A study of the Preparation and Reactivity of Potassium Ferrate

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Abstract

In the context of water treatment, the ferrate ($[FeO_4]^{2-}$) ion has long been known for its strong oxidizing power and for producing a coagulant from its reduced form (i.e. Fe(III)). However, it has not been studied extensively owing to difficulties with its preparation and its instability in water. This paper describes an improved procedure for preparing solid phase potassium ferrate of high purity (99%) and with a high yield (50-70%). The characteristics of solid potassium ferrate were investigated and from XRD spectra it was found that samples of the solid have a tetrahedral structure with a space group of D_{2h} (Pnma) and a = 7.705 Å, b = 5.863 Å, and c = 10.36 Å. The aqueous stability of potassium ferrate at various pH values and different concentrations was investigated. It was found that potassium ferrate solution had a maximum stability at pH 9-10 and that ferrate solution at low concentration (0.25 mM) was more stable than at high concentration (0.51 mM). The aqueous reaction of ferrate with bisphenol A (BPA), a known endocrine disrupter compound, was also investigated with a molar ratio of Fe(VI):BPA in the range of 1:1-5:1. The optimal pH for BPA degradation was 9.4, and at this pH and a Fe(VI):BPA molar ratio of 5:1, approximately 90% of the BPA was degraded after 60 s.

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1. Introduction

The problems of water pollution continue to be of concern and as a consequence the regulated standards for drinking water supply and wastewater discharge are becoming more stringent. Hence there is a continuing interest in the application of more efficient water treatment chemical reagents to achieve higher water quality. Fe(VI) in the form of potassium ferrate (K_2FeO_4) has been found to be a powerful oxidant over a wide pH range and many studies have considered its role as an oxidant in water and wastewater treatment (Jiang and Lloyd, 2002). During the aqueous oxidation reaction, Fe(VI) is reduced to Fe(III) or an insoluble end-product, ($Fe[OH]_3$) (Sharma, 2002). The standard half-cell reduction potential of ferrate has been estimated to be from +2.20 V to +0.72 V in acidic and basic solution, respectively (cf. +2.07 V and +1.24 V for ozone) (Wood, 1958). Thus the oxidation potential of potassium ferrate in acidic solution is the strongest of all the oxidants/disinfectants used in water and wastewater treatment, including chlorine, hypochlorite, chlorine dioxide, ozone, hydrogen peroxide, dissolved oxygen, and permanganate (Jiang and Lloyd, 2002). In addition, the ferric hydrolysis species including insoluble ferric hydroxide formed during ferrate oxidation are conventional coagulants, which mean that ferrate is a dual-function chemical reagent which has the potential to perform both oxidation and coagulation in a single treatment step (Deluca et al., 1992). The expected benefits of this combined effect in advanced water and wastewater treatment are higher water quality (particularly a lower risk of producing hazardous chemical byproducts), and lower operational and capital costs. Previous investigations have considered aspects of Fe(VI) treatment such as the inactivation of micro-organisms (Kazama, 1995), its reactivity with a wide range of aqueous contaminants, such as ammonia and heavy metals

(Murmann and Robinson, 1974) and the treatment of industrial and municipal wastewaters (Delaude and Laszlo, 1996; Johnson and Read, 1996; Norcross et al., 1997; Read et al., 1998; Sharma et al., 1999). Recently we reported on the degradation of phenol and chlorophenols by potassium ferrate (Graham et al., 2004). Owing to problems with the stability of the concentrated ferrate chemical, it is not available commercially and previous studies have required the ferrate to be freshly prepared in the laboratory. Currently, there is a need for further studies concerned with improving the method of ferrate preparation, such as increasing the stability and yield, and the reactivity of ferrate with contaminants of concern.

In general, there are three methods (Bielski and Thomas, 1987) for the synthesis of Fe(VI): (1) the electrochemical method by which anodic oxidation uses iron or alloy as the anode and NaOH/KOH as the electrolyte. The production yield is revealed to be strongly dependent on the electrolyte temperature and current density; (2) the dry method by which various iron-oxide-containing minerals are heated or melted under strong alkaline conditions and with oxygen flow. This method proves to be quite dangerous and difficult, since the synthesis process could cause detonation at elevated temperatures; (3) the wet method by which a Fe(III) salt is oxidized under strong alkaline conditions and either hypochlorite or chlorine is used as an oxidant. The third approach is widely considered to be the most practical. In 1951, Thompson et al. described the preparation of potassium ferrate by the wet method. In this case, potassium ferrate was prepared according to the following scheme:

$$KMnO_4 + 8HCl \rightarrow MnCl_2 + 5/2Cl_2\uparrow + 4H_2O + KCl$$

$$Cl_2 + 2KOH \rightarrow KClO + KCl + H_2O$$

$$Fe\,(NO_3)_3.9H_2O + 5KOH + 3/2KClO \rightarrow 3/2KCl + 23/2H_2O + K_2FeO_4 + 3KNO_3$$
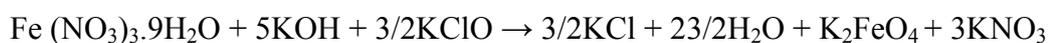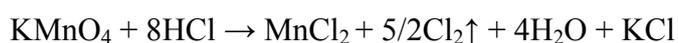
This method of preparation gave a purity of only about 70% and a 10-15% yield.

Bisphenol A (BPA) is a commonly used name for 2,2-(4,4-dihydroxydiphenyl) propane. The structure of BPA is obtained from 2 mol of phenol with one mol of acetone. It is manufactured in high quantities, 90% or more being used as a monomer for polyester-styrene resins and flame retardants (Stoyanova et al., 2003). It is also generated during the decomposition of polycarbonate flasks. It is well known that BPA has an estrogenic activity that serves as an endocrine disrupting chemical (EDC) and causes an abnormal increase in the growth of yeast cells in polycarbonate flasks. Moreover, BPA contributes significantly to the general environmental problem of EDCs as evidenced by a number of recent studies on the effects of BPA in the "low dose" range, including its effects even at a ppt level (Inoue et al., 2003). Thus the degradation of BPA and its removal from the environment are of public concern. However, as far as is known, little has been reported on the aqueous degradation of BPA and EDCs in general by potassium ferrate. In the present study, an improved method of preparing solid phase potassium ferrate is proposed which gives a product of very high purity (99%) and a much greater yield (50-70%). The characteristics of the solid potassium ferrate were analyzed by X-ray diffraction (XRD) spectroscopy. In addition, we report the results of laboratory experiments involving the degradation of BPA by potassium ferrate in which the molar ratio of Fe(VI):BPA was in the range of 1:1-5:1.

2. Materials and methods

2.1. Chemicals

K_2FeO_4 was prepared with high purity (99%) by the oxidation of ferric nitrate with hypochlorite. The main chemicals used were ferric nitrate (from Acros), potassium hydroxide (from BDH), potassium permanganate (from Sigma Aldrich), and bisphenol A (from Aldrich). These chemicals were used without any further purification. The solutions were prepared with water that had been

distilled and then passed through an 18 MΩ Milli-Q water purification system.

2.2. Experimental procedures

2.2.1. Potassium ferrate preparation

165 ml of 37% HCl was slowly reacted with 26.7 g of $KMnO_4$ to produce chlorine. The chlorine was subsequently added to pre-chilled KOH solution (60 g of KOH in 100 ml of water) with stirring for over 2 h. A quantity of 90 g of KOH was then added into this solution and the resulting suspension was cooled. The precipitate of KCl was removed from the suspension by filtration using a GF/C filter paper, leaving a concentrated and strongly alkaline solution of potassium hypochlorite. This yellow solution of KClO was then stirred rapidly while 37.5 g of pulverized $Fe(NO_3)_3.9H_2O$ was added slowly for over 1 h under cooling conditions (< 5 °C). In these conditions, the Fe(III) ion was readily oxidized to Fe(VI) and the solution became dark purple in colour. A quantity of 30 g of KOH was then added in small portions to the Fe(VI) solution and the mixture was stirred for 20 min. The resulting solution was allowed to stand for a further 40 min. The resulting dark purple slurry was filtered with a glass filter (P-0), after which the filtrate was discarded, and the precipitate was washed six times with a 25 ml quantity every time of cold 1 M aqueous KOH solution. The filtrate from the washings was collected and added to a flask containing 300 ml of a chilled saturated KOH solution. The solution was mixed, allowed to stand for 10 min, and then filtered initially with a glass filter (P-3), followed by double filtering with GF/A filter papers (Whatman Φ70mm). The precipitate was flushed with n-hexane (four times × 25 ml), n-pentane (four times × 25 ml), methanol (four times × 10 ml), and diethyl ether (two times × 10 ml). The final product, solid potassium ferrate (black in color), was collected and stored in a vacuum desiccator prior to further use.

2.2.2. Characterization of solid potassium ferrate

XRD patterns were obtained by using filtered Cu Kα reaction with a Philips recording diffractometer. Data were recorded over the range of 10° to 50° (2θ) at a 1° min^{-1} recording speed.

2.2.3. Decomposition of Fe(VI)

To determine the stability of potassium ferrate in aqueous solution, the prepared potassium ferrate solid was dissolved in deionzed distilled water to produce ferrate concentrations of 0.25 and 0.51 mM. The pH values of ferrate solutions were controlled with different pH buffers. These were: di-sodium hydrogen orthophosphate and sodium di-hydrogen orthophosphate for pH 7.1 and 8.0, and di-sodium hydrogen orthophosphate, sodium tetraborate and sodium hydroxide for pH 9.0, pH 9.2, pH 9.4, pH 10.3 and pH 11.9. The decomposition of Fe(VI) was monitored by determining the Fe(VI) concentration at different time intervals. The experiments were carried out to study the decomposition of Fe(VI) at different pH values.

2.2.4. Degradation of BPA

An aqueous solution of BPA was prepared by dissolving 2 mg BPA granules in 100 ml deionized distilled water. Fresh potassium ferrate solution was prepared with deionized distilled water and pH buffer solution immediately prior to each test to minimize the rapid decomposition of ferrate in aqueous solution. The oxidation tests were carried out by rapid mixing of the two chemical solutions (BPA and ferrate) at given pH values in the range of 8.2-12. In addition, similar oxidation tests were carried out in which different molar ratios of Fe(VI):BPA were applied in the range of 1:1-5:1. In the oxidation tests, samples were taken periodically up to 20 min. At each sampling time,

sodium sulfite solution was added immediately to the sample when it was taken to stop any further reaction. The samples were then centrifuged at 4000 rpm for 15 min before analysis. All experiments were carried out at room temperature (23 ± 2 °C).

2.2.5. Analytical methods

In this study, the concentration of potassium ferrate in an aqueous solution was determined by UV/VIS spectroscopy. K_2FeO_4 dissolved as FeO_4^{2-}, has a distinctive UV/VIS spectrum with a maximum absorbance at 510 nm. The molar absorptivity at 510 nm has been determined as 1,150 $M^{-1}cm^{-1}$ by Bielski and Thomas in 1987. In this analysis, colloidal ferric oxide interference is minimized by a 385 nm baseline correction (Licht et al., 2001). Other reaction species such as iron(II) and iron(III) phosphate have no interference at 510 nm (Huang et al., 2001). BPA concentration was determined by using a high performance liquid chromatograph, with a high pressure pump (Spectrasystem HPLC P4000), a UV detector (UV 6000LP), and an auto sampler (AS3000). In the HPLC analysis, a pinnacle II C18 column (5 μm particle size, 250 mm length, and 4.6 mm inner diameter) was employed and a mobile phase of acetonitrile/water (7:3, v/v) was used at a flow rate of 0.8 ml min^{-1}. An injection volume of 20 μl was used and the concentration of BPA was determined by the UV detector at 278 nm.

3. Results and Discussion

3.1. Preparation of potassium ferrate solid

In this study, the previous 'wet' method of preparation has been significantly improved in several ways. Firstly, the use of iron(III) nitrate rather than any other iron salt produced the best result. It is believed that the nitrate ion is more stable towards oxidation by the Fe(VI) ion than any of the other

anions. These include the chloride, sulfate, and phosphate ions (Williams and Riley, 1974). Secondly, in the preparation of the hypochlorite solution process, insoluble potassium chloride was removed with filter paper GF/C and not with fritted glass as was used by the Delaude and Laszlo method, because filter paper GF/C has a much smaller pore size (pore index = 1.2 μm) than the coarse glass filter P-0 (160 μm ≤ pore index < 250 μm) and can decrease the impurity of the ferrate solution. Thirdly, after KOH was added to the ferrate solution to precipitate potassium ferrate, the solution was allowed to stand for a further 40 min to improve the yield of potassium ferrate crystals. Fourthly, the yield of potassium ferrate increased by using additional double filtration with GF/A filter papers which have a smaller pore size (pore index = 1.6 μm) than that of glass filter P-3 (40 μm ≤ pore index < 16 μm) used as a pre-filter. Finally, during the drying process, n-hexane, n-pentane, methanol, diethyl ether, and negative pressure vacuum were used, rather than the methods used by others, viz.: benzene, ethyl alcohol used by Thompson et al.(Thompson et al., 1951); benzene, ethanol, and ether used by Williams and Riley (Williams and Riley, 1974); n-pentane, methanol, diethyl ether used by Delaude and Laszlo. Methanol usually is a better solvent than ethanol and dissolves many inorganic salts. Hence methanol was employed in this study to dissolve the hydroxide, chloride, and nitrate impurities in the precipitation. N-hexane and n-pentane replaced benzene that was used in earlier procedures for health and safety reasons. N-hexane was added to thoroughly dry the potassium ferrate to prevent it being degraded before washing with methanol. The purity of the potassium ferrate solid prepared in this study was found to be as high as 99% by use of the improved procedure.

3.2. Characteristics of potassium ferrate sample

Compared with previously used methods, the preparation procedure in this study is more efficient

in producing solid potassium ferrate with a higher purity. The prepared potassium ferrate crystal is black in colour and remains stable for more than a year if moisture is excluded. It is isomorphous with K_2SO_4 and K_2MnO_4. The FeO_4^{2-} has a tetrahedral structure in the crystal form (Jiang et al., 2001). To further determine the characteristics of the potassium ferrate, three potassium ferrate samples, prepared with different purity (75%, 90%, and 99%), were examined by XRD analysis. The XRD patterns of three samples are shown in Fig. 1.

[Fig. 1]

The peaks of 002, 111, 211, and 013 in the XRD spectra, shown in Fig. 1, correspond to solid potassium ferrate. The main peak (013) is at 30.1° (2θ). The main peak intensities of the 75%, 90% and 99% ferrate samples are 767, 912 and 1001, respectively. It can be seen that the potassium ferrate sample with the highest purity (99%) shows a sharper peak and a stronger response in the XRD spectra. The XRD results also indicate that the prepared potassium ferrate sample has a tetrahedral geometrical structure with a space group of D_{2h} (Pnma) and a = 7.705 Å, b = 5.863 Å, and c = 10.36 Å, obtained from Eq. (1).

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{1}$$

The concentration of potassium ferrate in an aqueous solution was determined by UV/VIS spectroscopy and the visible absorbance spectra for the ferrate concentrations of 0.25 mM and 0.51 mM are shown in Fig. 2.

[Fig. 2]

It can be seen from Fig. 2 that the potassium ferrate solution has a distinctive UV/VIS spectrum with a maximum absorbance at approximately 510 nm. The molar absorptivity at 510 nm has been determined previously as 1,150 $M^{-1} cm^{-1}$ by Bielski and Thomas (1987).

3.3. Decomposition of Fe(VI) in aqueous solution

A set of aqueous K_2FeO_4 solutions with an initial concentration of 0.25 mM was freshly prepared with different pH values from 7.1 to 11.9. The temporal change in Fe(VI) concentration was measured by UV/VIS spectroscopy every 30 s. It is assumed that the kinetics of K_2FeO_4 decomposition in aqueous solution follows $\frac{d[FeO_4^{2-}]}{dt} = k[FeO_4^{2-}]$. The experimental results are plotted in Fig. 3. The kinetic constant (k) was calculated for each pH condition and the values are shown in Table 1.

[Table 1]

[Fig. 3]

The decomposition kinetic constants shown graphically in Fig. 3 indicate that Fe(VI) is more stable in strongly alkaline conditions, and the rate constant has a minimum between pH 9.2 and 9.4. Visually, the decomposition of ferrate is accompanied by a marked change in solution colour. Initially, the ferrate solution is purple in colour and this rapidly becomes to a yellowish colour as decomposition occurs, before the solution finally becomes colourless with some yellowish precipitates evident at the bottom of the flask. It can be seen that under acidic conditions ferrate has a high oxidation potential that leads to rapid redox reactions with water leading to the reduction of Fe(VI) to Fe(III). For pH> 10, it is believed that ferrate follows a different reduction pathway leading to the formation of anionic ion species (eg. $Fe(OH)_4^-$ and $Fe(OH)_6^{3-}$) instead of $Fe(OH)_3(s)$,

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at the particular ferrate concentration used (Sharma et al., 2000; Graham et al., 2004).

Fe(VI) in aqueous solution occurs in four forms that depend on pH as shown below:

$$H_3FeO_4^+ \leftrightarrow H^+ + H_2FeO_4 \qquad pK_a = 1.6 \pm 0.2 \qquad \text{(Licht et al., 2001)}$$

$$H_2FeO_4 \leftrightarrow H^+ + HFeO_4^- \qquad pK_a = 3.5 \qquad \text{(Licht et al., 2001; Sharma, 2002)}$$

$$HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \qquad pK_a = 7.3 \pm 0.1 \qquad \text{(Licht et al., 2001; Sharma, 2002)}$$
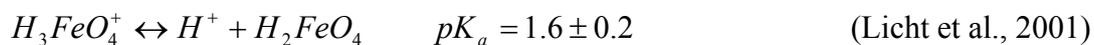
On the basis of the above pKa values, the fractions of each form ($H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^{2-}) against pH can be calculated and are shown in Fig. 5.

[Fig. 4]

The pattern of speciation (Fig. 4) indicates that FeO_4^{2-} is the dominant species in alkaline conditions, and $HFeO_4^-$ predominates in mildly acidic conditions. This explains the instability of FeO_4^{2-} in acidic conditions. However, ferrate has a higher oxidation potential at low pH than in the alkaline condition and the oxidation state of FeO_4^{2-} can be rapidly changed from +6 in acidic conditions to +3 in alkaline conditions (Wood, 1958) as shown below:

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \qquad\qquad E^0 = 2.20 \text{ V}$$

$$FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \qquad\qquad E^0 = 0.72 \text{ V}$$

Therefore, the optimal performance of ferrate as an oxidizing chemical may correspond to pH conditions of between 9 and 10, representing the overall combined effect of its lower oxidation potential but greater stability.

3.4. Degradation of BPA in aqueous solution by ferrate

BPA dissociates in aqueous conditions and has a pKa of 8.2 at 25 $^{\circ}$C. To study the reaction of BPA in its dissociated state with potassium ferrate, and the influence of pH, a set of tests was carried out with BPA (0.1 mM) and potassium ferrate (0.1 mM) at different pH values from pH 8.2 to pH 10.3. The experimental results are shown in Fig. 5.

[Fig. 5]

It is evident from Fig. 5 that the extent of degradation of BPA after 20 min was a maximum at approximately pH 9.4, and there was less degradation below and above this pH. The occurrence of a maximum BPA degradation at pH 9.4 appears to coincide closely to the pH value for maximum ferrate stability (Fig. 3), which suggests that ferrate stability is a decisive factor in the oxidation reaction. The possible reasons for the reduced degradation at pH values above and below pH 9.4 will be discussed later.

The influence of molar ratio of the reacting compounds on the degradation of BPA in water was studied. A set of tests was carried out at pH 9.4 using different molar ratios of Fe(VI):BPA from 1:1 to 5:1. A summary of the experimental results for the degradation of BPA at different reaction times with various Fe(VI):BPA molar ratios is shown in Fig. 6.

[Fig. 6]

It can be seen from Fig. 6 that the reaction between the BPA and the ferrate was very rapid, with a major degradation of BPA occurring during the first 60 s, followed by a more gradual further degradation over the next 10-20 min. This was the case for all the molar ratios of Fe(VI):BPA from

1:1 to 5:1, and it was evident that the rate of reaction increased sharply with molar ratio. The results indicate that BPA was reduced after 20 min by 70%, 78%, 87%, 95%, and 100% with the molar ratios of 1:1, 2:1, 3:1, 4:1, and 5:1, respectively. However, for a molar ratio of 5:1 the BPA degradation was approximately 90% after only 60 s. Overall, these results indicate that BPA is very readily degraded by ferrate under these conditions.

3.5. Overall effects

Previous work by some of the authors has demonstrated that pH is very influential in reactions between ferrate and dissociating compounds (Graham et al., 2004). The redox potential and aqueous stability of the ferrate ion, and the reactivity of dissociating compounds, are known to be pH dependent. Thus, for a given ferrate concentration, the stability of the ferrate increases and the oxidation potential decreases with increasing pH. In contrast, the degree of dissociation of the compound increases with pH and de-protonated compounds have been found to be more readily oxidized (Hoigné and Bader, 1983). In the previous study of the reactivity of phenol and chlorophenols with ferrate (Graham et al., 2004), the optimal pH for compound degradation (ie maximum degradation) appeared to be very close to the compound pKa, as can be seen in Table 2. In this study, the optimal pH for BPA degradation was found to be 9.4 which is above the pKa of 8.2. By comparing the BPA reactivity variation shown in Fig. 5 with the ferrate stability variation shown in Fig. 3, suggests that the optimal degradation requires the BPA to be in its de-protonated form and the ferrate to be stable. The trend of decreasing BPA degradation with pH above 9.4 is believed to be due principally to the reducing redox potential of ferrate.

Conclusion

In this study, solid potassium ferrate was successfully prepared by an improved preparation procedure and had a high purity up to 99%. Experiments have demonstrated that the stability of ferrate in aqueous solution is highly affected by pH values. However, Fe(VI) is relatively stable in an alkaline condition between pH 9-10. In this work, BPA was studied as a model endocrine disrupting chemical and was successfully degraded by different dosages of Fe(VI) in the range of molar ratio from 1:1 to 5:1.

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Table 1: Variation of kinetic constant (k) of Fe(VI) decomposition with pH

pH	k, s^{-1}
7.1	39×10^{-4}
8.0	16×10^{-4}
9.0	6×10^{-4}
9.2	1×10^{-4}
9.4	1×10^{-4}
10.3	4×10^{-4}
11.9	8×10^{-4}

Table 2: Optimal pH of compound degradation (ferrate:compound molar ratio 5:1)   (Graham et al., 2004)

Compound	pKa[a]	Optimal pH	Compound degradation (%)
phenol	9.9	9.2	83
4-chlorophenol	9.2	9.2	95
2,4-dichlorophenol	7.8	~ 8	87
2,4,6-trichlorophenol	6.1	~ 7	87

[a] Hoigné and Bader (1983)

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Fig.1: XRD spectra of three K_2FeO_4 samples

Fig.2: Visible spectra of Fe(VI) in aqueous solution

Fig.3: Decomposition kinetic constant, *k*, of Fe(VI) at different pH

Fig.4: Variation of Fe(VI) species with pH (Delaude and Laszlo, 1996)

Fig.5: Degradation of BPA with pH (reaction time = 20 min)

Fig.6: Degradation of BPA for different Fe(VI):BPA molar ratios and at different reaction times at pH 9.4

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6