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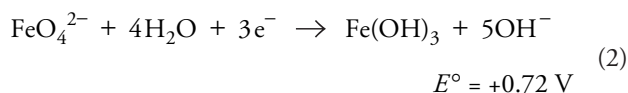
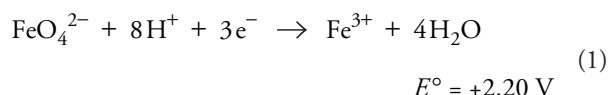


Part 6: Microscale Production of Ferrate

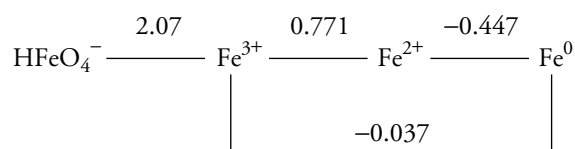
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Environmentally friendly, fast acting, and powerful oxidizing and disinfecting agents are needed for a variety of applications such as the removal of trace organic materials from potable water supplies, the removal of organics and inorganics from aqueous process streams, the disinfection of water, and so forth. There is a modern trend to reduce the use of chlorine for these purposes owing to the possible formation of harmful chlorinated organics (mainly trihalomethanes) in the presence of organic matter. Oxygen-based agents (ozone, hydrogen peroxide, and dioxygen) have gained popularity as a result of their powerful oxidizing and disinfecting properties as well as the cleanliness of their decomposition products. Another alternative that has been known for over a century and a half (but not studied for these purposes until recently) is a highly oxidized iron species called ferrate (FeO_4^{2-}), where the +6 oxidation state of iron makes it a very good oxidizer (1–3). The standard potential of the Fe(VI)/Fe(III) couple in acidic or basic media is (4):



The Latimer diagram of the main oxidation states of Fe (including Fe^{6+}) can be drawn as (5, 6):



From here, the Frost diagram (6) can also be calculated and drawn (Figure 1). The highly oxidizing power of ferrate is easily observed in this diagram.

In addition to the high standard potential of ferrate, another advantage is that iron is normally innocuous to the environment. Furthermore, solid K_2FeO_4 is stable in a dry environment for up to several months. It is interesting to note that these facts have also led to the proposal of using ferrate

as a cathode for the so-called “super iron battery” (1, 7–9) in which a zinc anode and a ferrate cathode form an environmentally benign battery capable of producing 1.8 V and of storing over 50% more energy than commercial alkaline batteries.

An added advantage in the use of ferrate for the remediation applications mentioned earlier is that Fe(OH)_3 , a well-known coagulating–flocculating agent capable of removing a large variety of pollutants, is normally the reaction product of ferrate in neutral or alkaline conditions. It has been shown that ferrate can destroy harmful organic and inorganic species like nitrosamines, phenol, nitrilotriacetic acid, hydrazine, thiourea, sulfides, cyanide, thioacetamide, ammonia, thiocyanate, soluble oils, as well as viruses and bacteria (1, 3, 4, 10–15). Ferrate can also be used for biofouling control (16) and for the removal of other pollutants such as metals, non-metals and radionuclides (1). Thus, ferrate can function as a multipurpose wastewater chemical for coagulation, disinfection, and oxidation (1, 15).

Ferrate is a tetrahedral ion, where all the Fe–O bonds are equivalent and covalent. It can be prepared either chemically or electrochemically. In the chemical synthesis a strong

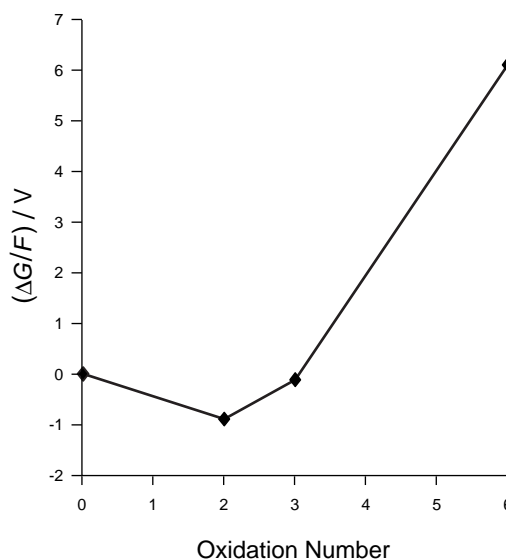
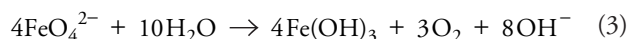


Figure 1. Frost diagram of iron species.

alkaline solution of hypochlorite oxidizes Fe(III) (17, 18). Monoperoxosulfate (HSO_5^-) can be used as a nonchlorinated oxidant (19). A preparation that requires more drastic conditions involves the heating of an intimate mixture of iron powder and potassium nitrate (as the oxidizer) (20). In the electrochemical synthesis, elemental iron is oxidized anodically to Fe(VI) in strongly alkaline solutions (typically 14–19 M NaOH) either at high voltages (100 V) (20), with constant current electrolysis (3, 21), using current reversal (3), or by superimposing alternating current on a dc supply (22). Since none of these electrochemical preparations is suitable for an introductory laboratory course, we investigated and probed different experimental conditions so that students taking general, inorganic, or introductory environmental chemistry laboratory could prepare ferrate electrochemically (and chemically), identify it, and use it for simulated environmentally relevant applications. This can be done with simple laboratory equipment and supplies at room temperature.

Experimental and Discussion

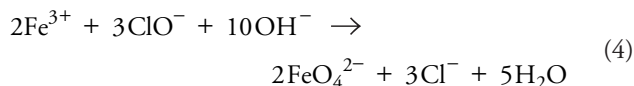
Ferrate is unstable in acidic and weakly alkaline solutions. This is unfortunate, since it is a stronger oxidant upon protonation, which occurs at low pH values (10). The source of such instability is its capacity for oxidizing water (3):



Ferrate is fairly stable in strongly alkaline media, as can be deduced from the application of LeChâtelier's principle to this equation. This is the reason for its preparation in concentrated NaOH or KOH solutions. The region of stability of ferrate ions can be found at high potentials and high pH values in the Pourbaix diagram of Fe (see, for example, ref 23).

Chemical Preparation of Ferrate

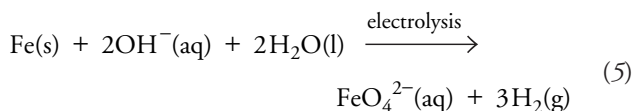
Ferrate has been traditionally prepared as (17,18):



To perform this reaction in microscale, place 2 mL of a commercial NaOCl solution in a 10-mL beaker (approximate concentration is 5–6%; more concentrated NaOCl solutions produce larger quantities of ferrate). Add 1 g of NaOH powder (or finely crushed pellets). Stir to dissolve. Once most of the solid hydroxide has dissolved, and while the mixture is still hot, add 40 μL (or a couple of tiny drops) of a 0.3 M FeCl_3 solution. Stir the reaction mixture for a few seconds and allow it to cool by itself. Sometimes a little foam is produced that may be removed mechanically if desired (e.g., with a filter paper). The color of the solid formed upon addition of the Fe(III) solution goes from light brown to dark brown or purple. Filter the resulting mixture preferably through sintered glass or a glass wool plug. A purple filtrate signals the presence of ferrate ions. Tests can be performed to identify ferrate.

Electrochemical Preparation of Ferrate (3, 15, 20–22)

The anodic oxidation of Fe in basic media involves a complicated mechanism (24). For simplicity, the overall reaction (i.e., anodic and cathodic) for the production of ferrate may be represented as (20):



To perform this reaction, prepare a 6 M NaOH solution (higher NaOH concentration reduces the time required for the production of ferrate, although it increases the danger associated with the experiment). Using your fingers make a small “paper ball” from a piece of filter paper. Using forceps, wet the ball with the NaOH solution and insert it in the bottom of a U-tube made from a 10-cm long piece of glass tube. A cotton ball can be used instead of the filter paper in a similar way. Fill both arms of the tube with the same NaOH solution prepared earlier. Then, place a 1 in. (about 2.5 cm) iron nail in each arm (make sure not to use steel nails). Connect each nail with an alligator clip to one terminal of a 9 V battery or a dc power source, set between 8 and 10 V. In a few minutes, a purple color will appear at the anode. Once the purple color in the anodic compartment is clearly visible, the power source can be disconnected. (Longer reaction times yield higher ferrate concentrations.) Tests for ferrate can be performed. Thorough acid washing of the iron electrodes after the experiment permits their reuse in subsequent experiments (3).

Tests for Ferrate

Spectrophotometric Response of Ferrate

After preparing ferrate by either method, place a few drops of the resulting solution in a spectrophotometric cell. Perform a wavelength scan in the visible region. If required, dilute the solution to get a reading in the instrument's range. A peak in the vicinity of 505 nm (2) indicates the presence of ferrate (Figure 2). This peak can be used to determine fer-

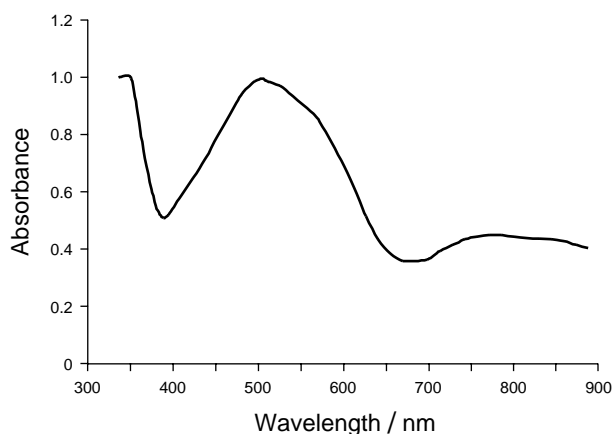


Figure 2. Spectrophotometric response of ferrate.

rate concentration using its extinction coefficient of $1070 \text{ M}^{-1} \text{ cm}^{-1}$ at 505 nm (2, 3). If a spectrophotometer is not available, a qualitative observation of a dark purple color indicates the presence of ferrate.

Oxidation of Organic Species (1–3)

Ferrate has attracted the attention of organic chemists for the selective oxidation of organic species to desired products. From an environmental perspective, it is normally desirable to oxidize such pollutants all the way to the nontoxic species CO_2 . For this purpose, place 0.5 mL of the ferrate solution obtained either chemically or electrochemically in a small vial. Add 0.5 mL of a surrogate organic pollutant (absolute or normal ethanol work well) to the vial. Oxidation of the alcohol takes place with a concomitant dramatic discoloration due to the reduction of Fe(VI) to Fe(III) . When a concentrated ferrate solution is used, tiny bubbles (presumably of CO_2) can be observed during the first few seconds of the reaction. If the resulting clear solution is allowed to stand in air for a few minutes (shaking speeds up the process), a brownish color due to the formation of Fe(III) oxide or hydroxide develops.

Oxidation of Inorganic Species (25)

Ferrate is capable of oxidizing insoluble Cr(III) to soluble chromates in alkaline high-level radioactive tank waste, facilitating removal of Cr(III) (19). In another application, Cr(VI) solutions are used for cleaning metal surfaces to remove oxides, dirtiness, et cetera. This produces Cr(III) , which renders the chromium useless for this application. It is desirable to oxidize Cr(III) back to Cr(VI) to regenerate the original reagent. Ferrate ions can be used to produce or regenerate Cr(VI) from Cr(III) .

To do this, place 1–2 mL of a dilute solution of a soluble Cr(III) salt (e.g., $\text{Cr}_2(\text{SO}_4)_3$) in two small test tubes. Record the visible absorption spectrum. Add dropwise to the first test tube 0.5–1 mL of the ferrate ion solution produced earlier. Shake the tube for a couple of minutes and compare the color obtained to that of the solution in the second test tube (blank). The first test tube now contains yellow Cr(VI) ions, whereas the second does not. Draw an aliquot of the resulting solution from the first tube with a pipet, and pour it in a spectrophotometric cuvette. Take its visible absorption spectrum. A new peak at ca. 350–370 nm confirms the production of Cr(VI) . In another application, Cr(III) oxidation by ferrate ions has been used to analyze the concentration of ferrate by quantitation of the Cr(VI) produced (17).

Oxidation of Water (1, 3, 18)

Acidic aqueous solutions will quickly reduce ferrate ions. Simply add a couple of drops of 2 M H_2SO_4 with a Pasteur pipet to a small test tube (e.g., 5-mm long, 0.5-mm diameter) containing 0.5 mL of the ferrate solution obtained earlier. Watch the color change from purple to colorless to golden brown. Tiny oxygen bubbles due to the oxidation of water by ferrate ions are also produced (see eq 3). Careful measurement of the volume of oxygen produced has been used for the quantitation of ferrate (18).

Hazards and Treatment of Residues

The NaOH solution is very caustic. Care has to be taken to prevent contact with the skin and especially with the eyes. The dissolution of NaOH in aqueous NaOCl is exothermic and caution is required.

Electrolysis (eq 5) produces gases as byproducts and as a result some splashing of the solution may occur. Be careful since this may contain NaOH and a powerful oxidizer (ferrate). In addition, a potentially explosive mixture of hydrogen and oxygen is produced. In a well-ventilated area this should not be a problem.

Cr(VI) compounds are suspected carcinogens. Do not touch this solution with your bare hands.

Some of the residues generated in these experiments are hazardous; they should be managed and disposed of according to applicable laws and regulations. For example, residual NaOH must be neutralized with acid. As this reaction is exothermic, the neutralization should be done slowly, preferably cooling the neutralization vessel with tap water or with a cold-water bath. Alkaline end products from some of the ferrate reactions also require neutralization. Disposal or remediation of dilute Cr(VI) solutions sometimes involves reduction to the much less toxic Cr(III) species by addition of a reducing agent (e.g., H_2O_2 , sulfite ions, active metal dust) (26), followed by neutralization to produce insoluble Cr(OH)_3 .

Conclusions

Ferrate, a powerful oxidizing and disinfecting agent, can be synthesized chemically and electrochemically in the undergraduate laboratory with simple equipment and under very mild conditions. Tests are given to characterize it and to observe its action in simulated environmental applications. Related problems are included in the Supplemental Materials.^W

Acknowledgments

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^WSupplemental Material

Instructions and a problem set for the students, and notes and answers for the problem set for the instructor are available in this issue of *JCE Online*.

Literature Cited

- Sharma, V. K. *Preprints of Extended Abstracts*, American Chemical Society Meeting, San Francisco, CA, Mar 26–30, 2000;

- American Chemical Society: Washington, DC, 2000; Vol. 40, No. 1, Paper #10, pp 131–132.
2. Wood, R. H. *J. Am. Chem. Soc.* **1958**, *80*, 2038–2041.
3. Denvir, A.; Pletcher, D. *J. Appl. Electrochem.* **1996**, *26*, 815–822.
4. Sharma, V. K.; Rivera, W.; Smith, J. O.; O'Brien, B. *Environ. Sci. Technol.* **1998**, *32*, 2608–2613.
5. Huhee, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993; Chapter 14.
6. Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; W. Freeman: New York, 1994; Chapter 7.
7. Freemantle, M. *Chem. Eng. News* **1999**, *77* (Aug 16), 4.
8. Licht, S.; Wang, B.; Xu, G.; Li, J.; Naschitz, V. *Electrochem. Comm.* **1999**, *1*, 527–531.
9. Licht, S.; Wang, B.; Gosh, S.; Li, J.; Naschitz, V. *Electrochem. Comm.* **1999**, *1*, 522–526.
10. Sharma, V. K.; Smith, J. O.; Millero, F. J. *Environ. Sci. Technol.* **1997**, *31*, 2486–2491.
11. Sharma, V. K. *Environ. Sci. Health* **1998**, *A33*, 635–650.
12. Sharma, V. K.; Burnett, C. R.; O'Connor, D. B. *Preprints of Extended Abstracts*, American Chemical Society Meeting, Washington, DC, Aug 20–24, 2000; American Chemical Society: Washington, DC, 2000; Vol. 40, No. 2, Paper #278, pp 600–602.
13. Sharma, V. K.; Rivera, W.; Smith, J. O.; O'Brien, B. *Environ. Sci. Technol.* **1999**, *33*, 2645–2650.
14. Johnson, M. D.; Hornstein, B.; Wingo, R. *Int. J. Environ. Consc. Des. Manufact.* **1995**, *4*, 27–30.
15. Lescuras-Darrou, V.; Lapique, F.; Valentin, G. *J. Appl. Electrochem.* **2002**, *32*, 57–63.
16. Walte, T.; Fagan, J. *Environ. Sci. Technol.* **1983**, *17*, 123–125.
17. Goff, H.; Murmann, K. *J. Am. Chem. Soc.* **1971**, *93*, 6058–6065.
18. Dyer, J.; Bennett, C. In *A Proceedings on a Cost Effective Chemistry: Ideas for Hands-on Activities*; Towse, P., Huseh, A., Eds.; Institute for Chemical Education: University of Wisconsin: Madison, WI, 1997; pp 105–106.
19. Johnson, M. D. Method for Synthesizing Ferrate and Ferrate Produced Thereby. U. S. Patent No. 5,746,994, May 5, 1998.
20. Ealy, B. J.; Ealy, J. L. *Visualizing Chemistry*; The American Chemical Society: Washington, DC, 1995; pp 175–177, 183–185.
21. Denvir, A.; Pletcher, D. *J. Appl. Electrochem.* **1996**, *26*, 823–827.
22. Bouzek, K.; Schmidt, M. J.; Wragg, A. A. Proc. 13th Int. Congr. Chem. Proc. Eng., Paper 0393; Prague, Czech Republic, Aug 23–28, 1998.
23. Barnum, D. W. *J. Chem. Educ.* **1982**, *59*, 809–812.
24. Zhang, H.; Park, S-M. *J. Electrochem. Soc.* **1994**, *141*, 718–724.
25. Sylvester, P.; Rutherford, L. A., Jr.; Gonzalez-Martin, A.; Kim, J.; Rapko, B. M.; Lumetta, G. J. *Environ. Sci. Technol.* **2001**, *35*, 216–221.
26. Pettine, M.; Campanella, L.; Millero, F. J. *Environ. Sci. Technol.* **2002**, *36*, 901–907.