Iron VI

Mary Anne Armstrong Literature Seminar November 4, 1999

There is currently a resurgence of interest in the study of iron (VI) and its properties. Although Fe in this uncommon oxidation state has been known since the early eighteenth century, it was not thoroughly characterized until much later.[1,2] It is a very strong oxidizing agent,[3] and many of its potential applications utilize this property. It is a useful oxidizing agent for many organic compounds,[1,4,5] for use in wastewater treatment,[6-8] as well as replacing current battery cathodes to create batteries with larger charge capacities.[9]

Potassium ferrate, K_2FeO_4, is the most commonly studied iron (VI) salt. There are currently three different methods of synthesizing this substance: dry,[10] wet,[11] and electrochemical.[12] The wet synthesis is preferred and is carried out by adding $Fe(NO_3)_3$ to a basic solution of KClO. Enough potassium hydroxide is then added to saturate the solution and cause K_2FeO_4 to precipitate. It forms dark purple crystals that have been determined to have an orthorhombic unit cell, with the FeO_4^{2-} anions in a tetrahedral geometry.[13] (Figure 1)[14] The tetrahedral geometry is slightly distorted in the lattice structure, reducing the symmetry to C_s.[15] This effect is quite small, but its effect on the spectral properties is measurable.[16]

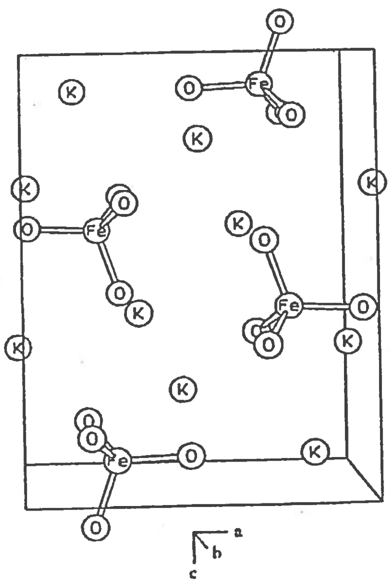

Figure 1

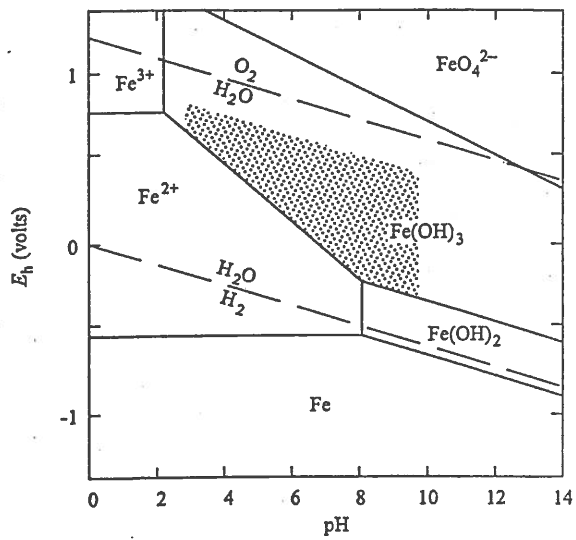

Figure 2

The largest issue that must be faced in the study of ferrate chemistry is that of its stability in water. With reduction potentials of 2.20 V in acidic solutions and 0.72 V in basic conditions, it oxidizes water to molecular oxygen quite readily at most pH values.[3] As ferrate salts are insoluble in anything but water,[1] this creates concern that any application using it as an oxidizing agent will have to compete with the oxidation of water. An interesting note is that kinetic studies on the oxidation of water by ferrate show the reaction to be slowest in a pH range of 9.4-9.7.[17] However, the Pourbaix diagram for Fe (Figure 2) shows that ferrate should not be stable except above a pH of about 13.[18]

Potassium ferrate has been shown to oxidize a wide variety of organic compounds, including alcohols, amines, thiols, and hydrocarbons.[1] The kinetics and mechanism of the selective oxidation of secondary alcohols to ketones has been studied in detail. The kinetics indicate a second order reaction, first order in both the ferrate and the alcohol after taking into account the competing water oxidation.[4,17] The mechanism of oxidation is still unclear. There is evidence in the literature to support both a 2+2 addition[17] and an indirect hydride transfer mechanism.[4] These mechanisms appear to describe the observed behavior in different pH regimes.

Most organic oxidations must occur in either aqueous or mixed solvents due to ferrate solubility. However, a method of heterogeneous oxidation has been developed that has been shown to improve product yields and reduce the difficulty of separations. Solid potassium ferrate is mixed with K10 montmorillonite clay and added to a solution of the substrate to be oxidized. This system was found to achieve quantitative formation of benzaldehyde from benzyl alcohol, with no overoxidation to benzoic acid. It was also utilized in the oxidation of a series of other organic species, including cyclic and linear alkanes.[1]

Since ferrate has such a high reduction potential, as well as being less toxic than many other oxidizing agents, it makes an excellent candidate for wastewater treatment. Investigations have shown that ferrate can oxidize H_2S to sulfate in groundwater,[6] cyanide to HCO_3^- and NO_2^- in industrial rinsewaters,[7] and thiourea to urea and sulfate in industrial cleaning wastes.[8] Not only does it oxidize these pollutants to safer compounds, but it coprecipitates with heavy metals and can act as a disinfectant.[19]

Another recent development has been the use of potassium ferrate and other ferrate salts as a cathode for traditional batteries. Potassium ferrate has a charge capacity of 406 mA h/g, which is higher than the current cathodes used in both alkaline (MnO2, 308 mA h/g) and rechargeable (NiOOH, 290 mA h/g) batteries. Also, ferrate salts can be engineered and used as a direct replacement for the cathodes in use now, without the need for cell redesign.[9]

In summary, iron (VI), specifically as a ferrate ion, has great potential and many applications as an oxidizing agent. The rapid reduction of ferrate in water remains an obstacle to be overcome in order to use it in practical applications, but the possibilities for its uses once this is overcome are tremendous.

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