PHOTOCHEMICAL DISSOLUTION OF GOETHITE IN ACID/OXALATE SOLUTION

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Abstract—During photochemical dissolution of goethite in acid/oxalate solution, Fe$^{3+}$, Fe$^{2+}$, and CO$_2$ were released and towards the end of the reaction ferrous oxalate precipitated. The dissolution process involved an initial slow stage followed by a much faster reaction. The slow stage was eliminated by addition of 20 ppm Fe$^{2+}$ to the system at the start of the reaction. The presence of this Fe$^{2+}$ did not accelerate the secondary dissolution process. Both protons and oxalate ions appear to have been involved in the dissolution process. Dissolution was accelerated by an increase in oxalate concentration (from 0.0025 to 0.025 M) in the system and also depended on pH, reaching a maximum rate at pH 2.6. Highly substituted (15.9 mole % Al) goethite dissolved more slowly per unit area than unsubstituted goethite. Lepidocrocite (γ-FeOOH) dissolved faster than goethite. The first stage of the dissolution process probably proceeded by slow release of Fe$^{3+}$ through complexation with oxalate adsorbed on the goethite surface. The faster, secondary step appears to have been a reductive dissolution reaction involving adsorbed ferrous oxalate.

Key Words—Goethite, Iron, Lepidocrocite, Photochemical dissolution, Oxalate.

INTRODUCTION

Dissolution of goethite (α-FeOOH) can proceed by a variety of pathways. In the laboratory, the dissolution of synthetic goethite by proton attack was studied intensively by Cornell et al. (1974, 1976) and Schwertmann (1984); however, the action of dissolution agents more applicable to natural systems has been neglected. The dissolution of goethite in soils involves complexation by organic chelating agents and/or reductive dissolution (Schwertmann, 1985). In natural waters and sediments, photochemical dissolution may also be important (Finden et al., 1984).

Oxalic acid is particularly effective at dissolving iron oxides both by complexation and by reduction (Sellars and Williams, 1984). This acid is produced in soils and sediments in comparatively large quantities by microbial action (Stone, 1987) and may assist the breakdown of soil iron oxides. It is also a component of the oxalic acid/ammonium oxalate solution that is widely used by soil scientists to dissolve noncrystalline iron oxides from mixtures of noncrystalline and crystalline oxides (Schwertmann, 1964). Several investigations have established the mechanism by which iron oxides dissolve in oxalic acid in the absence of light (DeEndreddy, 1963; Baumgartner et al., 1983; Segal and Sellars, 1984; Zinder et al., 1986; Miller et al., 1986). Although ultraviolet light has been shown to accelerate the reaction, the mechanism involved has not been fully established (DeEndreddy, 1963).

Recently, various studies of the photochemical dissolution of iron oxides in the presence of complexing agents such as citric acid and thiol compounds have been carried out (Waite and Morel, 1984; Waite et al., 1986 and references therein).

The present work is concerned with the photochemical dissolution of goethite in acid/oxalate solution. The aims are threefold; to identify the reaction products, to determine the factors that govern the reaction rate, and to propose a mechanism by which the reaction takes place. These data should provide further insight into the mechanisms by which photochemical dissolution of iron oxides takes place in natural systems.

EXPERIMENTAL

For a typical kinetic experiment, a suspension containing 40 mg of goethite in 50 ml of H$_2$C$_2$O$_4$/K$_2$C$_2$O$_4$ solution (total [oxalate] = 0.025 M) of ionic strength, I = 1.0 M (KCl), was equilibrated at 25°C in a thermostated glass cell. The cover of the cell was equipped with inlet ports for N$_2$ flow, sampling, electrodes and stirrer. The pH of the suspension was varied by adjusting the ratio of H$_2$C$_2$O$_4$ to K$_2$C$_2$O$_4$; most experiments were performed at pH 2.6.

Before and during an experiment, the suspension was purged with N$_2$ to minimize dissolved O$_2$. The initial purging was carried out in the dark; during this period (60 min), no dissolution took place. The suspension was agitated with a magnetic stirrer.

After the initial purging, the suspension was subjected to eight 5-min periods of illumination by unfiltered UV radiation ($\lambda_{max} = 254, 302, 313, 366, 546,$ and 577 nm), using a high-pressure Hg lamp (Hanau GmbH). The lamp was contained in a water-cooled quartz envelope and positioned 20 cm from the sus-
In solution. To exclude other sources of illumination, the apparatus was mounted in a box which could be closed during the experiment.

During an experiment the pH was held constant by the addition of small amounts of 0.1 M HCl in 1.0 M KCl. The initial pH was maintained with the aid of a potentiostat. The volume of acid consumed by the dissolution reaction was recorded as a function of time, and the progress of the reaction was usually measured in terms of proton consumption. Linear regression of H+ consumption as a function of time, to the point at which 20% of the oxide had been dissolved, was used to calculate the initial rates of dissolution.

CO2 release during the dissolution process was monitored by passing the CO2 produced (together with the N2 outflow) into solutions of CO2-free NaOH (0.025 M) in Duran glass bottles. During CO2 collection, the receiving vessels were sealed with Parafilm M. The collection vessel was replaced with a new one after each burst of radiation. The amount of CO2 released was measured by precipitation with excess BaCl2, followed by back titration with 0.1 M HCl.

In some experiments, subsamples were withdrawn after each burst of irradiation and filtered through a 0.22-μm Millipore filter. The amount of Fe(total) and Fe2+ was determined by atomic absorption spectroscopy and a colorimetric technique involving complexation with bathyphenanthroline, respectively.

Goethite was prepared by heating ferrihydrite at pH 12.2 and 70°C for 60 hr. Ferrihydrite was precipitated from ferric nitrate solution (0.1 M) with 1.0 M KOH. The preparation and properties of Al-substituted goethites were described by Schulze and Schwertmann (1984); their series-12 samples were used in the present experiments. Lepidocrocite (γ-FeOOH) was prepared by passing air through a FeCl3 solution held at pH 6 (see Giovanoli and Brutsch, 1974).

Speciation calculations were carried out using FITEQL, a general, nonlinear regression program for chemical equilibrium problems developed by Westall (1982). Dissociation and stability constants were taken from Sillen and Martell (1964).

For adsorption measurements, 0.1 g of goethite was suspended in 20 ml of H2C2O4/K2C2O4 solution in which total [oxalate] = 0.025 M and KNO3 = 1.0 M. The pH of the suspensions ranged from 1.7 to 4.9. The suspensions were equilibrated in the absence of light by shaking for 60 min, centrifuged and the concentration of oxalate remaining in the supernatant liquid was measured by liquid scintillation counting. 14C-labeled oxalic acid was obtained from the Radiochemical Centre, Amersham. X-ray powder diffraction (XRD) patterns were obtained using a Guinier-Enraf camera (Mk.IV) with FeKα1 radiation.

RESULTS

Reaction products

The reaction products were Fe3+, Fe2+, CO2, and ferrous oxalate. Initially, only Fe3+ was released. As dissolution proceeded, Fe2+ was also produced and CO2 was released in about equal amounts (Figure 1). Towards the end of the reaction, ferrous oxalate started to precipitate. The bulk of the precipitation took place at a decreasing rate during the 2 hr following the completion of the experiment and the cessation of UV illumination.

Ferrous oxalate exists in two modifications (Deyrioux and Peneloux, 1969). The α-form (monoclinic) is common and results if oxalic acid or oxalate ion is in considerable excess. The β-form (orthorhombic), however, is rare and forms only if stoichiometric amounts of Fe2+ and oxalic acid are mixed. In the present work, XRD showed that β-ferrous oxalate precipitated. UV illumination appears to have accelerated precipitation; solutions containing similar levels of Fe2+ and oxalic acid, but held in the dark, took several weeks to produce a precipitate.

Precipitation of ferrous oxalate interfered with the determination of the amount of Fe released—a further reason for following the reaction as a function of proton consumption, rather than as a function of Fe release.

Kinetics

A plot of H+ consumed, or, alternatively, Fe released, vs. time (Figures 1 and 2) shows an initial slow stage followed by a much faster reaction, in agreement with the qualitative observations of DeEndreddy (1963) who reported that photochemical dissolution of iron oxides in an oxalic acid/oxalate solution appeared to
be autocatalytic. Rates of dissolution were measured from the linear part of the reaction curve.

The initial slow stage was eliminated by the addition of ≥20 ppm Fe²⁺ (as ferrous sulfate) to the system before the start of dissolution (Figure 2). The presence of Fe²⁺ did not accelerate the secondary dissolution process, the rate of which appeared to be independent of Fe²⁺, at least over the range 20–100 ppm. The addition of 500 ppm Fe²⁺ inhibited the reaction, presumably because the oxalate was precipitated as ferrous oxalate. Most investigations were concerned with the second, faster dissolution process because this process accounts for the bulk of the reaction. In most experiments, therefore, 50 ppm Fe²⁺ was added to the system before the start of the reaction, in order to bypass the slow stage.

The effect of oxalate concentration was investigated at pH 2.6, and 1:1 mixtures of H₂C₂O₄ and K₂C₂O₄ were diluted in stages to keep the pH constant as [oxalate] varied. The rate of dissolution increased linearly over the range 0.0025 to 0.025 M oxalate and thereafter remained constant (Figure 3). Adsorption experiments showed that a monolayer of oxalate ions was adsorbed on goethite from a solution of 0.025 M oxalate. The maximum dissolution rate, therefore, corresponded to surface saturation by oxalate. Other experiments showed that oxalate adsorption on goethite was at a maximum at pH 2–4 and decreased at higher pHs (Figure 4). Both protons and oxalate ions appear to have been involved in the dissolution process. Because the concentration of H⁺ increased with decreasing pH, whereas the concentration of oxalate ions increased with rising pH, the maximum dissolution probably reflected a combination of two opposing factors. Figure 5A shows the speciation in bulk solution for oxalic acid as a function of pH. The predominant species at pH 2.6 was H₂C₂O₄⁻, suggesting that the proton concentration was equal to the oxalate concentration at this pH.

Replacement of KCl as the supporting electrolyte by MgCl₂ markedly reduced the rate of dissolution. The effect of MgCl₂ was counteracted to some extent by increasing [oxalate].

**Nature of the oxyhydroxide**

Aluminous goethite containing 9 mole % Al dissolved at almost the same rate/unit area as unsubstituted goethite.
Figure 5. Speciation in bulk solution as a function of pH for (A) oxalic acid; (B) Fe^{2+}/oxalic acid.

tuated goethite (Table 1). For an Al substitution of 15.9 mole %, however, the rate/unit area decreased to some extent. The rate of dissolution of these samples by proton attack also decreases with increasing degree of Al substitution (Schwertmann, 1984). Possibly the decrease in the number of intergrowths/crystals with increasing degree of Al substitution (Mann et al., 1985) is responsible for the decrease in the rate of dissolution in acid media; the boundaries between intergrowths in goethite are preferential sites of acid attack, and their presence can accelerate the dissolution of synthetic goethite (Cornell et al., 1974; Schwertmann, 1984; Comell and Giovanoli, 1986).

Lepidocrocite dissolved faster than goethite despite having a much smaller surface area (Table 1). The dissolution of these oxyhydroxides by proton attack is similar (Sidhu et al., 1981). The enhanced reactivity of lepidocrocite can be related to its open structure which consists of sheets of Fe(O,OH)\_6 octahedra held together by hydrogen bonds. Goethite, on the other hand, does not have a layer structure. Detachment of the structural metal ion is usually rate-limiting for dissolution, and a layer structure may present a greater proportion of metal atoms in active sites, i.e., sites having fewer structural bonds at the edges of the sheets.

**DISCUSSION**

Photochemical dissolution of goethite in oxalate solution appears to be a two-stage reaction: (1) comparatively slow release of Fe^{3+} through complexation by adsorbed oxalate and (2) a faster, secondary, reductive dissolution step involving ferrous oxalate, which accounts for the bulk of the dissolution.

Oxalate adsorbs extensively on goethite in the pH range of these experiments. The first step in the slow dissolution process appears to be the formation of a surface Fe^{3+}-oxalate complex. The Fe–O bond is polarized by complex formation and further weakened by protonation of adjacent surface hydroxyl groups (cf. the dissolution model of Zinder et al., 1986). Both effects combine to promote detachment of the Fe^{3+}-oxalate complex from the oxide, i.e., adsorbed oxalate assists dissolution by complexation. If structural ferric ions had been reduced by adsorbed oxalate, Fe^{2+} rather than Fe^{3+} should have been released from the start of the reaction. In fact, reductive dissolution involving adsorbed oxalate has only been reported for oxygenated suspensions of hematite (Hermann et al., 1983) or, for goethite, if an additional electron donor (ascorbic acid) was present in solution (Zinder et al., 1986). UV irradiation probably promotes the release of ferric oxalate complexes from the oxide structure in the same manner as does an increase in temperature (Sellars and Williams, 1984).

The subsequent formation of Fe^{2+} arises from photochemical decomposition of ferric oxalate complexes in solution, as suggested by Parker (1953). Speciation calculations showed that under the conditions of the present experiments, the predominant ferric oxalate species is the tris-oxalate complex. Decomposition of this species can be represented by:

$$2[Fe^{3+}(C\_2O\_4)^3\_] \rightarrow 2Fe^{2+}(C\_2O\_4)^2\_ + 3C\_2O\_4^{2-} + 2CO\_2$$

According to this equation, Fe^{2+} and CO_2 are produced in equal molar amounts during the dissolution process, if there is no other source of CO_2, for example, the decomposition of adsorbed oxalate. Experimentally, the formation of Fe^{2+} matched that of CO_2; hence, the reaction shown above can be assumed to be responsible for CO_2 production.

When sufficient ferrous oxalate has formed, the secondary, reductive-dissolution step becomes operative. A possible mechanism is outlined in Figure 6. The essential step shown here is the interfacial electron transfer between adsorbed ferrous oxide and structural ferric ions. This transfer results in reoxidation of the adsorbed species to ferric oxalate which, because of its altered molecular structure, desorbs from the oxide surface. Structural Fe^{3+} is simultaneously reduced. Desorption of reduced metal ions from the structure is the rate-determining step and is facilitated by adsorption of H\(^+\) and oxalate species. Because the Fe^{2+}–O bond is longer than the Fe^{3+}–O bond, ferrous ions leave the structure more readily than do ferric ions, which accounts for the greater speed of reductive dissolution.
Figure 6. Schematic outline of the mechanism of the fast reductive dissolution step. Roman numerals generally indicate surface species; arabic numerals indicate solution species. Fe$^{II}$ = surface.

According to this mechanism, UV light is responsible for the production of the active dissolution agent, i.e., ferrous oxalate; however, it is not clear whether UV light also accelerates electron transfer at the oxide surface. The surface reaction regenerates the ferrous oxalate involved in electron transfer, and, thus, equal amounts of Fe$^{II}$ and Fe$^{III}$ are released into solution. Because with increasing dissolution, the quantity of ferric oxalate available for photochemical decomposition increases, the concentration of ferrous oxalate also increases; hence, an autocatalytic reaction occurs.

Fischer (1973) reported that the presence of Fe$^{II}$ enhances dissolution of ferrihydrite; however, his study was carried out at pH 6–7. At lower pHs adsorption of Fe$^{II}$ on goethite is negligible, and the reducing species in the present work must be ferrous oxalate, which is the predominant ferrous species at pH 2.6 (Figure 5B). Some support for this hypothesis comes from the marked reduction in rate of dissolution observed if 0.1 M MgCl$_2$ replaces KCl as the supporting electrolyte. Mg$^{2+}$ and Fe$^{2+}$ form oxalate complexes of similar stability (log K = 2.39 and 3.05, respectively), and the presence of Mg$^{2+}$, therefore, reduces the formation of ferrous oxalate. If the latter species is the reducing agent, then because Mg (with only one oxidation state) cannot promote reductive dissolution of goethite, the reaction rate should decrease.

No evidence exists that suggests that ferrous oxalate adsorbs on goethite to form an inner-sphere complex. Probably, the Fe$^{2+}$ is associated with adsorbed oxalate as an outer-sphere complex in the same way that ascorbic acid associates with adsorbed oxalate (Zinder et al., 1986).

Autocatalytic dissolution has been observed for magnetite and hematite in de-aerated oxalic acid solutions (Segal and Sellars, 1984; Baumgartner et al., 1983). In both investigations, the shape of the kinetic curve was attributed to accelerated dissolution promoted by adsorbed ferrous oxalate. Autocatalytic dissolution was replaced by a much slower reaction if oxygen was not excluded from the system. Segal and Sellars (1984) suggested that the effect of oxygen was to prevent the formation of Fe$^{II}$.

Interestingly, in de-aerated oxalate solutions with or without UV illumination, the reducing species are Fe$_2$C$_2$O$_4$ or Fe(C$_2$O$_4$)$_2$$^{2-}$, depending on pH. For magnetite, Fe$^{II}$ presumably came initially from the oxide structure, whereas for hematite (dissolution at 80°C), reduction of Fe$^{III}$ by oxalic acid in solution provided a source of Fe$^{II}$. In both systems, light was excluded. Thus, a variety of circumstances can apparently lead to formation of ferrous oxalate and so promote accelerated, reductive dissolution of iron oxides in oxalic acid. This mechanism may also operate in natural environments in which Fe$^{II}$, adsorbing organic acids, and iron oxides coexist.

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