of environmentally important substances chosen for our investigation. Acrylonitrile (AN) is primarily used in the manufacture of acrylic and modacrylic fibers. It is also used as a raw material in the manufacture of plastics (acrylonitrile-butadiene-styrene and styrene-acrylonitrile resins), adiponitrile, acrylamide, and nitrile rubbers and barrier resins [35, 36]. Based on limited evidence in humans and evidence in rats, EPA has classified AN as a probable human carcinogen (Group B1).

Vynilacetate (VA) is primarily used as a monomer in the production of polyvinyl acetate and polyvinyl alcohol. VA is also used as a raw material in the production of other chemicals, in adhesives, water-based paints, nonwoven textile fibers, textile sizings and finishes, paper coatings, inks, films, and lacquers [37, 38]. When VA is disposed of at waste sites or
elsewhere in the environment, it can enter the soil, air, and water. VA will break down in the environment.

VA caused tumors in animal. The International Agency for Research on Cancer (IARC) has determined that VA is possibly carcinogenic to humans (Group 2B) [37].

Vynil bromide (VB) is primarily used in the manufacture of flame retardant synthetic fibers. Its copolymer with vinyl chloride is also used for preparing films, for laminating fibers, and as a rubber substitute [39, 40]. VB has been shown to be a potent carcinogen in rats exposed by inhalation, producing liver angiosarcomas [40]. EPA has classified VB as a Group B2, probable human carcinogen.

**Advantages of ozone treatment of drinking water.** Ozone application in drinking water treatment has dramatically increased in Europe since the early 1900s and in North America for the past three decades. The many advantages of ozone as a multi-platform treatment technology are well documented, but an often overlooked aspect is ozonation as a cost saving method versus other technologies. Here are some examples [41]:

- Ozone as a floculating agent results in rapid microfloculation of raw waters.

- Some pollutants can only be oxidized by ozone. *Cryptosporidium parvum*, for example, are very resistant to most chemical disinfectants but are economically and effectively destroyed by ozonation. The US Food and Drug Administration and EPA found that ozone effectively destroys 99.9992 % of pathogens, including Giardia and Cryptosporidium. The American Water Works Association did research in 1991 that found ozone effectively neutralized viruses, bacteria, amoeba, protozoa and spores in municipal water supplies. In contrary, most other applicable methods including UV-disinfection act only as barriers to cysts but do not actually destroy them.

- The higher oxidation potential of ozone versus chlorine results in a reduced contact time. Ozone can totally replace chlorine, chloramines or chlorine dioxide in the preoxidation and main oxidation stages.

With recent advancements in ozone generation technology, the cost of ozone from both capital and operating investment is less than half of what it was only seven years ago. These savings have been demonstrated in many cities around the world, including Los Angeles, Orlando, Mexico City, Barcelona, Singapore, Paris, Shanghai and Zurich [41].

In arid countries, where drinking-water resources are scarce, ozone is widely used in the so-called reclamation process, where waste water is processed in several steps for re-use as drinking water.

Ozone treatment prevents formation of trihalomethanes and other organochlorine compounds by decomposing humic acids [42]. Humic acids react with chlorine to produce this class of substances. Ozone deodorizes drinking water by breaking down two major compounds that contribute to musty smell, geosmine and 2-methylisoborneol, which other processes do not remove [42]. Ozone has long been used as a decolorizing agent to decompose humic acids and other pigmented compounds, and therefore ozone removal of humic substances reduces the potential for trihalomethane formation.
Advantages of ozone as an oxidant of inorganics and organics are well established [43]. For example, sulfide and nitrite are oxidized to sulfates and nitrate ions, which are stable and innocuous.

1.2. Motivation

All subjects studied in this work have a direct or close relation to the above mentioned ecological problems. Major aspects are questions of the degradation mechanisms of typical water pollutants and the processes during the ozone treatment of drinking water.

Taking into the consideration all mentioned above advantages of radiation chemistry compared to other AOTs methods, we have chosen it as a major tool to investigate free-radical processes of degradation or transformation of environmentally important organic compounds in aqueous solutions (see Chapter 3).

For a better understanding of the studied degradation processes, ozonolysis has been selected as another priority tool (see Chapter 4). Our interest in ozone chemistry is due to its wide use in drinking water treatment. In this work, we really have learnt to appreciate ozone chemistry as the best method to generate and investigate reactive fates of key molecular intermediates of degradation processes such as organic hydroperoxides.

Free-radical degradation of organic compounds in the presence of dioxygen very often proceeds via simultaneous formation of hydrogen peroxide and organic (hydro)peroxides, especially in aqueous solutions. In ozone reactions, these products are common as well. For any mechanistic study a material balance is a prerequisite. However, very often the well-established hydroperoxide assays do not allow to distinguish between $\text{H}_2\text{O}_2$ and $\text{ROOH}$ making their quantitative determination impossible. This stimulate us to look for further improvements of analytical methods of simultaneous determination of $\text{ROOH}$ and $\text{H}_2\text{O}_2$.

The questions of free-radical degradation of halogenated organics in the environment (air, water, ground and living organisms) were a subject of numerous investigations in the last 3-4 decades. However, even for halogenated methanes, despite the stereotype of simplicity of C-1 chemistry, the detailed mechanisms are not known. The reason for this is that no model systems have been proposed to study independently the reactive fates of the most important intermediates, namely halogenated hydroperoxides, alkoxyl and peroxyl radicals. In this work we are introducing such model systems (see Chapter 3).

Surprisingly little is known at present about the reactions of ozone in aqueous solutions. Therefore, a detailed knowledge of these reactions is a prerequisite for any further evaluation of a wider application of ozone, especially in the reclamation technology. This work will shed some light on the major pathways of ozone reactions in aqueous solution.

Regarding ozone treatment of drinking water there is, however, an increasing concern as to the final products [44, 45]. For any future risk assessment, predictions as to the potential products of identified raw-water contaminants are required. These will have to be based on mechanistically oriented studies. For disinfection, the viability of the pathogens must be
suppressed. In the case of viruses, and potentially to some extent also in case of bacteria, this may be due to ozone-induced DNA damage. Our investigation on thymine, thymidine and members of the uracil family is the first mechanistically oriented study of the reaction of ozone with a DNA constituent.

1.3. Basic Processes in Radiolysis and Ozonolysis in Aqueous Solutions

1.3.1. Radiolysis of Water

Radiation chemistry relies on the generation of highly reactive electrons, radical ions and neutral radical species upon exposing matter, e.g. an aqueous solution, to high-energy radiation. The latter may be electromagnetic waves such as \( \gamma \)-rays from a \(^{60}\)Co-source. These are known to interact with matter predominantly via the Compton effect in which one of the electrons from the interacting atom’s pool is ejected. The energy of these electrons is still high (close to one MeV). An alternative source of high energy electrons are high voltage Van-de-Graaff or linear accelerators (LINAC). For further details and insight the reader is kindly referred to Radiation Chemistry textbooks [46-49] and/or explanatory articles [50].

In an irradiated aqueous system the overall primary chemical result of the high-energy radiation impact is the formation of three highly reactive radical species: hydrated electrons (\( e_{aq}^- \)), hydrogen atoms (\( H^\bullet \)), and hydroxyl radicals (\( OH^\bullet \)) [51]. In addition, some hydrogen peroxide, hydrated protons, and molecular hydrogen are formed, as summarized in eq. 1.1.

\[
H_2O \xrightarrow{\text{irradiation, electron beam}} e_{aq}^-, H^\bullet, OH^\bullet, H_2O_2, H_{aq}^+, H_2
\]  

(1.1)

The radiation chemical yield of these species, \( G \), ranges from about 0.6 (\( H^\bullet \)) to 2.8 (\( e_{aq}^- \) and \( OH^\bullet \) species) per 100 eV of absorbed energy (in new units \( 1 \, G \approx 1.036 \times 10^{-7} \, \text{mol J}^{-1} \)). Starting from here all radiation chemical yields, \( G \), are given without the factor of \( \times 10^{-7} \, \text{mol J}^{-1} \) for reason of simplification).

Both, \( e_{aq}^- \) and \( H^\bullet \), are strongly reducing species – corresponding reduction potentials are – 2.9 and – 2.4 V [52]. The most typical reactions of the hydrated electron with haloid-containing compounds are reduction (reaction 1.2), except \( \text{Hal} = F \):

\[
e_{aq}^- + R\text{Hal} \rightarrow R^\bullet + \text{Hal}^-
\]  

(1.2)

Addition of the hydrated electron to C=O bond with the formation of the corresponding radical-anion \( >\text{C-O}^- \) and addition to conjugated olefins or aromatic compounds is also important. The hydrogen atom is a weaker reductant compared to \( e_{aq}^- \). On the other hand, H-atoms easily undergo addition to C=C bonds [51]. Both hydrogen atom and hydrated electron react very fast with molecular oxygen (corresponding rate constants are 1.2 and 1.9 \times 10^{10} \, \text{dm}^3 \, \text{mol}^{-1} \, \text{s}^{-1} [51]) giving the simplest peroxy radicals, superoxide and its conjugated acid, hydroperoxyl radicals:

\[
e_{aq}^-/H^\bullet + O_2 \rightarrow O_2^-/HO_2^\bullet
\]  

(1.3a,b)

The \( HO_2^\bullet \) radical has a \( pK_a \) of 4.8 [53], i.e. in neutral solutions \( O_2^- \) predominates.
\[ \text{HO}_2^* \Leftrightarrow \text{O}_2^* + \text{H}^+ \] (1.4)

The \( ^* \text{OH} \) radical is one of the strongest oxidant known (reduction potential \( [E(\text{^*OH}/\text{OH}^-) = + 1.9 \text{ V}] \) [54]; \( E(\text{^*OH}, \text{H}^+\text{H}_2\text{O}) = + 2.73 \text{ V}] \) [52]. The 1-e oxidation (very often via an intermediate OH-adduct) is a typical reaction of \( ^* \text{OH} \) radicals. Another common reactions of these species are addition to C=C bonds or to free electron pairs, as well as H atom abstraction from C-H bonds. The latter reaction is characterized by high exothermicity (\( \Delta \text{H} \) in the range of \(-85 \text{ to } -110 \text{ kJ mol}^{-1} \) [55] and, therefore, low selectivity.

In order to simplify radiolytical systems, some of the primary water radicals have to be selectively scavenged. Hydrated electrons react very fast, for example with protons (\( k = 2.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [51]) giving H-atoms:

\[ \text{e}_\text{aq}^- + \text{H}^+ \rightarrow \text{H}^- \] (1.5)

The reactions of hydrogen atoms alone can be studied in strongly acidic solutions and employing some suitable \( ^* \text{OH} \) radical scavenger.

On the other hand, \( \text{e}_\text{aq}^- \) are effectively transformed to \( ^* \text{OH} \) via fast reaction with \( \text{N}_2\text{O} \) (\( k = 9.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [56]). Radiolysis of water saturated with \( \text{N}_2\text{O} \) represents a well-defined radical system which generates 90% of hydroxyl radicals and 10% of H atoms.

\[ \text{e}_\text{aq}^- + \text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow ^* \text{OH} + \text{N}_2 + \text{OH}^- \] (1.6)

The radiation chemical yield of the radicals derived from an \( ^* \text{OH} \) scavenger in \( \text{N}_2\text{O} \)-saturated solutions, \( G(S) \), can be evaluated by eq. 1.7 proposed by Schuler et al. [57]:

\[ G(S) = 5.2 + 3.0 \frac{\sqrt{k_S[S]/\lambda}}{1 + \sqrt{k_S[S]/\lambda}} \] (1.7)

In this equation the product \( k_S[S] \) represents the pseudo-first order rate constant for the \( ^* \text{OH} \) scavenging process, and \( \lambda \) is a so-called track recombination frequency of \( 4.7 \times 10^8 \text{ s}^{-1} \).

When the reaction of hydrated electrons with substrates is studied, the possible influence of hydroxyl radicals can be suppressed by the use of \( ^* \text{OH} \) scavenger. Dimethylsulfoxide and alcohols such as \( \text{MeOH}, \text{EtOH}, \text{2-PrOH} \) and \( \text{t-BuOH} \) are the most often used scavengers. The reaction of DMSO is a selective source of methyl radicals (reaction 1.8a, 92% yield) with a minor contribution of \( \beta \)-hydrogen abstraction (reaction 1.8b, 8%) [58]:

\[ \text{HO}^* + (\text{CH}_3)_2\text{S}=\text{O} \rightarrow \text{CH}_3^* + \text{CH}_3\text{S(O)}\text{OH}/\text{H}_2\text{O} + ^*\text{CH}_2\text{S(\text{CH}_3)}=\text{O} \] (1.8a,b)

Abstraction of an \( \alpha \)-hydrogen atom is a major route for the alcohols in their reaction with \( ^* \text{OH} \) radical:

\[ ^* \text{OH} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{H}_2\text{O} + (\text{CH}_3)_2\text{C}^*\text{OH}/^*\text{CH}_2\text{CH(\text{CH}_3)}\text{OH} \] (1.9a,b)

The yields of \( \alpha \)-hydroxyalkyl radicals generated in reaction like 1.9a amount to about 85%, 89% and 93% for 2-PrOH, EtOH and MeOH, respectively [59]. The remainder accounts for
\( \beta \)-hydrogen abstraction (reaction like 1.9b) and O–H cleavage [59]. The latter has usually a negligible contribution with exception of t-BuOH (5% yield, reaction 1.10b):

\[
{^\cdot}\text{OH} + (\text{CH}_3)_3\text{COH} \rightarrow \text{H}_2\text{O} + {^\cdot}\text{CH}_2(\text{CH}_3)_2\text{COH} / (\text{CH}_3)_3\text{CO}^* \tag{1.10a,b}
\]

In the case of t-BuOH there are no \( \alpha \)-hydrogen atoms available and \( \beta \)-hydrogen abstraction becomes a dominant pathway (95% contribution of reaction 1.10a). In oxygenated solutions alkyl radicals from alcohols are quickly transformed into corresponding peroxyl radicals, whose further reactions are discussed in details later (see subsection 1.3.3 and section 4.1).

### 1.3.2. Ozonolysis of Olefins in Aqueous Solutions

The ozonolysis of olefins in aqueous solution is adequately described by the Criegee mechanism [60, 61]. Free radicals are not formed in these reactions. They do, however, play a role in the ozonolysis of phenol and related compounds [62] and in adenine and its derivatives [14].

In an olefin containing electron donating (D) and electron-withdrawing (A) substituents such as in 1, the electrophilic ozone molecule will seek the position of the highest electron density at this polarized C–C double bond (see Scheme 1.1).

**Scheme 1.1**

In the first step zwitterion 2 is formed (reaction 1.11) which subsequently closes the ring giving rise to the Criegee ozonide 3 (reaction 1.12). The latter can cleave heterolytically into 4 and 5 (reactions 1.13 and 1.14, respectively). A \( \beta \)-cleavage gives rise to the secondary...
zwitterions [6 and 9, reactions 1.15 and 1.17). The strong directing effects of the substituents A and D have led to the suggestion that reactions 1.13 and 1.14 may be reversible and that reaction 1.15 is faster than reaction 1.17, because the electron donating substituent D would stabilise zwitterion 6 in comparison to zwitterion 9.

1.3.3. Fate of Peroxyl Radicals

1.3.3.1. Formation of peroxy radicals

Details of the formation and decay of peroxy radicals in an aqueous environment have been described in the literature [63, 64], only the most important features will be mentioned here.

The great majority of alkyl radicals react practically irreversibly with O$_2$ at close to diffusion-controlled rates (typical rate constant of $2 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$), *i.e.* in air-saturated aqueous solutions ($[O_2] = 2.8 \times 10^{-4}$ mol dm$^{-3}$), the half-life of a radical $R^\cdot$ will be ca. 1.2 µs (reaction 1.19). For a compilation of rate constants see [65-67].

$$R^\cdot + O_2 \rightarrow RO_2^\cdot$$  \hspace{1cm} (1.19)

This high rate constant for the oxygen addition reflects both, the electrophilic nature of the oxygen and the electron density at the radical site. Considerable reversibility of reaction 1.19 has been established for the cyclohexadienyl radicals, which have unusually low $R^\cdot OO^\cdot$ bond dissociation energies of only 25 kJ mol$^{-1}$, whereas a typical value for alkylperoxyl radicals is about 125 kJ mol$^{-1}$ [68]. Reversibility was found also for thiy/thiylperoxyl radicals [69, 70].

1.3.3.2. Oxidative properties of peroxy radicals

Peroxyl radicals are known as moderate oxidants [71, 72]. In their reactions with suitable molecules, M, this may manifest as an electron transfer (eq. 1.20) or as an H-atom abstraction (eq. 1.21). In both cases the peroxy are reduced to the corresponding hydroperoxide

$$ROO^\cdot + M \rightarrow ROO^- + M^{\cdot+}$$  \hspace{1cm} (1.20)

$$ROO^\cdot + M \rightarrow ROOH + M(-H)^\cdot$$  \hspace{1cm} (1.21)

It can plausibly be expected that α-halogenation increases the oxidative power of peroxy radicals because electron density delocalization into the halogen atoms reduces the electron density at the peroxy functionality. Indeed, the reduction potential of non-substituted alkylperoxy radicals is calculated to be $E^\circ = 0.77$ V vs. NHE, and it is markedly increased by electron-withdrawing substituents [cf. $E^\circ(CCl_3OO^\cdot) = 1.15$ V and $E^\circ(CH_3C(O)OO^\cdot) = 1.6$ V] [73]. Accordingly, the $CCl_3OO^\cdot$ is the best and $CH_3OO^\cdot$ is the worst oxidant within the series:

$CCl_3OO^\cdot > CHCl_2OO^\cdot > CH_2CIOO^\cdot > CH_3OO^\cdot$

However, while this is well in line with a number of experimental observations concerning, for example, the oxidation of certain phenolic compounds, ascorbate and phenothiazines [74], there are other findings which seemingly contradict this conclusion [75-77]. The rate constant for the general oxidation reaction (eq. 1.22) does, in fact, not necessarily coincide with expectation (D = electron donor; $D^{\cdot\cdot+} =$ one-electron oxidized form of a donor). Another
observation is, for example, that despite high rate constants the yields of D$$^{**}$$ are lower than the yield of peroxyl radicals.

$$\text{CCl}_3\text{OO}^\cdot + D \rightarrow \text{CCl}_3\text{OO}^- + D^{**}$$ (1.22)

1.3.3.3. 2-e Oxidation processes

The rationale for all this is that halogenated peroxyl radicals do not seem to undergo a classical one-electron transfer but rather engage in addition/elimination mechanisms [78-80]. This is exemplified in Scheme 1.2 for the oxidation of organic sulfides by halogenated peroxyl radicals.

**Scheme 1.2**

Mechanistically, the peroxyl radical-induced oxidation of a sulfide proceeds as shown in the Scheme 1.2. In the first instance the peroxyl radical adds to the sulfur. From the redox point of view, this constitutes a first one-electron oxidation step. The resulting sulfuranyl radical is polarized with slight positive charge at sulfur and a corresponding negative charge at the adjacent oxygen. In aqueous solution this facilitates protonation of the oxygen and hydroxylation of the sulfur. The next step is the transfer of the radical electron, which initially resides at sulfur, into the peroxide bridge. This step constitutes a second one-electron oxidation of the sulfur which thus has undergone an overall two-electron oxidation and consequently has assumed the oxidation level as in a sulfoxide. In fact, the charge separated transient resulting from this second oxidation step is now formally composed of a reduced hydroperoxide and a protonated sulfoxide moiety. It is easy to predict a decay of such a transient into a sulfoxide and an oxyl radical (besides OH$$^-$$ and H$$^+$$). With respect to the peroxyl moiety this mechanism is reminiscent of the well-known Fenton chemistry (see, for example ref. [12]). It also explains the experimentally observed fact that the sulfoxide oxygen comes from the solvent water and is not one of the peroxyl oxygens [79].

A further argument in favour of this overall two-electron transfer mechanism is the possibility to intercept the one-electron intermediate sulfuranyl radical. Reaction of the latter
with a second molecule of sulfide leads to a three-electron bonded dimer radical cation which is also formed as a transient in any one-electron oxidation (e.g. by •OH) and is easily detectable through its characteristic and strong optical absorption [81, 82].

A most important parameter which helped to evaluate the mechanism are the sulfoxide yields which may differ significantly depending on the nature of the oxidant. Typically, they are much lower for a one-electron oxidation which leads to radical cations as intermediates. In the •OH-induced oxidation the sulfoxide yields are about 20% (in deoxygenated solution) while an oxidation initiated by CHCl\textsubscript{2}OO• results in sulfoxide yields of up to 100% [79-81].

Bonifacij et. al. [78] showed that RHalOO• may indeed engage in a multi-electron oxidation step. It has been found, that the CCl\textsubscript{3}OO• radical adds to the iodide ion (reaction 1.23a) with subsequent decomposition into the CCl\textsubscript{3}O• radical (reaction 1.23b, 2-e oxidation) which is further reduced by iodide into trichloromethanol (reaction 1.24, 1-e oxidation) [78]. The latter decays much faster (reaction 1.25, \(k \geq 8 \times 10^4 \text{ s}^{-1}\)) than the subsequent hydrolysis of phosgene (reaction 1.26, \(k = 9 \text{ s}^{-1}\) at 25 °C, \(E_a = 53 \text{ kJ mol}^{-1}\)) [83].

\[
\begin{align*}
\text{CCl}_3\text{OO}^* + \Gamma &\rightarrow [\text{CCl}_3\text{OO-I}]^* H^+ \rightarrow \text{I}_2 + \text{CCl}_3\text{O}^* & (1.23a,b) \\
\text{CCl}_3\text{O}^* + \Gamma + \text{H}^+ &\rightarrow \text{I}^* + \text{CCl}_3\text{OH} & (1.24) \\
\text{CCl}_3\text{OH} &\rightarrow \text{HCl} + \text{COCl}_2 & (1.25) \\
\text{COCl}_2 &\rightarrow \text{HCl} + \text{CO}_2 & (1.26)
\end{align*}
\]

The most important features of oxyl radicals are well described for the gas-phase [84] and for nonhalogenated ones also in aqueous solutions [71]. Reactive modes of halogenated oxyl radicals in aqueous solutions are studied poorly mostly because no model systems have been proposed so far to study this question adequately. This has been one of the major aims of the present work and is discussed in details in Chapter 3.

### 1.3.3.4. Unimolecular reactions of peroxyl radicals

The most studied unimolecular reactions of peroxyl radicals are HO\textsubscript{2}•/O\textsubscript{2}•-eliminations (see reaction 1.27). They are, for example, the major mode of decay for peroxyl radicals derived from carbohydrates [85].

\[
(\text{CH}_3)_2\text{C(OH)OO}^* \rightarrow \text{HO}_2^* + (\text{CH}_3)_2\text{C}=\text{O} \quad (1.27)
\]

The rate of HO\textsubscript{2}• elimination from α-hydroxyalky peroxy radicals strongly depends on the substituents in α-position to the peroxy moiety (for a compilation see [64]).

The O\textsubscript{2}•-elimination reactions are very typical for the peroxy radicals with an –OH or –NH\textsubscript{2} function in the α-position. Deprotonation at the heteroatom by OH\textsuperscript{-} (reaction 1.28) leads to a short-lived peroxy radical anion, which subsequently eliminates superoxide with a rate proportional to \(k_{1.28} \times [\text{OH}^-]\), even at high [OH\textsuperscript{-}] [86]. Similar observations were made for other α-hydroxyalkyl peroxy radical anions [87-89]. Electron donating groups such as methyl raises the \(pK_a\) values and enhance the rate of O\textsubscript{2}•-release.
The driving force for both HO$_2^*$ and O$_2^-$-elimination reactions is the formation of a double bond; cf. (reactions 1.27 and 1.29) [86, 88, 90-93].

\[(\text{CH}_3)_2\text{C(OH)OO}^* + \text{OH}^- \rightarrow \text{H}_2\text{O} + (\text{CH}_3)_2\text{C(O)}^-\text{OO}^* \rightarrow \text{O}_2^- + (\text{CH}_3)_2\text{C=O} \quad (1.28-29)\]

### 1.3.3.5. Bimolecular decay of peroxy radicals

Recombination of peroxy radicals leads to a tetroxide intermediate (reaction 1.30):

\[2 \text{ ROO}^* \rightarrow \text{R-O}_4^-\text{R} \quad (1.30)\]

Formation of the tetroxide was observed in organic solvents at low temperatures [94-99]. However, its formation has not been detected in aqueous solutions as yet. Since ROO--OOR bond strengths are estimated at 21 to 33 kJ mol$^{-1}$ [100-103], therefore the reverse reaction 1.30 and decay reactions of tetroxide into products [reactions (1.31)--(1.34), R = alkyl or H] maintain non-detectable steady-state concentration of tetroxide. For many peroxy radicals, the values of $k_{1,30}$ are typically in the range of $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ [66], i.e. they are close to the diffusion-controlled ones.

Reaction 1.31 applies, in principle, to all peroxy radicals and affords the formation of oxyl radicals. Reactions 1.32 and 1.33 require the presence of at least one H-atom at the peroxy carrying carbon. The termination process according to eq. 1.32 has been described by Russell [101] who suggested that this reaction is a concerted process and proceeds via a cyclic six-membered ring transition state as depicted below. The tetroxide decomposes to the carbonyl and hydroxyl compounds together with dioxygen in the ratio 1:1:1, the latter probably in the singlet state (O$_2^1\Delta_g$) [104, 105].

Reaction 1.33, sometimes called Bennett mechanism, yields hydrogen peroxide and two carbonyl compounds. It is also considered to be concerted, proceeding via two five-membered [106, 107] or two six-membered rings involving two water molecules (see above).

\[
\begin{align*}
\text{R}_2\text{CH-O}_4^-\text{CHR}_2 &\rightarrow 2 \text{ R}_2\text{CHO}^* + \text{O}_2 \\
\text{R}_2\text{CH-O}_4^-\text{CHR}_2 &\rightarrow \text{R}_2\text{C}=\text{O} + \text{R}_2\text{CHOH} + \text{O}_2 \\
\text{R}_2\text{CH-O}_4^-\text{CHR}_2 &\rightarrow 2 \text{ R}_2\text{C}=\text{O} + \text{H}_2\text{O}_2 \\
\text{R}_2\text{CH-O}_4^-\text{CHR}_2 &\rightarrow \text{R}_2\text{CHOOCHR}_2 + \text{O}_2
\end{align*}
\]

Khusran et al. [108, 109] have proposed a mechanism alternative to Russell’s and Bennet’s ones. It is based on asymmetric O–O bond homolysis of the tetroxide as a first step to products formation:
Further reactions of \( R_2CHOOO^- \) and \( \cdot OCHR_2 \) yield the same final products as predicted by Russell’s or Bennet’s mechanism. However, this hypothesis contradicts to other data (see [103] and [110]).

In the systems generating several types of peroxyl radicals they may disappear not only via self-termination, as schematically given by the reactions 1.30-1.34, but also via cross-termination reaction. The investigation of the latter type of reactions are well-known for the organic phase [111-113].

However, cross-termination reactions have not been studied and are usually neglected for aqueous systems. A possible cross-termination is the reaction of peroxyl radicals with superoxide, \( O_2^- \), a species commonly present in many radiolytical systems. Not much information is available for this reaction. It is known that its rate constant is strongly dependent on the oxidative power of the peroxyl radicals. The rate constant for at present the most powerful peroxyl radical known, the \( CH_3C(O)OO^- \) radical, with \( O_2^- \) is \( k_{1.36} \approx 2 \times 10^9 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) [114], whereas the \( \alpha \)-hydroxyethylperoxyl radical reacts with \( O_2^- \) with a rate constant of ca. \( 10^7 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) only [88].

\[
CH_3C(O)OO^- + O_2^- \rightarrow CH_3C(O)OO^- + O_2
\] (1.36)

An intermediate reactivity pertains to peroxyl radicals derived from c-hexane, c- \( C_6H_{11}OO^- \) (\( k \approx 2.5 \times 10^8 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\)) [115].

In many works of C. von Sonntag et al it was possible to evaluate the contribution of the cross-termination reaction of peroxyl radicals with superoxide, the yield of which, however, was never higher than 15-20% [114, 116-121]. Section 3.3 of the present work is devoted to the importance of the cross-termination of the halogenated peroxyl radicals and superoxide.

The most convenient and, therefore, the most used method of \( O_2^- \) detection is based on its reaction with tetrinitromethane (reaction 1.37, \( k = 1.9 \times 10^9 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\)) [122, 123] yielding the strongly absorbing nitroform anion (\( \varepsilon \) at 350 nm = 15,000 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)).

\[
O_2^- + C(NO_2)_4 \rightarrow O_2 + C(NO_2)_3^- + \cdot NO_2
\] (1.37)

Except for the above mentioned cross-termination with peroxyl radicals and reduction of some strong oxidants like TNM, superoxide species are not very reactive in aqueous solutions (for a compilation of rate constants see [53]).
1.4. Goals of the Work

Detailed studies of degradation mechanisms of the environmentally relevant organic compounds in water induced by $\gamma$-radiolysis or ozonolysis is the major issue of this work. To achieve this objective a complete product analysis in combination with time-resolved studies of the transients are mandatory. The principal point of the present work has been to get a total material balance at low turnover.

Two decisive goals of our radiation chemistry works were:

- to improve existing analytical methods of side by side determination of hydroperoxides and $\text{H}_2\text{O}_2$ as the most important molecular intermediates in the free-radical degradation or ozonation processes (see section 3.2);
- to develop a model systems which allow to generate selectively halogenated hydroperoxides or oxyl radicals and study independently their reactive fates; based on this knowledge to elucidate the reaction modes of the corresponding peroxy radicals (see sections 3.4 and 3.5).

The principal goals of our ozone investigations were:

- development of experimental methods of determination of key radical intermediates ($\cdot\text{OH}$, and $\text{O}_2\cdot^-\text{radicals}$, see section 4.1);
- ozone treatment of vinyl compounds known as environmental pollutants (see section 4.2);
- determination of the rate constants of reaction of ozone with DNA constituents and related compounds needed for better understanding of the inactivation of viruses and bacteria by ozone (see section 4.3);
- to conduct a mechanistically-oriented studies on the reactions of ozone in aqueous solutions (see section 4.4) to predict potential oxidation by-products and also to get some insight into the mechanism of the ozone-induced degradation of the nucleic acid, a reaction that must be of importance in the disinfection of viruses and possibly also contributes to the disinfection of bacteria.
2. EXPERIMENTAL PART

2.1. Instrumentation

The pulse radiolysis experiments were carried out with:

a) 1.55 MeV Van-de-Graaff accelerator (500 ns electron pulses, Hahn-Meitner-Institut, Berlin, Germany) [124];

b) 8 MeV linear electron accelerator (50 ns electron pulses, LINAC, Notre Dame Radiation Laboratory, USA) [125];

c) 12 MeV LINAC (20-200 ns electron pulses, ISOF, Bologna, Italy) [126];

d) 2.8 MeV Van-de-Graaff accelerator (400 ns electron pulses, MPI für Strahlenchemie, Mülheim-an-der-Ruhr, Germany); for preparative pulse radiolysis 2 µs pulses were employed [127];

e) 12 MeV linear electron accelerator (50 ns electron pulses, Institut für Oberflächenmodifizierung e. V., Leipzig, Germany) [128];

Intermediates were monitored by optical and conductometric detection. The pulse radiolysis set-up has been described previously [127]. For dosimetry, N₂O-saturated 10⁻² mol dm⁻³ thiocyanate solution was used for optical detection [125, 129]. For conductometric detection, N₂O-saturated 10⁻² mol dm⁻³ DMSO solution at pH 4 was used as dosimeter, taking \( G(H^+) = G(CH_3SO_2^-) = 5.8 \times 10^{-7} \) mol J⁻¹ [130]. Experimental error limits are estimated to be ± 10% unless specifically noted.

The \( \gamma \)-radiolysis was carried out in the field of a \( ^{60} \)Co \( \gamma \)-source. Total absorbed doses were typically in the range 50-300 Gy (1 Gy = 1 J kg⁻¹ = 100 rad). The dose rates were varied between 0.011 and 0.165 Gy s⁻¹ as determined by the Fricke dosimetry [131].

Stopped-flow experiments were carried out with the help of a Biologic (SF3) instrument equipped with a diode array system (Tidas–16, J&M, Aalen) for optical detection. The conductometric detection device was home-made and practically identical to that described before [132, 133].

Conductometric measurements on the longer time-scale were carried out with a conductometer (CDM3, Radiometer).

UV-Vis spectra were recorded on UV spectrophotometer (Lambda 16, Perkin Elmer).

Kinetic simulations were carried out with the help of the Chemical Kinetics Simulator TM software, version 1.01 (from IBM, Almaden Research Center).

Solutions for pulse- and \( \gamma \)-radiolysis as well as for ozone experiments were made up in Milli-Q-filtered (Millipore) water.

2.2. Product Analysis

Oxygen concentration in aqueous solutions was determined with an oxygen-sensitive Clark-electrode. Ozone was generated with the help of a dioxygen-fed ozonator.
The ozone concentration was determined spectrophotometrically using $\varepsilon(260 \text{ nm}) = 3300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ [134, 135]. Singlet dioxygen was analysed for as described previously in [136].

Ionic products were analysed by IC employing a Dionex 2010i. CO$_2$ was determined in the form of HCO$_3^-$ ions by IC or by GC after its transformation to methane.

The yields of CO were analysed by GC, using Molecular Sieve 5A column, helium as a carrier gas, thermoconductivity detector and head-space technique. In ozone treated samples, CO was detected by means of CO electrochemical sensor described in [61, 137].

The yields of MetSO were determined by HPLC (Inertsil column — 250 x 4.6 mm, 5 $\mu$, ODS II, H$_2$O/CH$_3$OH = 95/5 vol.% as eluent at 1 dm$^3$ min$^{-1}$, UV-detection at 210 nm).

DMSeO was determined by HPLC using Millipore water as an eluent and UV detection at 205 nm. Reference DMSeO was prepared in the solution of 0.1 mol dm$^{-3}$ DMSe and 0.001 mol dm$^{-3}$ H$_2$O$_2$ under stirring at room temperature within 24 hours. 100-fold excess of DMSe was taken in order to avoid further oxidation of DMSeO to dimethylselenone, (CH$_3$)$_2$SeO$_2$.

Hydroperoxides were determined using Allen’s reagent [138]. In this assay, equal amounts of the two reagents and the solution to be assayed were mixed in a 1:1:1 ratio if not stated otherwise. Reagent A: 0.4 mol dm$^{-3}$ KI, $3.6 \times 10^{-4}$ mol dm$^{-3}$ KOH, $1.6 \times 10^{-4}$ mol dm$^{-3}$ (NH$_4$)$_6$Mo$_7$O$_{24}$; reagent B: 0.1 mol dm$^{-3}$ potassium hydrogen phthalate. The absorption of I$_3^-$, $\varepsilon(350 \text{ nm}) = 25,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, is read. Some experiments have also been carried out without molybdate as catalyst to differentiate between highly reactive hydroperoxides and hydrogen peroxide. The latter reacts very slowly under these conditions. Further developments of hydroperoxides determination are described in the Section 3.2.

αSeparation of the (hydro)peroxides by HPLC was on a 25 cm reversed phase column using water as eluent. The (hydro)peroxides were detected by post-column reaction with molybdate-activated iodide. In addition, some unstable organic peroxides were identified by LCMS-ESI.

FPA was generated by the ozonolysis of an aqueous solution 1,2-dichloroethene [61].

Formaldehyde was determined by the Hantzsch method [139] or by HPLC of its 2,4-dinitrophenyl-hydrazone [140]. TFAAld was analysed in the form of TFAA by means of IC after oxidation with excess NaOBr at pH 12.3 (see ref. [6]).

### 2.3. Quantum Chemical Calculations

The calculations were carried out using the Gaussian 03 package [141]. For the systems under study, geometries were optimised applying the density functional theory (DFT) approach with B3LYP hybrid functional [142, 143]. Stationary points were characterised by frequency calculations. For geometry optimisations, the standard 6-31+G(d,p) basis [144] sets were used. To investigate the influence of a solvent on the molecular structure of the radicals, geometry optimisations were carried out using self-consistent reaction field (SCRF) polarized continuum the PCM model [145, 146].
3. THE MECHANISMS OF RADIATION INDUCED REACTIONS IN AQUEOUS SOLUTIONS

It has been shown that degradation of the halogenated hydrocarbons in the environment may eventually lead to complete mineralization, i.e., to CO₂ and the respective hydrogen halides [147]. Several molecular organic intermediates such as halogenated alcohols, aldehydes, ketones and organic acids have been identified en route to these inorganic substrates. Under anaerobic conditions most studies have only been concerned with the liberation of halide ions with little attention being paid to the other products, particularly with respect to a satisfactory material balance. The principal feature of this work is that we have tried to obtain a complete material balance wherever possible. Based on this, and also kinetic investigations, we will propose mechanisms of degradation of some environmentally and biologically important organic compounds.


The majority of the studies dealing with the mineralization process in oxygen containing environment still lack a detailed mechanistic insight into the degradation of the above mentioned molecular organic intermediates, particularly the organic acids.

An environmentally potentially very important halogenated acid is trifluoroacetic acid (TFAA). It is the exclusive or partial molecular product generated in the free radical or photocatalytically induced degradation of practically all C₂- and C₃-compounds carrying a CF₃-function, such as anaesthetic halothane CF₃CHBrCl (see section 3.5), or HFC-124a (CF₃CFH₂). The latter is considered to be one of the more ozone-friendly alternatives to fully halogenated freons for different applications [148].

Yet, there is hardly any knowledge about the reactivity of CF₃CO₂H toward free radicals. Only two absolute rate constants have been reported, namely, for its reactions with e⁻ₐ₉ (k < 1.4 x 10⁶ dm³ mol⁻¹ s⁻¹) [149] and with NO₃ radicals (k = 3.9 x 10³ dm³ mol⁻¹ s⁻¹) [150]. Other equally strong oxidants such as Cl₂⁻, SO₄²⁻, or the TiO₂-based hᵥB⁺ (all with E° ≈ 2.4 V) [52, 151] fail to do the job [1]. The bulk of existing data suggests that TFAA is resistant to biodegradation in natural environments and since both e⁻ₐ₉ and NO₃⁻ are naturally not very abundant, this leaves CF₃CO₂H as a chemically almost undegradable, long lasting environmental sink in fluorocarbon chemistry.

More information is available on the degradation mechanisms of chlorinated acetic acids. Some studies [152, 153], concerning the photocatalytic degradation of CCl₃CO₂H on TiO₂ surfaces, reveals that the oxidative process may be induced via valence band holes generated in a light-exposed semiconductor. In this case, the reaction proceeds via the photo-Kolbe mechanism, i.e., oxidation of the carboxylate group and subsequent decarboxylation.
Potentially critical are also trichloro- and tribromoacetic acids (TCAA and TBAA) which are formed as chlorination or bromination disinfection by-products when the chlorine or bromine, used to disinfect drinking water, reacts with naturally occurring organic matter in water.

Practically no information is available, so far, on the degradation of brominated acetic acids. The following study is, therefore, focusing on pulse and steady-state radiolysis investigations of TBAA with emphasis on the formation and properties of radical intermediates and a complete material balance for the molecular products. Some relevant information on the transients and products formed from the chlorine and fluorine analogue acids is also included.

3.1.1. Time–resolved measurements

Reduction of TBAA by \( e_{\text{aq}}^- \) and other reductive species. Pulse radiolysis experiment conducted with an \( N_2 \)-saturated solution of \( 1.3 \times 10^{-4} \text{ mol dm}^{-3} \) TBAA and 1% (v/v) 2-PrOH at pH 10 shows the formation of a transient absorption in the UV range with a maximum at 290 nm. The kinetics of the absorption–time traces recorded at 720 nm, the maximum of the \( e_{\text{aq}}^- \) absorption, and at 290 nm, were identical (\( t_{\frac{1}{2}} = 300 \text{ ns} \)), identifying the 290 nm species as a direct product from the \( e_{\text{aq}}^- \)-induced reduction of TBAA, assigned to the •CBr\(_2\)CO\(_2^-\) radical formed in reaction 3.1:

\[
e_{\text{aq}}^- + \text{CBr}_3\text{CO}_2^- \rightarrow \text{Br}^- + \cdot\text{CBr}_2\text{CO}_2^- \tag{3.1}
\]

The same differential absorption spectrum has been observed also in the reaction of TBAA with other reductive species. The absorption coefficient for •CBr\(_2\)CO\(_2^-\) at 290 nm has been determined to be \( \varepsilon = 2580 \pm 200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \). From the linear relationship between the observed first–order rate constant for the build-up of absorbance at 290 nm, \( k_{\text{obs}} \), and [TBAA], the absolute rate constants were obtained. They are equal to \( 1.8 \times 10^{10}, 1.5 \times 10^{10}, 2.8 \times 10^9, 1.6 \times 10^9, 2.3 \times 10^9 \) and \( 3.0 \times 10^9 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) for the reactions of TBAA with \( e_{\text{aq}}^- \), H\(^+\), CO\(_2\)^\(^-\), \( \cdot\text{CH}_2\text{OH}, \text{CH}_3\text{C}^\cdot\text{HOH} \) and \( (\text{CH}_3)_2\text{C}^\cdot\text{OH} \).

Degradation of TBAA induced by the alkyl radicals. The generation of the •CBr\(_2\)CO\(_2^-\) species from the TBAA can be achieved also through non-reducing alkyl radicals such as methyl radicals produced via the reaction of •OH radicals with DMSO in an \( N_2\)-O-saturated, aqueous solution (see reaction 1.8a). In this system, the formation kinetics of the •CBr\(_2\)CO\(_2^-\) absorption reveals two distinct contributions. A small, fast initial growth is attributed to a direct reaction of TBAA with all H\(^-\)-atoms. The second and slower component is much larger in yield and reflects a bromine atom abstraction according to reaction (\( k_{3,2} = 3.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \)).

\[
\cdot\text{CH}_3 + \text{CBr}_3\text{CO}_2^- \rightarrow \text{CH}_3\text{Br} + \cdot\text{CBr}_2\text{CO}_2^- \tag{3.2}
\]

The same picture was observed for the non-reducing •CH\(_2\)C(\( \text{CH}_3 \))\(_2\)OH radicals generated in the reaction of •OH with t-BuOH (\( k_{3,3} = 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \)).
\[ \cdot \text{CH}_2\text{C(CH}_3\text{)}_2\text{OH} + \text{CBr}_3\text{CO}_2^- \rightarrow \text{CH}_2\text{Br}-\text{C(CH}_3\text{)}_2\text{OH} + \cdot \text{CBr}_2\text{CO}_2^- \] (3.3)

**Reactions of \( \cdot \text{CBr}_2\text{CO}_2^- \).** In the absence of suitable molecular reaction partners the \( \cdot \text{CBr}_2\text{CO}_2^- \) radicals decay by a second order process \((2k_{3,4} = 2.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\):

\[ 2 \cdot \text{CBr}_2\text{CO}_2^- \rightarrow -\text{O}_2\text{C}--\text{CBr}_2--\text{CBr}_2--\text{CO}_2^- \] (3.4)

In the experiments in air-saturated solution the second-order decay of the initially formed radical changes into a faster exponential decay due to the formation of the respective peroxyl radical \((k_{3,5} = 1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\):

\[ \cdot \text{CBr}_2\text{CO}_2^- + \text{O}_2 \rightarrow \cdot \text{OOCBr}_2\text{CO}_2^- \] (3.5)

**Formation of \( \cdot \text{CCl}_2\text{CO}_2^- \) and \( \cdot \text{CF}_2\text{CO}_2^- \).** Reduction of \( \text{CCl}_3\text{CO}_2^- \) \((10^{-2} \text{ mol dm}^{-3})\) by hydrated electrons \((k = 8.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) [154] in \( \text{N}_2\text{-saturated solution} \) yielded a transient differential absorption spectrum attributable to \( \cdot \text{CCl}_2\text{CO}_2^- \) with \( \lambda_{\text{max}} = 330 \text{ nm} \) \((\varepsilon_{330} = 3000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})\).

The \( \cdot \text{CF}_2\text{CO}_2^- \) radical was generated upon pulse radiolysis of an \( \text{N}_2\text{O-saturated solution} \) of \( 0.1 \text{ mol dm}^{-3} \) \( \text{CF}_2\text{HCO}_2^- \) (eq. 3.6). Assuming that the reaction is quantitative, the calculated extinction coefficient, \( \varepsilon_{\text{max}} \approx 660 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \), is much lower than that for \( \cdot \text{CBr}_2\text{CO}_2^- \) and \( \cdot \text{CCl}_2\text{CO}_2^- \). This may reflect electronic reasons.

\[ \cdot \text{OH} + \text{CF}_2\text{HCO}_2^- \rightarrow \text{H}_2\text{O} + \cdot \text{CF}_2\text{CO}_2^- \] (3.6)

**3.1.2. \( \gamma \)-Radiolysis of \( \text{CBr}_3\text{CO}_2^- \) solutions**

**Products and material balance.** Six different systems were subjected to a detailed product study, all of them consisting of \( 2 \times 10^{-4} \text{ mol dm}^{-3} \) aqueous TBAA solutions at \( \text{pH} 10 \).

They are listed below:

I: \( 10^{-3} \text{ mol dm}^{-3} \) \( \text{HC(O)}\text{O}^-/\text{N}_2\text{O-saturated} \)

II: 1% \((v/v)\) \( \text{C}_2\text{H}_5\text{OH}/\text{N}_2\text{O-saturated} \)

III: 1% \((v/v)\) \( \text{(CH}_3\text{)}_3\text{COH}/\text{N}_2\text{O-saturated} \)

IV: 1% \((v/v)\) \( \text{(CH}_3\text{)}_2\text{SO}/\text{N}_2\text{O-saturated} \)

V: \( \text{N}_2\text{O-saturated} \)

VI: \( \text{N}_2\text{-saturated} \)

The products obtained upon \( \gamma \)-radiolysis of the above systems are summarized in Table 3.1. The main products were hydrogen bromide, tribromoacrylic acid (TBAcrA), and \( \text{CO}_2 \). In system (IV) also appreciable yields of \( \text{CH}_3\text{Br} \) were formed. In all systems, some small amounts of \( \text{CO}, \text{ dibromofumaric} \) and dibromomaleic acid (DBFA and DBMA) were detected.

The absolute TBAA degradation yields agree well with those expected on the basis of commonly used yields for scavengable \( e_{\text{aq}}^- \) \((G \approx 2.8)\), \( \cdot \text{OH} \) \((G \approx 2.8)\), and \( \cdot \text{H} \) \((G \approx 0.6)\), denoted as classical yields, or those predicted by a more sophisticated formula (see eq. 1.7, subsection 1.3.1) evaluated by Schuler *et al.* [57] for the scavenging of \( \cdot \text{OH} \) radicals in \( \text{N}_2\text{-O-} \)

---

27
saturated solutions. For more details about TBAA degradation yields in each particular system see ref. [4].

**Table 3.1. Yields of products from γ-irradiated, pH 10, aqueous solutions of 2 x 10^{-4} mol dm^{-3} TBAA under various conditions. All yields are given in terms of G values.**

<table>
<thead>
<tr>
<th>System</th>
<th>-TBAA</th>
<th>Br⁻</th>
<th>TBAcrA</th>
<th>CO₂</th>
<th>CO</th>
<th>DBFuA+ DBMaA</th>
<th>CH₃Br</th>
<th>Total Br</th>
<th>Total C</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6.25</td>
<td>9.65</td>
<td>3.0</td>
<td>3.1a</td>
<td>0.1</td>
<td>0.2</td>
<td>n.a.</td>
<td>3.05</td>
<td>2.08</td>
</tr>
<tr>
<td>II</td>
<td>6.45</td>
<td>10.5</td>
<td>3.2</td>
<td>3.4</td>
<td>0.1</td>
<td>0.1</td>
<td>n.a.</td>
<td>3.15</td>
<td>2.09</td>
</tr>
<tr>
<td>III</td>
<td>6.0</td>
<td>9.1</td>
<td>2.75</td>
<td>3.4</td>
<td>0.1</td>
<td>0.1</td>
<td>n.a.</td>
<td>2.93</td>
<td>2.03</td>
</tr>
<tr>
<td>IV</td>
<td>6.1</td>
<td>3.7</td>
<td>2.8</td>
<td>3.1</td>
<td>0.2</td>
<td>0.1</td>
<td>5.5</td>
<td>2.92</td>
<td>1.98</td>
</tr>
<tr>
<td>V</td>
<td>3.4</td>
<td>7.5</td>
<td>0.9</td>
<td>3.9</td>
<td>0.2</td>
<td>≤ 0.1</td>
<td>n.a.</td>
<td>3.0</td>
<td>≈ 2.0</td>
</tr>
<tr>
<td>VI</td>
<td>3.9</td>
<td>9.0</td>
<td>0.9</td>
<td>4.2</td>
<td>0.3</td>
<td>0.1</td>
<td>n.a.</td>
<td>3.05</td>
<td>1.95</td>
</tr>
</tbody>
</table>

a Difference between measured total $G(\text{CO}_2) = 9.1$ and $G(\text{CO}_2) = 6.0$ formed through 100% of •OH and 40% of H⁺.

One common finding for all systems is a complete material balance. With “Total Br” denoting the overall yield of bromine in the products (Br⁻, CH₃Br, 3 x TBAcrA, 2 x DBFuA, 2 x DBMaA), “Total C” that of the carbon in the products (CO₂, CO, 3 x TBAcrA, 4 x DBFuA, 4 x DBMaA), and { –TBAA} the measured degradation of TBAA, the ratios of “Total Br”/{–TBAA} and “Total C”/{–TBAA} in all systems match the theoretically predicted values of 3.0 and 2.0, respectively, within an error margin of ≤ 5%. This is an excellent agreement considering that the TBAA degradation is measured as a difference between two relatively large concentrations.

**Origin of tribromoacrylic acid (TBAcrA).** The yields of Br⁻, TBAcrA, and CO₂ measured in the immediate analysis of the room temperature samples always fell short from the maximum values by an approximate 1:1:1 ratio. This observation suggests that all these three products originate from a common precursor formed as a result of the irradiation but not directly detectable in the analysis. The stoichiometric sum of Br⁻, TBAcrA and CO₂ constitutes tetrabromosuccinic acid (TetBSA) acid which formally results from combination of two **CBr₂CO₂⁻** radicals (eq. 3.4). Accordingly, we assign the formation of the final products to the subsequent decomposition of TetBSA (eq. 3.7).

\[
\text{TetBSA} \rightarrow \text{Br}⁻ + \text{CO}_2 + \text{CBr}_2=\text{CBr}–\text{CO}_2⁻
\]

A similar mechanism has been forwarded for TetCSA which, in a process analogous to eq. 3.7, was found to decay into trichloroacrylic acid with a half-life of 9 min at 80 °C [155]. Our present investigation shows that TetBSA, on the other hand, is already completely decomposed after heating the sample for 20 min at 55 °C. For comparison, we also generated
TetFSA from dimerization of °CF\(_2\)CO\(_2\) – radicals in N\(_2\)O-saturated solutions of CHF\(_2\)CO\(_2\) –. In this case no traces of fluoride (i.e. ≤ 1 µmol) could be detected in the irradiated sample, even after heating at 90 °C for 7 hours.

In connection with the formation of TBAcra still another aspect is worth mentioning. This acid, necessary for initial chromatographic reference, is not available commercially but has to be synthesized by a two-stage procedure in analogy to a patent literature for diiodo-monobromoacrylic acid [156]. It is certainly interesting to note that γ-irradiation of an aqueous solution of TBAA provides a fast, one-step pathway to TBAcra which can conveniently be obtained in good quantities by appropriate preparative chromatography.

The formation mechanisms of DBFA, DBMA and CO are described in [4].

**Reaction of Br° atoms with TBAA.** In the systems (V) and (VI) no °OH scavenger is present. Our pulse radiolysis experiments have shown that there is no °CBr\(_2\)CO\(_2\) – formation associable with a direct reaction between °OH and TBAA. These findings suggest that °OH radicals participate only indirectly in the degradation mechanism. The most likely scenario involves the °OH-induced oxidation of the bromide liberated in the H° and e\(_{aq}^-\) reactions with TBAA and formation of Br\(_2\)° – species

\[
\text{°OH} + 2 \text{Br}^- \rightarrow \text{Br}_2\text{°}^- \quad (3.8)
\]

Indeed, a transient absorption with all characteristic features of Br\(_2\)° – is observed to grow in after the pulse (\(t_{1/2} \approx 20 \mu\text{s}, \lambda_{\text{max}} = 360 \text{ nm as for Br}_2\text{°}^- [157]\)). This absorption is not present upon addition of any °OH scavenger in excess to Br\(^-\).

The yield of TBAA degradation in the γ-radiolysis is thus likely to be due to a reaction of Br\(_2\)° – or Br° atoms which exist in equilibrium 3.9.

\[
\text{Br}_2\text{°}^- \Leftrightarrow \text{Br}^° + \text{Br}^- \quad (3.9)
\]

The more reactive of these two species is clearly the free Br° atom. For example, bromine atom is involved in hydrogen abstraction [158], whereas Br\(_2\)° – species is not. In the present system, there is good evidence that Br° atoms are able to induce TBAA degradation via direct bromine abstraction (eq. 3.10)

\[
\text{Br}° + \text{CBr}_3\text{CO}_2^- \rightarrow \text{Br}_2 + °\text{CBr}_2\text{CO}_2^- \quad (3.10)
\]

\[
\text{Br}° + \text{CBr}_3\text{CO}_2^- \rightarrow \text{Br}^- + \text{CBr}_3\text{CO}_2° \quad (3.11)
\]

\[
\text{CBr}_3\text{CO}_2° \rightarrow °\text{CBr}_3 + \text{CO}_2 \quad (3.12)
\]

Looking at the yields listed in Table 3.1, it is noted that in the systems (V) and (VI) the measured CO\(_2\) yields are higher than the TBAA degradation yields. A plausible explanation would be an oxidation of the carboxyl function according to reaction 3.11 followed by fast decarboxylation (eq. 3.12). Bromine atoms are known to be strong 1e-oxidants – the reduction potential was recently estimated as \(E^°(\text{Br}°/\text{Br}^-) = 1.96 \text{ V vs NHE} [158]\), which is higher than that of Br\(_2\)° –/2Br\(^-\) couple \((E^° = 1.63 \text{ V vs. NHE}) [54]\).
3.1.3. γ-Radiolysis of CCl$_2$CO$_2^-$ and CHF$_2$CO$_2^-$ solutions

In N$_2$- and N$_2$O-saturated, pH 10, 2 x 10$^{-4}$ mol dm$^{-3}$ aqueous solutions of TCAA, the corresponding degradation yields ($G = 3.9$ and 0.9, respectively) also exceed the yield of reducing equivalents, e$_{aq}^-$ and H$^*$, ($G = 3.4$ and 0.6). The excess may, therefore, be due to a reaction of Cl$^*$ atoms with TCAA, in analogy to reaction 3.10. The chlorine atoms are suggested to be formed in a reaction of Cl$^-$ with $^*$OH, possibly via an intermediate Cl(OH)$^*$--adduct radical anion. The $G$(Cl$^-$)/$G$(-TCAA) ratio, measured immediately after the irradiation, amounts to 1.0 (± 0.1), reflecting the relative stability of the TetCSA as compared to TetBSA.

The reductive TCAA degradation process can also effectively be induced by CO$_2$. This is interesting since CO$_2^*$, for example, is not able to reduce CCl$_4$ [159]. If DFAA was subjected to reaction with $^*$OH radicals, the yield of $^*$CF$_2$CO$_2^-$ radicals is almost quantitative. This is deduced from the yield of TetFSA, $G = 2.6$, obtained in γ-irradiated N$_2$O-saturated solution of DFAA at pH 10.

This study provides a detailed mechanistic and quantitative account for the free-radical-induced degradation of TBAA. It elaborates on certain principles applicable to the reactions of halogenated organic acids, in general, but also addresses on a number of points specifically. With halogenated organic acids being important molecular intermediates in the degradation of many environmentally hazardous compounds en route to mineralization our results are considered to be of value for a quantitative understanding of detoxification and water remediation processes.

3.2. Characterisation and Quantitative Determination of (Hydro)Peroxides Formed in the Radiolysis of Dioxygen-Containing Systems and Upon Ozonolysis

Free-radical degradation of organic compounds in the presence of dioxygen very often proceeds via simultaneous formation of hydrogen peroxide and organic (hydro)peroxides, especially in aqueous solutions. In ozone reactions, these products are common as well. Because of the essential role of ROOH and H$_2$O$_2$ analysis for our work, possible routes of hydroperoxides formation are shortly discussed below. For the studies dealing with hydroperoxide chemistry, reliable assays which allow their quantitative determination are required. Therefore, some established assays are discussed and some new ones are presented in this sections.

3.2.1. Formation of organic hydroperoxides

In paragraph 1.3.3.5 it has been mentioned that organic dialkyl peroxide, ROOR, could be a product of the recombination of two peroxy radicals.

$\text{HO}_2^*/\text{O}_2^-$ may disproportionate into H$_2$O$_2$ and O$_2$ ($k = 1 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$)[53], reaction 3.13), but O$_2^-$ can also undergo electron transfer to ROO$^*$ giving rise to organic hydroperoxides (see reaction 1.36). In competition to above mentioned reactions, $\text{HO}_2^*/\text{O}_2^-$
may also react by addition to ROO• (reaction 3.14). This reaction is leading to short-lived hydrotetroxides [116, 160].

\[
\text{HO}_2^* + \text{O}_2^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\]  
(3.13)

\[
\text{ROO}^* + \text{O}_2^- + \text{H}^+ \rightarrow \text{ROOOOH}
\]  
(3.14)

Due to the comparatively fast reaction of two ROO• with one another and the relative slowness of the self-termination of O₂•− (see reaction 3.28 further below), O₂•−/HO₂• build up to rather high steady-state concentrations under continuous radiolysis. Therefore, reactions 3.13 and cross-termination of O₂•− with ROO• may become of considerable importance even if their rate constants are only moderate, i.e., in the order of \(k_{3.13}\). Their contribution should be pH-dependent since \(k_{3.13}\) is strongly pH-dependent [53].

Other ways leading to organic hydroperoxides via 1-e transfer or H-abstraction by means of peroxyl radicals are already mentioned in the paragraph 1.3.3.2 (see reactions 1.20 and 1.21). It is necessary to point out that the first reaction is more typical for highly reactive peroxyl radicals such as halogenated ones [75, 161-165]. H-abstraction by ROO• is a slow process, since the ROO−H bond is only weak. This reaction occurs intermolecularly or intramolecularly. In dilute solutions, the latter often markedly predominates, when a favourable (e.g., six-membered) transition state allows the transfer of a weakly-bound hydrogen (e.g., in ethers [166-168]). Rate constants for such reactions are around 1 s⁻¹.

The hydroperoxides are very different regarding the reactivity. They are sometimes too short-lived to be detectable by a peroxide assay, and their formation can only be inferred from the final products. However, there is a wide span of hydroperoxides that live seconds, minutes or “for ever”. Hydrogen peroxide is such a long-lived hydroperoxide, but it may react with primary products of radiolysis or ozonolysis, and then it can fade away even on the time scale of typical analytical procedures. An example of that will be given further below for the chemistry of 2-hydroxyperoxy-2-hydroxy-2-acetic acid. More on the rich hydroperoxides chemistry will be presented in this and the next chapters of this work.

3.2.2. Methods of (hydro)peroxides determination

Titanyl sulfate assay. This assay is based on the complexation of H₂O₂ by Ti(IV) in sulfuric acid solution that gives rise to a yellow color and is often used for the determination of H₂O₂. However, the molar absorption coefficient is only low (\(\varepsilon = 710 \text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}\) at 410 nm) [169, 170], i.e. the method is not very sensitive. Organic hydroperoxides give rise to this assay only after hydrolysis which may be slow and incomplete [170].

Destruction of H₂O₂ by catalase [14]. The destruction of H₂O₂ with the help of catalase is often a most useful tool to distinguish between H₂O₂ and organic hydroperoxides. The addition of 10 µl catalase to 10 dm³ 1 × 10⁻⁴ mol dm⁻³ H₂O₂ solution eliminates H₂O₂ in less than 2 seconds, while organic hydroperoxides are typically not or only very little affected [14]. For example, at a catalase concentration of 0.8 mg dm⁻³ CH₃OOH decays with a half-
life of a day [117]. In contrast, we now found that formic peracid (FPA) is rapidly destroyed by catalase [14].

**Oxidation of sulfides and disulfides by reactive hydroperoxides** [14]. Reactive hydroperoxides such FPA and hydroperoxides of a similar reactivity are capable of oxidizing sulfides and disulfides by O-transfer (cf. reaction 3.15).

\[
\text{HC(O)}\text{OOH} + \text{R}_2\text{S} \rightarrow \text{HC(O)}\text{O}^- + \text{H}^+ + \text{R}_2\text{SO} \tag{3.15}
\]

This reaction can be readily followed by conductance measurements, because formate ions and protons are liberated in this reaction (pK\text{a}(formic peracid) = 7.1, pK\text{a}(formic acid) = 3.8). The rate constant of the reaction of FPA with bis(2-hydroxyethyl)sulfide is determined to be 220 dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1} [13, 14]. The reactivity of H\textsubscript{2}O\textsubscript{2} toward this sulfide is negligible. The reaction with the sulfide can be used to reduce reactive organic hydroperoxides [13].

Simple aliphatic sulfoxides do not have sufficiently strong absorptions at \(\lambda > 200\) nm to use them for the quantitative determination of reactive hydroperoxides. Methionine (MetS) also undergoes this reaction. Its sulfoxide (MetSO) absorbs more strongly in the UV, and, therefore, MetS can be used with advantage to quantify reactive hydroperoxides.

**Fe(II)-based assays.** Aqua-Fe\textsuperscript{2+} is known to reduce H\textsubscript{2}O\textsubscript{2} and organic hydroperoxides. This ready reaction of Fe\textsuperscript{2+} with hydroperoxides has often been used for their quantification (e.g., ref.[171, 172]), but the question has to be put ahead whether one can rely on such data.

The stoichiometry of the reaction of hydroperoxides with Fe\textsuperscript{2+} is simple, *i.e.* one mol hydroperoxide may yield two mol Fe\textsuperscript{3+} (reactions 3.16-3.17; \(k_{17} = 3 \times 10^8\) dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1} [173]).

\[
\text{Fe}^{2+} + \text{ROOH} \rightarrow \text{Fe}^{3+} + \text{RO}^* + \text{OH}^- \tag{3.16}
\]

\[
\text{Fe}^{2+} + \text{RO}^* + \text{H}^+ \rightarrow \text{ROH} + \text{Fe}^{3+} \tag{3.17}
\]

A system which seems to follow this sequence of reactions with practically no side reaction is the reaction of FPA with Fe(CN)\textsubscript{6}\textsuperscript{4-} [14]. At pH \(\sim 3.7\) the rate constant of this reaction is 4.3 dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}, and \(\sim 1.9\) mol Fe(CN)\textsubscript{6}\textsuperscript{3-} and \(\sim 0.9\) mol formic acid are formed. Reaction 3.17 does not consider competing reactions. In reality, however, the RO\textsuperscript{*} radicals are usually very short-lived and may react with the substrate RH (reaction 3.18, \(k \approx 3 \times 10^5\) dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1} for the tert-butoxyl [174] and the methoxyl [175] radicals with methanol), decompose by \(\beta\)-fragmentation [176] or undergo an 1,2-H-shift [177-179] when \(\alpha\)-hydrogens are available (e.g., reaction 3.19). In water, the 1,2-shift reaction is also very fast (\(\sim 10^6\) s\textsuperscript{-1}).

\[
\text{RO}^* + \text{R}_1\text{H} \rightarrow \text{ROH} + \text{R}_1\text{•} \tag{3.18}
\]

\[
\text{CH}_3\text{O•} \rightarrow \text{•CH}_2\text{OH} \tag{3.19}
\]

In the presence of dioxygen, the alkyl radicals are rapidly converted into the corresponding peroxyl radicals which are subsequently reduced by Fe\textsuperscript{2+} into hydroperoxides (reaction 3.20).
ROO\(^*\) + Fe\(^{2+}\) + H\(^+\) → ROOH + Fe\(^{3+}\)  \(\text{(3.20)}\)

Thus, a short chain reaction is induced and it is no longer guaranteed that even at low substrate concentrations two mol Fe\(^{3+}\) are formed per mol of hydroperoxide reacted.

We would like to give three examples of systems investigated by us, which are leading to higher than stoichiometric 2 : 1 ratios:

a) the reaction of one from three organic hydroperoxides derived from thymine ozonolysis (for the details see Section 4.4) with Fe(CN)\(_6\)\(^{4-}\) yields 2.9 mol Fe(CN)\(_6\)\(^{3-}\) \([13]\);

b) the reaction of tertiary butylhydroperoxide with Fe\(^{2+}\) in air-saturated solution leads to the formation of 4 mol Fe\(^{3+}\) \([14]\);

c) the reaction of H\(_2\)O\(_2\) with Fe\(^{2+}\) in the presence of 2-PrOH, where up to 11 mol Fe\(^{3+}\) per 1 mol H\(_2\)O\(_2\) could be formed at high 2-PrOH concentration \([14]\).

The reason for this is the occurrence of the fast unimolecular reactions of alkoxyl radicals which may undergo fragmentation yielding alkyl radicals; subsequent O\(_2\)-addition and reduction gives rise to new hydroperoxides.

It is thus concluded that Fe\(^{2+}\)-based hydroperoxide assays, although most useful for their detection, are often not well-suited for their quantification (cf. also ref. \([180]\)).

**The molybdate-activated iodide assay.** The stoichiometry of this assay is given by equation 3.21. At the high iodide concentration used in this assay, the iodine formed is complexed by I\(^-\) (reaction 3.22), and the strong absorption of I\(_3^-\) is monitored. For the characterisation of the (hydro)peroxides, their kinetics with molybdate-activated iodide \([138]\) is used.

\[
\text{ROOH} + 2 \Gamma + 2 \text{H}^+ \rightarrow \text{ROH} + \text{I}_2 + \text{H}_2\text{O}  \quad \text{\(\text{(3.21)}\)}
\]

\[
\text{I}_2 + \Gamma \rightarrow \text{I}_3^-  \quad \text{\(\text{(3.22)}\)}
\]

Although most ROOH require catalysis, some strongly oxidising ROOH such as FPA and a hydroperoxide formed in the ozonolysis of thymine react equally fast with iodide in the presence and in the absence of molybdate catalyst \([14]\).

For the quantitative determination of (hydro)peroxides, the molybdate-catalysed iodide assay has the advantage over Fe\(^{2+}\)-based assays, because no free-radical chain reactions are induced which can lead to considerable errors.

In the next section some examples are given for the radiolytic formation of some (hydro)peroxides from commonly-used \(\cdot\)OH radical scavengers and their characterisation by the kinetics of the iodide assay. This subject is important for the understanding of free-radical degradation of RHal. Since most of them react efficiently with e\(_{\text{aq}}^-\) and much more slowly with \(\cdot\)OH radicals, their degradation can be induced more conveniently via reductive mechanism. Therefore, an appropriate \(\cdot\)OH scavenger should be chosen to suppress possible reaction of \(\cdot\)OH radicals with RHal. In order to clarify the origin of any organic peroxide in such system, possible ROOH (ROOR) from \(\cdot\)OH-scavenger and their properties have to be known.
3.2.3. Determination of hydroperoxides in typical γ-radiolytical systems [9]

The DMSO system. The reactions of CH$_3$OO$^*$ radicals generated in the radiolysis of pressurised CH$_4$/N$_2$O/O$_2$ solutions have been investigated in some detail. Methylhydroperoxide ($G = 0.9$; as a remainder, all radiation chemical yields are given without the factor of $10^{-7}$ mol J$^{-1}$ for reason of simplification) was determined with Allen’s reagent after destruction of H$_2$O$_2$ with catalase [117]. In O$_2$-saturated DMSO solutions at pH 5, three major products were identified: CH$_3$OOH ($G = 2.0$), H$_2$O$_2$ ($G = 1.0$) and formaldehyde ($G = 0.54$) [9]. Under the present conditions, more O$_2^*$ than CH$_3$OO$^*$ are generated upon radiolysis (ratio of $G$ values: 3.2/2.8) than in the previous study [58], where this ratio was 0.6/5.6. This explains why $G$(CH$_3$OOH) is higher under the present conditions. Upon HPLC, H$_2$O$_2$ and CH$_3$OOH are well separated [9]. In the presence of tetr anitromethane (TNM) which scavenges readily O$_2^*$ (see reaction 1.37), the organic peroxide is absent. This is taken as strong evidence that we, indeed, deal with the ROOH, as already suggested earlier [117].

The 2-PrOH system. The reaction of •OH with 2-PrOH in the presence of oxygen leads mainly to the formation of the corresponding peroxy radicals, *OOC(CH$_3$)$_2$OH (∼85.5% based on *OH yields) and *OOCH$_2$CH(CH$_3$)OH (13.3%), respectively [59]. The former eliminates rapidly HO$_2^*$/O$_2^*$ (see reaction 1.27, $k = 650$ s$^{-1}$ [86]). As a consequence, O$_2^*$ and *OOCH$_2$CH(CH$_3$)OH are formed in a ratio of around 13:1. Thus, the probability for *OOCH$_2$CH(CH$_3$)OH of reacting with O$_2^*$, yielding the corresponding hydroperoxide as compared to its self-termination is high.

The yield of ROOH is $G = 0.3$ in O$_2$-saturated solutions, i.e. it corresponds to the yield of the minor radical in this system. In the presence of TNM, ROOH is no longer formed. We therefore attribute it to a hydroperoxide, HOOCH$_2$CH(CH$_3$)OH [9].

The t-BuOH system. The reaction of *OH with t-BuOH in the presence of oxygen give rise to *OOCH$_2$C(CH$_3$)$_2$OH in 95% yield [59]. Here, one may expect two organic peroxides, namely the peroxide HOC(CH$_3$)$_2$CH$_2$OOCH$_2$C(CH$_3$)$_2$OH and the hydroperoxide HOOCH$_2$C(CH$_3$)$_2$OH. In a preceding detailed study [160] it had been concluded that ROOR, but not ROOH is formed. Indeed, we have now shown that the addition of TNM does not diminish the yield of the ROOR and only one organic peroxidic compound ($G = 0.4$ in O$_2$-saturated solution) was detected by HPLC [9].

3.2.4. Formation and decay of 2-hydroperoxy-2-hydroxy-acetic acid as an example of “fast” H$_2$O$_2$ transformations [11]

Studying the ozonolysis of cinnamic acid [11] we have observed that when an ozonated cinnamate solution (pH ∼6.5) is kept for some time, glyoxylic acid is progressively converted into formic acid due to the presence of H$_2$O$_2$ which is thereby consumed.

Glyoxylic acid and H$_2$O$_2$ give rise to 2-hydroperoxy-2-hydroxyacetate (reactions 3.24-3.25, Scheme 3.1) which decarboxylates into formic acid and carbon dioxide (reaction 3.27) [181-184].
Very little was known about the kinetics of these reactions. The $^1$H NMR spectrum of glyoxylic acid in $D_2O$ shows a strong signal at $\delta = 5.04$ ppm (hydrate form, 98.2%, cf. equilibrium 3.24) and a much weaker one at $\delta = 9.35$ ppm (aldehyde form, 1.8%). For the formation of the 2-hydroperoxy-2-hydroxy-acetic acid, the free carbonyl form is required (cf. reaction 3.24), and since the anion of $H_2O_2$, $HO_2^-$, is a much better nucleophile, in alkaline solution the rate of reaction should increase with pH [$pK_a(H_2O_2) = 11.8$], which is observed.

The kinetics of the reaction of glyoxylic acid with $H_2O_2$ is given by equation 3.23, whereby $k_{obs}$ is the observed second-order rate constant.

$$k_{obs} = k_{3.25} \times [H_2O_2] + k_{3.26} \times [HO_2^-]$$  (3.23)

The rate of the 2-hydroperoxy-2-hydroxy-acetate ion decomposition has been estimated as $k_{3.27} > 1 \text{ s}^{-1}$ [11]. On the other hand, the hydrolysis of 2-hydroperoxy-2-hydroxy-acetic acid into glyoxylic acid and hydrogen peroxide [reaction (−3.25)], must be slow in comparison.

### 3.2.5. Recommendations for the determination of hydro(peroxide) yields in aqueous solutions [9]

The rate of reaction of different (hydro)peroxides with Allen’s reagent varies by seven orders of magnitude. The corresponding half-lives change from 3 ms for FPA to about 10 hours for HOCl(CH$_3$)$_2$OOH [9].

Assuming that $H_2O_2$ is not undergoing fast transformations, we may come up with recommendations for the determination of (hydro)peroxide yields in aqueous solution.

Conventional UV spectroscopy (time-drive mode) may be used to determine $H_2O_2$ and organic (hydro)peroxides of lower reactivity side by side. In general, a difference of a factor of $\sim 10$ in reactivity is required for a clear kinetic separation of two components.

If the (hydro)peroxide reacts faster than $H_2O_2$ the stopped-flow technique is required.

Very reactive (hydro)peroxides (e.g., formic peracid, FPA) react also fast with iodide without molybdate catalysis while $H_2O_2$ does not. This difference in reactivity may be used to differentiate between $H_2O_2$ and a very reactive (hydro)peroxide.
If H$_2$O$_2$ and the organic (hydro)peroxide are of similar reactivity H$_2$O$_2$ may be destroyed with catalase, and from experiments with and without catalase their yields can be assessed. Note that FPA also reacts fast with catalase, and it is as yet not known whether other (hydro)peroxides do as well.

Reactive (hydro)peroxides can be readily eliminated with sulfides, \textit{e.g.} bis-2-hydroxyethylsulfide [13, 14]. Slowly reacting (hydro)peroxides and H$_2$O$_2$ remain.

HPLC PCD allows to locate the (hydro)peroxides on the chromatogram. This approach can also be used to determine reasonably reactive (hydro)peroxides (including H$_2$O$_2$) quantitatively.

3.3. Importance of Cross-Termination Reaction Between Halogenated Peroxyl Radicals and Superoxide [3]

Both O$_2$•$^-$ and H$_2$O$_2$ are present in practically all oxygenated samples exposed to radiation. Particularly in the photocatalysis involving TiO$_2$ relatively high concentrations of superoxide have to be considered since molecular oxygen is one of the few substrates reducible by the conduction band electrons of this semiconductor. Nonetheless, reactions involving O$_2$•$^-$ are often neglected. Because O$_2$•$^-$ is not very reactive towards other substrates in an aqueous environment, its dismutation with conjugated acid, HO$_2$•, (see reaction 3.13) leading to H$_2$O$_2$ is usually the only reaction which is considered. Self-termination of superoxide (reaction 3.28) is a very slow process ($2k_{3.28} \leq 0.35$ dm$^3$ mol$^{-1}$ s$^{-1}$ [53]) and usually is not taken into consideration.

\[
2 \text{O}_2\cdot^- + 2 \text{H}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}_2
\]  

For the reaction of O$_2$•$^-$ with peroxy radical, commonly named as cross-termination, in fact, only three rate constant estimates have been published (see paragraph 1.3.3.5).

The particular system serving to demonstrate the importance of the cross-termination, is an aqueous, pH 6, air-saturated solution containing CClF$_2$CO$_2$• and HCO$_2$•. Exposed to \textgamma-irradiation, the following primary reactions (eqs. 3.29-3.32) lead to the key players in the system, namely, O$_2$•$^-$ and *OOCF$_2$CO$_2$•.

The total yields of O$_2$•$^-$ and *OOCF$_2$CO$_2$•, in terms of $G$-values, are 3.7 and 2.5, respectively, \textit{i.e.}, superoxide is formed in some excess. These numbers emerge from the total CClF$_2$CO$_2$• degradation which was measured to be $G = 2.5$. The figure for the O$_2$•$^-$ yield includes all e$_{\text{aq}}$ and H• which react directly with O$_2$ but not with the acid ($G = 0.9$), and the entire *OH and H• contribution to the O$_2$•$^-$ formation through reactions 3.31 and 3.32.

The yields of the products, listed in the Table 3.2 show a 100% material balance with respect to chlorine, fluorine and carbon. The fact that practically all carbon shows up as CO$_2$ indicate an almost complete breakdown of the carbon skeleton.
Mechanistically two scenarios have to be considered for the product formation. The first considers only self-termination processes of the O$_2$•$^-$ and •OOCF$_2$CO$_2$• radicals, respectively, while the second allows also for mutual cross-termination.

**Self-termination:**
Further degradation of •OOCF$_2$CO$_2$• could proceed via self-termination:

$$2 \text{•OOCF}_2\text{CO}_2^- \rightarrow \text{O}_2 + 2 \text{•OCF}_2\text{CO}_2^-$$

**Cross-termination:**
The cross-termination is considered to yield a hydroperoxide according to reaction 3.35. The hydroperoxide may cleave HOF or, after hydrolysis, H$_2$O$_2$. However, this would again leave F(O)CCO$_2$•, discarded already as major intermediate based on oxalate yields. Hydroperoxides of the type R–CY$_2$–OOH have, on the other hand, been found to break down

$$\text{•CF}_2\text{CO}_2^- + \text{O}_2 \rightarrow \text{•OOCF}_2\text{CO}_2^-$$

$$\text{•OH} / \text{H}^+ + \text{HCO}_2^- \rightarrow \text{CO}_2^• + \text{H}_2\text{O} / \text{H}_2$$

$$\text{CO}_2^• + \text{O}_2 \rightarrow \text{O}_2^• + \text{CO}_2$$

Table 3.2. Degradation of CDFAA. The yields of the products (in terms of G-units) obtained upon irradiation of an aqueous, pH 6, air-saturated solution containing 0.02 mol dm$^{-3}$ CClF$_2$CO$_2$– and 0.002 mol dm$^{-3}$ HCO$_2$–.

<table>
<thead>
<tr>
<th>degradation</th>
<th>formation</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CClF$_2$CO$_2$–</td>
<td>2.5</td>
<td>Cl$^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F$^-$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>(CO$_2^-$)$_2$</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

β-Cleavage includes two options. Fluorine atom elimination from the resulting oxyl radical is unfeasible because of the strong C–F bond. More probable is C–C cleavage:

$$\text{•OOCF}_2\text{CO}_2^- \rightarrow \text{CF}_2\text{O} + \text{CO}_2^•$$

Hydrolysis of CF$_2$O, and reaction of CO$_2$•$^-$ with O$_2$ converts both carbon fragments into CO$_2$ and, furthermore, via reaction 3.32, generates additional O$_2$•$^-$.

In summary, this mechanism calls for the breakdown of each •OOCF$_2$CO$_2$• species into 2 of F$^-$ and 2 of CO$_2$.

The other self-termination process taking place under this premise is the superoxide conversion into H$_2$O$_2$ as formulated in reaction 3.28 (or self-termination of its conjugated acid HO$_2^+$ or mutual termination of HO$_2^+$ with O$_2$•$^-$, see reaction 3.13).

**Cross-termination:**
The cross-termination is considered to yield a hydroperoxide according to reaction 3.35. The hydroperoxide may cleave HOF or, after hydrolysis, H$_2$O$_2$. However, this would again leave F(O)CCO$_2$•, discarded already as major intermediate based on oxalate yields. Hydroperoxides of the type R–CY$_2$–OOH have, on the other hand, been found to break down
into ROH and CY\textsubscript{2}O [185-187]. With R = CO\textsubscript{2}\textsuperscript{−} and Y = F, as in our case, the products would be HCO\textsubscript{3}\textsuperscript{−} and CF\textsubscript{2}O, i.e., ultimately two equivalents of F\textsuperscript{−} and CO\textsubscript{2} would emerge from each •OOCF\textsubscript{2}CO\textsubscript{2}\textsuperscript{−} peroxyl radical also in this case. Self- and cross-termination routes are, therefore, indistinguishable by looking at the constituency products from the original acid.

\[
O_2^{•−} + \cdot\text{OOCF}_2\text{CO}_2^{•−} + H^+ \rightarrow O_2 + \text{HOOCF}_2\text{CO}_2^{−}
\]  

(3.35)

A distinction can, however, be made on the basis of the H\textsubscript{2}O\textsubscript{2} yields, i.e., the yields of a product which is often neglected. Upon radiolysis of an aqueous solution containing e\textsubscript{aq}− and •OH scavengers, the primary H\textsubscript{2}O\textsubscript{2} yield of \( G = 0.7 \) is always present [55]. Additional H\textsubscript{2}O\textsubscript{2} is formed through the superoxide termination processes.

The numerical H\textsubscript{2}O\textsubscript{2} yields, calculated on the basis of the outlined mechanisms, are \( G = 3.8 \) and 1.0 for self- and cross-termination, respectively. The experimentally measured value of \( G = 1.5 (\pm 0.1) \) clearly indicates that cross-termination constitutes the major reaction route [4]. Evaluation of the data shows that, in this particular experiment, at least 80% of all •OOCF\textsubscript{2}CO\textsubscript{2}− react with O\textsubscript{2}•−, and this percentage goes up to 100% if the \([O_2^{•−}] / [\cdot\text{OOCF}_2\text{CO}_2^{•−}]\) ratio is further shifted in favour of O\textsubscript{2}•− at higher \([O_2] / [\text{CClF}_2\text{CO}_2^{−}]\) concentration ratios [4].

Cross-termination between peroxyl radicals and superoxide thus appears to be a very efficient process, occurring with rate constants exceeding those for the radicals’ self-termination. Since, for peroxyl radicals, the latter are on the order of \( 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) (e.g. \( 2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) for CCl\textsubscript{3}OO• [188]), the cross-termination rate constants would accordingly be more around the \( 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) range, substantiating the few published values [114, 115].

Although our example has only referred to homogeneous radiolysis conditions the principle conclusion should also apply for the heterogeneous photocatalytic systems. Cross-termination should, in particular, be taken into consideration in any degradation mechanism of organic compounds which involves simultaneous generation of peroxyl radicals and superoxide in significant quantities at the semiconductor surface. This has, of course, also an immediate bearing on the interpretation of any H\textsubscript{2}O\textsubscript{2} yields measured in such systems.

3.4. Radiation Chemistry of Halogenated Methanes. Model Systems to Study Reactive Fates of Halogenated Alkoxyl Radicals

3.4.1. Introduction

Free-radical degradation of halogenated hydrocarbons in an oxygen-containing environment involves halogenated peroxyl radicals (RHalOO•) as the first common key intermediates. Detailed knowledge about the ultimate fate of the halogenated peroxyl radicals, especially in aqueous phase, is still relatively poor. The same is true for halogenated alkoxyl radicals (RHalO•) which in the presence of certain donors such as organic sulfides [79] or
inorganic iodide [189], as well as in donor-free systems are important secondary intermediates in the transformations of the peroxy radicals [190]. In many cases it is very difficult to distinguish between the final stable products derived from RHalOO• or RHalO• as they are often the same. Here, we would like to introduce model systems in which the chemistry of RHalO• in aqueous solutions appears, however, to be distinctly different from that of RHalOO•. They are based on the reactions of RHalOO• and an organic selenide or sulfide (dimethylselenide or methionine) as oxidizable, biologically important compounds. It will be shown that in such systems RHalOO• are quantitatively transformed into corresponding RHalO•, further reactions of which can be conveniently studied. The use of such well-defined model systems allows us to make a qualitative progress in understanding of the degradation processes.

**Biological importance of selenorganic compounds.** Selenium, in the form of selenite or selenomethionine, functions as an essential micronutrient at levels of ~0.1 ppm (mg/kg) in the animal diet, but it becomes a toxin at levels of 8-10 ppm [191]. Clark et al. [192] have found that supplementation of the people with selenized brewer's yeast was capable of decreasing the overall cancer morbidity and mortality by nearly 50%.

The article [193] reviews the progress in basic research of selenium and cancer prevention during the past decade. In this work the questions of chemical forms of selenium and their anticarcinogenic activity as well as selenium-enriched food are described. Selenium metabolic pathways involve selenomethionine or dimethylselenide (DMSe).

In contrast to biochemistry, the free-radical chemistry of selenium-containing compounds has been investigated only very poorly. This and also their high biological importance encouraged us to study the chemical fate of DMSe as a model electron-donating compound in the reactions with free radicals, especially RHalOO•.

**Literature data on radiation chemistry of DMSe [194].** OH radicals react with DMSe with the overall rate constant of 7.7 x 10^9 dm^3 mol^{-1} s^{-1}, mostly via an addition mechanism (79%, reaction 3.36a), with minor route being H atom abstraction reaction from the methyl group (21%, reaction 3.36b):

\[ \cdot\text{OH} + \text{DMSe} \rightarrow \text{HO–DMSe}^-/\text{H}_2\text{O} + \text{CH}_3\text{SeCH}_2^- \]  \hspace{1cm} (3.36a, b)

The adduct HO–DMSe• has an optical absorption maximum at 330 nm with \( \varepsilon = 1.1 \times 10^4 \) mol^{-1} dm^3 cm^{-1}. No direct evidence was found for the possible formation of a monomer radical cation DMSe•+ from HO–DMSe•:

\[ \text{HO–DMSe}^- \rightarrow \text{OH}^- + \text{DMSe}^{++} \]  \hspace{1cm} (3.37)

Instead, the radical–adduct appears to react further with a second DMSe molecule via reaction 3.38a \( (k_{3.38a} = 1.4 \times 10^9 \) dm^3 mol^{-1} s^{-1}) to give (DMSe)_2•++ , a radical species showing an absorption maximum at 470 nm \( (\varepsilon = 1.1 \times 10^4 \) mol^{-1} dm^3 cm^{-1}).

\[ \text{HO–DMSe}^- + \text{DMSe} \Rightarrow \text{OH}^- + (\text{DMSe})_2^{++} \]  \hspace{1cm} (3.38a, b)

In acidic solutions the OH• ions are neutralized by reaction with H^+:
$$\text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}$$  \hspace{1cm} (3.39)

The measured $G(\text{DMSe})_2^{•+} = 4.4$ in $\text{N}_2\text{O}$-saturated solutions corresponds to 79% of $^{1}\text{OH}$ radicals (generated in the system containing 0.001 mol dm$^{-3}$ DMSe with $G = 5.5$ as calculated via Schuler's formula [57], see eq. 1.7).

Radical $\text{CH}_3\text{SeCH}_2^{•}$, formed in reaction 3.36b, has an optical absorption maximum at 290 nm. Other oxidants such as $\text{Br}_2^{•-}$ and $\text{N}_3^{•}$ in their reaction with DMSe, also yield $(\text{DMSe})_2^{•+}$, i.e. involve a second DMSe molecule.

The decay of $(\text{DMSe})_2^{•+}$ in $\text{N}_2\text{O}$ or $\text{N}_2\text{O}/\text{O}_2$-saturated solutions obeyed second-order kinetics within the time range of the pulse radiolysis experiment (at times up to 160 microseconds). In analogy to the established fate of analogous sulfur species $(\text{DMS})_2^{•+}$ [81], the termination mechanism of $(\text{DMSe})_2^{•+}$ species is supposed to be a disproportionation via elimination of two DMSe molecules and formation of a dimer dication, which reacts instantly with water giving one equivalent of DMSeO [194]:

$$2(\text{DMSe})_2^{•+} \rightarrow 2\text{DMSe} + (\text{DMSe})_2^{2+}$$  \hspace{1cm} (3.40)

$$(\text{DMSe})_2^{2+} + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{DMSeO} + \text{DMSe}$$  \hspace{1cm} (3.41)

This mechanism predicts the formation of DMSeO with 50% yield, relative to the yield of $(\text{DMSe})_2^{•+}$. However, only a 27% yield of DMSeO has been found in our steady-state radiolysis experiment carried out with 0.001 mol dm$^{-3}$ DMSe in $\text{N}_2\text{O}$-saturated solution ($G = 1.2$, whereas $G(\text{DMSe})_2^{•+} = 4.4$). An even lower yield of DMSO was detected in a DMSO-containing system in the absence of oxygen under similar conditions [80]. A possible reason for this low DMSeO yield could be the involvement of other than a second $(\text{DMSe})_2^{•+}$ species in the overall termination processes. Species like $\text{CH}_3\text{SeCH}_2^{•}$ (reaction 3.36 b) and H-DMSe$^{•}$ adduct (reaction 3.42) as partner of $(\text{DMSe})_2^{•+}$ are among them.

$$\text{H}^{•} + (\text{CH}_3)_2\text{Se} \rightarrow (\text{CH}_3)_2\text{Se}^{•-}\text{H}$$  \hspace{1cm} (3.42)

### 3.4.2. Results and Discussion

#### Rate constants for the reactions of $\text{RHalOO}^{•}$ with DMSe. Yields of $(\text{DMSe})_2^{•+}$ radical.

Radical degradation of halogenated methanes, RHal, was initiated by their reactions with hydrated electrons (see reaction 1.2) and other reductive species generated in the systems. In order to reveal the specific feature of the reaction of $\text{RHalOO}^{•}$ with DMSe, the reactions were investigated in air-saturated aqueous solutions containing 1% 2-PrOH (an $^•\text{OH}$ radicals scavenger) and $10^{-2}$ mol dm$^{-3}$ RHal in the absence or in the presence of $10^{-3}$ mol dm$^{-3}$ DMSe.

Rate constants for the reactions of $\text{RHalOO}^{•}$ with DMSe have been determined pulse-radiolytically from the slope of the initial linear part of the plot: $k_{obs}$ (formation kinetics of the dimer radical–cation $(\text{DMSe})_2^{•+}$ absorbance at 470 nm) vs. [DMSe]. Obtained rate constants are compiled in Table 3.3.
At higher DMSe concentrations the $k_{\text{obs}}$ vs. [DMSe] correlation deviates from the linearity and is leveling off (see Fig. 3.1 for the reaction of CHBr$_2$OO$^*$ radicals). This is typical for the reactions of the halogenated peroxyl radicals with electron–donating compounds as it was established in [163]. The plateau value of $k_{\text{obs}}$, if divided by $[O_2]_{\text{air–sat.}}$, gives the rate constant for the reaction of oxygen addition to the corresponding halogenated alkyl radicals. In the case of the reaction of CHBr$_2$• + O$_2$ $k = 2.1 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ has been calculated as for the majority of organic radicals.

![Figure 3.1. Dependences of $k_{\text{obs}}$ for build-up of (DMSe)$_2^{•+}$ in the reaction of DMSe with CH$_2$BrOO$^*$ in the system consisting of 0.01 mol dm$^{-3}$ BF, 0.001 mol dm$^{-3}$ DMSe, 1% 2-PrOH in aqueous, air-saturated solution.](image)

No difference was found for the rate constant of radicals with equal number of bromine or chlorine substituents, which just reflects a very high reactivity of DMSe in this reaction. Rate constants for the reactions of DMSe with peroxy radicals carrying more halogen atoms are higher. For example, a 3-4 fold increase of the rate constants was observed for the reactions of CHCl$_2$OO$^*$ and CHBr$_2$OO$^*$ with DMSe compared to the analogue reactions of less substituted radicals, namely CH$_2$ClOO$^*$ and CH$_2$BrOO$^*$. However, the reactivity of the CCl$_3$OO$^*$ species is slightly lower than that of CHCl$_2$OO$^*$ and CHBr$_2$OO$^*$. It should also be noted that the rate constants obtained for DMS and DMSe in their reactions with CCl$_3$OO$^*$ are very close, whereas analogous values for CHCl$_2$OO$^*$ differ by a factor of 25. This unexpected observation will be explained later. Here it is important to point out that the (DMSe)$_2^{•+}$ yields are much lower than the yields of initial oxidants, i.e. RHalOO$^*$. According to Table 3.3, 16 - 17% yields have been determined in the case of CF and DCM and about 29-30% in DBM and CT-containing systems. The only exception is the system with BF (for the explanation see later), where (DMSe)$_2^{•+}$ has been formed with the yield equal to 66% of RHalOO$^*$. However, taking into account that only 27% of (DMSe)$_2^{•+}$ are leading to DMSeO (see above), the
The maximal possible contribution of 1-e oxidation mechanism of DMSe into DMSeO will be minor (<18% for BF system and much lower yields for other systems).

**Table 3.3. Rate constants for the reaction of RHalOO• with DMSe and the yield of (DMSe)2•+ radical measured at natural pH.**

<table>
<thead>
<tr>
<th>Radical</th>
<th>$10^{-8} \times k$, dm$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>(DMSe)$_2$•+ yield, %$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$ClOO•</td>
<td>0.75 ± 0.07</td>
<td>17.4</td>
</tr>
<tr>
<td>CH$_2$BrOO•</td>
<td>0.60 ± 0.10</td>
<td>28.6</td>
</tr>
<tr>
<td>CHCl$_2$OO•</td>
<td>2.5 ± 0.4 (0.1)$^b$</td>
<td>16.4</td>
</tr>
<tr>
<td>CHBr$_2$OO•</td>
<td>2.6 ± 0.5</td>
<td>66.2</td>
</tr>
<tr>
<td>CCl$_3$OO•</td>
<td>1.8 ± 0.4 (1.3)$^c$</td>
<td>30.0</td>
</tr>
</tbody>
</table>

$^a$ – calculated as 100% x $G$(DMSe)$_2$•+/$G$(RHalOO•), where $G$(DMSe)$_2$•+ values were corrected for the yield of this species formed in the direct reaction of DMSe with •OH (taken from the blank experiment in the system consisting of 1 mM DMSe, 1% 2-PrOH, N$_2$/O$_2$, nat. pH). Since the yield of •OH in this system is twice as high compared to the systems containing RHal, $G$(DMSe)$_2$•+ = 0.08 was subtracted from the observed $G$(DMSe)$_2$•+ for all RHal; $^b, c$ – values in parenthesis gives a rate constant for the reaction of RHalOO• with dimethylsulfide, taken from the ref. [79] and [161], respectively.

**DMSeO yields.** Experimentally observed DMSeO yields in all RHal-containing systems are much higher than $G$(DMSeO)$_2$•+ and are even exceeding the yield of oxidants in the RHal-containing systems (see Table 3.4). Post-irradiation effects have been found in each system studied. For example, $G$(DMSeO) = 3.2 has been measured in the system containing DCM, DMSe and 2-PrOH directly after γ-irradiation. This value increased to $G$ = 4.0 during the post-irradiation time (3.5 hours at room temperature in dark). Since the chloride yield did not changed ($G$ = 4.6), the increase of $G$(DMSeO) can be attributed to the slow molecular reaction of DMSe and H$_2$O$_2$. Taking into account that irradiation and short post-irradiation time before DMSeO analysis were always minimized (<20 minutes), the post-irradiation effect in the studied systems can be neglected.

**SOD experiments.** In order to establish a possible role of superoxide, O$_2$•–, in the overall reaction mechanism, especially on the DMSeO formation, an experiment was conducted in the presence of superoxide dismutase (SOD). No difference in the yield of DMSeO (as well as Br–) was detected in the irradiated air-saturated solutions consisting of BF, DMSe and 2-PrOH without and in the presence of 50 mg dm$^{-3}$ SOD. In these systems the (DMSe)$_2$•+ species are formed in a significant excess to superoxide (their yields are equal to $G$ = 4.4 and $G$ = 0.85, respectively). If the reaction of both species would lead to DMSeO (100% yield relative to superoxide), then the DMSeO yield should be higher by $G$ = 0.85 than the one for RHalOO•. This is almost three times more than the error limit for DMSeO determination and should therefore be detectable. However, no difference was found. These results suggest that in the studied systems superoxide disappears mostly via dismutation (see reaction 3.13 [53]).
Table 3.4. Yields of DMSeO and \((\text{DMSe})_2^{•+}\) in aqueous solution of 0.001 mol dm\(^{-3}\) DMSe at natural pH due to the reaction of DMSe with different oxidants as measured by means of steady-state (dose rate 0.37 Gy s\(^{-3}\)) and pulse radiolysis.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>(G(\text{DMSeO}))</th>
<th>(G(\text{DMSe})_2^{•+})</th>
<th>(G(\text{RHalOO}^{•})) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mM DMSe, (\text{N}_2\text{O}) [9]</td>
<td>1.2</td>
<td>4.4 [206]</td>
<td>5.5 ((•\text{OH}))</td>
</tr>
<tr>
<td>10 mM DCM, 1 mM DMSe, 1% 2-PrOH (^a)</td>
<td>3.2</td>
<td>0.40</td>
<td>2.3 (^b)</td>
</tr>
<tr>
<td>10 mM DBM, 1 mM DMSe, 1% 2-PrOH (^a)</td>
<td>3.6</td>
<td>0.90</td>
<td>3.15 (^b)</td>
</tr>
<tr>
<td>10 mM CF, 1 mM DMSe, 1% 2-PrOH (^a)</td>
<td>3.4</td>
<td>0.50</td>
<td>3.05 (^b)</td>
</tr>
<tr>
<td>10 mM BF, 1 mM DMSe, 1% 2-PrOH (^a)</td>
<td>6.6</td>
<td>4.3</td>
<td>6.5 (^b)</td>
</tr>
<tr>
<td>10 mM CT, 1 mM DMSe, 3% 2-PrOH (^a)</td>
<td>3.7</td>
<td>0.95</td>
<td>3.2 (^b)</td>
</tr>
</tbody>
</table>

\(^a\) – air-saturated solutions; \(^b\) – \(G(\text{RHalOO}^{•})\) denotes the yields of halogenated peroxyl radicals as oxidant calculated from the yields of corresponding \(\text{HCl}\) (in the case of DCM, CF and CT) or \(\text{HBr}\) (in the case of DBM and BF) determined in steady-state experiments (see later).

The question about the origin of \((\text{DMSe})_2^{•+}\) is important for the interpretation of the determined rate constants. Interaction of \(\text{RHalOO}^{•}\) with DMSe may proceed via formation of the transient adduct (reaction 3.43), which could undergo further transformations via three alternative pathways depicted by equations 3.44, 3.46 or 3.47:

\[
\begin{align*}
\text{RHalOO}^{•} + \text{Se(CH}_3)_2 & \rightarrow \text{RHalOO}–\text{Se}•(\text{CH}_3)_2 \quad (3.43) \\
\text{RHalOO}–\text{Se}•(\text{CH}_3)_2 & \rightarrow \text{RHalOO}^{–} + \text{•Se(CH}_3)_2 \quad (3.44) \\
\text{•Se(CH}_3)_2 + \text{Se(CH}_3)_2 & \equiv [\text{Se(CH}_3)_2]^{•+} \quad (3.45a,b) \\
\text{R(Hal)OO–DMSe}^{•} + \text{DMSe} & \rightarrow \text{RHalOO}^{–} + (\text{DMSe})_2^{•+} \quad (3.46)
\end{align*}
\]

Heterolytic dissociation of an adduct depicted by reaction 3.44 is leading to generation of the halogenated peroxyl anion and the monomer radical–cation from DMSe, \((\text{CH}_3)_2\text{Se}^{•+}\), which, in a fast reaction 3.45a, will give \((\text{DMSe})_2^{•+}\).

Reaction 3.46 predicts an interaction of \(\text{RHalOO–DMSe}^{•}\) adduct with a second DMSe molecule with formation of the halogenated peroxyl anion and the dimer radical–cation. The latter pathway is proposed in analogy to the reactions of \(^•\text{OH}\) radicals with organic sulfides and DMSe (depicted here as D), where it was established that \(\text{D}_2^{•+}\) is formed not via direct formation of \(\text{D}^{•+}\), despite the high oxidation potential of \(^•\text{OH}\) radicals. As \(\text{RHalOO}^{•}\) possess lower oxidation potentials than \(^•\text{OH}\) radicals, the assumption about the sequence of the reactions (3.43 + 3.46) is quite reasonable. In fact, the latter route is stoichiometrically equal to the one given by the sequences of reactions 3.43, 3.44 and 3.45a. However, it will be shown below that both of these routes should be discarded based on the product analysis. Thus, the only route leading to \((\text{DMSe})_2^{•+}\) could be based on the reactions of halogenated alkoxyl radicals. In the case of chlorinated methanes, and most likely also DBM, this is shown by reaction 3.47:
RHalO• + Se(CH3)2 → RHalO− + •Se(CH3)2

In the case of BF, it will be not alkoxyl radicals, but bromine atoms which are responsible for generation of (DMSe)2•+ (see below).

Finally, the R(Hal)OO–Se•(CH3)2 adduct may undergo homolytic cleavage which formally constitutes an oxygen transfer reaction (but, in fact, it is a 2-electron transfer process with the assistance of water molecule) via formation of halogenated alkoxyl radicals and DMSeO (reaction 3.48):

\[
\text{R(Hal)OO–Se•(CH}_3\text{)}_2 \rightarrow \text{H}_2\text{O} \rightarrow \text{R(Hal)O• + O=Se(CH}_3\text{)}_2
\]

As it appears from Table 3.4, the contribution of the 2-e oxidation pathway always prevails (≥ 70 % based on maximal (DMSe)2•+ yields < 30%, which represents alternative, 1-e oxidation pathway).

3.4.3. Oxidation of dimethylselenide to dimethylselenoxide by chloromethylperoxyl and bromomethylperoxyl radicals. Reactions of CH2ClO• and CH2BrO• radicals

Detailed study of the products derived from the reaction of chloromethylperoxyl and bromomethylperoxyl radicals with DMSe has been undertaken and the results obtained are presented in Table 3.5.

Material balance. Material balance with regard to carbon is satisfactory. Also, \(G(HCl)\) or \(G(HBr)\) amount to twice the \(G(\text{Total C})\) of the products originating from DCM (or DBM), calculated as the sum of \(G(\text{CO}_2) + G(\text{CO}) + G(\text{HCO}_2\text{H}) + G(\text{CH}_2\text{O})\), reflecting the same proportion of 2 : 1 as in the molecule of DCM (or DBM).

Only 17.5 and 28 % RHalOO• available in these systems are leading to (DMSe)2•+. Taking into the account that only 27 % of them will end up as DMSeO, the contribution of the 1-e transfer mechanism can be neglected and, hence, the 2-e oxidation must prevail.

In the following various reaction routes and their associated stoichiometry are presented and discussed.

Two-electron transfer mechanism

The 2e-transfer mechanism leads to alkoxyl radicals formation and, therefore, all the products derived from DCM will be coming from further reactions of CH2ClO•:

\[
\text{CH}_2\text{ClOO• + (CH}_3\text{)}_2\text{Se} \rightarrow \text{CH}_2\text{ClO• + (CH}_3\text{)}_2\text{SeO}
\]

Reactions of CH2ClO• radicals

Route 1. Alkoxyl radicals are known as a strong one-electron oxidant [73], more powerful than the corresponding peroxyl radicals. For example, a reduction potential of \(E^\circ = 2.3 \pm 0.3\) V has been calculated for the reaction \(\text{CCl}_3\text{O• + e}^- \rightarrow \text{CCl}_3\text{O}^-\) whereas only \(E^\circ = 1.15 \pm 0.16\) V has been reported for \(\text{CCl}_3\text{OO• + e}^- \rightarrow \text{CCl}_3\text{OO}^-\) [73].

Hence it is quite reasonable to assume such an e-transfer reaction to occur:
\[
\text{CH}_2\text{ClO}^* + 2 \text{DMSe} \rightarrow \text{CH}_2\text{ClO}^- + (\text{DMSe})_2^{*+} \quad (3.50)
\]
\[
\text{CH}_2\text{ClO}^- \rightarrow \text{Cl}^- + \text{CH}_2\text{O} \quad (3.51)
\]

This reaction explains formation of \((\text{DMSe})_2^{*+}\) as an intermediate and formaldehyde as a final product, both with radiation yields of \(G = 0.4\). The contribution of this route is 17.4 %.

**Stoichiometric equation for Route 1:** 2 \(\text{HCl} + \text{CH}_2\text{O} + \text{DMSeO} + (\text{DMSe})_2^{*+}\)

---

**Route 2.** Possible chlorine atom elimination from the radicals \(\text{CH}_2\text{ClO}^*\) (reaction 3.52) is neglected for the following reasons:

\[
\text{CH}_2\text{ClO}^* \rightarrow \text{CH}_2\text{O} + \text{Cl}^* \quad (3.52)
\]

a) the absence of extra yields of acetone (an ultimate product from the reaction of Cl atoms and 2-PrOH, see below CF system for the explanation) compared to the blank system without DCM and DMSe, where acetone is formed due to \(^*\text{OH}\) scavenging by 2-PrOH and followed reactions;

b) as shown by quantum-chemical calculations reaction 3.52 is endothermic by about 68.6 kJ mol\(^{-1}\), whereas 1,2-H shift is exothermic (\(\Delta \text{H} = -17.6\) kJ mol\(^{-1}\), see further below Table 3.8), making the latter much more probable;

c) this reaction was found to be unimportant in the gas phase [195].

**Stoichiometric equation for Route 2:** 2 \(\text{HCl} + \text{CH}_2\text{O} + \text{DMSeO}\)

---

**Table 3.5. \(\gamma\)-Radiolysis of air-saturated solutions of 0.01 mol dm\(^{-3}\) DCM (0.01 mol dm\(^{-3}\) DBM) in the presence of 1 % 2-PrOH and 0.001 mol dm\(^{-3}\) DMSe, pH 6, dose rate 0.37 Gy s\(^{-1}\). Products, their radiation yields and selectivities of formation.**

<table>
<thead>
<tr>
<th>Product</th>
<th>DCM (G)-values</th>
<th>DCM Selectivity, % (^c)</th>
<th>DBM (G)-values</th>
<th>DBM Selectivity, % (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{HHal})</td>
<td>4.6</td>
<td>200</td>
<td>6.4</td>
<td>200</td>
</tr>
<tr>
<td>(\text{HC(O)OH})</td>
<td>0.3</td>
<td>13</td>
<td>0.3</td>
<td>9.5</td>
</tr>
<tr>
<td>(\text{CH}_2\text{O})</td>
<td>0.4</td>
<td>17.5</td>
<td>0.9</td>
<td>28</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>0.7</td>
<td>30.5</td>
<td>0.8</td>
<td>25.0</td>
</tr>
<tr>
<td>(\text{CO})</td>
<td>0.9</td>
<td>39</td>
<td>1.2</td>
<td>37.5</td>
</tr>
<tr>
<td>(\text{DMSeO}^a)</td>
<td>2.7</td>
<td>117</td>
<td>4.0</td>
<td>125</td>
</tr>
<tr>
<td>[(\text{CH}_3)_2\text{Se}]_2^{*+}d</td>
<td>0.4</td>
<td>17.5 (^d)</td>
<td>0.9</td>
<td>28 (^d)</td>
</tr>
<tr>
<td>Total carbon (^b)</td>
<td>2.3</td>
<td>100</td>
<td>3.2</td>
<td>100</td>
</tr>
</tbody>
</table>

\(^a\) – Yields corrected for the formation of DMSeO in the system without RHal; \(^b\) – Total carbon yield is calculated as the sum of the radiation yields of formic acid, formaldehyde, carbon monoxide and carbon dioxide; \(^c\) – calculated as 100 % x \(G(\text{product})/G(\text{Total carbon});^{d}\) – calculated as 100 % x \(G((\text{DMSe})_2^{*+})/G(\text{CH}_2\text{HalOO}^*).\)
Routes 3a, b. Reaction 3.53 represents a 1,2-H shift in analogy to other alkoxyl radicals [166, 177-179, 196] with typical rate constants in the order of $10^5$-$10^6$ s$^{-1}$. For halogenated methyl alkoxyl radicals such rearrangement had been proposed in [197]. The carbon-centered product radicals will add oxygen, eliminate HO$_2^*$ (reaction 3.54 is known for $\alpha$-hydroxylalkylperoxyl radicals [198]) and the resulting formyl chloride will mostly (94 %) decompose to carbon monoxide (reaction 3.55, $k = 10^4$ s$^{-1}$ [137]) and, to a minor extent, hydrolyse to formic acid (6%, reaction 3.56) [137].

\[
\text{CH}_2\text{ClO}^* \rightarrow \text{CHCl(OH)} \quad (3.53)
\]

\[
\text{*CHCl(OH)} + \text{O}_2 \rightarrow \text{HO}_2^* + \text{CHClO} \quad (3.54)
\]

\[
\text{HC(O)Cl} \rightarrow \text{HCl} + \text{CO} \quad (3.55)
\]

\[
\text{HC(O)Cl} + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HC(O)OH} \quad (3.56)
\]

The sequence of reactions 3.53 + 3.54 is stoichiometrically equal to the gas-phase reaction of the alkoxyl radicals CH$_2$ClO* with oxygen

\[
\text{CH}_2\text{ClO}^* + \text{O}_2 \rightarrow \text{HO}_2^* + \text{CHClO} \quad (3.57)
\]

for which the rate constant $k = 6.3 \times 10^{-14}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$ has been determined in [195]. This value corresponds to $3.8 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ for liquid phase and in air-saturated solution with [O$_2$] = $2.8 \times 10^{-4}$ mol dm$^{-3}$ the pseudo–first order rate constant for reaction 3.57 will be equal to $1.1 \times 10^4$ s$^{-1}$. Water-assisted reaction 3.53 will be definitely much faster and could thus be comparable with the rate of the main reaction between CH$_2$ClO$_2^*$ and DMSe at these conditions ($k_{obs} \approx 7.5 \times 10^4$ s$^{-1}$ at $10^{-3}$ mol dm$^{-3}$ DMSe).

**Stoichiometric equation for Route 3a**: 2 HCl + CO + DMSeO

**Stoichiometric equation for Route 3b**: 2 HCl + HCO$_2$H + DMSeO

Based on the CO yield the contribution of Route 3a (the only source of CO in the present system) in the overall degradation of DCM is calculated to be 39.2%. Since CO and formic acid are coming from the common precursor, namely HC(O)Cl, only up to $G(\text{HCO}_2\text{H}) = 0.05$ (or only 2.2 % of the overall degradation) could be assigned to the Route 3b. The remaining $G(\text{HCO}_2\text{H}) = 0.25$ (see below) have to be formed via another route.

Route 4. An alternative to oxygen addition to *CHCl(OH) radical is a fast HCl elimination (reaction 3.58) and generation of the formyl radicals, H–C*=O:

\[
\text{*CHCl(OH)} \rightarrow \text{HCl} + \text{H–C*=O} \quad (3.58)
\]

In the gas phase, reaction of HCl elimination from alkoxyl radicals is known to occur from a 3-centered transition state with the rate constant of $k_{3.59} = 1.3 \times 10^4$ s$^{-1}$ [195]:

\[
\text{CH}_2\text{ClO}^* \rightarrow \text{HCl} + \text{H–C*=O} \quad (3.59)
\]

Reaction 3.59 is stoichiometrically equal to the combination of reactions 3.53 + 3.58. Reaction 3.53 could be significantly accelerated due to water assistance and deprotonation of the rearranged radical *CHCl(OH) with a subsequent rapid chloride elimination.
Species H–C•=O, as acyl type of radicals, may undergo hydration reaction 3.60, followed up by fast oxygen addition (reaction 3.61):

\[
\begin{align*}
\text{H–C}{}^{\cdot}=\text{O} + \text{H}_2\text{O} & \rightarrow \text{HC}{}^{\cdot}(\text{OH})_2 \\
\text{HC}{}^{\cdot}(\text{OH})_2 + \text{O}_2 & \rightarrow \text{HC(OH)}_2\text{OO}{}^{\cdot}
\end{align*}
\] (3.60) (3.61)

So formed dihydroxymethylperoxyl radicals decompose fast \((k_{3.62} > 10^6 \text{ s}^{-1})\):

\[
\text{HC(OH)}_2\text{OO}{}^{\cdot} \rightarrow \text{O}_2{}^{\cdot}+ \text{H}^+ + \text{HCO}_2\text{H}
\] (3.62)

**Stoichiometric equation for Route 4:** 2 HCl + HCO₂H + DMSeO

Based on \(G(\text{HCO}_2\text{H}) = 0.25\), the contribution of the Route 4 is about 10.8%.

**Route 5.** An oxygen addition (reaction 3.63) would be an alternative to the hydration of formyl radicals:

\[
\text{H–C}{}^{\cdot}=\text{O} + \text{O}_2 \rightarrow \text{HC(O)}\text{OO}{}^{\cdot}
\] (3.63)

So far nothing is known about the reactivity and even existence of HC(O)OO• radicals in aqueous solutions. Formylperoxyl radicals HC(O)OO• and its dimer [HC(O)OOI]₂ were successfully matrix isolated in solid O₂ at 13–18 K from UV photooxidation of solid O₂/H₂CO and O₂/trans-H₂C₂O₂ samples, respectively [199]. In [200-202] an assumption has been made that HC(O)OO• is probably a precursor intermediate to the atmospheric reaction 3.64 \((k_{3.64} = 6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})\):

\[
\text{H–C}{}^{\cdot}=\text{O} + \text{O}_2 \rightarrow \text{HO}_2{}^{\cdot} + \text{CO}
\] (3.64)

At \([\text{O}_2] = 2.8 \times 10^{-4} \text{ mol dm}^{-3}\) the calculated \(k_{\text{obs}}\) for reaction 3.64 is 10³ s⁻¹. This is too slow to compete with a possible reaction of HC(O)OO• with DMSe (in the order of \(7.5 \times 10^4 \text{ s}^{-1}\) at 10⁻³ mol dm⁻³ DMSe). The value of \(k_{\text{obs}} = 7.5 \times 10^4 \text{ s}^{-1}\) at 10⁻³ mol dm⁻³ DMSe is calculated for the reaction of peroxyl radical CH₂ClO₂• with DMSe. Formylperoxyl radicals HC(O)OO• represent, in fact, the simplest acylperoxyl radicals. It has been shown that its nearest analogue, namely acetylperoxyl radical CH₃C(O)OO• [114] is one of the most reactive peroxyl radicals known. Hence, reactivity of formylperoxyl radicals should be higher than of CH₂ClO₂• radicals. Therefore, H–C•=O radicals can be neglected as any significant source of CO in the studied system.

**Stoichiometric equation for Route 5:** 2 HCl + CO + DMSeO

**Route 6.** An overall 2-e oxidation of DMSe by means of formylperoxyl radicals will give DMSeO and formyloxyl radicals (reaction 3.65). The latter, as many alkoxyl radicals, will undergo 1,2-H atom shift (reaction 3.66) followed by fast interaction with oxygen producing carbon dioxide and HO₂• radicals (reaction 3.67, \(k = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) [203])
\[ \text{HC(O)OO}^* + \text{DMSe} \rightarrow \text{HC(O)O}^* + \text{DMSeO} \quad (3.65) \]
\[ \text{HC(O)O}^* \rightarrow \cdot\text{C(O)OH} \quad (3.66) \]
\[ \cdot\text{C(O)OH} + \text{O}_2 \rightarrow \text{HO}_2^* + \text{CO}_2 \quad (3.67) \]

**Stoichiometric equation for Route 6:** \( 2 \text{HCl} + \text{CO}_2 \rightarrow 2 \text{DMSeO} \)

This route is the only one able to explain the appearance of carbon dioxide among the products. This product is very informative because only alkoxyl radicals, which further suffer 1,2 H-shift, could be its precursor. It should be noted that no carbon dioxide has been found upon \( \gamma \)-radiolysis of the same system in the absence of DMSe. This shows the essential role of DMSe for the formation of \( \text{CH}_2\text{ClO}^* \) species. Based on \( G(\text{CO}_2) = 0.7 \) the contribution of the Route 6 is 30.4 %.

**Mechanistical Considerations.** Below is the list of routes necessary to explain the formation of all products measured.

- **Route 1:** \( 2 \text{HCl} + \text{CH}_2\text{O} + \text{DMSeO} + (\text{DMSe})_2^{2+} \)
- **Route 3 a:** \( 2 \text{HCl} + \text{CO} + \text{DMSeO} \)
- **Route 3 b:** \( 2 \text{HCl} + \text{HCO}_2\text{H} + \text{DMSeO} \)
- **Route 4:** \( 2 \text{HCl} + \text{HCO}_2\text{H} + \text{DMSeO} \)
- **Route 6:** \( 2 \text{HCl} + \text{CO}_2 \rightarrow 2 \text{DMSeO} \)

Each of the route gives one particular product from DCM together with DMSeO, but only Route 1 is explaining formation of \( (\text{DMSe})_2^{2+} \) radical cations.

Calculated yields of the products based on the selected Routes agree very well with experimentally measured values.

Assuming that all \( \text{CH}_2\text{ClOO}^* \) radicals are transformed into alkoxyl radicals \( \text{CH}_2\text{ClO}^* \) (a small part of which is reacting further with DMSe via 1-e oxidation Route 4, 17.4 %) is able to accommodate all the observed products. All carbon-containing products from DCM (CO, CO\(_2\) and HCO\(_2\)H), except formaldehyde, originate from \( \cdot\text{CH(OH)Cl} \) radicals, the yield of which is calculated as the sum of \( G(\text{CO}) \), \( G(\text{CO}_2) \) and \( G(\text{HCO}_2\text{H}) \), i.e. \( 0.9 + 0.7 + 0.3 = 1.9 \). This accounts for 83 % of all \( \text{CH}_2\text{ClO}^* \) radicals taking \( G = 2.3 \) as their primary yield. Based on the obtained data and proposed mechanism, it is possible to estimate rate constants for some key reactions. For example, based on \( G = 0.4 \) for the Route 1 and \( G = 1.9 \) for the Routes 3a, b + 4 + 6 (representing the reactions of the isomerised alkoxyl radical) and assuming \( k_{3,54} = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) as for the great majority of alkyl radicals, the rate constant for the isomerisation of \( \text{CH}_2\text{ClO}^* \) radical \( k_{3,53} = 3.6 \times 10^5 \text{ s}^{-1} \) can be obtained. By assuming \( k_{3,61} = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) and using the radiation yields of the Routes 4 and 6, the rate constant \( k_{3,60} = 2.0 \times 10^5 \text{ s}^{-1} \) for the hydration of the formyl radical is obtained. This value is one order of magnitude higher than one obtained for hydration of acetyl radical \( \text{CH}_3\text{C}^\bullet=\text{O} \) [114]. The difference can be explained by the much stronger electron-donating influence of the methyl group compared to H atom, resulting in a significantly lower positive charge on the carbonyl oxygen in \( \text{CH}_3\text{C}^\bullet=\text{O} \). Finally, \( k_{3,58} = 5.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) for the HCl elimination from
\*CH(OH)Cl radical is calculated based on the radiation yields of competing Routes 3 a,b and 4 + 6. All the estimated rate constants are well in accordance with known values for analogue reactions (see above).

**Dibromomethane (DBM) system.** The DBM system reveals, in principle, the same results as the DCM-containing one. The same basic mechanism can be proposed for DBM degradation with differing quantitative contribution of the various routes, which, however will not be discussed in further details. It is interesting to note, that the rate constants for HBr elimination (like reaction 3.58) and hydration of H-C*=O radicals, calculated from the data in the DBM system, are in perfect agreement to those obtained for the DCM system, namely $5.6 \times 10^5$ s$^{-1}$ and $2.1 \times 10^5$ s$^{-1}$. It should be pointed out, that in both, DCM and DBM systems without DMSe, no carbon dioxide has been found, clearly indicating that the corresponding alkoxyl radicals, a necessary precursor for this product, are not formed. Hence, the mechanism of DCM and DBM degradation is totally different in the absence and in the presence of DMSe. Another interesting observation is the absence of any extra-acetone as a product, ruling out any significant formation of free halogen atoms from alkoxyl radicals in the systems discussed. This is in sharp contrast to the results presented below for CF and BF containing systems.

### 3.4.4. Chloro- and bromoform degradation in the presence and absence of dimethylselenide. Reactions of dichloro- and dibromomethylperoxyl radicals

Results of the detailed study of products formed due to the free-radical degradation of CF/BF in the presence and in the absence of DMSe are presented in Table 3.6.

The experimentally found yield $G(\text{CHCl}_2\text{OO}^*) = 3.0$ is slightly exceeding the yield predicted for the reactions of CF with H atoms and hydrated electrons, $G(-\text{CF}) = 2.80$. The remaining $G(-\text{CF}) = 0.2$ could come from the reduction of CF by (CH$_3$)$_2$C•(OH) (an estimated rate constant should be in the range of $5 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$, which is in agreement with $k < 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ from [204].

As it has been discussed before, there are no evidences that peroxyl radicals react with DMSe via 1-e-transfer mechanism, i.e. reaction 3.68 (Scheme 3.2) is giving 100% yield of corresponding alkoxyl radicals. Hence, reaction 3.68 is a major route to DMSeO ($G = 3.0$, or 86% from the overall DMSeO yield). Up to $G(\text{DMSeO}) = 0.2$ is expected from the disproportionation of [(CH$_3$)$_2$Se]$_2$•+ species and the rest $G(\text{DMSeO}) = 0.3$ is coming from the oxidation of DMSe by side reactions discussed above.

Alkoxyl radicals may undergo Cl atoms cleavage, accompanied with the formation of formyl chloride (reaction 3.69). Chlorine atoms are rapidly scavenged by 2-PrOH ($k_{3.70\text{a,b}} = 6 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ [205] at used [2-PrOH] = 0.13 mol dm$^{-3}$, $t_{1/2} = 0.9$ ns). It means that in the studied systems a possible reaction of Cl atoms with DMSe has no chance to compete with reactions 3.70a,b. Hence, CHCl$_2$O• radicals are the only oxidant responsible for the generation of [(CH$_3$)$_2$Se]$_2$•+. Based on the yield of [(CH$_3$)$_2$Se]$_2$•+, the fraction of CHCl$_2$O• radicals reacting with DMSe is equal to $\approx 17\%$. 49
Table 3.6. Reductive degradation of CF and BF in 0.01 mol dm\(^{-3}\) air-saturated aqueous solution containing 1% 2-PrOH in the presence and in the absence of 0.001 mol dm\(^{-3}\) DMSe. Intermediates, products and their yields (G-values). Dose rate 0.37 Gy s\(^{-1}\).

<table>
<thead>
<tr>
<th>Product</th>
<th>CF + DMSe</th>
<th>CF without DMSe</th>
<th>BF + DMSe</th>
<th>BF without DMSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHal</td>
<td>9.0</td>
<td>9.0</td>
<td>19.5</td>
<td>81</td>
</tr>
<tr>
<td>RHalOO(^{a})</td>
<td>3.0</td>
<td>3.0</td>
<td>6.5</td>
<td>27</td>
</tr>
<tr>
<td>DMSeO</td>
<td>3.5</td>
<td>-</td>
<td>6.5</td>
<td>-</td>
</tr>
<tr>
<td>[DMSe](^{2+})</td>
<td>0.5</td>
<td>-</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>2.8</td>
<td>0.4</td>
<td>6.2</td>
<td>4.0</td>
</tr>
<tr>
<td>HCO(_2)H</td>
<td>0.15</td>
<td>2.3(^{b})</td>
<td>0.2</td>
<td>23(^{b})</td>
</tr>
<tr>
<td>MetSO</td>
<td>-</td>
<td>2.3(^{b})</td>
<td>-</td>
<td>23(^{b})</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>&lt; 0.1</td>
<td>0.3</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Acetone(^{c})</td>
<td>2.2</td>
<td>2.0</td>
<td>1.7</td>
<td>25.5</td>
</tr>
<tr>
<td>Total Carbon(^{d})</td>
<td>3.0</td>
<td>3.0</td>
<td>6.5</td>
<td>27</td>
</tr>
</tbody>
</table>

\(^{a}\) – calculated as \(G(HHal)/3\); \(^{b}\) – determined after treatment of irradiated samples with 0.002 mol dm\(^{-3}\) MetS (the reaction of FPA with methionine is fast and leads to 100% yields of formic acid and MetSO); \(^{c}\) – extra-yield of acetone determined as a difference of acetone yields in the studied systems and the one obtained in air-saturated solution containing 1 vol. % of 2-PrOH (due to the reaction of \(\cdot\)OH with 2-PrOH); \(^{d}\) – the sum of the radiation yields of all carbon-containing products derived from CF or BF.

Dichloromethanol, formed in reaction 3.71, is rapidly losing HCl as geminal chlorohydrine, leading to formyl chloride which decomposes mostly to carbon monoxide besides of minor yield of formic acid (reactions 3.72, 3.55 and 3.56). The ratio \(G(HCO\(_2\)H)/G(CO) = 0.15/2.8\) agrees very well with the 6% yield of formic acid from formyl chloride [137]. In the present system Cl atoms are the only species responsible for the extra-acetone formation \((G = 2.2)\) as a result of oxygen addition to 2-hydroxyprop-2-yl radicals generated in reaction 3.70a. Hence reactions 3.68 and 3.70a together correspond to \(G = 2.7\), which is 90% of the available alkoxyl radicals. The remaining 10% missing could be explained by the assumption that Cl atoms, in analogy to \(\cdot\)OH radicals, may abstract H atoms also from methyl groups of 2-PrOH giving \(\cdot\)CH\(_2\)CH(CH\(_3\))OH radicals (reaction 3.70b), which do not result in acetone in their further transformations.

Reaction 3.69 is the basic one for Scheme 3.2. The question is whether there are some alternative routes which might lead to Cl atoms and formyl chloride and/or carbon monoxide as well. Isomerization via 1,2–H atom shift will lead to \(\alpha\)-hydroxyalkyl radicals which may undergo fast oxygen addition with rapid HO\(_2\)\(^{\cdot}\) elimination and formation of phosgene (see reactions 3.73a-c). The latter will hydrolyse giving carbon dioxide. Since carbon dioxide has not been found \((G \leq 0.1)\), reactions 3.73b,c can be neglected.
Scheme 3.2

\[
\text{CHCl}_2\text{OO}^* + (\text{CH}_3)_2\text{Se} \rightarrow \text{CHCl}_2\text{O}^* + (\text{CH}_3)_2\text{SeO} 
\]

(3.68)

\[
\text{CHCl}_2\text{O}^* \rightarrow \text{Cl}^* + \text{HC(O)Cl} 
\]

(3.69)

\[
\text{Cl}^* + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{HCl} + (\text{CH}_3)_2\text{C}^*\text{OH/CH}_2\text{CH(CH}_3\text{)OH} 
\]

(3.70a,b)

\[
\text{CHCl}_2\text{O}^* + (\text{CH}_3)_2\text{Se} + \text{H}^+ \rightarrow \text{CHCl}_2\text{OH} + (\text{CH}_3)_2\text{Se}^* 
\]

(3.71)

\[
\text{CHCl}_2\text{OH} \rightarrow \text{HCl} + \text{HC(O)Cl} 
\]

(3.72)

\[
\text{CHCl}_2\text{O}^* \rightarrow \text{CCl}_2\text{OH} \rightarrow \text{HO}_2^* + \text{COCl}_2 
\]

(3.73 a,b,c)

Formed in reaction 3.73a, \text{CCl}_2\text{OH} radicals may alternatively undergo fast HCl elimination reaction :

\[
\text{CCl}_2\text{OH} \rightarrow \text{HCl} + \text{O=C}^*\text{–Cl} 
\]

(3.74)

Radicals O=C^*–Cl potentially may decompose to carbon monoxide and a Cl atom (reaction 3.75), pretending to be one of the major routes of alkoxyl radical disappearance in the present system. However, according to [206, 207] C-Cl bond energy in formylchloride radical is equal to 30 kJ mol\(^{-1}\). This is high enough to guarantee a sufficient lifetime of the latter to react with oxygen (reaction 3.76).

Experimental evidence has been found in [208] that reaction 3.76 is strongly dominating over reaction 3.75. Carbon dioxide is an ultimate product from further transformation of O=CClOO* radicals [208]. Due to a very small yield of CO\(_2\), if formed at all, a sequence of reactions 3.73a, 3.74 and 3.76 can be neglected. Therefore, the only likely source of Cl atoms is reaction 3.69, which is the major feature of the CHCl\(_2\)O* radical decay mechanism in the studied system. Chlorine atom elimination is a dominant pathway also for the decomposition of CHCl\(_2\)O* radicals in the gas phase as it has been established in the work [209] based on \textit{ab initio} calculations.

\[
\text{O=C}^*\text{–Cl} \rightarrow \text{CO} + \text{Cl}^* 
\]

(3.75)

\[
\text{O=C}^*\text{–Cl} + \text{O}_2 \rightarrow \text{O=CClOO}^* 
\]

(3.76)

3.4.5. Chloroform degradation in the absence of dimethylselenide

As it can be seen from Table 3.6, the yields of the products derived from CF in the absence and in the presence of DMSe are very different. Despite the same chloride yield of \(G = 9.0\), the CO yield is lower by almost one order of magnitude, indicating a very low yield of CHCl\(_2\)O* radicals in the absence of DMSe. On the other hand, the formic acid yield, after immediate treatment of the irradiated solution with 2 \(\times\) 10\(^{-3}\) mol dm\(^{-3}\) solution of methionine (MetS), is now increased by more then 10 times, \(G = 2.3\). This is equal to \(G(\text{MetSO})\) in the
system with DMSe present. The kinetics of conductance build-up upon the mixing of irradiated solution with MetS in the conductivity cell is identical to one obtained for the reaction of MetS with formic peracid (FPA) in a separate experiment. On the other hand, $G_{\text{FPA}}$ is close to $G_{\text{acetone}} = 2.0$, which means that the majority of FPA ($G = 2.0$ from overall $G = 2.3$) is coming from the transformations of CHCl$_2$OOH, formed via H atom abstraction from 2-PrOH by CHCl$_2$O• radicals (reaction 3.77). 2-PrOH contains a weak secondary C–H bond which can easily be cleaved in reactions with free radicals. However quantitative kinetic data about such a reaction are not available so far. The only known estimation is $k_{3.78} < 7 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ [210]:

$$\text{CHCl}_2\text{OO}^\bullet + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{CHCl}_2\text{OOH} + (\text{CH}_3)_2\text{C}^\bullet\text{OH} \tag{3.77}$$

$$\text{CCl}_3\text{OO}^\bullet + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{CCl}_3\text{OOH} + (\text{CH}_3)_2\text{C}^\bullet\text{OH} \tag{3.78}$$

Transformations of CHCl$_2$OOH into PFA could be rationalized by equations 3.79 and 3.80.

$$\text{CHCl}_2\text{OOH} \xrightarrow{H^+} \text{HCl} + \text{HOCHClOOH} \tag{3.79}$$

$$\text{HOCHClOOH} \rightarrow \text{HCl} + \text{HC(O)OOH} \tag{3.80}$$

The rate constants for individual steps of these transformations are unknown. However, it is very likely that reaction 3.79, leading to α-hydroxyhydroperoxides, is the rate determining step. Reaction 3.80 illustrates fast HCl elimination from α-chlorohydrine leading finally to FPA. To the best of our knowledge, formation of peracids due to the free-radical degradation of halogenated hydrocarbons, has not been described so far.

Additional $G_{\text{FPA}} = 0.3$ (corresponding to 10% of the overall CF degradation) could be explained by the cross-termination between CHCl$_2$O• and superoxide radicals

$$\text{CHCl}_2\text{OO}^\bullet + \text{O}_2^\cdot + H^+ \rightarrow \text{CHCl}_2\text{OOH} + \text{O}_2 \tag{3.81}$$

To confirm reaction 3.81, CF radiolysis was conducted also in the presence of t-BuOH used as an *OH radical scavenger instead of 2-PrOH. Because of the relatively strong C-H bonds in t-BuOH compared to 2-PrOH, a reaction like 3.77 is impossible with t-BuOH, i.e. the reaction 3.81 is the only source of the halogenated hydroperoxide in this system. After radiolysis and MetS treatment, the experimentally found $G_{\text{FPA}} = 0.5$ corresponds to 17% of the yield of FPA based on $G_{\text{CHCl}_2\text{OO}^\bullet} = 2.9$ determined in this system.

In competition to reactions 3.77 and 3.81, peroxyl radicals from CF will undergo also self-termination reactions. Since CO$_2$ and CO are considered to be the major termination products, both formed with $G = 0.3$, the most likely termination mechanism could be the Russell’s one:

$$2 \text{CHCl}_2\text{OO}^\bullet \rightarrow \text{O}_2 + \text{CHCl}_2\text{OH} + \text{COCl}_2 \xrightarrow{H^+} 4 \text{HCl} + \text{CO} + \text{CO}_2 \tag{3.82 a,b,c}$$

Contribution of the self-termination step is calculated as ≈ 27%.

It is worth mentioning that the data for the system without DMSe clearly show that CHCl$_2$O• radicals (the same is true for CHBr$_2$O•, see below) are not reacting with DMSe via a 1-e oxidation mechanism (directly or via addition-elimination steps). Otherwise,
halogenated peroxyl anions formed in this reaction, and after their fast protonation, would give corresponding hydroperoxides leading to FPA, which should react further with DMSe to DMSeO and formic acid. The latter, however, was found in only a very minor yield.

3.4.6. Bromoform degradation in the presence of dimethylselenide

In both BF-containing systems halogenated peroxyl radicals are generated much more efficiently compared to the analogue CF-containing systems (see Table 3.4). In the presence of DMSe, extra $G(–BF)$ is calculated from $G(–BF)_{\text{experiment}} – G(–BF)_{\text{H}\text{•} + \text{e}_{\text{aq}}^{-}} = 6.5 – 3.0 = 3.5$, which is due to efficient reduction of BF by 2-hydroxyprop-2-yl radicals ($\text{(CH}_3\text{)}_2\text{C}\text{•}\text{OH}$):

$$\text{(CH}_3\text{)}_2\text{C}\text{•}\text{OH} + \text{CHBr}_3 \rightarrow \text{HBr} + (\text{CH}_3\text{)}_2\text{CO} + \text{•CHBr}_2$$  \hspace{1cm} (3.83)

Based on the rate constant $k_{3.83} = 4.6 \times 10^{8} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (determined by us in a separate experiment), known $k = 4.2 \times 10^{9} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (for (CH$_3$)$_2$C•OH + O$_2$) [211] and applied concentrations of BF and oxygen, it is calculated that $\approx 80 \%$ of all (CH$_3$)$_2$C•OH react with BF and the remaining 20 % is scavenged by oxygen. Observed $G(2\text{-hydroxyprop-2-yl radicals}) = 4.4$, all of which are quantitatively leading to acetone. Indeed, G(acetone) = 4.4 was observed. Since CHBr$_2$OO• radicals react with DMSe giving exclusively DMSeO and CHBr$_2$O• radicals ($G = 6.5$), only the latter could be responsible for the observed extra-yield of acetone. The most likely reaction would be a fast bromine atom elimination from alkoxyl radical:

$$\text{CHBr}_2\text{O•} \rightarrow \text{Br•} + \text{HC(O)Br}$$  \hspace{1cm} (3.84)

As it was illustrated for the gas-phase [212], reaction 3.84 is the only important one for CHBr$_2$O• degradation, occurring with $k > 4 \times 10^{6} \text{ s}^{-1}$ at 298 K and 700 Torr total pressure. In analogy to HC(O)Cl, formylbromide formed in reaction 3.84 will mostly decompose giving CO, whereas a very minor fraction hydrolyses to formic acid (for details see section 4.2). The ratio of the yields of these products confirms that both of them are originating from a common precursor, i.e. formylbromide. On the other hand, the absence of carbon dioxide is ruling out all other reactions than reaction 3.84 for the alkoxyl radical disappearance (for example, reactions 3.73, 3.75 + 3.76 in the case of CF).

Bromine atoms react with 2-PrOH presumably in the same way as *OH radicals, namely via abstraction of H atoms from $\alpha$- or $\beta$-C position (reaction 3.85a should strongly dominate)

$$\text{Br•} + (\text{CH}_3\text{)}_2\text{CHOH} \rightarrow \text{HBr} + (\text{CH}_3\text{)}_2\text{C•OH/•CH}_2\text{CH(CH}_3\text{)}\text{OH}$$  \hspace{1cm} (3.85 a,b)

The yield of acetone via reaction 3.85a can be calculated as $G = 2.0$, taking the difference between the observed yield of acetone and the one calculated from the reaction of 2-PrOH with *OH radicals (4.4 and 2.4, respectively). Then, the remaining $G(\text{Br•}) = 4.3$ should have reacted with DMSe, giving $G([\text{DMSe}_2\text{•}^+]) = 4.3$. The yield of the latter species is equal to 90 % Br atoms available. Based on the yields of extra-acetone and (DMSe)$_2$•$^+$ and $k_{3.85a} = 1.8 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction of Br atoms with 2-PrOH (determined by us in a separate experiment), the rate constant $k_{3.86a} = 4.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ can be estimated. The latter
value is close to the one obtained for the reaction of \(^{\cdot}\)OH radicals with DMSe [194], confirming the high reactivity of DMSe in both reactions.

\[
\text{Br}^{\cdot} + \text{DMSe} \rightarrow \text{Br}^{-} + (\text{DMSe})_2^{\cdot+}
\]  

(3.86 a,b)

In the present system \(G(\text{DMSe})_2^{\cdot+} = 6.5\) is equal to \(G(\text{CHBr}_2\text{OO}^{\cdot})\) and, therefore, there is no reason to consider \((\text{DMSe})_2^{\cdot+}\) to be involved into DMSeO formation. We assume, that \((\text{DMSe})_2^{\cdot+}\) in BF-containing system decay mostly via interaction with superoxide or deprotonation:

\[
(\text{DMSe})_2^{\cdot+} + \text{O}_2^{\cdot-} \rightarrow 2 \text{DMSe} + \text{O}_2
\]  

(3.87)

\[
(\text{DMSe})_2^{\cdot+} \rightarrow \text{H}^{\cdot} + \cdot\text{CH}_2\text{SeCH}_3 + \text{(CH}_3)_2\text{Se}
\]  

(3.88)

### 3.4.7. Bromoform degradation in the absence of dimethylselenide

BF degradation proceeds in this case via a free-radical chain mechanism. The measured \(G(\text{CHBr}_2\text{OO}^{\cdot}) = 27\) is about 5 times higher than the initial value of \(G(\text{CHBr}_2\text{OO}^{\cdot}) = 5.0\) calculated from the yields of \(e_{\text{aq}}^{-}\), \(\cdot\text{H}\) and \((\text{CH}_3)_2\text{C}^{\cdot}\text{OH}\) reacting with BF. This means that about 80 % of CHBr\(_2\text{OO}^{\cdot}\) radicals \((G = 22)\) have been formed in the propagation step which includes H-abstraction from 2-PrOH by CHBr\(_2\text{OO}^{\cdot}\) (in analogy to reaction 3.77) followed by fast oxygen addition to CHBr\(_2^{\cdot}\). The halogenated hydroperoxide formed in the former reaction ends up as FPA (in analogy to reactions 3.79-3.80). Experimentally found DMSeO and FPA yields are equal \((G = 23)\) and are only very slightly exceeding the expected one. This small excess, namely \(G = 1.0\) may just reflect the error limit, but could also be attributed to the competing cross-termination reaction of CHBr\(_2\text{OO}^{\cdot}\) with superoxide (in analogy to reaction 3.81). To confirm such a reaction, BF degradation was conducted also in the presence of t-BuOH instead of 2-PrOH. The yield of FPA was reaching 20 % from that of \(G(-\text{BF})\) at those conditions, similarly to the CF system with t-BuOH. The remaining \(G(\text{CHBr}_2\text{OO}^{\cdot}) = 4.0\) (a difference between total \(G = 27\) and \(G(\text{FPA}) = 23\)) which are not involved into the propagation step or cross-termination with superoxide should undergo self-termination leading exclusively to carbon monoxide. Self-termination via Russell’s mechanism and concerted mechanisms should be disregarded due to the absence of \(\text{CO}_2\) as a product. Therefore, the only termination mechanism satisfying all experimental data is reaction 3.89, i.e. formation of two alkoxyl radicals which suffer bromine atom cleavage (reaction 3.84)

\[
\text{CHBr}_2\text{OO}^{\cdot} \rightarrow 2 \text{CHBr}_2\text{O}^{\cdot} + \text{O}_2
\]  

(3.89)

Finally, an expected \(G(\text{acetone})_{\text{extra}} = 26\) can be calculated as a sum of the yields from the reaction of CHBr\(_2\text{OO}^{\cdot}\) with 2-PrOH \((G = 22.0)\) and reaction 3.89 \((G = 4.0)\). The experimentally observed value \(G(\text{acetone})_{\text{extra}} = 25.5\) is very close to this value.
3.4.8. Carbon tetrachloride degradation in the presence and in the absence of dimethylselenide

Interaction of CCl$_3$OO$^*$ with DMSe may occur via two pathways, namely e-transfer (reaction 3.90) or via formation of alkoxyl radicals and DMSeO (reaction 3.91):

$$ \text{CCl}_3\text{OO}^* + 2 \text{DMSe} \rightarrow \text{CCl}_3\text{OO}^- + (\text{DMSe})_2^{++} \quad (3.90) $$

$$ \text{Cl}_3\text{OO}^* + \text{DMSe} \rightarrow \text{CCl}_3\text{O}^* + \text{DMSeO} \quad (3.91) $$

$$ \text{CCl}_3\text{O}^* + 2 \text{DMSe} \rightarrow \text{CCl}_3\text{O}^- + (\text{DMSe})_2^{++} \quad (3.92) $$

$$ \text{CCl}_3\text{O}^* \rightarrow \text{Cl}^* + \text{CCl}_2\text{O} \quad (3.93) $$

$$ (\text{CH}_3)_2\text{C}^*\text{OH} + \text{CCl}_4 \rightarrow \text{HCl} + \text{CCl}_3^* + (\text{CH}_3)_2\text{CO} \quad (3.94) $$

Table 3.7. Reductive degradation of CT in its 0.01 mol dm$^{-3}$ air-saturated aqueous solution containing 1 vol. % 2-PrOH in the presence and in the absence of 0.001 mol dm$^{-3}$ DMSe. Products and their radiation yields ($G$-values). Dose rate 0.37 Gy s$^{-1}$.

<table>
<thead>
<tr>
<th>Product</th>
<th>with DMSe</th>
<th>without DMSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>12.8</td>
<td>14.8</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.2</td>
<td>3.7</td>
</tr>
<tr>
<td>DMSeO</td>
<td>3.7</td>
<td>-</td>
</tr>
<tr>
<td>Acetone (corrected)</td>
<td>1.9</td>
<td>3.9</td>
</tr>
</tbody>
</table>

As it was shown above for the case of DCM, CF and BF, corresponding alkoxyl radicals, or a product derived from them are responsible for the generation of (DMSe)$_2^{++}$ dimer radical cations. If in the case of CT the latter species came directly from the reaction of primary peroxy radicals with DMSe (reaction 3.90), then a significant deficit of $G$(DMSeO) compared to $G$(CCl$_3$OO$^*$) should be observed. This is, however, not the case. Therefore, it is postulated that in the present system all CCl$_3$OO$^*$ radicals are also transformed into corresponding alkoxyl radicals via reaction with DMSe (reaction 3.91). Some part of CCl$_3$O$^*$ oxidizes DMSe to (DMSe)$_2^{++}$(reaction 3.92, $G = 0.95$), the rest is undergoing chlorine atom elimination (reaction 3.93, $G = 2.25$). Chlorine atoms will react with 2-PrOH via reactions 3.70 a,b. According to Table 3.7, the extra-yield of acetone is equal to $G = 1.9$, which is giving 84 % and 16 % contributions for the reactions 3.70a and 3.70b, respectively. 2-Hydroxyprop-2-yl radicals react predominantly with oxygen (84%) and a minor part is reducing CT via reaction 3.94, causing some extra yield of CT degradation ($G = 0.7$) in addition to $G$(CT) $= 2.5$ via reaction with electrons. The rate constant $k_{3.94} = 7.6 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ calculated from these data is very close to the experimentally determined value of 1 x 10$^8$ dm$^3$ mol$^{-1}$ s$^{-1}$ measured by pulse radiolysis with conductivity detection [159].

In the absence of DMSe, CCl$_3$OO$^*$ radicals react with 2-PrOH via H abstraction:
CCl\textsubscript{3}OO\textsuperscript{*} + (CH\textsubscript{3})\textsubscript{2}CHOH \rightarrow CCl\textsubscript{3}OOH + (CH\textsubscript{3})\textsubscript{2}C\textsuperscript{*}OH \hspace{1cm} (3.95)

The reactivity of CCl\textsubscript{3}OO\textsuperscript{*} radicals in this reaction should be higher than that for CHCl\textsubscript{2}OO\textsuperscript{*} radicals, 2/3 of which are reacting with 2-PrOH and 1/3 undergoing termination routes (see discussion above). In analogy to CHCl\textsubscript{2}OOH transformation, further reactions of CCl\textsubscript{3}OOH can be formulated as follows

\[ \text{CCl}_3\text{OOH} \xrightarrow{H, \delta} \text{HCl} + \text{HOCCl}_2\text{OOH} \rightarrow \text{HCl} + \text{ClC(O)OOH} \] \hspace{1cm} (3.96 a,b)

\[ \text{Cl-C(O)OOH} \xrightarrow{H, \delta} \text{HCl} + \text{HOC(O)OOH} \] \hspace{1cm} (3.97)

### 3.4.9. The fate of halogenated oxyl radicals

As it appears from the results and discussion above, the reaction of halogenated peroxyl radicals with DMSe is leading to quantitative transformation into corresponding oxyl radicals. Some part of the latter species further oxidizes DMSe. The rest is undergoing a 1,2-H shift reaction (as was found for DCM and DBM systems) or suffers C-Hal cleavage via halogen atom elimination (see CF and BF systems).

To better understand the difference of reactive fates of the discussed oxyl radicals quantum chemical calculations have been performed taking into account the influence of water as a continuum. As it appears from Table 3.8, cleavage of halogen atoms from CH\textsubscript{2}ClO\textsuperscript{*} and CH\textsubscript{2}BrO\textsuperscript{*} radicals is an endothermic process, especially for the first species (\( \Delta H = 68.6 \text{ kJ mol}^{-1} \)). In contrast, the 1,2-H shift is an exothermic process with \( \Delta H = -17.6 \) and -20.9 kJ mol\(^{-1}\), respectively. Despite that these reactions possess high activation energies (\( E_a \) in the range of 140 kJ mol\(^{-1}\)), the latter are most likely strongly reduced by water assistance (in a 5-member ring transition state), which could not be fully estimated in our calculations. In the case of more substituted oxyl radicals such as CHCl\textsubscript{2}O\textsuperscript{*} and CHBr\textsubscript{2}O\textsuperscript{*} both type of reactions are exothermic. Elimination of chlorine atom from CHCl\textsubscript{2}O\textsuperscript{*} species is about 26 kJ mol\(^{-1}\) less exothermic compared to isomerization. However, an extraordinary large difference of the corresponding activation energies (9.6 vs. 125 kJ mol\(^{-1}\)) gives a much higher probability for the chlorine atom abstraction. This trend will be even more pronounced for CHBr\textsubscript{2}O\textsuperscript{*} radicals. Elimination of Cl\textsuperscript{*} is an exclusive reaction of the alkoxyl radicals derived from CT having almost zero \( E_a \) and high exothermicity of \( \Delta H = -74.4 \text{ kJ mol}^{-1} \).

Below is given a list of the major reactions of the studied halogenated oxyl radicals together with the estimated rate constants. The latter were calculated based on the determined rate constants for oxidation of DMSe by the corresponding RH\textsubscript{a}OO\textsuperscript{*} radicals and the yields of (DMSe)\textsubscript{2}\textsuperscript{•+} (see Table 3.3), taking [DMSe] = 1 \times 10^{-3} \text{ mol dm}^{-3}.

\[ \text{CH}_2\text{ClO}^\text{*} \rightarrow \cdot\text{CHCl(OH)} \hspace{1cm} k_{3.53} = 3.6 \times 10^5 \text{ s}^{-1} \] \hspace{1cm} (3.53)

\[ \text{CH}_2\text{BrO}^\text{*} \rightarrow \cdot\text{CHBr(OH)} \hspace{1cm} k_{3.53} = 1.5 \times 10^5 \text{ s}^{-1} \] \hspace{1cm} (3.53)

\[ \text{CHCl}_2\text{O}^\text{*} \rightarrow \text{Cl}^\cdot + \text{HC(O)Cl} \hspace{1cm} k_{3.69} = 1.3 \times 10^6 \text{ s}^{-1} \] \hspace{1cm} (3.69)

\[ \text{CHBr}_2\text{O}^\text{*} \rightarrow \text{Br}^\cdot + \text{HC(O)Br} \hspace{1cm} k_{3.84} > 2.6 \times 10^6 \text{ s}^{-1} \] \hspace{1cm} (3.84)
CCl$_3$O$^\bullet$ → Cl$^\bullet$ + CCl$_2$O  \hspace{1cm} k_{3.93} = 4.3 \times 10^5 \text{ s}^{-1}  \hspace{1cm} (3.93)

Table 3.8. Activation energies $E_a$ (kJ mol$^{-1}$) and reaction enthalpies $\Delta H$ (kJ mol$^{-1}$) calculated in water with B3LYP/6-31G(d,p)//SCRF=PCM for the reactions of halogenated methyloxyl radicals.

<table>
<thead>
<tr>
<th>Alkoxy radical</th>
<th>Reaction</th>
<th>Products</th>
<th>$E_a$, kJ mol$^{-1}$</th>
<th>$\Delta H$, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$ClO$^\bullet$</td>
<td>H-shift</td>
<td>*CHClOH</td>
<td>137</td>
<td>-17.6</td>
</tr>
<tr>
<td>CH$_2$ClO$^\bullet$</td>
<td>X-abstr.</td>
<td>Cl$^\bullet$ + CH$_2$O</td>
<td>-</td>
<td>+68.6</td>
</tr>
<tr>
<td>CH$_2$BrO$^\bullet$</td>
<td>H-shift</td>
<td>*CHBrOH</td>
<td>146</td>
<td>-20.9</td>
</tr>
<tr>
<td>CH$_2$BrO$^\bullet$</td>
<td>X-abstr.</td>
<td>Br$^\bullet$ + CH$_2$O</td>
<td>-</td>
<td>+26.4</td>
</tr>
<tr>
<td>CHCl$_2$O$^\bullet$</td>
<td>H-shift</td>
<td>*CCl$_2$OH</td>
<td>125</td>
<td>-32.6</td>
</tr>
<tr>
<td>CHCl$_2$O$^\bullet$</td>
<td>X-abstr.</td>
<td>Cl$^\bullet$ + CHClO</td>
<td>9.6</td>
<td>-6.7</td>
</tr>
<tr>
<td>CHBr$_2$O$^\bullet$</td>
<td>H-shift</td>
<td>*CBr$_2$OH</td>
<td>126</td>
<td>-25.0</td>
</tr>
<tr>
<td>CHBr$_2$O$^\bullet$</td>
<td>X-abstr.</td>
<td>Br$^\bullet$ + CHBrO</td>
<td>10.5</td>
<td>-25.5</td>
</tr>
<tr>
<td>CCl$_3$O$^\bullet$</td>
<td>X-abstr.</td>
<td>Cl$^\bullet$ + COCl$_2$</td>
<td>2.1</td>
<td>-74.4</td>
</tr>
</tbody>
</table>

The 1,2-H shift reaction is a major one for CH$_2$ClO$^\bullet$ and CH$_2$BrO$^\bullet$ radicals. The respective rate constants for the latter species is 2 times lower compared to those for the chlorinated analogues. This could be explained by a larger size of the bromine atom and, as a result, slower water entrance to the 5-membered transition state. For the same reason the 1,2-H shift in the more substituted radicals CHCl$_2$O$^\bullet$ and CHBr$_2$O$^\bullet$ is most likely even more inhibited. On the other hand, the energy of C-Hall bonds in these species are much lower compared to the less substituted analogues. As a result, halogen atom elimination becomes a major reaction of CHCl$_2$O$^\bullet$ and CHBr$_2$O$^\bullet$ radicals. An estimation of $k_{3.84} > 2.6 \times 10^6 \text{ s}^{-1}$ was derived from the fact, that at $[\text{DMSe}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $k_{\text{obs.}} = 2.6 \times 10^5 \text{ s}^{-1}$ represents the rate-determining step, i.e. reaction of CHBr$_2$OO$^\bullet$ with DMSe. Assuming 10 % error for a radiation chemical experiment, reaction 3.84 should be at least 10 times faster.

3.5. Radiation Chemistry of Halogenated Anaesthetics. The Mechanism of Radical-Induced Degradation of Halothane and the Fate of its Alkoxy Radicals

As it has been shown in the previous section, the organic selenide DMSe can be successfully used as 2-e donor to transform RHalOO$^\bullet$, derived from halogenated methanes, into corresponding RHalO$^\bullet$. This section represents another system leading to the same principal results. It is based on halothane as a source of peroxy radicals, and methionine, CH$_3$SCH$_2$CH$_2$CH(NH$_3^+$)CO$_2^-$ (MetS), as a marker for the free-radical oxidation processes.
Table 3.9 summarizes the various products and their yields, which have been obtained upon γ-irradiation of an aqueous, air-saturated, pH 6 solution containing 5% t-BuOH, $10^{-2}$ mol dm$^{-3}$ or no CF$_3$CHClBr, and $10^{-3}$ mol dm$^{-3}$ or no MetS [6].

Table 3.9. Reductive degradation of halothane in 10 mM air-saturated aqueous solution containing 5 vol. % t-BuOH in the absence or presence of 1 mM MetS. Products and their yields ($G$-values). Dose rate 0.3 Gy s$^{-1}$.

<table>
<thead>
<tr>
<th>Product</th>
<th>Without MetS (system I)</th>
<th>With MetS (system II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBr</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>HCl</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>HF</td>
<td>0.4</td>
<td>6.1</td>
</tr>
<tr>
<td>CF$_3$C(O)OH (TFAA)</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>CF$_3$CHO (TFAAld)</td>
<td>1.7</td>
<td>0</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.15</td>
<td>3.8</td>
</tr>
<tr>
<td>HC(O)OH</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>HO(O)CC(O)OH</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>CO</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>MetSO</td>
<td>–</td>
<td>5.6</td>
</tr>
<tr>
<td>Total Fluorine</td>
<td>10.3 (100%)</td>
<td>10.3 (100%)</td>
</tr>
<tr>
<td>Total carbon</td>
<td>6.8 (100%)</td>
<td>6.6 (&gt; 97%)</td>
</tr>
</tbody>
</table>

The yield of bromide ions identifies the yield of halothane reduction (eq. 3.98) and, since the follow-up reaction of the thus formed CF$_3$C•HCl radical with O$_2$ (eq. 3.99) is fast and quantitative, also equal to the yield of CF$_3$CHClOO• peroxyl radicals. As can be seen there is no difference between the system with and without MetS up to this point.  

\[
\text{CF}_3\text{CHClBr} + e_{aq}^- / \text{reducing radicals} \rightarrow \text{CF}_3\text{C}^*\text{HCl} + \text{Br}^- \tag{3.98}
\]

\[
\text{CF}_3\text{C}^*\text{HCl} + \text{O}_2 \rightarrow \text{CF}_3\text{CHClOO}^* \tag{3.99}
\]

It is noted that the chloride yield also quantitatively matches the bromide and peroxyl yields. Almost equal yields in both systems with and without MetS are also observed for TFAA, although, as will be shown below, they are formed via different routes. The yields of CO and oxalate are almost negligible ($G < 0.1$). Dramatic differences become apparent, however, for the yields of the other products. Fluoride ions and CO$_2$ are practically only formed in the presence of MetS, while TFAAld is generated only in its absence. It should
further be recognized that the MetSO yield is almost negligible in a system which was devoid of halothane. Finally, it should be noted that the MetSO yield in the halothane systems significantly exceeds the yield of primary peroxyl radicals ($G = 5.6$ vs $3.4$). All this clearly shows that (i) the peroxyl radicals derived from halothane induce an oxidation different to that of typical one-electron oxidants, and (ii) the peroxyl radical alone, nevertheless, cannot account for the entire MetSO yield.

In the system without MetS the halothane peroxyl radicals will exclusively undergo a bimolecular termination process. The most likely will be the Russell mechanism (see section 3.3) yielding equal amounts of trifluoroacetyl chloride, CF$_3$C(O)Cl, and 1,1,1-trifluoro-2-chloroethanol, CF$_3$CH(OH)Cl (eq. 3.100).

$$2 \text{CF}_3\text{CHClOO}^* \rightarrow \text{O}_2 + \text{CF}_3\text{C(O)Cl} + \text{CF}_3\text{CH(OH)Cl}$$ (3.100)

Hydrolysis of these compounds directly yields the observed products, CF$_3$CO$_2^-$ + Cl$^-$, and CF$_3$CHO + Cl$^-$. For an initial peroxyl radical yield of $G = 3.4$, the expected TFAA, TFAAld and chloride yields would be 1.7, 1.7 and 3.4, respectively, in agreement with the experimentally measured values (see Table 3.9).

In the system with MetS a bimolecular radical-radical termination cannot compete anymore with a peroxyl radical reaction with the MetS. A possible one-electron oxidation to yield either the sulfur-oxidized radical cation Met(S$^{**}$) or its three-electron bonded dimer (MetS : : SMet)$^+$ together with the hydroperoxide CF$_3$CHClOOH (reaction 3.101) can practically be discarded. Neither these radical cations could be detected at significant yields in time-resolved pulse radiolysis nor the one-electron oxidation initiated by $^*$OH and other typical 1 electron-oxidants leads to such high sulfoxide yields [80].

$$\text{CF}_3\text{CHClOO}^* + \text{MetS} \rightarrow \text{CF}_3\text{CHClO}^- + \text{Met(S}^{**})$$ (3.101)

We can reasonably assume that the efficiency of the sulfoxide formation via reaction 3.102 is close to 100%, i.e. $G$(MetSO) generated this way is equal to the yield of CF$_3$CHClOO$^*$ radicals, $G = 3.4$):

$$\text{CF}_3\text{CHClOO}^* + \text{MetS} \rightarrow \text{CF}_3\text{CHClO}^* + \text{MetSO}$$ (3.102)

This, in turn, means that the remainder of $G = 2.2$ to the actually measured yield ($G = 5.6$) must be formed in secondary processes. Not yet accounted for are also the yields of fluoride, CO$_2$, and TFAA. Consequently, we conclude that the CF$_3$CHClO$^*$ oxyl radical, the only remaining reactive radical species, must be responsible, directly and/or indirectly, for all other products listed in Table 3.9 for the MetS containing system.

Oxyl radicals offer, in general, a greater wealth of reaction possibilities than peroxyl radicals. A prominent property of oxyl radicals is, for example, their capability to undergo one-electron oxidations [71]. With respect to MetS such a reaction would yield the sulfur-centered MetS radical cation and TFAAld (eq. 3.103) both of which were not detected. Consequently, this possibility must be discarded.
\[
\text{CF}_3\text{CHClO}^\bullet + \text{MetS} \rightarrow \text{CF}_3\text{CHClO}^- + \text{Met(S}^\bullet) 
\]  \hspace{1cm} (3.103)

The same applies to a possible H-atom abstraction by the oxyl radical from any suitable functional group (eq. 3.104). Hydrolysis of the chloroalcohol formed in this reaction would also lead to the not observed TFAAld.

\[
\text{CF}_3\text{CHClO}^\bullet + \text{RH} \rightarrow \text{R}^\bullet + \text{CF}_3\text{CHClOH} \rightarrow \text{CF}_3\text{CHO} + \text{HCl} 
\]  \hspace{1cm} (3.104 a,b)

Another type of reaction oxyl radicals readily undergo are \(\beta\)-fragmentations [71]. As outlined in Scheme 3.3, two such processes can be envisaged.

**Scheme 3.3**

The first alternative would be cleavage of a chlorine atom. This possibility must, however, be dismissed because of the lack of \(\text{CF}_3\text{CHO}\) formation. The second possibility involves C–C cleavage and formation of trifluoromethyl radicals and formyl chloride. This route must, however, also be neglected because the simultaneously generated formyl chloride should give rise to CO [137], a product which is formed in negligible yield.

**Scheme 3.4**

Hydrogen shift reaction is another reaction oxyl radicals readily undergo [177-179, 196, 197], by which the oxygen-centered radical is converted into a carbon-centered radical, as shown in the first reaction of Scheme 3.4. The newly formed C-centered radical is likely to add oxygen with subsequent fast \(\text{HO}_2^\bullet\) elimination, thereby yielding trifluoroacetyl chloride which subsequently hydrolyzes to TFAA. Assuming that this rearrangement-based
mechanism is indeed the one responsible for the TFAA, the measured yield of the latter \((G = 1.4)\) accounts for about 40\% of the maximum oxyl radical yield \((G \leq 3.4)\).

A competing route leading to high yields of fluoride and CO\(_2\), MetSO is based on the reactions of the rearranged, C-centered radical CF\(_3\)C*Cl(OH) or its hydrolyzed form CF\(_3\)C*(OH)\(_2\). This assumption is based on the results of an *OH-induced oxidation of TFAAld which generates CF\(_3\)C*(OH)\(_2\) and, in the presence of oxygen and MetS, yields all the products in question [6]: CF\(_3\)CO\(_2\), F\(^-\), CO\(_2\) and MetSO (eq. 3.105), as well.

A key question in this proposed mechanism concerns the elimination of fluorine from the CF\(_3\)-group. We hypothesize that this takes place from, e.g., the CF\(_3\)C•(OH)\(_2\) radical, possibly its deprotonated form CF\(_3\)C•(OH)(O\(^-\))\(_2\), as depicted in the encircled section of Scheme 3.5. Elimination of one fluoride ion would leave the difluoroacetyl radical CF\(_2\)CO\(_2\)\(^-\). This, upon oxygen addition, would convert into the OOCF\(_2\)CO\(_2\)\(^-\) radical which could then oxidize additional MetS via the 2-electron mechanism outlined above in Scheme 3.5 and thus account for the still missing MetSO. As a result of this process we would be left with OOCF\(_2\)CO\(_2\)\(^-\) oxyl radicals which are prone for \(\beta\)-fragmentation into CF\(_2\)O and CO\(_2\)*. Hydrolysis of CF\(_2\)O and electron transfer from the CO\(_2\)* to oxygen would finally result in the experimentally observed "mineralization" products.

\[
\text{CF}_3\text{CH(OH)}_2 + \cdot\text{OH} \rightarrow \text{CF}_3\text{C}^*(\text{OH})_2 + \text{O}_2/\text{MetS} \rightarrow \text{CF}_3\text{CO}_2^- + \text{F}^- + \text{CO}_2 + \text{MetSO} \quad (3.105)
\]

In Table 3.10 the results of quantum-chemical calculations for the reactions of halogenated radical-anions related to this study are presented. As can be seen, there is a strong change in the calculated \(\Delta H\) upon the structure of these species. According to calculations \(\Delta H = 76.1 \text{kJ mol}^{-1}\) species CF\(_3\)C*(O\(^-\))CF\(_3\) is not releasing fluoride, which is in a total agreement with experiment [213]. Much lower endothermicity is predicted for species 2 \(\Delta H = 18.8 \text{kJ mol}^{-1}\), which allows fluoride anion elimination as it has been proved experimentally [214]. Fluoride ion elimination from CF\(_3\)C*(O\(^-\))OH species is about 40 kJ mol\(^{-1}\) more favourable compared to species CF\(_3\)C*(O\(^-\))H, and hence, should be much faster. Species CCl\(_3\)C*(O\(^-\))OH as a chlorinated analogue of former one possess even more pronounced exothermicity (at least \(\Delta H = -54.3 \text{kJ mol}^{-1}\)) resulting in a great instability of that radical anion.

**Table 3.10.** B3LYP/6-31+G(d,p)//(SCRF=PCM) (G03) calculated reaction enthalpies \(\Delta H\) (kJ mol\(^{-1}\)), \(L(C-X)\)\(_\text{max}\) (Angstrom; X = F, Cl), Q-Mulliken atomic charge, S-atomic spin density on C and O atoms respectively.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta H) (G03)</th>
<th>(L(C-X))(_\text{max})</th>
<th>Q</th>
<th>(C)</th>
<th>S(O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF(_3)C*(O(^-))CF(_3) \rightarrow \text{F}^- + \cdot\text{CF}_2\text{C}(O)\text{CF}_3</td>
<td>+ 76.1</td>
<td>1.397</td>
<td>-0.362</td>
<td>0.577</td>
<td>0.353</td>
</tr>
<tr>
<td>CF(_3)C*(O(^-))H \rightarrow \text{F}^- + \cdot\text{CF}_2\text{C}(O)\text{H}</td>
<td>+ 18.8</td>
<td>1.422</td>
<td>-0.390</td>
<td>0.615</td>
<td>0.295</td>
</tr>
<tr>
<td>CF(_3)C*(O(^-))OH \rightarrow \text{F}^- + \cdot\text{CF}_2\text{C}(O)\text{OH}</td>
<td>- 20.1</td>
<td>1.410</td>
<td>-0.392</td>
<td>0.883</td>
<td>0.202</td>
</tr>
<tr>
<td>CCl(_3)C*(O(^-))OH \rightarrow \text{Cl}^- + \cdot\text{CCl}_2\text{C}(O)\text{OH}</td>
<td>&gt; -54.3</td>
<td>unstable</td>
<td>-0.252</td>
<td>0.427</td>
<td>0.122</td>
</tr>
</tbody>
</table>
The calculated $\Delta H$ are in a good agreement with calculated C-X bond lengths and electron distribution in radical anions. The more unpaired electron distribution is localized on C-atom, the longer is C-X bond leading to more fast halogen anion elimination. The proposed mechanism is supported also by comparison of calculated harmonic vibrations of C-F bond in neutral molecule and radical anion. In case of CF$_3$C($\cdot$(O')H species, the intensity of C-F bond stretch vibrations increases up to 15 times going from the neutral molecule to the radical anion. At the same time, the C-F frequency changes from 833 cm$^{-1}$ to 788 cm$^{-1}$ indicating a strong weakening of C-F bond.

Scheme 3.5

This entire mechanistic idea is corroborated by an experiment in which the *CF$_2$CO$_2$* radical is generated via reduction of CF$_2$BrCO$_2$ by $e_{aq}$ and from which, in the presence of oxygen and MetS, the same products are formed as outlined in the lower section of Scheme 3.5.

Under the assumption that the mechanisms outlined in Schemes 3.4 and 3.5 contribute with 40 and 60%, respectively, we can now calculate the various product yields in the MetS-containing system and compare them with the experimental data (see Table 3.11). As can be seen, the material balance is excellent. The largest deviation amounts to just $G = 0.2$ (for MetSO), way below the typical radiation chemical error limit of ±10%.

This agreement between experimental and calculated yields can certainly be viewed as a most credible support for the proposed mechanism.

One important conclusion based on the proposed mechanism is following. Fluoride as a product are originated exclusively from the alkoxyl radicals, the yield of which in the presence of MetS is 100%. Then the yield of the alkoxyl in the absence of MetS can be calculated as about 7 % taking the ratio of fluoride yields in the systems without and with MetS (100% x 0.4/6.1).
Table 3.11. Comparison of the calculated and experimental yields of products in the system II (with MetS).

<table>
<thead>
<tr>
<th>Product</th>
<th>HCl</th>
<th>HF</th>
<th>CF$_3$(O)OH</th>
<th>CO$_2$</th>
<th>MetSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated*</td>
<td>3.4</td>
<td>6.0</td>
<td>1.4</td>
<td>3.7</td>
<td>5.4</td>
</tr>
<tr>
<td>Experimental</td>
<td>3.4</td>
<td>6.1</td>
<td>1.4</td>
<td>3.8</td>
<td>5.6</td>
</tr>
</tbody>
</table>

* - on basis of discussed mechanism and $G$(HBr) = 3.4.

Based on this study the toxicological side effects of halothane could be associated with formation of highly reactive halogenated peroxyl radicals (CF$_3$CHClOO$^\cdot$ and *OOCF$_2$CO$_2^-$) as well as toxic final products such as HF, HCl, CF$_2$O and CF$_3$(O)OH.

**Scheme 3.6**

![Scheme 3.6 diagram]

The fates of *OCCl$_2$CO$_2^-$ and *OCBr$_2$CO$_2^-$ radicals. By having chosen halothane as source for the peroxyl and oxyl radicals some light could be shed on the different behavior of fluorine, chlorine and bromine substituents. In this context, let us finally look at one more example. With reference to Scheme 3.5 and the described degradation of *OCF$_2$CO$_2^-$ into two equivalents each of F$^-$ and CO$_2$, it is interesting to note, that the decay mechanism of the dichloro and dibromo analogues of the *OCF$_2$CO$_2^-$ radical follows entirely the opposite pattern, as depicted in Scheme 3.6.

In both cases it appears to be the halogen atom (Cl$^\cdot$ and Br$^\cdot$) which is exclusively eliminated as radical component in the β-fragmentation, leaving the corresponding oxalylchloride and oxalylbromide. This conclusion is drawn from the observation that these two oxalyhalides decay under halide elimination into an equal yield of CO and CO$_2$ [8]. (Note: this is different to the oxalylfluoride which quantitatively hydrolyzes to oxalate!). The formation of the highly oxidizing and reactive chlorine and bromine atoms is noteworthy. In their follow-up reactions they will usually end up as halide ions.

The examples discussed in this section indicate the great wealth of reactions halogenated oxyl and peroxyl radicals engage in. They also demonstrate how mechanisms may be
influenced by the identity of the halogen atom, revealing in particular the special role of fluorine substituents. Furthermore, it clearly emerges from these studies that caution is advised for extrapolations from one halocarbon to another. Discussed above results clearly illustrate that an additional benefits may be drawn from quantum-chemical calculations at appropriate levels.

3.6. The Mechanism of Radiolytically Induced Chain Process Mediated by Peroxyl Radicals in Aqueous Solutions. Methanesulfinic Acid as an Example

Methanesulfinic acid, CH₃S(O)OH (MSA), is a convenient model compound, structurally similar to inorganic hydrogen sulfite HSO₃⁻, and an important intermediate in the atmospheric chemistry of sulfur dioxide [215]. On the other hand, MSA is a major product of the reaction of DMSO with •OH radicals (see reaction 1.8a) and plays an important role in further transformations of DMSO in the atmosphere and sea water. Finally, MSA can serve as a model compound in the oxidation of organic thiols through the intermediacy of sulfenic and sulfonic acids (RSOH and RS(O)OH, respectively) leading finally to sulfonic acids:

\[ \text{RSH} \rightarrow \text{RSOH} \rightarrow \text{RS(O)OH} \rightarrow \text{RSO}_3\text{H} \]

For example, in the reaction between a protein thiol and hydrogen peroxide protein sulfinic and sulfonic acid can be formed [216].

3.6.1. Radiation chemistry of MSA in oxygen-free solutions [7]

In the pulse radiolysis of N₂O-saturated solution of the MSA at pH 7, an intermediate is formed with absorption maximum at 330 nm (Fig.3.2), which is assigned to the CH₃S(O)O• radical (cf. also ref. [217]). Assuming \( G(\text{radicals}) = 4.8 \) (85 % of •OH, see below) the absorption coefficient of 1080 ± 100 dm⁻³ mol⁻¹ cm⁻¹ at 330 nm is calculated, well in agreement with an earlier study [217].

If its reaction with sulfoxides [217] (see Chapter 1, reaction 1.8a) is a good guide, one must assume that also in the present system •OH mainly adds to MSA (reaction 3.106) and that H-abstraction at the methyl group probably plays only a minor role (reaction 3.107). The •OH-adduct may decompose by β-fragmentation in two directions. It either eliminates OH⁻ to give the CH₃S(O)O• radical (reaction 3.108, major pathway), or it may split off a methyl radical, the other product being the bisulfite anion (reaction 3.109, minor pathway). The latter pathway is supported by the formation of sulfate and methane/ethane (see below). These products have the methyl radical as precursor.

\[
\begin{align*}
\HO\cdot + \text{CH}_3\text{S(O)O}^- & \rightarrow \text{CH}_3\text{S}^\cdot(\text{OH})(\text{O})\text{O}^- & (3.106) \\
\HO\cdot + \text{CH}_3\text{S(O)O}^- & \rightarrow \cdot\text{CH}_2\text{S(O)O}^- + \text{H}_2\text{O} & (3.107) \\
\text{CH}_3\text{S}^\cdot(\text{OH})(\text{O})\text{O}^- & \rightarrow \text{CH}_3\text{S(O)O}^\cdot + \text{OH}^- & (3.108) \\
\text{CH}_3\text{S}^\cdot(\text{OH})(\text{O})\text{O}^- & \rightarrow \text{CH}_3^\cdot + \text{HSO}_3^- & (3.109)
\end{align*}
\]
Figure 3.2. Comparison of the spectra (5 µs after the pulse) of radicals produced in the pulsed radiolysis (of ~5 Gy/pulse) N₂O-saturated solution of MSA (10⁻³ mol dm⁻³) at pH 7.2 in the absence (●) and presence of sodium azide (10⁻² mol dm⁻³) at pH 8.5 (△).

The overall rate constant of •OH with the methanesulfinate anion (reactions 3.106-107) has been determined by competition kinetics with thiocyanate to be \( k = 5.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \).

The CH₃S(O)O• radical is strongly oxidising. Its reaction with Fe(CN)₆⁴⁻ (equation 3.110) has been followed by absorption build-up of Fe(CN)₆³⁻ at 420 nm (\( \varepsilon = 1020 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \)) in the pulse radiolysis of a N₂O-saturated solution of MSA and Fe(CN)₆⁴⁻. The rate constant \( k_{3.110} = 2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) is obtained.

Similarly, it was found that the CH₃S(O)O• radical rapidly oxidises ascorbate (\( k = 1.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) was obtained by monitoring the build-up of the ascorbate radical) and sulfite (\( k = 1.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) obtained by monitoring the decay of the CH₃S(O)O• radical at 360 nm).

\[
\text{CH}_3\text{S(O)O}^+ + \text{Fe(CN)}_6^{4-} \rightarrow \text{CH}_3\text{S(O)O}^- + \text{Fe(CN)}_6^{3-} \quad (3.110)
\]

The CH₃S(O)O• radical decays mainly by bimolecular disproportionation or recombination (head-to-tail) and hydrolysis of the mixed anhydride, leading finally to one mol of each, MSA and methanesulfonic acid (see Table 3.11). The formation of methane, ethane and dimethylsulfone (see Table 3.11) provides direct evidence for the methyl radical formed in reaction 3.109. The small amount of methyl radicals can undergo either hydrogen abstraction with the starting material to give methane, or recombination to give ethane, or cross-termination with CH₃S(O)O•, the major radical in this system, leading to dimethylsulfone. For more details about the mechanism of MSA degradation in the absence of oxygen see ref. [7].
Table 3.12. Products and their $G$-values of the $\gamma$-radiolysis of sodium methanesulfinate ($10^{-3}$ mol dm$^{-3}$) in N$_2$O-saturated solution at pH 6.8.

<table>
<thead>
<tr>
<th>Products</th>
<th>$G$-values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanesulfonate</td>
<td>2.1</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.7</td>
</tr>
<tr>
<td>Dimethylsulfone</td>
<td>detected, not quantified</td>
</tr>
<tr>
<td>Methane</td>
<td>0.3</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The fact that sulfate (0.7) instead of bisulfite or sulfite (reaction 3.109) was observed as a final product can be explained by the rapid oxidation of sulfite by the CH$_3$S(O)O$^•$ radical (reactions 3.111-3.112, $k_{3.111} = 1.7 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$, see above).

\[
\text{CH}_3\text{S(O)O}^• + \text{SO}_3^{2−} \rightarrow \text{CH}_3\text{S(O)}^- + \text{SO}_3^- \quad (3.111)
\]
\[
\text{CH}_3\text{S(O)O}^• + \cdot\text{SO}_3^- + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{S(O)}^- + \text{SO}_4^{2−} + 2\text{ H}^+ \quad (3.112)
\]

Altogether two CH$_3$S(O)O$^•$ radicals will be reduced by one sulfite. This will leave $G$(CH$_3$S(O)O$^•$) = 4.2 (i.e. 75 %) for bimolecular self-termination. The yield found for methanesulfonate fits this material balance. Thus we can conclude from the above product analysis that $\sim$88 % of •OH reacting with MSA lead to the formation of the CH$_3$S(O)O$^•$ radical, $\sim$12 % to CH$_3$•+ HSO$_3$−, leaving very little room for reaction 3.107.

3.6.2. Reactions in the presence of oxygen [7]

**Pulse radiolysis observations.** In the pulse radiolysis of N$_2$O/O$_2$ (4:1)-saturated solution of MSA, the absorption of the CH$_3$S(O)O$^•$ radical at 330 nm decays rapidly during the first 5–10 µs. This is then followed by a much slower decay ($t_{1/2}$ about 100 µs). As reported in the earlier study [217] we also observe depending on the ratio of dioxygen to MSA, a residual absorption of the methanesulfonyl radical after the initial fast decay. The amount of initial absorbance decrease is only 10 % at a MSA concentration of $1 \times 10^{-3}$ mol dm$^{-3}$ and a dioxygen concentration of $1.3 \times 10^{-4}$ mol dm$^{-3}$. This amount increases to 80 % at the lower MSA concentration of $4 \times 10^{-4}$ mol dm$^{-3}$ and higher dioxygen concentration of $6.5 \times 10^{-4}$ mol dm$^{-3}$. From the kinetics of the initial fast decay (reaction 3.113) $k_{3.113} \sim 8 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$ has been estimated in fair agreement with the published value of $1.2 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ [217].

\[
\text{CH}_3\text{S(O)O}^• + \text{O}_2 \rightarrow \text{CH}_3\text{S(O}_2\text{O)}^• \quad (3.113)
\]

Following the initial fast decay of the absorbance of the CH$_3$S(O)O$^•$ radical, which can be attributed to reaction 3.113, the subsequent evolution of the remaining absorbance at 330 nm suggests the existence of an “equilibrium” concentration of the CH$_3$S(O)O$^•$ radical. The assumption of a reversibility of the dioxygen addition reaction 3.113, which has been observed in the case of certain thyl radicals [69, 70] can, however, not explain the above
observations that the “equilibrium” concentration of the CH\textsubscript{3}S(O)\textsuperscript{O•} radical does not only depend on the dioxygen concentration, but also on the MSA concentration. It was suggested by Sehested and Holcman [217] that the methanesulfonylperoxyl radical CH\textsubscript{3}S(O)\textsubscript{2}OO• initiates a chain reaction by rapidly oxidising the substrate to re-form the CH\textsubscript{3}S(O)\textsuperscript{O•} radical (reaction 3.114, \(k = 6.2 \times 10^8\) dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}). Indeed, the sulfonylperoxyl radical has been considered as one of the most reactive peroxyl radicals [218]. The propagating radicals would thus be CH\textsubscript{3}S(O)O• and CH\textsubscript{3}S(O)\textsubscript{2}OO•. The intermediate product, CH\textsubscript{3}SO\textsubscript{2}OOH, formed in reaction 3.114, was suggested to react with MSA to give two molecules of the methanesulfonic acid (reaction 3.115, \(k \approx 5 \times 10^3\) dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}) [217].

\[
\begin{align*}
\text{CH}_3\text{S(O}_2\text{)OO• + CH}_3\text{S(O)O}^- &\rightarrow \text{CH}_3\text{S(O}_2\text{)OO• + CH}_3\text{S(O)O}^• & (3.114) \\
\text{CH}_3\text{SO}_2\text{OOH + CH}_3\text{SO}_2\text{H} &\rightarrow 2 \text{CH}_3\text{SO}_3\text{H} & (3.115)
\end{align*}
\]

**Products of the chain reaction.** Upon γ-radiolysis of N\textsubscript{2}O/O\textsubscript{2} (4:1)-saturated solutions, dioxygen is consumed with a \(G\) value of 125 and methanesulfonic acid is formed with \(G = 250\) (cf. Table 3.12). A noticeable break in the further formation of methanesulfonic acid is observed after the depletion of dioxygen. The overall stoichiometry for the formation of the major product, methanesulfonate, can be described by reaction 3.116.

\[
\text{2 CH}_3\text{S(O)OH + O}_2 \rightarrow 2 \text{CH}_3\text{S(O)OH} \
\]

(3.116)

This chain reaction is characterised by the fact that the chain length is independent of the concentration of the two major components, MSA and dioxygen. The chain length is also independent of the dose rate in the range of 0.011 to 0.165 Gy s\textsuperscript{-1} (γ-radiolysis). Only at very much higher dose rates of pulse radiolysis do the chain lengths become noticeably shorter.

3.6.2.1. The nature of the chain reaction

From their pulse radiolysis data, Sehested and Holcman [217] convincingly concluded that the steady-state concentration of the methylsulfonyl radicals depends on the [dioxygen]/[MSA] ratio. Under our experimental conditions the steady-state concentration of the methylsulfonyl radicals is rather high. Accordingly, reaction 3.114, combined with the rapid addition of dioxygen (\(k_{3.113} \approx 1.2 \times 10^9\) dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}), is expected to lead to a very fast chain reaction. In fact, such a chain reaction would proceed so fast that the bimolecular termination of the methylsulfonyl radical, although its rate is close to diffusion controlled, cannot compete effectively with its propagation. Thus the chain would continue to run until one of the components, dioxygen or MSA, is exhausted. The branching (reactions 3.108-109) occurs at the initiation stage and does not impact the reaction chain postulated [217] (reactions 3.113-3.114). Moreover, taking into account the rates of bimolecular termination of all the radicals involved, assumed to be diffusion-controlled, it can be readily shown by a computer simulation that these do not alter the situation substantially. Thus, the simple mechanism suggested in [217] cannot explain the limited extent of the chain reaction determined by our product studies.
Table 3.13. Products and their G-values in the γ-radiolysis (dose rate 0.011 Gy s⁻¹) and pulse radiolysis (6 Gy per pulse)* of MSA (10⁻³ mol dm⁻³) in N₂O/O₂ (4:1 v/v)-saturated solution at pH 6.8. The G(H₂O₂) value includes G = 0.75 formed in the radiolysis of water.

<table>
<thead>
<tr>
<th>Products</th>
<th>G-values</th>
<th>γ-Radiolysis</th>
<th>Pulse radiolysis*</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSA consumption</td>
<td>270</td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>Methanesulfonate</td>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen consumption</td>
<td>125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen peroxide**</td>
<td>2</td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>Sulfate</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* - for data on other conditions see text; ** - the value for H₂O₂ includes G = 0.75 formed in the radiolysis of water.

An efficient chain breaking process is required to limit the chain length, e.g. to G ~250, i.e. a turnover of ~50, as under our experimental conditions. We propose that, as in the peroxyl-radical-induced oxidation of organic sulfides [6, 79, 219], the CH₃S(O)₂OO• peroxy radical reacts with MSA by an overall two-electron oxidation to yield the CH₃S(O)₂O• oxyl-type radical. This is then proposed to be followed by an electron transfer from the MSA to the strongly oxidising CH₃S(O)₂O• (reaction 3.118), whereby the CH₃S(O)O• radical is regenerated [6, 79, 219]. The difference between our extended mechanism and that proposed by Sehested and Holcman [217] is that the propagating radicals in our case include the CH₃S(O)₂O•, besides the CH₃S(O)O• and CH₃S(O)₂OO• radicals.

CH₃S(O)₂OO• + CH₃S(O)O⁻ → CH₃S(O)₂O• + CH₃S(O)₂O⁻  \hspace{1cm} (3.117)
CH₃S(O)₂O• + CH₃S(O)O⁻ → CH₃S(O)₂O⁻ + CH₃S(O)O•  \hspace{1cm} (3.118)
CH₃S(O)₂O• + CH₃S(O)O⁻ → CH₃S(O)₂OH + CH₃S(O)O⁻  \hspace{1cm} (3.119)
•CH₂S(O)O⁻ + O₂ → •OOCH₂S(O)O⁻  \hspace{1cm} (3.120)

The CH₃S(O)₂O• radical possesses a reactivity intermediate between •OH (good H-abstractor) and SO₄•⁻ (good electron abstractor). Hence parallel to the chain-propagating step (reaction 3.118), a branching reaction in the form of H-abstraction by the CH₃S(O)₂O• radical to give the carbon-centred radical and methanesulfonic acid (reaction 3.119) can take place. The alkylperoxyl radical ensuing from the carbon-centered radical in its reaction with dioxygen (reaction 3.120) has a much lower oxidising power compared to the chain carrying S-centered peroxy and oxyl radicals in this system. The relatively inert •OOCH₂S(O)O⁻ radical may thus undergo termination reactions rather than propagating the chain. The chain length of about 50 suggests a branching ratio \(k_{3.119}/k_{3.119}\) in the order of \(10^2\).
4. THE MECHANISMS OF OZONE INDUCED REACTIONS IN AQUEOUS SOLUTIONS

Chapter 4 is focused mainly on the investigations of the most important radicals and molecular intermediates as well as end products of ozonation processes of environmentally and biologically important organic compounds. This approach combined with kinetic studies provides a basis for the new mechanisms of ozonation proposed in this work.

4.1. Determination of \( ^*\text{OH} \) and \( \text{O}_2\cdot^- \) Yields in Ozone Reactions in Aqueous Solution

4.1.1. Introduction

In ozone reactions in aqueous solutions, \( ^*\text{OH} \), and \( \text{O}_2\cdot^- \) are often generated as short-lived intermediates. For example, in the reaction of ozone with amines, including the chelators NTA and EDTA, a non-negligible pathway proceeds via \( ^*\text{OH} \) and \( \text{O}_2\cdot^- \) radicals as intermediates [220]. In the present chapter a number of ozone reactions will be described, in which \( ^*\text{OH}/\text{O}_2\cdot^- \) play an important role.

For a detailed understanding of ozone reactions in water, \( ^*\text{OH} \) and \( \text{O}_2\cdot^- \) yields have to be known. For monitoring \( ^*\text{OH} \) formation, one approach is to follow the consumption of an added ozone refractory compound [221, 222]. This procedure has the advantage that the low additive concentration does not effectively alter the progress of the reaction, but it has also the disadvantage that the ensuing reactions of the \( ^*\text{OH} \) radical are not effectively suppressed.

In our work, we have used a different approach. The addition of a large excess of t-BuOH which readily reacts with \( ^*\text{OH} \) (see reactions 1.10 a,b, \( k = 6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [51]) but is practically inert against ozone (\( k = 1 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [223], \( 3 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [224]) allows to scavenge all \( ^*\text{OH} \) and to follow the reaction by measuring one of the ensuing products, formaldehyde.

An example where \( ^*\text{OH} \) formation becomes the only process is the reaction of \( \text{H}_2\text{O}_2 \) with ozone. This reaction has found a pronounced interest considering its potential to eliminate ozone-refractory compounds in drinking-water processing with the help of the highly reactive \( ^*\text{OH} \) radical (for reviews see, \( e.g. \), refs. [225, 226]; for compilations of ozone and \( ^*\text{OH} \) rate constants see ref. [224] and ref. [51], respectively).

At low pH, where \( \text{H}_2\text{O}_2 \) predominates (\( \text{pK}_a(\text{H}_2\text{O}_2) = 11.6 \)), the reaction is slow (\( \leq 0.01 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \), \( k = 0.036 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [227]), and in neutral solutions the reaction is mainly governed by the fast reaction of \( \text{HO}_2^- \) in equilibrium (\( k_{4,1} = 5.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [228]). The initiation step may proceed \( via \) a short-lived adduct (a hydroperoxide anion) which decomposes into \( ^*\text{OH}, \text{O}_2, \) and \( \text{O}_2\cdot^- \) (reaction 4.1). The subsequent reaction of \( \text{O}_2\cdot^- \) with ozone is very fast (reaction 4.2, \( k = 1.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [229, 230]). The ozonide radical anion is only stable at very high pH (equilibrium 4.3, \( k_{4,3} = 2.1 \times 10^3 \text{ s}^{-1} \), \( k_{4,(-3)} = 3.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [231]. Due to the fast protonation of \( \text{O}_2\cdot^- \) by water (equilibrium 4.4; \( \text{pK}_a(\text{OH}) = 11.8 \) [51]), equilibrium 4.4 is rapidly drawn to the left at neutral pH (\( k_4 \approx 10^9 \text{ s}^{-1} \)). As a consequence, \( ^*\text{OH} \) is formed at pH \( \geq 7 \) closely at the same rate as \( \text{O}_3\cdot^- \) decays (reaction 4.3).
In acid solutions and in neutral solution in the presence of buffer, $\text{O}_3^-$ is protonated and $^\bullet\text{OH}$ formation is caused via the short-lived $\text{HO}_3^\bullet$ radical [229].

\[
\text{HO}_2^- + \text{O}_3 \rightarrow [\text{HO}_5^-] \rightarrow ^\bullet\text{OH} + \text{O}_2 + \text{O}_2^- \tag{4.1}
\]

\[
\text{O}_2^\bullet^- + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_3^- \tag{4.2}
\]

\[
\text{O}_3^- \rightleftharpoons \text{O}^- + \text{O}_2 \tag{4.3}
\]

\[
\text{O}^- + \text{H}_2\text{O} \rightleftharpoons ^\bullet\text{OH} + \text{OH}^- \tag{4.4}
\]

The reaction of ozone with organic substrates can lead to $\text{O}_3^-$ (by electron transfer, reaction 4.5) and to $\text{O}_2^\bullet^-$ (by an addition/elimination process, reaction 4.6). Both processes lead to the formation of $^\bullet\text{OH}$ (cf. reactions 4.2–4.4).

\[
\text{RH} + \text{O}_3 \rightarrow \text{RH}^\bullet^+ + \text{O}_3^- \tag{4.5}
\]

\[
\text{RH} + \text{O}_3 \rightarrow \text{RO}^\bullet + \text{O}_2^\bullet^- + \text{H}^+ \tag{4.6}
\]

The situation can become very complex at low substrate concentrations, since $^\bullet\text{OH}$ reacts rapidly with ozone (reaction 4.7, $k = 1 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$) [224] and thus can initiate a chain reaction with $\text{HO}_2^\bullet^7\text{O}_2^-\text{O}_2^-\text{O}_2^-$ as intermediates (cf. equilibrium 1.4, $pK_a(\text{HO}_2^\bullet) = 4.8$) [53]. This chain reaction may lead to an unwanted self-destruction of ozone.

\[
^\bullet\text{OH} + \text{O}_3 \rightarrow \text{HO}_2^\bullet + \text{O}_2 \tag{4.7}
\]

4.1.2. The t-BuOH system [14]

As was already described in subsection 1.3.1, the reaction of hydroxyl radicals with t-BuOH in the presence of oxygen leads mainly to $^\bullet\text{OOCH}_2\text{C(CH}_3)_2\text{OH}$ (95%). They decay bimolecularly, whereby a tetroxide is formed as a short-lived intermediate (reaction 4.8) which decomposes via different pathways. One of them leads to dioxygen, 2-methyl-2-hydroxypropanol and 2-methyl-2-hydroxypropanal (reaction 4.9) [160]. Reaction 4.10 gives rise to hydrogen peroxide and two mol 2-methyl-2-hydroxypropanal. The third reaction pathway leads to the formation of two mol formaldehyde, one mol dioxygen and two mol 2-hydroxyprop-2-yl radicals in a concerted reaction 4.11 (cf. ref. [118]). The same products may be formed via oxyl radicals (reactions 4.12 and 4.13). The 2-hydroxyprop-2-yl radical readily adds dioxygen, and then undergoes fast elimination of $\text{HO}_2^\bullet$ leading to acetone ($k = 650$ s$^{-1}$ [86], see paragraph 1.3.3.4, reaction 1.27).

The yields of the main products, formaldehyde, acetone, 2-hydroxy-2-methylpropanal and 2-methyl-2-hydroxypropanal have been determined in the radiolytic study [160]. However, the formation of considerable amounts of $\text{HO}_2^\bullet/\text{O}_2^\bullet$ in this system, which also interact with $^\bullet\text{OOCH}_2\text{C(CH}_3)_2\text{OH}$ radicals, prevents a quantitative comparison with the present system, where any $\text{O}_2^\bullet^-$ formed in the course of the t-BuOH-derived peroxyl radicals are immediately converted by ozone into further $^\bullet\text{OH}$ (cf. reactions 4.2–4.4). The regeneration of $^\bullet\text{OH}$,
however, does not lead to an efficient chain reaction because of the two competing pathways 4.9 and 4.10.

\[
2 \cdot OOC(CH_3)_2CH_2OH \rightarrow [HOC(CH_3)_2CH_2OO]_2 \quad (4.8)
\]

\[
[HOC(CH_3)_2CH_2OO]_2 \rightarrow O_2 + HOC(CH_3)_2CH_2OH + HOC(CH_3)_2CHO \quad (4.9)
\]

\[
[HOC(CH_3)_2CH_2OO]_2 \rightarrow H_2O_2 + 2 HOC(CH_3)_2CHO \quad (4.10)
\]

\[
[HOC(CH_3)_2CH_2OO]_2 \rightarrow O_2 + 2 CH_2O + 2 \cdot C(CH_3)_2OH \quad (4.11)
\]

\[
[HOC(CH_3)_2CH_2OO]_2 \rightarrow O_2 + 2 HOC(CH_3)_2CH_2O^* \quad (4.12)
\]

\[
HOC(CH_3)_2CH_2O^* \rightarrow CH_2O + \cdot C(CH_3)_2OH \quad (4.13)
\]

It has been recently shown that the t-BuOH-derived peroxyl radicals react with ozone in competition [232], leading to the formation of oxyl radicals (reaction 4.14) and to an increase in the yields of CH_2O and HOC(CH_3)_2CHO (cf. reactions 4.9, 4.10 and 4.13) [233].

\[
HOC(CH_3)_2CH_2OO^* + O_3 \rightarrow O_2 + HOC(CH_3)_2CH_2O^* \quad (4.14)
\]

Reaction 4.14 is slow \((k = 1.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) [232] and has to compete with the bimolecular decay of the t-BuOH-derived peroxyl radicals \((2k = 8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} [160])\). Moreover, alkyl radicals also react with ozone with a rate comparable to that of dioxygen [234]. This reaction gains in importance at high \([O_3]/[O_2]\) ratios.

In the radiolytic system, the formaldehyde yield was found to be \(~25\%\) of \(^*\)OH, and the ratio of the 2-hydroxy-2-methylpropanal and formaldehyde yields was \(\sim 1.5\) [160]. We have determined the formaldehyde and 2-hydroxy-2-methylpropanal yields in the ozone / hydrogen peroxide / t-BuOH system. We have obtained \((30\pm4)\%\) for the formaldehyde yield and a value of 1.3–1.4 for the 2-hydroxy-2-methylpropanal to formaldehyde ratio [14].

Thus, for the quantification of \(^*\)OH formation in ozone reactions by its scavenging with t-BuOH it usually suffices to determine the formaldehyde yield formed in reactions 4.11 and 4.13 by the methods described in [139].

4.1.3. The DMSO system [14]

As it was already mentioned, DMSO in its reaction with \(^*\)OH will give selectively MSA (92\% yield, see subsection 1.3.1, reaction 1.8a) [58]. MSA is readily detected by IC. The use of DMSO as \(^*\)OH scavenger in ozone reactions has the disadvantage since DMSO reacts reasonably fast with ozone \((k = 8.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\), and also the product of its reaction with \(^*\)OH radicals, the anion of MSA, is rapidly further oxidized by ozone to methanesulfonate \((k_{4.15} = 2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) [7], with singlet dioxygen \(O_2(\Delta_g)\) as the other product [7, 136].

\[
\text{CH}_3\text{S(O)O}^- + O_3 \rightarrow \text{CH}_3\text{S(O)}_2\text{O}^- + O_2(\Delta_g) \quad (4.15)
\]

The combined yields of MSA and methanesulfonic acid, determined by IC analysis, allow conclusions as to the yield of \(^*\)OH formation.
4.1.4. The tetranitromethane/nitroform anion system [14]

For the use TNM as an O$_2^-$ scavenger in ozone reactions, it is of importance to know the ozone rate constants with TNM and its primary product, the nitroform anion (NF$^-$). Moreover, the reaction products of ozone with TNM and NF$^-$ may also react with ozone, and for this reason they and their yields must be known as well. To generate NF$^-$, the hydrolysis of TNM is the most convenient method. However, in the literature there are conflicting reports as to the products [235, 236]. This required a reinvestigation of the hydrolysis of TNM.

TNM is stable in acid and neutral solutions but hydrolyses quite rapidly in basic solutions [235, 236]. After completion of the hydrolysis of TNM, we find [NO$_3^-$]/[NO$_2^-$] = 0.4 and an NF$^-$ yield of 62%, in good agreement with the earlier report [235]. In this context, the rate of TNM hydrolysis was redetermined by following the build-up of NF$^-$ as a function of the OH$^-$ concentration. The value of $k = 0.27$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 20 °C obtained by us is in reasonable agreement with reported [236] value of $0.4$ dm$^3$ mol$^{-1}$ s$^{-1}$ (at 25 °C).

**Reaction of TNM with ozone [6, 14, 219].** TNM reacts slowly with ozone. The reaction has been followed spectrophotometrically at 260 nm as well as by changes in conductance as a function of time. From these data, rate constant of $k = 10$ dm$^3$ mol$^{-1}$ s$^{-1}$ is calculated. This rate constant is low compared to many other ozone rate constants, but noticeably higher than the one with t-BuOH mentioned above.

In the reaction of TNM with ozone, four mol ozone are consumed and four mol nitrate ion are formed (C(NO$_2$)$_4$ + 4 O$_3$ + 2 H$_2$O → 4 HNO$_3$ + 4 O$_2$ + CO$_2$). This is shown by conductance measurements and by IC. The formation of NF$^-$ is not observed, and nitrite yields are very small (< 2% of nitrate). It is suggested that this reaction proceeds by a bipolar addition of ozone at nitrogen. The subsequent elimination of dioxygen may be followed by a rearrangement into trinitromethyl nitrate (reaction 4.16), which hydrolyses (reaction 4.17) much faster than C(NO$_2$)$_4$.

\[
\text{C(NO}_2\text{)}_4 + \text{O}_3 \rightarrow (\text{NO}_2)_3\text{CONO}_2 + \text{O}_2
\]

(4.16)

\[
(\text{NO}_2)_3\text{CONO}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + (\text{NO}_2)_3\text{COH} + \text{H}^+
\]

(4.17)

The trinitromethanol thus formed immediately loses nitrous acid (reaction 4.18) followed by fast hydrolysis of dinitro carbon monoxide (reaction 4.19).

\[
(\text{NO}_2)_3\text{COH} \rightarrow \text{H}^+ + \text{NO}_2^- + (\text{NO}_2)_2\text{C}=\text{O}
\]

(4.18)

\[
(\text{NO}_2)_2\text{C}=\text{O} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{H}^+ + 2 \text{NO}_2^-
\]

(4.19)

\[
\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2(\text{I}^\Delta_g)
\]

(4.20)

Nitrite is then readily oxidized by ozone (reaction 4.20, $k = 3.7 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ [237]).

**Reaction of the nitroform anion with ozone [14].** Using the stopped-flow technique, the decay of NF$^-$ at 350 nm was followed in the presence of a large excess of ozone, and from such data a rate constant of $k = 1.4 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$ is obtained. This value is ~30 times lower than the rate constant of ozone with nitrite.

It is suggested that the reaction of ozone with the NF$^-$ proceeds by O-atom transfer:
\[(\text{NO}_2)_3 \text{C}^- + \text{O}_3 \rightarrow (\text{NO}_2)_3 \text{CO}^- + \text{O}_2\]  \hspace{1cm} (4.21)

This reaction is followed by a rapid release of nitrite (reaction 4.22) with a subsequent hydrolysis of \((\text{NO}_2)_2\text{C}=\text{O}\) (reaction 4.19):

\[(\text{NO}_2)_3 \text{CO}^- \rightarrow (\text{NO}_2)_2\text{C}=\text{O} + \text{NO}_2^-\]  \hspace{1cm} (4.22)

4.1.5. Factors to be taken into account in the determination of \(^{\bullet}\text{OH}\) in ozone reactions with the t-BuOH/formaldehyde assay [14]

It has been shown above, that in the reaction of \(^{\bullet}\text{OH}\) with t-BuOH the formation of formaldehyde is connected with the concomitant release of \(\text{O}_2^{\bullet-}\). Since the latter reacts rapidly with ozone giving rise to further \(^{\bullet}\text{OH}\), this additional source of formaldehyde has to be taken into account when the primary \(^{\bullet}\text{OH}\) yield is calculated from such data. Applied to our system, a correction factor of 0.48±0.08 is obtained by which the measured formaldehyde yield has to be divided to arrive at the precursor \(^{\bullet}\text{OH}\) yield, i.e. as a rule of thumb one can take twice the formaldehyde yield.

When the initial \(^{\bullet}\text{OH}\) yield is high, ozone depletion due to the secondary formation of \(^{\bullet}\text{OH}\) in this assay has to be taken into account in material balance calculations. Furthermore, when the rate of reaction of ozone with the substrate is very fast, \(\text{O}_2^{\bullet-}\) released in the t-BuOH-derived peroxy radical reactions may no longer be able to react with ozone and thus the correction factor mentioned above may not have to be applied. A case in point may be \(N,N,N,N\)-tetramethylphenylenediamine (\(\text{cf.}\) data in Table 4.1). In addition, when \(^{\bullet}\text{OH}\) formation in ozone reactions becomes a major process, there are always substrate radicals which will interact with the t-BuOH-derived peroxy radicals. This must have an influence on the formaldehyde yield. Whether this will lead either to an increase or a decrease cannot be predicted.

As a consequence, the t-BuOH assay is an excellent tool for the detection of \(^{\bullet}\text{OH}\) in ozone reactions, but as its quantitative aspect is concerned, it is fraught with an error beyond the experimental one, especially when the formaldehyde \((^{\bullet}\text{OH})\) yield is found to be high.

4.1.6. Formation of \(^{\bullet}\text{OH}\) in ozone reactions [14]

It has been mentioned above that \(^{\bullet}\text{OH}\) may be formed in an electron-transfer process (reaction 4.5). This reaction has always to compete with other reactions of ozone. Thus, the differences in the reduction potentials of substrate and ozone are not expected to be a measure of the electron transfer efficiency, although a larger difference will favour electron transfer and thus \(^{\bullet}\text{OH}\) formation. Most experiments reported here were carried out at pH ~7. For assessing the reduction potential difference, one has to take the ozone reduction potential at pH 7. It is more reasonable to take the value \(E^\circ(\text{O}_3^{\bullet-}/\text{O}_3) = 1.01\ \text{V}\) measured [238] at high pH also for experiments at pH 7. Thus, ozone is a rather weak one-electron oxidant.

For a number of substrates, the formaldehyde yields in the presence of an excess t-BuOH, the \(^{\bullet}\text{OH}\) yields calculated (see above) from these data, together with the substrate reduction potentials at pH 7 are given in Table 4.1.
Table 4.1. Reduction potentials at pH 7 of various substrates [52], their difference against the reduction potential of ozone (1.01 V), formaldehyde yields in the presence of t-BuOH and the yields of •OH calculated therefrom.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>E\textsuperscript{7}/V</th>
<th>ΔE/V</th>
<th>CH\textsubscript{2}O yield/ %</th>
<th>OH yield/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N,N,N- Tetramethylphenylene-diamine</td>
<td>0.24</td>
<td>0.77</td>
<td>34</td>
<td>See text</td>
</tr>
<tr>
<td>o-Phenylenediamine</td>
<td>0.34</td>
<td>0.67</td>
<td>14</td>
<td>30±5</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>0.45</td>
<td>0.56</td>
<td>20</td>
<td>43±7</td>
</tr>
<tr>
<td>Catechol</td>
<td>0.53</td>
<td>0.48</td>
<td>11</td>
<td>24±4</td>
</tr>
<tr>
<td>Fe(CN)\textsubscript{6}\textsuperscript{3−}</td>
<td>0.77</td>
<td>0.34</td>
<td>~70 a</td>
<td></td>
</tr>
<tr>
<td>N,N-Diethylaniline</td>
<td>0.86</td>
<td>0.15</td>
<td>13</td>
<td>28±5</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.86</td>
<td>0.15</td>
<td>11</td>
<td>24±4</td>
</tr>
<tr>
<td>Triethylamine [220]</td>
<td>1.04</td>
<td></td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>1,3,5-Trimethoxybenzene</td>
<td>(1.23)\textsuperscript{b}</td>
<td>(-0.22)\textsuperscript{b}</td>
<td>7.4</td>
<td>16±2.5</td>
</tr>
<tr>
<td></td>
<td>(1.27)\textsuperscript{b}</td>
<td>(-0.26)\textsuperscript{b}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iodide</td>
<td>1.28</td>
<td>-0.27</td>
<td>&lt;0.5</td>
<td>0</td>
</tr>
<tr>
<td>Guanosine [239]</td>
<td>1.29</td>
<td>-0.28</td>
<td>0 [10]</td>
<td>0 [10]</td>
</tr>
<tr>
<td>1,4-Dimethoxybenzene</td>
<td>1.30 [240]</td>
<td>-0.29</td>
<td>8.4</td>
<td>18±3</td>
</tr>
<tr>
<td>1,2-Dimethoxybenzene</td>
<td>1.44 [240]</td>
<td>-0.43</td>
<td>6.8</td>
<td>15±2</td>
</tr>
<tr>
<td>Adenosine [239]</td>
<td>1.56</td>
<td>-0.55</td>
<td>20</td>
<td>43±7</td>
</tr>
<tr>
<td>Anisole [240]</td>
<td>1.62</td>
<td>-0.61</td>
<td>4.1</td>
<td>9±1.5</td>
</tr>
<tr>
<td>Bromide</td>
<td>2.00</td>
<td>-0.99</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} From experiments with DMSO, \textsuperscript{b} based on values in acetonitrile of 1.49 V vs. SCE [241] and 1.25 V vs. a silver electrode [242].

Of the substrates compiled in Table 4.1, the compound with the lowest reduction potential is N,N,N,N-tetramethylphenylenediamine. Although ΔE\textsuperscript{°} = 0.77 V, and thus the only expected reaction is electron transfer [243], it is not. As it is evident from the 9% yield of singlet dioxygen, O\textsubscript{2}(\textsuperscript{1}Δ\textsubscript{g}), O-transfer competes [136]. A short-lived adduct to nitrogen is the likely precursor for both reaction channels. A tertiary amine with a higher reduction potential is triethylamine. Here, an adduct has also been assumed to be the primary product (reaction 4.23), but now the route to the N-oxide and singlet dioxygen (reaction 4.24) is the preferred pathway, and electron transfer (reaction 4.25) occurs with a much lower yield (Table 4.1) [220].
\[
\text{N(CH}_2\text{CH}_3)_3 + \text{O}_3 \to ^+\text{N(CH}_2\text{CH}_3)_3\text{OOO}^-
\]
(4.23)
\[
^+\text{N(CH}_2\text{CH}_3)_3\text{OOO}^- \to (\text{CH}_2\text{CH}_3)_3\text{NO} + \text{O}_2(1\Delta_g)
\]
(4.24)
\[
^+\text{N(CH}_2\text{CH}_3)_3\text{OOO}^- \to (\text{CH}_2\text{CH}_3)_3\text{N}^{++} + \text{O}_3^-
\]
(4.25)

Kinetic evidence for short-lived adduct has been found with bromide which does not react very fast with ozone (reactions 4.26 and 4.27). Reaction 4.26 is close to isoenergetic, and thus the first step is even reversible [244].

\[
\text{Br}^- + \text{O}_3 \rightleftharpoons \text{BrOOO}^- \to \text{BrO}^- + \text{O}_2(1\Delta_g)
\]
(4.26-4.27)

The reaction of I\(^-\) with ozone is, however, very fast \((k = 1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) [244], and the endothermic electron transfer does not compete effectively (cf. Table 4.1) with O-transfer:

\[
\Gamma + \text{O}_3 \to [\text{IOOO}^-] \to \text{IO}^- + \text{O}_2(1\Delta_g)
\]
(4.28-4.29)

Support for a certain lifetime of such adducts comes from the \(\text{O}_2(1\Delta_g)\) yields in these systems. While with other systems, e.g. various sulfur- and nitrogen-containing compounds \(\text{O}_2(1\Delta_g)\) yields are 100% when an O-transfer occurs, it is only 54% in the case of \(\text{Br}^-\) and 14% in the case of \(\Gamma\) [136]. This low \(\text{O}_2(1\Delta_g)\) yield is readily explained if the adducts (IOOO\(^-\) and BrOOO\(^-\)) are sufficiently long-lived to allow heavy-atom-assisted spin conversion and release of triplet (ground-state) dioxygen. This effect would be more pronounced with \(\Gamma\) than with the lighter \(\text{Br}^-\), as observed.

The preference of forming adducts rather than undergoing outer-sphere electron transfer is also given by the much stronger oxidant, the \(^*\text{OH}\) radical \((E^* = 2.73 \text{ V})\) [52], and even in the very few cases, where electron transfer is observed (e.g., ref. [245]), short-lived adducts are not fully excluded.

4.1.7. Use of tetranitromethane for the detection of superoxide in ozone reactions [14]

When the ozone rate constant with the substrate is much lower than that with NF\(^-\), the TNM assay, when only based on the formation of NF\(^-\), may underestimate the \(\text{O}_2(1\Delta_g)\) yield because of a consumption of NF\(^-\) by ozone. Raising the substrate concentration to account for this may not be always possible due to solubility limitations. In order to minimize the reaction of ozone with \(\text{O}_2(1\Delta_g)\), TNM should be present at a \(\sim 10\)-fold concentration with respect to ozone.

Adenine and its derivatives react slowly with ozone \((k(\text{Ado} + \text{O}_3) = 12 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) [10] and are known [246, 247] to produce \(^*\text{OH}\) in remarkable yields [10] despite its high reduction potential (Table 4.1). The \(^*\text{OH}\) that were detected would then have \(\text{O}_2(1\Delta_g)\) as the precursor.

We have carried out an experiment where the ratio of \([\text{Ado}]/[\text{TNM}] \sim 10\) in order to protect TNM from being attacked by ozone. The TNM concentration was chosen as high as possible, and the ozone concentration was kept as low as possible in order to prevent \(\text{O}_2(1\Delta_g)\) from reacting with ozone to a major extent. Moreover, t-BuOH was added at a \(\sim 100\)-fold excess over Ado to ensure that \(^*\text{OH}\) would react with t-BuOH. However, our experimental data for the key
products nitroform anion (for $O_2^*$), nitrate, formaldehyde (for $^*OH$) and 2-hydroxy-2-methylpropanal yields ruled out any significant contribution of the reaction 4.6.

From the experiments in the absence of TNM, it was concluded that in this system $^*OH$ are generated in ~43% yield. We came to the conclusion that ozone reacts with adenosine by electron transfer despite the fact that the reaction is endothermic. The absence of other very efficient competing reactions allows this reaction to proceed nevertheless.

### 4.2. Ozonolysis of Vinyl Compounds, $\text{CH}_2\text{=CH}\cdot X$, in Aqueous Solution – the Chemistries of the Ensuing Formyl Compounds and Hydroperoxides

This chapter is dealing with ozonolysis of some substituted vinyl compounds, great part of which is of high environmental consideration [35-40]. It will be shown that their ozonolysis can be successfully used to study the formation and decay of mixed anhydrides of formic acid whose rates of hydrolysis (or alternative decomposition) are as yet unknown. The advantages of stopped-flow technique with conductivity detection will be clearly demonstrated. The products and the kinetics of the ozonolysis of vinyl cyanide (acrylonitrile, AN), vinyl acetate (VA), vinyl phosphonic acid (VPA), diethyl vinylphosphonate (DethVP), vinylsulfonylic acid (VPA), vinyl phenylphosphonate (PhVS), vinyl bromide (VB), 1,2-dibromoethylene (1,2-DBEth) and vinylene carbonate (VC) will be reported. The characterisation of short-lived intermediates allows us to draw conclusions concerning some mechanistic details.

**Ozone rate constants** [15]. The rate constants of ozone with the substrates were either determined directly by stopped flow (following the decay of the 260 nm absorption of ozone) or by competition [248]. Nitrite (product: nitrate, 100%) [10, 237], cis-1,2-dichloroethene ($k = 540 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, product: chloride, 200%) [61] or buten-3-ol (product: formaldehyde, 100%) [61] were used as competitors. When the rate constant is $\leq 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, a competition with buten-3-ol is no longer feasible. In this range, the indigo method [249, 250] has been used. The remaining ozone was titrated as a function of reaction time by the addition of indigotrisulfonate [250] which is practically instantaneously ($k = 9.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [248]) bleached by the ozone still present.

The rate constants thus obtained are compiled in Table 4.2.

Ozone is an electrophilic agent [251], and compared to their parent ethene ($k = 1.8 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [61] the substrates studied here react more slowly, i.e. the rate of reaction is reduced by the electron-withdrawing substituents. In VPA, the electron density in the C–C double bond increases upon dissociation and so does the rate of ozone reaction (Table 4.2).

#### 4.2.1. Ozonolysis of AN – hydrolysis of formyl cyanide [15]

Upon ozonolysis of AN in aqueous solution, the formaldehyde and formic acid yields increase linearly with increasing ozone concentrations (data not shown). They are equal to the amount of ozone consumed. The total hydroperoxide yield is also 100%. Based on a kinetic
analysis of its reaction with molybdate-activated iodide, it is assigned to hydroxymethylhydroperoxide CH$_2$OH(OOH) (called further HMHP). The yields of H$_2$O$_2$ and other fast-reacting hydroperoxides such as FPA are < 5%.

In principle, the hydrolysis of the Criegee intermediate, formed in the first step (see below) may take two routes (reactions 4.30 and 4.31), but the electron-withdrawing cyano substituent disfavours the carbocation formed as an intermediate in reaction 4.33, and hence reaction 4.32 becomes practically the only process. Formyl cyanide and HMHP are the products.

The identification of the organic hydroperoxide as HMHP is not in contradiction with the above statement that the formaldehyde yield is 100%, because under the conditions of the Hantzsch reaction used for the determination of formaldehyde HMHP is quantitatively converted into formaldehyde (reaction 4.36, for the equilibrium constant see ref. [198]).
The rate constant of formyl cyanide hydrolysis at pH \(\sim 7\) (reaction 4.34) is 3 \(s^{-1}\) as determined from the data presented in Fig. 4.1 (for a compilation of hydrolysis rate constants see Table 4.3).

\[
\text{HC(O)CN} + H_2O \rightarrow \text{HC(O)O}^- + H^+ + HCN
\]  \hspace{1cm} (4.34)

\[
\text{HC(O)CN} + OH^- \rightarrow \text{HC(O)O}^- + CN^- + H^+
\]  \hspace{1cm} (4.35)

\[
\text{CH}_2(OH)OOH \rightleftharpoons H_2O_2 + \text{CH}_3O
\]  \hspace{1cm} (4.36)

A plot of \(k_{\text{obs}}\) vs. the OH\(^-\) concentration yields a straight line (data not shown), wherefrom the rate constant of reaction 4.35 was calculated.

**4.2.2. Ozonolysis of VA – hydrolysis of formyl acetate [14]**

The yields of formaldehyde and formate ion are both 100%. Acetate cannot be measured, because VA itself hydrolyses into acetaldehyde and acetic acid too quickly (2 \(dm^3\) \(mol^{-1}\) \(s^{-1}\)). The hydroperoxide yield is also 100%, and a kinetic analysis of its reaction with molybdate-activated iodide shows that it has to be assigned to HMHP. The absence of significant amounts of FPA and \(H_2O_2\) indicates that reactions 4.38, 4.40 and 4.41 can be neglected.
Table 4.3. Compilation of hydrolysis rate constants determined in ref. [15].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC(O)Cl + H₂O → HC(O)OH + HCl</td>
<td>6 × 10² s⁻¹ [137]</td>
</tr>
<tr>
<td>HC(O)CN + H₂O → HC(O)OH + HCN</td>
<td>3 s⁻¹</td>
</tr>
<tr>
<td>HC(O)OC(O)CH₃ + H₂O → HC(O)OH + CH₃C(O)OH</td>
<td>0.25 s⁻¹</td>
</tr>
<tr>
<td>HC(O)S(O)₂O⁻ + H₂O → HC(O)OH + HSO₃⁻</td>
<td>3 s⁻¹</td>
</tr>
<tr>
<td>HC(O)S(O)₂OPh + H₂O → HC(O)OH + SO₂ + PhOH</td>
<td>~5 s⁻¹</td>
</tr>
<tr>
<td>HOOCH(OH)OC(O)OC(O)OH → HC(O)OH + CO₂ + HC(O)OOH</td>
<td>0.33 s⁻¹</td>
</tr>
<tr>
<td>HC(O)PO₃²⁻ + OH⁻ → HC(O)OH + PO₃³⁻</td>
<td>~5 dm³ mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td>HC(O)Cl + OH⁻ → HC(O)OH + Cl⁻ [137]</td>
<td>2.5 × 10⁴ dm³ mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td>HC(O)CN + OH⁻ → HC(O)OH + CN⁻</td>
<td>3.8 × 10⁵ dm³ mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td>HC(O)S(O)₂O⁻ + OH⁻ → HC(O)OH + SO₃²⁻</td>
<td>2 × 10⁴ dm³ mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td>HC(O)P(O)(OEt)₂ + OH⁻ → HC(O)OH + HOP(OEt)₂</td>
<td>3.2 × 10⁴ dm³ mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td>HC(O)PO₃²⁻ + OH⁻ → HC(O)OH + PO₃³⁻</td>
<td>~5 dm³ mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td>Vinylene carbonate + OH⁻ → Products</td>
<td>~10 dm³ mol⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>

In the major reaction 4.37, one of the products is formyl acetate, the mixed anhydride of formic and acetic acid. The rate of its hydrolysis is equal to 0.25 s⁻¹ (see Table 4.3).
4.2.3. Ozonolysis of VB and 1,2-DBEth – decomposition and hydrolysis of formyl bromide [14]

The chemistry of VB (reactions 4.43–4.45) is very similar to that of vinyl chloride discussed in [61].

\[
\begin{align*}
\text{H}_2\text{CBr} & \xrightarrow{\text{O}_3} \text{H}_2\text{CBr} + \text{Br}^- \\
\text{H}_2\text{CCH}_2 & \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{CCH}_2 + \text{H}_2\text{O} \\
\end{align*}
\]

The bromide yield is practically quantitative (~92%) and that of formate is 3.6%; CO was detected in large amounts but not quantified. So, HC(O)Br decomposes giving mostly CO and HBr (reaction 4.45).

In its reaction with ozone, the cis/trans mixture of 1,2-DBEth yields Br⁻ (200%) and FPA (95%, kinetic analysis; cf. [9, 61]). The formate yield after reduction of FPA with S(CH₂CH₂OH)₂ is 100%. The Criegee ozonide must decompose into BrCH(OH)OOH and formyl bromide. The former must lose HBr within a few µs [83, 159] thereby forming FPA.

For the details of the ozonation mechanisms of other vinyl compounds see ref. [15].

In summary one can say that there is a wide spread (five orders of magnitude) of the hydrolysis rates in water of the mixed anhydrides of formic acid with some other acids ranging from 600 s⁻¹ (formyl chloride [61, 137] to $7 \times 10^{-3}$ s⁻¹ (formyl diethylphosphonate). The rate constant for the OH⁻-induced hydrolysis ranges in the order of $10^4$ to $10^5$ dm³ mol⁻¹ s⁻¹ for formyl cyanide, sulfonate and diethylphosphonate. However the rate of the OH⁻-induced hydrolysis of formyl phosphonate di-anion is only in the order of $5$ dm³ mol⁻¹ s⁻¹.

4.3. Reactions of Ozone with Nucleobases, their Related Compounds and DNA

4.3.1. Rate Constants of Ozone Reactions with DNA Constituents and Related Compounds [10]

4.3.1.1. General Consideration

Mechanistic details of the inactivation of bacteria and viruses by ozone are as yet not fully understood. Some $10^8$ ozone molecules are required for the inactivation of a bacterium [252, 253]. It has been suggested that this is due to a destruction of the bacterial cell wall and subsequent leakage of cellular contents [252]. However, ozone also causes mutations [254-256]. This may be taken as evidence for damage of its DNA (with the cell remaining adequately intact), but it cannot be excluded that ozone by-products (e.g. formed in the reaction with the cell wall) have caused the mutagenic effect. For example, hydroperoxides
and H₂O₂ are typical ozonation by-products, and the latter is known to be weakly mutagenic [257, 258].

There is already quite a body of information on the reaction of ozone with nucleic acids and their constituents [13, 246, 247, 259-267]. However, in order to reach a better understanding of the inactivation of viruses and bacteria by ozone, a firm set of rate constants on which further studies can be based is required. The determination of the rate of reaction of ozone with the nucleic acids and their constituents by e.g. the stopped-flow technique is difficult because of the strong overlap of the absorption spectra of the nucleobases with that of ozone (for the data presently available see Table 4.4).

Therefore, we have used a competition kinetics [248]. Deprotonation or protonation of substrates has a dramatic effect on the rate of ozone reactions. The most striking example is phenol, whose ozone rate constant increases six orders of magnitude upon deprotonation [268]. Similarly, amines no longer react with ozone when protonated [220, 248]. Also in the reaction of ozone with the nucleobases, one has to take their protonation/deprotonation equilibria into account. Thus, a detailed study covering a large pH range is required for a better understanding of the kinetics of ozone with the nucleobases and with DNA.

4.3.1.2. Results

Around pH 7, all nucleobases are present largely in their uncharged forms (cf. Table 4.4). In the case of the uracil family and guanine derivatives, protonation occurs only at very low pH. On the other hand, cytosine, adenine and their derivatives become protonated already at around pH 4. At high pH, the uracil family deprotonates at pH ~9.8, as long as one of the nitrogens remains unsubstituted. In thymine, for example, the second nitrogen may also deprotonate at very high pH. Most of the reported pKₐ values of 6-methyl-uracil range around 9.8 as well [269]. As can be seen from Table 4.4, the rate constants span more than five orders of magnitude.

In their reactions with ozone, nitrogen-containing compounds, e.g. amines [220], can give rise to the formation of •OH, and the ensuing •OH-induced reactions can distort the kinetics considerably. For this reason, the •OH scavenger t-BuOH has been added to test, whether its presence has an influence on the rate of reaction [14]. As will be shown below, this precaution is only necessary in the case of adenine and its derivatives, i.e. also in DNA. Here, however, it is essential.

4.3.1.3. Uracil, thymine and their derivatives

Under the conditions, where neutral forms of thymine predominate, the reaction is relatively slow, but with increasing pH the rate of reaction increases (Fig. 4.2). The position of the methyl group at the C(5)-C(6) double bond has a noticeable effect on the rate of reaction. Comparing the values at low pH, thymine reacts more than two orders of magnitude faster than 6-methyl-uracil. The other uracil derivatives fall in between. In contrast, the rate constants of the corresponding deprotonated forms are very similar; they all center at around 10⁶ dm³ mol⁻¹ s⁻¹ (cf. Table 4.4).
At pH 13, a value of $6.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is found and attributed to the rate constant for doubly deprotonated thymine. The rate constant for the mono-deprotonated thymine is fraught with some error and can only be estimated from the inflection point near pH 10, wherefrom we obtain a value of $\sim 3 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

As can be seen from Fig. 4.2, there is a considerable disagreement between the measured pH dependencies (dotted lines) and the ones calculated on the basis the $pK_a$ values and rate constants given in Table 4.4 (solid lines). The experimental curves suggest reactions of compounds which are noticeably more acidic than represented by their $pK_a$ values. In the reaction of ozone with olefins, there is evidence at low temperatures for the formation of a charge transfer complex which subsequently decays into products [270, 271]. In this context, it is intriguing that only a small if any deviation is found for thymidine (inset in Fig. 4.2), uracil and 5-chloro-uracil (data not shown) and also no such deviation is found for the cytosine, adenine and guanine systems.

It is remarkable that the position of the methyl group, i.e. when the rate of reaction with thymine is compared with that of 6-methyl-uracil, has such a dramatic effect (a factor of 300, cf. Table 4.4). Even more surprising is the observation that the rate constant of 6-methyl-uracil is lower than that of uracil. Typically, an additional methyl group at the reacting $C=C$ double bond increases the rate of ozone reaction by a factor of $\sim 4$ [61]. A marked difference between these uracil derivatives and simple olefins is also noticed when 6-methyl-uracil is compared with 5-chloro-uracil. One would have expected that the former reacts considerably faster with ozone than the latter, but the reverse has been observed (cf. Table 4.4).
Table 4.4. Compilation of rate constants of ozone with nucleobases and related compounds (in units of \( \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \)) at different stages of protonation as determined in the present study. Literature values [246] in brackets.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( pK_a ) values (^a)</th>
<th>protonated</th>
<th>neutral</th>
<th>deprotonated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thymine</td>
<td>9.9, &gt;12</td>
<td>–</td>
<td>( 4.2 \times 10^4 )</td>
<td>( \sim 3 \times 10^6 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( (2.3 \times 10^4) )</td>
<td></td>
</tr>
<tr>
<td>Thymidine</td>
<td>9.8</td>
<td>–</td>
<td>( 3.0 \times 10^4 )</td>
<td>( 1.2 \times 10^6 )</td>
</tr>
<tr>
<td>5’-dTMP</td>
<td>10.0</td>
<td>–</td>
<td>( (1.6 \times 10^4) )</td>
<td></td>
</tr>
<tr>
<td>1,3-Dimethyl-uracil</td>
<td>–</td>
<td>–</td>
<td>( 2.8 \times 10^3 )</td>
<td>–</td>
</tr>
<tr>
<td>Uracil</td>
<td>9.5, &gt;13</td>
<td>–</td>
<td>650</td>
<td>( 9.2 \times 10^5 )</td>
</tr>
<tr>
<td>6-Methyl-uracil</td>
<td>9.8</td>
<td>–</td>
<td>140</td>
<td>( 6.0 \times 10^5 )</td>
</tr>
<tr>
<td>5-Chloro-uracil</td>
<td>8.0</td>
<td>–</td>
<td>( 4.3 \times 10^3 )</td>
<td>( 1.3 \times 10^6 )</td>
</tr>
<tr>
<td>Orotic acid (^b)</td>
<td>2.1, 9.45</td>
<td>–</td>
<td>( 5.9 \times 10^3 )</td>
<td>n. d. (^e)</td>
</tr>
<tr>
<td>Iso-oortic acid (^b)</td>
<td>4.2, 8.9</td>
<td>–</td>
<td>( 3.7 \times 10^3 )</td>
<td>n. d.</td>
</tr>
<tr>
<td>Cytosine</td>
<td>4.6, 12.2</td>
<td>18</td>
<td>1.4 \times 10^3 ( (930) )</td>
<td>( 1.5 \times 10^6 )</td>
</tr>
<tr>
<td>2’-Deoxyctydine</td>
<td>4.3</td>
<td>44</td>
<td>3.5 \times 10^3</td>
<td>–</td>
</tr>
<tr>
<td>Cytidine</td>
<td>4.15</td>
<td>40</td>
<td>3.5 \times 10^3</td>
<td>–</td>
</tr>
<tr>
<td>5’-dCMP</td>
<td>4.6</td>
<td>–</td>
<td>( (1.4 \times 10^3) )</td>
<td></td>
</tr>
<tr>
<td>Adenine (^d)</td>
<td>4.15, 9.8</td>
<td>5</td>
<td>12</td>
<td>( 1.3 \times 10^5 )</td>
</tr>
<tr>
<td>2’-Deoxyadenosine (^d)</td>
<td>3.8</td>
<td>5</td>
<td>14</td>
<td>( e)</td>
</tr>
<tr>
<td>Adenosine (^d)</td>
<td>3.5</td>
<td>5</td>
<td>16</td>
<td>( e)</td>
</tr>
<tr>
<td>5’-dAMP</td>
<td>4.4</td>
<td>–</td>
<td>( (200) )</td>
<td></td>
</tr>
<tr>
<td>Guanosine</td>
<td>2.5, 9.2</td>
<td>&lt; 300</td>
<td>1.6 \times 10^4</td>
<td>( 4.0 \times 10^6 )</td>
</tr>
<tr>
<td>2’-Deoxyguanosine</td>
<td>2.5, 9.2</td>
<td>n. d.</td>
<td>1.9 \times 10^4</td>
<td>n. d.</td>
</tr>
<tr>
<td>5’-dGMP</td>
<td>2.9, 9.7</td>
<td>–</td>
<td>( (5 \times 10^4) )</td>
<td></td>
</tr>
<tr>
<td>DNA</td>
<td></td>
<td>–</td>
<td>410 (^{d, f})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) - \( pK_a \) values taken from ref. [272], 5-chloro-uracil [273], orotic acid and iso-ortotic acid [274]; \(^b\) - rate constant determined at pH 7, where the carboxylate group is deprotonated, but not yet one of the nitrogens; \(^c\) - n. d. = not determined; \(^d\) - in the presence of 0.2 mol dm\(^{-3}\) t-BuOH; \(^e\) - see text; \(^f\) - the average molecular weight of the nucleotides in DNA is taken as 350 Da.

The observed increase in rate upon deprotonation of thymine is connected with a change in the reaction mechanism. While the neutral nucleobase does not give rise to the formation of singlet dioxygen (\( O_2^{1\Delta_g} \)), deprotonated thymine yields \( O_2^{1\Delta_g} \) in \( \sim 8\% \) yield [136].

5-Chloro-uracil reveals even bigger differences: no singlet dioxygen (\( O_2^{1\Delta_g} \)) is formed at pH \( \sim 3.5 \), but it becomes a major product (\( \sim 42\% \)) for the reaction of its dissociated form [136].

4.3.1.4. Cytosine, cytidine and 2’-deoxycytidine

As can be seen from Fig. 4.3, cytidine and 2’-deoxycytidine react somewhat faster than the free base. This is most likely due to the electron-donating property of the sugar moiety. Upon
protonation their rate of reaction drops by two orders of magnitude. Whereas the nucleosides
do not show an increase in rate at high pH, cytosine does. At high pH, the latter deprotonates
\( pK_a = 12.2 \). A similar \( pK_a \) value (\( pK_a = 12.5 \)) is reported for cytidine, but here deprotonation
is suggested to occur at C(2’) [275]. Apparently deprotonation of the sugar moiety has
practically no effect on the reactivity of these compounds with ozone.

4.3.1.5. Adenine, adenosine and 2’-deoxyadenosine

In the case of adenine and its derivatives, the addition of t-BuOH has a dramatic effect on
the observed rate of reaction (see subsection 4.1.7, cf. also refs. [246, 247]). In its absence, the
rate constant with adenine became too fast for the indigo method, \( i.e. \) the apparent
bimolecular rate constant must have been faster than \( \sim 10^3 \) \( \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \). This points to the
intermediacy of \( \cdot \text{OH} \) at one stage. Indeed, when t-BuOH is added in large excess (0.1 mol
\( \text{dm}^{-3} \)), we observed the formation of considerable amounts of formaldehyde (\( \sim 0.2 \) mol per
mol ozone) in the case of adenine, adenosine (see subsection 4.1.7) and 2’-deoxyadenosine.
The observed formaldehyde yield of \( \sim 20\% \) relates to \( \sim 43\% \) \( \cdot \text{OH} \) [14] in the reaction of
adenosine with ozone. Adenine and 2’-deoxyadenosine gave a very similar results. As it was
already discussed, for the case of adenosine, \( \cdot \text{OH} \) have to be formed due to an electron
transfer reaction. Addition of t-BuOH reduces the observed rate by two orders of magnitude.
This indicates that the radicals that are formed upon \( \cdot \text{OH} \) attack on adenine/2’-
deoxyadenosine must induce a chain reaction. The reaction of ozone with the cyanide ion also
proceeds \( \text{via} \) a chain reaction [276]. There, t-BuOH cannot fully suppress it, \( i.e. \) there must be
an additional chain carrier. A similar situation may prevail here.

4.3.1.6. Guanosine and 2’-deoxyguanosine

Guanosine and 2’-deoxyguanosine react about equally fast with ozone (Table 4.4). Upon
deprotonation, the rate of reaction increases 250-fold. In contrast to thymine, there are no
deviation between the measured and the calculated pH dependencies. Addition of t-BuOH had
no effect on the rate of reaction nor was any formaldehyde formed under these conditions.
This excludes any electron transfer from the guanine moiety to ozone, although guanine has
the lowest reduction potential of all nucleobases [239, 277] and especially in basic solutions
where it’s anion predominates it is readily oxidized by many otherwise only weakly oxidizing
agents (\( cf. \) ref.[278]).
Figure 4.3. Observed rate constant of the reaction of ozone with cytosine (●), cytidine (▲) and 2’-deoxycytidine (△) as a function of pH. The solid line is calculated on the basis of the rate constants and the pH values given in Table 4.4.

4.3.1.7. DNA

As has been noticed before [247], and has been confirmed by us [14], *OH plays an important role in the reaction of ozone with DNA. From ref. [14, 246] it is clear that *OH radical formation must be due to the reaction of ozone with the adenine moiety. For the determination of the intrinsic ozone rate constant with DNA, t-BuOH has to be added. Under such conditions, the rate of reaction of DNA is only 410 dm$^3$ mol$^{-1}$ s$^{-1}$ (in the absence of t-BuOH $k_{obs} = 1.1 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$), i.e. much lower than that of the weighed average of the nucleobases. In the case of *OH which reacts with the nucleobases and their derivatives at close to diffusion-controlled rates ($k \approx 3 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$) [51], the rate of reaction of *OH with DNA is considerably lower ($k = 2.5 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$) [279], since in this non-homogeneous reaction with the macromolecule DNA two terms, a diffusion term ($k_{diff}$) and a reaction term ($k$) have to be considered [280]. The observed overall rate constant ($k_{obs}$) is the harmonic means of these two rate constants (cf. eq. 4.46).

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{1}{k_{diff}} \quad (4.46)$$

Since, in contrast to *OH, ozone reacts with the nucleobases at rates much below the diffusion-controlled limit, the second term must fall away, and the rate of reaction of ozone with the nucleic acids is only given by the first term, i.e. it should be close to that of the weighed average of the concentrations of the various nucleobases in the nucleic acid times
their rate constants with ozone. This is not observed. Structural effects such as hydrogen bonding between the nucleobases may be a reason for the strong reduction in rate.

Corresponding experiments with RNA were not carried out, because it was not guaranteed that the commercially available RNA is of similar purity and sufficiently double-stranded to yield complementary data. From the rate constants given in Table 4.4, one would assume that in RNA the guanine moiety is the most likely one to become degraded upon ozone treatment. This has been indeed observed [259]. In DNA, the situation might be somewhat different. Besides guanine, thymine may be the other preferred target.

4.3.2. Primary and stable products and mechanistic aspects

4.3.2.1. Introduction

Ozone is increasingly used in drinking-water processing for disinfection and oxidation [44]. Our mechanistically-oriented studies on the reactions of ozone in aqueous solution are mainly undertaken to be able to predict potential oxidation by-products, but also to get some insight into the mechanism of the ozone-induced degradation of the nucleic acid, a reaction that must be of importance in the disinfection of viruses and possibly also contributes to the disinfection of bacteria [7, 10, 11, 13-15, 61, 62, 136, 220, 233, 248, 281, 282].

The reaction of ozone with nucleic acids and their constituents has already found some attention [246, 247, 259-267]. As it was concluded in the previous section, the guanine and thymine moieties are considerably more reactive than the cytosine and adenine ones. In the present section the ozone reactions with pyrimidines such as uracil, thymine (and its nucleoside thymidine for comparison reason), 6-methyluracil, 5-chlorouracil and 1,3-dimethyluracil (corresponding abbreviations are: Ura, Thy, Thd, 6MeUra, 5ClUra, 1,3Me2Ura) have been studied:

![Chemical structures](image)

Proposed in the literature mechanisms of ozone reactions with pyrimidines suggest the formation of highly unstable intermediates A and B with hydroperoxide moiety in position 5 or 6 which eliminate promptly H₂O₂ [259]. So, hydrogen peroxide is considered as the only primary peroxide.
Following recommendations for the hydroperoxide analysis (see subsection 3.2.5), we have found that it is not true for Thy, 5ClUra, 6MeUra and 1,3Me2Ura. This encouraged us very much to investigate the reaction of ozone with Thy in various details. The reaction of ozone with Thd has already been studied [266] but a number of questions, especially as to mechanistic details remained open. For this reason, we have also reinvestigated the Thd system based on what we have learnt from a detailed study on the products, part of them short-lived intermediates, of its base moiety, Thy.

4.3.2.2. Reactions of thymine with ozone [13]

Primary products. Ozonolysis of Thy \((k = 3.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) leads to the formation of the acidic hydroperoxide 1-hydroperoxymethyl-3-(2-oxo-propanoyl)-urea 5 (34%), neutral hydroperoxides (1-hydroperoxyhydroxymethyl-3-(2-oxo-propanoyl)-urea 6 (41%) and \(\text{H}_2\text{O}_2\) (25%, with corresponding formation of 1-formyl-5-hydroxy-5-methylhydantoin 11, see Table 4.5 and Scheme 4.2). This statement is based on the following evidences:

a) right after ozonolysis the yield of total hydroperoxide is 100% as assayed with molybdate-activated iodide;

b) upon treatment of the ozonated solution with catalase, the hydroperoxide yield is reduced to 75%. To distinguish between \(\text{H}_2\text{O}_2\) and FPA, \(\text{bis}(2\text{-hydroxyethyl})\text{sulfide}\) has been added to the solution immediately after ozonation. The remaining peroxide was found in the 25% yield in agreement with catalase assay. IC analysis of this solution reveals no formic acid, i.e. FPA is not formed. Based on the catalase and the sulfide assays, it is hence concluded that \(\text{H}_2\text{O}_2\) is present in 25% yield right after ozonation.

Hydroperoxide 5 has been proved by LCMS-ESI technique in the positive mode by a peak at \(m/z = 175\), \((\text{M}+\text{H})^+\) in sample ozonated at 3 °C. When 5 had decayed, the mass spectrum of 18 (see Scheme 4.3) could be taken and showed a pronounced \(m/z = 147\), \((\text{M}+\text{H})^+\), i.e. its molecular weight is 146 Da.
Right after ozonolysis, a strongly UV-absorbing ($\lambda_{\text{max}} = 256$ nm, $\varepsilon = 2.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) product (assigned to $5a$, deprotonated form of 5) is observed by HPLC. There is also a second product (assigned to 11). This has only an end-absorption tailing towards 220 nm. Hydroperoxide 6 compared to 5, is expected to have a much weaker UV-absorption (absence of conjugation in structure in contrast to 5) and may be masked if its retention time is very close to that of 5. The suggestion that 5 and 6 coelute is supported by HPLC PCD with molybdate-activated iodide, where right after ozonolysis only two peaks (22% yield, $\text{H}_2\text{O}_2$) and a rather broad peak (78% yield, due to 5 and 6) were detected.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Prompt” acid formation (conductometry)</td>
<td>~34</td>
</tr>
<tr>
<td>Formic acid at ~100 min (conductometry and IC)</td>
<td>~75</td>
</tr>
<tr>
<td>Formic acid at high pH (IC)</td>
<td>100</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>absent</td>
</tr>
<tr>
<td>Total hydroperoxide (immediate/after 2 h)</td>
<td>100/93</td>
</tr>
<tr>
<td>Hydrogen peroxide (immediate/after 1 h, catalase and R2S assays)</td>
<td>25/40</td>
</tr>
<tr>
<td>Organic hydroperoxides (immediate/after 1 h)</td>
<td>75/53</td>
</tr>
<tr>
<td>1-Hydroperoxymethyl-3-(2-oxo-propanoyl)-urea 5</td>
<td>34</td>
</tr>
<tr>
<td>5-Hydroperoxy-5-methylhydantoin 18 (after 1 h)</td>
<td>53</td>
</tr>
<tr>
<td>5-Hydroxy-5-methylhydantoin 13 (after R2S treatment)</td>
<td>67</td>
</tr>
<tr>
<td>5-Hydroxy-5-methylhydantoin 13 (after R2S and OH− treatment)</td>
<td>100</td>
</tr>
<tr>
<td>Singlet dioxygen (at high pH)</td>
<td>8 [136]</td>
</tr>
</tbody>
</table>

**Conductometry and ion chromatography.** When the ozonolysis is carried out in a conductometric cell, the conductance rises with biphasic kinetics (Fig. 4.4). The first step is too fast to be resolved kinetically by means of conventional conductometry (see Fig. 4.4). The second step shows a half-life of 10.5 min at room temperature ($k \approx 1.1 \times 10^{-3} \text{ s}^{-1}$). At 3 °C, the conductance build-up is eight times slower ($k \approx 1.3 \times 10^{-4} \text{ s}^{-1}$, cf. inset in Fig. 4.4).

The “prompt” acid yield corrected for partial protonation is then calculated at ~34% (of ozone consumed). Further acid is released in the slow process whereby its yield increases to ~75%. The difference between final and prompt acid yield, 41%, is attributed to the yield of 6 as additional precursor of formic acid.

The prompt acid release can be resolved kinetically using stopped-flow technique with conductometric detection. As can be seen from Fig. 4.4, the build-up of conductance follows first order-kinetics, and the rate of reaction depends on the Thy concentration. The rate constant derived from the data shown in the inset of Fig. 4.5 ($k = 3.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) agrees reasonably with the value obtained by competition kinetics ($4.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [10]. It is thus concluded that the reaction of ozone with Thy is the rate-determining step in this fast conductance increase.
Ozonolysis of thymine in aqueous solution at 18 °C. Formation of acid as a function of time as followed by: Figure 4.4. Steady-state conductance measurements. Inset: the slow part of conductance increase at 3 °C (○) and 18 °C (●) plotted as if it were of first-order kinetics. Figure 4.5. Stopped-flow with conductometric detection. The solid line through the data points is a first-order fit. Inset: $k_{obs}$ as a function of the thymine concentration.

To establish the product(s), responsible for obtained conductivity results, IC has been employed. From the results presented in Table 4.5 on could conclude that formic acid could be responsible for both, fast and slow, conductance increase. However, when sulfide was added to a conductometric cell immediately after ozonation of Thy, a decrease in the conductance occurs ($k = 50 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), and the “slow” increase in conductance shown in Fig. 4.4 is also suppressed. IC analysis of this solution reveals no acids, including formic acid as a product of the reaction of FPA with sulfide. This means, that:

1) FPA is not formed;

2) The organic product formed in 25% yield together with hydrogen peroxide is not an acid and does not transform itself into acidic product, i.e. it could not be responsible for any conductivity increase;

3) Organic peroxides are responsible for both, fast and slow conductivity increase. Dissociation of 5 gives a prompt conductivity increase. Further slow increase is due to transformations of 5 together with 6 (see Scheme 4.3) with release of formic acid. Compared to the reaction of ozone with Thy which gives rise to the Thy-derived Criegee ozonide, the decay of this Criegee ozonide (leading to 5) and the subsequent deprotonation of 5 are fast.

The absence of formic acid in the experiment with sulfide does not contradict to its 43% yield detected in the absence of sulfide 5 min after ozonation of Thy. The eluent used for IC (10^{-2} \text{ mol dm}^{-3} \text{ bicarbonate}, pH 8.6) is slightly basic and thus labile formyl compounds may release formic acid upon chromatography.
Based on these observations the mechanism of the formation of primary products can be proposed as depicted in the Scheme 4.2.

**Mechanistic aspects.** Ozone is a strongly electrophilic agent [251] and will hence preferentially add to the C(5)-position of Thy 1 (reaction 4.47), as other electrophilic agents such as the •OH radical and the H* atom do (cf. ref. [55]). The zwitterion 2 will close the ring thereby forming the Criegee intermediate 3 (reaction 4.48). The Criegee intermediate 3 can now open the ring into two directions (reactions 4.49 and 4.53). The zwitterion 4 can eliminate the proton at the neighbouring nitrogen (reaction 4.50). Hydroperoxides have generally high pKₐ values [cf. pKₐ(H₂O₂) = 11.8; pKₐ(HC(O)OOH) = 7.1], and the hydroperoxide function of 5 will thus remain protonated at a pH < 7. The acidity observed for 5 [pKₐ(5) = 4.0] is thus due to a deprotonation at N(3) (reaction 4.52). In competition with reaction 4.50, the zwitterion 4 may react with water yielding the α-hydroxyalkyhydroperoxide 6 (reaction 4.51).

The Criegee intermediate 3 can decay according to reaction 4.53. The zwitterion 7 may gives rise to the hydroperoxides 8 and 9 (reactions 4.54–4.56). The hydroperoxide 9 is an α-hydroxyalkyhydroperoxide. Such hydroperoxides often eliminate H₂O₂ so rapidly that it is not possible to determine their lifetime. We suggest that the H₂O₂ observed right after ozonolysis is due to reactions 4.57 and/or 4.59.

The resulting product 10 will convert to 1-formyl-5-hydroxy-5-methylhydantoin 11. The yields of immediate H₂O₂ and formic acid released at high pH are both ~25%. It is thus suggested that reaction 4.55 dominates over reaction 4.56 and the latter is slow compared to reactions 4.57 and/or 4.59. We suggest that H₂O₂ is released in the concerted pathway 4.59 which may well proceed with a relay of water molecules to accommodate a good transition state for the reaction to take place. The reduction of hydroperoxide 5 by sulfide is depicted in reaction 4.60 (followed by reactions 4.61 and 4.58) (hydroperoxide 6 will undergo analogous reactions), leading to 1-formyl-5-hydroxy-5-methylhydantoin 11, which eliminates formic acid only at high pH (reaction 4.62), giving finally 5-hydroxy-5-methylhydantoin 13 (100% after the addition of sulfide and base).
Scheme 4.2

\[
\text{1} \xrightarrow{(4.47)} \text{O}_3 \\
\text{2} \quad \text{3} \quad \xrightarrow{(4.48)} \\
\text{4} \xrightarrow{(4.49)} \\
\text{5} \xrightarrow{(4.50)} \text{H}_2\text{O} \xrightarrow{(4.51)} \\
\text{6} \xrightarrow{(4.52)} \text{pK}_a = 4 \\
\text{7} \xrightarrow{(4.53)} \\
\text{8} \xrightarrow{(4.54)} \text{H}_2\text{O} \xrightarrow{(4.55)} \\
\text{9} \xrightarrow{(4.56)} \text{10} \xrightarrow{(4.57)} \text{11} \xrightarrow{(4.58)} \\
\text{10} \xrightarrow{(4.59)} \\
\]
Transformations of hydroperoxides. The decay of the organic hydroperoxides 5 and 6 yields partly H$_2$O$_2$, whose yield increases from initial 25% to final 40% (data not shown). This reaction proceeds with a half-life of ~12 min [13]. Within error limits, it follows the same kinetics as the “slow” acid release reported above (t$_{1/2}$ = 10.5 min), i.e. a new organic hydroperoxide (assigned to 18) appears during the decay of 5 and 6. This transformation could be followed by stopped flow with optical detection employing the reaction with non-activated iodide. The hydroperoxides present right after ozonolysis 5 and 6 react with iodide more rapidly (k = 43 dm$^3$ mol$^{-1}$ s$^{-1}$) than the one remaining after one hour (18, k = 7.5 dm$^3$ mol$^{-1}$ s$^{-1}$).
mol\(^{-1}\) s\(^{-1}\)). Accordingly, the apparent \(k_{\text{obs}}\) of the reaction changes with time with a halflife of \(~13\text{ min}\) (data not shown).

One hour after ozonation the \(\text{H}_2\text{O}_2\) peak has increased (39% of total hydroperoxide), and the peak of the organic hydroperoxide (61%, 18) is now sharp.

When the pH of the eluent is decreased, 5 elutes somewhat later with a concomitant shift of its absorption maximum towards 237 nm. From the dependence of percentage of protonated form versus pH, the \(pK_a\) value of 5 is calculated at 4.0 [15].

The hydroperoxide 5 decays by the same kinetics \((k = 1.0 \times 10^{-3} \text{ s}^{-1})\) as found for the release of formic acid \((k = 1.1 \times 10^{-3} \text{ s}^{-1})\). The hydroperoxides 5 and 18 are both wiped out upon the addition of bis(2-hydroxyethyl)sulfide. The hydroperoxides 5 and 6 are reduced to 11, while 18 is reduced to 13. When the sulfide was added one hour after ozonation (to let the primary hydroperoxides 5 and 6 decay into 18), the yield of 5-hydroxy-5-methylhydantoin 13 was 67%. When this solution was subsequently treated with NaOH at pH 10.5 overnight, product 11 also disappeared, and the yield of 5-hydroxy-5-methylhydantoin 13 increased to \(~100\%\). When the sulfide is added immediately after ozonolysis, 1-formyl-5-hydroxy-5-methylhydantoin 11 is the only observed product. As expected from the above, 11 does not loose formic acid at natural pH, i.e. it does not decay into 13 under these conditions.

Hydroperoxides 5 and 18 are eliminated by the addition of bis-(2-hydroxyethyl)-sulfide.

The “slow” release of formic acid with concomitant decay of hydroperoxides 5 and 6 may be rationalised by assuming that these hydroperoxides form \(\alpha\)-hydroxyendoperoxides such as 14 (equilibrium 4.63, Scheme 4.3).

Hydroperoxides readily undergo such a reaction with carbonyl compounds and in our case, it would be even more efficient due to intramolecular addition. Addition of water to 14 leads to 15 (reaction 4.64). It is noted that upon endoperoxide formation, 6 immediately gives rise to 15. Its further transformation (reaction 4.65) leads to the amide 16. This may then undergo ring closure forming the hydantoin derivative 17 (reaction 4.66) which subsequently hydrolyses to 18 (reaction 4.67). Reduction of the latter by sulfide to 5-hydroxy-5-methylhydantoin is giving 13 (reaction 4.68). It has been mentioned above that the decay kinetics of 5 and the build-up of formic acid are practically identical and do not deviate too much from a first-order rate law (cf. inset in Fig. 4.5). This could be accounted for if the rate determining step in this sequence of reactions is the formation of the endoperoxide 14 (or 15 from 6).

In the absence of sulfide, the hydroperoxides 5 and 6 mainly decay into the hydroperoxide 18 and formic acid. A small fraction also looses \(\text{H}_2\text{O}_2\) in competition. Since the suggested mechanism involves an \(\alpha\)-hydroxyalkylperoxide as intermediate (15 may convert into 9), this is not unexpected.
4.3.2.3. Ozonation of thymidine [13]

Thd reacts with ozone with a rate constant of $3 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$ and its anion with a rate constant of $1.2 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ [10]. In contrast to Thy, no singlet dioxygen is formed at high pH [136]. The products that have been reported in an earlier study [266] are also markedly different from those reported above for the Thy reaction, that it seemed worthwhile to have closer look at mechanistic details.

Conductometry and IC. Similarly to Thy, there is a fast and a slow build up of conductance upon the addition of an ozone to Thy solution. In contrast to Thy, the fast process is two orders of magnitude slower (0.55 s$^{-1}$) than the reaction of Thd with ozone under these conditions (60 s$^{-1}$), i.e. cannot be due to the formation of an acidic hydroperoxide (as 5 in the case of Thy). Besides formic acid, acetic acid is formed here as well (the latter is absent in the case of Thy). The yield of this fast acid formation is $\sim$18%, in agreement with the yield of acetic acid (see Table 4.6). Addition of sulfide 30 s after ozonation suppressed significantly the yield of formic acid but did not influence the acetic acid yield. It is thus concluded that acetic acid is released during this fast conductance rise.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>18</td>
</tr>
<tr>
<td>Fast acid release (as acetic acid, conductometry)</td>
<td>$\sim$18</td>
</tr>
<tr>
<td>Acid release (8 min, as acetic plus formic acids, conductometry)</td>
<td>$\sim$40–45</td>
</tr>
<tr>
<td>Formic acid (immediate and after 2 h at high pH, IC)</td>
<td>76 (100)</td>
</tr>
<tr>
<td>Total hydroperoxide (immediate)</td>
<td>$\sim$100</td>
</tr>
<tr>
<td>Total hydroperoxide (25 s – 1.5 h)</td>
<td>78</td>
</tr>
<tr>
<td>Hydrogen peroxide (25 s -1 h, catalase and R$_2$S assays)</td>
<td>8</td>
</tr>
<tr>
<td>Organic hydroperoxides (25 s - 1 h)</td>
<td>70</td>
</tr>
<tr>
<td>$N_1$(2-deoxy-$\beta$-D-erythropentofuranosyl)-5-hydroxy-5-methylhydantoin, two isomers 21</td>
<td>19.5 [266]</td>
</tr>
<tr>
<td>$N_1$(2-deoxy-$\beta$-D-erythropentofuranosyl)-5-hydroxy-5-methylhydantoin, two isomers 21 (after R$_2$S treatment)</td>
<td>43–50</td>
</tr>
<tr>
<td>$N$(2-deoxy-$\beta$-D-erythropentofuranosyl)-formamide 19</td>
<td>19 [266]</td>
</tr>
<tr>
<td>$N$(2-deoxy-$\beta$-D-erythropentofuranosyl)-formylurea 20</td>
<td>18 [266]</td>
</tr>
<tr>
<td>Singlet dioxygen (at high pH)</td>
<td>absent</td>
</tr>
</tbody>
</table>

The slower part of the conductance rise is due to the formation of formic acid ($k = 9 \times 10^{-3}$ s$^{-1}$). When the ozonated sample was kept for two hours at pH 11.6, the formic acid yield increased from $\sim$76% to $\sim$100%. For a compilation of yields see Table 4.6.

Formation and decay of hydroperoxides. When the molybdate-activated iodide reagent is added immediately, i.e. $\sim$1–2 s after the addition of ozone, the total hydroperoxide yields thus determined is close to 100%. When the reagent is added after 25 s, only $\sim$78%
hydroperoxides are detected. Hence, there must be a very short-lived organic hydroperoxide with a yield of $\sim 22\%$. The yield of $\text{H}_2\text{O}_2$ is $8\%$ only. After the rapid loss, the total hydroperoxide yield remains practically stable over time, and in contrast to Thy no $\text{H}_2\text{O}_2$ is released. Upon the addition of sulfide, the organic hydroperoxides are eliminated. The remaining hydroperoxide detectable with molybdate-activated iodide is $\text{H}_2\text{O}_2$ (confirmed by its kinetics).

**HPLC, LCMS and UV-spectroscopy.** HPLC PCD with molybdate-activated iodide allows to monitor hydroperoxides (inclusive $\text{H}_2\text{O}_2$) and quantify their yields (the first number is a retention time with water as eluent, the second number is the yield: $7.6$ min, $\text{H}_2\text{O}_2$ ($11.5\%$), $9.5$ min ($13.5\%$), $15.3$ min ($37\%$), $25.4$ min ($4\%$), $26.4$ min ($4\%$), $29.9$ min ($3\%$), $32.5$ min ($5\%$). The larger number of products as compared to Thy is largely due to the fact that now meso/d,l isomers are formed. In contrast to Thy, after five hours only small changes (retention times, number of peaks, yields) are observed in this HPLC chromatogram and an acidic hydroperoxide is not formed.

Upon LCMS of a sample ozonated at $3\,^\circ\text{C}$, three species were detected with characteristic peaks at $m/z = 162$ (the M$^+$ ion), $m/z = 177$ (together with 117 and 353) and $m/z = 263$ (together with 117). Upon reduction with bis(2-hydroxyethyl)sulfide the product characterised by $m/z = 263$ disappeared, and a new product with $m/z = 247$ (together with 117) is observed. Thus, the $m/z = 263$ species must be a hydroperoxide. The $m/z = 117$ peak in these mass spectra is typical for the 2-deoxyribosyl moiety, i.e. all these products retain the sugar moiety.

These products are assigned to:

- $\text{N(2-deoxy-}\beta\text{-D-erythropentofuranosyl)-formamide 19 (MW = 161);}$
- $\text{N(2-deoxy-}\beta\text{-D-erythropentofuranosyl)-urea 20 (MW = 176);}$
- $\text{N$_1$(2-deoxy-}\beta\text{-D-erythropentofuranosyl)-5-hydroperoxy-5-methylhydantoin 22 (MW = 262);}$
- $\text{N$_1$(2-deoxy-}\beta\text{-D-erythropentofuranosyl)-5-hydroxy-5-methylhydantoin 21 (MW = 246).}$

![Chemical structures](https://example.com/structures.png)

The formation of the product 19 has been described and its yield determined at $19\%$ [266]. The previous study [266] does not report the formation of the products 20 and 22.

The formation of 21 has been observed before [266]. We have obtained the $m/z = 247$ signal for the product 21 only after reduction of ozonated solution with sulfide, so its precursor is hydroperoxide 22 (two isomers are expected).

The combined yield of the two hydantoines 21 was determined at $43\%$, i.e. is much higher than the reported [266] value of only $19.5\%$. In the latter study [266], the hydroperoxides
were subjected without prior reduction to a laborious work-up, and possibly only a fraction underwent \( \text{H}_2\text{O}_2 \) elimination, while the rest was degraded.

UV-spectroscopy of the mixture of Thd and ozone solutions reveals that the species with \( \lambda_{\text{max}} = 238 \text{ nm} \) decays, one with \( \lambda_{\text{max}} = 226 \text{ nm} \) builds up. The kinetics at these two wavelengths are the same \( (k \approx 9 \times 10^{-3} \text{ s}^{-1}) \). This value agrees with the release of formic acid. The same results have been obtained by stopped-flow.

**Mechanistic aspects.** Although there are considerable similarities between Thy and Thd in their reactions with ozone, there are also marked differences. In the case of Thy, the total hydroperoxide yield is 100%. With Thd, the hydroperoxide yield is close to 100% only right after ozonolysis, but already after 25 s it has dropped to \( \sim 78\% \). Formation of \( \text{H}_2\text{O}_2 \) is important \( (25\%) \) with Thy, but minor \( (8\%) \) with Thd. In Thd, there is a rapid \( (0.55 \text{ s}^{-1}) \) release of acetic acid \( (18\%) \), a product that is not formed in the case of Thy. An acidic hydroperoxide such as 5 \( (34\% \text{ in the case of Thy}) \) is not formed with Thd. Common for both systems is the full yield \( \sim 100\% \) of formic acid after reduction of hydroperoxides with sulfide and treatment at high pH. Yet, while 5-hydroxy-5-methylhydantoin 13 then reaches 100% in the case of Thy, the corresponding Thd product 21 is only formed in a 43% yield. Much of this deficit can be accounted for by fragment products such as \( N(2\text{-deoxy-}\beta\text{-d-erythropento-furanosyl)}\)-formamide 19 and \( N(2\text{-deoxy-}\beta\text{-d-erythropento-furanosyl})\text{formylurea} \) 20. A major problem in presenting a somewhat detailed mechanism for Thy ozonolysis, is the lack of a material balance. It has already been pointed out above that we also cannot rely on the yields presented in the earlier study [266], since considerable degradation of hydroperoxodic material must have occurred upon work up. Mechanistically, they [266] account for the formation of the \( N_1(2\text{-deoxy-}\beta\text{-d-erythropento-furanosyl})\)5-hydroxy-5-methylhydantoines 21 which are their \( \text{and also our}) \) major products by an elimination of \( \text{H}_2\text{O}_2 \). However, \( \text{H}_2\text{O}_2 \) is only formed in 8% yield, and 22 is stable for hours. In the earlier study [266], it has also not been realised that acetic acid is a major product \( (18\%). \) Especially the formation of the latter is a kind of key to mechanistic differences between Thy and its nucleoside.

It is reasonable to assume that in both systems ozone attack will be preferentially at C(5) with the subsequent formation of the Criegee ozonide \( \text{cf. reactions 4.47 and 4.48).} \) Subsequent ring opening according to the major pathway \( \text{cf. reaction 4.49} \) leads to a zwitterion which only can deprotonate and yield a C–N double bond, when the nitrogen carries a hydrogen as substituent (as in Thy). Since in Thd \( N(1) \) carries the 2-deoxyribosyl group instead, deprotonation and concomitant formation of an acidic hydroperoxide such as 5 is no longer possible. Here, the reaction analogous to reaction 4.51 that would lead to 2-deoxyribosyl-substituted 6 is the most likely one to occur. For this species we do not have mass-spectral evidence, but it is tempting to attribute the 238 nm species to this intermediate. The subsequent formation of formic acid will lead to 22 via an endoperoxide \( \text{cf. 6} \to 15 \to 16 \to 17 \to 18 \) as depicted for the aglycon in reactions 4.66-4.68. The release of formic acid which occurs at the same rate as the decay of the 238 nm species could account for the formation of \( N_1(2\text{-deoxy-}\beta\text{-d-erythropento-furanosyl})\)5-hydroperoxy-5-methylhydantoin 22 and the latter may thus have an absorption maximum at 226 nm. This is in agreement with the
UV spectra of the hydroperoxides detected by HPLC. For 22 there is also mass spectral evidence (see above).

For the minor pathway of the decay of the Criegee ozonide shown for Thy as reaction 4.53 the fast hydantoin formation and concomitant release of H\textsubscript{2}O\textsubscript{2} does not take place due to the lack of the hydrogen at N(1) (see above). Instead, acetic acid is released. The elimination of acetic acid with a concomitant drop in the total hydroperoxide yield (see Scheme 4.4) is reminiscent of the rapid decay of 2-hydroperoxy-2-hydroxyacetic acid (see Scheme 3.1) [13].

**Scheme 4.4**

Here, we suggest that the primary hydroperoxide 23 can deprotonate at N(3) (reaction 4.69), the N(3)H is acidified by two carbonyls in α-position and further electron-withdrawing groups in β-position) and that the ensuing anion undergoes the fragmentation reaction 4.70. The product of reaction 4.70, 25, will be unstable and hydrolyse thereby eliminating CO\textsubscript{2} (reaction 4.71). The product that is formed in this reaction, N(2-deoxy-β-D-erythropentofuranosyl)-formylurea 26, as well as its further degradation product N(2-deoxy-β-D-erythropentofuranosyl)-formamide 19 (cf. reaction 4.73) has been reported to be formed in high yield (cf. Table 4.6) [266]. Above, it has been suggested that N(2-deoxy-β-D-erythropentofuranosyl)-urea 20 (cf. reaction 4.72) may also be among the products.

The sum of the reported yields [266] of 19 and 26 are too high (37%) to balance the formation of acetic acid (18%, this work). Thus, they must be formed from other precursors (e.g. 24) during work-up as well.

**Conclusion.** Although the ozonolysis of Thy and Thd have many mechanistic aspects in common, there is a noticeable influence of the substituent at N(1) on the pathways taken
beyond the formation of the Criegee ozonide. In Thy, the Criegee ozonide opens into an intermediate that is capable of deprotonation at the neighbouring \( N(1)H \). This new kind of reaction in ozone chemistry is not available to Thd due to the lack of a hydrogen at this position. There are also big differences in the minor pathway. While acetic acid is released in the case of Thd (18%), no such process occurs with Thy. Concerning ozone-induced DNA damage, it may be of importance that highly reactive hydroperoxides are formed which may lead to further DNA lesions, \( e.g. \), upon reaction of these hydroperoxides with transition metal ions (\( cf. \) Fenton-type reactions) [12]. On the other hand, these hydroperoxides might be readily destroyed by sulfur compound such as glutathione which is quite abundant (near millimolar) [283] in cells. In eukariotic cells where it is difficult to rationalise how ozone may reach the nucleus, DNA lesions such as 8-hydroxyguanine [284] may even be caused by hydroperoxidic intermediates generated in the reaction of ozone with cellular components other than DNA. Certainly, there must be a long chain of events from the first reaction of ozone with cellular components to the dramatic morphologic alterations observed [285], \( e.g. \), in cells of the lung exposed to ozone.

4.3.2.4. Formation of peracids and hydroperoxides in the ozonolysis of uracil and its derivatives

In the previous subsection it has been shown that the ozonolysis of Thy and Thd differ dramatically, \( i.e. \) the substituent at \( N(1) \) strongly influences the sequence of reactions following ozone addition. In the present subsection, we present data on the hydroperoxides formed in the ozonolysis of Ura, 6MeUra, 1,3Me\(_2\)Ura and 5ClUra.

It will be shown that these pyrimidines, although closely related to Thy, behave markedly differently in their reactions with ozone. These data provide some more general insight into the mechanism of ozone reactions in aqueous solution beyond the narrow area of nucleic acid ozone chemistry.

If the Criegee’s mechanism depicted by Scheme 4.1 is applied to the pyrimidines one would expect two hydroperoxides with a hydroperoxide moiety in the position 5 or 6 (intermediates A and B). This has indeed be assumed, but the example with Thy clearly shows that the situation may be more complex than that [13]. We will show below that the hydroperoxides A and B are often only very short-lived intermediates, and in certain cases one might have to postulate even other products/intermediates.

Detection and quantification of the hydroperoxides have been done using various techniques described in Section 3.2, namely the molybdate-activated and non-activated iodide assays, reduction with organic sulfides, HPLC PCD etc. Their yields are given in Table 4.7.
Table 4.7. Ozonolysis of Ura and some of its derivatives in aqueous solutions. Characterisation and yields (in % per ozone consumed) of the hydroperoxides and their yields.

<table>
<thead>
<tr>
<th>Pyrimidine</th>
<th>Hydroperoxide</th>
<th>Yield, %</th>
<th>Characterisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ura</td>
<td>HC(O)OOH</td>
<td>16</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>H_2O_2</td>
<td>84</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>HC(O)C(O)NHC(O)N=C(H)OOH</td>
<td>traces</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td>Thy</td>
<td>ROOH (type B)</td>
<td>0</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>ROOH (type A)</td>
<td>34</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>CH_2C(O)C(O)NHC(O)N=C(H)OOH</td>
<td>41</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>HC(O)OOH</td>
<td>absent</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>H_2O_2</td>
<td>25</td>
<td>HPLC</td>
</tr>
<tr>
<td>6MeUra</td>
<td>CH_3C(O)OOH</td>
<td>15</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>H_2O_2</td>
<td>50</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>ROOH (types A or B)</td>
<td>–</td>
<td>not detected</td>
</tr>
<tr>
<td>5ClUra</td>
<td>HC(O)OOH</td>
<td>100</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td>1,3Me2Ura</td>
<td>HC(O)OOH</td>
<td>12</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>R_1OOH</td>
<td>55</td>
<td>HPLC PCD</td>
</tr>
<tr>
<td></td>
<td>R_2OOH</td>
<td>33</td>
<td>HPLC PCD</td>
</tr>
</tbody>
</table>

There is no doubt about the formation of FPA from hydroperoxide B in the case of 5ClUra. This is confirmed by 100% yields of HCl and parabanic acid (determined by IC and HPLC, respectively) in agreement with Scheme 4.5.

The detection of organic peracids as products is the most interesting finding for all studied pyrimidines (see Table 4.7 and Scheme 4.5). Total yield of initial peroxides was quantitative for all systems studied, except 6MeUra, which gives only 65 % yield based on the consumed ozone. This is similar to the Thd system, in which the total peroxide yield has been falling down from 100% immediately after ozonation to 78% after 25 s (see previous subsection). However, no such effect has been found in the case of 6MeUra: the total peroxide yield was equal to 65% already 2 s after ozonation and did not change further. It consists of hydrogen peroxide (50%) and acetic peracid (15%). Obviously, acetic peracid is much more stable compared to formic peracid regarding hydrolysis to the corresponding acid and hydrogen peroxide. The formation of CH_3C(O)OOH could be explained by the decomposition of initial hydroxyhydroperoxide B only (see Scheme 4.5). Based on our results, it is not possible to identify the origin of H_2O_2 – the decomposition of the hydroperoxides in position 5 or 6 (A or B or both of them).
Two hydroperoxides experimentally found in the case of 1,3Me₂Ura could be attributed to A and B. At present no distinction could be given between two of them regarding their yields.

The origination of PFA in this system is unclear. PFA is disappearing with a rate comparable with its hydrolysis to formic acid and hydrogen peroxide ($k = 1.6 \times 10^{-4} \text{ s}^{-1}$ [61]). The total peroxide decreases in this system much slower ($k = 2.3 \times 10^{-5} \text{ s}^{-1}$). Based on this observations one could state that the hydroperoxides $R_1\text{OOH}$ and $R_2\text{OOH}$ could not be precursors of FPA in 1,3Me₂Ura system. If this would be the case, the lifetime of PFA in the present system should be longer than observed. Therefore, we think that hydroperoxide B instantly decomposes giving FPA (as depicted in Scheme 4.5) and hydroperoxides $R_1\text{OOH}$ and $R_2\text{OOH}$ may thus represent hydroperoxide A and another one. The latter is possibly 1,3-dimethyl-5-hydroperoxyhydantoin in analogy to Thy system (hydroperoxide 18, see previous subsection).
5. CONCLUSIONS

The major aim of this work was a detailed study of the degradation mechanisms of environmentally important organic compounds. This was achieved by employing radiation chemistry and ozonolysis as complementary scientific tools. The proposed mechanisms are based on the detailed product analysis, a complete material balance, use of different analytical methods and techniques, allowing to monitor the most important radicals and molecular intermediates as well as stable end products.

The most important innovations which led to a deeper understanding of the degradation processes are:

- improvement of analytical methods for determination of organic hydroperoxides as the key molecular intermediates;
- design and development of model systems, in which the chemistry of the key species such as halogenated alkoxyl radicals and hydroperoxides can be studied separately from their precursors, halogenated peroxyl radicals.
- development of experimental methods for determination of key radical intermediates (•OH, and O$_2$$^•$− radicals) in reactions involving ozone.

The existing analytical methods for determination of organic peroxides and H$_2$O$_2$ have been critically reviewed and new analytical methods have been proposed. It has been shown that the pseudo-first-order kinetics for the reaction of organic (hydro)peroxides with molybdate-activated iodide allows to characterise a given peroxide, since the respective half-lives vary by more than seven orders of magnitude. For the reactive peroxides, including H$_2$O$_2$, HPLC with post-column reaction is a convenient method for spotting a (hydro)peroxide in the chromatogram and for its quantitative determination. Peracids could be distinguished from H$_2$O$_2$ and/or other peroxides due to their quantitative and fast reaction with organic sulfides. Recommendations are given how to analyse the mixtures of (hydro)peroxides of different reactivity.

The degradation of halogenated acetic acids has been studied in some detail. Optical spectra of •CBr$_2$COO−, •CCl$_2$COO− and •CF$_2$COO− radicals have been obtained for the first time. It has been shown that CBr$_3$COOH posseses a high reactivity in the reaction with reducing radicals like CO$_2$$^•$−, •CH$_2$OH, CH$_3$C•HOH, (CH$_3$)$_2$C•OH, e$_{aq}^−$ and H$^•$ (corresponding rate constants are in the range of 10$^{9}$-10$^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$). Non-reducing alkyl radicals •CH$_3$ react with CBr$_3$COOH via bromine atom abstraction ($k = 3.0 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$). Self-termination of •CBr$_2$COO− radicals leads to the formation of tetrabromosuccinic acid, which is unstable and thermally decomposes into HBr, CO$_2$ and tribromoacrylic acid. Efficient reductive degradation of CCl$_3$COOH can be initiated by e$_{aq}^−$ and CO$_2$$^•$− radicals. In contrast, CF$_3$COOH exhibits a high stability toward ionizing irradiation and is practically resistant to any reductive attack.

The importance of the reactions of the superoxide radical anion, O$_2$$^•$−, in the degradation processes is often neglected. Using γ-radiolytic model systems which simultaneously generate
•OOCF₂CO₂⁻ and O₂⁻, a high efficiency of their cross-termination (70 - 100 %), as opposed to the self-termination was established. This aspect is considered to be of particular significance for systems where peroxyl radicals and superoxide are present simultaneously, e.g., in biological environment or in the photocatalytic degradation of organic material.

Free-radical degradation of halogenated organics in the environment has been studied in the last decades very intensively. However, the mechanisms presented in the literature have to be critically reconsidered. The lack of suitable model systems for the separate investigation of the reactive fates of the major intermediates makes an establishment of the origin of end products often difficult, if not impossible at all. Similarly, analytical difficulties (for example, to separate and determine side by side, highly reactive organic hydroperoxides and H₂O₂) complicated very much an evaluation of the overall degradation mechanisms. These problems are solved in the present work.

The family of halogenated methanes representing a broad class of environmental pollutants was selected. Dichloro- and dibromomethanes (DCM and DBM), chloro- and bromoform (CF and BF) and carbon tetrachloride (CT) were used to generate and to study reactive fates of halogenated peroxy radicals (CH₂ClOO•, CH₂BrOO•, CHCl₂OO•, CHBr₂OO• and CCl₃OO• in aqueous solutions. It was established for the first time that dimethylselenide (DMSe) can be used for their quantitative transformation into the corresponding alkoxyl radicals. The major fraction of halogenated oxyl radicals undergo a 1,2-H shift reaction (as was found for DCM and DBM systems) or suffer C-Hal cleavage via halogen atom elimination (in the case of CF, BF and CT). The experimental findings on the reactive fates of the studied halogenated oxyl radicals were supported by quantum chemical calculations (B3LYP/6-31G(d,p)//SCRF=PCM) which take into account the influence of water as a continuum.

It is well-known for many years that RHalOOH are the products of 1-e oxidation of electron-donating compounds by means of RHalOO• and hundreds of rate constants have been measured for such reactions. However, it was impossible to evaluate the reactive fates of RHalOOH, since the latter react further with electron donors. Therefore, alternative model systems were created, in which RHalOOH can be generated almost quantitatively via H-atom abstraction by RHalOO• and the cross-termination of the latter with O₂⁻. It allowed, for the first time, demonstration that halogenated hydroperoxides derived from CF and BF end up as formic peracid. Based on detailed product studies, mechanisms of the degradation of halogenated methanes were proposed.

Fluorinated anaesthetic halothane, CF₃CHClBr, was used to generate and to study the reactive fates of halogenated peroxy radicals CF₃CHClOO•, which oxidize quantitatively methionine (MetS) to the sulfoxide (MetSO) with simultaneous formation of the corresponding alkoxyl radicals CF₃CHClO•. The latter radicals undergo 1,2-hydrogen shift giving α-hydroxyalkylradicals, CF₃C(OH)Cl, for which two reaction pathways were recognized. The first pathway is fast oxygen addition with subsequent HO₂• elimination. The second pathway proceeds via HCl elimination with the simultaneous generation of CF₃C=O radicals. The latter undergo hydration giving CF₃C(OH)₂ species which deprotonate and
suffer fluoride elimination. The resulting secondary halogenated alkyl radicals, upon oxygen addition, give highly reactive peroxyl radicals $^\bullet$OOCF$_2$CO$_2$ that are responsible for extra production of MetSO in the systems studied.

The mechanisms of free radical degradation of halothane were proposed based on detailed product studies, mechanistic considerations and supporting quantum-chemical calculations. Toxic side effects of halothane could be caused by the generation of highly reactive peroxyl and oxyl radicals as well as by toxic final products such as HF, HCl, CF$_2$O and CF$_3$C(O)OH.

Methylsulfonyl radical, CH$_3$S(O)O$^\bullet$ is formed as the main intermediate in the reaction of methanesulfinic acid (CH$_3$S(O)O$^-$, MSA) with $^\bullet$OH. This radical is oxidative in nature: Fe(CN)$_6^{4-}$, ascorbate and sulfite are all oxidised by CH$_3$S(O)O$^\bullet$ with a rate constant of $\sim 2 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. Steady-state radiolysis of MSA showed that methanesulfonic acid is the major product ($G = 2.1 \times 10^{-7}$ mol J$^{-1}$) in the absence of oxygen. In the presence of dioxygen, a chain reaction sets in. In the $\gamma$-radiolytical experiments, $G$(methanesulfonic acid) $\approx 250 \times 10^{-7}$ mol J$^{-1}$ was found to be almost independent of dose rate and concentration of MSA and dioxygen. An efficient chain process was also observed upon electron beam irradiation. A specific feature of the studied chain process is the presence of two chain carriers, namely methanesulfonylperoxyl and methanesulfonyloxyl radicals (CH$_3$S(O$_2$)OO$^\bullet$ and CH$_3$S(O$_2$)O$^\bullet$). Branching and partial removal CH$_3$S(O$_2$)O$^\bullet$ radicals by H-abstraction from the substrate leads to the generation of relatively inert $^\bullet$OOCH$_2$S(O)O$^-$ radicals responsible for chain termination.

Concerning the determination of $^\bullet$OH and O$_2$$^-$$^\bullet$ yields in ozone reactions new experimental methods are proposed. t-BuOH reacts with ozone only very slowly but readily with $^\bullet$OH, and in the presence of dioxygen formaldehyde is a prominent final product, (30±4)% whose ready determination can be used as an assay for $^\bullet$OH. Although DMSO reacts much more readily with ozone, its fast reaction with $^\bullet$OH, which gives rise to MSA, can also be applied for the determination of $^\bullet$OH, at least in fast ozone reactions. The formation of O$_2$$^-$$^\bullet$ can be assayed with tetranitromethane (TNM) which yields nitroform anion (NF$^-$) at close to diffusion-controlled rate. It was established that both, TNM and its product NF$^-$, react with O$_3$ ($k = 10$ and $1.4 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively). In the case of slow ozone reactions, these reactions have to be taken into account. Some examples of $^\bullet$OH and O$_2$$^-$$^\bullet$ formation in ozone reactions are given.

The reactions of ozone with some vinyl compounds of environmental consideration with general structure CH$_2$=CH$^-$X were studied in aqueous solution and the corresponding rate constants were determined. The main pathway leads to the formation of HOOC$_2$OH and HC(O)X. The latter may undergo rapid hydrolysis by water, e.g. HC(O)CN (3 s$^{-1}$), as measured by stopped flow with conductometric detection. Other HC(O)X hydrolyse much slower, e.g. HC(O)PO$_3$(Et)$_2$ (7 $\times$ 10$^{-3}$ s$^{-1}$). HC(O)Br mainly decomposes rapidly into CO and Br$^-$ and H$, and the competing hydrolysis is of minor importance (about 4%).

The rate constants of the reaction of ozone with DNA, its constituents and related compounds were determined as a function of pH by competition with nitrite and/or buten-3-ol and the indigo method. Depending on the degree of protonation, the rate constants (in units of
dm³ mol⁻¹ s⁻¹) vary substantially, e.g. in the case of cytosine, \( k = 18 \) (protonated), \( k = 1.4 \times 10^3 \) (neutral) and \( k = 1.5 \times 10^6 \) (deprotonated). A similar variation was found with the other nucleobases. The mechanism of the ozone reaction may also change upon deprotonation; e.g., no singlet dioxygen \( (\text{O}_2^1 \Delta_g) \) is formed in its reaction with 5-chloro-uracil, but when the 5-chloro-uracilate ion predominates it becomes a major product (≈42%). In the case of adenine and its derivatives, and thus also in the case of DNA, •OH is produced (via \( \text{O}_2^- \)) as an intermediate.

The ozonolysis of thymine and thymidine (Thy and Thd) was investigated by a product study complemented by kinetic studies using spectrophotometry, conductometry and stopped-flow with optical and conductometric detection. Material balance was obtained. Ozonolysis of Thy leads to the formation of the acidic \( (pK_a = 4) \) hydroperoxide 1-hydroperoxymethylene-3-(2-oxo-propanoyl)-urea (≈34%), neutral hydroperoxides (1-hydroperoxymethyl-3-(2-oxo-propanoyl)-urea, ≈41%) and \( \text{H}_2\text{O}_2 \) (25%, with corresponding formation of 1-formyl-5-hydroxy-5-methylhydantoin). The organic hydroperoxides decay \( (k \sim 1.1 \times 10^{-3} \text{ s}^{-1} \text{ at } 20 \degree \text{C}) \) releasing formic acid (formation of 5-hydroperoxy-5-methylhydantoin) and also to some extent \( \text{H}_2\text{O}_2 \). In basic solution, singlet dioxygen is formed (8%).

In the ozonolysis of Thd, the rapid formation of conductance \( (k = 0.55 \text{ s}^{-1}) \) is due to the release of acetic acid (18%). In this reaction a short-lived hydroperoxide is destroyed. An acidic hydroperoxide such as in the case of Thy is not among the products. Upon sulfide reduction, the organic hydroperoxides yield mainly (43–50%) \( N_1(2\text{-deoxy-}\beta\text{-D-erythropentofuranosyl})-5\text{-hydroxy-5-methylhydantoin} \). The reasons for some striking differences in the ozonolyses of Thy and Thd are discussed.

Ozonolysis of Ura, 6MeUra, 1,3Me₂Ura and 5ClUra in aqueous solution was investigated. It was found that these pyrimidines, although closely related the Thy, behave markedly differently in their reactions with ozone. The new pathway leading to the formation of organic peracids was established. Formic peracid is a minor product in the case of Ura, 1,3Me₂Ura, whereas its yield is equal to 100% in the 5ClUra system. Acetic peracid in 15% yield and \( \text{H}_2\text{O}_2 \) (50%) was detected upon ozonation of 6MeUra. The initial \( \text{H}_2\text{O}_2 \) yield is almost quantitative in Ura system, however no traces of \( \text{H}_2\text{O}_2 \) could be detected in the 1,3Me₂Ura and 5ClUra systems. Acidic organic hydroperoxide similar to the case of Thy were not found except for the Ura system, where its traces could be detected. The data provide some more general insight into the mechanism of ozone reactions in aqueous solution beyond the narrow area of nucleic acid ozone chemistry.
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7. REFERENCE LIST


