Hydrocarbon Formation in Metallic Iron/Water Systems

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Chlorinated ethenes can be reduced in metallic (zero-valent) iron/water systems to produce a suite of non-chlorinated hydrocarbons. When ^{13}C-labeled trichloroethylene is reduced, ^{13}C-labeled hydrocarbons are produced. In the absence of chlorinated ethenes, however, lower concentrations of many of the same hydrocarbons (methane and C_2-C_6 alkanes and alkenes) are also produced. Hardy and Gillham (1996) proposed that these background hydrocarbons were due to the reduction of aqueous CO_2 by metallic iron. In the present study, we examined the production of these hydrocarbons by various batch experiments. Several of the systems examined produced hydrocarbons in excess of the carbon available from aqueous CO_2. In addition, carbon from aqueous ^{13}C-labeled CO_2 was not incorporated into the hydrocarbons produced. The reduction of aqueous CO_2 was not a major source of carbon for the background hydrocarbons. Acid dissolution of gray cast irons containing both carbide and graphite carbon yielded hydrocarbons and a substantial amount of graphite residual. The dissolution of metallic irons containing only carbide carbon yielded total carbon conversion to hydrocarbons. Carbide carbon in the iron appears to be the most likely carbon source for the production of the background hydrocarbons. Mechanisms, analogous to the Fischer−Tropsch synthesis of hydrocarbons, are proposed for hydrocarbon production from carbide carbon. Similar mechanisms may also contribute to the formation of some of the hydrocarbons produced during the reduction of chlorinated ethenes by metallic iron.

Introduction

Chlorinated aliphatic compounds (e.g., trichloroethylene and perchloroethylene) have been widely used as solvents, degreasing agents, and chemical synthesis intermediates. The release of these compounds into subsurface environments has contaminated many groundwater aquifers, prompting concerns due to their possible effects on human health and persistence in aquatic environments. Recently, it has been shown that chlorinated solvents can be reduced by metallic iron (1−9). Nontoxic hydrocarbons are the major reduction products of chlorinated solvents such as trichloroethylene (TCE) (3, 6, 9) and perchloroethylene (PCE) (9). The reduction

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reactions take place on the iron surfaces and are linked to the anaerobic corrosion of the iron (5, 10). A new technology based upon this process has been proposed by researchers at the University of Waterloo, in which a permeable iron wall is placed within the aquifer to degrade chlorinated solvents as the contaminated groundwater passes through the reactive wall (4). This passive approach to groundwater remediation may provide significant advantages over traditional pump-and-treat technologies in many complex contamination sites (11).

In order to validate this technology and to optimize design parameters, reaction products and intermediates, mass balances, kinetics, and reaction mechanisms must be investigated. For chlorinated ethylenes, reductive β-elimination and sequential hydrogenolysis are the primary reaction pathways leading to the formation of C_2 hydrocarbons (acetylene, ethene, and ethane) (8, 9). The observation of methane and C_3-C_5 alkenes and alkanes as 5−10% of the reaction product mass (9), however, cannot be explained by these mechanisms.

Efforts to examine the reduction products, kinetics, and mechanisms have been complicated by the production of many of the same hydrocarbons in the metallic iron/water system in the absence of chlorinated solvents (2, 9, 12). Possible carbon sources for these background hydrocarbons include the following: (1) carbon impurities in the metallic iron; (2) aqueous CO_2; and (3) other organic compounds dissolved in water.

In a study examining the reduction of aqueous 1,1,2,2-tetrachloroethane (TCA) by iron powder, Senzaki and Kumagai (2) observed the production of methane and ethane in the controls containing no TCA. They postulated that the background hydrocarbons were due to the transformation of other, unidentified organic compounds present in the water, but did not provide supporting evidence.

Hardy and Gillham (12) examined the production of hydrocarbons in water/iron batch and column systems in the absence of chlorinated aliphatic compounds. They reported the formation of methane, ethane, ethene, propane, propene, butene isomers, and C_5 compounds and hypothesized, primarily based on the Anderson−Schultz−Flory (ASF) distributions of the hydrocarbons produced, that these hydrocarbons were formed from the reduction of aqueous CO_2 by zero-valent iron. Fischer−Tropsch (F-T) synthesis of hydrocarbons from CO and H_2 in the presence of metals such as Fe, Ni, and Co are known to result in ASF product distributions under some conditions (13−15). Enhanced production of hydrocarbons, however, was not observed when additional carbonate was added. Their results did not preclude carbon within the iron as the source of carbon for the hydrocarbons produced.

Campbell et al. (9) reported that, in an iron/water system, many of the same C_1-C_5 alkanes and alkenes were produced in the presence and absence of PCE or TCE, although hydrocarbon concentrations were higher when a chloroethylene was present. An experiment using ^{13}C-labeled TCE showed that the carbon in the C_1-C_5 compounds was derived predominantly from the TCE. Using Ar-purged water and CO_2-amended water, no differences were observed in the background (chloroethylene-free) hydrocarbon production. It was hypothesized that carbon impurities in the iron may be the source of carbon in the formation of the background hydrocarbons. Mechanisms for the formation of the background hydrocarbons or the similar hydrocarbons in the presence of a chloroethylene were not investigated.

This study examines the source of carbon for background hydrocarbon production in metallic iron/water systems.

TABLE 1. Iron Content, Surface Area, and Carbon Content of Metallic Irons Used in This Study

iron sources	Fe content (%)	C content (%)	surface area (m^2/g)
Fisher iron filings	>85[a]	3.09	1.18
Master Builder (MB) iron filings	90[b]	2.79	1.88
electrolytic iron	>99[a]	<0.002	0.30
Sigma iron powder	>97[a]	0.83	0.47
Leco iron wire 1	nd[c]	0.0067[a]	nd
Leco iron wire 2	nd	0.032[a]	nd
Leco iron wire 3	nd	0.065[a]	nd
Leco iron wire 4	nd	0.895[a]	nd

[a] As reported by supplier. [b] Ref 12. [c] nd, not determined.

Evidence is presented that indicates that carbon impurities within the metallic iron are the dominant source of carbon for the background hydrocarbons. Carbide carbon is implicated as the form of carbon primarily responsible. A mechanism analogous to the Fischer–Tropsch synthesis of hydrocarbons is proposed for the production of background hydrocarbons in the metallic iron/water system. A similar F-T analogous mechanism is proposed for the formation of some of the hydrocarbons produced in the metallic iron/water system in the presence of chloroethylenes such as TCE and PCE.

Experimental Section

Chemicals. Deionized Milli-Q water (18 MΩ·cm resistivity and <1 mg/L total organic carbon, Millipore Corp.) was used in all experiments. CO_2 gas (99+%) was obtained from Air Products and Chemicals, and ^{13}C-labeled CO_2 (99%) was from Aldrich. C_1 and C_2 hydrocarbon gases (1% each of methane, ethylene, and ethane in N_2) were supplied by Scott Specialty Gases. Propane (1% in N_2), propene (99+%), n-butane (10% in N_2), 1-butene (99+%), and 1-pentene (99+%) were obtained from Aldrich. Heptane (HPLC grade) was from Mallinckrodt, and pentane (HPLC grade) was from Baxter. Graphite powder (99%) was supplied by Fisher.

Irons examined in this study (see Table 1) included Fisher iron filings (40 mesh, Fisher Scientific), electrolytic iron (powder, Fisher Scientific), MB iron filings (a commercial source of iron filings from Master Builders, Cleveland, OH), Sigma iron powder [97+% iron produced by the reduction of $Fe(CO)_5$ by hydrogen, Sigma], and Leco iron wires (C calibration standards, Leco). The iron filings and powders were washed with Ar-purged 1.0 N HCl for 30 min, rinsed 15 times with Ar-purged water, dried at 100 °C under N_2 atmosphere, and kept in N_2 or Ar atmosphere prior to use. This treatment yielded gray-colored irons with strong metallic luster. The N_2-BET surface areas of the treated irons were measured using a Micromeritics FlowSorb 2300. The carbon content (w/w %) was measured on a Leco WR-112 carbon analyzer. When irons were treated with 6.0 M HCl under Ar atmosphere, all were completely dissolved except Fisher and MB iron filings, which produced black residuals containing 33 and 34% carbon, respectively. X-ray diffraction analysis (APD1700 automated powder diffractometer system) showed that graphite was the major mineral in the residues from both Fisher and MB iron filings.

Experimental Systems. Experiments with low and high CO_2 concentrations were conducted in zero-headspace systems. Carbon dioxide present in air can dissolve in water, thus preparation of metallic iron/water system with low CO_2 concentration must start with low CO_2 water. Milli-Q water was acidified by HCl to pH 4.0 and boiled for 30 min under continuous Ar purge. The water bottle was closed with a gas-tight plug and was placed into a small Ar-filled glovebox after cooling. FTIR analysis indicated that CO_2 in the water and in the glovebox atmosphere was below the detection limit (2.5×10^{-5} atm). GC/FID analysis showed no detectable hydrocarbons in the glovebox. Reaction bottles (15.0-mL serum vials) containing 5.00 g of the specified iron as well as control bottles containing no iron were filled completely with the low CO_2 water and crimp-sealed with Teflon septa in the Ar chamber. Upon addition of the iron, the pH quickly increased to pH 5–7. The reaction and control bottles were then mixed on a rotor drum at 8 rpm in a dark incubator at 20 °C. Similar experiments with a high CO_2 concentration were set up in a small glovebox with 1.0 atm CO_2, in which reaction and control bottles were completely filled without headspace using water in equilibrium with 1 atm CO_2.

Total amount of carbon dioxide dissolved in water is the sum of CO_3^{2-}, HCO_3^-, and $H_2CO_3^*$ [$H_2CO_3 + CO_2$(aq)], which varies as a function of CO_2 partial pressure and pH. Equilibrium calculations were performed using the computer program HYDRAQL (16). The waters in low and high CO_2 experiments were calculated to contain less than 1.0 μM and approximately 0.02 M total dissolved CO_2, respectively.

Hydrocarbons were monitored for approximately 6 weeks by analyzing two reaction bottles and one control bottle at each time point. Since there was no headspace in the low and high CO_2 experiments but headspace injection was needed to get high sensitivity for hydrocarbon analysis, an assay system with headspace was first created by displacing supernatant in a reaction bottle into an empty 10-mL crimp-sealed assay bottle through a stainless steel cannula. By injecting 5.00 mL of air into the reaction bottle employing a gas-tight syringe and at the same time venting the 10-mL assay bottle employing a stainless steel needle, quantitative liquid transfer (5.00 ± 0.05 mL) was achieved. The cannula and needle were withdrawn immediately after the transfer. The assay bottle was kept upside down after the supernatant transfer in order to minimize the loss of hydrocarbons, as suggested by Gossett (17). Five microliters of pentane solution (50.0 mg of pentane in 50 mL of methanol) was added into the assay bottle as the analytical internal standard. The assay bottle was vortexed for 10 s and incubated for at least 15 min at 20 °C before 100 μL of headspace was sampled and analyzed using gas chromatography (GC).

An experiment was conducted using ^{13}C-labeled CO_2 to further determine if CO_2 was being reduced by iron to form the hydrocarbons observed. The batch reaction system was set up, in duplicate, by adding 10.0 mL of Ar-sparged water and 20.0 g of Fisher iron filings to 26-mL serum bottles in an anaerobic glovebox (5% H_2 with N_2 balance) and crimp-sealing with Teflon-lined septa. The headspace in the reaction system was 13 mL. A gas-tight syringe was used to add 10 mL of $^{13}CO_2$ (99%) to the bottle, introducing approximately 400 μmol of $^{13}CO_2$ into the reaction system. The reaction bottles were mixed in the dark on a rotor drum at 8 rpm at a constant temperature of 20 °C. After a sufficient quantity of hydrocarbons was produced, the vapor phase was sampled and analyzed by GC/MS to determine the isotopic composition of the hydrocarbons and CO_2.

Experiments were conducted in duplicate to determine the amount of hydrocarbons produced upon dissolution of iron samples with HCl. In one set of experiments, each of the irons (less than 30 mg) was dissolved in 5.0 mL of 6.0 M

HCl in a Teflon-lined septa crimp-sealed 160-mL bottle. Reaction bottles were gently heated on a hot plate until all metal had dissolved and then allowed to cool back down to 20 °C. The hydrocarbons in headspace were analyzed by GC using an external standard calibration rather than internal standard in order to avoid introduction of any other source of carbon into the system. In a second set of experiments, a range of Sigma iron masses were dissolved in 6.0 M HCl, allowed to react as described above, and then analyzed for hydrocarbons. During iron dissolution, an internal pressure was built up in the reaction system mainly due to H_2 production, which would affect the hydrocarbon analysis based on the external calibration. The internal pressure was estimated by water displacement arising from this pressure and by calculation based on the reaction: $Fe^0(s) + 2H^+ = Fe^{2+} + H_2(g)$. Both methods generated the same results of internal pressure as a function of iron dissolved, and the effect of the pressure on the hydrocarbon analysis was corrected. The correction was less than 6% for all iron samples except Sigma iron, where the correction was up to 25% because larger samples were used.

Analytical Methods. Hydrocarbons were analyzed by GC with vapor phase injection. A Hewlett Packard 5890 Series II gas chromatograph equipped with a GS-Q fused silica capillary column (J&W Scientific, Inc., 30 m length, i.d. 0.53 mm) and a flame ionization detector was used. Helium was used as the carrier gas with a flow rate of 4.0 mL/min. The oven was programmed as follows: hold at 50 °C for 2 min, ramp at 30 °C/min to 200 °C, and hold for 3 min. Injector and detector temperature were 210 and 240 °C, respectively. For zero-headspace experiments with low and high CO_2, relative response factors (RRFs) were determined for analytes by equilibrating known masses of analytes and internal standard (pentane) at 20 °C in Teflon-lined crimp-sealed serum vials that had the same water/vapor ratio as the assay vials to account for the vapor/water partitioning of the analytes. The RRF for 1-butene was used to estimate the total mass of C_4 compounds. The peak areas of hydrocarbons that coelute with pentane (the internal standard) was much lower than 5% of the internal standard peak area, thus their effect on quantification was minimal. Hydrocarbons were identified by comparing retention time with authentic standards under different chromatographic conditions. Further confirmation of hydrocarbons and identification of unknowns was accomplished by GC/MS (HP 5890 GC and HP 5971 quadrapole mass selective detector using the GS-Q column). The isotopic compositions of hydrocarbons and CO_2 were also determined by the GC/MS system. Detection limits for ^{13}C-labeled hydrocarbons were less than 2 μM.

CO_2 concentrations in gas phase samples were determined by FTIR on a Magna-IR spectrometer 750 (Nicolet Instruments Corp.). The detection limit of the method was less than 25 ppm (i.e., partial pressure of 2.5×10^{-5} atm).

Solution pH was measured in filtered samples (0.20 μm nanapore nylon filter, Gelman Sciences) employing a Fisher Accumet model 25 pH meter, which was calibrated daily using standard pH solutions.

Results

Hydrocarbons produced in the Fe/H_2O systems with low and high aqueous CO_2 are shown in Tables 2 and 3, respectively. The quantifiable compounds include methane, ethylene, ethane, propene, propane, 1-butene, butane, and 1-propene. Further analysis using GC/MS indicated that small amounts of 2-butene (E), 2-butene (Z), 2-pentene (E or Z), 3-methyl-1-pentene, 1-hexene, and hexane were also present at the later stage of the reaction. The total hydrocarbon yield reported as C_1 (μM) over the course of both experiments is shown in Figure 1. No hydrocarbon products were detected in control bottles without iron.

TABLE 2. Hydrocarbon Concentrations (Values Reported as Mean of Duplicates) in Metallic Iron/Water Systems Containing a Low Initial Aqueous CO_2 Concentration (<1.5 μM)

	time (h)							
	15	65	116	184	308	454	664	954
Fisher 40 Mesh Iron
methane	0.18	0.34	0.72	0.74	0.76	1.02	1.08	1.95
ethene	0.12	0.24	0.38	0.49	0.67	0.94	1.22	1.82
ethane	0.05	0.10	0.14	0.19	0.23	0.29	0.37	0.52
propene	0.07	0.17	0.28	0.43	0.64	0.94	1.27	1.96
propane	<[b]	<	0.03	0.03	0.04	0.06	0.08	0.12
butenes	<	<	0.07	0.11	0.22	0.30	0.43	0.66
pentene	<	<	<	<	<	<	0.03	0.06
Master Builders Iron
methane	<	<	0.40	0.34	0.57	0.60	0.55	1.01
ethene	<	0.04	0.31	0.33	0.49	0.59	0.68	1.07
ethane	<	<	0.06	0.11	0.18	0.26	0.37	0.50
propene	<	<	<	0.05	0.08	0.13	0.18	0.29
Electrolytic Iron
no hydrocarbons were detected

[a] Hydrocarbon concentration in μM. [b] <, less than component detection limit.

TABLE 3. Hydrocarbon Concentrations (Values Reported as Mean of Duplicates) in Metallic Iron/Water Systems Containing a High Initial Aqueous CO_2 Concentration (0.03 M)[a]

	time (h)							
	22	52	118	216	310	483	695	985
Fisher 40 Mesh Iron
methane	1.07	1.98	2.44	2.45	1.83	3.40	3.95	4.45
ethene	0.31	0.46	0.33	0.40	0.41	1.02	1.21	1.24
ethane	0.25	0.43	0.54	0.62	0.55	1.06	1.15	1.21
propene	0.26	0.32	0.32	0.51	0.54	1.25	1.25	1.65
propane	0.04	0.09	0.10	0.12	0.12	0.24	0.25	0.27
butenes	0.10	0.13	0.08	0.18	0.18	0.45	0.66	0.59
butane	<[b]	<	<	0.02	0.04	0.06	0.09	0.10
pentene	<	<	<	0.02	0.04	<	0.03	0.05	0.05
Master Builders Iron
methane	0.40	0.64	1.13	1.86	1.32	1.65	2.23	3.67
ethene	0.07	0.12	0.17	0.44	0.40	0.66	0.70	0.92
ethane	0.10	0.15	0.17	0.42	0.59	0.92	1.23	2.59
propene	<	<	<	0.10	0.12	0.10	0.39	0.86
propane	<	<	<	<	<	<	0.06	0.15
butenes	<	<	<	<	<	<	<	0.04
Electrolytic Iron
methane	0.06	0.24	0.27	0.45	nd[c]	nd	nd	nd
ethene	<	0.08	0.11	0.21	nd	nd	nd	nd

[a] Hydrocarbon concentration in μM. [b] <, less than component detection limit. [c] nd, not determined.

In the low aqueous CO_2 system (Figure 1a), the total hydrocarbon concentration increases in a nearly linear fashion as a function of time, reaching 15 μM for Fisher iron filings and 5 μM for MB iron filings after approximately 40 days. The total hydrocarbon concentrations in the system with Fisher iron filings are consistently higher than for MB iron filings over the course of the reaction. The maximum possible amount of aqueous CO_2 at the beginning of the experiments (approximately 1.5 μM) is also shown in Figure 1a. The total amounts of carbon present in hydrocarbons at the end of the experiments are 10 times (Fisher iron fillings) and 3 times (MB iron filings) higher than the maximum amount of aqueous CO_2. This indicates that aqueous CO_2 originally dissolved in water is not a major source of carbon in the background hydrocarbons formed. In the electrolytic iron/water system, no hydrocarbons were detected.
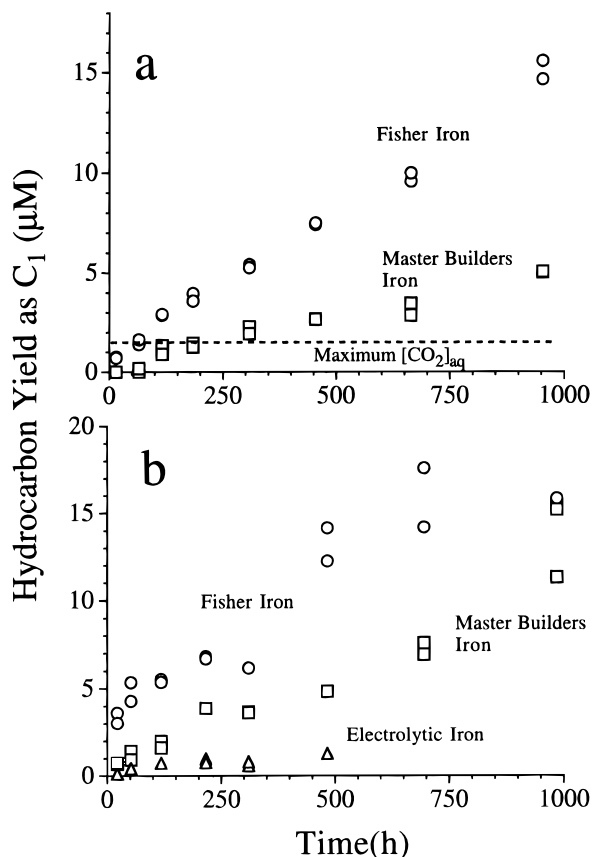
FIGURE 1. Total hydrocarbon yields as C_1 produced in the low CO_2 (a) and high CO_2 (b) metallic iron/water systems. Open circles, squares, and triangles correspond to Fisher iron filings, MB iron filings, and electrolytic iron powder, respectively.

In the high aqueous CO_2 system (Figure 1b), total hydrocarbon concentrations also increase in an approximately linear fashion as a function of time. The hydrocarbon yield as C_1 over the experimental time period is more than 3 orders of magnitude lower than the aqueous CO_2 concentration at the beginning of experiments (approximately 0.020 M). The hydrocarbon production rate is higher in a high CO_2 system than in a low CO_2 system by a factor of 1.5 for Fisher iron filings and 2 for MB iron filings. Small amounts of methane and ethene (less than 1 μM total hydrocarbon as C_1) were produced in the electrolytic iron system with high CO_2, which is different from the electrolytic iron system with low aqueous CO_2 where no hydrocarbons were detected.

The carbon isotopic composition of hydrocarbons produced in the presence of a significant amount of $^{13}CO_2$ was determined by GC/MS. Reduction of as little as 0.1% of the $^{13}CO_2$ present would have produced concentrations of ^{13}C-labeled hydrocarbons greater than the GC/MS detection limit. Examination of the mass spectra of the hydrocarbons produced indicates that no ^{13}C was transferred from $^{13}CO_2$ into the hydrocarbons. As an illustration, Figure 2 shows the mass spectra of a propene standard (with normal carbon isotope distribution) and propene produced in the iron/water system in the presence of $^{13}CO_2$. The nearly identical spectra indicate that propene produced in the presence of $^{13}CO_2$ is not ^{13}C-labeled and is thus not produced from the reduction of aqueous CO_2.

When the irons were dissolved in hydrochloric acid, the same hydrocarbons were produced as in the iron corrosion experiments discussed earlier. The total hydrocarbon yield as C_1 is directly proportional to the amount of Sigma iron powder dissolved in acid (see Figure 3). The dashed line in Figure 3 denotes the theoretical yield if all carbon in the iron (see Table 1) is converted into hydrocarbons. The experi-
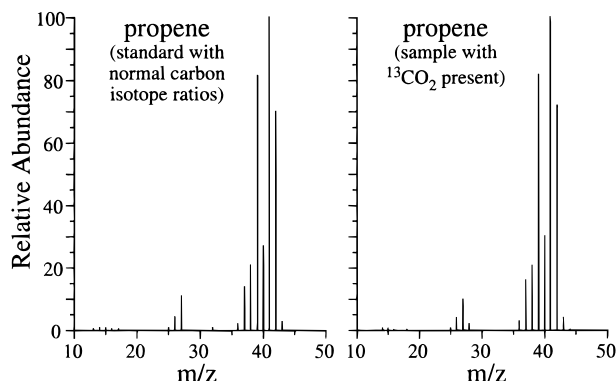

FIGURE 2. Mass spectra for propene standard with normal carbon isotopic composition and for propene produced in a metallic iron (Fisher iron filings)/water system in the presence of $^{13}CO_2$.
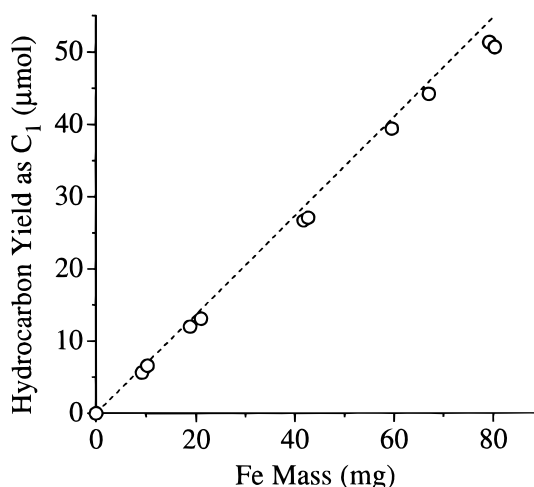

FIGURE 3. Hydrocarbon yields as C_1 produced by acid dissolution of Sigma iron containing carbide carbon. Dashed line corresponds to theoretical 100% conversion of carbon in the iron (see Table 1) into hydrocarbons.
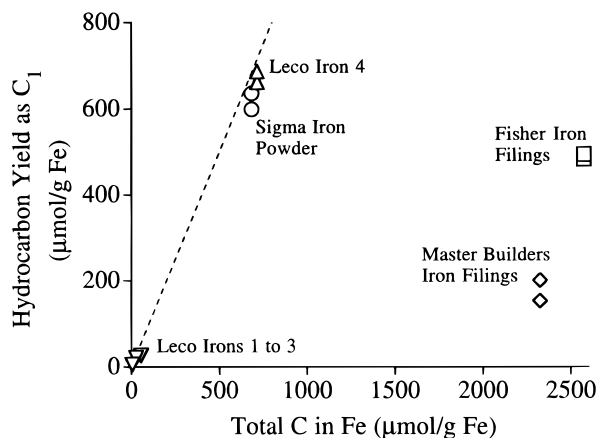

FIGURE 4. Hydrocarbon yields as C_1 produced by acid dissolution of a variety of iron samples. Dashed line corresponds to theoretical 100% conversion of carbon in the iron (see Table 1) into hydrocarbons.

mental data indicate a near 100% conversion of carbon from Sigma iron powder into hydrocarbons. Figure 4 shows the total hydrocarbon production as C_1 on a per mass iron basis (μmol/g of iron) from the dissolution of various iron samples in hydrochloric acid. The dashed line again indicates the carbon yield when all the carbon present in the iron samples is quantitatively converted into hydrocarbons. A close to 100% conversion is observed for the Leco iron wires and Sigma iron powder but is only 40 and 20% for Fisher and MB iron filings, respectively. The dissolution of both Fisher and MB

iron filings left black-gray residues. X-ray diffraction analysis showed that graphite was a major component in the residuals. In order to examine if graphite alone can produce hydrocarbons in strong acid, a separate test was performed. No GC/FID detectable hydrocarbons were produced in a system containing 0.10 g of graphite and 40.0 mL of 2.0 M HCl, indicating that graphitic carbon is not being converted into hydrocarbons.

Discussion

A possible source of carbon in the formation of hydrocarbons observed in this study is organic matter dissolved in Milli-Q water. The total organic carbon (TOC) in the water, however, is found to be low (<1 mg/L, the detection limit of TOC analysis). Control experiments containing no iron showed no detectable hydrocarbons on GC/FID. Experiments in systems containing electrolytic iron and Suwannee River water with 22 mg/L TOC also showed no hydrocarbon products (our unpublished data). It is unlikely, therefore, that background organic compounds dissolved in Milli-Q water act as a major carbon source in the formation of hydrocarbons in metallic iron/water systems.

The results from the low CO_2 experiments (Figure 1a) and the ^{13}C-labeled CO_2 experiments (Figure 2) clearly show that the reduction of aqueous CO_2 is a minor, if not negligible, process in the formation of background hydrocarbons in metallic iron/water systems. This contradicts the conclusion of Hardy and Gillham (12) that the reduction of aqueous CO_2 was the primary process in the formation of the background hydrocarbons.

Although the aqueous CO_2 concentration in high CO_2 experiments is more than 3 orders of magnitude greater than in the low CO_2 experiments, hydrocarbon production is increased by less than 2-fold (Figure 1b). This small increase in hydrocarbon concentration may result from the following (1) rate increases in iron corrosion due to CO_2 (i.e., carbon is from the iron itself) and/or (2) the reduction of CO_2 on iron surface. It has been reported that CO_2 dissolved in water enhances iron corrosion by chemical–electrochemical mechanisms (18–20). We observed in our experiments that more gas (H_2) was produced in high CO_2 systems than in low CO_2 systems. Thus, the enhanced rate of iron corrosion due to dissolved CO_2 may partially contribute to the higher hydrocarbon production in high CO_2 system.

The low level of hydrocarbon production with electrolytic iron in the high CO_2 experiment (see Table 2 and Figure 1b) indicates that at very high aqueous CO_2 levels the reduction of aqueous CO_2 may be possible since electrolytic iron contains very little carbon. Electrochemical reduction of CO_2 has been observed for various metal electrodes, carbon dioxide pressures, and solvents (18–26). Chemical CO_2 reduction normally requires more stringent reaction conditions such as high temperature and organometallic clusters as catalysts (27–29). Energetically, the following reaction is feasible:

$$H_2CO_3^*(aq) + 4Fe_{(s)} + 8H^+(aq) =$$
$$CH_{4\ (aq)} + 4Fe^{2+}(aq) + 3H_2O \quad \Delta G° = -438.21 \text{ kJ mol}^{-1}$$
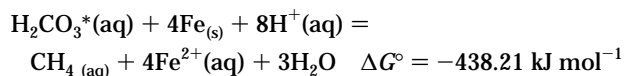
Thus, the slow observed CO_2 reduction by metallic iron is limited by kinetics. In any event, aqueous CO_2 reduction by iron does not represent a major source of carbon for the hydrocarbons formed under present experimental conditions, particularly under low aqueous CO_2 conditions likely to be encountered in the application of this technology.

A major portion of the carbon present in the metallic iron/water systems in this study is impurities in the iron (see Table 1). These carbon impurities are the most likely source of carbon for the formation of the background hydrocarbons. Cast irons, such as Fisher and MB iron filings, are primarily alloys of iron containing at least 2% carbon (30, 31). The two
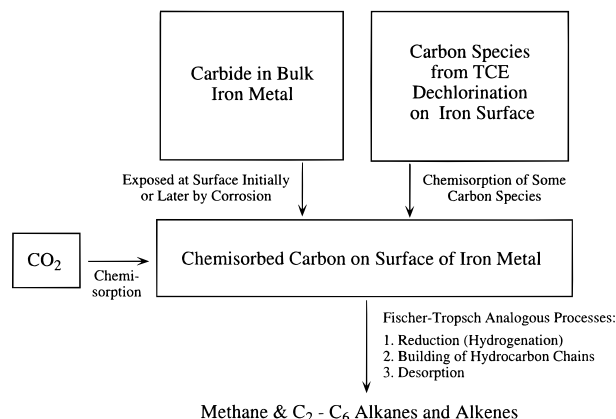

FIGURE 5. Proposed mechanisms for the formation of hydrocarbons (methane and $C_2–C_6$ alkanes and alkenes) in metallic iron/water systems with or without a chloroethene (e.g., TCE). See text for detailed discussion.

major forms of carbon in cast irons are (1) carbide, in which single carbon atoms are bonded to iron lattice, and (2) graphite, a separate phase of crystalline carbon (30). Among iron samples used in this study, graphite exists only in Fisher and MB iron filings based upon their graphite residues upon acid dissolution of the iron. It is reasonable to conclude that the carbon in the other iron samples (Sigma iron powder and Leco iron wires) exists primarily in carbide form since no residue remained upon the acid treatment. The near 100% conversion of carbon impurities in the Sigma iron powder and Leco iron wires to hydrocarbons (see Figures 3 and 4) strongly suggests that it is the carbide form of carbon that is being converted into the hydrocarbons. The two cast irons (Fisher and MB iron filings) gave incomplete conversion of carbon to hydrocarbons upon acid treatment due to the presence of graphite. Cast irons are of particular interest in the practical application of metallic iron in the reductive dechlorination of chlorinated solvents since their usage may be more cost-effective.

Hardy and Gillham (12) observed Anderson–Schultz–Flory product distributions for background hydrocarbons produced in iron/water systems, which suggested a possible connection to Fischer–Tropsch synthesis of hydrocarbons. They proposed that the connection to F-T synthesis was in the reduction of aqueous CO_2.

We propose an alternative connection to F-T synthesis to explain the observation of background hydrocarbons produced in metallic iron/water systems. In F-T synthesis, hydrocarbons are produced from synthesis gas ($CO + H_2$) in the presence of various metal (including Fe) or metal oxide catalysts at a few hundred degrees Celsius (13, 32, 33). It has been observed that both CO and H_2 can chemisorb onto the metal surface, decompose, and form methylidyne (carbide), methylene, and methyl reaction intermediates (34, 35). Recent work suggests that hydrocarbon chain growth is propagated in a catalytic cycle in which surface vinyl or alkenyl groups react with surface methylenes (36). Detachment at the metal surface releases the hydrocarbon. Additional evidence suggesting that carbide intermediates are possible in F-T synthesis comes from the observation that nickel carbide reacts with H_2 at elevated temperatures to form hydrocarbon gases (37). The carbon formed by the dissociation of CO and the carbide carbon originally present on the metal surfaces may not be distinguishable, and thus similar reaction mechanisms may be responsible for hydrocarbon formation in both cases. We propose that iron carbide will react by Fischer–Tropsch analogous processes to produce the background hydrocarbons formed in metallic iron/water systems. An illustrative schematic is shown in Figure 5.

It has been mentioned earlier that the reduction of chlorinated ethylenes by metallic iron yields the same kinds

of hydrocarbons as in iron corrosion alone (i.e., background hydrocarbons). When ^{13}C-labeled trichloroethylene is reduced, ^{13}C-labeled hydrocarbons are produced (9). Two dechlorination mechanisms exist for chloroethylenes: hydrogenolysis in which a halogen is replaced by a hydrogen, and reductive β-elimination in which two halide ions are released (8). Using TCE as an example, hydrogenolysis generates dichloroethylene (DCE) isomers, vinyl chloride, and ethylene while reductive β-elimination can generate chloroacetylene that undergoes hydrogenolysis to acetylene. Our experiments (unpublished data) have shown that acetylene reduction by iron can produce methane and C_2–C_6 alkanes and alkenes. It is likely that acetylene is one of the intermediates involved in the formation of methane and C_2 and larger hydrocarbons. We propose that acetylene and certain other components produced during the reductive dechlorination of chlorinated ethenes will chemisorb to the iron surface. Occasional cleavage of the carbon–carbon bond would be required to account for the formation of methane. F-T analogous processes would occur to form the long-chain hydrocarbons. The schematic shown in Figure 5 illustrates the common nature of how some of the hydrocarbons are proposed to be produced in (1) the background hydrocarbon formation examined in this study, (2) the hydrocarbon formation in chlorinated ethylene reduction, (3) and F-T synthesis. The commonality begins at the point in which carbon is chemisorbed onto the iron surface.

The results of this study show that iron carbide is the primary source of carbon in the formation of background hydrocarbons in metallic iron/water systems. Mechanisms, analogous to the Fischer–Tropsch synthesis of hydrocarbons, are proposed for hydrocarbon formation from carbide. Similar mechanisms are also proposed for the formation of some of the hydrocarbons produced during the reduction of chlorinated ethenes by metallic iron.

Acknowledgments

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