LETTER

The formation of CO₂ by fulvic acid on the surface of goethite studied using ultraviolet and infrared spectroscopy

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Changes in the absorption intensity (absorbance) at 254 nm of a fulvic acid solution in the presence of goethite powder were monitored in situ in a liquid cell at a temperature of 80 °C in a UV-visible spectrometer. The absorbance at 254 nm decreased rapidly with time in the initial stage in the presence of goethite with a first-order rate constant of $k_1^{\text{UV}} = 3 \times 10^{-4} \text{ s}^{-1}$, while in the absence of goethite, the absorbance at 254 nm decreased slowly with time, with a first-order rate constant of $k_0^{\text{UV}} = 6 \times 10^{-7} \text{ s}^{-1}$. A hydrothermal vessel was connected to a long-path gas cell infrared spectrometer to monitor the volatile compounds formed on heating the fulvic acid at 80 °C. Carbon dioxide formed gradually over time from the fulvic acid solution in the absence of goethite ($k_0^{\text{CO}_2} = 1.5 \times 10^{-6} \text{ s}^{-1}$). The formation of CO₂ in the presence of goethite occurred via two first-order reactions. The initial first-order rate constant of CO₂ formation from fulvic acid in the presence of goethite ($k_1^{\text{CO}_2} = 3.2 \times 10^{-4} \text{ s}^{-1}$) had the same magnitude as the decrease in absorbance at 254 nm. The second rate constant of CO₂ formation ($k_2^{\text{CO}_2} = 1.8 \times 10^{-6} \text{ s}^{-1}$) had the same magnitude as CO₂ formation in the absence of goethite. These results suggest that the formation of CO₂ from the fulvic acid is greatly accelerated by the presence of goethite, possibly through the adsorption of the fulvic acid on the goethite surface with subsequent redox reactions occurring.

Keywords: CO₂ formation, Organic-inorganic reaction, Fulvic acid, Goethite

INTRODUCTION

Organic compounds are supposed to be decomposed and finally oxidized to CO₂ on geological surfaces as $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ (Berner, 1980). On the other hand, various interactions of organic matter with minerals are commonly observed on the Earth's surface (Stumm and Morgan, 1996; Blesa et al., 2000). Recently, enhanced CO₂ formation from organic matter was found on oxide minerals (Majcher et al., 2000; Wang and Huang, 2000). However, the mechanism and rate of CO₂ formation on oxide minerals are not known.

Common dissolved organic compounds existing in the environment, such as fulvic acid, have been reported to be adsorbed on oxide minerals, such as goethite (Gu et al., 1994; Filius et al., 2000; Zhou et al., 2001). The ferric iron in iron hydroxides is often reduced to ferrous iron in the presence of organic matter (LaKind and Stone, 1989; Chorover and Amistadi, 2001; Pullin and Cabaniss, 2003). Although organic compounds are supposed to be oxidized in turn, and have the capability to form CO₂, the

details of these redox reactions are not yet understood. To investigate the possible formation of CO₂ from organic matter in the presence of iron hydroxides, in this study, we carried interaction experiments between a representative dissolved organic compound, fulvic acid, and a representative iron hydroxide, goethite. The interaction experiments were conducted at 80 °C to accelerate the reactions. The decrease in fulvic acid in solution was monitored in situ using ultraviolet-visible (UV-Vis) spectroscopy by measuring the absorption intensity at 254 nm, which is commonly used as a measure of dissolved organic carbon content (Korshin et al., 1997). Long-path gas cell infrared (IR) spectroscopy (Ishikawa et al., 2007) was employed to quantify the gaseous products produced, including CO₂, from the fulvic acid. Using these spectroscopic methods, the reaction kinetics of fulvic acid in the presence of goethite was investigated.

MATERIALS AND METHODS

Goethite and fulvic acid solution

The goethite samples were prepared using the method of Schwertmann and Cornell (2000). Iron hydroxide was

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precipitated in a polyethylene vessel by adding 180 mL of a 5 M potassium hydroxide solution to 100 mL of a 0.1 M Fe(NO₃)₃ solution. The suspension was immediately diluted to a volume of 2 L using pure water (MilliQ-UV), and incubated at 70 °C for a period of 60 h. The yellowish-brown precipitate obtained was centrifuged and then washed. The product was identified as goethite using X-ray diffraction and FT-IR spectroscopy (Nagano et al., 1992).

A fulvic acid standard, Nordic aquatic fulvic acid powder, was obtained from the International Humic Substances Society (IHSS), with an elemental composition of: C = 52.3, H = 4.0, O = 45.1, and N = 0.7 wt%. The functional group content was: COOH = 11.2 mmol/gC (13.4 wt% of the carbon was in the form of COOH) and OH = 3.2 mmol/gC (Ritchie and Perdue, 2003). Stock solutions containing 200 and 500 mg/L of Nordic fulvic acid were prepared using pure water. The pH of these solutions was adjusted to pH = 4 using 0.01 M HCl and 0.01 M NaOH solutions.

Batch hydrothermal experiments

A steel-lined PTFE (Teflon) reaction vessel was connected to a long-path gas cell (10-m path length) placed in a Bomem MB154 Fourier transform infrared (FT-IR) spectrometer (Fig. 1). Reflecting IR mirrors were set at both ends of the 25-cm long cell to obtain a 40 times reflection, yielding a full 10 m optical path length. A 20 mL plastic syringe was used to introduce the sample solutions and for the sampling products (Fig. 1). A vacuum pump and a N₂ gas bombe (99.9999% purity) were connected to the lines to obtain a non-oxidizing atmosphere throughout the entire system.

A volume of 15 mL of a 200 mg/L fulvic acid solution and a volume of 15 mL of a 20 g/L goethite suspension were purged with 99.9999% nitrogen gas in advance. The fulvic acid solution was then added to the goethite suspension in the hydrothermal reaction system described above under a nitrogen atmosphere.

Figure 1. The 10-m long path gas cell Bomem MB154 FT-IR spectrometer connected to the steel-lined PTFE (Teflon) hydrothermal reaction vessel.

The hydrothermal experiments were conducted at a temperature of 80 °C for periods of 0 and 24 h in the absence of goethite, and for periods of 0, 2, 4, 6, 9, 12, 18, and 24 h in the presence of goethite. The product solutions were filtered using a 0.45- μ m MF-membraneTM filter. The UV-Vis spectra of the filtered solutions were obtained using a Jasco V-570 UV-Vis spectrophotometer using 1.0 cm quartz cells. The gaseous products formed during the hydrothermal reactions were introduced by the nitrogen gas to the long-path gas cell FT-IR (Fig. 1) to measure their IR spectra.

In situ hydrothermal experiments

In situ hydrothermal experiments were conducted at 80 °C for periods of 0 to 24 h in the presence / absence of goethite using a heatable liquid cell set in a Jasco V-530 UV-Vis spectrophotometer. A mass of 1.25 mg of goethite powder was added to a volume of 25 μ L of the 500 mg/L fulvic acid solution in the heatable liquid cell. The UV-Vis spectra of the mixture were measured every 2 min while maintaining the solution at 80 °C. The weight ratio of goethite to fulvic acid was set to a value of (100:1) for the batch and in situ hydrothermal experiments.

RESULTS AND DISCUSSION

Decrease rate of absorbance at 254 nm by fulvic acid in the presence / absence of goethite

The UV-Vis spectra of the product solutions at 80 °C for periods of 0 and 24 h in the absence of goethite did not

Figure 2. Ultraviolet-visible spectra obtained from the product solutions at 80 °C for periods of 0 and 24 h in the absence of goethite, and for periods of 2 and 24 h in the presence of goethite, taken using the batch hydrothermal experimental apparatus shown in Figure 1.

Figure 3. Change in the absorbance at 254 nm with time at 80 °C in the presence / absence of goethite during the batch and in situ hydrothermal experiments. The value of the absorbance at 254 nm was normalized by the initial value. The in situ data in the initial stage up to a period of 3 h are shown in the inset as a semi-logarithmic plot. Consult the main text for the curve fitting information used to obtain the first-order rate constants of $k_0^{\text{UV}} = 6 \times 10^{-7} \text{ s}^{-1}$ and $k_1^{\text{UV}} = 3 \times 10^{-4} \text{ s}^{-1}$.

show any significant difference from that of the initial Nordic fulvic acid solution (Fig. 2). On the other hand, the spectra in the presence of goethite showed a marked decrease in their absorbance within a period of 2 h. The absorption intensity (absorbance) at 254 nm of the fulvic acid solution is due to the π - π^* electron transfer originating from substituted aromatic structures, and is commonly used as a measure of dissolved organic matter content (Korshin et al., 1997). Therefore, the absorbance values at 254 nm of the product solutions are plotted versus time in Figure 3. In the absence of goethite, the absorbance at 254 nm showed only a slight decrease on heating at 80 °C for a period of 24 h, while it decreased to a value of about 0.1 of the initial value within a period of 2 h, and then remained mostly unchanged around a value of 0.05 in the presence of goethite.

In situ UV-Vis experiments were conducted to study the rapid changes in the absorbance at 254 nm. The in situ data for the absorbance at 254 nm showed a slow decrease at 80 °C in the absence of goethite (Fig. 3). The batch data for a period of 24 h in the absence of goethite closely followed this trend. On the other hand, the in situ data at 80 °C in the presence of goethite appeared to decrease very rapidly (Fig. 3). The batch data in the presence of goethite were about 0.1 lower than the in situ data. This difference may be due to light scattering and absorption by the goethite particles in the in situ experiments and from the loss of adsorbed fulvic acid on the goethite during filtering in the batch experiment.

Figure 4. The cumulative formation of CO_2 with time from fulvic acid at 80 °C in the presence / absence of goethite during the batch hydrothermal experiments. Consult the main text for the curve fitting information used to obtain the first-order rate constants of $k_0^{\text{CO}_2} = 1.5 \times 10^{-6} \text{ s}^{-1}$, $k_1^{\text{CO}_2} = 3.2 \times 10^{-4} \text{ s}^{-1}$, and $k_2^{\text{CO}_2} = 1.8 \times 10^{-6} \text{ s}^{-1}$.

The slow decrease in absorbance at 254 nm of the fulvic acid in the absence of goethite can be used to determine the first-order reaction rate constant ($k_0^{\text{UV}} = 6 \times 10^{-7} \text{ s}^{-1}$) by fitting the data until a period of 24 h using an exponential curve. The absorbance at 254 nm decreased in the presence of goethite rapidly during the initial stage, but became slower at a later stage, reaching a constant value, indicating the contribution of several processes. These processes can be modeled, for example, by the sum of two independent first-order reactions, or three successive first-order reactions. Our simulations gave a rate constant for the initial stage, k_1^{UV} , of between $2 \times 10^{-4} \text{ s}^{-1}$ and $5 \times 10^{-4} \text{ s}^{-1}$. Alternatively, the data in the period up to 1 h, which showed a quasi-linear trend in a semi-logarithmic plot (insert in Fig. 3), can be fitted using an exponential curve to obtain the apparent first-order reaction rate constant of $k_1^{\text{UV}} = 3 \times 10^{-4} \text{ s}^{-1}$. Since this value is of the same order as the above complex simulation, and a precise kinetic treatment will need further experimental data, we used this initial stage first-order rate constant in our study. The rapid decrease in fulvic acid from solution suggests it was adsorbed on the goethite.

Rate of formation of CO_2 from fulvic acid in the presence / absence of goethite

The gaseous products formed in the batch hydrothermal experiments and analyzed using gas cell FT-IR spectroscopy indicated that only CO_2 was formed as a recognizable species. Carbon monoxide and other incomplete combustion gases were not detected. In the absence of

goethite, the cumulative amount of CO₂ formed gradually increased with time (Fig. 4). By assuming that the maximum formation of CO₂ was limited by the initial carboxylic group content of the fulvic acid, $C_0 = 1.75 \times 10^{-5}$ mol for 3 mg of fulvic acid, then the rate of formation of CO₂ can be modeled using the first-order kinetics by assuming this value of C_0 {where $C = C_0[1 - \exp(k_0^{\text{CO}_2}t)]$ }. The calculated first-order rate of formation of CO₂ was $k_0^{\text{CO}_2} = 1.5 \times 10^{-6} \text{ s}^{-1}$.

On the other hand, the CO₂ formed in the presence of goethite showed a rapid increase in the initial stage, and then the release of CO₂ increased gradually with time (Fig. 4). Assuming that the CO₂ was formed by two independent first-order reactions $\{C = C_1[1 - \exp(k_1^{\text{CO}_2}t)] + (C_0 - C_1)[1 - \exp(k_2^{\text{CO}_2}t)]\}$, then the first-order rate of formation of CO₂ can be obtained by fitting the data up to a period of 24 h using the above equation (Fig. 4) ($k_1^{\text{CO}_2} = 3.2 \times 10^{-4} \text{ s}^{-1}$ and $k_2^{\text{CO}_2} = 1.8 \times 10^{-6} \text{ s}^{-1}$ for $C_1 = 1.1 \times 10^{-6} \text{ mol}$). The amount of CO₂ formed in the presence of goethite, C_1 , comprises only about 6% of the initial carboxyl content, C_0 .

The first-order rate of formation of CO₂ from fulvic acid in the presence of goethite ($k_1^{\text{CO}_2} = 3.2 \times 10^{-4} \text{ s}^{-1}$) is of the same order as the above initial first-order rate in the decrease in absorbance at 254 nm ($k_1^{\text{UV}} = 3 \times 10^{-4} \text{ s}^{-1}$). This indicates that the mechanism of formation of CO₂ may be related to the adsorption of fulvic acid on the goethite. The first-order rate of formation of CO₂ in the presence of goethite in the second stage ($k_2^{\text{CO}_2} = 1.8 \times 10^{-6} \text{ s}^{-1}$) agrees with the rate in the absence of goethite ($k_0^{\text{CO}_2} = 1.5 \times 10^{-6} \text{ s}^{-1}$).

These results suggest that the hydrothermal transformation of fulvic acid to produce CO₂ is greatly accelerated by the presence of goethite, possibly through the adsorption of the fulvic acid on the goethite surface followed by subsequent redox reactions. Further studies are needed to clarify the mechanism of the surface interaction of fulvic acid with goethite.

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