Doctoral Thesis

Reductive dehalogenation of chlorinated hydrocarbons by surface-bound Fe(II) kinetic and mechanistic aspects

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Reductive Dehalogenation of Chlorinated Hydrocarbons by Surface-Bound Fe(II) – Kinetic and Mechanistic Aspects

A dissertation submitted to the Swiss Federal Institute of Technology Zürich for the degree of Doctor of Natural Sciences

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Zusammenfassung

Halogenierte kurzkettige Kohlenwasserstoffe wurden über Jahrzehnte weltweit in großem Massstab eingesetzt, u.a. als explosionssichere Treibgase, Kühlmittel, Lösemittel und Löschmedien. Dies führte zu gravierenden Umweltproblemen. Flüchtige Fluorchlorkohlenwasserstoffe (FCKW) zerstören die Ozonschicht und tragen zum Treibhauseffekt bei, während die hohe Dichte von chlorierten Kohlenwasserstoffen (CKW) dazu führt, dass sie den Untergrund durchdringen und sich am Boden von Wasser führenden Schichten (Aquiferen) ansammeln. Die Giftigkeit einiger dieser Verbindungen stellt eine ernste Gefahr für Trinkwasservorkommen dar. CKW sind relativ persistent unter oxischen Bedingungen, können jedoch in anoxischem Milieu im Untergrund reduktiv dehalogeniert werden, z.B. in mikrobieller biotischer Transformation. Dort werden auch grössere Mengen an gelöstem reduziertem Eisen (Fe(II)) generiert, durch mikrobielle Reduktion von oxidierten Eisen (Fe(III)). Wenn Fe(II) an Mineraloberflächen gebunden ist, konnte beobachtet werden, dass seine Reaktivität als abiotischer Reduktand enorm zunahm. Soche Fe(II) Spezies sind zusätzlich von Interesse, weil sie sich auch an der Oberfläche von reaktiven Eisen(0) Barrieren bilden, die zur in-situ Reinigung von kontaminierten Böden verwendet werden.

Im zweiten Kapitel dieser Arbeit wurde die Reaktivität von Oberflächen gebundenem Fe(II) für verschiedene umweltrelevante Mineralien verglichen: Siderit (FeCO₃), Hämatit (α-Fe₂O₃), Lepidokrokit (γ-FeOOH), Nontronit (ein eisenhaltiges Tonmineral), Goethit (α-FeOOH), Magnetit (Fe₃O₄), Grüner Rost (FeII₄FeIII₂(OH)₁₂SO₄·⁴H₂O), Pyrit (FeS₂) und FeS. Im Gegensatz zu früheren Studien wurden alle Mineralien unter konstanten Bedingungen untersucht (pH 7,2, 25 m² Mineraloberfläche/L, 1 mM gelöstes Fe(II)), wodurch die Reaktionsraten auf Mineraloberflächen normiert und verglichen werden konnten. Die Reaktivitäten der Mineralien unterschieden sich um Grössenordnungen für beide untersuchte Modellsubstanzen, Hexachlorethan (Dechlorierung) und 4-Chlornitrobenzen (Reduktion der Nitrogruppe). Geschwindigkeitskonstanten folgten dem generellen Trend „Fe(II) + Siderit“ <

Dehalogenierung unter Eisen-reduzierenden Bedingungen kann zu einer raschen Entgiftung führen (z.B. Bildung von CO, CO₂ und Formiat aus Tetrachlorkohlenstoff (CCl₄)), unter Umständen aber auch Hydrogenolyse-Produkte generieren (z.B. Chloroform (CHCl₃) aus CCl₄), die toxisch und unter reduzierenden Bedingungen sehr persistent sind. Ein simultaner Transfer von zwei Elektronen und Bruch zweier C-Cl-Bindungen im ersten, geschwindigkeitsbestimmenden Schritt dieser Reaktion würde eine solche Bildung von Chloroform vollständig vermeiden. Um diese Möglichkeit zu untersuchen, wurde im dritten Kapitel der kinetische Kohlenstoff-Isotopeneffekt in Reaktionen mit Fe(II)/Goethit untersucht (isotopischer Anreicherungsfaktor ε = -26.5 ‰) und mit dem von Modellreaktanden für den Bruch einer C-Cl Bindung verglichen, Fe(II)porphyrin (ein-Elektronen Transfer, ε = -26.1 ‰) und Polysulfid (partieller zwei-Elektronen Transfer, ε = -22.2 ‰). Alle ε-Werte weichen signifikant vom Schätzwert für einen simultanen Bruch zweier C-Cl Bindungen (ε = -50 ‰) ab, was daraufhin deutet, dass im entscheidenden ersten Schritt der Reaktion nur eine C-Cl Bindung gebrochen wird.

Hauptprodukte der Reaktion von CCl₄ mit an Goethit sorbiertem Fe(II) waren CHCl₃, CO und Formiat. Als wichtige kurzlebige Zwischenprodukte wurden freie Trichlormethyl-Radikale in Lösung identifiziert, was auf einen Ein-Elektronen-Transfer an der Fe(II)/Goethit Oberfläche hindeutet. Dagegen spielten freie Trichlormethyl-Carbanionen keine Rolle, was ein Indiz für eine mögliche Oberflächen-Stabilisierung von Intermediaten ist. Dies deutet darauf


Kapitel 5 beschreibt den Entwurf und die Synthese von neuartigen Probemolekülen, von der Art a) $\text{CCl}_3\text{-CH}_2\text{-X}$ (-X = -OPO$_3^2^-$, -OSO$_3^-$, -N(CH$_3$)$_3^+$) und b) $\text{CCl}_3\text{-CH}_2\text{-CHOR-CH}_2\text{-CH}_2\text{-CH=CH}_2$ (R = H, Phosphat). Die funktionelle $\text{CCl}_3$-Gruppe ahmt die Reaktivität von prominenten Umweltkontaminanten wie $\text{CCl}_4$, CHCl$_3$ oder CH$_3$CCl$_3$ nach. Sie ist mit einer Ankergruppe verbunden, die für hinreichende Wasserlöslichkeit (-OH) und/oder Festlegung an Oberflächen sorgt (-OPO$_3^2^-$, -OSO$_3^-$, -N(CH$_3$)$_3^+$). Die Doppelbindung schliesslich fängt kurzlebige Zwischenprodukte wie Radikale und Carbene in einer Zyklisierungsreaktion ab. Diese Art von Probemolekülen kann in zukünftigen Studien helfen, die Rolle von Radikalen und Oberflächen gebundenen Intermediaten in reduktiven Dehalogenierungen weiter aufzuklären.
Summary

Over decades, halogenated C₁- and C₂- hydrocarbons have been used extensively all over the world, for example, as non-explosive propellants, refrigerants, solvents and fire extinguishing agents. This has generated major environmental problems. Volatile chlorofluoro(hydro)carbons (CFCs) were found to cause depletion of the stratospheric ozone layer and add to global warming, whereas dense chlorinated (hydro)carbons (CHCs) tend to penetrate the subsurface in pure phase and accumulate at the bottom of aquifers. Because of their toxicity, some of these compounds pose a severe threat to drinking water resources. Chlorinated (hydro)carbons are rather persistent under oxic conditions, but they may undergo reductive dehalogenation in reducing subsurface environments, for example, by microbially mediated biotic transformation. In addition, microbial ferric iron (Fe(III)) reduction produces considerable quantities of dissolved ferrous iron (Fe(II)) in the subsurface. This Fe(II) has been shown to gain enormously in reactivity as an abiotic reductant when sorbed to mineral surfaces. Such surface bound Fe(II) species are of great interest; they are also thought to form also in long-time applications on reactive Fe(0) subsurface barriers.

In the second chapter of this thesis the reactivity of surface-bound Fe(II) was investigated in a comparative study including environmentally important minerals such as siderite (FeCO₃), hematite (α-Fe₂O₃), lepidocrocite (γ-FeOOH), nontronite (a ferruginous clay mineral), goethite (α-FeOOH), magnetite (Fe₃O₄), green rust (Fe^{II}_4Fe^{III}_2(OH)_{12}SO₄·4H₂O), pyrite (FeS₂) and FeS. In contrast to previous studies, all minerals were studied under constant conditions (pH 7.2, 25 m² mineral/L, 1 mM dissolved Fe(II)), which allowed a comparison based on surface-normalized rate constants. With hexachloroethane (dechlorination) and 4-chloronitrobenzene (nitro group-reduction) as reducible organic probe compounds, reactivities were observed to vary by orders of magnitude among the different minerals. As a general trend, rate constants increased in the order Fe(II) + siderite < Fe(II) + iron oxides < Fe(II) + iron sulfides. 4-Chloronitrobenzene reacted consistently about three orders of magnitude faster
than hexachloroethane, however, with Fe(II) on hematite and pyrite as interesting exceptions, where reaction rates of the nitroaromatic compound were unusually small. This indicates that a) the reactivities of surface bound Fe(II) species with respect to transformation of reducible contaminants depend strongly on the geological composition of the environment and that b) general reactivity trends may sometimes be influenced by specific substance-related effects so that care has to be taken in extrapolating reaction rates between very different contaminant classes.

Dehalogenation under iron-reducing conditions can in some cases lead to a rapid detoxification (e.g., production of CO, CO₂ and formate from carbon tetrachloride (CCl₄)). However, depending on the conditions, hydrogenolysis products may be formed (e.g., chloroform (CHCl₃) from CCl₄) that are toxic and more recalcitrant in reducing environments. A simultaneous transfer of two electrons and cleavage of two C-Cl bonds of CCl₄ in the initial rate-determining step of the reaction would completely circumvent such chloroform production. To distinguish between initial one- or two-bond-cleavage, in the third chapter ¹³C-isotope fractionation of CCl₄ was studied for reactions with Fe(II)/goethite (isotopic enrichment factor ε = -26.5‰) and with model systems for one C-Cl bond cleavage and either single-electron transfer (Fe(II) porphyrin, ε = -26.1‰) or partial two-electron transfer (polysulfide, ε = -22.2‰). These ε-values differed significantly from calculations for simultaneous cleavage of two C-Cl bonds (ε ≈ -50‰) indicating that only one C-Cl bond is broken in the critical first step of the reaction.

CHCl₃, CO and formate were found to be major products in the the reaction of CCl₄ with Fe(II) sorbed on goethite. Free trichloromethyl radicals in solution could be identified as important intermediates, which points to an initial one-electron transfer by surface-bound Fe(II). Conversely, free trichloromethyl anions in solution were not found to play a significant role, which indicates their possible stabilization as surface complexes. This suggests that radical and surface-mediated reactions may be more important for the outcome of this reaction than commonly thought. The reaction of CO to formate was observed to be catalyzed at the surface of goethite/Fe(II), however, not sufficiently fast to
explain the amounts of formate observed in dehalogenation experiments. Complementary to these mechanistic studies, Fe(II) sorption on goethite was investigated in the absence of external buffers. For the first time we could measure directly the release of two protons per Fe(II) adsorbed and obtain evidence for S-O-Fe(II)-OH as the predominant surface species.

Chapter 4 critically discusses way in isotope fractionation is currently quantified in environmental studies. Instead of the common application of the Rayleigh equation, a more accurate evaluation scheme is presented that considers 1) the effect of invariant isotope ratios at non-reactive positions and 2) the intramolecular competition of chemically equivalent, reactive positions.

In chapter 5 the design and synthesis of novel probe molecules is described, of the types a) CCl$_3$-CH$_2$-X ( -X = -OPO$_3$$^{2-}$, -OSO$_3$$^-$$, -$N$(CH$_3$)$_3$$^+$ ) and b) CCl$_3$-CH$_2$-CHOR-CH$_2$-CH$_2$-CH=CH$_2$ (R = H, phosphate). The CCl$_3$- group mimics the reactivity of major environmental contaminants such as CCl$_4$, CHCl$_3$ or CH$_3$CCl$_3$. It is linked to an anchor group that ensures water solubility (-OH), and/or attachment at surfaces (-OPO$_3$$^{2-}$, -OSO$_3$$^-$, -$N$(CH$_3$)$_3$$^+$ ). The presence of the double bond ensures trapping of radicals and carbenes in an intramolecular cyclization reaction. Such probe molecules may be helpful in future studies to further elucidate the role of radical and surface-mediated reactions in reductive dehalogenation.
General Introduction
1.1 Polyhalogenated Hydrocarbons

Over decades, polyhalogenated alkanes and alkenes have been produced and applied extensively all over the world. That they are fairly unreactive with oxygen or water made them attractive as non-explosive propellants, refrigerants, blowing agents, solvents, dry cleaning agents and fire extinguishing agents, in addition to their role as pesticides and chemical intermediates [19, 44, 16, 20, 1]. They were regarded as unproblematic and universally applicable, until evidence emerged, about 25 years ago, for carcinogenic effects in mammals (e.g., introduction in [19, 52]) and their potential to deplete the stratospheric ozone layer [15, 32, 31]. In the wake of regulatory acts such as the Montreal protocol, industrial production decreased strongly in the 1990s [43, 2, 36]. By then, however, their ubiquitous and unguarded application over many years had already created major environmental problems. Volatile chlorofluoro-(hydro)carbons (CFCs) lead to the destruction of the ozone layer and contribute to global warming, whereas dense chlorinated (hydro)carbons (CHCs) have started to pose a severe threat to drinking water resources. Because of their high density, these compounds can penetrate the subsurface in pure phase and accumulate at the bottom of aquifers [50]. In surveys of groundwater at hazardous waste disposal sites, chlorinated C\textsubscript{1} and C\textsubscript{2} hydrocarbons have regularly been identified as the most notorious pollutants [42, 33, 56, 34, 58, 48, 5, 12]. Prominent examples are tetra- and trichloroethene, 1,1,1-trichloroethane and chlorinated methanes such as methylene chloride, chloroform and tetrachloromethane (CCl\textsubscript{4}). Among them, CCl\textsubscript{4} is especially important because of its high toxicity (liver toxin and carcinogen [4]) and frequent occurrence [51].

1.2 Pathways for Reductive Dehalogenation of CCl\textsubscript{4}

Polychlorinated alkanes such as CCl\textsubscript{4} contain carbon atoms in a high oxidation state. This renders them very persistent under oxic conditions, but makes them susceptible to reductive dehalogenation under anoxic conditions in the subsurface, either by natural transformation or in reactive iron(0) subsurface barriers [47]. This reaction can be regarded as decisive for the pollutant’s long-
term fate in contaminated groundwaters. Either a C-Cl bond is converted into a C-H bond (hydrogenolysis), or two C-Cl bonds are reduced under release of two chloride ions (dichloroelimination) [49]. For CCl₄, the second case typically gives rise to benign products that are completely dechlorinated, such as CO, CO₂ or formate. (Although CO is highly toxic, it is referred to herein as ‘benign’ because it is readily transformed to nontoxic species such as formate.) In the first case, however, chloroform (CHCl₃) is produced, which is also toxic, but not as highly oxidized as CCl₄. It is therefore more persistent in anoxic environments, which intensifies the problem of groundwater pollution under anoxic conditions (in contrast to a better degradation, however, in oxic environments). Whether hydrolysis or dichloroelimination dominates depends on the reaction circumstances. A key role is thought to be played by very short-lived intermediates, radicals and carbenes. This has created great interest in the reaction mechanism as well as the influence of environmental conditions on product formation.

1.3 Importance of Iron-Reducing Zones in the Subsurface

Downstream of waste disposal sites, water is typically very rich in dissolved organic matter, which serves as a carbon and nutrient source for a variety of microorganisms. Under such conditions the available oxygen is quickly depleted, and many microorganisms specialize in using alternative terminal electron acceptors for respiration, such as nitrate, iron(III) and manganese(IV) minerals, sulfate or organic substances (in order of decreasing attractiveness). Consequently, on a large scale, a sequence of redox zones is created, with the most reducing (methanogenic) conditions commonly closest to a landfill, and nitrate-reducing conditions furthest downstream. The different redox zones can be more or less pronounced, depending on the relative abundance of the respective electron acceptors.

Iron is the most abundant transition element in the earth’s crust (5-6%), where it occurs in the oxidation states +II and +III. It is originally released from Fe(II)-containing magmatic (“primary”) rocks through aerobic weathering, and reprecipitates as iron(III) (hydr)oxides or in silicates. Microbial reduction [54] or
chemical complexation [53] can enhance the dissolution of these oxides and produce aqueous Fe(II), which, under exposure to oxygen, may be reoxidized to insoluble Fe(III). This interplay between reductive dissolution and oxidative reprecipitation in new compartments is one example of many natural processes that lead to a ubiquitous distribution of iron in the environment, with an average content in soils of about 3.2% [35]. Consequently, ferrogenic conditions typically represent a predominant redox zone downstream of waste disposal sites. In a Danish field study, for example, iron-reducing conditions were found to extend over 200 m downgradient of a landfill. At an average groundwater velocity of 150-200 m/year, this represents a very significant reaction zone. Indeed, transformation could be observed there for a range of reducible pollutants, among them halogenated hydrocarbons [12, 11].

1.4 The Importance of Surface-bound Fe(II) as Reductant in Iron-Reducing Zones

Natural in-situ reduction of chlorinated alkanes and alkenes has long been thought to occur almost exclusively in biotic transformations through dehalogenating bacteria [6, 13]. An increasing number of cultures and even isolated organisms have been discovered that can reduce chlorinated hydrocarbons, either by co-metabolic activities or because they use them as terminal electron acceptors for respiration [17, 22, 18, 27]. Such well adapted behavior, however, has mainly been encountered under strongly competitive conditions, such as in methanogenic [28] or sulfate-reducing environments (see also overview in [17]). In contrast to this highly localized occurrence, recent, increasing evidence indicates that dissipative iron-reducing microorganisms are present almost ubiquitously in the subsurface [37] [25]. These bacteria are largely responsible for the formation of iron-reducing zones, because they couple the oxidation of organic substrates to reduction of Fe(III) in minerals [26, 54]. This gives rise to considerable amounts of Fe(II), which may be contained inside iron(III) minerals, bound to their surface or released in solution, from whence Fe(II) can sorb again to other minerals. Under such conditions, abiotic reaction of reducible contaminants through surface-bound Fe(II) can become
important relative to direct biotic transformation. In a Danish field study, an injection experiment with nitroaromatic compounds as reactive tracers provided strong evidence that surface-bound Fe(II) was the single most important mediator in the reduction of aromatic nitro groups [46]. At the same site evidence was also obtained for significant abiotic dehalogenation of CCl₄ through Fe(II) species [38, 45, 7]. In addition, McCormick et al. [29] observed that reductive dehalogenation of CCl₄ in the presence of iron-reducing bacteria was mainly caused by Fe(II) at the surface of biogenic magnetite, and only to a small part by direct enzymatic dehalogenation. Wielinga et al. [57] came to a similar conclusion in the case of chromate reduction. Very recent results of Lee and Batchelor show finally that even very persistent chlorinated alkenes can be dehalogenated by mineral-bound Fe(II) [24, 23]. How much reactions are accelerated by Fe(II) at surfaces in comparison to Fe(II) in solution is illustrated by a wide range of studies addressing the reductive transformation of many different pollutants with ferrous iron. Transformation rates in reactions with Fe(II) were regularly found to be orders of magnitude higher in the presence of iron oxide surfaces [8, 21, 39, 10]. Last but not least, surface bound Fe(II) is thought to play an important role in the long-term performance of zero-valent iron reactive subsurface barriers [47].

### 1.5 Challenges in Investigating Reductive Dehalogenation by Surface-Bound Fe(II)

Several main difficulties obstruct the detailed investigation of dehalogenation by surface-bound Fe(II), characteristic for heterogeneous reactions of trace compounds at surfaces present in aquatic environments:

1) The actual reactive iron(II) species at the surface are very difficult to distinguish from the bulk mineral phase underneath. Analytical techniques such as X-ray diffraction (XRD, for determination of crystal structures) or Mössbauer spectroscopy (sensitive to the symmetry and chemical environment of Fe in a mineral) are typical “bulk-phase techniques”. Even fairly surface-sensitive methods like Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) or Micro-Raman Spectroscopy (both for identification of minerals by
means of vibrational spectra) have light beam penetration depths of about 1 μm and “see” therefore exclusively bulk mineral phases. Many truly surface-specific methods, finally, such as Scanning Tunneling Microscopy (STM) (for investigation of surface nanostructures) or X-ray Photoelectron Spectroscopy (XPS) (to obtain oxidation states of surface atoms) cannot be directly used, because in the aqueous suspension under investigation no high vacuum can be applied. Little is therefore known about the exact nature of ferrous iron species bound to the surfaces of different iron minerals. They could possibly represent surface complexes of more or less uniform reactivity, which would make rough estimates for the persistence of reducible pollutants under ferrogenic conditions rather easy. Contrarily, they may depend strongly on the crystal structure and chemical composition of the mineral bulk phase underneath. Presently, elucidation can, therefore, primarily be expected from experiments with reducible contaminants as reactive tracers.

In chapter two of this thesis, a comparative reactivity study was conducted with a range of important iron-bearing minerals in nature: iron(II) sulfides, iron(II) carbonate, a ferruginous clay mineral and a number of iron (hydr)oxides such as goethite (α-FeOOH), lepidocrocite (γ-FeOOH), hematite (α-Fe₂O₃) magnetite (Fe₃O₄) and green rust (Fe²⁺₄Fe³⁺₂(OH)₂SO₄·4H₂O) [14, 3]. They were equilibrated with 1 mM ferrous iron in solution, and allowed to react with the reducible pollutants hexachloroethane and 4-chloronitrobenzene, two representatives of major contaminant classes [49]. Reactivities of the different minerals are compared on the basis of surface-normalized rate constants.

2) A second major difficulty in investigating dehalogenation by surface-bound Fe(II) is related to the extremely low concentrations of intermediate organic species formed during the reaction. This is partly due to the general low solubility of chlorinated hydrocarbons in water and to the fact that only a fraction of the dissolved substrate is present at the reactive surface. Secondly, however, the dehalogenation progress is very fast once the reaction has started. The lifetime of intermediate radicals and carbenes is therefore so short that their direct analytical detection (e.g. by magnetic resonance techniques) is impossible. Indirect evidence is necessary to infer their existence and to reconstruct the
reaction pathway for better understanding factors that lead to product formation.

In chapter three of this thesis the reaction of CCl\textsubscript{4} with Fe(II) sorbed to the surface of goethite was partly investigated by rather conventional methods. The influence of environmental parameters was studied, such as pH and organic matter (H\textsuperscript{+} donor) in the form of added perdeuterated isopropanol. These experiments were complemented by sorption studies of Fe(II) on goethite to gain information about possible Fe(II) surface species. The results are discussed in terms of possible reaction mechanisms and environmental implications.

Then two new methodical approaches to the difficult mechanistic elucidation of surface-catalyzed dehalogenation reactions are presented: i) application of isotope fractionation studies (chapter 3 & 4) and ii) the synthesis of suitable probe molecules for substrate enrichment at surfaces and trapping of intermediates.

In chapter three carbon isotope fractionation was measured in reactions of CCl\textsubscript{4} with iron(II) porphyrin (initial one-electron transfer, one C-Cl bond broken [41, 9]), with polysulfide (partial two-electron transfer, one C-Cl bond broken [40, 30]) and with goethite/Fe(II) (to be investigated). The extent of observed fractionation was taken to infer on the number of C-Cl bonds broken in the first rate determining step of the reaction. The use of isotope fractionation in environmental studies is also subject of chapter four, where the Rayleigh equation, a common evaluation procedure in environmental chemistry, is subjected to a critical evaluation.

In chapter five, finally, the optimized design and synthesis of novel model compounds is presented. They include a charged anchor group such as a phosphate group that ensures water solubility and/or attachment at reactive surfaces. In addition, these molecules contain a reactive CCl\textsubscript{3}- group, which mimics the reactivity of chlorinated alkanes such as CCl\textsubscript{4}, and a double bond for trapping intermediate radicals and carbenes. These novel molecules were designed to exhibit very little susceptibility to side reactions, which represented a major problem in previous studies [55].

In chapter six the results of this thesis are summarized, and an outlook is given on possible future applications of the methods presented.
1.6 References

[16] D. A. Fisher and P. M. Midgley, The production and release to the atmosphere of


[32] M. J. Molina and F. S. Rowland, Stratospheric Sink for Chlorofluoromethanes -


General Introduction


Reactivity of Fe(II)-Bearing Minerals towards Reductive Transformation of Organic Contaminants*

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Abstract

Fe(II) present at surfaces of iron-containing minerals can play a significant role in the overall transformation of reducible subsurface contaminants. The effect of various minerals on the reactivity of surficial Fe(II)-species was evaluated in a comparative study including siderite (FeCO$_3$), nontronite (ferruginous smectite SWa-1), hematite (α-Fe$_2$O$_3$), lepidocrocite (γ-FeOOH), goethite (α-FeOOH), magnetite (Fe$_3$O$_4$), sulfate green rust (Fe$^{II}$_4Fe$^{III}$_2(OH)$_{12}$SO$_4$·4H$_2$O), pyrite (FeS$_2$) and mackinawite (FeS). The reactivities of the different minerals were investigated in aqueous suspension under similar conditions (pH 7.2, 25 m$^2$ mineral/L, 1 mM Fe(II)$_{aq}$, O$_2$ (aq) ≤ 0.1 µg/L) which enables a comparison based on surface-normalized pseudo first-order rate constants for organic pollutant reduction. Hexachloroethane and 4-chloronitrobenzene were used as probe compounds for reducible organic contaminants representing dehalogenation and nitroaryl reduction reactions. The reactivities of the different Fe(II)-containing minerals varied greatly and systematically both within each data set obtained with either probe compound as well as between the two data sets. As a general trend, surface area-normalized reaction rates increased in the order Fe(II) + siderite < Fe(II) + iron oxides < Fe(II) + iron sulfides. 4-Chloronitrobenzene was transformed much more rapidly than hexachloroethane, except for suspensions of hematite, pyrite and nontronite. The results indicate that a reactivity trend of Fe(II) bearing minerals observed for one particular reaction can be dominated by specific interactions of the oxidant with the surface. Care must, therefore, be taken in extrapolating reactivity data of surface-bound Fe(II) between different compound classes.
2.1 Introduction

Numerous previous studies have pointed out the high reactivity of ferrous iron when bound to ferric oxide minerals (“surface-bound Fe(II)”) in comparison to Fe(II)\textsubscript{aq} in solution. Surface-bound Fe(II) was found to enhance dramatically transformation rates of many reducible pollutants, such as nitroaromatic compounds (NACs) \[25, 37, 21\], polyhalogenated alkanes \[16, 1, 33\], chromium(VI) \[5\], technetium(VI) \[12\], uranium(VI) \[31\], oxamyl and related carbamate pesticides \[43\] or disinfectants such as monochloramine \[48\]. Considering that surface-bound Fe(II) may be continuously regenerated in the subsurface, for example, by microbial iron-reduction \[3, 10\], it is one of the most potent natural mediators for reductive in-situ transformation of contaminants. Field studies have demonstrated that even in geochemically complex polluted aquifers surface-bound Fe(II) was the predominant reductant of nitroaromatic compounds \[37\]. A very recent study on reduction of polyhalogenated methanes in iron- and sulfate-reducing sediments came up with similar conclusions \[23\]. The reactivity of surface-bound Fe(II) can be rationalized within the framework of surface complexation theory. Hydroxo ligands greatly enhance the oxidation of Fe(II) \[32\] due to both increased electron density at the Fe(II) center and stabilization of the product Fe(III) \[47\]. A surface complex of the type =Fe(III)-O-Fe(II)-OH was proposed \[9\], irrespective of mineral stoichiometry and crystal structure of the iron oxide bulk phase. From an environmental engineering point of view, the existence of such defined Fe(II) surface species of uniform reactivity would largely simplify predictions of the fate of reducible pollutants at contaminated sites where iron-reducing conditions prevail.

There are, however, several reasons why this approach may be an oversimplification for a wider range of minerals: i) Reactive ferrous iron does not only form on oxides, but also on surfaces of other major iron minerals such as iron sulfide (FeS), pyrite (FeS\textsubscript{2}) or siderite (FeCO\textsubscript{3}). ii) Among the oxide minerals, mixed Fe(II)/Fe(III) phases such as magnetite (Fe\textsubscript{3}O\textsubscript{4}), green rust or reduced ferruginous clay minerals may differ in reactivity from Fe(II) at pure iron(III) oxides, owing to the presence of structural Fe(II) within the mineral
lattice. iii) Even various ferric (hydr)oxides such as goethite (α-FeOOH), lepidocrocite (γ-FeOOH) or hematite (α-Fe₂O₃) have distinctive crystallography and likely display different surface structures and reactivities. In addition, evidence for reactive internal surfaces has been found in layered minerals such as green rust and clay minerals [18, 17, 20]. Because of all these effects, the co-existence of an array of Fe(II) species with differences in reactivity is very likely.

In contrast to solution chemistry, where linear free energy relationships (LFERs) between reduction potential and rate constants could be derived for various dissolved Fe(II) complexes [6, 49, 45, 44], the reduction potential of Fe(II) bound at surfaces is not known. In an alternative approach, however, a probe compound might be used to measure the reactivity of Fe(II) in the presence of different minerals so that surface-bound Fe(II) species could be classified according to the probe compounds reaction rates. If it is possible to normalize these rates to the density of reactive sites, two extreme cases can be imagined. (a) Fe(II) on different minerals reacts with a given probe compound at a uniform rate. This would support the picture of one “representative” surface complex such as =Fe(III)-O-Fe(II)-OH (Figure 2-1a). (b) The reactivity of Fe(II) at different minerals differs greatly. This would be indicative of various Fe(II) surface sites with different intrinsic reactivities (Figure 2-1b). Such a reactivity pattern can then be compared to one obtained with a second reducible probe from a different compound class. Again two cases can be imagined. (c) Reaction rates of Fe(II) with the second probe follow very closely the trend of the first. Rates would then be controlled by 1) the intrinsic reactivity of Fe(II) on a given surface as “calibrated” with the first probe compound and 2) the reduction potential of the probe compounds. Different reaction mechanisms would not play a major role, simplifying greatly predictions of reductive pollutant transformation (Figure 2-1c). Finally (d): Reaction rates of one probe compound do not follow the trend observed with the other. This would indicate that specific reaction mechanisms and/or the accessibility to different surface sites determined their reactivity, complicating extrapolations of Fe(II) reactivities between different compound classes (Figure 2-1d).
Figure 2-1. Classification of Fe(II) on different minerals according to probe compound reaction rates that are normalized to reactive site densities. Possible scenarios: (a) “uniform reactivity”, (b) different intrinsic reactivities; (c) similar and (d) different patterns with different contaminants.

Quantitative reactivity patterns of Fe(II) bound to different minerals are, however, very difficult to derive from the presently available literature data. Major obstacles are 1) the lack of consistent data sets generated under comparable experimental conditions and 2) the difficulty in determining true concentrations of reactive Fe(II) surface-sites to normalize the observed reaction rates accordingly. In addition to studies of Fe(II) sorbed on Fe(III) oxides, the wide range of Fe(II)-containing minerals studied in reductive transformations of organic pollutants includes magnetite [41, 19, 28], various forms of FeS (troilite, mackinawite; [41, 7]), green rusts [14, 28], lattice bound Fe(II) in tectosilicates (e.g., biotite [27] and smectites [20, 8]). However, these studies were conducted with different reducible pollutants, at different pH values, different mineral
concentrations and different degrees of surface saturation by Fe(II) so that quantitative comparisons are not feasible. In studies dealing with the reactivity of Fe(II) bound to the surface of pure iron(III) minerals, observed rate constants were sometimes normalized to the concentration of surface-bound Fe(II) determined in adsorption experiments. However, because mixed valent Fe(II)/Fe(III)-minerals contain potentially reactive Fe(II) in their mineral structure, this approach is not generally applicable. In addition, the measured total concentration of surface bound Fe(II) may overestimate the concentration of reactive sites, as in the case of nontronite, where only edge-bound Fe(II) has been found to be reactive whereas Fe(II) sorbed at siloxane surfaces was unreactive [20]. Alternatively, reaction rates could be normalized to the total BET-surface area of the mineral. The surface areas of oxygen-sensitive minerals, however, have not always been determined in such studies, owing to experimental difficulties in performing lyophilization and BET-measurement under anoxic conditions.

In this study we investigated the reactivity of surface bound Fe(II) for a series of environmentally relevant minerals under similar and defined conditions, i.e. at pH 7.2, at a concentration of 25 m² mineral surface per liter and 1 mM of dissolved Fe(II). Fe(II) was present in excess to ensure saturation of surface sorption sites so that comparable conditions prevailed during the experiment. Hexachloroethane and 4-chloronitrobenzene were used as probe compounds, as representatives of polyhalogenated alkanes and nitroaromatic compounds, respectively, two important classes of reducible organic contaminants [38]. The major goals of this study were 1) to assess the reactivity of surface-bound Fe(II) present on different minerals and 2) to explore the possibility of predicting reaction rates of one probe compound from measured data of another, such as sketched in Figure 2-1.

2.2 Materials and Methods

*Maintenance of Anoxic Conditions.* If not mentioned otherwise, manipulations were carried out inside an oxygen free glovebox (23°C) with external regenerator, in which the O₂-level was continually controlled by an
oxygen sensor (TOS 1.0, Ionic Systems) and kept below 0.1 ppm. As an additional visual control, siderite (FeCO₃) was periodically exposed to the glovebox atmosphere. Siderite maintains its white color under strict exclusion of oxygen, whereas it turns brown within seconds and then red when exposed to small amounts of oxygen (low ppm level). The fact that FeCO₃ remained white during all manipulations performed inside and (in closed containers) outside the box, such as lyophilisation, BET-surface measurements, flame sealing of ampules or agitating of vials, was taken as visual evidence for overall strictly anoxic conditions.

2.2.1 Materials / Synthesis and Characterization of Minerals

All air-sensitive minerals were synthesized in the glovebox, washed repeatedly with deionized oxygen-free water (prepared by heating to 90°C and subsequently purging with argon for 3 hours) and freeze-dried. The BET-surface areas of the resulting dry powders is listed in Table 1. Crystal structures were confirmed by XRD-analysis (see Figure A1-1 in the Appendix A1).

Goethite, lepidocrocite and hematite were purchased as fine powder from Bayer (Bayferrox 910, 943 and 105 M, respectively). Their crystal structure has been confirmed in previous studies [33]. Pyrite was purchased in chunks (Alfa Aesar) and ground in a mortar in the glovebox.

Fe(II)-solutions were prepared by adding 28 g (0.5 mol) iron powder (Merck) to 1 L of 1 M deoxygenated HCl. The mixture was brought to reaction by heating to 70°C under gentle stirring (60 rpm) during 2-2.5 h, until evolution of H₂ ceased (gas outlet for pressure release!). The solution was then filtered within the glovebox through a 0.2 µL PTFE filter to remove excess iron powder. The exact concentration of dissolved Fe(II) was determined photometrically according to the phenanthroline method [15].

Siderite was synthesized by mixing 500 mL of 1 M NaHCO₃ and 500 mL of 0.5 M FeCl₂ under stirring for 14 h in a closed container. From time to time the lid was opened to release CO₂. After sedimentation, the supernatant was decanted and the mineral was repeatedly resuspended, until the supernatant had a pH of 7, followed by freeze-drying.
Mackinawite was synthesized by mixing 300 mL of 0.5 M Na₂S (32 g Na₂S·7-9 H₂O (Fluka)) and 300 mL of FeCl₂ under stirring for 48 h. The mixture was repeatedly centrifuged (6000 rpm) and resuspended in 10 mM NaCl solution (2x) and water (1x). The wet paste that remained after centrifugation was stored for 2 years before lyophilization.

Sulfate green rust, GR₅O₄ was prepared by mixing 250 mL of 150 mM Fe(II)SO₄ and 100 mL 25 mM iron(III) sulfate (prepared from desiccated Fe₂(SO₄)₃), adding 200 mL 0.3 M NaOH and titrating with 25 mM iron(III) sulfate solution to pH 7. The suspension was stirred for 7 days, and the pH was repeatedly adjusted to pH 7. Finally the suspension was washed in a glass filter funnel and thereafter quickly freeze-dried.

Magnetite was prepared following a procedure by Regazzoni et al. [34]. Briefly, 0.5 L 0.25 M FeCl₃ solution and 0.5 L 0.5 M FeCl₂ solution were mixed, heated to 80°C and titrated with 2 M NaOH to pH 7. The mixture was stirred for one month, and the pH was repeatedly adjusted to 7 by addition of HCl. The mineral was washed several times by sedimentation and decantation, before lyophilization.

Chemically reduced nontronite (ferruginous smectite SWa-1) purchased from Source Clay Mineral Repository (University of Missouri Columbia, MO) was prepared in the glovebox according to a method adapted from Stucki et al. [46], as described in detail by Hofstetter et al. [20]. Briefly, assays containing 0.25 g finely ground clay mineral (size fraction < 2 µm) were suspended in 12.5 mL citrate-bicarbonate buffer and diluted with water to 50 mL. After stirring for 15 min, 0.75 g Na₂S₂O₄ salt was added. After 8 days the clay was washed and homoionized by pressurized filtration (80 mL ultrafiltration cell, Millipore AG, Volketswil, Switzerland), three times with 1 M NaCl and once with pure water (0.2 µm Fluoropore (PTFE) membrane filters, 47 mm diameter, Millipore).

Lyophilisation of all minerals was carried out according to the Schlenk method [40]. Mineral suspensions were filled into a 200 mL glass finger connected to an empty 1 L round bottom flask via a U-shaped lyophilisation bridge, which was equipped with an outlet with stopcock for evacuation. The
whole apparatus was assembled inside the glovebox, closed and taken out. The suspension was frozen by submerging the glass finger (not the fitting!) for 2 hours in liquid nitrogen. The outlet of the stopcock was then connected via a metal hose to a vacuum pump (vacuum $2 \cdot 10^{-3}$ mbar), the hose was flushed several times by quickly opening and closing the stopcock and the apparatus was finally evacuated for 5 minutes. After disconnecting the pump, the glass finger was taken out of the coolant, and instead the round bottom flask was immersed in liquid nitrogen for 2-3 days. Thus, because of the low pressure, the ice sublimated completely from the frozen sample suspension to the cooled round bottom flask leaving the mineral as a fine, dry powder in the glass finger. The apparatus was subsequently transferred back into the glovebox, demounted, and the powder was stored in a closed container in the glovebox.

*Surface areas* of the minerals were determined by adsorption of nitrogen according to the BET-method [4] using a Sorptomatic 1990, Fisons device. Burettes were equipped with a stopcock, which could be filled and closed inside the glovebox. They were then evacuated on an external vacuum line, closed and connected to the BET-instrument. Prior to opening the stopcock and starting the analysis, all connections inside the instrument were evacuated and flushed several times with nitrogen.

*X-ray diffraction measurements* were performed on an XRD Siemens D 5000 and XDS 2000, Scintag, Cu Kα source, with a scanning rate of 1 °/min so that measurements took about 70 min. The thin-layered samples were prepared in the glovebox and kept in air-tight containers until immediately before the measurement.

*Hexachloroethane* (Fluka), *tetrachloroethene* (Aldrich), *bromoform* (Fluka), *4-chloronitrobenzene* (Fluka) and *4-chloronitroaniline* (Fluka) were of the highest purity available. They were stored at 4°C in the dark and used without further purification. Spike solutions of 50 – 100 µM were prepared in degassed, anoxic methanol (Scharlau).
2.2.2 Experimental Conditions

Experiments were conducted in 10-14 mL sample containers at 23°C, with mineral suspensions of 25 m²/L surface concentration, contaminant concentrations of 0.5 - 3 μM, 1 mM dissolved Fe(II), a pH of 7.2 and ionic strengths of 3.4 – 11.0 mM (see Table A1-1 in the Appendix A1). A pH of 7.2 was chosen because of its environmental relevance, notwithstanding the fact that sorption of Fe²⁺ on mineral surfaces is strongly pH-dependent and leads to different degrees of surface saturation at different minerals [11]. We chose small initial contaminant concentrations of 0.5 to 3 μM to minimize limitations of reaction kinetics by surface sites. Further, we added predetermined amounts of FeCl₂ to the mineral systems to obtain – after 48h sorption time – concentrations of Fe(II) of 1 mM. This was (a) high enough to ensure maximum sorption at this pH, (b) low enough to prevent precipitation of Fe(OH)₂ (K = 4.8 10⁻¹⁷, [30]) and (c) reflects conditions that may be encountered in iron-reducing natural environments [3]. A relatively low concentration of mineral surface (25 m²/L) was chosen to prevent coagulation of particles that may limit the accessibility of the surface for sorption of Fe(II) and reaction [1]. In experiments conducted with hexachloroethane and goethite/Fe(II), the ionic strength was systematically varied from 5 to 25 mM, which corresponds to a 20-fold to 100-fold excess in comparison to the volumetric concentration of surface bound Fe(II). No significant differences in reaction rates could be observed (data not shown). We therefore did not use an ionic strength buffer, except for mackinawite, where sedimentation and filtration of particles were hampered by the low ionic strength.

Preparation of Mineral Suspensions. An aliquot of mineral corresponding to 25 m²/L surface area was suspended in anoxic, deionized water. The pH was adjusted to 7.2 (1 N HCl / NaOH), aliquots of FeCl₂ were added and the pH adjusted again, until the concentration of Fe(II) in solution was 1 mM. For magnetite and green rust, Fe(II)ₐq concentrations were slightly higher, because Fe(II) was released from the surface of the freshly prepared minerals. Suspensions were buffered at pH 7.2, either through the intrinsic buffer capacity of the mineral surface or by small amounts (0.4 - 1.2 mM) of added
4-morpholinopropanesulfonic acid (MOPS). A pH adjustment to 7.2 was not feasible for sulfate green rust, because addition of HCl or MOPS resulted in rapid formation of a secondary black phase. For this mineral, two different set-ups were prepared: a) without external buffer, at pH 8; under these conditions, green rust maintained its green color for hours and was thus considered sufficiently stable for our purposes; b) with addition of MOPS, at pH 7.5; under these conditions, a rapid color change to black could be observed. The exact ionic composition of all experiments is reported in Table A1-1 in the Appendix A1.

**Kinetic Experiments.** Kinetic experiments were initiated by addition of 0.1 to 0.5 mL methanolic contaminant stock solutions, and they were stopped by filtration through 0.2 µm filters in the case of 4-chloronitrobenzene and by liquid/liquid extraction with hexane in the case of hexachloroethane. The sampling schema was adapted to the time scale of the experiments, which embraced half-lives of less than 10 seconds to several weeks. Experiments with 4-chloronitrobenzene were mostly performed inside the glovebox, typically conducted in 14 mL glass flasks with stopcock and magnetic stirrer. Every 1-2 minutes, the flasks were quickly opened, a 1 mL aliquot was withdrawn with a polypropylene syringe (BD Plastipak™) and was subsequently filtered into autosampler vials. Losses of the nitroaromatic compound through volatilization and sorption were found to be negligible. For some extremely fast reactions, 10 mL of mineral suspensions were drawn into a polypropylene syringe (BD Plastipak™). The reaction was initiated by adding a contaminant stock solution, a PTFE filter (25 mm x 0.2 µM, BGB Analytik) was then quickly emplaced and the syringe was shaken for 5 seconds, before the solution was filtered into 1 mL autosampler vials with sampling intervals of about 5 seconds. In experiments lasting longer than one hour batches were set up in crimp serum cap vials with Viton stoppers, removed from the glovebox and agitated on a reciprocating shaker at 23°C in the dark until analysis. Nearly all experiments in this study were therefore conducted in 9 - 16 identical batches of 10 mL suspensions. For each sampling point, one batch was sacrificed and used for 2-3 replicates that were analyzed by GC-ECD and HPLC, respectively (see below). Longer lasting experiments (duration one to several weeks) were conducted in glass ampules.
(10 mL gold band, Wheaton). Inside the glovebox, ampules were filled with 10 mL mineral suspension, spiked with contaminant stock solutions and closed with Viton stoppers (prepared from Viton strings). The suspensions were frozen outside the box and then flame-sealed. To avoid bursting of the glass during flame sealing, the Viton stopper was pierced for pressure release by a cannula (1.2 mm diameter, Microlance 3), which was loosely kept inside an argon-flushed hose.

2.2.3 Analytical Procedures

For analysis of chlorinated hydrocarbons, 0.4 mL mineral suspension was extracted with 0.35 mL hexane (Merck), which contained 5 µM CHBr\textsubscript{3} as internal standard. Extraction took place for 45 seconds on a vortex shaker, in 0.8 mL autosampler vials with PTFE-coated butyl rubber septa. Six calibration standards were prepared in water and extracted in an identical way, except for pentachloroethane, which eliminates HCl in aqueous solution so that standards were prepared directly in hexane/CHBr\textsubscript{3}. Samples and standards were either analyzed within 2 days or stored at -30°C until analysis. Analysis took place on a gas chromatograph with electron capture detector (GC/ECD, Carlo Erba HRGC 5160 with autosampler AS200 and a Carlo Erba ECD 400 with a Ni-63 source) equipped with a DB-624 column (i.d. 0.32 mm, 1.8 µm film thickness, J&W). The injector and detector temperatures were 250°C and 320°C respectively, carrier gas flow 1.5 mL/min (hydrogen), make-up gas flow 12 mL/min (90% argon, 10% methane). The parameters for measurement were as follows: injection of 1.5 µL splitless, 60°C (1 min.), ramp 10°C/min to 175°C (0 min.), ramp 30°C/min to 250°C (6 min.).

Aqueous filtrates for analysis of 4-chloronitrobenzene and 4-chloroaniline were kept in 1 mL autosampler vials with PTFE septa at -30°C and then analyzed without further treatment. Analysis took place by gradient high performance liquid chromatography (HPLC) on an RP-8 reversed-phase column (125 x 4 mm) equipped with a precolumn (4 x 4 mm; both LiChroCart stainless steel cartridge, 5 µm spheres; Merck) connected to a pumping system (Gynkotek M480 with gradient pump Henggeler DG4) supplemented with an autosampler
Reactivity of Fe(II)-Bearing Minerals  25

(Gina 50; Gynkotek) and a diode array UV detector (340S, Gynkotek). The injected volume was 100 µL, the flow 1 mL/min, the eluents were (A) methanol, (B) 5 mM phosphate (pH 7) in H₂O, (C) H₂O, and the gradient program was as follows: 5 min. prior to injection: 20% A, 20% B, 60% C; ramp to 4 min prior to injection: 20% A, 50% B, 30% C; ramp to 0 min (injection): 20% A, 80% B; ramp to 5 min: 60% A, 20%B, 20% C; ramp to 10 min: 60% A, 40% C; ramp to 13 min: 90% A, 10% C; ramp to 15 min (end): 20%A, 80%C; 4-chloronitrobenzene (t_{ret} = 10.9 min) was quantified at 276 nm, 4-chloroaniline (t_{ret} = 8.7 min) at 245 nm. Frequently an additional peak (probably 4-chlorophenyl hydroxylamine, see Results and Discussion, λ_{max} = 240 nm) appeared at t_{ret} = 7.7 min. Its area increased and decreased with the missing mass balance observed in the experiments (see Figure 2-2c).

2.3 Results and Discussion

2.3.1 Reaction kinetics and product formation

The reactions of hexachloroethane and 4-chloronitrobenzene with mineral bound Fe(II) generally followed pseudo first-order behavior (see examples in Figure 2-2). Reaction of hexachloroethane produced quantitatively tetrachloroethene (C₂Cl₄) for all minerals. No further dechlorination of C₂Cl₄ was observed during the short period of our measurements (2-3 half-lives of the reaction of hexachloroethane). In the case of fast transformation (half-lives of a few hours) small amounts of pentachloroethane (C₂HCl₅) and traces of trichloroethene (C₂HCl₃), its dechlorination product, were detected (see Figure 2-2a and Scheme 2-1).

\[
\text{Dichloroelimination: } \quad \text{C}_2\text{Cl}_6 + 2e^- + 2\text{Cl}^- \rightarrow \text{C}_2\text{Cl}_4 + \text{HCl} \\
\text{Hydrogenolysis: } \quad \text{C}_2\text{Cl}_6 + \text{H}^+ + \text{Cl}^- \rightarrow \text{C}_2\text{HCl}_5 + 2\text{Cl}^- + 2e^-
\]

\text{Scheme 2-1}

Roberts et al. [36, 35] have argued that the pentachloroethyl carbanion decomposes quickly without significant protonation in aqueous solution,
indicating that formation of $\text{C}_2\text{HCl}_5$ may be diagnostic for formation of pentachloroethyl radicals. At our experimental conditions, i.e., in the absence of efficient H-donors, we do not expect nor find significant formation of pentachloroethane, even if the reaction mechanism involves pentachloroethy radicals.

In most experiments with 4-chloronitrobenzene, disappearance of the parent compound was more rapid than the formation of 4-chloroaniline (Figure 2-2c). We attributed a peak in the HPLC chromatogram observed at intermediate reaction times (see Materials and Methods), to transient accumulation of the intermediate 4-chlorophenyl hydroxylamine based on its elution time in proximity of 4-chloroaniline and its UV-spectrum. In analogy to earlier studies by Dunnivant et al. [13] and Klausen et al. [25] (see Scheme 2-2); no indication for 4-chloronitrosobenzene was found, except for possible traces in reactions with magnetite (data not shown).

$$
\begin{align*}
\text{Ar-NO}_2 & \xrightarrow{2e^-, 2\text{H}^+, \text{H}_2\text{O}} \text{Ar-NO} & + 2e^-, 2\text{H}^+ & \xrightarrow{2e^-, 2\text{H}^+, \text{H}_2\text{O}} \text{Ar-NHOH} \\
\text{Ar-NH}_2 & & & \text{Ar-NH}_2
\end{align*}
$$

Scheme 2-2

Pseudo-first-order rate constants $k_{\text{obs}}$ for 4-chloronitrobenzene (4-Cl-NB) were determined from $\ln \left( \frac{[4-\text{Cl-NB}]}{[4-\text{Cl-NB}]_{t=0}} \right)$ vs. time plots using data points at the beginning of the experiment. After complete disappearance of 4-chloronitrobenzene at a time $t'$, pseudo-first-order rate constants were also calculated for 4-chlorophenyl hydroxylamine (4-Cl-NOH), from $\ln \left( \frac{[4-\text{Cl-NOH}]}{[4-\text{Cl-NOH}]_{t=t'}} \right)$ vs. time plots, starting at time $t'$ and using calculated concentrations of the intermediate by assuming a complete mass balance. As can be seen from Figure 2-2c, experimental data could be fitted well using this assumption of consecutive reactions. Exceptions are experiments with siderite, hematite, pyrite and with Fe(II) in homogeneous solution, where no accumulation of 4-chlorophenyl hydroxylamine was observed (Figure 2-2d), and with green rust, where initial disappearance of 4-chloronitrobenzene was too rapid to be quantified.
Experimental reaction rates constants $k_{obs}$ were checked for artifacts such as i) mass-transfer limitations or ii) saturation kinetics at the surface. i) Mass-transfer may become rate-limiting if surface-reactions are so fast that contaminant diffusion to the surface becomes the slow step in the overall process [2]. Values of $k_{obs}$ are then of similar magnitude as estimates for $a \cdot k_L$, where $k_{obs}$ is the observed pseudo first-order rate constant, $a$ the ratio of external (geometric) particle surface area to volume of solution (m$^{-1}$) and $k_L$ the calculated mass transfer coefficient (ms$^{-1}$). Our estimates of $a \cdot k_L$ (see Supporting
Information in the Appendix A1 and Table 2-1) indicate that mass transfer was possibly rate-limiting only in the reaction of 4-chloronitrobenzene with mackinawite (FeS) (100%), goethite (40%) and magnetite (30%), but not in reactions of hexachloroethane. ii) Saturation kinetics at the surface occurs, if competition between substrates for a restricted number of surface sites poses a limit to the overall reactivity. This effect was investigated with pyrite/Fe(II) and lepidocrocite/Fe(II) at elevated concentrations of 4-chloronitrobenzene. Our results (see Supporting Information in the Appendix A1) indicate that surface competition was not likely to play a role at the low contaminant concentrations of 0.8 – 2 µM used in this study (see Figure 2-2), but may become important at higher substrate loadings (5-20 µM at 25 m²/L mineral surface concentrations).

2.3.2 Reactivity of different Fe(II)-containing minerals with hexachloroethane

Surface-area-normalized reaction rate constants \( k_{obs}' \) \( (k_{obs}' = k_{obs}/\{\text{surface area [m²/L]}\}) \) of hexachloroethane differed greatly for Fe(II) bound on different minerals (see Figure 2-3a), in a way similar to the sketch in Figure 2-1b. The reactivity increased in the order \( \text{Fe(II)}_{aq} + \text{siderite} < \text{Fe(II)} + \text{iron oxides} < \text{Fe(II)} + \text{iron sulfides} \), with the ferruginous clay mineral nontronite ranking between the iron oxides. This observed reactivity pattern can be an indication of different intrinsic reactivities of surface-bound Fe(II), but it could also be caused by a) different surface-densities of reactive Fe(II) or b) specific interactions of the contaminant with the surface (e.g., precursor complex formation). For minerals where Fe(II)-sorption had been determined (see Table 2-1), reaction rates could alternatively be normalized to the sorption-density of Fe(II), rather than to BET surface areas (Figure 2-3b). In the case of iron oxides both normalization procedures lead to values for hexachloroethane that were consistent within half an order of magnitude (see Figure 2-3a and 2-3b). This indicates that a) the reactivity of Fe(II) on various iron oxides may indeed be attributable to similarly reactive \( =\text{Fe(III)}-\text{O}-\text{Fe(II)}-\text{OH} \) surface complexes such as sketched in Figure 2-1a and that b) normalizations on surface area and/or Fe(II)-sorption-site-density give both practical approximations to the true concentration of reactive sites that cannot be measured directly. The large differences in
Figure 2-3. Logarithmic pseudo-first-order rate constants for different Fe(II) containing minerals with the reducible contaminants (□) hexachloroethane, (□) 4-chloronitrobenzene and (○) 4-chlorophenyl hydroxylamine. (a) Surface area-normalized, (b) normalized to sorbed Fe(II).
<table>
<thead>
<tr>
<th>Minerals</th>
<th>Hexachloroethane</th>
<th>4-Chlorophenyl hydroxylamine a</th>
<th>4-Chloronitrobenzene</th>
<th>Mass Transfer constants (a kL / 25) b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>surface area [m²/g]</td>
<td>Fe(II)ads [µmol/m²]</td>
<td>log ( k_{obs} )</td>
<td>( k_{obs} ) [h⁻¹m²L]</td>
</tr>
<tr>
<td>Mackinawite (FeS)</td>
<td>12.6</td>
<td>10.4</td>
<td>-1.79</td>
<td>1.6 10⁻²</td>
</tr>
<tr>
<td>Pyrite (FeS2)</td>
<td>0.88</td>
<td>-1.4</td>
<td>-1.80</td>
<td>1.6 10⁻²</td>
</tr>
<tr>
<td>Green rust (GR₅O₄)</td>
<td>45.7</td>
<td>-15.2</td>
<td>-2.12</td>
<td>7.5 10⁻³</td>
</tr>
<tr>
<td>GR₅O₄ + 10 mM MOPS</td>
<td>45.7</td>
<td>-48</td>
<td>-2.94</td>
<td>1.1 10⁻³</td>
</tr>
<tr>
<td>Goethite (α-FeOOH)</td>
<td>16.2</td>
<td>11.2</td>
<td>-3.04</td>
<td>9.1 10⁻⁴</td>
</tr>
<tr>
<td>Magnetite (Fe₃O₄)</td>
<td>19.2</td>
<td>-53.6</td>
<td>-3.12</td>
<td>7.6 10⁻⁴</td>
</tr>
<tr>
<td>Nontronite (clay mineral)</td>
<td>103.4</td>
<td>3.64</td>
<td>-3.70</td>
<td>2.0 10⁻⁴</td>
</tr>
<tr>
<td>Lepidocrocite (γ-FeOOH)</td>
<td>17.6</td>
<td>5.6</td>
<td>-3.74</td>
<td>1.8 10⁻⁴</td>
</tr>
<tr>
<td>Hematite (Fe₂O₃)</td>
<td>13.7</td>
<td>1.2</td>
<td>-3.82</td>
<td>1.5 10⁻⁴</td>
</tr>
<tr>
<td>Siderite (FeCO₃)</td>
<td>38.3</td>
<td>-10.8</td>
<td>-4.76</td>
<td>1.7 10⁻⁵</td>
</tr>
<tr>
<td>No mineral</td>
<td>-5.09</td>
<td>8.2 10⁶</td>
<td>3.3 10⁻⁷</td>
<td>1</td>
</tr>
</tbody>
</table>
Rate constants for 4-chlorophenyl hydroxylamine are only reported in cases, where accumulation of the intermediate took place.

Experiments were conducted with 25 m² mineral surface per liter, reported rate constants, however, are normalized to 1 m²/L. For the sake of comparability, calculated lower and upper estimates for mass transfer constants (see supplementary information) are reported as values divided by 25, as well.

For calculation see also Table A1-1 in the Appendix A1.

SD = Standard deviation, either determined from the average of repetitive experiments (“#”) or from the standard deviation of pseudo-first-order plots in long experiments conducted in several independent batches.

# = number of experiments
reactivity observed with hexachloroethane (Figure 2-3a) for iron minerals of different chemical composition are thus primarily due to different intrinsic surface-reactivities of the minerals such as sketched in Figure 2-1b because variations of Fe(II) sorption densities are not likely to vary by several orders of magnitudes, and, in the case of hexachloroethane, specific surface interactions do not seem to play an important role. Reactivity differences between the mineral classes may be rationalized as follows:

- Fe(II) on FeCO₃. Earlier studies [24] found that carbonate ligands in solution enhanced oxidation of Fe(II). In contrast, our data suggest that Fe(II) within the siderite lattice was a poor promoter of electron transfer to organic pollutants. The low reactivity of Fe(II) at siderite may be explained by stabilisation of Fe(II) compared to Fe(III) within FeCO₃.

- Conversely, the great reaction rates in FeS or FeS₂ may be attributable to reduced sulfide or disulfide ligands. These sulfide entities may either act as promoters of electron transfer by Fe(II), as known from iron-sulfur clusters in non-heme iron proteins [42], reduce Fe(III) centers formed after e-transfer from Fe(II), or they might even convey electrons directly to the contaminant.

- The intermediate reactivity of iron oxides may be attributable to the extent by which the coordination at the oxide surface promotes electron transfer from =Fe(III)-O-Fe(II)-OH complexes. The comparatively low reactivity of nontronite, finally, suggests that structural Fe(II) in interlayers played only a minor role in the transformation of hexachloroethane. Recent data suggest (19) that Fe(II) coordinated to edge surface hydroxyls dominates the reactivity of nontronite. Conversely, green rust at pH 8 was very reactive, which points either to a simple pH effect, to a high reactivity of Fe(II) associated with the mineral or to a large number of surface sites, possibly located in readily accessible mineral interlayers [18]. An X-ray diffractogram of resuspended sulfate green rust after one month showed peaks at smaller interlayer distances, which could indicate a partial anion exchange in the interlayer, and, thus, a certain interlayer accessibility for contaminants (see Figure A1-1 in the Appendix A1). The overall high reactivity of green rust is in agreement with results from Pecher et al. who found an observed increased reactivity of goethite/Fe(II) at higher pH
values which they attributed to the formation of more reactive secondary mineral precipitates including green rust [33]. Conversely, when green rust was buffered at pH 7.5, it turned black and the reaction rate dropped to the level of magnetite and goethite. This indicates that a thin layer of a less reactive secondary precipitate (probably magnetite) started to form at the surface, and dominated the reactivity, irrespective of the properties of green rust in the bulk phase underneath. Green rust could thus be identified as an exceptionally reactive iron (hydr)oxide phase.

Comparison of reaction rates with earlier studies. Whereas the measured reaction rate of hexachloroethane with goethite/Fe(II) (0.00091 Lm⁻²h⁻¹) compares reasonably well with data by Pecher et al. [33] (0.002 Lm⁻²h⁻¹), the value for mackinawite (0.016 Lm⁻²h⁻¹) is six times smaller than reported by Butler et al. [7] (0.1 Lm⁻²h⁻¹ at pH 7.1). The difference may be caused by different experimental conditions (mineral loading / total surface area / concentration of Fe(II) in solution). The overall fairly good agreement between our values and comparable literature data, however, indicates that normalization to the BET surface is an expedient approach to comparing such data.

2.3.3 Reactivity of different Fe(II)-containing minerals with 4-chloronitrobenzene

Rate constants of 4-chloronitrobenzene were consistently higher than observed for hexachloroethane for the same mineral suspension, and they did not show a similar reactivity pattern Fe(II) + siderite < Fe(II) + iron oxides < Fe(II) + iron sulfides (Figure 2-3a/b). Deviations were observed for pyrite/Fe(II), hematite/Fe(II) and, to a lesser degree, for nontronite/Fe(II), similar to the sketch in Figure 2-1d. Specific reaction mechanisms and/or the accessibility to different surface sites must therefore play a role in determining the overall reactivity. Possibly, 4-chloronitrobenzene was transformed at reactive sites different from those of hexachloroethane and such “4-chloronitrobenzene-specific” sites were less abundant in hematite and pyrite suspensions. This explanation would be consistent with previous observations made in iron-reducing aquifer columns [22, 39] and a long-time study with granular iron(0) [26], where indirect evidence suggested that chlorinated hydrocarbons and nitroaromatic compounds
reacted at least partially at different reaction sites. An alternative explanation is specific sorption of 4-chloronitrobenzene, either (a) at unreactive sites, which would retard the reaction in some cases, or, less probably, (b) at reactive sites, which would lead to accelerated rates for the majority of minerals. Recent evidence for sorption of nitroaromatic compounds at non-reactive sites comes from experiments with ferruginous clay minerals, where an observed retarded transformation was attributed to sorption at non-reactive siloxane surfaces [20]. This may explain why in our study 4-chloroaniline was formed much more slowly in suspensions of nontronite as compared to batches with iron oxides (Figure 2-3). The cases of atypically low reactivity of 4-chloronitrobenzene in our study may thus be an interesting starting point for further investigations of specific surface reactivities of nitroaromatic compounds. They compromise, however, attempts to establish reactivity rankings (see Figure 1c) that would make it possible to estimate reaction rates of one type of contaminant (e.g., a nitroaromatic compound) from data of other compound classes (e.g., chlorinated alkanes).

2.3.4 Extrapolation of reaction rates between structurally related compounds

To address the question whether reactivity pattern as discussed above may be similar for structurally related compounds, such as sketched in Figure 2-1c, our values for the aliphatic chlorinated hydrocarbon hexachloroethane may be compared to literature data of an olefinic chlorinated hydrocarbon, trichloroethene (see Figure 2-4). Recently published [28, 29] rate constants for trichloroethene (green rust: $8.55 \times 10^{-5} \text{ L m}^{-2} \text{ day}^{-1}$, pyrite: $2.53 \times 10^{-5} \text{ L m}^{-2} \text{ day}^{-1}$, magnetite: $7.21 \times 10^{-7} \text{ L m}^{-2} \text{ day}^{-1}$) show a similar reactivity trend as observed with hexachloroethane. Earlier data by Sivavec et al. [41] for trichloroethene in reaction with troilite (an iron sulfide, $5.52 \times 10^{-2} \text{ L m}^{-2} \text{ day}^{-1}$) and magnetite ($4.56 \times 10^{-4} \text{ L m}^{-2} \text{ day}^{-1}$) show a similar relative trend, despite large differences in absolute rate constants. (A discussion of these differences is difficult, because the experimental conditions of that study are not well specified.) These trends suggest that it may be possible to extrapolate reactivity patterns with different Fe(II) bearing minerals within the class of aliphatic/olefinic hydrocarbons. In contrast, a recent study addressing the reactivity of polyhalogenated methanes in
sulfate- and iron-reducing sediments [23] found reactivity patterns in both types of sediments similar to those of Fe(II)/goethite suspensions, but differed from those of FeS batches. However, as the commercial FeS used in the study contained impurities of Fe(0), the pattern attributed to FeS may have been characteristic for zero valent iron rather than for iron sulfide. In conclusion, the reactivity trends observed for hexachloroethane in the present study may be valuable for predictions of relative reactivities of structurally related chlorinated hydrocarbons. Prospects and limitations of such predictions, however, need to be validated by future studies.

**Figure 2-4.** Logarithmic pseudo-first-order rate constants for reactions of (□) hexachloroethane (this study), and trichloroethene (□ Sivavec et al. [41] / ▲ Lee et al. [28, 29]) with different Fe(II) bearing minerals.

### 2.4 Environmental Significance

The strong dependence of reaction rates on the chemical composition of Fe(II) containing minerals indicates that natural abiotic transformation reactions involving such species in the field may vary strongly with (bio)geochemical conditions. Based on our data, one would expect reductive transformation of hexachloroethane by Fe(II) to be fastest either at coexisting sulfate- and iron-reducing conditions, where Fe(II) sulfides can form, or under rapidly changing...
oxic/anoxic redox conditions, where green rusts may form. An intermediate reactivity would be expected for iron(III)oxide-rich soils, when dissolved Fe(II) is present in the pore water. Lowest transformation rates would finally be anticipated in strictly anoxic calcite-rich grounds, where siderite-formation will take place.

A back-of-the-envelope calculation for the case of iron oxide-rich sediments follows. If we assume an iron-reducing model sediment with a porosity of 0.3, mineral density of 2.5 g/cm³ and an iron oxide content of 2 % with a specific surface area 10 m²/g, we arrive at (700 cm³ mineral/L · 2.5 g/cm³ · 2/100 · 10 m²/g = ) 350 m² iron-oxide-surface / L sediment. This rough estimate is supported by results of Kenneke and Weber [23] who isolated the reactive silt and clay fraction from an iron-reducing pond sediment and, after ten-fold dilution, obtained 16 g/L with a specific surface area of 22 m²/g, corresponding to (10 · 16 g/L · 22 m²/g = ) 3520 m² silt-and-clay-surface per L sediment. This material transformed halogenated methanes about ten times more slowly than goethite/Fe(II) (based on surface-normalized reaction rates), indicating that its reactivity was equivalent to 352 m² iron oxide / L sediment. We can now apply the rate constant determined with goethite/Fe(II) in our study to calculate the half-life of hexachloroethane in the iron-reducing model sediment as ln(2) / (9.1·10⁻⁴ Lm⁻²h⁻¹ · 350 m²/L) = 2.2 h at 23°C. Results of Pecher et al. [33] with goethite/Fe(II) may further be used to estimate also transformation rates of polyhalogenated methanes. Tetrachloromethane, for example, was found to react 3.2 times slower than hexachloroethane in their study, so that the half-life in the model sediment can be calculated to (2.3 · 2.2 h = ) 6.9 h at 23°C. An educated guess for trichloroethene transformation can be made using data of Lee and Batchelor [28]. As can be seen from Figure 2-4, their observed reaction rate for trichloroethene with magnetite was about 2.5 10⁴ times smaller than the one for hexachloroethane, resulting in an estimated half-life of about (2.5 10⁴ · 2.2 h = ) 5.6 10⁴ hours or 6.4 years at 23°C in the iron-reducing model sediment.

We can further calculate how much reactive surface area would have to be present if iron oxides in the sediment were substituted by iron(II) carbonate or
iron(II) sulfides. Reaction rates of hexachloroethane in our study were 52 times smaller with FeCO₃/Fe(II) in comparison to goethite/Fe(II) (see Table 2-1) so that that an unrealistically high surface of 20 000 m²/L would be required in the case of FeCO₃ for equal reactivity. Conversely, reaction rates with Fe(II) sulfides were 17 times greater so that a surface of only 20 m²/L would be sufficient in the case of iron sulfides. Kenneke and Weber [23] compared the reactivity of sulfate- and iron-reducing sediment samples and found little differences in halomethane reduction rates. In the light of our data, their conclusion that Fe(II) on iron oxides was the dominating reductant in both sediments suggests that the exposed surface area of sulfide minerals was very low.

Such estimates illustrate how data from this study may be used to calculate the persistence of structurally related compounds such as halogenated alkanes and, possibly, also alkenes in natural environments. However, because reactivity patterns in our laboratory experiments showed different trends for different classes of contaminants (4-chloronitrobenzene / hexachloroethane), such calculations may not be applied to estimate reaction rates of different contaminant classes (e.g. nitroaromatic compounds). The influence of specific reaction mechanisms and/or specific contaminant/surface interactions, which may contribute to the overall reactivity, prevents such simple extrapolations. When making such interpretations, finally, care has to be taken that the surface reaction is really the rate-determining step in the overall natural process. Heijman et al. [19] investigated the transformation of highly reactive nitroaromatic compounds at elevated concentrations in iron-reducing aquifer columns, and found that the overall reactivity was limited by microbial regeneration of a limited number of reactive sites, rather than by the actual abiotic transformation itself. The transformation rates reported in this study should, therefore, be regarded as maximum values per surface area, for the case that dissolved ferrous iron is provided in excess by in-situ microbial activity.

**Supporting Information Available in the Appendix A1.** Figure A1-1: X-ray diffractograms of synthesized minerals; Table A1-1: Ionic composition and ionic strength in the experiments. Calculations of mass transfer estimates; Figure A1-2: effect of compound concentrations on $k_{obs}$; Figure A1-3:
Correlations between logarithmic rate constants of hexachloroethane and 4-chloronitrobenzene / 4-chlorophenyl hydroxylamine.

2.5 References


Mechanisms and Products of Surface-Mediated Reductive Dehalogenation of Carbon Tetrachloride by Fe(II) on Goethite

* Martin Elsner, René P. Schwarzenbach, Thomas Kellerhals, Samuel Luzi, Luc Zwank, Werner Angst, Stefan B. Haderlein; submitted to Environmental Science and Technology
Abstract

Natural attenuation processes of chlorinated solvents in soils and groundwaters are increasingly considered as options to manage contaminated sites. At anoxic conditions, reactions with ferrous iron sorbed at iron(hyrox)ides may dominate the overall transformation of carbon tetrachloride (CCl₄) and other chlorinated aliphatic hydrocarbons. We investigated mechanisms and product formation of CCl₄-reduction by Fe(II) sorbed to goethite which may lead to completely dehalogenated products and/or to chloroform (CHCl₃), a toxic product which is fairly persistent under anoxic conditions. A simultaneous transfer of two electrons and cleavage of two C-Cl bonds of CCl₄ would completely circumvent chloroform production. To distinguish between initial one- or two-bond-cleavage, ¹³C-isotope fractionation of CCl₄ was studied for reactions with Fe(II)/goethite (isotopic enrichment factor ε = -26.5‰) and with model systems for one C-Cl bond cleavage and either single-electron transfer (Fe(II) porphyrin, ε = - 26.1‰) or partial two-electron transfer (polysulfide, ε = -22.2‰). These ε-values differ significantly from calculations for simultaneous cleavage of two C-Cl bonds (ε ≈ -50‰) indicating that only one C-Cl bond is broken in the critical first step of the reaction. At pH 7, reduction of CCl₄ by Fe(II)/goethite produced about 33% CHCl₃, 20% carbon monoxide (CO) and up to 40% formate (HCOO⁻). Addition of d₈-isopropanol resulted in 33% CDCl₃ and only 4% CO, indicating that both products were generated from trichloromethyl radicals (’CCl₃), chloroform by reaction with hydrogen radical donors and CO by an alternative pathway likely to involve surface-bound intermediates. Hydrolysis of CO to HCOO⁻ was surface-catalyzed by goethite but too slow to account for the measured formate concentrations. Chloroform yields slightly increased with pH at constant Fe(II) sorption density, suggesting that pH-dependent surface processes direct product branching ratios. Surface-stabilized intermediates may thus facilitate abiotic mineralization of CCl₄, whereas the presence of H radical donors such as natural organic matter enhances formation of toxic CHCl₃.
3.1 Introduction

Aliphatic chlorinated hydrocarbons including carbon tetrachloride (CCl₄) are widespread groundwater contaminants [3, 10, 35, 40]. While such compounds are rather persistent under oxic conditions, they may undergo reductive dehalogenation under reducing conditions in the subsurface. Depending on the predominating environmental conditions, dehalogenation of CCl₄ can lead to harmless end products, but also to more persistent compounds. The majority of studies on abiotic reductive dehalogenation of CCl₄ reported hydrogenolysis to chloroform (CHCl₃), which is toxic and more recalcitrant than CCl₄ under anoxic conditions. Most studies, however, also report incomplete mass balances [32, 2] and/or partial conversion of CCl₄ to completely dehalogenated products that are indicative of alternative dehalogenation pathways of CCl₄ ([15, 37, 28, 27, 48, 14, 29, 22], see also summary in Appendix A2). Formate (HCOO⁻), carbon monoxide (CO) and carbon dioxide (CO₂) were found during electrolytic dehalogenation of CCl₄ at a silver electrode [15], formate in the reaction of CCl₄ with goethite/Fe(II) [37], CO and CO₂ in the reaction with pyrite or with sulfide in the presence of layer silicates [28, 27] as well as in photochemical transformation of CCl₄ in water (ice) films [48]. Transformation of CCl₄ by Pseudomonas stutzeri KC is the only case of biotransformation where readily degradable (thio)phosgene (S=CCl₂/ O=CCl₂) and CO₂ accounted for most of the mass balance and only traces of chloroform were found [14, 29]. Other microorganisms studied produced chloroform as major product [22]. Therefore, hydrogenolysis and complete dehalogenation are concurrent and thus competing pathways in the dehalogenation of CCl₄ by various reductants, and knowledge about the conditions that favor either pathway is of great interest, both for evaluation of natural attenuation and for the design of remediation schemes.

Reduction of CCl₄ is believed to start in most cases with a single electron transfer and simultaneous cleavage of one C-Cl bond, which leads to short-lived trichloromethyl radicals (single-electron-transfer, scheme 3-1).
In such a case the product formation is determined by radical reactions of \( ^\cdot\text{CCl}_3 \) with system components. Presence of molecular oxygen, for example, causes re-oxidation to phosgene / \( \text{CO}_2 \) \[36, 48\], sulfide creates sulfur adducts \[6, 28, 27\], transfer of a second electron causes further reduction and H-radical donors such as organic compounds favor \( \text{CHCl}_3 \) formation \[4, 6, 29\]. Alternatively, a concerted transfer of two electrons with simultaneous cleavage of one C-Cl bond is believed to take place in a nucleophilic attack of strong reductands at the halogen center (X-philic reactions, scheme 3-2, \[49, 6\], thus leading directly to short-lived trichloromethyl anion intermediates.

In such a case the product formation is governed by the rate of \( \text{H}^+ \) transfer relative to that of self-decomposition of \( \text{CCl}_3^- \) \[21\]. Proton transfer leads to chloroform, decomposition of \( \text{CCl}_3^- \), however, to dichlorocarbene, which rapidly hydrolyses to formyl chloride (HCOCI) \[39\] and, eventually, to \( \text{CO} \) \[16\]. Because both, case 1 as well as case 2, can lead to \( \text{CHCl}_3 \), it is intrinsically impossible to circumvent chloroform production, except for a theoretical third case in which two electrons are transferred and, simultaneously, two C-Cl bonds are broken in the initial reaction step so that dichlorocarbene is formed directly \[37\] (case 3, scheme 3-3).
Simultaneous cleavage of two C-Cl bonds, however, is highly endergonic, whereas the postulate of transition state theory requires that the reaction-coordinate proceeds along a path of lowest activation energy. In solution, i.e., without stabilization of the respective intermediate(s), generally only one C-Cl bond will thus be initially broken; the situation, however, may be different on surfaces, where a transition state of the kind $=S---Cl---CCl_2---Cl---S=$ can be imagined that may reduce the activation energy for simultaneous cleavage of two bonds (where $=S$ denotes surface groups).

Because of the great importance and ubiquitous occurrence of ferrous iron sorbed at natural mineral surfaces, we focus in this study on elucidating the pathways of reductive dehalogenation of CCl$_4$ by reactive surface-bound Fe(II) species. McCormick et al. [33] reported that reductive dehalogenation of CCl$_4$ in the presence of iron-reducing bacteria was mainly due to abiotic reaction with Fe(II) at the surface of biogenic magnetite, and only to a small extent to direct enzymatic dehalogenation. In many other studies, Fe(II) sorbed to mineral surfaces was found to be by orders of magnitude more reactive than Fe(II) in solution [5, 26, 31, 17]. It has been found that for some contaminants including carbon tetrachloride (CCl$_4$), reactions with Fe(II) sorbed at iron(hydro)xides may be the dominating removal process under anoxic conditions [43],[25]. Surface-bound Fe(II) is finally thought to play also a role to support the long-term reactivity of metal iron reactive walls that are increasingly used to clean up contaminated aquifers [45].

Pecher et al. [37] identified chloroform and formate as major products of the reaction of carbon tetrachloride with Fe(II) sorbed to goethite at circumneutral pH and found increasing yields of chloroform with higher pH. Amonette et al. [2] observed in similar systems under acidic conditions second-order kinetics with respect to sorbed Fe(II) and postulated a termolecular initial two-electron reaction step in which each of two adjacent Fe(II) surface sites conveyed simultaneously one electron to a CCl$_4$ molecule.

To date, the reaction mechanisms and conditions that cause formation of toxic chloroform vs. completely dehalogenated products are not well understood for this reaction. In particular, it remains unclear whether and under which
conditions a simultaneous two-electron transfer associated with two-bond-cleavage process can occur, and whether formation of chloroform may be attributable to an initial single-electron transfer or, alternatively, generation of formate to an initial two-electron transfer. The objectives of our study, thus, were

1) to complete the mass balance of the reductive dehalogenation of CCl₄ by goethite/Fe(II) and to investigate what environmental conditions (pH, Fe(II) surface site coverage, presence of 'H donors) favor generation of chloroform, formate and potentially other products;

2) to elucidate the mechanism of this product formation with information from product studies and trapping experiments as well as a complementary isotope fractionation study.

To distinguish between initial one- or two-bond-cleavage processes, ¹³C-isotope fractionation during dehalogenation of CCl₄ was studied with various electron donors. Completion of mass balances was attempted by comprehensive analyses of reaction products at pH 7, including CO₂, CHCl₃ and formate. To trap intermediate CCl₃ radicals, an efficient D-radical donor (perdeuterated isopropanol) was used or, alternatively, great care was taken to exclude possible H-radical donors from the experimental system such as organic buffers (e.g., MOPS, HEPES). To distinguish the influence of pH from that of Fe(II) surface site coverage, experiments were conducted at different pH, but constant Fe(II) sorption site density.

### 3.2 Materials and Methods

Great care was taken in experiments with goethite/Fe(II) to minimize organic residues which could serve as possible H radical donors in the experimental system: a) Prior to experiments, the goethite was repeatedly washed with deionized water to remove organic acids known to be present at the surface [18, 24]. b) Organic (“Goods”) buffers were avoided, since they are known to transfer H’ atoms to ’CCl₃ radicals and, thus, generate chloroform (see scheme 3-1, [29]); instead, pH-control was ensured by the intrinsic buffer
capacity of $\equiv$S-O-Fe(II)-OH surface groups (see Results and Discussion).

3.2.1 Synthesis and Preparation of Materials

*Goethite (α-FeOOH)* (17±1 m$^2$/g BET-surface, determined by N$_2$-adsorption with Sorptomatic 1990, Fisons Instruments) was purchased from Bayer (Bayferrox 910, Standard 86). Tetrachloromethane (Fluka), dichloromethane (Fluka), chloroform (Aldrich) and trichloroethene (Aldrich) were of the greatest available purity (≥ 99 %) and were used without further treatment. Methanol free CCl$_4$ spike solutions were prepared by adding 3.5 µL CCl$_4$ of pure liquid (>99.5%, Fluka) to 110 mL anoxic water (3 h purged with Ar) and stirred for at least 24 h prior to transfer into an anoxic glovebox.

*Fe(II)-stock solutions* (0.5 M, pH 5) were prepared by adding 3.63 g (0.065 mol) iron powder (Merck) to 100 mL of a 1.00 M HCl solution (prepared from 32% HCl p.a., Merck) that had been purged with argon for 1 hour. The mixture was heated to 80°C under slow stirring for 2 hours, until most of the powder had dissolved and visible hydrogen evolution ceased. The mixture was subsequently transferred into a glovebox and was filtered through a 0.2 µm PTFE filter to remove excess iron powder. The exact Fe(II) concentration was determined photometrically after complexation with phenanthrolene [19].

*Washing procedure.* To remove traces of organic residues, the glassware used in experiments for formate analysis was 1) soaked in ethanol for several hours, 2) rinsed with deionised water, 3) soaked in 1.5 M HNO$_3$ for several hours, 4) rinsed six times with deionised water immediately before use.

*Preparation of goethite/Fe(II) suspensions.* An amount of goethite corresponding to 50 m$^2$/L was suspended three times in deionised water in order to remove adsorbed ions from the surface. The resulting suspension was purged with argon for 4 hours and subsequently transferred into an anoxic glovebox with external regenerator (Vaccum Atmospheres Corp.) at an oxygen level of ≤ 0.5 ppm O$_2$ as controlled by an oxygen sensor (PBI Dansensor, Module ISM-3). There, the pH (initially about 5) was adjusted with 0.1 M NaOH (Titrisol, Merck) to pH = 7.0. FeCl$_2$ solution was added and the pH adjusted again until the desired conditions were obtained (generally 1 mM Fe(II) in solution at
pH 7). If necessary, pH and Fe(II) were readjusted after an equilibration time of 48 h. Two additional sets of experiments were conducted at different conditions: One assay contained 3% (vol) of perdeuterated 2-propanol (Aldrich) the other only 0.45 mM Fe(II) total (all sorbed to goethite) at a pH of 8.

“Iron(II) porphyrin” (meso-tetrakis(N-methylpyridyl) iron(II) porphyrin) was prepared from meso-tetrakis(N-methylpyridyl) iron(III) porphyrin kindly provided by Buschmann [6] according to the following method from Wade and Castro [47]: 13 g iron powder (>99.5%, Merck) were treated with 1 N HCl for 1 h, transferred into the glovebox and washed three times with anoxic water. The iron was then added to 0.25 L 0.5 mM iron(III) porphyrin, the mixture was shaken for 15 minutes and subsequently filtered through a 0.2 µM PTFE filter (BGB Analytik). During reduction the color of the solution changed from green to red, as verified by UV-VIS spectroscopy (see Figure A3-1 in the Appendix A3). In isotope fractionation experiments, the iron(II) porphyrin concentration was adjusted to 150 µM, and 200 µM 4-morpholino-propanesulfonic acid (MOPS, Fluka) were added as buffer at pH 7.

Polysulfide-solutions were prepared by mixing of 49 g (0.2 mol) Na₂S·xH₂O (puriss. p.a., 32-38% S, Fluka) with 50 g sulfur powder in 1L deionized anoxic water for 2 months (pH 9) [38]. In isotope fractionation experiments the polysulfide concentration was adjusted to 40 mM total S(-II), at pH 8.3.

3.2.2 Transformation experiments of CCl₄

Experiments were set up in the glovebox. For each experiment, eighteen replicates were prepared in parallel by weighing 49 g (96 g) of the stirred suspension into 57 mL (115mL) serum vials. (Values in parentheses describe the setup in isotope fractionation experiments.) Then freshly prepared CCl₄ spike-solution was added to yield a start concentration of 40-50 µM in the product study and of 10 µM in the isotope fractionation experiments. The vials were closed with Viton© stoppers, taken out of the glovebox and agitated on a horizontal shaker at 25°C / 140 rpm in the dark until they were sacrificed for analysis. Experiments to study the reaction of CO to formate were set up at pH 7
in 57 mL vials, with a) 10 mL goethite/Fe(II) suspension, b) 10 mL water. Outside the glovebox the headspace was filled with pure CO gas via a cannula through the Viton© septum, corresponding to a concentration of CO in solution of about 1 mM.

For sampling in the product study, first two 1-mL-aliquots of gas were taken from the headspace of the vials by piercing the Viton© stopper with a gas syringe (A2, 1 mL, 0.29”x 0.12”x 2”, VICI AG) with side-port taper, under simultaneous introduction of 2x 1 mL water with a second syringe. These gas samples were subsequently analyzed for CO. Then 7 mL of liquid were withdrawn, to which 300 µL 0.1 M NaOH was added in order to precipitate Fe(II). This sample was filtered with a 0.2 µm PTFE filter and stored at -20°C until analysis for formate. Finally, 8 mL diethyl ether (Merck) containing 10 µM trichloroethene as internal standard were added to the remaining suspension. Extraction took place on a reciprocating shaker for 10 minutes, and 3x 0.8 mL aliquots of extracts were taken for analysis of chlorinated hydrocarbons.

In isotope fractionation experiments 10 mL diethyl ether containing 9 µM benzene (>99.5%, Fluka) as internal standard were added into the headspace of the reaction vials, followed by extraction for 10 minutes in a reciprocating shaker. Then the cannula of a 1 mL Hamilton© glass syringe without piston was bored through the Viton© stopper. The ether phase (about 1 mL remained after equilibration) was risen into the glass tube of the syringe by injecting water into the reaction vial through a second cannula; 3x 200 µL of the ether extract were taken for analysis by GC-C-IRMS.

3.2.3 Analytical Methods

For all analytical methods, external standards were prepared in exactly the same way as the samples. Standards for chlorinated alkanes were set up in serum vials with goethite suspensions (but without Fe(II)), and they were extracted according to the same procedures. Formate standards were set up in goethite/Fe(II) suspensions, which were filtered after addition of NaOH. They had to be prepared daily, as nearly complete disappearance of formate was observed in the goethite/Fe(II) standards at room temperature within a week. CO
standards were prepared by mixing varying volumes of a 900 ppm standard with air.

**CO analysis.** CO was determined on a gas chromatograph with thermal conductivity detector (GC/TCD, Shimadzu GC-8A) and a packed column (molecular sieve 8 Å 80/100, Brechbühler, Switzerland). Helium (99.999%) was used as carrier gas at 25 ml/min, the oven temperature was isothermal at 80°C, injector and detector temperatures were at 150°C, the detector current was set at 140 mA. The detection limit of the method was about 150 ppm.

**Formate analysis.** Formate was quantified after enzymatic reaction by measuring the production of NADH photometrically at 339 nm, according to a procedure modified from Schaller and Triebig [44]. A mixture of 0.5 mL of a β-NAD solution (20 mM), 1 mL phosphate buffer (0.15 M, pH 7.5) and 1.5 mL sample solution was prepared in a polystyrene vial (Semadeni, all chemicals from Fluka). The photometric absorption of the solution was measured at 339 nm in a quartz precision cuvette (Suprasil, Hellma, 5 cm length). The solution was subsequently transferred back into the polystyrene vial, where 10 µL formate dehydrogenase solution was added (formate dehydrogenase Pseudomonas spec., recombinant mutant to 79900 from E.coli; ca. 175 U/mL, Fluka Biochemicals, 75274). After an incubation time of 30-60 minutes at room temperature, the mixture was transferred to the quartz cuvette, which had been cleaned by rinsing twice with deionised water, and the absorption was measured again. The difference between absorption before and after incubation with formate dehydrogenase was used for quantification. The detection limit of this method was about 2 µM formate (sample concentration in experiment).

**Quantification of volatile halogenated compounds.** CCl₄ and CHCl₃ as well as CDCl₃ were quantified on a GC/MS (GC Fisons 8000 Series, autosampler Fisons AS 800, quadrupole MS Fisons MD 800) equipped with a 60 m x 0.32 mm Stabilwax fused silica column (film thickness 1 µm) and a 8 m x 0.53 mm deactivated guard column. Injection was 1 µL on-column, the temperature program was 40°C (2 min.), ramp 8°C/min. to 130°C (0 min.), ramp 30°C/min. to 200°C (5 min.). Quantification was carried out in the single ion monitoring
mode, for CCl₄ at m/z = 84, 123, for CHCl₃ at m/z = 47, 87 and for CDCl₃ at m/z = 88. The detection limit of this method was about 0.1 µM.

**GC-C-IRMS analysis.** Concentrations and isotope ratios in isotope fractionation experiments were determined on a GC-C-IRMS (gas chromatograph with combustion unit and isotope ratio mass spectrometer, Finnigan MAT delta plus XL™), with a Combi Pal autosampler (CTC Analytics) and a 60 m x 0.32 mm Rtx©-VMS column (Restek, Bellefonte, PA, USA). Injection was 9 µL on-column, the temperature program was 40°C (2 min.), 8°C/min., 100°C (5 min.), 20°C/min., 210°C (8 min.). All measurements were run in triplicates (3 samples from the extract of the same reaction vial). δ¹³C values of CCl₄ were automatically determined relative to a CO₂ reference gas. Concentrations of CCl₄ were determined by the peak area ratio of CCl₄ and the internal standard benzene using IRMS data. This yielded calibrations with R² of 0.998 (5 points, Fe(II)porphyrin and polysulfide) and 0.996 (4 points, goethite/Fe(II)), respectively. The goethite used contained trace contaminations of ethyl acetate, which could not be completely baseline-separated from the analyte peak of CCl₄. Their influence on δ¹³C values of CCl₄ was corrected for by an empirical function obtained from the calibration standards:

\[
\delta^{13}C_{\text{measured}} - \delta^{13}C_{\text{true}} = \frac{1}{2} \left( -2.3153 \ln(I^{44}) + 18.439 \right)
\]  

(3-1)

where I^{44} is the intensity of the ion beam at the mass 44. The uncertainty of this correction is reflected in a larger error in the goethite/Fe(II) system compared to experiments with Fe(II) porphyrin and polysulfide. Likewise, impurities of tetrahydrofurane in the diethyl ether co-eluted with CHCl₃. δ¹³C data for this compound could therefore not be obtained. Concentrations of CCl₄ and δ¹³C values were evaluated according to the Rayleigh equation (see Figure 3-2 and A3-3 in the Appendix A3), with progression of experimental errors in x and y direction using the software Lin2d [20]. The total experimental error, however, is likely to be overestimated by this method so that the errors reported for the resulting enrichment factors describe a confidence interval of greater than 95%.
3.3 Theoretical Background

Kinetic isotope fractionation can be expressed by the fractionation factor $\alpha$ or the enrichment factor ($\epsilon = \alpha - 1$) evaluated according to the Rayleigh-equation

$$\ln \frac{R}{R_0} = \ln \left[ f \cdot \frac{(1+R_0)}{(1+R)} \right]^{(\alpha - 1)}$$

$$= \ln \left[ f \cdot \frac{(1+R_0)}{(1+R)} \right] \approx \ln f^{\epsilon} = \epsilon \cdot \ln f$$

with

$$\ln \frac{R}{R_0} = \ln \left[ \left( \frac{\delta^{13}C_{Cl_4}}{1000} + 1 \right) \left/ \left( \frac{\delta^{13}C_{0,Cl_4}}{1000} + 1 \right) \right. \right]$$

where $R$ is the isotope ratio $^{13}C / ^{12}C$ in $Cl_4$ at time $t$, $\delta^{13}C$ the isotopic enrichment (in ‰) with respect to the international VPDB standard and $f$ the remaining substrate fraction at time $t$, where the subscript index “0” denotes values at time 0 (start of experiment). Because $Cl_4$ contains only one C atom, all carbon isotopes of the molecule take part in the reaction and the fractionation factor $\alpha$ obtained by a Rayleigh-type analysis of experimental data is directly equivalent to the inverse kinetic isotope effect at the reactive site

$$\alpha = \left( \frac{^{12}k}{^{13}k} \right)^{-1}$$

where $^{12}k$ and $^{13}k$ are the rate constants for C-Cl bond cleavage involving $^{12}C$ and $^{13}C$ carbon isotopes, respectively.

Such kinetic isotope effects are independent of the absolute value of the activation energy, but strongly influenced by changes in bond strength affecting the vibrational zero-point energy levels in the transition state (TS) [34]. Reductive dehalogenation of $Cl_4$ proceeds via a dissociative electron transfer, that is, electron transfer and C-Cl bond cleavage occur simultaneously [12]. In such a simple bond-breaking process, the kinetic isotope effect, KIE, increases monotonously from unity for a very early (= reactant like) TS to a maximum for a very late (= product like) TS (see Figure 3-1 and, e.g., [23, 11]). Such maximum values, known as Streitwieser limits [23], can be estimated, the
calculated value for cleavage of a C-Cl bond (750 cm\(^{-1}\)) being about \((^{12}\!k/^{13}\!k)_{\text{max}} = 1.057\) [23]. This means that the KIE in reductive cleavage of a single C-Cl bond increases from 1.000 for a completely reactant-like TS to about 1.057 for a completely product-like TS and will in most cases adopt intermediate values (see Figure 3-1). If, however, two C-Cl bonds are broken at the same time then isotopic energy differences will be manifested in two weakened bonds in the transition state, and the KIE can be expected to be about twice as large \((1.057^2 = 1.117\) for the maximum KIE and correspondingly lower values for earlier transition states, see Figure 3-1). A vibrational analysis confirms this conclusion: The reactant CCl\(_4\), (point group \(T_d\)) possesses a triply degenerate asymmetric stretching mode (\(T_2\)) at 776 cm\(^{-1}\) [30], whereas the product :CCl\(_2\) (point group \(C_{2v}\)) has a non-degenerate asymmetric stretching mode (\(B_2\)) at about 750 cm\(^{-1}\) [9]). The two asymmetric stretching modes that are present in the reactant, but not in the product, correspond to the two vibrations that will be weakened and become non-periodic reaction motions in the transition state, if two C-Cl bonds are cleaved simultaneously.

![Figure 3-1. Theoretical dependence of the kinetic carbon isotope effect \(^{12}\!k/^{13}\!k\) on the extent of bond cleavage in the transition state, for one (solid line) and two broken bonds (dashed line). Small arrow-diagrams: Activation energies of isotopic bonds in a reactant-like TS (left), a symmetric TS (centre) and a product-like TS (right).](image-url)
3.4 Results and Discussion

3.4.1 $^{13}$C-Isotope fractionation study to evaluate the number of bonds broken in the initial reaction step

The kinetic carbon isotope effect in the reductive dehalogenation of $\text{CCl}_4$ by goethite/Fe(II) was investigated and compared to the KIE observed for two other model reductands, Fe(II) porphyrin (single-electron transfer, one C-Cl bond broken) and polysulfide (single- and two-electron transfer, one C-Cl bond broken). Evaluation of experimental data according to the Rayleigh equation (Figure 3-2 and A3-3 in the Appendix A3) gave kinetic isotope effects that were very similar for the Fe(II) porphyrin and goethite/Fe(II) systems but significantly different from that with the reductand polysulfide (see Table 3-1 and Figure 3-2c). This can be an indication that the reaction of $\text{CCl}_4$ with goethite/Fe(II), as with Fe(II) porphyrin, involved a single-electron transfer in the rate determining step, as opposed to a partial two-electron transfer in reaction with polysulfide. More importantly, however, all three model reductands yielded moderate carbon kinetic isotope effects of 1.027 (Fe(II) porphyrin, Fe(II)/goethite) and 1.023 (polysulfide), indicative of cleavage of a single C-Cl bond with about 50% and 40% bond weakening in the transition state (Figure 3-2c). In contrast, if two C-Cl bonds were cleaved simultaneously, the kinetic isotope effect would be expected to be twice as pronounced, around 1.046-1.054 (see Figure 3-1 and 3-2c) or, if both processes took place in parallel, a weighted average would be observed. From the KIE of 1.027 for goethite/Fe(II) it can thus be concluded that generally only one C-Cl bond was broken in the initial step of the reaction with goethite/Fe(II) and that a simultaneous two-electron transfer/two-bond cleavage process must be discarded.

Figure 3-2 (right). (a) Changes in concentration and isotopic signature of $\text{CCl}_4$ during reduction by goethite/Fe(II); (b) Evaluation of $\varepsilon$ according to the Rayleigh-equation; (c) Measured and expected isotope effects in reductive dehalogenation of $\text{CCl}_4$ with different reductants investigated in this study.
Dehalogenation of CCl₄ by Goethite/Fe(II)

(a) Transformation Goethite/Fe(II) + CCl₄

(b) Rayleigh-Plot Goethite/Fe(II) + CCl₄

(c) Measured Kinetic Isotope Effects $k_{12C}/k_{13C}$
### Table 3-1. Measured and expected isotope effects in reductive dehalogenation of $CCl_4$

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon$ (‰) (± 95% CI)</th>
<th>$\alpha = 1 + \varepsilon$ (± 95% CI)</th>
<th>$\alpha^{-1} = 12k/13k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron(II) porphyrin</td>
<td>-26.10 ± 1.25</td>
<td>0.97390 ± 0.00125</td>
<td>1.0268</td>
</tr>
<tr>
<td>(Single electron transfer, one C-Cl bond broken)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polysulfide</td>
<td>-22.22 ± 1.73</td>
<td>0.97778 ± 0.00173</td>
<td>1.0227</td>
</tr>
<tr>
<td>(Partial two electron transfer, one C-Cl bond broken)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expected range for two broken C-Cl bonds</td>
<td></td>
<td></td>
<td>1.046-1.054</td>
</tr>
<tr>
<td>Goethite/Fe(II)</td>
<td>-26.48 ± 2.79</td>
<td>0.97352 ± 0.00279</td>
<td>1.0272</td>
</tr>
</tbody>
</table>

#### 3.4.2 Characterization of the goethite/Fe(II) system with respect to Fe(II) sorption and buffer capacity

The experimentally determined sorption capacity of Fe(II) on goethite was 7-12 µmol/m² (or 4.2-7.2 sites/nm²) for suspensions containing 12.5 m²/L – 100 m²/L goethite (Figure 3-3a). Sorption of Fe(II) (i) showed a noticeable inverse dependence on the mineral concentration of the suspensions and (ii) continued to increase at higher Fe(II) concentrations, effects that have been attributed to (i) particle coagulation [2] and (ii) surface precipitation [37] in previous studies, as discussed in greater detail in the Supporting Information in Appendix A3. The intrinsic buffer capacity $dC/dpH$ of goethite/Fe(II) suspensions (50 m²/L, 1 mM Fe(II)ₐq) was 250-300 µM pH⁻¹ within the range of pH 7-8 (Figure 3-3b), which shows that sufficient pH control could be achieved by the capacity of sorbed Fe(II) alone, even in the absence of external buffers. (For calculation of the buffer capacity and estimates of corresponding pH changes during reaction of CCl₄ see Supporting Information in the Appendix A3). The measured buffer capacity could be used to calculate a ratio $R = (H^+ \text{ released}) / (Fe^{2+} \text{ sorbed})$ from small changes in pH that followed sorption of added Fe(II). Calculated values of R were consistently around 2 (Figure 3-3a), which provides strong experimental evidence for a Fe(II) sorption reaction of the
Dehalogenation of CCl₄ by Goethite/Fe(II)  59

type

\[
\text{surface-O-H} + \text{Fe}^{2+}_{\text{aq}} + \text{H}_2\text{O} \rightarrow \text{surface-O-Fe-OH} + 2 \text{H}^+ \quad (3-5)
\]

which was postulated already previously on the basis of surface complexation models ([13, 8, 31]; for further discussion see Supporting Information in the Appendix A3).

![Graph of Fe²⁺ sorbed vs Fe²⁺ dissolved](image1)

![Graph of H⁺ released vs pH](image2)

**Figure 3-3.** (a) Fe(II) sorption isotherms (left) and corresponding “proton release” isotherms (right) calculated from changes in pH values upon Fe(II) addition, calculated with the buffer intensity dC/dpH determined in Figure 3-3b. Solid circles: 12.5 m²/L, crosses: 25 m²/L, squares: 50 m²/L, triangles: 100 m²/L mineral loading. (b) Buffer capacity in suspensions containing 50 m²/L goethite (right), as determined in titrations with 0.1 M NaOH (left); (o) with 1.0 mM Fe(II)_{tot} and (x) without added Fe(II). Steps in the curve are caused by the effect of longer equilibration times (12-24 hours). Solid circles represent points where the suspension was titrated repeatedly with alternating addition of 0.1 M HCl and 0.1 M NaOH.
This shows that the buffer effect observed in goethite/Fe(II) suspensions is attributable, primarily, to ad- and desorption of Fe(II) at the surface according to equation (3-5) and that complex formation between adsorbed Fe(II) and Fe(II) in solution is not prevented by electrostatic repulsion, thus leading to high sorption densities and possibly even surface precipitation already at slightly alkaline pH and higher concentrations of Fe(II)\textsubscript{aq}. Both studies of Amonette et al. [2] and Pecher et al. [37] observed an enormous reactivity increase with higher sorption densities of Fe(II). This observation could not be explained by an increased number of isolated S-\text{OFe(II)}OH species alone, as otherwise reaction rates would have depended on their concentration per volume solution, not, as observed, on the sorption density per surface area. A general simultaneous transfer of two single electrons from two adjacent Fe(II) sites, as postulated by Amonette et al. [2], must also be excluded, owing to evidence in this study for an initial single-electron transfer (see below). An alternative explanation is therefore needed for the rate equation observed by Amonette et al.

\[ -\frac{d[\text{CCl}_4]}{dt} = k[\text{Fe(II)}]^2[\text{CCl}_4] \]  

(3-6)

(where k, [\text{Fe(II)}] and [\text{CCl}_4] are the rate constant, density of sorbed Fe(II) and concentration of \text{CCl}_4 in solution, respectively). Such an explanation could be the formation of reactive precursor complexes involving \textit{two} Fe(II) centers and subsequent \textit{single} electron transfer. (An analogous case (single-electron transfer / second order kinetics) has also been observed in the reduction of \text{CCl}_4 by \text{Cr(II)} [7].) Our evidence for S-\text{OFe(II)}OH complexes rather than S-\text{OFe(II)}\textsuperscript{+} corroborates such precursor formation, owing to the absence of repulsive electrostatic effects. Such processes could finally correspond to the slow rearrangement of surface bound Fe(II) postulated by Pecher et al. [37] and be a first step in the generation of surface precipitates observed by these authors at higher pH.
3.4.3 *Products in the dehalogenation of CCl₄*

Dehalogenation of CCl₄ by goethite/Fe(II) at pH 7 produced 33% CHCl₃, 20% CO and up to 40% HCOO⁻ (see Figure 3-4a). Other volatile halogenated compounds such as CH₂Cl₂, C₂Cl₆ or C₂Cl₄ were not detected. In a second experiment, 3 vol % perdeuterated isopropanol (d₈-isopropanol) was added, which has a weak tertiary C-D bond that facilitates abstraction of D-atoms by ‘CCl₃ radicals [6]. The formation of 33% CDCl₃ and only 11% CHCl₃ (Figure 3-4b) in the presence of d₈-isopropanol indicates a) that the total yield of chloroform (CHCl₃ and CDCl₃) was considerably higher due to addition of the ‘D-donor, and b) that a strong competition between ‘H- and ‘D-donors took place in the system leading to a much lower yield of CHCl₃. The results provide strong evidence that ‘CCl₃-radicals were intermediates in the reaction. This indicates that an initial single-electron transfer took place (scheme 3-1), in accordance with indications from ¹³C isotope fractionation experiments.

*Formation of CHCl₃.* Significant fractions of CHCl₃ were formed at all experimental conditions studied, despite our attempts to remove organic residues and, thus, possible alternative H’ donors from the experimental setup (see Materials and Methods). A possible pathway to explain this result involves the transfer of a second single electron to an initially formed ‘CCl₃-radical, leading to a trichloromethyl carbanion (:CCl₃⁻) (see scheme 3-1). In analogy to scheme 3-2, :CCl₃⁻ can either be protonated, thus explaining formation of chloroform, or decompose to dichlorocarbene, which reacts further to CO. Results by Pecher et al. [37], however, rule out the protonation of :CCl₃⁻, because no CDCl₃ was formed in experiments performed in deuterated water (D₂O). This leaves hydrogen (H’) transfer to trichloromethyl radicals (scheme 3-1) as most likely process, in spite of the enforced depletion in organic H’ donors. Traces of organic matter at the surface of goethite and/or present in the deionized water (f_organic ≤ 0.1 mg C / L) supposedly reacted as H’ donor with ‘CCl₃-radicals. This indicates that minute amounts of organic matter may have affected surface-catalized reductive dehalogenation of CCl₄, shifting product distribution towards chloroform.
Figure 3-4. Time course and product yield in the reaction of CCl₄ with goethite/Fe(II) (50 m²/L mineral, 23°C), (a) at pH 7, (b) at pH 7 with added perdeuterated isopropanol and (c) at pH 8. Solid diamonds represent CCl₄, upright triangles CHCl₃, downward triangles CDCl₃, solid squares HCOO⁻ and circles CO. Lines are exponential fits with pseudo-first-order rate constants (a) 0.0076 h⁻¹, (b) 0.0092 h⁻¹, (c) 0.0145 h⁻¹ and product yields (a) 33% CHCl₃/18% CO, (b) 33% CDCl₃/13% CHCl₃/4% CO, (c) 40% CHCl₃.
Formation of CO. Addition of perdeuterated isopropanol strongly decreased the yield of carbon monoxide (Figure 3-4a/b). The pathway to CO must, therefore, also involve ‘CCl₃ radicals as intermediates, since otherwise CO formation would not have been affected by the presence of the radical scavenger. The most plausible pathway from ‘CCl₃ to CO entails transfer of a second electron leading to :CCl₃⁻, then :CCl₂, HCOCl and finally CO (see scheme 3-1 and 3-2). Free trichloromethyl anions (:CCl₃⁻) in solution, however, must again be discarded on grounds of experiments by Pecher et al. [37] with D₂O (see above). This indicates that :CCl₃⁻ may be stabilized in some way, most probably as a short-lived surface complex. Evidence for such a stabilization by complex-formation with Fe-centers comes from experiments with microsomal cytochrome P-450, where carbenes and radicals were found to form iron(II) porphyrin complexes ([1], see also [50]), as opposed to free radicals, carbanions and carbenes in solution. One possibility could therefore be the formation of a surface complex of the type

\[
[ \text{S-Fe(II)} - \text{CCl}_3^- \rightleftharpoons \text{S-Fe(III)} - \text{CCl}_3 ] \rightarrow (+e^-, -\text{Cl}^-) \rightarrow [ \text{S-Fe(II)} = \text{CCl}_2 ]
\]

as short-lived intermediate in the reaction, where S-Fe(II) denotes surface entities. Formation of CO would thus be possible without transient occurrence of free :CCl₃⁻ in solution.

Formation of HCOO⁻. Formate was detected only in some of the reaction vials (see Figure 3-4), consistent with earlier experiments at lower CCl₄ concentrations (data not shown). Contamination can be ruled out, as formate was not found in blanks prepared according to the general strict washing protocol. On the contrary, HCOO⁻ often disappeared in calibration standards (identical in composition to the reaction vials) with a half-life of three to four days. It is therefore likely that formate was produced in all vials to the same extent, but disappeared from some of them in a subsequent reaction. Since all vials were set up identically with regard to their chemical content, but were not sterile (owing to their preparation in a glovebox and the fact that mineral suspensions cannot be filter-sterilized), microbial degradation of formate to CO₂ is a likely cause of the disappearance. Because the carbon based mass balance was essentially complete in cases where HCOO⁻ could be detected (see Figure 3-4a) and other
volatile halogenated compounds were not detected, we suggest that a deficit in the mass balance observed is attributable, primarily, to microbial oxidation of formate to CO$_2$. This interpretation is corroborated by recent findings that the iron reducing microorganism geobacter metallireducens (GS 15) is able to grow on formate present at low concentrations [46]. Production of formate cannot be rationalized by hydrolysis of formyl chloride (HCOCI, see scheme 3-2) because decomposition of this intermediate leads preferentially to CO at circumneutral pH [16]. Generation of formate by hydrolysis of CO at pH 7 is thermodynamically favorable ($\Delta G_r^\circ = -73.9$ kJ/mol, see Supporting Information in the Appendix A3), but was found to be very slow in homogeneous solution, with a half life of 275 years at our experimental conditions ($k = 8 \cdot 10^{-4}$ Lmol$^{-1}$ s$^{-1}$, [42] where $k = d[\text{HCOO}^-]/dt [\text{OH}^-][\text{CO}]^{-1}$ and species in brackets denote aqueous concentrations). To test for surface catalysis by goethite, CO hydrolysis was measured at pH 7, in pure water and in the presence of goethite/Fe(II). In both experiments the headspace contained pure carbon monoxide so that the aqueous concentration of CO corresponded to a saturated solution (17.7 ppm or 9.86$ \cdot 10^{-4}$ M [41]). Formate could neither be detected in batches with pure water nor in controls of goethite without CO, whereas 3.2 $\mu$M - 4.8 $\mu$M of formate was formed in the presence of goethite/Fe(II) after 36 to 67 days (see Figure A3-2 in the Appendix A3), indicating surface catalysis of CO hydrolysis by goethite/Fe(II). A rough estimate of the second-order rate constant ($k = d[\text{HCOO}^-]/dt [\text{OH}^-][\text{CO}]^{-1} = 1 \cdot 10^{-2}$ Lmol$^{-1}$ s$^{-1}$) based on these results reveals that the reaction was accelerated by the presence of goethite by a factor of about ten, which is, however, by far not sufficient to explain the amount of formate observed in the dehalogenation experiments of CCl$_4$. The pathway CO $\rightarrow$ HCOO$^-$ can therefore be discarded, in accordance with the observation that the radical scavenger $d_8$-isopropanol influenced CO formation, but had no effect on the missing mass balance (=product fraction attributable to formate) (see Figure 3-4b). Formate is therefore likely to be formed by an alternative pathway that does not involve free trichloromethyl radicals as intermediates, possibly because of specific stabilization of intermediates at the surface.
Influence of pH on product distribution. Pecher et al. [37] observed that higher Fe(II)-surface-site densities at constant pH decreased the fraction of CHCl₃ formed, whereas an increase of both, sorption site density and pH, led to increased chloroform production. In order to investigate the influence of pH alone, experiments were conducted at pH 7 and pH 8, with similar sorption site densities of Fe(II) on goethite. The chloroform yield increased slightly from 33% at pH 7 to about 40% at pH 8 (see Figure 3-4c). Direct involvement of H⁺ in the reaction of CCl₄ to CHCl₃ is very unlikely, because H₂O can be expected to be the most important proton donor at circumneutral pH. As discussed above, chloroform is formed by hydrogen (H⁻) transfer to trichloromethyl radicals rather than by H⁺ transfer to trichloromethyl anions. An increase of pH, however, changes the surface chemistry of goethite, leading, for example, to deprotonation of surface hydroxyl groups according to =S-OH + OH⁻ -> =S-O⁻ + H₂O. Such processes may affect the formation of surface stabilized intermediates and thus discriminate against alternative pathways in favor of chloroform production. Product formation can therefore be expected to be primarily influenced by changes in surface chemistry and only indirectly by pH.

3.5 Environmental Significance

By applying various complementary experimental techniques this study provides new mechanistic information for a better understanding of surface mediated reactions of chlorinated aliphatic contaminants by Fe(II) (see Figure 3-5). Our results indicate that the first step in reductive dehalogenation of CCl₄ by surface-bound Fe(II) involves 1) cleavage of only one C-Cl bond and 2) transfer of one electron. This initial reaction was found to generate partly trichloromethyl radicals and to lead partly to formate, possibly via surface-bound intermediates. Consequently, toxic chloroform was found to be produced, mainly, in consecutive radical reactions with H⁻ donors, whereas surface stabilization of short-lived intermediates may play a key role in the alternative formation of benign products.
Figure 3-5. Summary of mechanistic evidence obtained for the reaction of CCl₄ with goethite/Fe(II). Compounds in boxes were detected during the reaction. Bold arrows and ticks designate reaction paths for which experimental evidence (written in italic letters) could be obtained, whereas dashed arrows and crosses indicate pathways that must be excluded. Question marks point out hypothesized pathways and intermediates.

Product formation pathways therefore do not primarily depend on the competition between an initial one- or two-electron transfer, but rather on the presence of different radical scavengers and/or the properties of the mineral surface with respect to stabilization of reaction intermediates. The presence of oxygen and sulfur species can thus lead to completely dehalogenated products in radical reactions [48, 6], whereas even trace amounts of organic matter may result in chloroform formation as indicated by the results of this study. In addition, specific adsorption of major anions and/or pH effects may modify the capability of the goethite surface to stabilize short-lived radical intermediates.
The key to predicting product formation in reductive dehalogenation of CCl₄ by Fe(II) is therefore a profound understanding of the factors that determine the stabilization of radical intermediates at reactive Fe(II) surface sites. Further research is needed to address this topic including the effects of co-adsorbates such as inorganic ions and natural organic matter.

**Supporting Information Available in Appendix A3.** Figure A3-1: UV-VIS spectra of Fe(III) and Fe(II) porphyrin; - Buffer capacity in goethite/Fe(II) suspensions; - Dependence of Fe(II) sorption on mineral loading; - Characterization of Fe(II) surface complexes and discussion of possible reactive species; - Figure A3-2: Reaction of CO to formate in suspensions goethite/Fe(II); - Thermodynamic and Kinetic Data about the Reaction of CO und OH-to Formate - Figure A3-3: Changes in concentration and isotopic signature of CCl₄ during reduction by iron(II) porphyrin and polysulfide / Rayleigh-plots.

### 3.6 References


Current Application of the Rayleigh-Equation in Environmental Sciences: A Critical Discussion
Abstract

Inadequate applications of the Rayleigh equation presently hamper mechanistic insights from isotope fractionation studies in environmental chemistry. The reason is that GC-IRMS (gas chromatography - isotope ratio mass spectrometry) measures isotope ratios $R$ as average values over whole molecules, whereas the observed fractionation is only caused by some isotopes close to the reacting bond. In this chapter, a more accurate evaluation scheme is presented that considers 1) the effect of invariant isotope ratios at non-reactive positions and 2) the intramolecular competition of chemically equivalent, reactive positions. The most pronounced kinetic isotope effects can be expected in the absence of these factors. This is the case in compounds that contain only one atom of the element for which isotope fractionation is measured, such as carbon in carbon tetrachloride ($\text{CCl}_4$). For larger molecules containing several like atoms, however, attenuation of the site-specific fractionation will become important due to statistical effects, and the precision of GC-C-IRMS measurements may pose a limit to the method. The choice of suitable substrates may thus be essential to the outcome of mechanistic isotope studies in environmental sciences.
4.1 Introduction

Fractionation of stable isotopes during a variety of processes is an important and well established method for investigations in many scientific disciplines including geology, chemistry, biology and physics. Urey [26] was the first to derive a sound theoretical basis to explain that molecules of the same elemental composition have different bond strengths, depending on whether they are composed of heavy or light isotopes. This was shown to have two important implications: (1) The bond strengths affect the standard free enthalpy of formation of such compounds so that chemical equilibrium processes are subject to small, but measurable isotopic fractionations (thermodynamic isotope effect). (2) During an irreversible reaction, bonds of heavier isotopes may be broken more slowly and become enriched in the substrate, whereas lighter isotopes often accumulate in the products (kinetic isotope effect). In environmental sciences, and particularly in geology, changes in the natural ratio of stable isotopes (e.g. $^{2}\text{H}/^{1}\text{H}, ^{13}\text{C}/^{12}\text{C}$) have been used as tracers for processes such as past climatic changes (thermodynamic isotope effect) or activity of organisms (kinetic isotope effect). Contrary to this partly rather empirical use, chemical studies employ the kinetic isotope effect on a very detailed level, with specifically labeled isotopic substrates, to investigate the mechanism of elementary reactions. Accordingly, there are two different conventions to describe the kinetic isotope effect in the two disciplines:

1) In chemistry, the definition $k_L/k_H$ refers to elementary rate constants, for bonds containing the light ($k_L$) and heavy isotopes ($k_H$), respectively. (For example, in carbon isotope studies $k_L = k_{12}$ is the reaction rate of molecules with a $^{12}\text{C}-\text{Y}$ bond and $k_H = k_{13}$ that of molecules with a $^{13}\text{C}-\text{Y}$ bond, where Y is a non-specified element.) In the case of larger molecules this definition refers specifically to the bond that actually reacts. (see, e.g., [17]).
2) In environmental sciences, an observed isotopic enrichment $\varepsilon$ is usually expressed by the Rayleigh equation:

$$\frac{R}{R_0} = f(\alpha - 1) = f\varepsilon$$

where for a given reaction time $t$, the isotope ratio $R = \frac{N_t^*}{N_t}$ of heavier ($N_t^*$) and lighter ($N_t$) isotopes in the substrate, respectively, is linked to the remaining substrate fraction $f = \frac{N_l}{N_0}$ of the lighter isotope. (N_0$ and $R_0$ are values for isotope concentration and the isotope ratio, respectively, at time 0.)

In recent years, gas chromatographs that are coupled to an isotope ratio mass spectrometer (GC-IRMS) have become available for routine analysis. The isotope ratio in single compounds can now be determined even in the case of complex compound mixtures, provided that separation is possible by gas chromatography. This has rendered isotopic fractionation a new, promising tool in the field of environmental chemistry. One exciting application is the detection of natural in-situ transformation in contaminated subsurface sites. By monitoring contaminant concentrations only, it is often difficult to distinguish in-situ transformation from other attenuation processes such as dilution, sorption or evaporation. The isotope ratio within the contaminants, however, gives important complementary information, because the isotope ratio is only very slightly changed in partitioning processes [2, 6, 25, 9, 24], but often shows pronounced fractionation during transformations, owing to the kinetic isotope effect. Enrichment of heavy isotopes in the remaining substrate has been shown to be indicative of in-situ transformation in an increasing number of studies applying carbon [10, 23, 12, 4, 5, 3, 13, 8, 11, 1, 18, 19], hydrogen [8, 11, 27, 18, 19] and even chlorine [10, 21] isotope fractionation, for methyl t-butyl ether

\[1\] This expression is equivalent to the expression

\[f = \left(\frac{N_{tot,1}}{N_{tot,0}}\right) \cdot \left[\frac{(1 + R_0)}{(1 + R)}\right] \approx \frac{N_{tot,1}}{N_{tot,0}}\]

where $N_{tot,1} = N_t + N_t^*$ and $N_{tot,0} = N_0 + N_0^*$; for the case that the heavy isotope is of low natural abundance, the approximations $\left[\frac{(1 + R_0)}{(1 + R)}\right] \approx 1$, and $\frac{N_{tot,1}}{N_{tot,0}} \approx \frac{N_t}{N_0}$, can be made, see discussion later in the text.
[13, 8], chlorinated hydrocarbons [10, 23, 12, 4, 5, 3], toluene and other alkyl benzenes [11, 1, 27, 18, 19], in laboratory [10, 23, 4, 5, 3, 13, 8, 11, 1, 18, 21, 19] and field [12, 23] studies, for chemical [5, 3, 21] and biological [10, 23, 4, 8, 11, 1, 27, 18] transformations.

The potential of isotopic fractionation in environmental chemistry, however, goes well beyond this rather qualitative application. Depending on the extent to which the breaking of a bond is involved in the rate-determining step, kinetic isotope effects in the elementary reaction can vary, and they may be characteristic for different types of reactions [17, 28]. However, so far this mechanistic information has largely been overlooked in environmental fractionation studies, partially, because it is often masked by statistical artifacts related to an inappropriate application of the Rayleigh equation.

In the first part of this chapter, the properties and intrinsic assumptions of the Rayleigh expression are reviewed. It is demonstrated how artifacts can be generated by an inappropriate application, and an evaluation procedure is proposed by which the site-specific kinetic isotope effect $^{1}k^{H}/k^{L}$ can be extracted from experimental data.

### 4.2 Theoretical Considerations

In 1896 Lord Rayleigh developed an equation to describe vacuum distillation [20], which was later adopted by geologists to express isotopic fractionation in small compounds like $\text{CH}_4$, $\text{CO}_2$, $\text{NH}_4^{+}$ and $\text{NO}_3^{-}$ [15]. It is derived from the relation

$$\frac{dN^*}{dN} = \alpha \cdot \frac{N^*}{N} \quad (4-2)$$

which expresses simply that a heavy ($N^*$) and a light ($N$) isotope, respectively, disappear from a pool of substrate according to different rate constants $dN^* = k_{H}N^*$ and $dN = k_{L}N$, where $\alpha = k_{H} / k_{L}$. For such fractionation to take place, however, the isotope of interest must be close enough to the reacting bond to have an influence on its reactivity. It can either form part of the bond
(primary isotope effect) or be in its direct proximity (secondary isotope effect).

Instead of \( k_{H\cdot N^*} \) and \( k_{L\cdot N} \) it would therefore be more appropriate to write \( k_{H\cdot N_{(at\, reacting\, bond)}}^{*} \) and \( k_{L\cdot N_{(at\, reacting\, bond)}} \). On the other hand, compound specific isotope analysis by GC-IRMS can only determine the isotopic ratio \( R = N^*/N \) of whole molecules, i.e. the average value over all positions within a compound, irrespective of whether they are in proximity to a reacting bond or not. Instead of \( R = N^*/N \) it would therefore more appropriate to write \( R = N^*_{(average\, over\, molecule)}/N_{(average\, over\, molecule)} \). Hence, the R value measured by GC-IRMS is not necessarily identical to the ratio that determines the isotopic fractionation during the reaction. This effect must be taken into account for before integrating equation (4-2). Otherwise, any application of the Rayleigh equation is based on wrong assumptions and does not lead to meaningful results! Unfortunately, such inappropriate applications are found in most studies published in environmental chemistry so far. In the following, we propose necessary corrections based on standard evaluation procedures as, for example, described by Melander [17]. These corrections are illustrated by discussing three cases of carbon isotope fractionation in reductive dehalogenations of aliphatic chlorinated hydrocarbons (Fig. 4-1), where a C-Cl bond is broken in the rate-determining step.

In the following derivations, several assumptions are made. They will be mentioned when applied, and will be summarized and discussed in greater detail at the end of the section.
Figure 4-1 Bonds broken in the rate-determining step of dehalogenation reactions, under consideration that different carbon isotopes may be present in substrate molecules; $k_L$ and $k_H$ characterize rate constants of molecules containing lighter and heavier carbon isotopes, respectively, and the subscripts indicate the influence of primary and secondary kinetic isotope effects.
### 4.2.1 Case A: Carbon tetrachloride (CCl₄)

In carbon tetrachloride (CCl₄), there is only one carbon atom per molecule. It forms part of every C-Cl bond that can be broken and therefore contributes directly to the observed fractionation (primary isotope effect)². In this case the value \( R = \frac{N^*/N}{N} \) determined in GC-C-IRMS is identical to the ratio at the reacting bond. This means explicitly:

\[
R = \frac{^{13}C_{\text{average over molecule}}}{{}^{12}C_{\text{average over molecule}}} = \frac{[^{13}\text{CCl}_4]}{[^{12}\text{CCl}_4]} \tag{4-3}
\]

\[
- \frac{d[^{13}\text{CCl}_4]}{dt} = k_H [^{13}\text{CCl}_4] \tag{4-4}
\]

\[
- \frac{d[^{12}\text{CCl}_4]}{dt} = k_L [^{12}\text{CCl}_4] \tag{4-5}
\]

A combination of equations (4-4) and (4-5) gives:

\[
\frac{d[^{13}\text{CCl}_4]}{d[^{12}\text{CCl}_4]} = \frac{k_H}{k_L} \cdot \frac{[^{13}\text{CCl}_4]}{[^{12}\text{CCl}_4]} \tag{4-6}
\]

² In the following, only carbon isotope effects will be discussed. These effects are practically independent of the presence of different chlorine isotopes for the following reasons:

1) The *direct* kinetic chlorine isotope effect (C-³⁷Cl bonds react more slowly than C-³⁵Cl bonds) is not relevant if only carbon isotopes are analyzed, because chlorine atoms are randomly associated with both, ¹²C and ¹³C, and the effect averages out in measurements of carbon isotope fractionation.

2) The *indirect* influence on the carbon isotope effect: \( k \left( ^{13}\text{C}-^{35}\text{Cl} \right) / k \left( ^{12}\text{C}-^{35}\text{Cl} \right) \neq k \left( ^{13}\text{C}-^{37}\text{Cl} \right) / k \left( ^{12}\text{C}-^{37}\text{Cl} \right) \) (where \( k (X-Y) \) is the rate for scission of an X-Y bond) can be expected to be very small.
Integration leads to the well known Rayleigh equation

\[
\frac{R}{R_0} = f(\alpha - 1) = f\varepsilon, \tag{4-7}
\]

where

\[
\varepsilon = \alpha - 1 = \frac{k_H}{k_L} - 1 \tag{4-8}
\]

\[
f = \frac{(1 + R_0)}{(1 + R)} \frac{[\text{CCl}_4]}{[\text{CCl}_4]_0} \approx \frac{[\text{CCl}_4]}{[\text{CCl}_4]_0} \tag{4-9}
\]

(The approximation in equation (4-9) is only valid if the heavy isotope is of low abundance and does not become greatly enriched so that \(R << 1\) during the entire course of the reaction. Whereas this is not always the case for hydrogen isotope fractionation or in studies with isotopically enriched substrates ([17, 14], see discussion at the end of this section), this condition is generally fulfilled for carbon isotope fractionation in substrates of natural isotopic abundance.)

Isotope ratios are generally expressed as differences \(\delta^{13}\text{C}\) (in ‰) with respect to the international VPDB standard:

\[
\delta^{13}\text{C} = \left(\frac{(\text{C}^{13}/\text{C}^{12})_{\text{Sample}}}{(\text{C}^{13}/\text{C}^{12})_{\text{VPDB}}} - 1\right) \cdot 1000\% \text{ VPDB} \tag{4-10}
\]
Thus, equation (4-7) is often expressed in the form

$$\frac{1000 + \delta^{13}C}{1000 + \delta^{13}C_0} = \left( \frac{[CCl_3]}{[CCl_4]_0} \right)^{(\alpha - 1)} = \left( \frac{[CCl_4]}{[CCl_4]_0} \right)^{\varepsilon}$$

(4-11)

First applications of the Rayleigh equation for isotope fractionation in geology, such as $^{15}$N fractionation in $NH_4^+$ and $NO_3^-$, are correctly evaluated in the same way [15].

4.2.2 Case B: 1,1,1-Trichloroethane (CCl$_3$-CH$_3$)

In 1,1,1-trichloroethane (CCl$_3$-CH$_3$), carbon isotopes are located at two different positions in the molecule (see Figure 4-1b). A substrate pool of CCl$_3$-CH$_3$ can therefore be imagined to consist of $^{12}$CCl$_3$-$^{12}$CH$_3$ molecules (i) and small fractions of $^{12}$CCl$_3$-$^{13}$CH$_3$ (ii) as well as $^{13}$CCl$_3$-$^{12}$CH$_3$ molecules (iii). (Because of the low natural abundance of $^{13}$C, $^{13}$CCl$_3$-$^{13}$CH$_3$ species can be neglected for non-enriched substrates.) The isotope ratio $R$ determined by GC-C-IRMS is the average over all positions:

$$R = \frac{^{13}C_{\text{average over molecule}}}{^{12}C_{\text{average over molecule}}}$$

$$= \frac{[^{13}CCl_3-^{12}CH_3] + [^{12}CCl_3-^{13}CH_3]}{2[^{12}CCl_3-^{12}CH_3] + [^{13}CCl_3-^{12}CH_3] + [^{12}CCl_3-^{13}CH_3]}$$

$$\approx \frac{[^{13}CCl_3-^{12}CH_3] + [^{12}CCl_3-^{13}CH_3]}{2[^{12}CCl_3-^{12}CH_3]}$$

$$= \frac{1}{2} \frac{^{13}CCl_3-^{12}CH_3}{^{12}CCl_3-^{12}CH_3} + \frac{1}{2} \frac{^{12}CCl_3-^{13}CH_3}{^{12}CCl_3-^{12}CH_3}$$

(4-12)
and, therefore,

\[
\frac{d^{13}C_{\text{average over molecule}}}{d^{12}C_{\text{average over molecule}}} \approx \frac{1}{2} \frac{d^{13}\text{CCl}_3-^{12}\text{CH}_3}{d^{12}\text{CCl}_3-^{12}\text{CH}_3} + \frac{1}{2} \frac{d^{12}\text{CCl}_3-^{13}\text{CH}_3}{d^{12}\text{CCl}_3-^{12}\text{CH}_3} \quad (4-13)
\]

The observed isotopic enrichment is therefore the average of two independent reactions of \(^{13}\text{CCl}_3-^{12}\text{CH}_3\) and \(^{12}\text{CCl}_3-^{13}\text{CH}_3\), respectively. This is important, because they can now be considered in two separate mathematical treatments, and then the effect on the average value can be calculated. In the case of \(^{12}\text{CCl}_3-^{13}\text{CH}_3\) a secondary isotope effect can be expected, in the case of \(^{13}\text{CCl}_3-^{12}\text{CH}_3\) a primary isotope effect:

\[
\frac{d^{13}\text{CCl}_3-^{12}\text{CH}_3}{d^{12}\text{CCl}_3-^{12}\text{CH}_3} = \frac{k_{H,\text{primary}}}{k_L} \cdot \frac{[^{13}\text{CCl}_3-^{12}\text{CH}_3]}{[^{12}\text{CCl}_3-^{12}\text{CH}_3]} \quad (4-14)
\]

\[
\frac{d^{12}\text{CCl}_3-^{13}\text{CH}_3}{d^{12}\text{CCl}_3-^{12}\text{CH}_3} = \frac{k_{H,\text{secondary}}}{k_L} \cdot \frac{[^{12}\text{CCl}_3-^{13}\text{CH}_3]}{[^{12}\text{CCl}_3-^{12}\text{CH}_3]} \quad (4-15)
\]

Because these equations cannot be solved using experimental data of \(R\) alone, two assumptions need to be made for an approximate solution.

a) At the beginning of the reaction, carbon isotopes are assumed to be distributed evenly over the \(\text{CCl}_3\)-position and the \(\text{CH}_3\)-position of the molecule (for the validity of this assumption see discussion at the end of this section). Substitution into (4-12) then gives

\[
\left(\frac{[^{13}\text{CCl}_3-^{12}\text{CH}_3]}{[^{12}\text{CCl}_3-^{12}\text{CH}_3]}\right)_0 = \left(\frac{[^{12}\text{CCl}_3-^{13}\text{CH}_3]}{[^{12}\text{CCl}_3-^{12}\text{CH}_3]}\right)_0 = R_0 \quad (4-16)
\]

b) Secondary isotope effects, which are about one order of magnitude
weaker than primary effects, are neglected: \( k_{H, \text{secondary}} \approx k_L \). Equation (4-15) then simplifies to

\[
\frac{d[^{12}\text{CCl}_3^{-13}\text{CH}_3]}{d[^{12}\text{CCl}_3^{-12}\text{CH}_3]} = \frac{[^{12}\text{CCl}_3^{-13}\text{CH}_3]}{[^{12}\text{CCl}_3^{-12}\text{CH}_3]} \tag{4-17}
\]

Integration of (4-17) under the boundary condition (4-16) finally gives

\[
\left(\frac{[^{12}\text{CCl}_3^{-13}\text{CH}_3]}{[^{12}\text{CCl}_3^{-12}\text{CH}_3]}\right)_t = \left(\frac{[^{12}\text{CCl}_3^{-13}\text{CH}_3]}{[^{12}\text{CCl}_3^{-12}\text{CH}_3]}\right)_0 = R_0 \tag{4-18}
\]

This means that during a reaction, the isotope ratio does not change at non-reacting positions of a molecule. This result is rather intuitive, and it can be considered as representative for the case of larger molecules, where most of the atoms are far away from the reactive site and have no influence on the reaction rate. Very importantly, however, the invariant isotope ratio of such non-reactive sites attenuates the isotope effect measured by GC-C-IRMS (see 4-12)! If the change in \(^{13}\text{C}/^{12}\text{C}\) during a reaction could be determined at the \(-\text{CCl}_3\) position of \(\text{CCl}_3\text{-CH}_3\) alone, it would thus be about twice as large as the average change in \(\text{CCl}_3\text{-CH}_3\) measured by GC-C-IRMS. An unwary researcher, who might be tempted to infer \(k_H/k_L\) from application of the Rayleigh equation to \((R/R_0)\text{(average over molecule)}\), would thus be in error. It is intuitive to take this effect into account by multiplying the measured changes in isotopic ratios \((\Delta \delta^{13}\text{C} = \delta^{13}\text{C} - \delta^{13}\text{C}_0)\) by an appropriate statistical factor (in this case 2) and then applying the Rayleigh equation to \((R/R_0)\text{(at reactive site)}\).
Rayleigh-Equation: A Critical Discussion

\[
\left( \frac{R}{R_0} \right) \text{ at reactive site} = \frac{1000 + \delta^{13}C_0 + 2(\delta^{13}C - \delta^{13}C_0)}{1000 + \delta^{13}C_0}
\]

\[
= \left( \frac{[\text{CH}_3\text{CCl}_3]}{[\text{CH}_3\text{CCl}_3]_0} \right)^{(\alpha - 1)} = \left( \frac{[\text{CH}_3\text{CCl}_3]}{[\text{CH}_3\text{CCl}_3]_0} \right)^{\varepsilon} \quad (4-19)
\]

with \( \alpha \approx \frac{k_{\text{H, primary}}}{k_{\text{L}}} \).

Complementary to this rather intuitive introduction, a correct derivation of equation (4-19) is given in Appendix A4. In addition, a demonstration is given there that in cases such as “B” an inappropriate application of the Rayleigh equation leads to calculated \( \varepsilon \) values that do not have a physical meaning!

4.2.3 Case C: Hexachoroethane (CCl3-CCl3)

In hexachloroethane (CCl3-CCl3), isotopes are located at two symmetrical positions in the compound. A substrate pool of CCl3-CCl3 can therefore be imagined to consist of only two kinds of molecules, \(^{12}\text{CCl}_3-{^{12}\text{CCl}}_3\) and \(^{13}\text{CCl}_3-{^{12}\text{CCl}}_3\) (neglecting \(^{13}\text{CCl}_3-{^{13}\text{CCl}}_3\) because of its low abundance). For the measured isotope ratio \( R \):

\[
R = \frac{^{13}\text{C}}{^{12}\text{C}} \frac{\text{average over molecule}}{\text{average over molecule}}
\]

\[
= \frac{[^{13}\text{CCl}_3-^{12}\text{CCl}_3]}{2[^{12}\text{CCl}_3-^{12}\text{CCl}_3] + [^{13}\text{CCl}_3-^{12}\text{CCl}_3]} \approx \frac{[^{13}\text{CCl}_3-^{12}\text{CCl}_3]}{2[^{12}\text{CCl}_3-^{12}\text{CCl}_3]} \quad (4-20)
\]

\[
\frac{d^{13}\text{C}}{d^{12}\text{C}} \approx \frac{1}{2} \frac{d[^{13}\text{CCl}_3-^{12}\text{CCl}_3]}{d[^{12}\text{CCl}_3-^{12}\text{CCl}_3]} \quad (4-21)
\]
If we assume that only one C-Cl bond is broken in the rate determining step (such as in hydrogenolysis to pentachloroethane [22]) the reaction process can be regarded as localized at one carbon center (see “C1” in Figure 4-1). Contrary to the case of $^{13}\text{CCl}_3$-$^{12}\text{CH}_3$, however, where for 100% conversion every $^{13}\text{C}$ atom is bound to react sooner or later, dehalogenation of $^{13}\text{CCl}_3$-$^{12}\text{CCl}_3$ can take place at both the $^{13}\text{CCl}_3$ and the $^{12}\text{CCl}_3$ center so that part of the reaction circumvents the $^{13}\text{C}$ center! Besides intermolecular competition between a $^{13}\text{CCl}_3$-$^{12}\text{CCl}_3$ and a $^{12}\text{CCl}_3$-$^{12}\text{CCl}_3$ molecule, also intramolecular competition therefore takes place between the two sites within $^{13}\text{CCl}_3$-$^{12}\text{CCl}_3$! The corresponding rate expressions are (see Fig. 4-1)

$$\frac{d[^{13}\text{CCl}_3-^{12}\text{CCl}_3]}{dt} = k_{\text{H,primary}}[^{13}\text{CCl}_3] + k_{\text{H,secondary}}[^{12}\text{CCl}_3]$$

$$= (k_{\text{H,primary}} + k_{\text{H,secondary}})[^{13}\text{CCl}_3-^{12}\text{CCl}_3] \quad (4-22)$$

(where $[^{-12}\text{CCl}_3]$ and $[^{-13}\text{CCl}_3]$ denote the concentrations of $^{-12}\text{CCl}_3$ and $^{-13}\text{CCl}_3$ sites, respectively) and

$$\frac{d[^{12}\text{CCl}_3-^{12}\text{CCl}_3]}{dt} = k_{L}[^{12}\text{CCl}_3]$$

$$= 2k_{L}[^{12}\text{CCl}_3-^{12}\text{CCl}_3] \quad (4-23)$$

(There are two $^{-12}\text{CCl}_3$ sites in every $^{12}\text{CCl}_3$-$^{12}\text{CCl}_3$ molecule!)

---

3 Dichloroelimination (“C2” in Figure 1) as an alternative pathway will be discussed later in this chapter.
This leads to the expression

\[
\frac{d[^{13}\text{CCl}_3-^{12}\text{CCl}_3]}{d[^{12}\text{CCl}_3-^{12}\text{CCl}_3]} = \frac{(k_{\text{H,primary}} + k_{\text{H,secondary}})}{2 k_L} \cdot \frac{[^{13}\text{CCl}_3-^{12}\text{CCl}_3]}{[^{12}\text{CCl}_3-^{12}\text{CCl}_3]} \tag{4-24}
\]

or, with (4-20) and (4-21),

\[
\frac{d[^{13}\text{C}_{\text{average over molecule}}]}{d[^{12}\text{C}_{\text{average over molecule}}]} = \frac{(k_{\text{H,primary}} + k_{\text{H,secondary}})}{2 k_L} \cdot \frac{[^{13}\text{C}_{\text{average over molecule}}]}{[^{12}\text{C}_{\text{average over molecule}}]} \tag{4-25}
\]

As in the case of A, integration leads to the Rayleigh equation

\[
\frac{R}{R_0} = f^{(\alpha - 1)} = f^{\varepsilon} \tag{4-7}
\]

where

\[
f = \frac{(1 + 2R_0)}{(1 + 2R)} \cdot \frac{[^{13}\text{CCl}_3^{12}\text{CCl}_3]}{[^{13}\text{CCl}_3^{12}\text{CCl}_3]} \approx \frac{[^{13}\text{CCl}_3^{12}\text{CCl}_3]}{[^{13}\text{CCl}_3^{12}\text{CCl}_3]} \tag{4-26}
\]

(The approximation is valid for the case that \( R \ll 1 \)). Written in the delta notation:

\[
\frac{1000 + \delta^{13}C}{1000 + \delta^{13}C_0} = \left( \frac{[^{13}\text{CCl}_3^{12}\text{CCl}_3]}{[^{13}\text{CCl}_3^{12}\text{CCl}_3]} \right)^{(\alpha - 1)} = \left( \frac{[^{13}\text{CCl}_3^{12}\text{CCl}_3]}{[^{13}\text{CCl}_3^{12}\text{CCl}_3]} \right)^{\varepsilon} \tag{4-27}
\]
with

$$\varepsilon = \alpha - 1 = \frac{k_{H, \text{primary}} + k_{H, \text{secondary}}}{2k_L} - 1 \quad (4-28)$$

If the secondary isotope effect is neglected again ($k_{H, \text{secondary}} \approx k_L$), this expression reduces to

$$\varepsilon = \alpha - 1 = \frac{1}{2} \cdot \left( \frac{k_{H, \text{primary}}}{k_L} - 1 \right) \quad (4-29)$$

In general, if there are $x$ chemically equivalent sites inside a molecule competing for reaction, the determined enrichment factor $\varepsilon$ is

$$\varepsilon = \alpha - 1 = \frac{1}{x} \cdot \left( \frac{k_{H, \text{primary}}}{k_L} - 1 \right) \quad (4-30)$$

4.2.4 Generalization of the evaluation procedure: Toluene

The evaluation procedures presented can in principle be generalized and applied for all kinds of molecules. In most cases a combination of corrections as in case B and C has to be used. This can be illustrated for hydrogen isotope fractionation in the oxidation of toluene at the methyl group. Of the eight total hydrogen atoms, five positions in the ring have an invariant isotope ratio during the reaction, whereas the three hydrogen atoms of the methyl group are potentially reactive (see Fig. 4-2). The Rayleigh equation therefore takes the form
\[
\frac{1000 + \delta^{13}C_0 + 8/3 (\delta^{13}C - \delta^{13}C_0)}{1000 + \delta^{13}C_0} = \left( \frac{[\text{toluene-d}]}{[\text{toluene}]_0} \right)^{(\alpha - 1)} = \left( \frac{[\text{toluene-d}]}{[\text{toluene}]_0} \right)^{\varepsilon}
\]

(4-31)

where

\[
\varepsilon = \alpha - 1 = \frac{1}{3} \cdot \left( \frac{k_{H,\text{primary}}}{k_L} - 1 \right).
\]

(4-32)

---

**Figure 4-2:** Reactive and non-reactive positions in a toluene molecule, leading to both effects, intramolecular competition and attenuation through invariant isotope ratios.
4.2.5 *Approximations in the evaluation procedure*

It is important to bear in mind what approximations were made in deriving this equation.

1) An assumption used in equations (4-12)/(4-20) on the one hand and in (4-9)/(4-19)/(4-26) on the other is the low total abundance of the heavy isotope. This assumption may not be valid, if many C atoms are present in a molecule or if strong fractionation takes place such in the case of hydrogen. It is certainly not justified for isotopes of high natural abundance such as chlorine isotopes or in the case of isotopically enriched substrates, and the evaluation has then to be modified accordingly.

2) Isotopes are assumed to be distributed uniformly over the positions of the molecule so that the isotope ratio is the same at all sites at t = 0 (equation 4-16). There is overwhelming evidence that this is not exactly the case [7, 16, 21]. Reddy et al. [21] have made great efforts to determine the exact site specific Cl isotope ratio at different positions in DDT. In the case of elements other than hydrogen, however, deviations can be expected to be generally in the range of ten percent at most.

3) The largest error is probably introduced by neglecting secondary isotope effects (equations 4-17 and 4-29). As they are generally about one order of magnitude smaller than primary effects [17, 28], differences in kinetic isotope effects are likely to be overestimated by up to 10%.

4) In a group of chemically equivalent atoms (as for example hydrogen in the methyl group of toluene), only one of them at most is assumed to be a heavy isotope. Whereas this assumption is valid for isotopes of low natural abundance (see assumption 1), the case is different for isotopically enriched substrates. The assumption is introduced by stating equation (4-22), where the case $^{13}$CCl$_3$-$^{13}$CCl$_3$ has been neglected, with important consequences for the equations (4-29), (4-30) and (4-32). In perdeuterated toluene, for example, three deuterium isotopes are present in the methyl group, and the expression $\varepsilon = 1/x \left( k_H/k_L - 1 \right)$ in (4-30) changes to $\varepsilon = \left( k_H/k_L - 1 \right)$ (besides changes in other assumptions). Because this effect was neglected, a previous study reports greatly differing enrichment
factors $\varepsilon$ for natural and perdeuterated toluene, respectively [18]. This lead to considerable confusion, as can be seen in a recent letter exchange [14]. (There, the focus is on another evaluation error of this study, related to the approximation 1 in expressions (4-9, 4-19, 4-26); however, because the influence of approximation 4 is not taken into account, the correction was made only halfway, and no consistent results were obtained there.)

5) The most important presupposition for application of the above discussed evaluation scheme is certainly that a reaction mechanism must be postulated beforehand: reactive and unreactive positions inside a molecule have to be identified. As an alternative to hydrogenolysis, for example, hexachloroethane can also react via a dichloroelimination. If this reaction takes place in a concerted mechanism, both C-atoms will be involved ([22], see Fig. 4-1, C2). In this case there would be no intramolecular competition between a $^{13}$CCl$_3$ and a $^{12}$CCl$_3$ site, because they are both involved in the rate determining step. A different enrichment factor $\varepsilon = (k_H/k_L - 1)$ could therefore be expected.

This example, however, demonstrates the power of the proposed evaluation procedure: experimental data can be tested for different possible reaction mechanisms!

### 4.2.6 The “ideal” probe compound in isotope fractionation studies

As an important insight from the preceding discussion it can be stated that a determination of kinetic isotope effects $k_H/k_L$ is then more substantial, when compounds contain only one atom of the element for which isotope fractionation is measured, for example in small molecules such as $^{12/13}$CCl$_4$, $^{15/14}$NO$_3^-$, $^{34/32}$SO$_4^{2-}$ etc. Then no assumptions are necessary to apply the Rayleigh equation, and there is no attenuation due to non-reactive sites or intramolecular competition. We used this insight to address the question whether one or two bonds are broken in the first rate-determining step in dehalogenation by goethite/Fe(II) in the context of chapter three, with CCl$_4$ as a suitable probe compound in carbon isotope fractionation studies.
Supporting Information in Appendix A4: A4.1 Correct Derivation of Equation (4-19) for Case B in Chapter 4 (CCl₃-CH₃); A4.2 The Physical Meaning of Epsilon Values Determined by an Inappropriate Application of the Rayleigh Equation in Case B in Chapter 4 (CCl₃-CH₃)

4.3 References


Design and Synthesis of Probe Compounds for Mechanistic Studies of Dehalogenation at Reactive Surfaces
Abstract

Intermediate radicals and carbenes play a key role for the product distribution of many reductive dehalogenation reactions. Their detection is, however, hampered by the low water solubilities of the halogenated substrates as well as by the very short lifetimes of the intermediates. For an indirect detection, carbene and radical traps have been applied in previous studies, such as alkenoic acids, vicinal dibromide stereoisomers and radical clocks. Their use, however, was limited by trapping efficiencies, slow rotational equilibria at surfaces and fast decomposition of the traps. In addition, for the case of heterogeneous reactions, no attempts have been made to accumulate halogenated probe compounds specifically at reactive surfaces, for example by attachment of suitable charged anchor groups. In order to meet these criteria, we synthesized two classes of novel model compounds: a) CCl$_3$-CH$_2$-X (-X = -OPO$_3^{2-}$, -OSO$_3^{-}$, -N(CH$_3$)$_3^+$) and b) CCl$_3$-CH$_2$-CHOR-CH$_2$-CH$_2$-CH=CH$_2$ (R = H, phosphate). The CCl$_3$- group mimics the reactivity of major environmental contaminants such as CCl$_4$, CHCl$_3$ or CH$_3$CCl$_3$. It is linked to an anchor group that ensures water solubility (-OH), and/or attachment at surfaces. Whereas phosphate esters are likely to form inner-sphere complexes at (iron) oxide surfaces, sulfate groups are known for ion pair bonding, and trimethylammonium groups are in the diffuse counter-ion cloud of positively charged surfaces. The small probe compounds of group a) are therefore promising tools to investigate the electron transfer depending on the distance from the surface. In addition, they could be used to investigate the reactivity in interlayers of reactive sheet minerals such as green rust and ferruginous clay minerals. The probe molecules of group b) are optimized for trapping radicals and carbenes. Their trapping efficiency can be expected to be similar to that in previously described radical clocks; however, they are more reactive with respect to dehalogenation and less reactive in decomposition reactions such as hydrolysis. For the first time they contain anchor, trap and reactive group in one molecule. In this chapter the synthesis of these novel probe compounds is described. Initial experiments are currently in progress.
5.1 Introduction

Detailed mechanistic studies of reductive dehalogenation reactions by surface bound Fe(II) are hampered by two main difficulties. 1) Chlorinated aliphatic hydrocarbons are sparingly water soluble, only a small part is present at the surface, and of this part only a tiny fraction takes place in a reaction. 2) The slow initial step of the reaction contrasts with a rapid subsequent reaction. Intermediate radicals and carbenes, which play a key role in the product formation, have only a very short lifetime (see chapter 3). These species of interest not only form in trace amounts at the surface, they are also transient in nature, and their direct analytical detection (such as by magnetic resonance techniques) is very difficult. Alternatively, detection can be achieved indirectly, by adding radical or carbene traps. These are compounds that react rapidly with the intermediates and trap them to form characteristic products. However, they need to be chosen carefully, because many of them are very reactive and may be reduced rapidly in environments of low redox potential [11, 19].

Creative solutions to this problem have been applied in earlier work. Buschmann et al. [3] used perdeuterated isopropanol to detect chlorinated radicals (see also chapter 3) and synthesized 3-methyl but-3-en acid (following earlier studies by Fujita et al. [6]), which proved well suited for trapping dichlorocarbene (see Figure 5-1a); such traps, however, had to be added in large excess for satisfactory trapping efficiencies. Totten et al. [17] chose a different approach by using halogenated probe compounds that carried the trap already inside their molecular structure. As a first type they studied vicinal dibromide stereoisomers (inspired by earlier studies, see [1]), such as 2,3-dibromopentanes. If these stereochemical probes were reduced in a concerted two-electron transfer reaction, both bromine substituents were eliminated simultaneously, and the stereochemistry of the compounds was preserved. Conversely, a one electron transfer led to formation of radical intermediates, and bond rotations during their lifetime directed the stereochemistry towards the most stable products (see Figure 5-1b). These probes were successfully tested in homogeneous solution. Experiments with goethite/Fe(II), however, indicated that the rotational equilibrium was not established in proximity to the surface. Either the transfer of
the second electron was very fast, or bond rotations were hindered by the presence of the surface, in any case no conclusive information could be gained for heterogeneous catalysis [18]. Totten [18] took another approach with so-called radical clocks, which allow estimates of the lifetimes of intermediates (For a comprehensive overview see [8] and [12]). They also carry the trap inside their structure, for example in the form of a double bond. In compounds such as 6-bromo-1-hexene, the generation of 6-hexene radicals leads to two competing follow-up reactions: cyclisation vs. further reduction (see Figure 5-1c). Because the cyclisation rate is known, the lifetime of 6-hexene radicals can readily be estimated. These radical clocks were successfully applied in the reaction with zero valent iron. However, 6-bromo-1-hexene was found to hydrolyze rapidly in aqueous solution so that its application was restricted to very fast dehalogenation reactions and it could not be used in slower reductions such as for example by goethite/Fe(II).

Thus, the “ideal” probe compound for investigating reductive dehalogenation by surface bound Fe(II) has not been found yet. From past experiences, however, a list of desirable attributes can be summarized:

1) The reactive halogenated group and the trap should be part of the same probe compound. Trapping efficiencies are then increased enormously, and even the lifetime of intermediates may be estimated (use as a radical clock).

2) The halogenated group should be sufficiently reactive to allow rapid studies, and it should mimic the reactivity of major environmental contaminants.

3) Products of the reaction should be stable and easy to analyze by a single analytical technique.

4) The possibility of side reactions such as hydrolysis should be minimized.

5) The trapped information must not rely on stereospecific information that may be affected by the presence of a surface (such as for vicinal dibromides).

6) The probe compound used should be water soluble, or even better, accumulate at the surface of mineral oxides.

7) The compound should be obtained by a straightforward synthesis route.
Figure 5-1: Probe molecules used to investigate electron transfer and trap short-lived intermediates in previous studies: a) deuterated isopropanol and alkenoic acids [3], b) vicinal dibromides [18] and c) radical clocks [17].
5.2 Concept

5.2.1 Small charged reactivity probes (A)

A first class of probe molecules was synthesized to probe the reactivity at charged surfaces (see scheme 5-1). At a positively charged goethite/Fe(II) surface, phosphate forms inner-sphere surface complexes [7], sulfate is electrostatically bound in outer sphere complexes and monovalent cations are in the diffuse ion swarm of the electrical double layer ([15, 16], see Figure 5-2)). In addition, some Fe(II) containing minerals display a layered structure in which ions can be intercalated, such as anions in green rust and cations in ferruginous clay minerals. With regard to electron transfer reactions by surface bound Fe(II), two questions are of major interest: 1) Over what distances from the surface are electrons transferred? 2) To what extent are interlayers involved in reductive transformations? (Previous studies have indicated that this can be the case under certain circumstances [9].) To deal with these issues, a series of probe molecules was synthesized that are based on the 2,2,2-trichloroethyl group, which is used as a protective group in organic synthesis; it is there reductively removed by treatment with Zn(0) [10]. Advantages of these molecules are:

a) The introduction of a charged anchor group via ester bonds is relatively easy to accomplish. These anchor groups can be chosen as phosphate, sulfate or trimethyl ammonium so that they are likely to be bound in inner-sphere complexes, outer-sphere complexes, in the diffuse ion swarm or even in interlayers of certain minerals. The design of the anchor thus determines the position of the molecule and the distance to a charged surface.

b) These molecules are small so that the position of the reactive –CCl₃ group is determined by the anchor group with a precision of two to three bond lengths.

c) They can be expected to decompose during the reaction and produce the easily detectable product 1,1-dichloroethene (see scheme 5-1).
Although these molecules were chosen for convenience, their application is complicated by three factors: 1) It may not be sufficient to locate the reactive \( \text{CCl}_3 \) group with a precision of two to three bond lengths in order to investigate small distance variations at the surface, such as the difference between inner sphere and outer sphere complexes. 2) The interpretation of results is made difficult by additional electrostatic effects. They can be expected to have an influence on the activation energy of electron transfer reactions, as predicted by the Marcus theory [5]. 3) In order to compare reaction rates of different probe compounds at charged surfaces, they must be “calibrated” in their reaction with a non-charged reductant. However, to find and carry out such a reaction in water is not trivial. We therefore plan to apply the designed probe compounds of the 2,2,2-trichloroethyl-type in a rather qualitative fashion, to investigate the extent to which reductive dehalogenation reactions can be accelerated, if the substrate is fixed at a reactive surface. Such insight shall then be used to approach “yes / no”- questions, such as the reactivity in interlayers of minerals.

**Figure 5-2:** Mechanisms for adsorption of ions at surfaces: inner-sphere complex, outer-sphere complex and diffuse ion (from Stumm, 1996 [16], adapted from Sposito, 1989 [15])

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \text{Cl} \quad \text{Cl} \\
\end{array}
\quad + \quad 2e^- \quad -\text{Cl}^-
\end{align*}
\]
“Anchor and trap” compounds (B)

The design of the second class of model compounds is based on the idea of a triple functionality. These probes are supposed to contain 1) a reactive halogenated group, 2) a trap to catch intermediates and 3) a functional group that ensures water solubility or even accumulation at the surface (“anchor”, see Fig. 5-3). The trichloromethyl group, –CCl₃, is well suited as halogenated group, because it is reasonably reactive and it mimics properties of major contaminants such as carbon tetrachloride (CCl₄), chloroform (CHCl₃) or 1,1,1-trichloroethane. A more reactive alternative is the tribromomethyl group, -CBr₃. Both functional groups have the advantage that they are relatively inert towards hydrolysis as a possible major side reaction. A good candidate for the trap functionality is a double bond, because it is known to react with both radicals and carbenes (see Figure 5-1). Hydroxyl groups are finally suitable as “anchor” groups, for two reasons. 1) They make the probe compounds to a certain degree water soluble. 2) In addition they are convenient for the attachment of additional modules such as ionic phosphate groups via ester bonds. A phosphate ester group can be expected to act as a true anchor and fix the probe compound in proximity to surface-bound Fe(II), in analogy to the observed strong sorption of phosphates and phosphonates at iron oxides [7, 13].

Figure 5-3: The concept of “anchor and trap” compounds
Radical cyclization rates to n-membered rings decrease in the order 5 > 6 > 7 [4]. A similar effect can be expected for cyclisation by addition of carbenes to a double bonds. Fairly good trapping efficiencies can therefore be expected in formation of six-membered rings, when reactive group and double bond are four C atoms apart. (see Figure 5-5; remark: according to the Baldwin rule [2] cyclization reactions take place preferentially exo-trigonal, which means that the attack on the trigonal C-center of a double bond occurs in a way that the double bond is not included in the ring being formed (“exo”!). The backbone of the probe compound without anchor group thus takes the form \(\text{Cl}_3^\delta\text{C}-^\varepsilon\text{CH}_2-^\varepsilon\text{CH}_2-^\varepsilon\text{CH}_2-^\varepsilon\text{CH}_2-^\varepsilon\text{CH}=^\varepsilon\text{CH}_2\). If we chose to attach the anchor group at least one C atom away from both, the reactive group and the double bond, “e” and “d” remain as possible positions. When the hydroxyl group is introduced in position “e”, the two protons in position “f” (\(^\varepsilon\text{CH}_2\) ) experience the electron withdrawing effect of both the \(-\varepsilon\text{CHOH}\)- group and the \(\text{Cl}_3^\delta\text{C}\)- group, which may render them more acid and thus promote \(\beta\)-elimination of \(\text{HCl}\) or \(\text{H}_2\text{O}\) (see Figure 5-4). This could be critical, because such side reactions may make the compound useless as a probe in slower dehalogenation reactions. However, it may also have a beneficial effect. Once a phosphate group is introduced as anchor, the probe molecule is likely to stick to the surface, even after completion of the reaction. Not only is it then troublesome to desorb the products, it may also be difficult to extract and analyze them. A \(\beta\)-elimination that would remove the phosphate ester group at elevated temperature and/or lower pH could provide an elegant solution to the problem (see Fig. 5-4).

Figure 5-4: \(\beta\)-Elimination of the phosphate group as a convenient way to remove the anchor prior to analysis (left) vs. the possibility of an unwanted \(\beta\)-elimination of \(\text{HCl}\) and \(\text{H}_2\text{O}\) (right)
Because of the benefit of such a *forced* elimination, we evaluated the probability of an *unwanted* $\beta$-elimination by estimating the lifetime of $\text{Cl}_3\text{C}-^\text{f}\text{CH}_2-^\text{f}\text{CHOH}-^\text{d}\text{CH}_2-^\text{d}\text{CH}_2-^\text{b}\text{CH}=^\text{b}\text{CH}_2$ with respect to $\beta$-elimination of HX at circumneutral pH. Very helpful were Taft relationships from a comprehensive review by Roberts et al [14]. For our compound, they gave rough estimates for rather long half-lives of several decades at pH 7 (see Appendix A5), comparable to reported data about 1,1,1,2-tetrachloroethane ($\text{Cl}_3\text{C}-\text{CClH}_2$) [14]. No major problems should thus be expected from such unwanted side reactions.

![Figure 5-5: Possible reactions of “anchor and trap” - compounds](image)

The synthesis and characterization of all probe compounds are described in Appendix A5.
5.3 Conclusions and Outlook

Possible reactions of “anchor and trap” probe compounds are summarized in Figure 5-5. As with their predecessors (Figure 5-1), they should be well suited as radical and carbene scavengers: similar to radical clocks, they may even allow estimates of the lifetimes of these intermediates. Their new feature, however, is an “anchor” group that enables for the first time specific investigations of surface reactions. In chapter 3 evidence was obtained for the importance of radical versus surface-mediated reactions in the dehalogenation of CCl₄ by goethite/Fe(II). For several reasons, the newly synthesized probe compounds may just be the right tool to approach this question in future studies:

1) These compounds can be attached at the reactive surface, thereby increasing the probability of effective encounters for reaction.

2) Depending on the anchor group, these compounds can be chosen to be kept in proximity to the surface (phosphate) or to be allowed to diffuse back into solution (-OH). This adjustment of their residence time can be expected to have an influence on the formation of surface intermediates, and thus on the eventual product formation. This enables testing of mechanistic hypotheses made in chapter 3.

3) In the study of chapter 3, radicals were trapped with isopropanol. There, it could not be decided whether the formation of CDCl₃ was due to a rather slow second electron transfer at the surface or to a quick back-diffusion into solution. With “anchor and trap” molecules, the lifetime of radicals can be investigated with the trap as second, independent measure.

4) Due to the enrichment of probe molecules at the surface, Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR) may allow the in-situ observation of their reaction.

These features give an outlook on exciting possibilities in further investigations. Currently, first results are being evaluated from experiments with Cr(II) in homogeneous solution.
Results of experiments with 7,7,7-trichlorohepten-5-ol in reaction with Cr(II) available in Appendix A6.

These experiments were evaluated after submission of this thesis. Their results, conclusion and an outlook on further studies is given in Appendix A6.

5.4 References


3627-3633.


Conclusions and Outlook
The work presented in this dissertation is a contribution to understanding a) the reactivity of natural surface-bound iron(II) phases and b) the product formation in reductive dehalogenations catalyzed by such species. Several different approaches have been made to deal with the difficulties that are encountered when reactive surface species are investigated on the one hand and transient organic intermediates on the other. The methods provide an approach for new, interesting perspectives in future mechanistic studies.

Reducible organic contaminants as reactive probes were used in chapter two, to investigate the reactivity in suspensions of many different environmentally important iron minerals in the presence of dissolved Fe(II). Great differences in surface-normalized reaction rates were observed, with the general trend Fe(II) + iron(II) carbonate < Fe(II) + iron oxides < Fe(II) + iron(II) sulfides. This result highlights the importance of the chemical and mineralogical environment for the reactivity of surface bound Fe(II) in natural in-situ transformations of reducible contaminants (e.g., in ferruginous subsurface zones). Low reactivities can be expected in strictly anoxic calcite-rich grounds. They will increase in zones of changing oxic/anoxic conditions, where iron oxides form [3]. The highest reactivity can be expected in proximity to sulfate reducing zones, where iron sulfides are likely to be encountered. From an environmental engineering point of view, it is attractive to extrapolate such insight gained with one contaminant class (e.g. chlorinated hydrocarbons) to the behavior of another (e.g. nitroaromatic compounds). However, our study with hexachloroethane and 4-chloronitrobenzene as representatives of very different compound classes showed that reactivity trends could be transferred only very approximately. For some minerals they were dominated by possible mechanistic and/or sorption effects of 4-chloronitrobenzene. A better correlation, however, can be expected for similar compounds. This shows our comparison of results for hexachloroethane from this study with very recently published data for chlorinated ethenes [2]. Chapter 2 may therefore serve as a basis to qualitatively predict relative reactivity trends for chlorinated hydrocarbons in reactions with Fe(II)-bearing mineral surfaces.

In chapter three the focus was on mechanism and product formation in the
Conclusions and Outlook

dechlorination of carbon tetrachloride with Fe(II) on the surface of goethite. Like in previous studies, toxic (chloroform) as well as harmless compounds (formate and carbon monoxide) were observed as major products. In addition, mechanistic evidence was obtained for free trichloromethyl radicals (CCl$_3^\cdot$) indicative of an initial one-electron transfer. Conversely, free trichloromethyl carbanions could not be expected to play a major role. This evidence is important for an understanding of the product formation: 1) it stresses the importance of follow-up radical reactions (such as with organic matter) that can lead to chloroform and 2) it indicates that reaction to harmless products may involve intermediates that are stabilized in iron complexes at the surface. Conversely, we did not find evidence for an initial two-electron transfer that was thought to play a key role in previous investigations [1, 4]. We therefore suggest that radical and surface-mediated reactions may be more important in the dechlorination of CCl$_4$ by surface-bound Fe(II) than commonly assumed. Higher pH values were observed to lead to more chloroform, an effect that is probably related to changes in surface chemistry but cannot be fully explained with our present knowledge. Obviously, the behavior of radicals and the nature of surface stabilized intermediates still have to be better understood. Experimental approaches taken in this thesis could pave the way for such future investigations. A detail is the novel experimental setup applied in chapter three. There, the pH was kept constant by the intrinsic buffer capacity of the mineral surface; no organic or inorganic buffers were introduced with possible side effects on surface chemistry or product formation.

Fundamental methodical approaches that could be helpful in future mechanistic investigation are presented in chapter four and five. As shown in the context of chapter three, isotope fractionation studies can provide important mechanistic information such as about the number of bonds broken in the first rate-determining step of a reaction. In the future, isotope fractionation may therefore gain in importance for mechanistic studies in environmental chemistry. However, as prerequisite for such investigations, experimental fractionation data must be correctly evaluated. A critical evaluation of the commonly applied Rayleigh equation in chapter four discusses the nature of statistical artifacts in current evaluation procedures, and presents an evaluation scheme by which they
can be avoided in future investigations.

Chapter five gives an outlook on future studies of a different kind. There, the use of conveniently designed model compounds is suggested for the investigation of surface reactions and detection of intermediates. A new generation of probe compounds was synthesized that contain a reactive –CCl$_3$ group and a double bond as intramolecular trap for radicals and carbenes. In contrast to previous similar molecules, these compounds have higher water solubilities and a low probability of side reactions. In addition they can be attached to an ionic group (“anchor group”) that ensures binding at surfaces of mineral oxides so that the probe is attached in direct proximity of reactive sites. The following properties make these compounds especially attractive:

1) By the choice of the anchor group (strong / weak surface-binding), the residence time of the probe molecule at the surface can be adjusted.

2) The probe compound carries an internal radical clock. This means as soon as a radical is formed, it will react with a certain half-life in an intramolecular cyclization reaction.

An interesting example application is the following mechanistic study:

From chapter 3 and 4 it can be expected that the rate limiting transfer of a first electron to the –CCl$_3$ group leads to formation of a –CCl$_2^-$ radical. In addition, evidence from chapter 3 points to competing follow-up reactions of this radical, either to chloroform (e.g. in reactions with organic matter) or by stabilization in surface complexes. It is not known, however, whether such reactions take place in direct proximity to the surface or involve a diffusion of radicals away into solution, as suggested by Figure 3-11. An interesting case for CCl$_4$ would be the situation where reactions at the surface lead preferentially to non-toxic compounds, whereas in solution hydrogenolysis products are formed.

The new probe molecules offer the possibility to investigate both cases separately. No matter where the reaction takes place, the lifetime of radicals is indicated by the intramolecular cyclization reaction (“radical clock”). Depending on the anchor group and residence time at the surface, however, the yields of products formed in reactions with solution and/or surface components can vary.
considerably. Even formation of carbenes will be detected, as these intermediates also react in a cyclization reaction. By investigating the product formation with different anchor groups and, correspondingly, at different surface-residence times, valuable insight may thus be gained.

The full potential for applications of these probe molecules cannot be fully assessed yet. First experiments with Cr(II) in homogeneous solution are currently being evaluated. Further experiments are planned, where the functionality of the probe compounds shall be demonstrated in the reaction with goethite/Fe(II), with the aim to obtain new mechanistic insight, as discussed above. It will be tested whether it is possible to observe reactions of the surface-bound organic molecules by Attenuated Total Reflectance – Infrared (ATR-IR) spectroscopy.

In summary, the results of this study are important from a mechanistic as well as from a practical point of view. They allow qualitative estimates for the relative reactivity of Fe(II) bound at the surface of different minerals. New mechanistic insight for the reaction of CCl₄ by goethite/Fe(II) was obtained that helps understanding the formation or harmful and benign dehalogenation products in this reaction. Finally, two methodical approaches in this thesis, comparative fractionation studies and the synthesis of specific probe molecules, may be helpful in future mechanistic investigations.


Appendix 1
(Supporting Information of Chapter 2)
Figure A1-1. X-ray diffractograms of (a) mackinawite (Mw) and (b) sulphate green rust (SO4-GR) before and after suspension for one month, as well as (c) magnetite (Ma) and (d) pyrite (Py).
<table>
<thead>
<tr>
<th>Minerals</th>
<th>Added Concentrations</th>
<th>Measured Concentrations</th>
<th>Calculated Concentrations</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe(II) (mM)</td>
<td>NaOH (mM)</td>
<td>HCl (mM)</td>
<td>MOPS (mM)b</td>
</tr>
<tr>
<td>Siderite</td>
<td>1.00</td>
<td>0.30</td>
<td>1.00</td>
<td>4.00</td>
</tr>
<tr>
<td>Mackinawite</td>
<td>1.25</td>
<td>0.20</td>
<td>0.86</td>
<td>1.00</td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.00</td>
<td>1.80</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Goethite</td>
<td>1.24</td>
<td>0.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>1.14</td>
<td>0.38</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>1.04</td>
<td>0.12</td>
<td>0.02</td>
<td>0.40</td>
</tr>
<tr>
<td>Green Rust</td>
<td>1.00</td>
<td>0.10</td>
<td>10.00</td>
<td></td>
</tr>
<tr>
<td>Green Rust + MOPS</td>
<td>1.00</td>
<td>0.10</td>
<td>10.00</td>
<td></td>
</tr>
<tr>
<td>No mineral</td>
<td>1.00</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nontronite</td>
<td>1.09</td>
<td>0.04</td>
<td>0.08</td>
<td>0.80</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.96</td>
<td>0.04</td>
<td>0.08</td>
<td>1.20</td>
</tr>
</tbody>
</table>

a Reported values for surface-hydroxyl groups Fe(III)-OH (possible sorption sites for Fe(II)), adapted from Pecher et al. (1).

b Added MOPS (pH 7.2) consisted of 50% neutral molecules and 50% anionic species.

c Negative values indicate release of Fe(II) from mineral into solution.
A1.1 Estimate of Mass Transfer Coefficients for Transformation Experiments in Mineral Suspensions

As pointed out by Arnold et al. (2) surface catalyzed reactions may sometimes be mass transfer limited, even though the reaction rate is found to be insensitive to mixing speed. The overall reaction rate constant can then be represented by a system of resistances in series:

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{a} \left[ \frac{1}{k_L} + \frac{1}{k_{(\text{SA-geom})}} \right]
\]

where \( k_{\text{obs}} \) is the observed rate constant, \( k_L \) is the mass transfer coefficient (ms\(^{-1}\)), \( a \) is the ratio of external (geometric) particle surface area to volume of solution (m\(^{-1}\)) and \( k_{(\text{SA-geom})} \) is the intrinsic rate constant of the reaction normalized to external (geometric) surface area rather than the BET specific surface area. By calculating the contribution of \( a \cdot k_L \) and comparing it to the observed pseudo first order rate constant \( k_{\text{obs}} \) one can therefore evaluate the influence of mass transfer. If \( a \cdot k_L >> k_{\text{obs}} \), mass transfer has no influence on the observed reaction rate, if \( a \cdot k_L << k_{\text{obs}} \), mass transfer becomes the bottleneck to reaction.

1) Estimation of the particle diameter \( d_p \) and related quantities

A key parameter for calculation of both, the mass transfer coefficient \( k_L \) as well as the quantity \( a \), is the diameter of the mineral particles, \( d_p \). This quantity was estimated by measuring the terminal settling velocity \( u_t \) of discernible particles and then applying Stoke’s law (applicable because Reynolds numbers were found to be very much smaller than 1 in our systems)

\[
\begin{align*}
\frac{1}{u_t} &= \frac{g \cdot d_p^2 \cdot (\rho_p - \rho)}{18 \cdot \eta} \\
\Rightarrow d_p &= \sqrt{\frac{18 \cdot \eta \cdot u_t}{g \cdot (\rho_p - \rho)}}
\end{align*}
\]

where \( u_t \) is the terminal settling velocity in m\(^{-1}\)s\(^{-1}\), \( g = 9.81 \) m/s\(^2\) is the gravitational constant, \( \rho = 1000 \) kg/m\(^3\) is the density of water, \( \rho_p \) is the particle density in kg/m\(^3\) and \( \eta = 10^{-3} \) Pa*s is the viscosity of water. The corresponding Reynolds number was calculated according to
\[ \text{Re} = \frac{d_p \cdot u_t}{\nu} \]

where \( \nu = 10^{-6} \text{ m}^2/\text{s} \) is the kinematic viscosity of water.

Assuming spherical particles, the external (geometric) surface area in m\(^2\)/g was calculated according to

\[
\text{SA}_{\text{geom}} = \frac{\text{surface}_{\text{particle}}}{\text{volume}_{\text{particle}} \cdot (1000 \rho_p)} = \frac{\pi \cdot d_p^2}{\frac{1}{6} \pi \cdot d_p^3 \cdot (1000 \rho_p)} = \frac{6}{d_p \cdot (1000 \rho_p)}
\]

where \( \rho_p \) is the particle density in kg/m\(^3\). The quantity \( a \) is finally determined as the product of \( \text{SA}_{\text{geom}} \) and the amount of added mineral (in g) per m\(^3\) of solution.

<table>
<thead>
<tr>
<th></th>
<th>FeS</th>
<th>Pyrite</th>
<th>Goethite</th>
<th>Magnetite</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle density (kg/m(^3))</td>
<td>4300</td>
<td>5500</td>
<td>4000</td>
<td>5150</td>
</tr>
<tr>
<td>settling velocity ( u_t ) (m/s) (measured)</td>
<td>(3.3 \times 10^{-4})</td>
<td>(2.0 \times 10^{-3})</td>
<td>(3.3 \times 10^{-4})</td>
<td>(4.0 \times 10^{-4})</td>
</tr>
<tr>
<td>particle diameter ( d_p ) (m)</td>
<td>(1.36 \times 10^{-5})</td>
<td>(2.86 \times 10^{-5})</td>
<td>(1.43 \times 10^{-5})</td>
<td>(1.33 \times 10^{-5})</td>
</tr>
<tr>
<td>Reynolds number (-)</td>
<td>(4.54 \times 10^{-3})</td>
<td>(5.71 \times 10^{-2})</td>
<td>(4.76 \times 10^{-3})</td>
<td>(5.32 \times 10^{-3})</td>
</tr>
<tr>
<td>( \text{SA}_{\text{geom}} ) (m(^2)/g)</td>
<td>(1.02 \times 10^{-1})</td>
<td>(3.82 \times 10^{-2})</td>
<td>(1.05 \times 10^{-1})</td>
<td>(8.76 \times 10^{-2})</td>
</tr>
<tr>
<td>( a ) (m(^{-1}))</td>
<td>(2.46 \times 10^{2})</td>
<td>(1.08 \times 10^{3})</td>
<td>(1.65 \times 10^{2})</td>
<td>(1.72 \times 10^{2})</td>
</tr>
</tbody>
</table>

2) **Estimation of the diffusion coefficient of hexachloroethane and related quantities**

The molar volume of liquid hexachloroethane \( \overline{V}_\text{hexachloroethane} \) was extrapolated from values of the homologous compounds:

<table>
<thead>
<tr>
<th>molar volume (cm(^3)/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \overline{V} ) (1,1,1-trichloroethane)</td>
</tr>
<tr>
<td>( \overline{V} ) (1,1,1,2-tetrachloroethane)</td>
</tr>
<tr>
<td>( \overline{V} ) (1,1,2,2-tetrachloroethane)</td>
</tr>
<tr>
<td>( \overline{V} ) (pentachloroethane)</td>
</tr>
<tr>
<td>( \overline{V} ) (hexachloroethane) (extrapolated)</td>
</tr>
</tbody>
</table>
The diffusivity $D_{\text{hexachloroethane},w}$ of hexachloroethane in water (in m$^2$/s) could then be estimated according to Hayduk and Laudie (3):

$$D_{\text{hexachloroethane},w} = \frac{13.26 \cdot 10^{-9}}{\eta^{1.14} \cdot \sqrt[0.589]{V_{\text{hexachloroethane}}}}$$

where $\eta = 1$ centipoise = 1 mPa*s is the viscosity of water. The Schmidt number $Sc$ was finally calculated as the ratio of kinetic viscosity of water $\nu = 10^{-6}$ m$^2$/s and the diffusion coefficient $D_{\text{hexachloroethane},w}$ in m$^2$/s.

<table>
<thead>
<tr>
<th>$D_{\text{hexachloroethane},w}$ (m$^2$/s)</th>
<th>$7.4 \times 10^{-10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schmidt number $Sc$ (-)</td>
<td>1360</td>
</tr>
</tbody>
</table>

3) Calculation of the transfer coefficient $k_L$

Harriott (4) used a previously established relationship of Ranz and Marshall (5) for the Sherwood number to calculate a minimum value $k_{*L}$ of the mass transfer coefficient representing solid-fluid transfer for a particle falling at its terminal velocity:

$$Sh^{*} = \frac{k_{*L} \cdot d_p}{D_{\text{hexachloroethane},w}} = 2 + 0.6 \cdot \text{Re}^{1/2} \cdot \text{Sc}^{1/3}$$

$$<==> k_{*L} = \frac{(2 + 0.6 \cdot \text{Re}^{1/2} \cdot \text{Sc}^{1/3}) \cdot D_{\text{hexachloroethane},w}}{d_p}$$

The actual mass transfer coefficient $k_L$ was assumed to be 1.5 times greater than $k_{*L}$: $k_L = 1.5 \cdot k_{*L}$. This leads to the following values

<table>
<thead>
<tr>
<th></th>
<th>FeS</th>
<th>Pyrite</th>
<th>Goethite</th>
<th>Magnetite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{*L}$ (m/s)</td>
<td>$1.32 \times 10^{-4}$</td>
<td>$9.25 \times 10^{-5}$</td>
<td>$1.27 \times 10^{-4}$</td>
<td>$1.37 \times 10^{-4}$</td>
</tr>
<tr>
<td>$a \cdot k_L$ (h$^{-1}$)</td>
<td>176</td>
<td>542</td>
<td>113</td>
<td>130</td>
</tr>
</tbody>
</table>

It should be noted, however, that the calculated particle diameters are upper estimates, because the mineral suspensions were composed of a continuum of particle sizes and contained fractions with visibly lower settling velocities. Estimates from pore size distributions measured in adsorption experiments with liquid nitrogen are rather in the range of $2 \times 10^{-7} - 2 \times 10^{-6}$ m.. If these lower
estimates are used to compute $a_kL$, the following values are obtained

<table>
<thead>
<tr>
<th></th>
<th>FeS</th>
<th>Pyrite</th>
<th>Goethite</th>
<th>Magnetite</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle diameter $d_p$ (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>from liquid N$_2$ adsorption</td>
<td>2.0 $10^{-7}$</td>
<td>6.0 $10^{-6}$</td>
<td>8.0 $10^{-7}$</td>
<td>2.5 $10^{-6}$</td>
</tr>
<tr>
<td>$a$ (m$^{-1}$)</td>
<td>1.7 $10^4$</td>
<td>5.2 $10^3$</td>
<td>2.9 $10^3$</td>
<td>3.0 $10^4$</td>
</tr>
<tr>
<td>$k*L$ (m/s)</td>
<td>7.4 $10^{-3}$</td>
<td>2.6 $10^{-3}$</td>
<td>1.8 $10^{-3}$</td>
<td>6.0 $10^{-4}$</td>
</tr>
<tr>
<td>$a_kL$ (h$^{-1}$)</td>
<td>6.6 $10^5$</td>
<td>7.4 $10^4$</td>
<td>2.9 $10^4$</td>
<td>3.0 $10^4$</td>
</tr>
</tbody>
</table>

As can be seen by a comparison of $a_kL$ and $k_{obs}$ in Table 2-1 of the paper section, upper estimates for $a_kL$ exceed observed rate constants by at least two orders of magnitude and would thus rule out an influence of mass transfer. Lower estimates, however, show that mass transfer may become partially important in the case of iron sulfide (100%), goethite (40%) and magnetite (30%). The reaction of 4-chloronitrobenzene can thus be expected to be partly mass-transfer-limited for large particles (about $2*10^{-5}$ m), whereas it should occur unrestricted for smaller particles ($2*10^{-7}$-$2*10^{-6}$ m). Reactions of hexachloroethane were not subject to mass transfer limitations.

A1.2 Effect of compound concentrations on $k_{obs}$

Competition between substrates for a restricted number of surface sites may pose a limit to reactivity in heterogeneous catalysis. To evaluate whether such limitation played a role in our experiments, the effect of elevated concentrations of 4-chloronitrobenzene was investigated in experiments with pyrite/Fe(II) and lepidocrocite/Fe(II). In experiments with pyrite/Fe(II) no accumulation of 4-chlorophenyl hydroxylamine was observed and pseudo-first-order rate constants decreased sharply between 1 and 5 µM initial concentration corresponding to $0.04 - 0.2$ µmol/m$^2$ at a surface area of 25 m$^2$/L (Figure A1-2a). Considering that six electrons are necessary for complete reduction of the nitro group and assuming that each site contributes one electron, the concentration of highly reactive sites at the surface could thus be estimated to about $0.24 - 1.2$ µmol/m$^2$ or $6 - 30$ µmol/L. In the case of lepidocrocite/Fe(II) a similar decrease in reactivity was found between 12 and 18 µM initial substrate concentration.
(Figure A1-2b). Here, accumulation of the intermediate 4-chlorophenyl hydroxylamine was observed and was found to have a weak inhibitory effect on the reaction of 4-chloronitrobenzene. For both mineral systems reactive sites were thus present in excess to the substrate concentrations chosen (1 µM) so that surface competition was not likely to play a role in this study. However, our results indicate that higher substrate concentrations (5-10 µM at 25 m²/L mineral surface concentrations) may result into depletion of reactive sites, and reaction rates for natural, low contaminant conditions may then be underestimated in such laboratory experiments.

**Figure A1-2.** Competitive effects on the surface: observed pseudo-first-order rate constants versus initial substrate concentrations; a) reaction of 4-chloronitrobenzene with pyrite/Fe(II); b) reaction of 4-chloronitrobenzene with lepidocrocite c) reaction of 0.6 µM 4-chloronitrobenzene with goethite/Fe(II) in the presence of varied concentrations of hexachloroethane.
Figure A1-3. Correlation between logarithmic rate constants: 4-chloronitrobenzene and hexachloroethane (left), b) 4-chlorophenyl hydroxylamine and hexachloroethane (right).

References


Appendix 2

Observed Products in the Reductive Dehalogenation of CCl₄ with Various Abiotic Model Reductants (Overview)
Table A2-1. Product formation in the reductive dehalogenation of CCl₄ with a

<table>
<thead>
<tr>
<th>Reductands</th>
<th>CHCl₃</th>
<th>CH₂Cl₂</th>
<th>CH₃Cl</th>
<th>CH₄</th>
<th>CO₂</th>
<th>HCOO⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25%</td>
</tr>
<tr>
<td>Zn</td>
<td>(x)</td>
<td>(x)</td>
<td>(x)</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Sn</td>
<td>x</td>
<td>(x)</td>
<td>(x)</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>electrolytic reduction at Ag cathode</td>
<td>x</td>
<td>(x)</td>
<td>(x)</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Fe(0)</td>
<td>(x)</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(0)</td>
<td>40%</td>
<td>(x)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biotite &amp; HS⁻</td>
<td>5-15%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>81-86%</td>
</tr>
<tr>
<td>FeS₂, oxic</td>
<td>5-6%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>55%</td>
</tr>
<tr>
<td>FeS₂, anoxic</td>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5%</td>
</tr>
<tr>
<td>FeS₂, fresh</td>
<td>50%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5%</td>
</tr>
<tr>
<td>Freshly Precipitated FeS</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green Rust (GR)</td>
<td>90%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10%</td>
</tr>
<tr>
<td>Green Rust (GR)</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td>47%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8%</td>
</tr>
<tr>
<td>Fe(II) on Goethite</td>
<td>83-90%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(II) on Iron Oxides</td>
<td>20-25%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Aquocobalamin &amp; Ti(III)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Aquocobalamin &amp; Cysteine &amp; Na₂S</td>
<td>(x)</td>
<td></td>
<td></td>
<td>10%</td>
<td></td>
<td>8%</td>
</tr>
<tr>
<td>Cobalamin(II) &amp; 50 mM Dithiothreitol</td>
<td>(x)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Cobalamin &amp; Cysteine</td>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co Porphyrins</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni / Co -Porhyrins &amp; Dithiothreitol</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Michrosomal Cytochrome P-450</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50%</td>
</tr>
<tr>
<td>Hematin,Sulfide/Cysteine</td>
<td>x</td>
<td>(x)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe Porphyrin &amp; Cysteine</td>
<td>&lt;1%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cysteine</td>
<td>50%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>*</td>
</tr>
</tbody>
</table>
A variety of model chemical reductants.

<table>
<thead>
<tr>
<th>CO</th>
<th>CS₂</th>
<th>Remarks</th>
<th>Authors</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>75%</td>
<td></td>
<td>in DMF / water</td>
<td>Castro &amp; Kray 1966</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cridge &amp; McCarty 1991</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Matheson &amp; Tratnyek 1994</td>
<td>[18]</td>
</tr>
<tr>
<td>1-2%</td>
<td></td>
<td>mass balance not complete</td>
<td>Helland et al. 1995</td>
<td>[11]</td>
</tr>
<tr>
<td>15%</td>
<td></td>
<td>mass balance not complete, mass balance completed</td>
<td>Kriegman-King &amp; Reinhard 1992</td>
<td>[14]</td>
</tr>
<tr>
<td>20%</td>
<td></td>
<td>mass balance not complete, mass balance completed</td>
<td>Kriegman-King &amp; Reinhard 1994</td>
<td>[13]</td>
</tr>
<tr>
<td>2%</td>
<td></td>
<td>mass balance not complete, mass balance completed</td>
<td>Kriegman-King &amp; Reinhard 1994</td>
<td>[13]</td>
</tr>
<tr>
<td>x</td>
<td></td>
<td>mass balance not complete, CHCl₃/CS₂ ratio 2:1</td>
<td>Devlin 1999</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mass balance not complete, mass balance completed</td>
<td>O'Loughlin &amp; Burris 2000</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₅Cl₆, C₂Cl₄, very high substrate concentrations</td>
<td>Erbs &amp; Hansen 1999</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45% non-identified, completely dehalogenated</td>
<td>McCormick et al. 2000</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>yield of chloroform depends on mineral, pH, Fe(II)</td>
<td>Amonette et al. 2001</td>
<td>[2]</td>
</tr>
<tr>
<td>x</td>
<td></td>
<td>nonvolatile products</td>
<td>Krone et al. 1989 &amp; 1991</td>
<td>[15, 16]</td>
</tr>
<tr>
<td>15%</td>
<td></td>
<td>values after 20h reaction, 50% non volatile products</td>
<td>Stromeyer, 1992</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mass balance not complete</td>
<td>Assaf-Anid et al. 1994</td>
<td>[3]</td>
</tr>
<tr>
<td>3%</td>
<td></td>
<td>water soluble products, chloroform decreases with pH</td>
<td>Chiu &amp; Reinhard 1996</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 70% in aqueous phase</td>
<td>Ukrainczyk et al. 1995</td>
<td>[23]</td>
</tr>
<tr>
<td>x</td>
<td></td>
<td>80% in aqueous phase</td>
<td>Lewis et al. 1995</td>
<td>[17]</td>
</tr>
<tr>
<td>2.4%</td>
<td></td>
<td>lipid bound and protein bound products</td>
<td>Ahr et al. 1980</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>incomplete mass balance</td>
<td>Klecka &amp; Gonsior 1984</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* ≈ 100% N-formyl-cysteine</td>
<td>Buschmann et al. 1999</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* ≈ 50% N-formyl-cysteine</td>
<td>Buschmann et al. 1999</td>
<td>[5]</td>
</tr>
</tbody>
</table>
Figure A2-1. Competing reactions in the reductive dehalogenation of CCl₄: hydrogenolysis versus rapid mineralization in transformations with different chemical reductants (Summary of Table A2-1).

References


Dehalogenation of CCl₄ with Various Reductants


Appendix 3
(Supporting Information of Chapter 3)
A 3.1 Buffer capacity in goethite/Fe(II) suspensions

In the dehalogenation experiments addition of organic and inorganic buffers (such as 4-morpholinopropanesulfonic acid (MOPS) or 1,4-piperizine bis(ethanesulfonic)acid (PIPES)) was avoided to minimize the presence of H-donors and precipitates of Fe(II) or surface complexes of buffers. An experimental setup was used that relied solely on the intrinsic buffer capacity of the mineral surface. Hydroxyl groups at the goethite surface are known to have a rather limited buffer intensity of only about 0.5 µmol m⁻² pH⁻¹ in the pH range from 5 to 8 (2,3). However, specific adsorption of cations has been found to displace additional protons from the mineral surface and modify titration curves towards higher buffer capacities. Previous studies (4-6) were run at low surface loadings at pH ≤ 7.5, the onset for precipitation of Fe(OH)₂ (K = 4.8 10⁻¹⁷, (7)). In this study we characterized buffer capacities in suspensions of goethite/Fe(II)
Supporting Information of Chapter 3  XIX

at high surface loadings and up to pH 8.

### A 3.2 Measurements of buffer intensities

Base titrations (0.1 M NaOH; Titrisol, Merck) were performed in suspensions of 50 m²/L goethite (10 mM NaCl) with a) 1.0 mM Fe(II)ₜₒᵗ and, for comparison, b) without added Fe(II) (see Figure 3-3b). At least 15 minutes equilibration time were allowed after each addition, and several times the system was equilibrated for 16 hours to allow for slow secondary sorption / surface restructuring of Fe(II) as observed in previous studies (8-10). At pH 7 and 8, equilibration was allowed until the pH drift was lower than 0.01 units per 3 h, then the suspension was titrated repeatedly with alternating addition of 0.1 M HCl and 0.1 M NaOH (Titrisol, Merck). Buffer intensities \( \frac{dC}{dpH} \) were determined from the change of pH after addition of base aliquots according to

\[
\frac{dC}{dpH} \approx \frac{\Delta C_{\text{base added}}}{\Delta pH_{\text{measured}}} = \frac{V_{\text{base}} \cdot C_{\text{base}}}{V_{\text{suspension}} \cdot (pH_2 - pH_1)}
\]

where \( V_{\text{base}} \) is the volume of base added, \( C_{\text{base}} \) its concentration, \( V_{\text{suspension}} \) the volume of the mineral suspension and \( pH_2 \) and \( pH_1 \) the pH values before and after base addition, respectively.

Without Fe(II), buffer intensities were of the same magnitude as observed in previous studies, whereas Fe(II) addition increased them enormously (Figure 3-3b). In the presence of 1 mM Fe(II), values for \( \frac{dC}{dpH} \) ranged from about 3 μmol m⁻² pH⁻¹ (150 μM pH⁻¹) at pH 5 to 6-8 μmol m⁻² pH⁻¹ (300-400 μM pH⁻¹) at pH 7. This reflects the fact that at higher pH, more Fe(II) is sorbed to the surface of goethite. Unlike in the study of Zhang et al. (5), however, sufficient Fe(II) was present in solution to allow for additional sorption after increasing the pH to 8, and no rapid consumption of base could be observed that would be indicative of a sudden precipitation of Fe(OH)₂. Evidence, however, was found for a slow secondary sorption process following the initial rapid sorption of Fe(II), as reported from previous investigations (8-10): long equilibration intervals of 16-24 h led to a decrease in pH after which less protons were liberated per base addition. We therefore relied on the buffer intensity obtained...
by alternating titration after long equilibration times (5-6 µmol m\(^{-2}\) pH\(^{-1}\) or 250-300 µM pH\(^{-1}\), see solid circles in Figure 3-3b) to calculate how much the pH would change on average, if 50 µM CCl\(_4\) reacted completely in our experimental system. Calculations were based on hydrogenolysis (1) or dihaloelimination (2a and 2b) as possible reaction pathways:

\[
\begin{align*}
\text{CCl}_4 + 2 \equiv \text{Fe(II)-OH} & \rightarrow \text{CHCl}_3 + 2 \equiv \text{Fe(III)-O}^- + \text{H}^+ + \text{Cl}^- \quad (1) \\
\text{CCl}_4 + 2 \equiv \text{Fe(II)-OH} + \text{H}_2\text{O} & \rightarrow \text{CO} + 2 \equiv \text{Fe(III)-O}^- + 4 \text{H}^+ + 2 \text{Cl}^- \quad (2a) \\
\text{CCl}_4 + 2 \equiv \text{Fe(II)-OH} + \text{H}_2\text{O} & \rightarrow \text{HCOO}^- + 2 \equiv \text{Fe(III)-O}^- + 5 \text{H}^+ + 2 \text{Cl}^- \quad (2b)
\end{align*}
\]

Hence, for example, when using these reaction stoichiometries and assuming a production of 50% chloroform and 50% formate, 150 µM protons are calculated to be produced per turnover of 50 µM CCl\(_4\). At a buffer intensity of 250-300 µM pH\(^{-1}\) this would correspond to a pH drift of about 0.5 pH units in our experimental system. It should be noted that this approach is somewhat problematic, because the buffer capacity is provided by the very same \equiv \text{Fe(II)-OH} surface complexes that comprise the reactive species. Thus, a desorption of ferrous iron which buffers the pH will also lead to a decrease in reactivity with CCl\(_4\). However, this effect should be limited by the fact that total \equiv \text{Fe(II)} surface species were present in large excess compared to those that desorb because of a pH increase during reaction.

A 3.3 Dependence of Fe(II) sorption on mineral loading

For comparison between different studies, sorption isotherms are often normalized to the specific surface area as determined in BET measurements. (For an overview about sorption of Fe(II) on goethite see e.g. Mettler (10)). Amonette et al. (11) recently challenged the underlying assumption that sorption increases linearly with mineral concentration. They found that only about four times more Fe(II) was sorbed to the surface of goethite at ten times higher
Supporting Information of Chapter 3

mineral concentrations (55 vs. 550 m²/L, pH 7), corresponding to a decrease of 60% in sorption per unit surface. They postulated that coagulation of the particles took place, thus rendering parts of the surface to be no longer accessible for sorption of Fe(II). In our system we measured sorption isotherms at pH 7 for mineral concentrations varying by a factor of eight (12.5 m²/L, 25 m²/L, 50 m²/L and 100 m²/L, see Figure 3-3a). Within this range, sorption density differed by about 30%, which is considerably less than found by Amonette et al.. Sorption capacities at 50 m²/L were comparable in both studies (about 6-8 µmol m⁻²), despite goethite minerals from different sources and with different specific surface areas. We suggest that for comparability, results can be surface normalized, but that the total surface present in solution should always be indicated, as it may have an influence on coagulation and, therefore, on the accessible surface area.

Our data could not be fit satisfactorily by Langmuir isotherms. An increased sorption at higher Fe(II) concentrations was observed that may be indicative for a transition from surface complexation of Fe(II) to surface precipitation as postulated and modelled by Pecher et al. (8) according to the theory of Dzombak and Morel (12). The maximum sorption capacity of 7-12 µmol/m² (or 4.2-7.2 sites/nm²) which can be extracted from Figure 3-3a is therefore likely to be an overestimate. Previous studies reported values of 3.1 sites/nm² (surface precipitation model, (8)), 2.9 sites/nm² (10), 2.8 sites/nm² (13), 2.7 sites/nm² (14) and 1.6-3.6 sites/nm² (11).

A 3.4 Characterization of Fe(II) surface complexes and discussion of possible reactive species

Information on predominant surface complexes of Fe(II) can be derived from the number of protons that are liberated per Fe²⁺ sorbing to the surface. One proton is released in the formation of a charged mononuclear complex (S-OH + Fe²⁺ → S-Fe(II)²⁺ + H⁺), whereas two protons are produced from either a binuclear complex (2 S-OH + Fe²⁺ → (S-O)₂Fe(II)²⁺ + 2 H⁺) or an uncharged mononuclear complex (S-OH + Fe²⁺ + H₂O → S-Fe(II)OH + 2 H⁺), where S-OH denote surface hydroxyl groups. Application of surface
complexation models in previous adsorption studies suggested the formation of uncharged mononuclear S-OFe(II)OH complexes at iron oxide surfaces (6,13,15). This evidence, however, could not be backed up with measurements of proton release, because such studies were conducted at high concentrations of added buffers. In our approach without using added buffers we measured sorption isotherms at pH 7 by adding aliquots of Fe(II), adjusting the pH with NaOH and equilibrating for 72 hours (Figure 3-3a). We could thus measure “proton release isotherms” directly, by the drop in pH that followed addition of Fe(II), and with the previously determined buffer intensity of our suspensions (see Figure 3-3b). As can be seen from Figure 3-3a, sorption of one Fe(II) ion was found to produce two H⁺(aq) ions, evidence for either a binuclear complex (S-O)₂Fe(II) or an uncharged mononuclear complex (S-OFe(II)OH). The large release of up to 14 protons per nm² in our study, however, compares to reported values of 11 -14 (13,16) sites per nm² for total S-OH concentrations at the goethite surface. As it is most unlikely that this reservoir was already depleted at pH 7, the formation of binuclear complexes (S-O)₂Fe(II) is rather unlikely.

**Figure A3-2. Reaction of CO to formate in suspensions with 50 m²/L goethite in presence of 1 mM Fe(II), with a headspace of pure CO, corresponding to a saturation concentration of about 1 mM.**
Thermodynamic and Kinetic Data about the Reaction of CO und OH- to Formate

Kinetic Data (17)

\[
\frac{d[HCOO^-]}{dt} = k_3 \cdot [OH^-]_{aq} \cdot [CO]_{aq}
\]

\[ k_3 \approx 8 \cdot 10^{-4} \text{ s}^{-1} \text{ M}^{-1} \]

Pseudo first-order rate constant for \([OH^-] = 10^{-7} \) :

\[ k_{pseud 1.ord.} = 8 \cdot 10^{-4} \cdot 10^{-7} = 8 \cdot 10^{-11} \text{ s}^{-1} \]

Thermodynamic Data

\[ \text{CO(aq)} + \text{OH}^- (aq) = \text{HCOO}^- (aq) \]

\[ \Delta G_r^\circ = -73.9 \text{ kJ/mol} \]

\[ \ln K \approx 30 \]

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta G_r^\circ ) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOO(^\text{aq})</td>
<td>-351.04</td>
</tr>
<tr>
<td>CO(^\text{g})</td>
<td>-137.17</td>
</tr>
<tr>
<td>CO(^\text{aq})</td>
<td>-119.9</td>
</tr>
<tr>
<td>OH(^-\text{aq})</td>
<td>-157.24</td>
</tr>
</tbody>
</table>

\[ \Delta G_r^\circ (aq) = \Delta G_r^\circ (g) + RT \ln K_{H}[\text{atm/M}] \]

Henry coefficient of CO

0.00095 (mol/kg*bar)

0.00094 (mol/kg*atm) \( \approx 0.00094 \text{ (M/atm)} = 1064 \text{ (atm/M)} \)

\[ 0.08206 \text{ [atm/K} \cdot \text{M]} \cdot 298.15 \text{ [K]} = 43 \]

Water solubility of CO (20)

\[ x(aq) = \frac{n(aq)}{n(aq) + n(g)} = 1.7744 \cdot 10^{-5} \]
Figure A3-3. Changes in concentration and isotopic signature of CCl₄ during reduction by iron(II) porphyrin (a) and polysulfide (c) as well as corresponding evaluation of ε according to the Rayleigh-equation (b/d).

References


Appendix 4
Mathematical Derivations Related to the Rayleigh Equation
(Supporting Information of Chapter 4)
A4.1 Correct Derivation of Equation (4-19) for Case B in Chapter 4 (CCl₃-CH₃)

A combination of equations (4-13), (4-14), (4-17) and (4-18) gives

\[
\frac{d^{13}C_{\text{average over molecule}}}{d^{12}C_{\text{average over molecule}}} \approx \frac{1}{2} \cdot \frac{k_{H,\text{primary}}}{k_L} \cdot \frac{[^{13}\text{CCl}_3-^{12}\text{CH}_3]}{[^{12}\text{CCl}_3-^{12}\text{CH}_3]} + \frac{1}{2} \cdot R_0 \quad (A4-1)
\]

Equation (4-12), on the other hand, can be written in the form

\[
2 \cdot R \approx \frac{[^{13}\text{CCl}_3-^{12}\text{CH}_3]}{[^{12}\text{CCl}_3-^{12}\text{CH}_3]} + \frac{[^{12}\text{CCl}_3-^{13}\text{CH}_3]}{[^{12}\text{CCl}_3-^{12}\text{CH}_3]} \quad (A4-2)
\]

and, after introduction of (4-18),

\[
\frac{[^{13}\text{CCl}_3-^{12}\text{CH}_3]}{[^{12}\text{CCl}_3-^{12}\text{CH}_3]} \approx 2 \cdot R - \frac{[^{12}\text{CCl}_3-^{13}\text{CH}_3]}{[^{12}\text{CCl}_3-^{12}\text{CH}_3]} \approx 2 \cdot R - R_0 \quad (A4-3)
\]

Substitution of (A4-3) into (A4-1) gives (where \( R = ^{13}\text{C}/^{12}\text{C} \), and “\( d^{13}C \)” is short for “\( d^{13}C_{\text{average over molecule}} \)”)

\[
\frac{d^{13}C_{\text{average over molecule}}}{d^{12}C_{\text{average over molecule}}} \approx \frac{1}{2} \cdot \frac{k_{H,\text{primary}}}{k_L} \cdot \left(2 \cdot \frac{^{13}C}{^{12}C} - R_0\right) + \frac{1}{2} \cdot R_0 \quad (A4-4)
\]

\[
\frac{d^{13}C}{d^{12}C} \approx \frac{k_{H,\text{primary}}}{k_L} \cdot \frac{^{13}C}{^{12}C} + \frac{1}{2} \cdot R_0 \cdot \left(1 - \frac{k_{H,\text{primary}}}{k_L}\right) \quad (A4-5)
\]
The general solution of this first-order inhomogeneous differential equation is

\[
\frac{d^{13}C}{d^{12}C} - \frac{k_{H,\text{primary}}}{k_L} \cdot \frac{^{13}C}{^{12}C} = \frac{1}{2} \cdot R_0 \cdot \left(1 - \frac{k_{H,\text{primary}}}{k_L}\right)
\]  
(A4-6)

where \(\kappa\) is an arbitrary constant introduced by integration. Division by \(^{12}C\) gives

\[
^{13}C = \kappa \cdot ^{12}C \cdot \frac{k_L}{k_{H,\text{primary}}} + \frac{1}{2} \cdot R_0 \cdot ^{12}C
\]  
(A4-7)

This can be expressed for \(t = 0\):

\[
R_0 - \frac{1}{2} R_0 = \kappa \cdot ^{12}C \left(\frac{k_{H,\text{primary}}}{k_L} - 1\right)
\]  
(A4-10)
Division of the two equations gives

\[
\frac{R - \frac{1}{2} R_0}{\frac{1}{2} R_0} = \left( \frac{^{12}C}{^{12}C_0} \right) \left( \frac{k_{H,\text{primary}}}{k_L} - 1 \right)
\]  

(A4-11)

or

\[
\frac{2R - R_0}{R_0} = \frac{R_0 + 2(R - R_0)}{R_0} = \left( \frac{^{12}C}{^{12}C_0} \right) \left( \frac{k_{H,\text{primary}}}{k_L} - 1 \right)
\]

(A4-12)
A4.2 The Physical Meaning of Epsilon Values Determined by an Inappropriate Application of the Rayleigh Equation in Case B in Chapter 4 (CCl₃-CH₃)

As shown in chapter 4, the physical meaning of isotope ratios determined as average over the whole molecule of CCl₃-CH₃ is given by equation (4-12), and the meaning of relative changes in isotope concentrations is described by equation (4-13) in combination with (4-14) and (4-15):

\[
\frac{^{13}C}{^{12}C} \approx \frac{1}{2} \left( \frac{[^{13}CCl_3-^{12}CH_3]}{[^{12}CCl_3-^{12}CH_3]} + \frac{[^{12}CCl_3-^{13}CH_3]}{[^{12}CCl_3-^{12}CH_3]} \right) \tag{4-12}
\]

\[
\frac{d^{13}C}{d^{12}C} \approx \frac{1}{2} \left( \frac{k_{H,primary}}{k_L} \cdot \frac{[^{13}CCl_3-^{12}CH_3]}{[^{12}CCl_3-^{12}CH_3]} + \frac{k_{H,secondary}}{k_L} \cdot \frac{[^{12}CCl_3-^{13}CH_3]}{[^{12}CCl_3-^{12}CH_3]} \right) \tag{4-13}
\]

Setting

\[
\frac{[^{13}CCl_3-^{12}CH_3]}{[^{12}CCl_3-^{12}CH_3]} = x \quad \text{and} \quad \frac{[^{12}CCl_3-^{13}CH_3]}{[^{12}CCl_3-^{12}CH_3]} = y
\]

this can be written as

\[
\frac{^{13}C}{^{12}C} \approx \frac{1}{2} \cdot (x + y) \tag{4-12}
\]
and

\[ \frac{d^{13}C}{d^{12}C} \approx \frac{1}{2} \left( \frac{k_{H,\text{primary}}}{k_L} \cdot x + \frac{k_{H,\text{secondary}}}{k_L} \cdot y \right) \tag{4-13} \]

Division of (4-13) by (4-12) gives

\[ \frac{d\ln^{13}C}{d\ln^{12}C} \approx \left( \frac{k_{H,\text{primary}}}{k_L} \cdot x + \frac{k_{H,\text{secondary}}}{k_L} \cdot y \right) \frac{x + y}{x + y} \tag{A4-13} \]

and, with

\[ \left( \frac{k_{H,\text{primary}}}{k_L} \cdot x + \frac{k_{H,\text{secondary}}}{k_L} \cdot y \right) \frac{x + y}{x + y} = \beta, \]

\[ ^{13}C = \kappa \cdot \left( ^{12}C \right)^{\beta} \tag{A4-13} \]

where \( \kappa \) is an arbitrary integration constant. Division by \(^{12}C\) gives

\[ \frac{^{13}C}{^{12}C} = R = \kappa \cdot \left( ^{12}C \right)^{\beta} - 1 \tag{A4-14} \]
or, for \( t = 0 \)

\[
R_0 = \kappa \cdot \left( \frac{^{12}C}{C_0} \right) \beta - 1
\]

(A4-15)

Division of (A4-14) by (A4-15) finally leads to

\[
\frac{R}{R_0} = \left( \frac{^{12}C}{^{12}C_0} \right) \beta - 1
\]

(A4-16)

which corresponds to the expression that is obtained by the way the Rayleigh equation is commonly applied in such cases.

The value

\[
\varepsilon = \beta - 1 = \left( \frac{k_{H,\text{primary}}}{k_L} \cdot x + \frac{k_{H,\text{secondary}}}{k_L} \cdot y \right) \frac{x + y}{x + y} - 1
\]

(A4-17)

is thus obtained, which does not have the physical meaning of an enrichment factor!
Calculation of Rate Constants for An Unwanted β-Elimination of HX from Model Compounds

Synthesis of Probe Compounds

(Supporting Information of Chapter 5)
Calculation of Rate Constants for an Unwanted $\beta$-Elimination of HX from $X_3C$-$\text{CH}_2$-$\text{CHOH}$-$\text{CH}_2$-$\text{CH}_2$-$\text{CH}$=$\text{CH}_2$ ($X = \text{Cl, Br}$) using Taft Relationships Reported in Roberts et al. [2]

Relationships reported by Roberts et al.:

**Chlorinated substrates**

\[
\log_{10}(k_{\text{OH}^-}) = -10.73 (\pm 2.64) + 8.76 (\pm 2.87) \sum \sigma_1 \quad (A5-1)
\]

\[
\log_{10}(k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]) = -9.62 (\pm 2.94) - 0.02 (\pm 3.02) \sum \sigma_1 \quad (A5-2)
\]

**Brominated substrates**

\[
\log_{10}(k_{\text{OH}^-}) = -9.77 (\pm 1.13) + 8.82 (\pm 1.70) \sum \sigma_1 \quad (A5-3)
\]

\[
\log_{10}(k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]) = -7.42 (\pm 1.41) - 2.96 (\pm 2.09) \sum \sigma_1 \quad (A5-4)
\]

$\sigma_1$-values from Roberts et al. and Hine [1], p. 98:

$\sigma_1 = 0.17$ for $-\text{CH}_2\text{Cl}$, $0.10$ for $-\text{CH}_2\text{OH}$, and $0.163$ for $-\text{CH}_2\text{Br}$

For $\text{Cl}_3\text{C}$-$\text{CH}_2$-$\text{CHOH}$-$\text{CH}_2$-$\text{CH}_2$-$\text{CH}$=$\text{CH}_2$, this results in calculated rate constants for base catalysis and neutral reaction of $\log_{10}(k_{\text{OH}^-}) = -5.4$ and $\log_{10}(k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]) = -9.6$, respectively. At pH 7, this corresponds to half-lives of 7.4 $10^5$ and 128 years.

For $\text{Br}_3\text{C}$-$\text{CH}_2$-$\text{CHOH}$-$\text{CH}_2$-$\text{CH}_2$-$\text{CH}$=$\text{CH}_2$ the values are $\log_{10}(k_{\text{OH}^-}) = -4.6$ and $\log_{10}(k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]) = -9.1$, respectively, indicating half-lives at pH 7 of 1.1 $10^5$ and 44 years.


Synthesis of Probe Compounds Described in Chapter 5

Probe molecules of type A (small charged reactivity probes) were synthesized from trichloroacetic acid and trichloroethanol, respectively. Molecules of the type B were obtained by reaction of hexen-6-epoxide with trichloromethylolithium at low temperature and in the presence of boron trifluoride. A different approach, where introduction of the hydroxyl group was attempted by nucleophilic substitution of a bromine substituent by OH\(^-\), was not successful, indicating that the probe molecule is very inert towards S\(\text{N}_2\) reactions.

A) Small charged reactivity probes

**Trimethyl-(2,2,2-trichloroethyl)-ammonium chloride**

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2^- & \quad \text{HN(CH}_3\text{)}_2
\end{align*}
\]

\[
\begin{align*}
3.4 \text{ ppm} & \\
4.9 \text{ ppm}
\end{align*}
\]

**Dimethyl-(2,2,2-trichloroethyl)-amine**


5.119 g (50 mmole) N\(_2\)N\(_2\)N\(_2\)'N\(_2\)'-tetramethyl-aminomethane and 26.35 g (165 mmole) trichloroacetic acid were dissolved in 60 mL dioxane and stirred at 38°C for 3 h. After concentration under reduced pressure, the reaction mixture was treated with 50 mL 2 N NaOH followed by extraction with 5 x 20 mL diethylether. The extract was dried over K\(_2\)CO\(_3\). Evaporation of the ether
followed by distillation of the residue under reduced pressure gave the liquid product **dimethyl-(2,2,2-trichloroethyl)-amine**; yield 4.1 g (23 mmole, 46%), b.p. 67°C/20 mmHg, \(^1\)H-NMR (400 MHz in CDCl\(_3\)) \(\delta\): 2.53 (6H, s, CH\(_3\)), 3.39 (2H, s, CH\(_2\)), \(^13\)C-NMR (100 MHz in DMSO) \(\delta\): 46.5 (CH\(_3\)), 75.9 (CH\(_2\))

**Trimethyl-(2,2,2-trichloroethyl)-ammonium chloride**

Lit: Böhme H., Stammberger W.; Arch.Pharmaz. 305, 397-400 (1972)

3.5 g (20 mmole) dimethyl-(2,2,2-trichloroethyl)-amine were mixed with 4.6 mL (32 mmole) methyl iodide and allowed to react for 28 days. 5.08 g of the crystalline product were dissolved in 80 mL of a methanol/water mixture (1:1) and treated on an ion exchange column (90 mL (96.3 meq) Duolite A 147 (Fluka), Cl\(^-\) form). The crude product was recrystallized in methanol to give a white solid **trimethyl-(2,2,2-trichloroethyl)-ammonium chloride**; yield 2.9 g (13 mmole, 56%), \(^1\)H-NMR (400 MHz in CH\(_3\)OH) \(\delta\): 3.52 (9H, s, CH\(_3\)), 4.87 (2H, s, CH\(_2\)),

\[
\text{C}_3\text{H}_1\text{NCl}_4 \ 	ext{calc.} \ 	ext{C} \ 26.46 \quad \text{H} \ 4.88 \quad \text{N} \ 6.17 \quad \text{Cl} \ 62.48 \quad \text{I} \ 0.00
\]

\[
\text{found} \ 	ext{C} \ 26.64 \quad \text{H} \ 4.76 \quad \text{N} \ 6.10 \quad \text{Cl} \ 62.52 \quad \text{I} \ 0.00
\]

**Sodium 2,2,2-trichloroethyl-sulfate**

\[
\text{py} \cdot \text{SO}_3^+ + \text{Cl}^- \quad \rightarrow \quad \text{py}^+ + \text{Cl}^- \cdot \text{SO}_3^- \quad \rightarrow \quad \text{py}^+ + \text{Cl}^- \cdot \text{SO}_3^- \quad \rightarrow \quad \text{Na}^+ \cdot \text{Cl}^- \cdot \text{SO}_3^- \quad \rightarrow \quad \text{Na}^+ \cdot \text{Cl}^- \cdot \text{SO}_3^- \quad \rightarrow \quad \text{Na}^+ \cdot \text{Cl}^- \cdot \text{SO}_3^- 
\]

1) NaOH, extraction of py with CHCl\(_3\)
2) ion exchange column (Na\(^+\))
3) extraction of product with methanol

**Pyridinium 2,2,2-trichloroethyl-sulfate**

To 110 ml (1.14 mole) 2,2,2-trichloroethanol, 20 g (0.126 mole) of pyridine-sulfur trioxide were added. The mixture was stirred under argon at
35°C for 10 days. After distillation at 65°C/4 mbar, 34 g of a white crude product were obtained, which still contained about 30 mol% 2,2,2-trichloroethanol (intensity in NMR) pyridinium 2,2,2-trichloroethyl-hydrogensulfate; \(^1\)H-NMR (400 MHz in CH\(_3\)OH) \(\delta\): 4.53 (2H, s, CH\(_2\)), 8.15 (2H, trip., CH ar.), 8.68 (1H, quadr., CH ar.), 8.88 (2H, d, CH ar.)

*Sodium 2,2,2-trichloroethyl-sulfate*

The crude product was washed with hexane and dried under vacuum. 13 g (0.042 mol) of it were dissolved in 20 mL deionized water and treated on an ion exchange column (150 g (0.45 eq.) Dowex 50Wx8, 20-50 mesh, prepared from the H\(^+\)-form to the Na\(^+\)-form by treatment with 0.01 M NaOH and subsequent washing with deionized water until the pH of the effluent was neutral). Semiquantitative analysis by NMR-spectroscopy with 2,2,2-trichloroethanol as an external standard showed that the fractions of the ion exchange column contained Na\(_2\)SO\(_4\) in varying degrees, from 0 up to 100%. Sodium 2,2,2-trichloroethyl-sulfate could be obtained in the last fractions with a purity of 98% (1.2% 2,2,2-trichloroethanol, 0% pyridine (NMR-analysis)); \(^1\)H-NMR (400 MHz in CH\(_3\)OH) \(\delta\): 4.55 (2H, s, CH\(_2\))

**Additional Remarks:**

2,2,2-trichloroethyl-chlorosulfate could be obtained easily according to the procedure of Charalambous et al. (J. Chem. Soc. (1964) 5480-5482) However, mild hydrolysis of the chlorosulfate took place only slowly and did not yield 2,2,2-trichloroethyl-hydrogensulfate, but rather 2,2,2-trichloroethanol and sulfuric acid.

Direct reaction of an equimolar mixture of fuming sulfuric acid and 2,2,2-trichloro-ethanol according to Sandler and Karo (Organic Functional Group Preparations, in: Organic Chemistry Vol. 12, Ed. H. Wassermann, 1989) yielded a mixture of the educts and a product with a remarkably high NMR-shift of 6.3 (in methanol), possibly the diester di-(2,2,2-trichloroethyl)-sulfate. No signals of the monoester were observed in the NMR-spectrum.
**2,2,2-trichloroethyl-dihydrogenphosphate**


![Reaction Scheme]

\[ \text{POCl}_3 + \text{Cl}_2\text{CH}_2\text{OH} \rightarrow \begin{array}{c} \text{Cl} \\text{Cl} \\text{Cl} \\text{Cl} \\text{O} \\text{P} \\text{O} \\text{Cl} \\text{Cl} \\text{Cl} \\text{Cl} \\text{Cl} \\text{Cl} \\text{OH} \\ \text{1) + H}_2\text{O} \\ \text{2) Recrystallisation in benzene} \end{array} \]

2,2,2-trichloroethyl-phosphorodichloridate

31 g (0.205 mole) 2,2,2-trichloroethanol, 51 mL (0.555 mole) phosphoryl chloride and 0.07 g AlCl\textsubscript{3} were heated at 80°C under reflux for 4 h. The reaction mixture was allowed to cool down and distilled under reduced pressure to yield **2,2,2-trichloroethyl-phosphorodichloridate**; yield 37.49 g (0.14 mole, 68%), b.p. 105°C/20 Torr

2,2,2-trichloroethyl-dihydrogenphosphate

To 37.49 g (0.14 mole) of the crude product, 30 mL (1.67 mole) water were added, and the reaction mixture was heated to 80°C under reflux and stirring. The water was removed at 160°C and the product recrystallized to give a crude product of **2,2,2-trichloroethyl-dihydrogenphosphate**; yield 23.72 g (0.12 mole, 88%);

\[ ^1\text{H}-\text{NMR} \text{ (400 MHz in CDCl}_3\text{) } \delta: 4.46 \text{ (2H, d, CH}_2\text{, J}^4(\text{H-P}) = 5.9 \text{ Hz)}; \]
\[ ^31\text{P}-\text{NMR} \text{ (162 MHz): } \delta: -1.8 \text{ in CDCl}_3, -1.3 \text{ in CH}_3\text{OH (1P, t, J}^4(\text{H-P}) = 5.9 \text{ Hz)}; \]
\[ ^13\text{C}-\text{NMR} \text{ (100 MHz in CDCl}_3\text{) } \delta: 75.9 \text{ (CH}_2\text{, q, J}^3(\text{C-P}) = 3.4 \text{ Hz, J}^1(\text{C-H}) = 154.3 \text{ Hz), 96.3 (CCl}_3\text{, q, J}^4(\text{C-P}) = 12.1 \text{ Hz, J}^2(\text{C-H}) = 2.6 \text{ Hz)}; \]

The crude product was initially contaminated with 20% phosphoric acid (NMR-signal at 1.3 ppm in CH\textsubscript{3}OH) and was purified by recrystallization in benzene.
B) “Anchor and trap” compounds

7,7,7-trichlorohepten-5-ol


\[ \text{CCl}_3 \quad \text{OH} \]

\[
\begin{align*}
\text{THF, -115 °C} & \\
\text{CCl}_4 + \text{BuLi} & \quad \text{LiCCl}_3 \\
- \text{BuCl} & \\
\text{BF}_3 \text{OEt}_2 & \\
\end{align*}
\]

The synthesis was conducted in dry glassware and under argon. 27.6 mL (44.2 g, 0.29 mole) CCl\textsubscript{4} were dissolved in 600 mL freshly distilled tetrahydrofuran at -115°C (acetone/liquid nitrogen). Then, 200 mL (0.31 mole) butyl lithium were added dropwise over 1.5 hours. Finally, 26.8 mL (0.24 mmole) hex(1)en(5)epoxide and 34 mL (0.28 mmole) borotrifluoride etherate were added. The mixture was stirred for two hours at -115°C and was then allowed to warm to room temperature.

After 12 h, the mixture was poured on crushed ice, extracted twice with 100 mL diethylether, the extract was dried over sodium sulfate and reduced under vacuum. Flash chromatography with silica gel as stationary phase and a mixture of hexane and diethyl ether (4:1) as eluent separated two main fractions of about 7 g product and 11 g side product. The product was purified by distillation under reduced pressure to yield 7 g (0.032 mmole, 14%) 7,7,7-trichlorohepten-5-ol, b.p. 95°C/5 Torr; \textsuperscript{1}H-NMR (400 MHz in CDCl\textsubscript{3}) \( \delta \):

1.65, 1.71: CCl\textsubscript{3}-CH\textsubscript{a}H\textsubscript{b}-CHOH-CH\textsubscript{c}H\textsubscript{d}H\textsubscript{w}-CH\textsubscript{x}H\textsubscript{y}-CH=CH\textsubscript{cis}H\textsubscript{trans}, m,

\( ^3 \)J coupling constants of CH\textsubscript{a} (\( \delta = 1.65 \) ppm): 4.9 Hz, 7.1 Hz, 8.8 Hz;

\( ^3 \)J coupling constants of CH\textsubscript{w} (\( \delta = 1.71 \) ppm): 6.0 Hz, 8.0 Hz, 8.0 Hz;

\( ^2 \)J(CH\textsubscript{c}H\textsubscript{d}) = 13.9 Hz
2.16-2.31: CCl₃-CH₃H₂-CHOH-CH₄H₅=CH=CH₃ CH₅H₆ trans, m;
2.26: CCl₃-CH₃H₂-CHOH-CH₄H₅=CH=CH₃ CH₅H₆ trans, s;
2.86, 2.94: CCl₃-CH₃H₂-CHOH-CH₄H₅=CH=CH₃ CH₅H₆ trans, dd,
  ³J coupling constant of CH₃ (δ = 2.86 ppm): 2.3 Hz (³J(CH₃H₂-CHOH))
  ³J coupling constant of CH₅ (δ = 2.94 ppm): 7.1 Hz (³J(CH₃H₂-CHOH))
  ²J(CH₃H₂) = 15.2 Hz
5.08: CCl₃-CH₃H₂-CHOH-CH₄H₅=CH=CH₃ CH₅H₆ trans, dq
  ⁴J(CH₅H₆CH=CH₃ CH₅H₆ trans) = ⁴J(CH₅H₆CH=CH₃ CH₅H₆ trans) = 1.7 Hz,
  ³J(CH=CH₃ trans) = 17.2 Hz,
5.85: CCl₃-CH₃CH₃-COH-CH₄H₅=CH=CH₃ CH₅H₆ trans, m
  ³J(CH₅H₆CH=CH₃) / ³J(CH₅H₆CH=CH₃) = 6.7 Hz

¹³C-NMR (100 MHz in CDCl₃) δ: 29.5, 36.5, 61.8, 69.0, 98(?), 115.4, 137.7 ppm

7,7,7-trichlorohepten-5-yl dimethyl phosphate

The synthesis was conducted in dry glassware, with fresh reagents and under argon. 5 mL (6.25 g, 29 mmole) 7,7,7-trichlorohepten-5-ol and 9.4 mL (116 mmole) pyridine were dissolved in 150 mL dichloromethane. Separately, 14 g (55 mmole) iodine and 7 g (56 mmole) trimethylphosphite were added to 100 mL dichloromethane and brought to reaction at 0°C. The resulting solution of iododimethylphosphate was added in portions to the alcohol, and the mixture was stirred for 1 h at room temperature. After dilution with 200 mL diethylether, the mixture was washed two times with 100 mL 25% sodium hydrogensulfate solution and three times with 100 mL 10% NaHPO₄ buffer (pH 6). After drying
over sodium sulfate and treatment under vacuum, the crude product was purified
by flush chromatography with silica as stationary phase and ethyl acetate as
eluent to yield 2.1 g (7 mmole, 25%) 7,7,7-trichlorohepten-5-yl dimethyl
phosphate.

$^1$H-NMR (400 MHz in CH$_3$OH) $\delta$:

1.89-2.04: CCl$_3$-CH$_2$H$_b$-CHOPO(OCH$_3$)$_2$-CH=CH$_2$H$_y$-CH=CH$_{cis}$H$_{trans}$, m,

2.18-2.27: CCl$_3$-CH$_2$H$_b$-CHOPO(OCH$_3$)$_2$-CH$_2$H$_w$-CH$_2$H$_y$-CH=CH$_{cis}$H$_{trans}$, m;

3.13, 3.22: CCl$_3$-CH$_2$H$_b$-CHOPO(OCH$_3$)$_2$-CH$_2$H$_w$-CH$_2$H$_y$-CH=CH$_{cis}$H$_{trans}$, dq/dd
coupling constants of CH$_a$ ($\delta = 3.13$ ppm):
$^3$J (CH$_a$H$_b$-CHOPO(OCH$_3$)$_2$) = 3.8 Hz, $^4$J$_{H-P}$ (CH$_a$H$_b$-CHOPO(OCH$_3$)$_2$) = 2.6 Hz
coupling constants of CH$_b$ ($\delta = 2.94$ ppm):
$^3$J(CH$_a$H$_b$-CHOH) = 5.9 Hz, $^4$J$_{H-P}$ (CH$_a$H$_b$-CHOPO(OCH$_3$)$_2$) = 0 Hz
$^2$J(CH$_a$H$_b$) = 15.6 Hz

3.791, 3.789: CCl$_3$-CH$_2$H$_b$-CHOPO(OCH$_3$)$_2$-CH$_2$H$_w$-CH$_2$H$_y$-CH=CH$_{cis}$H$_{trans}$, 2xd
$^3$J$_{H-P}$ (CHOPO(OCH$_3$)$_2$) = 11.2 Hz

4.85: CCl$_3$-CH$_2$H$_b$-CHOPO(OCH$_3$)$_2$-CH$_2$H$_w$-CH$_2$H$_y$-CH=CH$_{cis}$H$_{trans}$, m
$^3$J (CHOPO(OCH$_3$)$_2$-CH$_2$H$_w$) = $^3$J (CHOPO(OCH$_3$)$_2$-CH$_2$H$_w$) = 5.8 Hz,
$^3$J$_{H-P}$ (CHOPO(OCH$_3$)$_2$) = 7.9 Hz

5.03: CCl$_3$-CH$_2$H$_b$-CHOH-CH$_2$H$_w$-CH$_2$H$_y$-CH=CH$_{cis}$H$_{trans}$, dq
$^4$J(CH$_x$CH$_y$CH=CH$_{cis}$H$_{trans}$) / $^4$J(CH$_x$CH$_y$CH=CH$_{cis}$H$_{trans}$) = 1.4 / 1.6 Hz,
$^3$J(CH=CH$_{cis}$) = 10.3 Hz,
$^2$J(CH$_{cis}$H$_{trans}$) = 1.6 Hz

5.11: CCl$_3$-CH$_2$H$_b$-CHOH-CH$_2$H$_w$-CH$_2$H$_y$-CH=CH$_{cis}$H$_{trans}$, dq
$^4$J(CH$_x$CH$_y$CH=CH$_{cis}$H$_{trans}$) = $^4$J(CH$_x$CH$_y$CH=CH$_{cis}$H$_{trans}$) = 1.7 Hz,
$^3$J(CH=CH$_{trans}$) = 17.1 Hz,

5.86: CCl$_3$-CH$_2$H$_b$-CHOH-CH$_2$CH$_w$-CH$_2$H$_y$-CH=CH$_{cis}$H$_{trans}$, m
$^3$J(CH$_x$CH$_y$CH=) = $^3$J(CH$_x$CH$_y$CH=) = 6.7 Hz
\[ ^{31}\text{P-NMR (162 MHz in CH}_3\text{OH)} \delta: -0.05 \text{ ppm;} \]
\[ ^3J_{\text{H-P}} \text{(CH}_2\text{OP(OCH}_3\text{)_2}) = 11.2 \text{ Hz, } ^3J_{\text{H-P}} \text{(CH}_2\text{OP(OCH}_3\text{)_2}) = 8.0 \text{ Hz,} \]
\[ ^4J_{\text{H-P}} \text{(CH}_3\text{H_b-CH}_2\text{OP(OCH}_3\text{)_2}) = 2.6 \text{ Hz} \]

7,7,7-trichlorohepten-5-yl monomethyl phosphate

0.5 g (1.5 mmole) 7,7,7-trichlorohepten-5-yl dimethyl phosphate and 1.5 g (10 mmole) sodium iodide were dissolved in 50 mL acetonitrile and stirred for 2 weeks at room temperature. The mixture was treated with 100 mL 25% sodium hydrogensulfate and extracted with diethyl ether. The ether phase was again extracted with 2x 30 mL 10% NaHPO\(_4\) buffer (pH 6), which was subsequently acidified to pH 2 and extracted with 2x 30 mL diethyl ether. After treatment of the organic phase under vacuum, 0.3 g (60%) 7,7,7-trichlorohepten-5-yl monomethyl phosphate were obtained.

Removal of the second methyl group was attempted in a solution of sodium iodide and sodium hydrogensulfate in acetonitrile. However, only about 70% completion could be obtained after 3 weeks (analysis by NMR).
Products in the Reaction of Model Compounds with Cr(II)

Outlook


Products in the Reaction of 7,7,7-trichlorohepten-5-ol with Cr(II)

A solution of 0.5-1 mM of 7,7,7-trichlorohepten-5-ol was brought to reaction with a) 0.1 mM Cr(II) (pH 4), b) 0.4 mM Cr(II) (pH 3.5) and c) 1 mM Cr(II) (pH 3). (Cr(II) solutions were prepared according to the same method as used by Totten et al., Environ. Sci. Technol. 2001, 35, 2268-2274). After 7 days the reaction mixture was extracted with hexane and analysed on a GC/MS (GC Fisons 8000 Series, autosampler Fisons AS 800, quadrupole MS Fisons MD 800) equipped with a 30 m DB-5 silica column. Injection was 1 µL on-column, the temperature program was 40°C (3 min.), ramp 8°C/min. to 100°C (0 min.), ramp 30°C/min. to 210°C (4 min.). To detect fragment ions of higher masses, mass spectra were alternatively acquired using mild chemical ionization (CI instead of EI with the Fisons mass analyzer), with isobutane as ionization gas and the following parameters: temperature 280°C, emission current 1000 mA, electron energy 30 eV, filament current 4 A, sensitivity 60 mV, mass range 100-300 m/z, scan speed 1 s/d, resolution 1000 m/Δm.

As can be seen from the chromatograms in Figure A6-1, reaction of the substrate (retention time 12.5 min.) generated major products with retention times at 11.7 min., 10.6 min. and 9.7 min. Nearly identical mass spectra of the products at retention times 10.6 min. and 9.7 min. (Figure A6-2) indicated that they were two cis-trans isomers (similar fragmentation pattern pointed towards an identical connectivity within the molecule, the greatly differing retention times, however, showed that they were not enantiomers), whereas the mass spectrum at retention time 10.7 min. indicated the generation of a distinctly different compound. The characteristic pattern of peaks at (m+1)/z = 129, 131 and (m+1)/z = 163, 165, 167, respectively, indicated that in the first two isomers only one Cl atom was present, whereas the second compound contained two Cl substituents. Figure A6-3 summarizes possible products of the reaction with distinguishable retention times. At first sight the mass spectra (CI) of Figure A6-2 point to products with molecular masses of m/z = 162 (11.7 min.) and m/z = 128 (9.7 / 10.6 min.). The fragmentation patterns (Δm/z = 18 (H₂O)), however, are not consistent with such an assumption, because all possible products with masses m/z = 128, 163 cannot eliminate H₂O.
Figure A6-1: Chromatograms (Total Ion Current MS) of hexane extracts to analyze products of the reaction of 7,7,7-trichlorohepten-5-ol with a) 0.1 mM Cr(II) (above), b) 0.4 mM Cr(II) (middle) and c) 1 mM Cr(II) (below)
Figure A6-2: Mass spectra of most important peaks (RT=retention time, EI = electron impact ionization, CI = chemical ionization with isobutene)
The true molecular mass of the isomers can therefore be expected to be $m/z = 146$ and that of the second peak $m/z = 180$. It can be assumed that these molecular mass fragments underwent elimination of water during fragmentation in the mass spectrometer so that their peaks could not be observed directly. As can be seen from Figure A6-3, the only possibility for the product at retention
time 11.7 min. is then 1,1-dichloro-1,6-heptadiene (“F”), whereas at first sight several structures with m/z = 146 are possible for the isomers at retention times 9.7 and 10.6 min. Unambiguous structure determination, however, can be achieved by an analysis of the mass spectra. As can be seen from Figure A6-4, the observed spectra are consistent with fragmentation reactions of cis/trans 1-chloro-1,6-heptadiene, whereas other possibilities of Figure A6-3 such as B1-4 or H1-4 would be expected to show a significantly different fragmentation.

**Figure A6-4:** Mass fragmentation of cis/trans 1-chloro-1,6-heptadiene, consistent with observed fragments in the spectra of isomeric products at retention times 9.7 min. and 10.6 min (see Figure A6-2).
Conclusion and Outlook

Observed reactions of 7,7,7-trichlorohepten-5-ol with Cr(II) at pH 3.5 are summarized in Figure A6-5. The dominating pathways have been found to be an unwanted dehydrohalogenation and a hydrogenolysis, followed again by an unwanted dehydrohalogenation. Cyclization reactions that would trap radicals and carbenes seem to be too slow to be of importance. The reactions for which these molecules were designed were therefore outcompeted by side reactions so that the design of this first generation of probe molecules was not successful.

![Figure A6-5](image_url)

**Figure A6-5:** Summary of reaction pathways observed in the reaction of 7,7,7-trichlorohepten-5-ol with Cr(II) at pH 3.5.

As a consequence of these experiences, the synthesis of a second generation is now planned with methyl groups in β-position to the CCl₃-group so that dehydrohalogenation is effectively avoided. In addition, the alkyl chain shall be shortened by one unit, thus enabling faster cyclization reactions to five-membered rings. A proposed synthesis route for these compounds is given in Figure A6-6.
Figure A6-6: Proposed synthesis route for a new generation of probe compounds
Curriculum Vitae

06.10.1972  Born in Hamburg, Germany

1983-1992  High School at Christianeum in Hamburg (Germany)

1992-1994  Student of Chemistry at the Albert-Ludwigs University, Freiburg i.Br. (D)

1994:  Vordiplom in Chemistry, at the Albert-Ludwigs University, Freiburg i.Br.(D)

1994/95  Visiting and Exchange Student at the University of Sussex in the Department of Chemistry, Brighton (U.K.)

1995:  Research Project: “Crystallographic Studies on C_{60}/IBr-crystals” in the group of Prof. Kroto (University of Brighton)

1995-1998  Studies in Chemistry at the Swiss Federal Institute of Technology (ETH), Zürich (CH)


1998:  M. Sc. (Diplom) in Chemistry, at the Swiss Federal Institute of Technology (ETH), Zürich (CH)

1998-2002  Doctoral Thesis at the Swiss Federal Institute for Environmental Sciences and Technology (EAWAG) under supervision of Prof. Dr. René. Schwarzenbach, Prof. Dr. Stefan Haderlein and Dr. Werner Angst

since 1998:  Teaching assistant in the Environmental Sciences Department, ETH Zürich