Chlorobenzenes and Chloronitrobenzenes Interaction with Iron (O)

Manuel Alejandro Serratos

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Chlorobenzenes and Chloronitrobenzenes

Interaction with Iron (O)

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BY

Manuel Alejandro Serratos

THESIS

SUBMITTED IN PARTIAL FULLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Science in Chemistry

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

2003

YEAR

I HEREBY RECOMMEND THAT THIS THESIS BE ACCEPTED AS FULFILLING THIS PART OF THE GRADUATE DEGREE CITED ABOVE

DATE 6/6/2003

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Abstract

Degradation of chlorobenzene, dichlorobenzenes and chloronitrobenzenes (ClB, x-Cl2B and x-ClNO2B) was tested by trying to make them react with metallic iron, Fe (0), in water solvent.

The experiments consisted of optimizing the parameters of the reactions (like minimum mass of iron needed) and analytical detection conditions. Analytical techniques used were gas and liquid chromatography (GC and HPLC), mass spectrometry (MS) and UV-Vis spectroscopy.

No substances other than the initial ClB and x-Cl2B were detected in their tests with Fe (0) after shaking for periods of up to three days, although 10% weight average decreases in concentration were observed.

The ClNO2B isomers were completely reduced into their respective chloroanilines in a minimum of 20 minutes. Nitrobenzene and the ortho and para isomers of ClNO2B showed pseudo-first order rate constants of $0.14 \pm 0.01$, $0.14 \pm 0.01$ and $0.10 \pm 0.01$ min$^{-1}$. The meta isomer behaved differently with a second order rate constant of $0.0068 \pm 0.0003$ ppm$^{-1}$ min$^{-1}$. 
DEDICATION

To the Eastern Illinois University and the American-tax payers, especially my wife April.
Acknowledgments

Thank you Dr. Klarup for your supervision and direction during all of this time which has been almost everything, but bored.

I have to recognize all the other researcher who got into my filed of work and helped us to make conclusions, especially to Dr. Tratnyek and his team from the Oregon Graduate Institute.

I also appreciate to the faculty, staff and other students of the chemistry department of the Eastern Illinois University. It was very nice being with them.

I want to thank my wife April for her company. And this may be pure coincident, but it was also when I started hanging around with her that my research begun to provide results. Anyway I want to mention it.

iii
Contents

I. Introduction

1.1 General Properties of the Reactants 2
1.2 Toxicity of Reactants 4
1.3 Previous Research on the Reactants Degradation 6
1.3.1 Influence of different factors on kinetics 9
1.4 Thermodynamics 10

II. Experimental

Reactants and Solvents 13
Equipment Used 13
2.1 Reaction Conditions in the Chlorobenzene/Fe (0) experiments 15
2.1.1 Head-space 15
2.1.2 Liquid-liquid Extractions 16
2.2 Reactions conditions in the dichlorobenzene/Fe (0) experiments 17
2.3 Reactions conditions in the chloronitrobenzene/Fe (0) experiments 17
2.4 Reactions conditions in the chloronitrobenzene/Fe (II) experiments 18
2.5 Reactions conditions in the chloronitrobenzene/Fe (0)/EDTA experiments 18

III. Results and Discussion

3.1 Results from Chlorobenzene/Fe (0) Reactions 19
3.1.1 Head-space Analyse 19
3.1.2 Results from Liquid-liquid extraction 20
3.2 Results from Dichlorobenzene/Fe (0) Reactions 20
3.3 Results from Chloronitrobenzenes/Fe (0) Reactions

3.3.1 Calibrations Curves

3.3.2 Product Analyses of x-Chloronitrobenzenes Reactions

3.3.3 Influence of pH on Reactions

3.3.4 Kinetic Analyses

3.3.5 Mechanism of Reaction

3.4 Results from Chloronitrobenzenes/Fe (II) Reactions

3.5 Results from Chloronitrobenzenes/Fe (0)/EDTA Reactions

3.6 Influence of the Mass Transport

3.7 General Discussion

Conclusions

List of Figures

Figure 1. Comparison of chlorobenzene head-space gas chromatograph signal with and without Fe (0).

Figure 2. Calibration Curve for o-dichlorobenzene at 220 nm.

Figure 3. Calibration Curve for m-dichlorobenzene at 220 nm.

Figure 4. Calibration Curve for p-dichlorobenzene at 220 nm.

Figure 5. HPLC Chromatograph of o-dichlorobenzene in water, 35.0 ppm.

Figure 6. HPLC Chromatograph of m-dichlorobenzene in water, 34.8 ppm.

Figure 7. HPLC Chromatograph of p-dichlorobenzene in water, 11.4 ppm.
Figure 8. Typical calibration curves for chloronitrobenzenes at 286 nm for the ortho and para isomers and 278 nm for the meta isomer.

Figure 9. HPLC Chromatograph of o-chloronitrobenzene in H2O, 46 ppm

Figure 10. HPLC Chromatograph of m-chloronitrobenzene in H2O, 48 ppm

Figure 11. HPLC Chromatograph of p-chloronitrobenzene in H2O, 44 ppm

Figure 12. HPLC Chromatograph of o-chloronitrobenzene (at 5.95 min) and its product o-chloroaniline (at 4.24 min) from reaction with Fe (0) 0.50 gFe/gsol

Figure 13. Gas chromatograph from the reaction of nitrobenzene with Fe (0) 0.50 gFe/gsol after 6 minutes.

Figure 14. Gas chromatogram from the reaction of o-chloronitrobenzene with Fe (0) 0.50 gFe/gsol after 6 minutes.

Figure 15. Gas chromatogram from the reaction of m-chloronitrobenzene with Fe (0) 0.50 gFe/gsol after 6 minutes.

Figure 16. Gas chromatogram from the reaction of p-chloronitrobenzene with Fe (0) 0.50 gFe/gsol after 6 minutes.

Figure 17. MS spectra of aniline, the nitrobenzene product reaction with Fe(0)

Figure 18. MS spectra of o-chloroaniline, the o-chloronitrobenzene product reaction with Fe(0).

Figure 19. MS spectra of m-chloroaniline, the m-chloronitrobenzene product reaction with Fe(0).

Figure 20. MS spectra of p-chloroaniline, the p-chloronitrobenzene reaction product with Fe(0).
Figure 21. MS spectra of the nitroso intermediate of o-chloronitrobenzene reaction with Fe(0).

Figure 22. MS spectra of the nitroso intermediate of m-chloronitrobenzene reaction with Fe(0).

Figure 23. MS spectra of the nitroso intermediate of p-chloronitrobenzene reaction with Fe(0).

Figure 24. MS spectra of the azo intermediate of the nitrobenzene reaction with Fe(0).

Figure 25. MS spectra of the azo intermediate of the o-chloronitrobenzene reaction with Fe(0).

Figure 26. MS spectra of the azo intermediate of the m-chloronitrobenzene reaction with Fe(0).

Figure 27. MS spectra of the azo intermediate of the p-chloronitrobenzene reaction with Fe(0).

Figure 28. Reduction rates of chloronitrobenzenes and nitrobenzene with Fe(0) 0.50 ± 0.01 g_{Fe}/g_{sol}.

Figure 29. Pseudo-first order disappearance of nitrobenzene and ortho and para chloronitrobenzene when reacting with Fe(0) 0.50 ± 0.01 g_{Fe}/g_{sol}.

Figure 30. Second-order disappearance of m-chloronitrobenzene when reacting with Fe(0) 0.50 ± 0.01 g_{Fe}/g_{sol}.

Figure 31. Disappearance of nitrobenzene and ortho and para chloronitrobenzene when reacting with Fe(0) 0.50 ± 0.01 g_{Fe}/g_{sol} according to second order kinetic model.
Figure 32. Disappearance of m-chloronitrobenzene when reacting with Fe (0) $0.50 \pm 0.01 \text{ g}_{\text{Fe}}/\text{g}_{\text{sol}}$ according to pseudo-first order kinetic model. 63

Figure 33. Product formation of o-ClNO2Benzene reaction with $0.50 \pm 0.01 \text{ g}_{\text{Fe}}/\text{g}_{\text{sol}}$ 64

Figure 34. Product formation of m-ClNO2Benzene reaction with $0.50 \pm 0.01 \text{ g}_{\text{Fe}}/\text{g}_{\text{sol}}$ 64

Figure 35. Product formation of p-ClNO2Benzene reaction with $0.50 \pm 0.01 \text{ g}_{\text{Fe}}/\text{g}_{\text{sol}}$ 65

**References** 66
I. Introduction

Over the last 10 years a treatment for chlorinated contaminants that has been used all around the world is iron metal (Fe 0) permeable reactive barriers or PRBs (1). PRBs have been proven to be reliable and cost effective in terms of maintenance and installation. Fe (0) is a relatively good reducing agent because of its oxidation potential of 0.440 V to turn into Fe (II).

Likely targets for these PRBs include chlorobenzene, dichlorobenzenes and chloronitrobenzenes which are important industrial chemicals and contaminants. It is of interest whether or not Fe (0) can turn these chlorobenzenes into benzene. Benzene, a possible reduction product, is a confirmed carcinogen (2) which means that this kind of treatment might need further improvements.

As for the chloronitrobenzenes, the parent compound, nitrobenzene (NO2B), is not considered to be carcinogen. But chloroanilines are carcinogenic and are irritants (3), so these technologies may also need further improvements.

We need to understand how Fe (0) interacts with these chlorocompounds and which parameters may control these interactions. Of particular interest is how isomers compare, since potential information relating to the reaction mechanism might be revealed. Experiments of Fe (0) with aqueous solutions of chlorobenzene, nitrobenzene and the isomers of dichlorobenzenes and chloronitrobenzenes were conducted in an attempt to address this issue.
1.1 General Information of Reactants

Table 1. Basic Properties of the Reactants

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point, °C</th>
<th>Boiling point, °C</th>
<th>Density at 20°C, g/ml</th>
<th>Water Sol., ppm</th>
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<tr>
<td>Chlorobenzene</td>
<td>-46</td>
<td>132</td>
<td>1.106</td>
<td>466</td>
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<td>o-dichlorobenzene</td>
<td>-17</td>
<td>180</td>
<td>1.306</td>
<td>147</td>
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<td>54</td>
<td>174</td>
<td>1.241</td>
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<td>32</td>
<td>245</td>
<td>1.305</td>
<td>307</td>
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<tr>
<td>1-chloro-3-nitrobenzene</td>
<td>46</td>
<td>236</td>
<td>1.534</td>
<td>256</td>
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<tr>
<td>1-chloro-4-nitrobenzene</td>
<td>83</td>
<td>242</td>
<td>1.520</td>
<td>154</td>
</tr>
</tbody>
</table>

Solubility data from
- [http://www.epa.gov/chemrtk/chlrnbnz/c14392tp.pdf](http://www.epa.gov/chemrtk/chlrnbnz/c14392tp.pdf)

Chlorobenzene

Chlorobenzene (CIB) is an important industrial compound. From one of the latest reports (4), the American CIB production in 1992 was 104.8 million kg (231 million pounds) made by three companies (5), Solutia Inc. (a Monsanto Co. spin-off) in Sauget, Illinois; PPG Ind. Inc., in Natrium, West Virginia; and Standard Chlorine Chemical Co. of Delaware, Inc. in Delaware City, Delaware. The biggest plant, located in Illinois, belongs to Monsanto which still produces CIB and uses it as a component of LARIAT®Flowable herbicide (or MON 29870) in less than 20% by weight. CIB has been used mostly (~40% of U.S. use) as a chemical intermediate in the production of rubber and agriculture chemicals, antioxidants, dyes and pigments (5) via ortho and para CIB nitration. Another source (6) mentions CIB was also used to produce phenol, DDT insecticide, aniline; as a solvent in the production of adhesives, paints, polishes, waxes, diisocyanates (surface coating), pharmaceuticals, natural rubber and surface coating
removers; as a fiber swelling agent and dye carrier in textile processing; as a tar and grease remover in cleaning fats and oils; and as heat-transfer medium.

**o-Dichlorobenzene**

o-Cl2B has been used mostly as a chemical intermediate and solvent. Specific uses are production of 3,4-dichloroaniline (via 3,4-dichloronitrobenzene) and many herbicides (7). As a solvent, it has been used to produce toluene diisocyanate. These uses account for about 70-90% of total o-Cl2B use. Other minor applications are as an insecticide, an intermediate in the manufacture of some dyes, as a deodorizing agent in garbage and sewage, as solvent for waxes, gums, resins, tars, rubbers, oils, asphalts, or as cleaners of engines, leather and wool.

**m-Dichlorobenzene**

m-Cl2B is used as a solvent, insecticide, fumigant, and chemical intermediate to manufacture dyes, chlorophenols and arylene sulfide polymers (8).

**p-Dichlorobenzene**

p-Cl2B has been sold not only to industries, but also to the general public as an insecticide for moths, molds and mildews, and as a deodorant for toilets and garbage containers. These uses have accounted for most of its uses (35-55%) from 1978 to 1998. About 34% is exported, about 27% is used in the production of polyphenylene sulfide (PPS) resin, and about 10% as an intermediate in the production of other chemicals such as 1,2,4-trichlorobenzene. Minor uses of p-Cl2B include control of certain tree-boring insects, ants and blue mold in tobacco seed beds (8,9).

p-Cl2B production was 65.3 million kilograms (144 million pounds) in 1997 (10) and is produced by the same factories as ClB.
Chloronitrobenzenes

The ortho and para isomers are used to produce dyes, plastics chemistry, munitions, pesticides (parathion), drugs (4-acetylamino phenol), lumber preservatives and photographic chemicals. They are manufactured by Solutia Inc. in the U.S.A. (11).

1.2 Toxicity of Reactants

Chlorobenzene

ClB can be irritating to the eyes and respiratory tract of humans and has neurotoxic effects. Chronic exposure may cause headaches, drowsiness, numbness of the extremities and spastic contractions of the muscles. Nonetheless, there have been no systematic studies of its toxicity in humans, nor has it been proven carcinogenic or genotoxic. Reports from ClB toxicity come from people accidentally exposed to it. It is in animals where plenty of toxicity data is available. Most small animals die quickly only after being exposed to extremely high doses of ClB. For example, exposure of rats by inhalation to 9000 ppm kills two thirds of these animals within 3 hours (12).

Anyway, all of these ClB concentrations are bigger than the reported ClB concentrations in the environment in 1989 (13). Atmospheric concentrations of ClB in rural areas were <0.02 ppb, and 0.8 ppb in cities, with a maximum value of 12 ppb. In drinking water, several U.S. cities reported concentrations of ≤ 5.6 ppb. The U.S. Environmental protection Agency (EPA) has proposed a Maximum Contaminant Level (MCL) of 0.1 ppm of ClB.
o-Cl₂B

The toxicity of o-Cl₂B resembles very much that of ClB. For example it has not been proven carcinogenic (14). Its environmental occurrence is also similar to ClB. Its concentration in air in the vicinity of chemical plants and waste disposals sites range from 0 to 1.3 µg/m³. In drinking water, o-Cl₂B has been found in concentration from 1 to 2.5 ppb (15). The MCL from the EPA is 0.6 ppm.

m-Cl₂B

m-Cl₂B is not carcinogenic for humans (16), but it is an irritant and may be absorbed through the skin. Some effects are nausea, vomiting, diarrhea, liver and kidney damage after chronic exposure. EPA has not proposed a MCL for m-Cl₂B.

p-Cl₂B

p-Cl₂B is a possible human carcinogen (17). It is an irritant. Overexposure provokes head-aches, eye irritation, nausea, anorexia, vomiting, weigh loss and cirrhosis. Its MCL is 0.075 ppm.

Chloronitrobenzenes

These compounds can be absorbed through the skin. They attack the central nervous system and provoke nausea, severe headaches, vomiting, dryness of throat, weakness, drowsiness, lethargy, coma, heart blocks and dermatitis (16). EPA has not proposed MCL for these compounds.
1.3 Previous Research on the Reactants Degradation

Several ways other than using Fe(0) have been developed to decompose chlorobenzenes:

- By pyrolysis in sealed ampoules with O\(_2\) at temperatures ranging from 200 to 600° C (18). There were no products below 380° C, but mostly at 500° C from times in the range of 10 minutes to 6 hours. These pyrolysis experiments released more toxic products like dibenzofurans, dichlorodibenzo furan, dichlorobenzodioxin, chlorinated biphenyls, trichlorobenzenes and chlorophenols. The reaction mechanisms were supposed to be through radicals. Their samples were analyzed by GC (Flame Ionization Detector, FID) and MS.

- With iron-treated char at more than 1500° C (19). ClB was fully converted into benzene by reacting with nascent hydrogen or hydrogen radicals. Nascent hydrogen is produced from water and FeO. Analyses were done by GC, and MS for the organic compounds, and X-ray diffraction for iron compounds.

- With Fenton’s reagent in round-bottom flasks (20). Under anaerobic conditions, chlorophenols, dichlorobiphenyls and phenolic polymers were the main products in up to 2 hours. With O\(_2\) present, less dichlorobiphenyls were formed. Chlorobenzoquinone, chlorinated and non chlorinated diols were obtained. Radicals were supposed to be the reaction intermediates again. Chemicals analysis was done by UV-Vis for iron and GC and MS for the organic compounds.

- Much research has been done with UV radiation. With air-saturated water, p-Cl\(_2\)B was converted into p-chlorophenol, hydroquinone, hydroxybenzoquinone and 2,5-dichlorophenol (21). With degassed water, p-Cl\(_2\)B forms phenol, 4,4,’dichlorobiphenyl
and 2,4',5-trichlorobiphenyl (21). With water over TiO$_2$ supported on molecular sieves (like NaY) irradiated with 300 nm light and 20° C, ClB, o-Cl$_2$B, and phenol were converted into CO$_2$ in a wide range of yield from 11.7 to 61.1% after 6 hours (22). In these experiments they had to determine surface areas and porosities of the inorganic materials by physical adsorption of nitrogen at -196° C (BET method). The surface areas of particles also covered a wide range from 6 to 1009 m$^2$/g. Other techniques used were X-ray diffraction to study crystal structure (the particles were crystalline), Transmission Electron Microscopy (TEM) to measure particle size and size distribution, and infrared (IR), Raman and UV-Vis spectroscopies. Organic substances were determined by GC (FID detector). CO$_2$ was determined by BaCO$_3$ precipitation by passing it over Ba(OH)$_2$ (22). In another report, UV radiation at the same wavelength of 300 nm and pure heat (from 200 to 500° C) also works, but in this patent details are not given (23).

Taneaki Yahata’s reactions just used CaO in combination with heat and produced CaCO$_3$ and CaCl$_2$ (24,25).

Life sciences. A major achievement happened when ClB was bio-degraded into hexa-1,6-dicarboxilic acid recently reported in Mar. 2003 (26). That degradation was achieved by using Ralstonia spp. bacteria isolated from a groundwater aquifer. The purpose of that research was mainly to determine which genes promote ClB degradation.

Iron has already been reported to dechlorinate the three Cl$_2$B isomers by 90% within a day by being mixed with either Pt or Pd and presented as nano-particles in order to maximize the reacting-surface-area from 0.9 to 33.5 m$^2$/g at 22° C (27). Fe was found to serve as electron donor, while the other metals were catalysts. The organic substances
were analyzed by GC (with Electron Capture Detector, ECD) and MS. Surface areas were determined by N₂ adsorption at −196°C (BET), TEM and X-ray diffraction.

Fe (0) is known to selectively reduce nitrogroups in aromatic compounds, but always by manipulating the pH, especially under acidic or buffered conditions (28). In this research, we also studied specifically the interaction between chloronitrobenzenes (x-ClNO₂B) and Fe (0) in water solvent alone.

Simple Fe (0) powder at room temperatures has been reported to reduce nitrobenzene to aniline without pretreatment, (29) or with previous HCl wash almost by 100% in 3 hours (30). Devlin et al. (31) found that granular Fe (0) reduced completely p-chloronitrobenzene (4ClNB) to p-chloroaniline at pH 10, room temperature and 0.008 M KNO₃ in 4 hours. Devlin set up these conditions in order to work in the most similar conditions to those in PRBs. X-ray diffraction was also used. Devlin group’s Fe had a relatively big surface area of 0.964 m²/g (BET). As a possible consequence of that big area, they performed most of their studies in how adsorbed aniline inhibits the reduction of NO₂B. Tratnyek’s Fe surface area was 0.038 m²/g (BET), and they did not discuss adsorption phenomena. Both groups used HPLC with reverse phase C-18 and UV-Vis detectors. In related experiments, trinitrotoluenes were reduced to the corresponding polyamines with Goethite rocks (Fe(III)hydroxides) covered by Fe(II) (32).
1.3.1 Influence of different factors on kinetics

The work of Agrawal and Tratnyek (30) shows how reduction rates are influenced by attaching other groups to NO2B and Fe (0) surface area and pH. When they reduced nitrobenzene, they obtained nitrosobenzene as an intermediate. Since nitrosobenzene is commercially available, they decided to do kinetics studies on nitrosobenzene and Fe (0) as well as NO2B. The reaction rate constants for these two compounds were close to each other, 0.0350 ± 0.001 and 0.0339 ± 0.001 min⁻¹ for nitrobenzene and nitrosobenzene respectively. Since nitrosobenzene and nitrobenzene have similar diffusion coefficients, they thought that these reduction reactions are controlled by diffusion of the analytes to the iron surface.

Then, they did more experiments with para-substituted nitrobenzenes with different diffusion constants (D). The effect of mass transport seemed demonstrated by parathion with the slowest rate constant and with the lowest diffusion coefficient due to its bulky p-(O,O-diethylphosphorothioate) substituent.

As for the influence of the Fe surface, Agrawal and Tratnyek showed that the reaction rate increases linearly with the mass of Fe (0) per unit reaction volume (g/L) which is supposed to be an adsorption effect. As for the pH, they did not show results, but said that there was not a clear effect on k₁ from 6-8 pH and only a small decrease below pH 6. This was considered congruent with their previous finding that these reductions of nitrocompounds are influenced by mass transport to reactive sites where pH might not be the same as in the bulk solution. They did not get aniline below pH 5. They believed that the aniline does not get desorbed because it is protonated at that pH. So, mass transfer influence may well matter below pH 5 in spite of being hindered by no product detection.
In summary, previous work with ClNO2Benzene compounds failed to determine if electronic or structural aspects played any role in ClNO2Benzene reactivity with the Fe (0) surface. This was due to mass transport limitations.

1.4 Thermodynamics

These paths have been proposed for chloroalkanes (33):

1. \( \text{Fe}^0 + \text{RCl} + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{RH} + \text{Cl}^- \)
2. \( \text{Fe}^0 + 2 \text{H}_2\text{O} \rightarrow 2 \text{OH}^- + \text{H}_2 + \text{Fe}^{2+} \)
2a. \( 2\text{Fe}^{2+} + \text{RCl} + \text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{RH} + \text{Cl}^- \)
3. Same as (2)
3a. \( \text{RCl} + \text{H}_2 \rightarrow \text{RH} + \text{Cl}^- + \text{H}^+ \) (catalyzed)

Path (1) seems to be the most likely to happen. In path (2), highly stable water is a reactant. In path (3) \( \text{H}_2 \) acts as a reactant, which has a lower oxidation potential than Fe (0) of 0.0 vs 0.440 V.

In order to know whether path 1 can spontaneously happen or not depends on the thermodynamic variables of free energy, enthalpy and entropy from all of the components of the general reactions above.
From the data in table 2, standard free energies for the possible reactions of the chlorobenzenes (with the exception of p-Cl2B) can be calculated at 298.1 K. For CIB, o-Cl2B and m-Cl2B successively, free energies of reduction with Fe are -198, -207 and -203 kJ/mol respectively. These negative free energies might indicate that the reactions between Fe and chlorobenzenes are possible; however, these enthalpies and entropies are valid for the pure chlorobenzenes in liquid state. Neither the effect of the water solvent, nor the Fe surface are taken into account because there is no available data for these cases. In order to find out if these numbers could be meaningful, it is proper to make calculations for these similar dechlorination reactions with Fe that proved effective (33).

Proven reactions:

4) \( H^+ + CCl_4 + Fe(s) \rightarrow HCCl_3 + Cl^- + Fe^{2+} \)

5) \( H^+ + HCCl_3 + Fe(s) \rightarrow H_2CCl_2 + Cl^- + Fe^{2+} \)
Table 3. Thermodynamic Data for Proven Reactions

<table>
<thead>
<tr>
<th>Component</th>
<th>$\Delta h_{\text{liq}}^o$, kJ/mol</th>
<th>$S_{\text{liq}}^o$, k J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>-128.4</td>
<td>0.2</td>
</tr>
<tr>
<td>HCCl$_3$</td>
<td>-134.3</td>
<td>0.2</td>
</tr>
<tr>
<td>H$_2$CCl$_2$</td>
<td>-124.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

From data in table 3 the free energies for reactions 4 and 5 are respectively -241 and -225 kJ/mol, which are negative values like those for reactions 1 - 3. Then, there might be some chances that Fe can react with the chlorobenzenes quantitatively as in reactions 4,5.
II. Experimental

Reactants and Solvents

In order to test the purity of the reactants, either gas or HPLC chromatograms were obtained.

- Powder metallic iron from Fisher, 100 mesh, purity 99%, no further purification.
  Surface area 0.31 m²/g determined from BET.
- Chlorobenzene, Analytical Grade (A.G.) from Eastman Kodak Co., without purity data from bottle or further purification.
- Dichloromethane, Toluene, o-dichlorobenzene, m-dichlorobenzene and p-dichlorobenzene, nitrobenzene, o-chloronitrobenzene, m-chloronitrobenzene and p-chloronitrobenzene and their respective chloroanilines from Aldrich Co. No one further purified.
- Deionized water provided from the chemistry department and degassed by bubbling N₂ for about an hour to volumes of 1 L. Its average resistance 3 \( \times \) 10⁵ ohms or conductivity 3 \( \mu \)MHo.
- Methanol grade HPLC, from Sigma-Aldrich Co.

Equipment Used

a) Schimadzu UV-160, UV-Vis Spectrophotometer. This instrument would tell us the proper wavelength to work with when using the HPLC instrument.
b) Hitachi HPLC with L-7100 pump, D-7000 interface, L-7200 autosamples, L-7300 column oven, L-7420 UV-Vis detector, reverse bonded-phase C-18, mobile phase 100% methanol.

-Sampling: Samples could be injected from the reaction medium right into the instrument after being filtered.

c) Hewlett Packard 5890 Gas Chromatograph.

-Stationary phase: Dimethyl Siloxane (J&WDB-1) 30m x 0.53 mm I.D.

-Mobile Phase: N₂, 15 psi head pressure.

-Detector: Ionization, with the aid of air and H₂.

-Detector and Injector Temperatures: 200 °C

-Retention times: They were manipulated by changing oven temperature instead of changing the column length or mobile phase flux because it was easy to do and compounds could be resolved quickly, in 3 minutes at most.

-Oven Temperatures: 50, 80, 85, 90 and 105 °C


e) pH meter, calibrated with a two-point calibration and verified with pH paper.

f) Inorganic membrane filters (Anatop10, 0.2 µm, 10 mm, Whatman®) to inject samples into the HPLC.

-General Preparation of Samples: Samples had to be shaken mechanically because magnetic stir bars attract all Fe. The other way of agitation, N₂ bubbling, takes chlorobenzenes off water. Water was degassed before adding any reagent.
2.1 Reaction conditions in the chlorobenzene/Fe (0) experiments

2.1.1 Head-Space

Head-Space is the space between the solution surface and the top of the flask. Those samples were, therefore, pure gases and were always injected into the GC without changes or additions. Samples from headspace could be useful because some compounds show a linear relation between their concentration in a given solution and their gaseous partial pressure from that solution. Then, by comparing blank solutions with a solutions containing Fe, we might find whether Fe and ClB interact in someway. We assumed that the Peak Area (PA) of a given compound has a linear relation with its partial pressure in the headspace.

A calibration curve was constructed by preparing one single solution and making five dilutions of it. For every concentration test four samples were analyzed, two with metallic iron, Fe, and two without Fe.

Since there is a linear relation between head-space pressure and ClB concentration, Henry’s Law can be used in this case to determine the ClB concentration in water.

From Henry’s Law, \[ P_x = K_x X_x \] (1)

And ideal gas formula, \[ P_x = n_g RT/V \] (2)

The moles of ClB in water can be determined.

\( P_x \), head-space pressure of a particular component in a solution.

\( K_x \), Henry’s constant for the particular component reported in NIST web site, http://webbook.nist.gov with an average value of 0.26 mol kg\(^{-1}\) atm\(^{-1}\).
X, Mol fraction of the particular component in the solution. Since we worked with very
dilute solutions, this factor can be simplified as \( n_s/n_{H2O} \).

\( n_G \), moles of component in the gas phase.

\( R \), ideal gas constant.

\( T \), temperature of experiment.

\( V \), volume where \( n_G \) exists (head-space).

From equations 1 and 2, the moles of some component in solution, \( n_s \), can be found by
developing a new equation,

\[
\begin{align*}
n_s &= n_T/ [1 + (K_x V/RT n_{H2O})] \\
&= n_T/ [1 + n_s V/RT n_{H2O}] \\
&= n_T/ [1 + n_s V/RT n_{H2O}]
\end{align*}
\]

The solution volumes were all 50 mL, taken with volumetric pipet. All samples with Fe
contained 1.00 g of the metal. Only crimped bottles were able to provide reproducible
results. Even more, the tips of the bottles had to be covered with aluminum from inside in
order to avoid CIB absorbtion into the rubber-made tops. Containers were dark-glass
made.

\( 2.1.2 \) Liquid-liquid Extractions

In order to make sure that the chlorobenzenes concentrations determined by using
head-space calibration curves were right, analysis from the solution was also done. We
analyzed the solutions when the CIB concentrations from mixtures with Fe were different
from blanks. Since water cannot be injected into the GC column, all organic compounds
in water had to be extracted by liquid-liquid extraction. Later, in order to be able to
determine the CIB concentration, an internal standard (I.S.) had to be added in the
samples to be analyzed by GC. The I.S. was toluene (Tol). Equations are as follows.
First, the ratio of Chromatographic Peak Areas (PA) for ClB and Tol is determined,

\[ R = \frac{[\text{ClB}]/\text{PA of ClB}}{[\text{Tol}]/\text{PA of Tol}} \]  

Only after getting R, quantifications can be performed,

\[ [\text{ClB}] = \text{PA}_{\text{ClB}} * R * [\text{Tol}]/\text{PA}_{\text{Tol}} \]  

This way of sampling was also useful with GC & Mass Spectrometry.

2.2 Reaction conditions in the dichlorobenzene/Fe (0) experiments

Direct Injection into HPLC. Calibration curves from prepared standards were obtained to monitor the concentration of compounds in the experiments. This technique was able to provide results with 1-5% of uncertainty. Tests for experimental samples were done 2-4 times and 1 for calibration curves unless the R coefficient was small. No head-space was left in these experiments.

In these experiments the initial concentration for each dichlorobenzene isomer was the same as the highest concentration from its respective calibration plot since these solutions came from the same initial standard used to make dilutions and obtain a calibration curve. Blank samples were subject to the same shaking and conditions as those with Fe (0).

2.3 Reaction conditions in the chloronitrobenzene/Fe (0) experiments

Initially, it was the same procedure of section 2.2. After getting products, reaction condition optimization was necessary. The optimum mass ratio of Fe (0) to solution was found to be 0.50 ± 0.01 gFe/gsol (iron mass was half of the aqueous solution) after increasing the mass ratio in different tests. The minimum reaction times to fully reduce
the $\text{x-ClNO}_2\text{B}$ was 20 minutes. In order to study the kinetics of the chloronitrobenzenes reduction, two solutions per each isomer were shaken during 20 minutes and 1 mL samples were extracted from each bottle with polypropylene syringes during certain intervals from 3-5 minutes; these samples were filtered when poured into HPLC vials, closed with septa and analyzed immediately. In order to minimize dilution effects after taking solution samples bigger flasks were used and a same amount of new solution was injected into the flask. The flasks contained 110 ± 2 g of solution.

2.4 Reaction conditions in the chloronitrobenzene/Fe (II) experiments

In order to test the influence of Fe (II) in our experiments, we first had to decide upon a given concentration of Fe (II). With the $0.50 \text{g}_\text{Fe(II)/g}_\text{sol}$ the pH was 9.50. The solubility product of $\text{Fe(OH)}_2$ ($k_{sp}$) is $8 \times 10^{-16}$. A pH 9.5 solution should have a concentration of $8 \times 10^{-7}$ M of Fe (II). Since we do not know the specific composition that might exist in our system, we can only consider $8 \times 10^{-7}$ as a minimum estimate. $10^{-4}$ and $10^{-5}$ M solutions of $\text{FeCl}_2.4\text{H}_2\text{O}$ were used to explore the role of Fe (II).

With the only exception of using Fe (II) instead of Fe (0), everything else was done in the same way as the kinetics experiments of section 2.3.

2.5 Reaction conditions in the chloronitrobenzene/Fe (0)/EDTA experiments

Tests with Fe (0) $0.50 \text{g}_\text{Fe}/\text{g}_\text{sol}$ and EDTA ($5 \times 10^{-3}$ M) were also done. Tratnyek did these same kind of tests with of alkyl chlorides in similar concentration of Fe (II) as ours without results. Nonetheless, they did not work with EDTA and Fe (0) alone (33). Blank tests of chloronitrobenzenes and EDTA were also performed. Everything else was done in the same way as in section 2.3.
III. Results and Discussion

3.1 Results from Chlorobenzene/Fe (0) Reactions

3.1.1 Head-Space Analysis

From table 4 we can see significant differences in ClB concentration after adding Fe (0) into the shaking flasks. Therefore, although no other signals than ClB and solvents were seen during the chromatographic analysis, it is likely that ClB was adsorbed onto Fe since it has a relatively high surface area of 0.31 m²/g. Data are plotted in fig. 1.

Table 4. Results from tests with ClB and 0.02 gFe/gsol in head-space analysis. Shaking time: 3 days.

<table>
<thead>
<tr>
<th>ClB conc, ppm</th>
<th>Signal of Pure ClB</th>
<th>Signal of ClB and Fe</th>
<th>ClB conc.*, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>115.0</td>
<td>141±4</td>
<td>108±6</td>
<td>87</td>
</tr>
<tr>
<td>103.5</td>
<td>129±7</td>
<td>103±6</td>
<td>83</td>
</tr>
<tr>
<td>92.0</td>
<td>117±5</td>
<td>96±7</td>
<td>78</td>
</tr>
<tr>
<td>46.0</td>
<td>57±1</td>
<td>44±1</td>
<td>38</td>
</tr>
<tr>
<td>23.0</td>
<td>23±1</td>
<td>20±2</td>
<td>19</td>
</tr>
<tr>
<td>11.5</td>
<td>21±2</td>
<td>18±1</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R²</td>
<td>0.998</td>
<td>0.999</td>
<td></td>
</tr>
</tbody>
</table>

ClB conc* stands for the ClB concentration in mixtures with Fe and is obtained from the calibration curve with pure ClB. The lowest signal was not included in the linear fit because the plot is not linear at the lowest concentrations, as can be seen in fig. 1 for both pure ClB and mixed with Fe. ClB concentrations in water are already corrected according to Henry's Law.
3.1.2 Results from Liquid-Liquid Extraction

Liquid-liquid extraction (with I.S.) results showed a difference of 10% between initial and final ClB aqueous concentration when mixed with Fe (0) with a solution 115 ppm. No other signal than I.S. and ClB were seen in the chromatographs. These results also indicate probable adsorption of ClB into Fe.

3.2 Results from Dichlorobenzenes/Fe (0) Reactions

Calibration data of the x-Cl2B isomers are plotted in figs. 2-4. The corresponding data is found in table 5. Examples of their HPLC chromatograms are shown in figs. 5-7. The retention times of the dichlorobenzenes were 7.58, 8.80 and 9.77 minutes for ortho, meta and para isomers respectively.

In the test with the x-Cl2B isomers, no other compounds than the original chlorocompounds were detected. The final concentrations of the organocompounds were lower than in their starting concentration which may indicate adsorption onto Fe (0) like with ClB. In table 6 it can be seen than the meta isomer presented a bigger percentage loss than the other two isomers, possibly indicating a higher affinity of the meta isomer for the iron surface.

Table 5. Data from calibration curves for x-Cl2B

<table>
<thead>
<tr>
<th>[o-Cl2B], ppm</th>
<th>Peak Areas (PA)</th>
<th>[m-Cl2B], ppm</th>
<th>Peak Areas (PA)</th>
<th>[p-Cl2B], ppm</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>84.4</td>
<td>657172</td>
<td>46.4</td>
<td>152834</td>
<td>21.4</td>
<td>2490873</td>
</tr>
<tr>
<td>67.5</td>
<td>390763</td>
<td>34.8</td>
<td>119601</td>
<td>32</td>
<td>2876897</td>
</tr>
<tr>
<td>63.3</td>
<td>341847</td>
<td>23.2</td>
<td>64395</td>
<td>42.7</td>
<td>3067475</td>
</tr>
<tr>
<td>56.3</td>
<td>184959</td>
<td>0</td>
<td>0</td>
<td>53.4</td>
<td>3307649</td>
</tr>
<tr>
<td>42.2</td>
<td>66838</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Zero point origin was only used in the calibration of the meta isomer.
Equations and $R$ for each slope:

$$R^2 = 0.980; \ PA = 14361[\text{o-Cl}_2\text{B}] - 572694$$  \hspace{1cm} (6)

$$R^2 = 0.989; \ PA = 3360[\text{m-Cl}_2\text{B}] - 3494$$  \hspace{1cm} (7)

$$R^2 = 0.976; \ PA = 2010989 + 24742[\text{p-Cl}_2\text{B}]$$  \hspace{1cm} (8)

**Table 6.** Changes in dichlorobenzenes concentrations (ppm) in solutions mixed with $0.04174 \pm 0.00174$ g$_{Fe}$/g$_{sol}$ after 3 days of shaking.

<table>
<thead>
<tr>
<th>Samples</th>
<th>[o-Cl$_2$B], start</th>
<th>[o-Cl$_2$B], final</th>
<th>[m-Cl$_2$B], start</th>
<th>[m-Cl$_2$B], final</th>
<th>[p-Cl$_2$B], start</th>
<th>[p-Cl$_2$B], final</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanks</td>
<td>84.4</td>
<td>76.0</td>
<td>58.0</td>
<td>57.1</td>
<td>53.4</td>
<td>51.6</td>
</tr>
<tr>
<td>Fe's</td>
<td>84.4</td>
<td>69.4</td>
<td>58.0</td>
<td>45.2</td>
<td>53.4</td>
<td>49.1</td>
</tr>
</tbody>
</table>

### 3.3 Results from Chloronitrobenzenes/Fe (0) Reactions

#### 3.3.1 Calibration Curves

Similar reactions were carried out with chloronitrobenzenes. These tests did provide products. Table 7 shows data from typical calibration curves. Data are plotted in fig. 8.

Examples of their HPLC chromatograms are shown in figs. 9-11.

**Table 7.** Typical data from calibration curves of x-ClN0$_2$B

<table>
<thead>
<tr>
<th>[Cl$_2$NO$_2$B], ppm</th>
<th>Peak Areas (PA)</th>
<th>[Cl$_3$NO$_2$B], ppm</th>
<th>Peak Areas (PA)</th>
<th>[Cl$_4$NO$_2$B], ppm</th>
<th>Peak Areas (PA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.4</td>
<td>628752</td>
<td>44.8</td>
<td>616597</td>
<td>44.0</td>
<td>342942</td>
</tr>
<tr>
<td>37.8</td>
<td>531903</td>
<td>37.3</td>
<td>488731</td>
<td>36.7</td>
<td>301123</td>
</tr>
<tr>
<td>30.3</td>
<td>376135</td>
<td>29.9</td>
<td>333140</td>
<td>29.3</td>
<td>196305</td>
</tr>
<tr>
<td>22.7</td>
<td>290610</td>
<td>22.4</td>
<td>232376</td>
<td>22.0</td>
<td>167699</td>
</tr>
<tr>
<td>15.1</td>
<td>172914</td>
<td>14.9</td>
<td>143056</td>
<td>7.3</td>
<td>37081</td>
</tr>
<tr>
<td>7.6</td>
<td>68884</td>
<td>7.5</td>
<td>69671</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: Zero point origin could be used for all of the calibrations.

Equations:

$$R^2 = 0.993; \ PA = -27571 + 14237[\text{Cl}_2\text{NO}_2\text{B}]$$  \hspace{1cm} (9)

$$R^2 = 0.978; \ PA = -39361 + 13770[\text{Cl}_3\text{NO}_2\text{B}]$$  \hspace{1cm} (10)

$$R^2 = 0.986; \ PA = -12038 + 8021[\text{Cl}_4\text{NO}_2\text{B}]$$  \hspace{1cm} (11)
Despite that the initial concentrations of x-ClNO2B seemed to be virtually the same (see table 8), the chromatograms of Fe reaction mixtures of each of the x-ClNO2B showed a new and unknown peak (see for example fig 12). That peak was compared with ClB and NO2B, but neither of them could be seen in the chromatograms. It was found that ClB and NO2B could not be seen at 286 or 278 nm, the working absorbances. The new peak did not appear in the blank tests either.

Table 8. Results from solutions of Chloronitrobenzenes (Cl,xNO2B) with 0.04174 ± 0.00174 gFe/gsol after 3 days of shaking:

<table>
<thead>
<tr>
<th>Samples</th>
<th>[x-ClNO2B], ppm</th>
<th>% from original</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanks of Cl,2NO2B</td>
<td>48.2</td>
<td>111.6</td>
</tr>
<tr>
<td>Fe's and Cl,2NO2B</td>
<td>47.2</td>
<td>109.2</td>
</tr>
<tr>
<td>Blanks of Cl,3NO2B</td>
<td>26.9</td>
<td>84.6</td>
</tr>
<tr>
<td>Fe's and Cl,3NO2B</td>
<td>25.1</td>
<td>78.9</td>
</tr>
<tr>
<td>Blanks of Cl,4NO2B</td>
<td>41.1</td>
<td>99.7</td>
</tr>
<tr>
<td>Fe's and Cl,4NO2B</td>
<td>38.7</td>
<td>93.9</td>
</tr>
</tbody>
</table>

3.3.2 Product Analysis of x-Chloronitrobenzene Reactions

Comparisons in HPLC and GC

Since our references mentioned reduction of the nitro groups to amines in chloroaromatic compounds (30, 31, 32), we compared the properties of amines, ClNO2B and ClNO2B products in GC (see table 9) and HPLC (see table 10). Conditions were optimized to enhance product formation whereupon all ClNO2B disappear from solution. Both tables, 9 and 10, show the statistically equal retention times for the chloronitrobenzene products and the corresponding chloroanilines that should be produced from each chloronitrobenzene. Differences were a bit bigger in GC, but the slight tendencies were of the para isomer to elute a little after the meta isomer were present in both amines and chloronitrobenzene products.
Table 9. Gas chromatography retention times for x-CINO2B products and x-CIAmines

<table>
<thead>
<tr>
<th>ChloroAmine isomer</th>
<th>ChloronitroBenzene isomer products with Fe (0)</th>
<th>Boiling Point, °C</th>
<th>Retent’ Time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomer</td>
<td>Ortho</td>
<td>Meta</td>
<td>Para</td>
</tr>
<tr>
<td>Ortho</td>
<td>209 ± 1</td>
<td>60 ± 1</td>
<td>60 ± 1</td>
</tr>
<tr>
<td>Meta</td>
<td>231 ± 3</td>
<td>71 ± 3</td>
<td>73 ± 3</td>
</tr>
<tr>
<td>Para</td>
<td>232 ± 2</td>
<td>73 ± 2</td>
<td>74 ± 2</td>
</tr>
</tbody>
</table>

Oven temp: 150°C. x-CINO2B products extracted with CH₂Cl₂. Retention (Retent’) times for ortho, meta and para CINO2B were 86, 82 and 84 sec. respectively, with boiling points 245, 236 and 242 °C in the same order. Number of tests, 5.

Table 10. HPLC retention times for x-CINO2Bs, products and x-CIAmines at 286 nm

<table>
<thead>
<tr>
<th>ChloroAmine Compounds</th>
<th>ChloronitroBenzene Compounds</th>
<th>ChloronitroBenzene Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomer</td>
<td>Retent’ Time, min</td>
<td>Isomer Retent’ Time, min</td>
</tr>
<tr>
<td>Ortho</td>
<td>4.11 ± 0.02</td>
<td>Ortho 5.99</td>
</tr>
<tr>
<td>Meta</td>
<td>3.50 ± 0.02</td>
<td>Meta 7.53</td>
</tr>
<tr>
<td>Para</td>
<td>3.53 ± 0.01</td>
<td>Para 8.33</td>
</tr>
</tbody>
</table>

Mass Spectra Analysis

Since CINO2B products seemed to convert into chloroanilines, we proceeded to confirm the structure of the products by Mass Spectrometry (MS). Nitrobenzene (NO2B) was included in the tests. Liquid-liquid extractions were done with 5 mL of CH₂Cl₂ from 50 mL of samples from reaction solutions and were analyzed by GC-MS. Their gas chromatographs are presented in figures 13-16. It was decided to obtain gas chromatograms from samples shaken for 6 minutes with Fe (0) because it is only at short times when intermediates can be seen. The products of the nitrocompounds turned out to be the respective chloroanilines for each isomer and aniline (figs. 17-20). Moreover, reaction intermediates mentioned by Agrawal and Tratnyek with nitroso (figs. 21-23) and azo (figs. 24-27) groups were detected in very small amounts as was expected from those not very stable compounds. The nitroso intermediate from nitrobenzene was not found.

The gas chromatograms of the three chloronitrobenzene products show two peaks at about the same times (12.9 and 10.9 min). The computer library identified one of these
(from the meta isomer products, eluted at 12.9 min) peaks as hexamethyl cyclotrisiloxane with main peaks at 149 and 207. The spectra of the other peaks are similar to this one and also have main peaks at 149 and 207, but the computer library could only identify them as dicarboxilic acids. The Nitrobenzene chromatograph showed these same 149 peaks at 7.5 and 8.3 min. We thought these two peaks must be artifacts or impurities of the column.

### 3.3.3 The pH of Reactions and Solutions

Since the pH of water and Fe (0) alone is basic (9.50), there had to be a thin hydroxide layer over its surface. Devlin (31) found that the hydroxide layer on the surface of their Master Builder’s iron had little effect on the reaction rates of nitroaromatic compounds at a starting and final pH 10, close to ours. However, at Devlin’s tests the pH was previously set and the basic water solution was constantly renewed (not buffered), which means that the hydroxide layer in their experiments should have been thicker than in our Fe (0). This may be the reason why their reactions were slower than ours (4 hours total).

We also measured the pH of the chloronitrobenzene solutions and product solutions. The product solutions pH values were compared to standard chloroaniline solution pH values. These chloroanilines were prepared in concentrations equivalent to the expected concentrations from the complete reduction of their respective parent compounds, the chloronitrobenzenes. The results are given in table 11. Note that all pH values are basic, confirming that some hydroxide layer would have most likely been present on the iron surface.
Table 11. Aqueous solutions pH. Water and 0.50 \( \text{g Fe/g H}_2\text{O} \) had a pH of 9.50

<table>
<thead>
<tr>
<th>Cl-Nitro Isomer</th>
<th>pH</th>
<th>pH of isomer product solution</th>
<th>Cl-Aniline isomer solution</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho, 43.2 ppm</td>
<td>8.55</td>
<td>9.33</td>
<td>Ortho, 31.2 ppm</td>
<td>9.44</td>
</tr>
<tr>
<td>Meta, 31.8 ppm</td>
<td>8.30</td>
<td>9.37</td>
<td>Meta, 23.0 ppm</td>
<td>9.26</td>
</tr>
<tr>
<td>Para, 41.2 ppm</td>
<td>8.50</td>
<td>9.74</td>
<td>Para, 29.8 ppm</td>
<td>9.70</td>
</tr>
</tbody>
</table>

Notes: It was found that 0.50 \( \text{g Fe/g H}_2\text{O} \) fully reduces the chloronitrobenzenes below 50 ppm. The aqueous solutions of chloroanilines did not contain Fe (0).

3.3.4 Kinetic Analysis

The progress of the reactions with time is presented in table 12 and illustrated in fig. 28. All of these compounds showed the same pseudo-first order kinetic pattern (fig. 29), with the exception of m-chloronitrobenzene which showed 2\( ^{nd} \) order kinetics (fig. 30). The half-lifes for the ortho and para isomers and NO2B are 5.0, 7.0 and 4.9 minutes respectively as calculated from the equations for first order kinetics. For the meta isomer, its half-life time was 3.1 minutes from the equation for second order kinetics.

Table 12. Data from kinetics studies. Two flasks analyzed per each compound. 0.50 ± 0.01 \( \text{g Fe/g H}_2\text{O} \)

<table>
<thead>
<tr>
<th>Time, min</th>
<th>[NO2B], ppm</th>
<th>[o-CINO2B], ppm</th>
<th>[m-CINO2B], ppm</th>
<th>[p-CINO2B], ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33.6 ± 0.5</td>
<td>45.9 ± 0.2</td>
<td>48.1 ± 0.8</td>
<td>44.3 ± 1.2</td>
</tr>
<tr>
<td>3</td>
<td>22.0 ± 1.6</td>
<td>28.3 ± 2.1</td>
<td>19.9 ± 5.7</td>
<td>23.4 ± 6.1</td>
</tr>
<tr>
<td>8</td>
<td>10.9 ± 2.0</td>
<td>15.4 ± 2.1</td>
<td>11.6 ± 1.4</td>
<td>16.8 ± 7.4</td>
</tr>
<tr>
<td>12</td>
<td>6.2 ± 1.0</td>
<td>9.6 ± 3.3</td>
<td>9.1 ± 0.8</td>
<td>12.0 ± 6.1</td>
</tr>
<tr>
<td>16</td>
<td>0 ± 0</td>
<td>3.6 ± 0.6</td>
<td>7.2 ± 0.9</td>
<td>7.9 ± 3.3</td>
</tr>
<tr>
<td>20</td>
<td>0 ± 0</td>
<td>3.3 ± 0.1</td>
<td>6.3 ± 0.2</td>
<td>0 ± 0</td>
</tr>
</tbody>
</table>

These are the rate equations of the nitroaromatic compounds:

\[
\ln[\text{NO2B}] = (3.514 ± 0.001) - [(\text{min.}) (0.141 ± 0.010)],
\]  \( \text{(12)} \)
\[
\ln[o-\text{ClNO2B}] = (3.802 \pm 0.131) - [(\text{min.})(0.139 \pm 0.011)] \quad (13)
\]
\[
\ln[p-\text{ClNO2B}] = (3.638 \pm 0.107) - [(\text{min.})(0.099 \pm 0.011)] \quad (14)
\]
\[
1/[m-\text{ClNO2B}] = (0.02688 \pm 0.00350) + [(\text{min})0.0068 \pm 0.0003] \quad (15)
\]

Equations 12-15 show pseudo-first order rate constants to be 0.141 \pm 0.010, 0.139 \pm 0.011 and 0.099 \pm 0.011 min\(^{-1}\) for NO2B, o-ClNO2B and p-ClNO2B. The meta isomer presented a second order rate constant of 0.0068 \pm 0.0003 ppm\(^{-1}\) min\(^{-1}\).

In order to verify that our models are properly assigned we also present graphs of the NO2B, o-ClNO2B and p-ClNO2B according to the second order kinetics model (fig. 31) and of the meta isomer according to first order kinetics (fig. 32). These figures confirm the pseudo first order character of the NO2B, ortho and para-ClNO2B reactions and the 2\(^{nd}\) order character of the meta isomer. Besides plots 31 and 32, we also present the \(R^2\) coefficients of both models for each isomer reaction in table 13 as further support of our assignments of the kinetic models for each nitroaromatic compound.

**Table 13.** \(R^2\) coefficients of the nitroaromatic compounds reactions with Fe (0) according to first and second order analyses.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(R^2) from 1(^{st}) order</th>
<th>(R^2) from 2(^{nd}) order</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO2Benzene</td>
<td>0.999</td>
<td>0.953</td>
</tr>
<tr>
<td>o-ClNO2Benzene</td>
<td>0.976</td>
<td>0.874</td>
</tr>
<tr>
<td>p-ClNO2Benzene</td>
<td>0.965</td>
<td>0.955</td>
</tr>
<tr>
<td>m-ClNO2Benzene</td>
<td>0.879</td>
<td>0.993</td>
</tr>
</tbody>
</table>

**3.3.5 Mechanism of Reaction**

The concentration of products were 25 \(\pm\) 10 % less than what was expected from calculated during the analyses, but tended to approach the expected 100% yield as time continued. Results are plotted in figs 33-35. During the initial tests that lasted three days, the chloroaniline concentration did correspond to 100% yield from the starting material.
Then, the loss shown in these 20 min. tests must be due to the formation of the nitroso and azo intermediates. We propose a reaction sequence similar to one of the possible mechanisms proposed by Tratnyek; these results confirm a specific route that we propose. The group \( Ar \) stands for any of the isomers rings and from nitrobenzene.

\[
\begin{align*}
\text{ArNO}_2 + \text{Fe (0)} & \leftrightarrow \text{Fe} - \text{ArNO}_2 \quad \text{(adsorption)} \\
2 \text{ArNO}_2 + 2 \text{Fe (0)} + 4 \text{H}^+ & \rightarrow 2 \text{ArNO} + 2 \text{Fe (II)} + 2 \text{H}_2\text{O} \\
2 \text{ArNO} + 2 \text{Fe (0)} + 4 \text{H}^+ & \rightarrow 2 \text{ArNHOH} + 2 \text{Fe (II)} \\
2 \text{ArNHOH} & \rightarrow \text{Ar} - \text{N}^+ = \text{N} - \text{Ar} + \text{H}_2\text{O} + \text{H}_2 \\
\text{Ar} - \text{N}^+ = \text{N} - \text{Ar} + \text{Fe (0)} + 2 \text{H}^+ & \rightarrow \text{Ar} - \text{N} = \text{N} - \text{Ar} + \text{Fe (II)} + \text{H}_2\text{O} \\
\text{Ar} - \text{N} = \text{N} - \text{Ar} + \text{Fe (0)} + 2 \text{H}^+ & \rightarrow \text{Ar} - \text{N} - \text{N} - \text{Ar} + \text{Fe (II)} \\
\text{Ar} - \text{N} - \text{N} - \text{Ar} + \text{Fe (0)} + 2 \text{H}^+ & \rightarrow 2 \text{ArNH}_2 + \text{Fe (II)} \\
2 \text{ArNO}_2 + 7 \text{Fe (0)} + 14 \text{H}^+ & \rightarrow 2 \text{ArNH}_2 + 7 \text{Fe (II)} + 4 \text{H}_2\text{O} + \text{H}_2
\end{align*}
\]

Since the kinetics for the nitroaromatics compounds were pseudo-first order, excluding the meta isomer, we could think that the first or second step in the proposed
sequence of reactions are the rate limiting. In the first steps we can see the reactions with only one molecule of iron and nitroaromatic compound.

For the reaction of the meta isomer, we can think that it is the fourth step the rate limiting. If the first three reactions are relatively fast, this could be the rate limiting step:

\[
2 \text{ArNHOH} \rightarrow \text{Ar} - \text{N}^+ (O') = \text{N} - \text{Ar} + \text{H}_2\text{O} + \text{H}_2
\]

If the first three reactions are relatively fast and in equilibrium, the concentration of ArNHOH could be equivalent to that of ArNO\textsubscript{2}. Then, this could be the reaction rate equation.

\[
\text{Rate} = [\text{ArNO}_2]^2 k_f \quad (16)
\]

It is possible that the combination of the two ArNHOH molecules occurs on the iron surface and this might explain why kinetics for the meta isomer were different from all the other compounds. This phenomenon may be explained with the models from Kastening and Holleck, who performed reductions of nitroaromatic compounds with iron by polarography (34), proposed that nitroaromatic compounds arrange themselves in two forms towards the Fe (0) surface: parallel to the surface in order to take electrons from Fe (0) and perpendicular to it to accept protons from water. Moreover, they considered that the reactive sites of iron were holes open enough that the organic molecules could land either parallel or perpendicular to the bottom of the hole. It might be difficult when the molecules have to stand up in the second step to accept protons; the ring has only one atom (chlorine or hydrogen) to be held in that moment. Another group in the meta position should help when holding the molecule in this second step, making the affinity of the meta isomer with the Fe (0) surface quite stable.
3.4 Results from Chloronitrobenzenes/Fe (II) Reactions

We did not find Fe (II) reacting at all with any of the nitroaromatic compounds after 8 minutes. This indicated that Fe (II) did not reduce the nitroaromatic compounds.

3.5 Results from Chloronitrobenzenes/Fe (0)/EDTA Reactions

The tests with EDTA and Fe (0), however, did make a difference. All reactions were much faster. NO2B, m-ClNO2B and p-ClNO2B disappeared in 8 minutes and o-ClNO2B in 3 minutes. Again, we worked with two flasks per compounds. By adding EDTA, the pH dropped from 9.50 to 8.15. A EDTA 5 x 10^{-3} M solution has pH 4.50. The problem is that the reproducibility of measurements was as bad as 50% in the three minutes measurement. The reactions conditions were difficult to control. It seems that EDTA cleaned the Fe surface from ions that inhibited reactions.

3.6 Influence of the Mass Transport

The rate constant for NO2B, ortho and para ClNO2B may reflect mass transport rates, rather than kinetic rates. The movement of these molecules to the surface depends upon the concentration gradient. The mass transport limited rate expression is

\[
\text{Rate} = D([\text{ArNO}_2]_{\text{Bulk}} - [\text{ArNO}_2]_{\text{Surface}}) \quad \text{or} \quad \text{Rate} = D[\text{ArNO}_2]_{\text{Bulk}} \quad \text{when} \quad [\text{ArNO}_2]_{\text{Surface}} \quad \text{is small. Note that this is the same form as the first order chemical rate expression. The second order kinetics for the meta isomer, however suggest that for this isomer, at least, the reaction is not mass transport limited. If all isomers have similar diffusion constants, nevertheless, then what we observed and report are indeed chemical rate constants.} \]
The rate limiting step for m-ClNO2B should occur after the molecules have been adsorbed over iron and the reduction sequence has started. Other possible evidences for our model is that the overall reduction of m-ClNO2B is slower than any of the other compounds, in spite that it has the shortest half-life, as should be. The other compounds had only one slow step at the beginning of their reduction sequences. The meta isomer underwent that same step and still one more in the coupling reaction which may be its rate limiting step. After 20 minutes, the concentration of m-ClNO2B was still twice that of o-ClNO2B and the other compounds had already been completely reduced.

As for other influences, we see in section 1.3.1 that the pH does not have a clear effect in these reactions. The influence of speed of shaking could not be studied because of our instrumentation could only shake by vibrating the samples at one frequency.

3.7 General Discussion

Taking into account that Fe (II) did not react with any of the nitroaromatic compounds and that Fe (0) reacted faster with EDTA, it seems that the hydroxide layer of Fe (II) or Fe (III) acts as an inhibitor by hindering the reactive sites of the Fe (0) surface.

Our reactions were faster than Tratnyek and Agrawal mainly because of two reasons: (1) The surface area of our iron (0.331 m²/g) was almost ten times than that from them (0.038 m²/g) (2) We used more iron (0.5 gFe(0)/gsoI) than them(0.03 gFe(0)/gsoI). The normalized rate of reaction was much slower. For example, if we normalize our rate constant of nitrobenzene by dividing the pseudo-first order rate constant (0.1408 m⁻¹) by the average Fe (0) surface area in our mixtures (182 m²/L), we get a constant of 7.7 x 10⁻⁴.
Lm$^{-2}$ s$^{-1}$, much lower than theirs ($2.8 \times 10^{-2}$ Lm$^{-2}$ s$^{-1}$). This same comparison should be done with the tests of Devlin, but they did not report reaction rates.

**Conclusions**

Fe (0) does not reduce CIB and x-Cl2B isomers, but they seem to adsorb because these compounds presented losses of approximately 10%. The m-Cl2B isomer presented a loss of 23% from its initial concentration. It is possible that they bond in specific ways to the Fe (0) surface.

The iron (0) surface is the main factor in the reaction reduction rate of NO2B, and the x-NO2B. This surface interacts in the same way with these nitroaromatic compounds, with the exception of the meta isomer which showed a second order kinetics. All the other compounds showed pseudo-first order kinetics. These reactions go through many steps that involve the nitroso and azo intermediates.
Figure 1. Comparison of chlorobenzene head-space signals with and without Fe (0).
Figure 2. Calibration Curve for o-dichlorobenzene at 220 nm.
Figure 3. Calibration Curve for m-dichlorobenzene at 220 nm.
Figure 4. Calibration Curve for p-dichlorobenzene at 220 nm.
Figure 5. HPLC Chromatograph of o-dichlorobenzene in water, 35.0 ppm.
Figure 6. HPLC Chromatograph of m-dichlorobenzene in H₂O, 34.8 ppm
Figure 7. HPLC Chromatograph of p-dichlorobenzene in H₂O, 11.4 ppm
Figure 8. Typical calibration curves for chloronitrobenzenes at 286 nm for the ortho and para isomers and 278 nm for the meta isomer.
Figure 9. HPLC Chromatograph of o-chloronitrobenzene in H₂O, 46 ppm
Figure 10. HPLC Chromatograph of m-chloronitrobenzene in H₂O, 48 ppm
Figure 11. HPLC Chromatograph of p-chloronitrobenzene in H₂O, 44 ppm
Figure 12. HPLC chromatograph of o-chloronitrobenzene (at 5.95 min) and its product o-chloroaniline (at 4.24 min) from reaction with Fe(0) 0.50 gFe/gsol
Figure 13. Gas chromatogram from the reaction of nitrobenzene with Fe (0) 0.50 gFe/gsol after 6 minutes. Aniline eluted at 3.6 min and azobenzene at 8.6 min. Other peaks are column impurities (see Mass Spectra Analysis)
Figure 14. Gas chromatogram from the reaction of o-chloronitrobenzene with Fe (0) 0.50 g$_{Fe}$/g$_{sol}$ after 6 minutes. o-chloroaniline eluted at 7.7 min, nitroso intermediate at 7.1 min and azobenzene at 13.3 min. Other peaks are column impurities (see Mass Spectra Analysis)
Figure 15. Gas chromatogram from the reaction of m-chloronitrobenzene with Fe (0) 0.50 gFe/gsol after 6 minutes. m-chloroaniline eluted at 8.2 min, nitroso intermediate at 6.4 min and azobenzene at 13.2 min. Other peaks are column impurities (see Mass Spectra Analysis)
Figure 16. Gas chromatogram from the reaction of p-chloronitrobenzene with Fe (0) 0.50 g_{Fe}/g_{sol} after 6 minutes. p-chloroaniline eluted at 8.2 min, nitroso intermediate at 6.4 min and azobenzene at 13.2 min. Other peaks are column impurities (see Mass Spectra Analysis)
Figure 17. MS spectra of aniline, the nitrobenzene reaction product with Fe(0)
Figure 18. MS spectra of o-chloroaniline the o-chloronitrobenzene reaction product with Fe(0).
Figure 19. MS spectra of m-chloroaniline, the m-chloronitrobenzene reaction product with Fe(0).
Figure 20. MS spectra of p-chloroaniline, the p-chloronitrobenzene reaction product with Fe(0).
Figure 21. MS spectra of the nitroso intermediate of o-chloronitrobenzene reaction with Fe(0).
Figure 22. MS spectra of the nitroso intermediate of m-chloronitrobenzene reaction with Fe(0).
Figure 23. MS spectra of the p-chloronitrobenzene nitroso reaction intermediate with Fe(0).
Figure 24. MS spectra of the azo intermediate of the nitrobenzene reaction with Fe(0).
Figure 25. MS spectra of the azo intermediate of the o-chloronitrobenzene reaction with Fe(0).
Figure 26. MS spectra of the azo intermediate of the m-chloronitrobenzene reaction with Fe(0).
Figure 27. MS spectra of the azo intermediate of the p-chloronitrobenzene reaction with Fe(0).
Figure 28. Reduction rates of chloronitrobenzenes and nitrobenzene with Fe (0) 0.50 ± 0.01 g Fe/g sol
Figure 29. Pseudo-first order disappearance of nitrobenzene and ortho and para chloronitrobenzene when reacting with Fe (0) 0.50 ± 0.01 gFe/gsol
Figure 30. Second-order disappearance of m-chloronitrobenzene when reacting with Fe (0) 0.50 ± 0.01 g_{Fe}/g_{sol}
Figure 31. Disappearance of nitrobenzene and ortho and para chloronitrobenzene when reacting with Fe (0) 0.50 ± 0.01 g_{Fe}/g_{sol} according to second order kinetic model.
Figure 32. Disappearance of m-chloronitrobenzene when reacting with Fe (0) 0.50 ± 0.01 g_Fe/g_sol according to pseudo-first order kinetic model.
Figure 33. Product formation of o-ClNO2Benzene reaction with 0.50 ± 0.01 gFe/gsol.

Figure 34. Product formation of m-ClNO2Benzene reaction with 0.50 ± 0.01 gFe/gsol.
Figure 35. Product of p-ClNO2Benzene reaction with 0.50 ± 0.01 g_Fe/g_sol
References


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