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Preparation and Alcohol Oxidation Studies of the Ferrate(VI) Ion, FeO_4^{2-}

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The preparation and properties of the very strong oxidizing ion, FeO_4^{2-}*, are reviewed. A shortened method for preparing samples of potassium ferrate(VI) which are usable in oxidation studies was developed. A study of the oxidation of various polyhydric alcohols by potassium ferrate(VI) indicates that the oxidation begins at terminal OH groups of the alcohols. During the course of the oxidation of some polyhydric alcohols by* K_2FeO_4*, polymerization of the alcohols is indicated.*

Introduction

The ferrate(VI) ion has long been known for its oxidizing power, but due to its instability, and difficulty of preparation, it has not been studied extensively. The salts that have been prepared are the alkali metal salts, calcium, strontium, and barium of the alkaline earth metals, and several of the transition metal salts. The stability of the alkali or alkaline earth metal salts increases as the size of the metal ion increases. The transition metal salts are all relatively unstable due to the tendency towards oxidation by the ferrate(VI) ion.[2,3,4]

A factor which contributes to the stability of $BaFeO_4$, the most stable ferrate(VI) salt, is its insolubility. Strontium and calcium ferrates are slightly soluble in water, whereas the alkali metal salts are all readily soluble. All the ferrate(VI) salts are insoluble in nonaqueous solvents.

The ferrate(VI) ion is relatively stable in concentrated alkaline solutions free of any reducing materials, and decomposes spontaneously at a very rapid rate in neutral or acid solution according to the following equation:

$$4\,FeO_4^{2-} + 10\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,OH^- + 3\,O_2$$

There are two efficient methods of preparing relatively pure solid potassium ferrate(VI).[5,6] Both make use of a strong oxidant to oxidize iron(III) in a concentrated alkali metal hydroxide solution, and both require a considerable amount of time for completion. In addition, copious quantities of starting materials are used to prepare and purify relatively small samples of the salt. In this work the purity of K_2FeO_4 was not critical, and a fast and easy method for preparing usable samples of this salt has been developed.

An important factor to consider in the preparation of K_2FeO_4 is its rapid removal from the reaction mixture, since prolonged contact of the product with the potential reducing materials in the solution would lead to partial decomposition of the salt. For this reason any ferrate(VI) salt should be precipitated quickly from aqueous solutions. Moeser[7] found that potassium ferrate(VI) is insoluble and stable in ethanol solutions containing less than 20 per cent water. This information along with solubilities of potassium hydroxide and chloride, the principal contaminants of potassium ferrate, in ethanol suggest that ethanol could be used to precipitate potassium ferrate from aqueous solutions. A preparation for potassium ferrate(VI) incorporating these ideas is outlined below.

The reduction potential for the half reaction:

$$FcO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$$

has been proposed to be 2.20 ± 0.03 volt by Wood[8] who also proposed that the reduction potential for the corresponding half reaction in base

$$FeO_4^{2-}\ 4H_2O + 3e^- \rightarrow Fe(OH)_3(s) + 5OH^-$$

to be 0.72 ± 0.03 volt. 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(VI) as typical of the observation reported by Moeser[7], that ammonia is oxidized by potassium ferrate(VI) solutions when cold, whereas potassium permanganate solutions react with ammonia only when hot.

The ferrate(VI) ion 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.

All water soluble organic substances reduce potassium ferrate(VI) with very few exceptions. It was desired to study the oxidation of various polyhydric alcohols by this salt, and to study extensively this oxidation process. This involved gathering information about the oxidation products, the extent of oxidation, and the relative rates by which the polyhydric alcohols are oxidized.

Lead tetraacetate reacts with polyhydric alcohols containing hydroxy groups on adjacent carbons (α-diols) to form aldehydes and ketones.[9] The interference in this reaction from hydroxy groups in other positions on the carbon chain, or with oxy-groups such as acids, aldehydes, and ketones is negligible. Lead tetraacetate was used to determine the amounts of some polyhydric alcohols remaining in solution after reaction with a given amount of K_2FeO_4.

Experimental

Materials and Reagents

The chlorine used was from a lecture bottle obtained from the Matheson Company. The polyhydric alcohols were supplied by the Aldrich Chemical Company. All other materials used were of reagent grade.

Preparation of K_2FeO_4

Ten grams of chlorine were slowly bubbled into 21 g of KOH in 35 ml of water at 0°. Thirty grams of KOH was 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°, filtered, and the yellow filtrate was stirred rapidly while 12.5 g of pulverized $Fe(NO_3)_3 \cdot 9H_2O$ was 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 $Fe(NO_3)_3 \cdot 9H_2O$ had been added. Twenty grams of KOH was then dissolved in the mixture and the slurry cooled to 0°. This was filtered using a 600 ml coarse porosity fritted glass filter. The precipitate on the filter was leached with three 15 ml portions of cold 1 *M* KOH, and the leachings collected in a filtering flask. The potassium ferrate(VI) solution was added slowly with vigorous stirring to 600 ml of 95% ethanol. After 20 minutes additional stirring the precipitate was filtered off using a coarse porosity filter, and washed on the filter with two 50 ml portions of 95% ethanol, and 50 ml of ether. Great care was taken to minimize the amount of air drawn through the filter. The sample was dried in a vacuum desiccator.

When more pure potassium ferrate(VI) was desired, samples were purified by dissolving the yield from one preparation 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 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 washed with two 50 ml portions of 95% ethanol and 50 ml of ether and dried in a vacuum desiccator. One purification results in samples of 80–90% K_2FeO_4 and an overall yield of greater than 75%. The analyses of the potassium ferrate(VI) samples were carried out using the chromite method developed by Schreyer, Thompson and Ockerman.[10]

Determination of the Extent of Oxidation of Alcohols by K_2FeO_4

Samples of K_2FeO_4 were allowed to react completely with an excess of 1,2-ethanediol, 1,2-propanediol, and 1,2,4-butanetriol under two conditions: (1) in aqueous solution, and (2) in neat alcohol. Any precipitated ferric oxide present after the reactions were complete was dissolved by adding acetic acid. A stock solution of each reaction solution was then prepared by diluting with H_2O in a volumetric flask, and the solutions were analyzed for the α-diol present in the following manner. Five milliliters of one of the above stock solutions and 10 ml of a standard $Pb(OAc)_4$ solution were stirred 10 minutes at 45° in a 500 ml Erlenmeyer flask. Ten milliliters of acetic acid, 3 g of KI, and 90 ml of H_2O were added, the flask stoppered and stirred 5 minutes. The stopper was rinsed with water and removed, and the mixture titrated with standard $Na_2S_2O_3$ until it turned from brown to yellow–brown. Two milliliters of a one percent starch solution was added, and the mixture titrated until the dark color disappeared leaving a yellow mixture. The lead tetraacetate solution was standardized prior to use by reacting 10 ml of approximately 0.05 *M* $Pb(OAc)_4$ in acetic acid with 3 g of KI in 25 ml of acetic acid for 10 minutes in a stoppered 500 ml flask. The mixture was then diluted to 125 ml and titrated with a standard $Na_2S_2O_3$ solution, using starch indicator. In the analyses of these alcohols, a standard solution of approximately the same concentration of each alcohol was prepared and analyzed under the same conditions for comparative results.

Products of the Reaction of Polyhydric Alcohols with K_2FeO_4

1,2-Ethanediol

Samples of K_2FeO_4 (2–5 g) were placed in 25 ml of 1,2-ethanediol and stirred. The reaction appeared complete in 15 min, but the mixtures were heated to approximately 100° and stirred for one hour. Any undissolved material was filtered off. Absolute ethanol and acetone were then added to the dark brown solution to obtain a brown precipitate which was filtered off, washed with acetone and recrystallized three times from 1,2-ethanediol–ethanol–acetone solutions. After drying in a vacuum desiccator the 1–2 g of yellow hygroscopic powder gave the elemental analyses results listed in Table II.

In another set of reactions, 5–7 g samples of K_2FeO_4 were reacted with 1,2-ethanediol as above, the solutions filtered and diluted to approximately 150 ml with water. Without much delay a dilute solution of HCl was added slowly with vigorous stirring, until the solution reached a pH of approximately 3, at which point a fine brown precipitate formed. The precipitate was filtered off, washed with H_2O and then dissolved in 0.01 *M* KOH solution. A brown precipitate was again formed by adding dilute HCl to the intense brown KOH solution until the pH reached 3. The precipitate was filtered off using a fine porosity filter, washed with H_2O and acetone, and dried in a vacuum desiccator. The results of elemental analyses are given in Table II.

1,2-Propanediol

Two grams of K_2FeO_4 was placed in 30 ml of 1,2-propanediol and the mixture stirred for 3 hours at 150°. After filtering a dark brown precipitate was obtained by adding methanol and acetone, which was filtered off and recrystallized from a methanol–acetone solution. After drying in a vacuum desiccator, the brown powder gave the following analyses: C, 26.7; H, 2.98; Fe, 19.2; K, 14.7%.

1,3-Propanediol

A sample of 7.5 g of K_2FeO_4 was placed in 50 ml of 1,3-propanediol and stirred at approximately 50° for 3 days. After filtering, a reddish-brown precipitate was obtained by adding methanol and acetone, which was recrystallized from a methanol–acetone solution, and dried in a vacuum desiccator. The 3 g yield of hygroscopic brown powder gave the following analyses: C, 23.1; H, 2.88; Fe, 24.1; K, 13.1%.

Oxidation Products

Oxidation products from the reaction of an excess of K_2FeO_4 with various polyhydric alcohols in aqueous solutions were determined using conventional "wet" methods of inorganic and organic qualitative analysis.

Infrared Spectra

Infrared spectra of the above compounds were recorded with a Beckman IR–8 spectrophotometer in the range of 4000–600 cm^{-1}. The potassium bromide pellet method was used, and the results of these measurements are given in Tables III and IV.

Results and Discussion

The most efficient way to prepare K_2FeO_4 was to use a 3-fold excess of the oxidant, KOCl, in a concentrated KOH solution, at a temperature of 35–40°. Higher temperatures promoted decomposition. The salt was precipitated from the concentrated KOH almost as quickly as it was formed. Adding more KOH before filtering resulted in almost complete precipitation. The use of iron(III) nitrate rather than any other iron salt produced the best results. It is believed that the nitrate ion is more stable towards oxidation by the ferrate(VI) ion than any of the other anions tried, which included the chloride, sulfate, and phosphate ions.

Aqueous solutions of K_2FeO_4 readily oxidize any soluble organic materials with the possible exception of the acetate ion, whereas organic solvents do not dissolve and are only slowly attacked by ferrate salts. Potassium ferrate(VI) can therefore be precipitated from ethanol solutions, as long as a large excess of the alcohol is present.

The purity of the K_2FeO_4 prepared by this procedure was sufficient for the purpose in mind, that of studying its oxidizing properties on various chemicals. Routine preparations of potassium ferrate(VI) using this procedure produced samples containing approximately 40% K_2FeO_4 and in yields greater than 90%. The time required to complete the procedure was approximately one-third that required to carry out the previously mentioned preparations.

In the analysis of the data concerning the extent of oxidation of the polyhydric alcohols, several factors had to be considered. There was a certain amount of iron(III) present in each sample (from the reduction of K_2FeO_4) which would oxidize the iodide ion to free iodine. Therefore the amount of standard $Na_2S_2O_3$ needed to titrate the liberated iodine had to be corrected for this iron(III). In other words, in 5 ml of stock solution the millimoles of α-diol is equal to the millimoles of $Pb(OAc)_4$ used minus the millimoles of standard $Na_2S_2O_3$ used (less one-half the millimoles of iron(III). By simple comparison this rough value was then corrected for the manner in which the standard samples of the α-diols behaved under the same conditions of analysis. The results are given in Table I.

Upon condensing the data from the Table, one finds that under the conditions of this experiment, the standard solution of 1,2-ethanediol analyzed to be 0.07514/0.8015 of its actual concentration. Using a simple comparison, one finds that the concentration of 1,2-ethanediol in water should be 0.05973 times 0.08015/0.07514 or 0.06371 *M*. Therefore 79.64 mmoles of the original 80.96 mmoles of the alcohol remain, and 1.32 mmoles were oxidized by 3.56 mmoles of K_2FeO_4, which gives a mole ratio of 1,2-ethanediol reacting with K_2FeO_4 of 1.00:2.70. In the reaction of this alcohol with K_2FeO_4, if the oxidation product were formic acid, or oxalic acid, or carbon dioxide the mole ratio of 1,2-ethanediol to K_2FeO_4 would be 1:2, 3:8, and 3:10, respectively. Actually all three of these products were identified in a reaction under conditions similar to those of this experiment. The ratio of 1.00:2.70 would indicate that a combination of these products, and possibly other products are being formed.

The 1,2-propanediol data from Table I can be treated similarly, giving a mole ratio of 1,2-propanediol reacting with K_2FeO_4 of 3.24:1.00. The simplest oxidation product of 1,2-propanediol would be 2-hy-

TABLE I. Extent of Oxidation of Polyhydric Alcohols.

Polyhydric Alcohol	Molar Concentration of α-diol from Analysis	Sample Source
1,2-ethanediol	0.07514	0.4975 g of 1,2-ethanediol in 100.0 ml of solution
1,2-ethanediol	0.05973	0.8849 g of 79.15% K_2FeO_4 with 5.0241 g of 1,2-ethanediol in 50 ml of H_2O – diluted to 1250 ml
1,2-ethanediol	0.05539	1.3040 g of 79.15% K_2FeO_4 with 22.2163 g of 1,2-ethanediol – diluted to 5000 ml
1,2-propanediol	0.09004	0.5909 g of 1,2-propanediol in 100.0 ml of solution
1,2-propanediol	0.04308	0.8611 g of 79.15% K_2FeO_4 with 4.3934 g of 1,2-propanediol in 50 ml of H_2O – diluted to 1250 ml
1,2-propanediol	0.06259	0.5002 g of 79.15% K_2FeO_4 with 22.0773 g of 1,2-propanediol – diluted to 5000 ml
1,2,4-butanetriol	0.04736	0.4215 g of 1,2,4-butanetriol in 100.0 ml of solution
1,2,4-butanetriol	0.05194	1.1802 g of 40.93% K_2FeO_4 with 1.1430 g of 1,2,4-butanetriol in 50 ml of H_2O – diluted to 250 ml
1,2,4-butanetriol	0.05621	1.0766 g of 40.93% K_2FeO_4 with 12.3732 g of 1,2,4-butanetriol – diluted to 2500 ml

droxypropanal, the mole ratio of 1,2-propanediol to K_2FeO_4 in a reaction yielding this product would be 3:2. It is obvious from this data that in the reaction of K_2FeO_4 with 1,2-propanediol, the ferrate(VI) ion in some way becomes involved with more than one molecule of the alcohol, and rearranges them in some manner so that they no longer behave as an α-diol. A simple test for the oxidation products from a reaction under similar conditions to those in the above experiment revealed that no acetic or oxalic acid was formed, indicating that the carbon to carbon linkage in the 1,2-propanediol molecule remains intact during such a reaction.

Looking at the 1,2,4-butanetriol results in Table I one finds after performing calculations similar to those above, that there was actually no noticeable change in the amount of α-diol used in the experiment. In a reaction between K_2FeO_4 and 1,2,4-butanetriol, carried out under conditions similar to these, there was no acetic or oxalic acid detected as an oxidation product. This information along with the above findings would indicate that the carbon chain of 1,2,4-butanetriol is not broken and that the oxidation of this alcohol under the above conditions apparently occurs at the number 4 carbon.

The remaining data from Table I involving the reaction of K_2FeO_4 with the neat alcohols offers some interesting information. In the analysis of 1,2-ethanediol upon treatment of the data as in the previous examples, one finds that the mole ratio of 1,2-ethanediol reacting with K_2FeO_4 is 11.9:1. Similarly, the mole ratio of 1,2-propanediol reacting with K_2FeO_4 is 9.81:1, but it was found with 1,2,4-butanetriol that there was no noticeable change in the concentration of α-diol, although oxidation of a portion of the 1,2,4-butanetriol, at the number 4 carbon, probably took place.

All the solutions obtained from the reaction of K_2FeO_4 with neat polyhydric alcohols possessed an intense brown color, and contained only a small amount of insoluble material after the reaction was complete. This observation indicates some type of compound formation between iron(III) and the reaction medium and products. The separation and analyses of various substances still leaves the work of ascertaining what these compounds are that are formed in these reactions.

If one looks at the reaction between K_2FeO_4 and 1,2-ethanediol, the possible oxidation products of 1,2-ethanediol are many, and included in the list are 2-hydroxyethanal, glycolic acid, formaldehyde, formic acid, oxalic acid, and carbon dioxide. The oxidation of 1,2-ethanediol by K_2FeO_4 in aqueous solutions was studied and the solutions examined for the presence of all the above substances except 2-hydroxyethanal and formaldehyde, and the tests were positive. However in a reaction between K_2FeO_4 and neat 1,2-ethanediol the production of any of these oxidation products in sufficient amounts to complex with the iron(III) present seems highly unlikely.

It therefore becomes necessary to rely on elemental analyses and spectral data to determine the nature of the compounds produced from the reactions of K_2FeO_4 with neat polyhydric alcohols. Taking the data in Table II, the following simplest formulas are obtained

TABLE II. Analyses of K_2FeO_4 and 1,2-Ethanediol Reaction Products.

% C	% H	% Fe	% K
From Non-aqueous Solutions			
(A) 22.00	3.67	31.5	7.20
(B) 19.03	2.72	31.9	8.96
(C)[a] 13.51	2.28	28.4	12.5
From Aqueous pH 3 Solutions			
(1) 10.99	2.71	46.1	0.0
(2) 10.61	2.44	45.5	0.0
(3) 8.75	2.73	44.1	0.0

[a] Recrystallized three times from methanol.

for the compounds resulting from the reaction of K_2FeO_4 with 1,2-ethanediol in non-aqueous solution; (A) $KFe_3(C_{10}H_{20}O_{12})$; (B) $KFe_3(C_7H_{12}O_{10})$; and (C) $K_2Fe_3(C_7H_{14}O_{16})$. The infrared spectra of the first two substances are almost identical, which would indicate that they have the same general structure. The infrared spectra of the two compounds are also very similar to the infrared spectrum of 1,2-ethanediol (Table III).

Miyake[12] has studied the infrared spectra of 1,2-ethanediol coordinated to the metal ions cobalt(II) and nickel(II). The infrared spectra of the dry salts were very similar to the spectrum of the free 1,2-ethanediol, but when the salts contained water, the appearance of a new band in the spectra at approximately 1600 cm^{-1} was observed.

If one compares the infrared spectrum of 1,2-ethanediol to the spectrum of compound A, it can be seen that the bands characteristic of $-CH_2$ and C–O stretching vibrations in the 1,2-ethanediol spectrum (2930 and 2880 cm^{-1} for CH_2; 1083 and 1073 cm^{-1} for C–O) are also present in the spectrum of A. The broad band at 870 cm^{-1} in the spectrum of A could be due to the $-CH_2$ rocking vibration, and the appearance of the broad band at 1595 cm^{-1} along with another broad band at 3430 cm^{-1} are due to the presence of water, as observed by Miyake.

TABLE III. Infrared Spectra of 1,2-Ethanediol and Reaction Products of K_2FeO_4 with 1,2-Ethanediol.[a,b]

$KFe_3(C_{10}H_{20}O_{12})$	$FeCH_3O_3$	1,2-Ethanediol
3430 s, b	3430 s, b	3330 s, b
2930 m	2930 vw	2930 m
2870 m	2860 vw	2880 m
1595 s, b	1625 s, b	
1440 w		1458 m
1360 m, b	1365 m, b	1268 m
1320 w, sh	1320 w, sh	1326 m
1215 vw	1230 vw	1248 w
		1202 m
1072 s	1077 m	1083 s
1035 s	1045 m, sh	1073 s
870 m, b	900 vw	881 m
		861 m

[a] Band positions are given in cm^{-1}. [b] Abbreviations: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad.

Considering the very reactive conditions under which the compounds in these experiments were prepared, and comparison of the elemental analyses of these compounds along with the infrared spectra suggest that these compounds are in part composed of the alkoxide of 1,2-ethanediol. The broad band at 870 cm^{-1}, along with shifts of the bands from 1368 to 1202 cm^{-1} to almost one broad band at 1360 cm^{-1} in the spectrum of A, occur from the formation of the alkoxide, which would restrict some of the vibrations of 1,2-ethanediol molecule. However, attempts to establish the composition of these compounds based on the alkoxide of 1,2-ethanediol were unsuccessful, indicating the presence of other organic species in the compounds.

Considering the remaining data in Table II, the elemental analyses for the substances produced from K_2FeO_4 and 1,2-ethanediol in aqueous pH 3 solution gives varied empirical formulas, but if an average of the elemental analyses is considered, the simplest formula, $FeCH_3O_3$, is obtained. The infrared spectra of all three of these substances were almost identical, and the absorption bands appearing in these spectra are also given in Table III. When this spectrum is compared to the spectra of 1,2-ethanediol and $KFe_3(C_{10}H_{20}O_{12})$, it can be seen that the same fundamental bands are present, but marked changes in the relative intensities of the bands assigned to the $-CH_2$ vibrations of 1,2-ethanediol occur, and the $-CH_2$ deformation band at 1458 cm^{-1} has disappeared. This suggests that in these compounds the same C–O linkage is present, but the 1,2-ethanediol molecule has been altered.

From the quantitative analyses of the potassium ferrate(VI) and neat 1,2-ethanediol reaction solution it was found that the alcohol reacted with K_2FeO_4 at a molar ratio of 11.9:1.00. This suggested polymerization of the 1,2-ethanediol. The reaction products of 1,2-ethanediol with K_2FeO_4 that were precipitated from acid solutions were also found to have varied composition which would also suggest a polymeric species. From the results of these studies it is proposed that the organic species present in these compounds is a polymer with a basic unit of $-(-CHO-)-^{1-}$. This would give rise to a very weak C–H stretching frequency around 2900 cm^{-1}, and possibly very weak bands in the same region that the $-CH_2$ vibrations of 1,2-ethanediol occurs.

It now remains to determine formulas for the various reaction products of 1,2-ethanediol with K_2FeO_4. These would be:

$KFe_3(C_{10}H_{20}O_{12}) = KFe_3\text{–(–CHO–)–}_4(C_2H_4O_2)_3 \cdot 2H_2O$

$KFe_3(C_7H_{12}O_{10}) = KFe_3\text{–(–CHO–)–}_5(C_2H_4O_2) \cdot (OH)_3$

$Fe(CH_3O_3) = Fe\text{–(–CHO–)–}(OH)_2$

The alkoxide of 1,2-ethanediol would readily undergo hydrolysis in aqueous solutions and be removed from the compound, leaving the polymeric compound. The same behavior would explain the results obtained for the third compound recrystallized methanol solutions in Table II. The behavior of this compound in aqueous solutions, that of being insoluble in acid solution, is probably due to the protonation of some sites on the polymer, the more probable site being the oxygen atom of the –(–CHO–)–$^{1-}$ group. When dissolved in basic solution, the compound would be soluble in water again, similar to the behavior of high molecular weight organic acids.

The elemental analysis of the compound isolated from a reaction of K_2FeO_4 with 1,2-propanediol gives the formula $KFeC_6H_8O_6$. Considering the results of the studies of the oxidation of 1,2-propanediol by potassium ferrate(VI) in aqueous solutions, which showed that the carbon chain was not broken, and that the number one carbon atom is oxidized, the compound could either be the salt of 2-hydroxypropanal, or 2-hydroxypropanoic acid. The formula for the latter would be $KFe(C_3H_4O_3)_2$, which agrees with the above analysis.

The bands observed in the infrared spectrum of this compound and of 2-hydroxypropanoic acid are given in Table IV. The similarity of the infrared spectra of $KFe(C_3H_4O_3)_2$ in the region of 1150 to 759 cm^{-1} and in the C–H stretching region around 2900 cm^{-1}, to the spectrum of 2-hydroxypropanoic acid offers strong evidence that the compound is the salt of this acid. Because of salt formation, the C=O (1730 cm^{-1}) stretching bands are replaced by asymmetric-CO_2 stretching bands at 1600 and 1375 cm^{-1}. Such a change is a well recognized sign of such chemical behavior.[12,13]

The analysis of the solution of K_2FeO_4 reacting with neat 1,2-propanediol showed that the mole ratio of this alcohol reacting with K_2FeO_4 is 9.81 : 1. The formation of 2-hydroxypropanoic acid will not account for this high ratio. These results indicate that some type of polymerization or condensation of the 1,2-propanediol is taking place in this solution, similar to the results obtained with 1,2-ethanediol. However, attempts to isolate an iron compound containing any polymeric materials were unsuccessful.

The hygroscopic brown iron compound isolated from the reaction of K_2FeO_4 with neat, 1,3-propanediol had the simplest formula, $K_3Fe_4C_{18}H_{27}O_{21}$, in the best agreement with elemental analysis data. By comparison with the bands in the infrared spectrum of 3-hydroxypropanoic acid, if one considers salt formation as in the previous example, we have assigned the formula $K_3Fe_4(C_3H_4O_3)_6(OH)_3$.

It is now appropriate to discuss the general reaction of K_2FeO_4 with polyhydric alcohols. It is proposed

TABLE IV. Infrared Spectra of the Reaction Products of K_2FeO_4 with 1,2-, and 1,3-Propanediols, and of 1- and 2-Hydroxypropanoic Acids.[a]

$KFe(C_3H_4O_3)_2$	$CH_3CHOHCOOH$(15)	$K_3Fe_4C_{18}H_{27}O_{21}$	CH_2OHCH_2COOH(14)
3430 s, b	3410 s, b	3430 s, b	3420 s, b
2970 w	2990 m	2920 m	2960 m
2930 w	2935 m	2860 m	2895 m
2870 w		1695 w, sh	1725 s
1690 w, sh	1730 s	1580 s	1650 w, sh
1600 s, b	1635 m		1455 w
1545 m, sh		1375 s	1395 m
1450 w	1455 m		1355 m
1402 w, sh		1235 vw	1250 m
1375 s, b	1375 m		1170 s
1340 m, sh		1115 m, sh	1100 vw
1290 m	1285 m	1075 m	1060 m
1240 vw	?	1040 m, sh	1030 m
1125 m	1125 s	935 vw	915 vw
1085 m	1095 s	845 w	875 w
1050 m	1045 m	820 w	815 w
925 vw	920 w		
860 m	865 w		
	820 m		
765 vw	745 w		

[a] See footnotes to Table III.

that the ferrate(VI) ion becomes involved with the end of the alcohol molecule as a first step in the oxidation process. The results of the oxidation studies of 1,2-propanediol and 1,2,4-butanetriol, and the isolation of the oxidation products of K_2FeO_4 with 1,2- and 1,3-propanediols would support this conclusion. As for the production of a polymeric species from 1,2-ethanediol, 1,2-propanediol, and the other polyhydric alcohols, the FeO_4^{2-} ion would conceivably become involved with more than one molecule of the alcohol, and would serve as a very active template for the combining of two or more of the molecules of the alcohol through the end carbon. In the case of 1,2-ethanediol, there is only one possible way in which the alcohol molecules could be combined to form a polymer, but in the case of the other alcohols, the branching and length of the carbon chains would present steric problems in the formation of such polymers. For this reason, it was possible to isolate only the polymeric material formed in the reaction of K_2FeO_4 with 1,2-ethanediol. When K_2FeO_4 reacted with 1,2-propanediol, combination of several of the molecules of the alcohol was indicated, but the bulkiness of the product would not allow the formation of a stable iron complex which could be isolated. The same reasoning would apply in the case of 1,2,4-butanetriol, and experiments with this compound resulted in the isolation of various iron containing samples that could not be characterized. A brown tarry mass which did not contain iron was isolated from the reaction mixtures of K_2FeO_4 with 1,3-butanediol, and with 2,3-butanediol.

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