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Donald H. Williams
University of Kentucky

J. T. Riley
University of Kentucky

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CHEMISTRY OF THE OXIDANT, FERRATE, ITS INTERACTION WITH
SPECIFIC ORGANICS FOUND IN WASTE WATER

Dr. Donald H. Williams
Principal Investigator

Graduate Student Assistant: J. T. Riley

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ABSTRACT

It became obvious during this investigation that while much work has been done with ferrate (VI) chemistry, discrepancies existed in the literature and very little attention had been given possible engineering uses. This work attempted to fulfill these two needs in an exploratory manner.

The preparative techniques were reviewed and mechanical improvements made in one which allowed improved yields. Essentially what was done was to enlarge and improve the filtering technique of the product and use cooler temperatures throughout the preparation. This greatly shortened the time required. Then it was learned that the addition of ethyl alcohol to the final filtrate, after product separation, produced more ferrate (VI) but of lower purity. Qualitative studies showed however, that for most situations high purity was not required. The procedure developed resulted in doubled yields and reduced time of preparation.

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WITH SPECIFIC ORGANICS FOUND IN WASTE WATER

(Project Completion Report)
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Donald H. Williams, Ph. D.
Principal Investigator
(April 1, 1966 to June 30, 1968)

Description of Research Performed

In order to learn as much about the chemistry of a little studied but powerful chemical oxidizing agent, the ferrate (VI) ion, $\text{FeO}_4^{=}$, and its interactions with contaminants found in waste water, an extensive bibliography has been compiled (Riley, 1968). Essentially all its chemistry is covered. In this study a great deal of attention was given to the preparation of the ferrate ion. The choice of preparative methods that existed before this study consisted of either investing approximately ten hours of laboratory time (using laboratory quantities) to obtain very small (20 g.) quantities of 95% pure ferrate ion or using approximately eight hours of time to double the yield at great sacrifice in purity (50%).

Studies to improve the preparation and investigate the effect of impurities were undertaken. It was found that concentrated KOC1 , saturated KOH and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ produced the best results. A combination of mechanical short-cuts and the use of ethanol as the precipating agent hastened the procedure to the point that in about three hours 40% pure K_2FeO_4 could be obtained in yields greater than 90%. A purification procedure was developed allowing 75% yields of 80-90% pure product.

The procedure is:

Materials and Reagents

The chlorine used was from a lecture bottle obtained from the Matheson Company. Potassium hydroxide and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were of reagent grade.

The analysis of the potassium ferrate samples were carried out using the chromite method of analysis developed by Schreyer, Thompson and Ockerman (1950).

Experimental

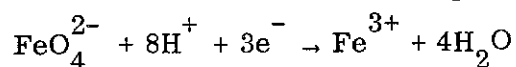
Twenty-one grams of KOH in 35 ml of water at 0° was chlorinated until 10 g of chlorine had been added. Thirty grams of KOH was then added to this solution, while the temperature was allowed to rise as high as 20° to aid in dissolving the KOH. The mixture was cooled to near 0° and the precipitated KCl was filtered off. The yellow filtrate was stirred rapidly and 12.5 g of pulverized $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ added slowly over a one hour period. The temperature was allowed to rise to 35-45° and the stirring continued 30 minutes after all the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ had been added. Twenty grams of KOH was then dissolved in the mixture and the slurry cooled to 0°. This was then filtered using a 600 ml coarse porosity fritted glass filter, which allowed any ferric hydroxide to pass through into the filtrate which was discarded. The precipitate on the filter, containing potassium ferrate and chloride was leached with three 15 ml portions of cold 1 M KOH, and these were collected in a filtering flask. The potassium ferrate solution was then added slowly with vigorous stirring to 600 ml of 95% ethanol. The mixture was stirred 20 minutes and the precipitate filtered off using a coarse porosity filter. The precipitate was washed on the filter with two 50 ml portions of 95% ethanol, and then with 50 ml of either. Great care was taken to minimize the amount of air drawn through the filter. The sample was then dried in a vacuum desiccator.

When more pure potassium ferrate (VI) was desired, samples prepared by this method were purified by dissolving the sample from one preparation (approximately 13 g) in 60 ml of cold 3 M KOH and adding this solution to 100 ml of cold saturated KOH. The precipitated K_2FeO_4 was then filtered off using a medium porosity fritted glass filter, and 15 ml of benzene added to force the water out of the filter. The sample was then washed with two 50 ml portions of 95% ethanol and then with 50 ml of ethyl ether and dried in a vacuum desiccator. The best temperature of preparation was 35-40°. Higher temperatures would promote decomposition.

The presence of impurities the ferrate sample had very little effect upon its use in the type studies undertaken. The impurities are KOH and KCl. The presence of the latter, although not of great importance, is of greater concern

than the presence of the former since it is capable of behaving as a reducing agent. The hydroxide tends to stabilize the oxidizing agent retarding its action as a clarifier.

The purity of the potassium ferrate prepared by this procedure was sufficient for the purpose in mind, that of studying its oxidizing properties on various chemicals. The reduction potential for the half reaction:



has been proposed to be 2.20 ± 0.03 v by Wood (1958), who also proposed that the reduction potential for the corresponding half reaction in base $\text{FeO}_4^{=}$ \rightarrow $\text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Fe}(\text{OH})_3 + 5\text{OH}^-$ to be 0.72 ± 0.03 v. These values were calculated from a measured heat of formation and an estimated entropy of the FeO_4^{2-} ion. Some of the early investigators were able to give a good estimation of the oxidizing power of the ferrate as typical of the observation reported by Moeser (1897), that ammonia is oxidized by potassium ferrate solutions when cold, whereas potassium permanganate solutions react with ammonia only when hot. The details concerning the effects of various impurities upon the stability of ferrate solutions has been studied elsewhere (Wagner, 1952; Rose, 1843). Some species were found to be retarding, while some aided decomposition slightly.

In general, soluble organic materials are readily oxidized by potassium ferrate and when this salt is in excess, the organic material is usually degraded to carbon dioxide and water. In slightly acid to strong basic solutions the oxidation of the organic material is accompanied by the separation of hydrous ferric oxide. Exceptions to this behavior occur in the case of some polyhydric alcohols such as glycerol, which complex with iron even in strongly basic solutions, especially when the organic material is present in a large excess. Another instance when the separation of hydrous ferric oxide does not occur is in solutions containing a high concentration of the PO_4^{3-} ion, which appears to complex with iron upon

decomposition of potassium ferrate (VI). These situations will be discussed below.

The ferrate (VI) ion also oxidizes some insoluble organic materials such as paper--making it impossible to filter solutions containing the FeO_4^{2-} ion with filter paper--and insoluble carbohydrates. It even slowly attacks such organic materials as benzene and ethyl ether--when a solution of K_2FeO_4 is shaken with ethyl ether, it is decolorized readily testifying to the reduction of ferrate and oxidization of the ether.

Thus the primary aim became to investigate more closely those situations preventing complete water clarification, and complete elimination of soluble contaminants and reactants. One semi quantitative investigation (Kinsley, 1950) existed indicating that in very alkaline solutions the highly soluble organic contaminants were more readily oxidized than the more insoluble. It also noted that not all the oxidation products were insoluble.

In this study the oxidation of organic compounds by potassium ferrate in various media was studied. The relative rates of oxidation of various organic compounds in 0.12 M and 8 M (dilute and concentrated) potassium hydroxide and phosphate buffer solutions of pH 8.04 were determined. Qualitative tests for the oxidation products from these and other aqueous solutions were performed. These results are given in Tables I-V.

The results from the oxidation of organic compounds by potassium ferrate in 8.0 M potassium hydroxide agree well with Kinsley's experiments. From the data shown in Tables I through V, it can be seen that soluble organic compounds, with the exception of potassium acetate, are oxidized by potassium ferrate. The fact that the acetate ion is not oxidized by potassium ferrate has previously been reported by Rosell. Alcohols are oxidized at a much more rapid rate than other oxygen containing organic compounds.

TABLE I

RELATIVE RATES OF OXIDATION OF ORGANIC COMPOUNDS
 BY 0.024 M K_2FeO_4 IN 8 M KOH SOLUTION.^{a, b}

Organic Compound	Weight, mg	Time of Reduction of K_2FeO_4
Methanol	50	2-3 min.
Absolute Ethanol	70	1-2 min.
Acetone	90	12-13 min.
1, 2-Ethenediol	100	Immediate
1, 2-Propanediol	120	15 sec.
1, 3-Propanediol	120	15 sec.
Glycerol	140	Immediate
1, 2, 4-Butanetriol	160	Immediate
α -Hydroxy Toluene	160	20 sec.
3-Amino-1-Propanol	130	1-2 min.
1, 2-Diaminopropane	130	1 min.
Ethyl Ether	160	45 min.
Benzene	130	None observed
Potassium Acetate	150	None observed

^aThe K_2FeO_4 solution was prepared from 71.05% K_2FeO_4 sample.

^bThe mole ratio of organic compound to K_2FeO_4 is approximately 2.5:1.

TABLE II

RELATIVE RATES OF OXIDATION OF ORGANIC COMPOUNDS

BY 0.012 M K_2FeO_4 IN 8 M KOH SOLUTION. ^{a, b}

Organic Compound	Weight, mg	Time of Reduction of K_2FeO_4
Methanol	50	1-2 min.
Absolute Ethanol	70	1 min.
1, 2-Ethenediol	100	Immediate
1, 2-Propanediol	120	10 sec.
Glycerol	140	Immediate
tert-Butanol	120	12 hours
1, 2, 4-Butanetriol	160	Immediate
3-Amino-1-Propanol	130	1-2 min.

^aThe K_2FeO_4 solution was prepared from 71.05% K_2FeO_4 sample.

^bThe mole ratio of organic compound to K_2FeO_4 is approximately 5:1.

TABLE III

RELATIVE RATES OF OXIDATION OF ORGANIC COMPOUNDS
 BY 0.023 M K_2FeO_4 IN 0.12 M KOH SOLUTION. ^{a, b}

Organic Compound	Weight, mg	Time of Reduction of K_2FeO_4
Methanol	50	27 min.
Absolute Ethanol	70	28 min.
Acetone	90	44 min.
1, 2-Ethenediol	100	10 min.
1, 2-Propanediol	120	14 min.
1, 3-Propanediol	120	10 min.
Glycerol	140	1-2 min.
1, 3-Butanediol	140	21 min.
1, 4-Butanediol	140	20 min.
2, 3-Butanediol	140	25 min.
1, 2, 4-Butanetriol	160	9 min.
1, 5-Pentanediol	160	22 min.
2, 5-Hexanediol	180	29 min.
1, 2, 6-Hexanetriol	200	14 min.
ϕ -Hydroxy Toluene	160	17 min.
3-Amino-1-Propanol	130	4 min.
1, 2-Diaminopropane	130	2-3 min.
Phenanthrene	270	39 min.
1, 4-Dioxane	130	42 min.
Blank		62 min.

^aThe K_2FeO_4 solution was prepared from 82.13% K_2FeO_4 sample.

^bThe mole ratio of organic compound to K_2FeO_4 is approximately 2.5:1.

TABLE IV
RELATIVE RATES OF OXIDATION OF ORGANIC COMPOUNDS
BY 0.0089 M K_2FeO_4 IN 0.12 M KOH SOLUTION. ^{a, b}

Organic Compound	Weight, mg	Time of Reduction of K_2FeO_4
Methanol	50	14 min.
Absolute Ethanol	70	15 min.
Acetone	90	35 min.
1, 2-Ethenediol	100	6-7 min.
1, 2-Propanediol	120	16-17 min.
1, 3-Propanediol	120	8 min.
Glycerol	140	1-2 min.
1, 3-Butanediol	140	10 min.
1, 4-Butanediol	140	10 min.
2, 3-Butanediol	140	30 min.
1, 2, 4-Butanetriol	160	4-5 min.
1, 5-Hexanediol	160	9-10 min.
2, 5-Hexanediol	180	13-14 min.
1, 2, 6-Hexanetriol	200	11 min.
α -Hydroxy Toluene	160	5 min.
3 - Amino-1Propanol	130	2-3 min.
1, 2-Diaminopropane	130	3 min.
1, 4-Dioxane	130	35 min.
Ethyl Ether	160	30 min.
Blank		52 min.

^aThe K_2FeO_4 solution was prepared from 71.05% K_2FeO_4 sample.

^bThe mole ratio of organic compound to K_2FeO_4 is approximately 7:1.

TABLE V
 RELATIVE RATES OF OXIDATION OF ORGANIC COMPOUNDS BY
 0.0087 M K_2FeO_4 IN pH 8, 04 PHOSPHATE
 BUFFER SOLUTION. ^{a, b}

Organic Compound	Weight, mg	Time of Reduction of K_2FeO_4
Methanol	30	2.25 hrs.
Absolute Ethanol	40	2.25 hrs.
Acetone	40	3.25 hrs.
1, 2-Ethenediol	50	35 min.
1, 2-Propanediol	50	38 min.
1, 3-Propanediol	50	22 min.
Glycerol	50	5 min.
1, 3-Butanediol	50	1.75 hrs.
1, 4-Butanediol	50	1.5 hrs.
2, 3-Butanediol	50	1.75 hrs.
1, 2, 4-Butanetriol	60	13 min.
1, 5-Pentanediol	60	1.5 hrs.
2, 5-Hexanediol	70	1.75 hrs.
1, 2, 6-Hexanetriol	70	24 min.
α -Hydroxy Toluene	60	43 min.
3 - Amino-1-Propanol	50	Immediate
1, 2-Diaminopropane	50	Immediate
tert-Butanol	50	1 day
Potassium Acetate	100	1 day
Blank		1.5 days

^aThe K_2FeO_4 solution was prepared from a 79.70% K_2FeO_4 sample.

^bThe mole ratio of organic compound to K_2FeO_4 is approximately 10:1.

When the rates of oxidation of alcohols are compared, the polyhydric alcohols are found to be oxidized much faster than monohydric alcohols. In addition, the polyhydric alcohols with more hydroxyl groups are oxidized at a more rapid rate than other alcohols with the same carbon skeleton. This is in evidence from the tables by the comparison of rates of oxidation of 1, 2-ethanediol, glycerol, and the triols to the rates of oxidation of the alcohols with the same carbon skeleton. For a series of alcohols such as the butanediols, the members of the series with hydroxy groups on the end carbons are oxidized faster.

The rates of oxidation of the organic compounds by potassium ferrate increase as the basicity of the reaction medium is increased. This behavior is similar to base-catalyzed reactions such as anion-type elimination reactions of organic compounds. The phosphate buffer solution is the least basic of the three media used, and together with the stability of potassium ferrate in this solution, this accounts for the relatively slow rates of oxidation of organic compounds.

When the concentration of potassium ferrate in the reaction solutions was doubled, the time required for the reduction of potassium ferrate was approximately doubled.

In a chemical sense we interpret this oxidation to proceed via initial bonding of the organic molecule to a ferrate ion. Alcohols with a minimal steric hindrance bond more easily and are degraded most quickly. From a more practical point of view it means that those species which contain more hydroxyl groups and that are thereby usually the more water soluble, are also the most easily and quickly destroyed.

Quantitative oxidation studies were made of alcohols either likely to be found in waste waters or of alcohols, the chemical nature of which, would allow insight to be gained relative to the products of the first kind. The results of these particular investigations were not especially encouraging from a practical

view point. Namely, it was found that in dilute solutions of alcohol (1%) and ferrate (1%) a relatively large amount of ferrate was required to oxidize the alcohol. On a mole basis the ratio of the amount of alcohol oxidized to the amount of potassium ferrate used is tabulated in Table VI.

TABLE VI
QUANTITATIVE ALCOHOL OXIDATION

<u>Alcohol</u>	<u>Alcohol/Ferrate</u>	<u>Presence of Soluble Product</u>
1, 2 ethanediol	1:2.5	None
1, 2 propanediol	1:8.0	slight
1, 2, 4 butanetriol	incomplete reaction	yes (iron-alcohol complex)
glycerol	1:2.0	slight
phenol	1:7.0	none

It was already known that the decomposition of potassium ferrate in alkaline or neutral solution results in the precipitation of ferric hydroxide. In acid solution the formation of ferric salts occurs. We have added to this general statement with specific examples.

In the studies of the ability of organic compounds to complex with the iron (III) from the decomposition of potassium ferrate, it was found that in water solutions, the compounds normally observed to complex with iron (III), did form complexes in the neutral solution. In 3 M potassium hydroxide solution, it was found that 1, 2-propanediol, glycerol, 1, 2, 4-butetriol, and phenol caused some complexing of iron along with precipitation of ferric hydroxide. In the presence of the very strong ligand, EDTA, the decomposition of potassium ferrate occurred with complete precipitation of the ferric ion as ferric hydroxide: The concentration of potassium ferrate in these solutions was approximately 0.08 M, while the concentration of the organic compounds ranged from approximately 0.11 M to 0.6 M, or in excess of the

amount required to reduce the potassium ferrate.

The reduction of potassium ferrate in the phosphate buffer solution by organic compounds resulted in the formation of brown solutions in all cases. The decomposition of potassium ferrate in the buffer solution resulted in a similar intense brown solution, which contradicted the observation of Kinsley (1950) that such a solution was colorless. Since the spectra were similar to the spectrum of a solution produced by the decomposition of potassium ferrate in the phosphate buffer solution, the color of these solutions is therefore due to the formation of ferric phosphates, and not to any type of complexing reaction between iron (III) and the organic compounds.

Some of the same studies as above were duplicated with ferrate and the pure alcohol. The reaction products of potassium and barium ferrates with 1, 2-ethanediol under anhydrous conditions were isolated, and the amount of 1, 2-ethanediol that reacted with potassium ferrate under these conditions was determined. A product isolated from this reaction was an iron (III) salt of the alkoxide of 1, 2-ethanediol and a polymeric species with a base unit of $\{CHO\}^{1-}$. When water is added to the system the alkoxide hydrolyzes leaving an iron (III) salt of the polymeric species. Potassium ferrate was found to react with 1, 2-ethanediol at a molar ratio of 1:11.9. Salts of glycolic acid were also formed in the reaction, but these could not always be isolated.

Potassium and barium ferrates were reacted with anhydrous solutions of other polyhydric alcohols and the products isolated. Iron (III) glyceroxide was isolated from the reaction of potassium ferrate with glycerol. The products isolated from the reactions of potassium and barium ferrates with 1, 2-propanediol were iron (III) salts of 2-hydroxypropanoic acid, and the reaction of potassium ferrate with 1, 3-propanediol produced an iron (III) salt of 3-hydroxypropanoic acid. Solutions of 1, 3- and 2, 3-butanediols, and 1, 2, 4--butanetriol containing small amounts of water were allowed to react with potassium ferrate. The product isolated from the 1, 2, 4-butanetriol reaction was an iron (III) salt

of the alkoxide and 3, 4-dihydroxybutanoic acid. Quantitative analysis of the reaction solution revealed that the hydroxy groups of the number one and two carbon atoms of 1, 2, 4-butanetriol were not oxidized. No iron containing compounds could be isolated from the reactions of 1, 3- and 2, 3-butanediol with potassium ferrate. A polymeric material which contained a high carbon percentage was isolated in each instance, but these could not be characterized.

The characterization of these products is based primarily upon elemental analysis, C, H and Fe, all performed in our laboratory, and careful infra-red spectral analysis. As noted, many of the products were polymeric and a tentative chemical model has been advanced in an effort to rationalize this behavior (Riley, 1968). It essentially notes that the bulkier polyhydric alcohols are oxidized more slowly and usually at a terminal - OH group where steric considerations are minimal.

For practical purposes these studies with the pure alcohol are not all pessimistic. While iron complexes result, one would not use this technique to prepare them, for the yields are very poor. Large quantities of insoluble iron hydroxide are formed. On a mole per mole basis we found the aqueous solution results reversed, that is, 11.9 moles of ethylene glycol were completely or partly oxidized for each mole of ferrate involved.

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