Reduction of CCl_4 by Iron Powder in Aqueous Solution

Irena Rusonik,[a] Haim Cohen,[a,b] and Dan Meyerstein*[a,b]

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$^{\cdot}CCl_3$ radicals formed in the first step of the CCl_4 degradation react with iron powder to form an intermediate with an Fe–C σ bond. In the absence of iron powder, $^{\cdot}CCl_3$ radicals formed by γ-irradiation react with 2-propanol in a chain reaction toward dechlorination. When the irradiated solution contains iron powder, the iron scavenges the $^{\cdot}CCl_3$ radicals, thus inhibiting the chain reaction. The minor product of the dechlorination of CCl_4 by iron powder in aqueous solution is CH_4, contrary to the results reported in the literature for the electrochemical reduction of CCl_4 on iron electrodes.

Introduction

The widespread use of chlorinated solvents in commerce has led to considerable groundwater contamination. Halocarbons, including carbon tetrachloride, have a cumulative toxicity and are carcinogenic. Research on the biological degradation of carbon tetrachloride has received much attention.[1,2] Nevertheless, the microbial degradation of CCl_4 can be relatively slow[3] and may be inhibited by the toxicity of CCl_4.

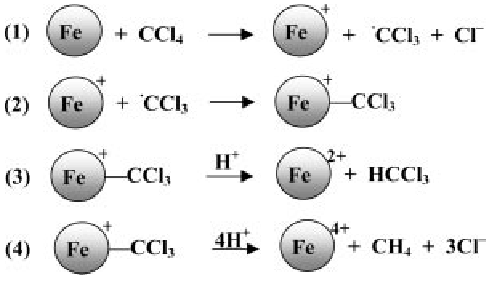
Many recent studies have focused on the abiotic transformation of CCl_4[4,5] and other ground-water pollutants[6,7] by naturally occurring soil minerals such as iron sulfide (FeS). This weak reducing agent reacts slowly with some halo-aliphatic compounds.[8] However, the mechanism of the process has not been elucidated.[8] Consequently, abiotic reductive dechlorination with reduced metals has received increased attention. The use of zero-valent metals has been an active research area[9–11], and most efforts have been concentrated on iron because of the success encountered with iron subsurface permeable walls[12] and the acceptance of zero-valent iron as being safe for the environment. The results indicate that significant CCl_4 reduction occurred at pits rather than on the passive oxide film on the metal.[13] Least-oxidized Fe^0 is the most reactive in CCl_4 degradation.[14]

The combination of ultrasound and Fe^0 has a positive synergistic effect on the dehalogenation of CCl_4. A mechanism involving the formation of $^{\cdot}CCl_3$ radicals was proposed.[15]

The electrochemical reduction of CCl_4 on Fe^0 electrodes was reported to yield CH_4 directly without the formation of $CHCl_3$, CH_2Cl_2, and CH_3Cl as intermediates,[16] though the latter compounds are reduced slower than CCl_4 by the Fe^0 electrode.[9,17–19] Iron is a reasonably strong reducing agent, thus it is not surprising that iron powder can reduce chloro-organic compounds.[20] Therefore it was of interest to investigate the mechanism of the dechlorination reaction of CCl_4 by iron powder, as this method is economically preferable to the electrochemical one.

Results and Discussion

The mechanism proposed to explain the latter results, involves the formation of carbenes.[16] However, this mechanism seems to be too complicated, and alternative simpler mechanisms can be proposed. In principle, the following mechanism is proposed (Scheme 1).



Scheme 1. Plausible mechanism of reduction of CCl_4 by iron powder immersed in aqueous solution.

The first reaction in this scheme is identical to that proposed in the literature.[16] However the second one is different; it is proposed that the radical formed in the first reaction, that is, the one near the iron surface, reacts with the resultant **1^+** particle to form an intermediate having an Fe–C σ bond, that is, a $–CCl_3$ bound to the iron powder.

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[a] Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel
[b] Department of Biological Chemistry, College of Judea and Samaria,
Ariel, Israel
Fax: +972-3-906-7440
E-mail: danmeyer@bgumail.bgu.ac.il

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Fe powder particles

Analogous transients are formed in the fast reaction of Fe^0 powder with CH_3.[21] The intermediate **1^+–CCl_3** thus formed might decompose by two alternative mechanisms:

1. Heterolysis of the Fe–C bond, reaction (3), as observed[21] for **1^+–CH_3**.
2. The iron particle can be considered as a microelectrode that can supply many electrons, which can reduce the $–CCl_3$ substituent directly to form methane, reaction (4).

In order to check the relative contribution of reactions (3) and (4) it was decided to study the reaction of $^{\cdot}CCl_3$ radicals with iron powder and measure the relative yields of $Cl^–$ and CH_4. The radicals were formed by γ-irradiating an aqueous solution containing CCl_4 (0.01 м) and 2-propanol (2.6 м). This solution was placed between the grains of iron powder.

$^{\cdot}CCl_3$ radicals formed in the first step of the CCl_4 degradation might react by two pathways:

1. Initiate a chain reaction by hydrogen abstraction from 2-propanol.[22–24]

$$^{\cdot}CCl_3 + HC(CH_3)_2OH \rightarrow HCCl_3 + {}^{\cdot}C(CH_3)_2OH$$
$$^{\cdot}C(CH_3)_2OH + CCl_4 \rightarrow C(CH_3)_2O + {}^{\cdot}CCl_3 + Cl^- + H_3O^+$$

2. React with the iron powder surface to form $CHCl_3$ or directly CH_4, as proposed in Scheme 1.

Therefore, dehalogenation of CCl_4 was investigated in three different systems (Table 1). Two of them contained iron powder and an aqueous solution containing CCl_4 and 2-propanol. One of these samples was irradiated, and the second served as a thermal blank. The light alkanes formed in the latter samples are due to traces of carbon in the analytical iron.[21] The main idea was to study the reaction of $^{\cdot}CCl_3$ radicals with the iron powder, where, in the nonirradiated system, the source of radicals is the dehalogenation process, and in the irradiated system, $^{\cdot}CCl_3$ radicals are derived from γ-irradiation in addition to the dehalogenation process. The third system contained the aqueous solution of CCl_4 and 2-propanol in the absence of iron powder and was irradiated. The latter blank system contributes to the investigation of the reaction of $^{\cdot}CCl_3$ radicals with 2-propanol in aqueous solution. The results of this blank experiment clearly demonstrate (Table 1) that indeed the chain process occurs, as the yield of $Cl^–$ is $G \sim 50–60$, even though the total primary radical yield is $G(\text{radicals}) \sim 6$.[25] G is defined as the number of molecules of each product per 100 eV of radiation absorbed by the solution. When the same solution is brought in contact with the iron powder, the yield of methane is approximately 1% of the $Cl^–$ yield (Table 1). This result clearly demonstrates that CH_4 is not the major product of the thermal dechlorination reaction and suggests that this process involves reactions (1), (2), and (3) in Scheme 1. This result clearly differs from that reported for the reduction of CCl_4 on Fe^0 electrodes.[16]

When the solution is irradiated in contact with the iron powder, the results (Table 1) point out that the $Cl^–$ yield is considerably smaller than the sum of the two blank experiments. The irradiation of the Fe^0-containing system adds only about 3×10^{-4} м to the $Cl^–$ yield when compared to the

Table 1. The relative yields of the organic gases and $Cl^–$ formed in the reduction of CCl_4 (radiation 3.3 Gy/min, 120 min).

[a]

Sample	Radiation	CH_4 [ppm]	CH_4[d] [м]	C_2H_4 [ppm]	C_2H_6 [ppm]	C_3H_6 [ppm]	C_3H_8 [ppm]	Cl^-[d] [м]	G
Fe^0(activ.), CCl_4, 2-propanol	+	143	2.0×10^{-5}	7.2	6.4	21.7	8.9	1.9×10^{-3}	–
Fe^0(activ.), CCl_4, 2-propanol	–	110	1.5×10^{-5}	5.2	4	10	3.4	1.6×10^{-3}	–
CCl_4, 2-propanol	+	80.6	1.1×10^{-5}	–	1.5	6.6	–	2.2×10^{-3}	55.6

[b]

Sample	Radiation	CH_4 [ppm]	CH_4[d] [м]	C_2H_4 [ppm]	C_2H_6 [ppm]	C_3H_6 [ppm]	C_3H_8 [ppm]	Cl^-[d] [м]	G
Fe^0(activ.), CCl_4, 2-propanol	+	127	1.8×10^{-5}	7	8	24	8.9	1.7×10^{-3}	–
Fe^0(activ.), CCl_4, 2-propanol	–	91.9	1.3×10^{-5}	6.4	5.9	4	3	1.3×10^{-3}	–
CCl_4, 2-propanol	+	64.3	9.0×10^{-6}	–	1	4.2	–	2.0×10^{-3}	50.5

[c]

Sample	Radiation	CH_4 [ppm]	CH_4[d] [м]	C_2H_4 [ppm]	C_2H_6 [ppm]	C_3H_6 [ppm]	C_3H_8 [ppm]	Cl^-[d] [м]	G
Fe^0(activ.), CCl_4, 2-propanol	+	184	2.6×10^{-5}	8.9	8.5	21.6	12	2.3×10^{-3}	–
Fe^0(activ.), CCl_4, 2-propanol	–	110.4	1.5×10^{-5}	7.4	7.4	5.6	7.5	2.0×10^{-3}	–
CCl_4, 2-propanol	+	69.5	9.7×10^{-6}	–	1.2	11	1.6	2.6×10^{-3}	65.7

[a] Activated Fe^0 powder (10 g), solution (2.5 mL) containing CCl_4 (0.01 м) and 2-propanol (2.6 м), phosphate buffer (0.01 м, pH 7.0), He sat., t = 3 h. [b] Activated Fe^0 powder (10 g), solution (2.5 mL) containing CCl_4 (0.01 м) and 2-propanol (2.6 м), phosphate buffer (0.01 м, pH 3.0), He sat., t = 3 h. [c] Activated Fe^0 powder (10 g), solution (2.5 mL) containing CCl_4 (0.01 м) and 2-propanol (2.6 м, pH 7.0), He sat., t = 3 h. [d] Error limit ±15%.

nonirradiated sample, that is, $G(Cl^-)$ under these conditions is $G(Cl^-) = 7.6$. This result clearly demonstrates that the Fe^0 powder scavenges the $^{\cdot}CCl_3$ and partially the $^{\cdot}C(CH_3)_2OH$ radicals, thus inhibiting the chain reaction. Also under these conditions where $G(^{\cdot}CCl_3) \geq 2.5$, as all the e^-_{aq} is expected to react with CCl_4, $G(CH_4) \leq 2\%$ of $G(Cl^-)$. This result clearly proves that reaction (4) in Scheme 1 is at most a side reaction in the process, and that reaction (3) is the major pathway.

The results are pH-independent in the range pH 3–7 (Table 1). Therefore, it was decided to omit the phosphate buffer from the solution. This action slightly increased the radiolytic yield of Cl^-. This result suggests that one of the reactions,

$$^{\cdot}C(CH_3)_2OH + H_2PO_4^- \rightarrow (CH_3)_2CHOH + HPO_4^{\cdot-}$$

$$^{\cdot}CCl_3 + H_2PO_4^- \rightarrow HCCl_3 + HPO_4^{\cdot-}$$

probably the latter, shortens the chain reaction. The effect of phosphate on the reduction of CCl_4 by Fe^0 is probably due to the precipitation of $Fe_3(PO_4)_2$ or $Fe(PO_4)$ on the surface of the iron particles, which decreases their activity.[21]

Finally it is suggested that, in the electrochemical reduction of CCl_4[16] on Fe^0, the potential of the cathode was negative enough to reduce the $-CCl_3$ groups bound to the surface by reaction (4). The redox potential of the iron particle is smaller; therefore $CHCl_3$ is obtained as the main product of the reduction of CCl_4 by the iron powder. This conclusion is highly complementary to the early studies of the reductive dehalogenation of CCl_4 by elementary iron.[9]

Experimental Section

The metal powder used in this study was Fe^0 powder Merck 99%, ≤10 µm. The solution was deaerated by bubbling He through it for 15 min by the syringe technique. The solution (2.5 mL) was then added over 2 min to a glass bulb (15 mL) sealed with a rubber septum and containing the Fe^0 powder (10 g), which was previously activated by H_2SO_4 (0.1 M), and then washed with water (7–8×8 mL). The bulb was also deaerated with He prior to the injection of the solution. Some of the samples were irradiated for 2 h in a ^{60}Co γ source with a dose rate of 3.3 Gy/min, within a 3-h reaction time span. After 3 h of reaction, the gas phase above the metal was analyzed with an HP 5890 GC fitted with an FID detector [Porapak QS GC column, 10 ft, 1/8 in; He (30 mL/min), T = 70 °C]. Concentrations of chloride ions were analyzed by a colorimetric method.[26]

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