Effect of Auxiliary Ligand. The frequency of the so-called "O–O" stretching band in various dioxygen or peroxy complexes has been discussed in the literature.[3,20] A slight variation of the frequency upon change of the halogen in Vaska's dioxygen complexes $IrX(O_2)(PPh_3)_2(CO)$, was interpreted to mean that this band is not a pure O–O stretching.[16] In our rhodium complexes the frequency is surprisingly constant when the anionic ligand is changed (*cf.* Table III). Substitution of PPh_3 with $AsPh_3$ also caused only a minor change of the frequency. A change of a substituent on the isocyanide again results in a very small change of the frequency in spite of the great influence on the reversibility of the oxygen addition (*cf.* Table III). The *tert*-butyl derivative irreversibly combines with oxygen, whereas the para tolyl derivative combines reversibly.[39] Thus, the O–O stretching vibration is little influenced by the electronic charge density of the metal coordination center. On the other hand, the "M–O" stretching frequency is more sensitive to these ligand effects and much more helpful for a better understanding of the metal–oxygen bond.

Although the data at hand are not sufficient to establish the effect of an auxiliary ligand, the following trend in the metal–oxygen stretching frequency (ν_{MO}) among the rhodium complexes is discernible: $Cl > Br > I$; $AsPh_3 > PPh_3$; *tert*-BuNC < c-$C_6H_{11}NC$ < *p*-$CH_3C_6H_4$-NC. The trend in the halogen triad may not be reflecting the electronic effect only. The mass effect may be operative here. The same reservation should be borne in mind for comparison of the PPh_3 derivatives with the $AsPh_3$ complex. However, only the electronic effect will be operative on changing the substituent of the isocyanide ligand. The trend suggests that the frequency increases in the order of electron attraction of the substituent and thus of the increase in partial positive charge of the metal. Examination of Table III further indicates that ν_{RhO} and ν_{RhCl} are both increased by an increase in the electron-attracting nature of the isocyanide ligand, *i.e.*, *tert*-Bu < c-C_6H_{11} < *p*-$CH_3C_6H_4$. This trend implies a stronger bond between the more positive rhodium and the anionic ligand. Hence, in comparison with the bonding in the nickel triad, the σ-donating interaction of a partially anionic oxygen ligand with the metal seems more important than the π interaction. This is in contrast with what was observed for Vaska's dioxygen complexes, where irreversible dioxygen coordination was realized in the presence of electron-donating ligands, *e.g.*, $[Ir(O_2)(dp)_2]^+$ (dp = 1,2-bis-diphenylphosphinoethane).[14] Thus, it should be pointed out that the trend in *metal–oxygen stretching* is not in accord with the evaluation of bond strength based on the reversibility of dioxygen coordination.[40]

Acknowledgment. We are grateful to Professor Kozo Hirota of Osaka University for helpful discussions and for making the facility for concentration of ^{18}O available. The help of Professor Kazuo Nakamoto of Marquette University in the redaction of this work is also gratefully acknowledged.

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(40) Note Added in Proof. Recent trends in nomenclature indicate that the ligand referred to in many places in this paper as "oxygen" should be called dioxygen throughout.

Studies on the Mechanism of Isotopic Oxygen Exchange and Reduction of Ferrate(VI) Ion (FeO_4^{2-})[1]

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Contribution from the Chemistry Department, University of Missouri, Columbia, Missouri 65201. *Received February 26, 1971*

Abstract: In basic media the rate of ^{18}O exchange between FeO_4^{2-} and water follows the law $R = k[FeO_4^{2-}]$, where $k = 1.62 \times 10^{-2}$ sec^{-1} at 25°, $\log A = 9.51 \pm 0.79$, and $E_a = 15.4 \pm 1.0$ kcal/mol. In aqueous media the ion of 6+ Fe is FeO_4^{2-} and all oxygens are kinetically equivalent. Both water exchange and water oxidation are accelerated by dilute acid. Stoichiometric, kinetic, and ^{18}O studies have been applied to the reaction of FeO_4^{2-} with H_2O, H_2O_2, and SO_3^{2-}, and the results are compared with other strong oxidizing agents. The reaction with H_2O_2 and SO_3^{2-} are quantitative and show simple stoichiometry. The reactions are first order in H_2O_2 and second order in SO_3^{2-}, but oxygen transfer from FeO_4^{2-} to the product (O_2 or SO_4^{2-}) occurs only in the latter case.

Methods for preparing and analyzing potassium ferrate, K_2FeO_4, of high purity (97–99%) have existed for some time, but little is known about its aqueous chemistry. K_2FeO_4(s) is usually prepared by OCl^- oxidation of freshly prepared iron hydroxide in strongly basic media and isolated from saturated KOH solution.[2–4] Electrolytic means may also be used.[5] Analysis consists of the oxidation of Cr(III) in basic media followed by titration of the Cr(VI) formed with

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acidic Fe(II) solution.[6] Only the reactions of FeO_4^{2-} of analytical interest have been studied in detail.[6-8] Qualitative studies include the oxidation of sulfurous acid,[3] ammonium ion,[3] hydrogen peroxide,[9] nitrite ion,[10] iodide ion,[3] and soluble organic materials.[5,10] FeO_4^{2-} is rapidly reduced by acidic water, yielding molecular oxygen and a complex iron(III) product. In basic media FeO_4^{2-} is the most stable with respect to decomposition in the pH region 10–11 and in concentrated base.[9,11,12] The standard half-cell oxidation potential has been estimated at −2.20 and −0.72 V in acid and base, respectively.[9] The visible,[9,13,14] ir,[15,16] and esr[17,18] spectra of metal ferrates have been measured and Mossbauer,[19] magnetic susceptibility,[2] and powder X-ray studies[20,21] have been carried out.

Little is known about the molecular nature of the ferrate ion in aqueous solution. It has been assumed that discrete FeO_4^{2-} ions exist in water solution (from studies on solids), but no information is available on the importance of dimerization or on the equivalence of or the lability to substitution of the bound oxygen atoms. Mechanistic studies utilizing FeO_4^{2-} as an oxidizing agent require a substantial knowledge of the molecular structure of the aqueous ion and of the kinetics of oxygen exchange with the solvent. This paper reports studies of the rate of oxygen exchange between FeO_4^{2-} and solvent water which, it turns out, is slow enough to determine the coordination number of the iron(VI) and thus give information about the aqueous formula of the ion in basic media. Some oxidation–reduction, kinetic, and tracer studies were carried out to initiate mechanistic investigations of ferrate ion reduction.

Experimental Section

Potassium ferrate was prepared by a method similar to that described by Thompson, Ockerman, and Schreyer,[4] and was analyzed by the chromite method.[6] The samples of K_2FeO_4 ranged between 94.8 and 97.2% pure, and no effect was noted which could be related to the K_2FeO_4 purity. Qualitative experiments revealed the absence of chloride ion, and the impurity was assumed to be iron(III) hydroxide[9] since traces were observed upon solution.

The solvent water was purified by at least two distillations: one from dilute $K_2Cr_2O_7$ solution and one from alkaline $KMnO_4$. The oxygen-18 enriched water, obtained from Yeda Research and Development Co., was triply distilled from an all-glass still. The second distillation was made from dilute alkaline $KMnO_4$ solution. Potassium perchlorate was prepared from AR grade K_2CO_3 + $HClO_4$ and was twice recrystallized from water. Reagent grade KNO_3 was twice recrystallized from water and dried under vacuum. All other materials were of reagent grade and were used directly.

Spectrophotometric measurements were made with either a Beckman Model B or a Cary Model 14 spectrophotometer. The Model B was equipped with thermostated cells and a strip chart recorder. For pH measurements, a Heath pH meter was used after calibration with standard buffers. The Nuclide RMS-16 dual collector mass spectrometer was used to measure the isotopic ratios. It was previously shown to be linear in the regions measured.

FeO_4^{2-}–$H_2{}^{18}O$ Exchange Studies. The reported[9] maximum stability of the ferrate ion in the pH range 10–11 was verified. An increased rate of decomposition with increased $[FeO_4^{2-}]$ was also observed. Consequently, most solvent-exchange experiments were restricted to the pH range 9.6–11.0, and the $[FeO_4^{2-}]$ was low, generally 5×10^{-3} *M*.

The FeO_4^{2-} solvent-exchange studies were initiated by dissolving K_2FeO_4 in oxygen-18 enriched water at constant temperature containing the desired amount of CO_2-free KOH solution and added salts. Samples of this solution (2 ml) were removed at intervals and cooled; $BaFeO_4$ was precipitated by adding a 0° barium chloride solution. Generally, six samples were taken spanning two to four exchange half-lives. The barium ferrate precipitate was separated by centrifugation and vacuum dried for several hours. In separate experiments it was shown that the presence of traces of $BaCl_2 \cdot 2H_2O$ did not affect the ^{18}O values. Some exchange, ≈3%, occurred when the samples were water washed before vacuum drying. Thus, the only samples which were washed were those containing added salts or a high [KOH]. Most reactions were carried out under nitrogen to prevent CO_2 absorption by the weakly basic, unbuffered solutions. Some ferrate ion oxidation of water occurred during the isotopic exchange runs. Maximum FeO_4^{2-} losses due to this reaction were experimentally determined by the chromite method.

The isotopic composition of the ferrate ion oxygens was determined by two different means, both of which gave the same results, ±1%. The first method, a modification of the Anbar and Guttmann technique,[22] consisted of sealing the sample, either $BaFeO_4$, K_2FeO_4 or H_2O, with anhydrous $Hg(CN)_2$ in an evacuated break-seal tube and heating at 400° for 3–4 hr. After cooling, the noncondensable gases were removed and the carbon dioxide and cyanogen were separated by gas chromatography using a 0.25 in. × 6 ft silicone oil on firebrick column.[23] The 46/(44 + 45) mass/charge ratios were measured on the resulting pure CO_2.

The second method of determining the isotopic composition of $BaFeO_4$ consisted of sealing the sample in an evacuated break-seal tube and heating at 250° for 30–45 min. This gave oxygen gas as one of the products, which was purified, and the 34/(32 + 33) mass/charge ratio was measured. Both methods were shown[1] to provide a reliable and consistent measure of the $BaFeO_4$ isotopic composition. Ferrate ion which was equilibrated with oxygen-18 enriched water for ten exchange half-lives ($t_{1/2}$ = 3 min at 25°), precipitated, and treated by both methods gave an ^{18}O content within 2% of that of the solvent determined separately.

The observed rate constant for exchange, k_{obsd}, was obtained from the slope of Calcomp graphs of $-\ln(1 - F)$ *vs.* time, where F refers to the fraction of exchange completed. A representative example is Figure 1. The slope was determined by a linear least-squares computer program, which also calculated the standard deviation in the slope. The overall rate of exchange, R is related to k_{obsd} by the expression

$$R = k_{obsd}\frac{4[FeO_4^{2-}][H_2O]}{4[FeO_4^{2-}] + [H_2O]}$$

Since $[H_2O]$ is very large with respect to $4[FeO_4^{2-}]$, a satisfactory approximation is

$$R = 4k_{obsd}[FeO_4^{2-}]$$

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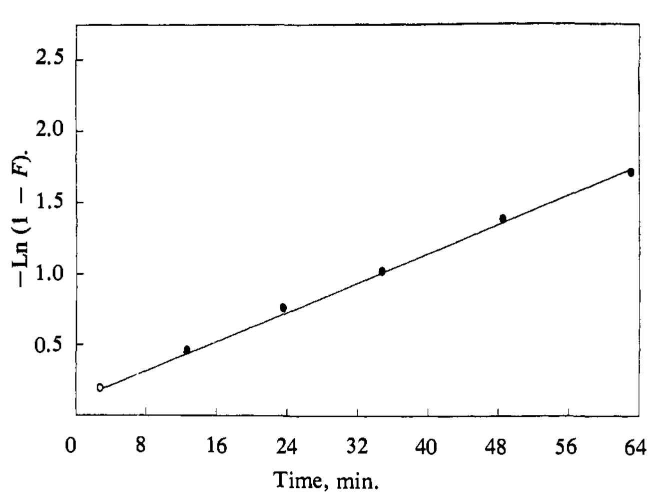

Figure 1. FeO_4^{2-}–H_2O exchange rate. −Ln (1 − F) *vs.* time. [FeO_4^{2-}] = 1.12×10^{-2}, pH 10.6–10.9, [$KClO_4$] = 0.0098, $t_{1/2}$ = 2020 sec, $k_{obsd} = 1.37 \pm 0.03 \times 10^{-3}$ sec^{-1}, 0.0°.

The values of k reported in this paper are defined by

$$k = 4k_{obsd} = R/[FeO_4^{2-}]$$

Kinetics of Reduction by Solvent. Preliminary experiments showed the rate of reduction by solvent to be very sensitive to pH and somewhat sensitive to the precipitated hydrolyzed products of Fe(III). Since the reaction, which may be written $4FeO_4^{2-} + 10H_2O \rightarrow 4Fe(OH)_3 + 3O_2 + 8(OH^-)$, generates OH^-, considerable pH changes occur in an unbuffered media. Therefore, phosphate ion buffers were used which had the additional quality of preventing precipitation by the formation of iron(III) phosphate complexes.

The rate of FeO_4^{2-} reduction by solvent in phosphate ion buffers was monitored spectrophotometrically at 5050 Å. Studies were carried out in the pH range 7.21–7.90. Buffers prepared from reagent grade K_2HPO_4 or KOH + H_3PO_4 or preoxidized K_2HPO_4 gave the same results. The reactions were carried out by bringing the buffer solution to constant temperature in the spectrophotometric cell and injecting a small amount of concentrated, freshly prepared, centrifuged K_2FeO_4 solution. Measurements showed that no pH change occurred during the reactions which were followed to 90–95% completion. The iron(III) product was complexed by the phosphate ions yielding clear solutions with the final absorbance being 2–3% of the initial.

The spectra of FeO_4^{2-} in 10^{-4} M KOH solution showed an absorption maximum at 5100 Å (ϵ 1103 ± 3) and 7850 Å (ϵ 379). These values have been corrected for decomposition which of necessity occurred before and during absorption measurement.[1] These agree with the literature values of 5050, 5100, and 7860 Å (ϵ 1070, 1130, 1120).[9,13,14]

Source of Oxygen in Acid Reduction of FeO_4^{2-}. Tracer studies were carried out to determine if the oxygen gas produced by the solvent reduction of FeO_4^{2-} in the low-pH region was derived from the solvent or from the ferrate ion. Since the order with respect to [H^+] was known for the decomposition but the H^+ order for exchange could not be determined in the acidic region because of decomposition, these data could give information about the latter.

Normal K_2FeO_4 and ^{18}O enriched water were used in all experiments. The isotopic composition of the O_2 formed upon complete reaction was studied as a function of [H^+]. Various acids and buffers altered the O_2 composition. The reactions were carried out under vacuum in a three-arm mixing tube, one arm being connected by a ground glass joint. In one arm was placed about 4 mg of K_2FeO_4(s); in the second arm, 2.0 ml of 10^{-4} M KOH solution made with enriched water; and, in the last arm, 1 ml of acid or buffer solution, made with enriched water. The two solutions were degassed, cooled to 0°, and the KOH solution added to the solid K_2FeO_4. The acid or buffer was immediately added to this mixture. The reaction appeared to be nearly as fast as mixing for the more acid solutions, but required up to a minute for the highest pH. Some reactions were carried out in which an acid or buffer solution was added directly to solid K_2FeO_4. After the reactions, the solutions were frozen (liquid N_2) and the oxygen gas was collected with a Toepler pump for mass spectrometric analysis.

The oxygen-18 content of the solvent water was determined by isotope-ratio measurement of a mixture of O_2 and H_2 produced by electrolysis under vacuum. This method gave the same results as the Anbar-Guttmann method ±0.5%.[1]

The FeO_4^{2-}–SO_3^{2-} Reaction. Kinetic, tracer, and stoichiometric studies were carried out on the FeO_4^{2-}–SO_3^{2-} reaction. The tracer studies were designed to determine if oxygen from the ferrate ion was transferred to the sulfite ion in the oxidation process. Reactions used isotopically normal SO_3^{2-} with ^{18}O enriched FeO_4^{2-} and water. Recently quantitative kinetic exchange studies between H_2O and SO_3^{2-} have been reported.[24] Previous to that report, we carried out brief exchange studies under the conditions used in the FeO_4^{2-}–SO_3^{2-} reactions. Reagent grade Na_2SO_3, 99.3% (manufacturers assay), was dissolved in dilute, deaerated solutions of KOH in $H_2{}^{18}O$. $BaSO_3$ samples were prepared by the addition of Ba^{2+}. The $BaSO_3$(s) was washed and vacuum dried, and its oxygen isotopic composition was determined with CO_2 prepared by its reaction with $Hg(CN)_2$ in a sealed tube. The results showed the exchange rate to be strongly H_{aq}^+ accelerated. At 25°, pH 10, the half-life for exchange was approximately 45 min, in reasonable agreement with the results given in ref 24.

Tracer studies with *excess FeO_4^{2-}* were accomplished by mixing solutions of Na_2SO_3 and K_2FeO_4, both in a 5×10^{-4} M KOH–$H_2{}^{18}O$ solution. The mixture was allowed to stand for 30 min at 0° to assure complete reaction, although it appeared complete in much less time. The mixture was brought to room temperature and $HClO_4$ was added to destroy the excess ferrate ion. Then KOH solution was added to precipitate $Fe(OH)_3$ which was removed. The solution was made 0.1 M in $HClO_4$ and $PbSO_4$ precipitated using 0.5 M lead acetate solution. The precipitate was washed three times with water and vacuum dried. When the reactant solutions were deaerated and the reaction handled under nitrogen, a slightly different result was obtained. This indicated that some air oxidation of SO_3^{2-} occurred in air.

Reactions were also carried out with $Fe^{18}O_4^{2-}$, $H_2{}^{18}O$, and normal SO_3^{2-}. A solution of 0.01 M K_2FeO_4 in 5×10^{-4} M KOH was allowed to equilibrate isotopically (about 10% decomposition occurred during this time period). This solution was treated with a Na_2SO_3 solution and converted to $PbSO_4$, whose ^{18}O content was measured as previously described. When conducted in the presence of air, some air oxidation of the sulfite ion occurred.

Reactions were carried out in *excess SO_3^{2-}* by mixing separate solutions (0°) of Na_2SO_3 and K_2FeO_4 in 5×10^{-4} M KOH–$H_2{}^{18}O$ solution. The reaction appeared to be complete in about 3 min. After reaction, the iron hydroxide was removed by centrifuging and the clear liquid was removed by decantation. The solution was made 0.5 M in $HClO_4$ and SO_2 was quickly removed under vacuum. $PbSO_4$ was precipitated using lead acetate and was given two washings with 0.5 M HNO_3 and two washings with water. Then it was vacuum dried for 5–10 hr.

Barium ion was first used to precipitate SO_4^{2-}, but numerous unsuccessful attempts were made to obtain a useful amount of CO_2 gas representative of the SO_4^{2-} oxygen from $BaSO_4$ at or below 500°.[22,25] Carbon dioxide was obtained from $PbSO_4$ by using mercuric cyanide,[25] and the CO_2 was purified by gas chromatography. Checks were made to determine the precision and accuracy of the SO_3^{2-} isotopic analysis. It was found that $PbSO_4$ had to be degassed under vacuum at a very high temperature or erroneous results were obtained. Degassing was accomplished with the sample in a platinum boat in a quartz tube. The tube was attached to the vacuum system and heated at 500–600° for 2 hr. A sample of normal SO_4^{2-} was precipitated from an oxygen-18 enriched solution, washed with enriched water, and dried in the manner above. The relative oxygen-18 abundance, where a normal sample has a value of 1.000, was found to be 1.013, where the enriched H_2O value was 3.191. Also, solutions of SO_3^{2-} (under N_2) and FeO_4^{2-} in deaerated ^{18}O water were allowed to isotopically equilibrate before reaction. When reacted, the $PbSO_4$ obtained gave relative abundances of 2.934 and 2.874 to be compared with the water values of 3.107 and 3.093. Thus, assuming that the SO_4^{2-} was of solvent composition, about 6% error is involved in measurements at this level of isotopic abundance. No study of the source of this error was made.

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The stoichiometry of the FeO_4^{2-}-SO_3^{2-} reaction was measured under the same concentration and pH conditions used in the tracer experiments. With excess FeO_4^{2-} the iron(III) product was removed as the hydroxide, and a standard $BaSO_4$ gravimetric determination was used to measure the amount of SO_4^{2-} produced. With excess SO_3^{2-}, an iodometric titration of the excess sulfite ion was used. NH_4HF_2 was present as a buffer and to prevent iron(III) oxidation of sulfite ion or iodide ion. A qualitative test showed no Fe(II) generation.

An iodometric determination of the Na_2SO_3(s) purity gave a value of 99.7 ± 0.3% Na_2SO_3 in the anhydrous reagent. The SO_4^{2-} content of the same material as shown by $BaSO_4$ precipitation gave 0.84 ± 0.01% Na_2SO_4. The uncertainties are the average deviation from the mean.

An analysis for dithionate ion was carried out on the product of the FeO_4^{2-}-SO_3^{2-} reaction (excess SO_3^{2-}) using the method of Murthy.[26] Only 1 ± 1% of the SO_3^{2-} was converted to dithionate ion.

The rate of reaction of SO_3^{2-} with FeO_4^{2-} was followed by absorption measurements at 5050 Å in K_2HPO_4-K_3PO_4 solutions. They were carried out by injecting a small volume of centrifuged K_2FeO_4 solution (in HPO_4^{2-} buffer) into the appropriate solution containing phosphate buffer and Na_2SO_3 at constant temperature. An excess of SO_3^{2-} was employed to assure first-order kinetics. The values of k_{obsd} were evaluated from linear least-squares evaluations of the first-order expression.

$FeO_4^{2-} + H_2O_2 \rightarrow Fe(III) + O_2$. Stoichiometry. A standard H_2O_2 solution (unstabilized AR grade) in 0.01 *M* Na_2HPO_4 was standardized against a standard Ce^{4+} solution. A fresh, dilute K_2FeO_4-0.10 *M* Na_2HPO_4 solution was centrifuged to remove solids and separated into two portions. The absorption at 5050 Å was measured on one sample and an exact volume of the other was added to a measured excess of standard H_2O_2 solution. After 12-15 min, acid was added to the latter until the solution was acidic, and the excess H_2O_2 was titrated with standard Ce^{4+} solution. Using the data obtained, the $FeO_4^{2-}:H_2O_2$ ratio was calculated. The time of contact had a slight effect. Below 8 min reaction time, the reaction was not complete, and beyond 20 min there was noticeable decomposition of the excess H_2O_2. Decomposition is somewhat faster in the presence of iron(III) products.

Kinetics. Preliminary experiments suggested that the reaction conformed to the rate law $-d[FeO_4^{2-}]/dt = k[FeO_4^{2-}][H_2O_2]$. The measurement of $[FeO_4^{2-}]$ *vs.* time was made spectrophotometrically at 5050 Å. Experiments were conducted in two ways. (1) A solution of Na_2HPO_4 and K_2FeO_4 was centrifuged and brought to temperature in a cell, and a small quantity of a standardized H_2O_2 solution was added. (2) A solution of Na_2HPO_4 and H_2O_2 was brought to temperature and a small volume of a centrifuged K_2FeO_4 solution added. The infinite absorption values were 2-5% of the original, depending on $[FeO_4^{2-}]$ and $[HPO_4^{2-}]$. The reactant concentrations were within a factor of 4 of each other and second-order equations, modified for the stoichiometry, were used.[27] For excess H_2O_2

$$\ln\left[\frac{a_0}{1.5b_0 + (a_0 - 1.5b_0)(A_0 - A_\infty/A_t - A_\infty)}\right] = (b_0 - 0.66a_0)kt$$

For excess FeO_4^{2-}

$$\ln\left[\frac{0.66a_0 + (b_0 - 0.66a_0)(A_0 - A_\infty)/A_t - A_\infty)}{b_0}\right] = (b_0 - 0.66a_0)kt$$

where $a_0 = [H_2O_2]$, $b_0 = [FeO_4^{2-}]$, and A_0, and A_∞, and A_t are the FeO_4^{2-} concentrations at 0, ∞, and time *t*, respectively. These equations were followed (Figure 2) over at least the 10-90% region, and the same rate constant (within experimental error) was found in excess H_2O_2 or excess FeO_4^{2-}. The observed rate constant was a function of Na_2HPO_4 concentration. This was due primarily to the change in $[H^+]$ concurrent with changing [buffer]. $[H^+]$ for each $[Na_2HPO_4]$ was calculated using the equation[28]

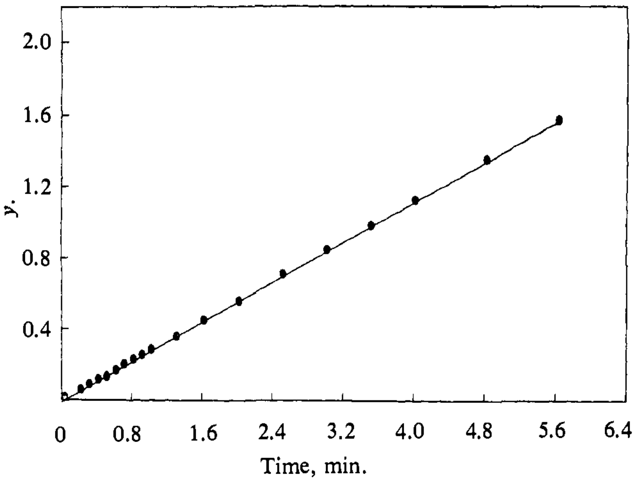

Figure 2. FeO_4^{2-}-H_2O_2 reaction rate. 15°, $[HPO_4^{-2}] = 0.10$, $[H_2O_2]_i = 6.28 \times 10^{-4}$, $[FeO_4^{2-}]_i = 2.93 \times 10^{-4}$, $A_0 = 0.322$, $A_\infty = 0.013$, $y = -\ln[a_0/1.5b_0 + [a_0 - 1.5b_0](A_0 - A_\infty/A_t - A_\infty)]$.

$$[H^+] = \left[\frac{CK_1K_2 + K_1K_W}{C + K_1}\right]^{1/2}$$

where $K_1 = 6.23 \times 10^{-8}$, $K_2 = 7.52 \times 10^{-13}$, and $K_W = 1 \times 10^{-14}$.

Oxygen-Transfer Experiments. ^{18}O enriched water and Na_2HPO_4 (0.1 *M*) were placed in one arm of a two-arm vacuum tube; in the other arm was placed solid K_2FeO_4. The solution was degassed and poured onto the K_2FeO_4. The released O_2 was collected after complete reaction (2 min) and dried, and the 34/(32 + 33) mass/charge was ratio measured. The ^{18}O content of H_2O was obtained by measuring CO_2 prepared by Anbar's method, K_2FeO_4 by thermal decomposition to O_2, and H_2O_2 by catalytic decomposition to O_2 in the presence of Fe(III). In certain cases the FeO_4^{2-} was equilibrated with enriched water before reaction.

Results and Discussion

The Aqueous Formula of the Iron(VI) Ion. In solid K_2FeO_4 the geometry of the negative ion is tetrahedral as shown by X-ray powder pattern studies.[20,21] A tetrahedral structure is consistent with the infrared spectra in aqueous solution.[16] The experiments presented in this study which show that K_2FeO_4 can be dissolved in ^{18}O enriched water and the FeO_4^{2-} ion removed as $BaFeO_4$(s) with less than 5% exchange prove that the primary coordination number does not rise above or fall below four in forming the aqueous solution. This applies to the pH region 9.6-14 and a $[FeO_4^{2-}] \sim 5 \pm 10^{-3}$ *M*. The linearity of graphs of $\ln(1 - F)$ *vs.* time (Figure 1) shows that no significant chemical changes occur, *i.e.*, dimerization, in the time scale of a $t_{1/2}$ for exchange (25 min) and that all four oxygens are equivalent. Thus, the ^{18}O measurements show that Fe(VI) in water solution has a primary coordination sphere of four oxygens. These are most likely tetrahedrally arranged.

Kinetics of FeO_4^{2-}-H_2O Exchange. In the region pH 9.6 to 1 *M* OH^- the overall rate of exchange, *R*, varies

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[27] J. Casey, Ph.D. Thesis, University of Missouri, 1969.

[28] W. C. Pierce and E. L. Haenisch, "Qualitative Analysis," Wiley, New York, N. Y., 1948, p 196.

Table I. Hydroxide Ion Dependence of the FeO_4^{2-}–$H_2{}^{18}O$ Exchange Reaction[a]

10^4[KOH] added	pH[b]	Estd decomp, %	$t_{1/2}$, sec[c]	10^3k, sec^{-1} [c]
0.48[d]	9.6–9.7	6	2010 ± 70	1.38 ± 0.05
5.0[d,f]	10.1	6	1730 ± 30	1.60 ± 0.03
5.0[e]	10.4	6	1850 ± 20	1.50 ± 0.02
9.6[d]	11.0–11.2	9	1280 ± 10	2.16 ± 0.02
9.9[d]	11.0–11.3	9	1370 ± 30	2.02 ± 0.04
99.0[e,g]		27	~1300	~2.1
1.0 × 10^4 [e,h]		6	3550 ± 60	0.78 ± 0.01

[a] 5 × 10^{-3} M K_2FeO_4, 0.0°. [b] Measured at 25 ± 0.1°. [c] Errors represent one standard deviation. [d] Isotopic analysis using thermal decomposition. [e] Isotopic analysis using $Hg(CN)_2$. [f] Reaction flask wrapped with aluminum foil. [g] Originally 9.7 × 10^{-3} M in K_2FeO_4. The large amount of decomposition made the results only approximate. Samples were taken for only 15 min. [h] Samples washed with normal water.

Table II. FeO_4^{2-}–$H_2{}^{18}O$ Exchange Rates

Run	$10^3[K_2FeO_4]^a$	Temp, °C	pH	[$KClO_4$]	μ	$t_{1/2}$, sec[f]	$10^3k'$, sec^{-1} [f]
8[d]	2.52	0.0	10.5[b]	0.0320	0.040	1700 ± 70	1.63 ± 0.06
9[d]	5.38	0.0	10.5[b]	0.0182	0.035	1820 ± 60	1.52 ± 0.05
10[e]	11.2	0.0	10.6–10.9[c]	0.0098	0.043	2020 ± 40	1.37 ± 0.03
3[d]	5.0	0.0	10.4[b]	0.000	0.016	1850 ± 20	1.50 ± 0.02
11[d,h]	5.0	0.0	10.5[b]	0.0132[i]	0.030	1620 ± 120	1.71 ± 0.13
12[d]	5.0	0.0	10.6[g]	0.0405	0.057	1760 ± 70	1.58 ± 0.06
13[d]	5.0	0.0	10.5[b]	0.375[i,j]	0.054	1840 ± 70	1.51 ± 0.06
k[d]	5.0	0.0	10			1810	1.53
14[d]	5.0	4.2[l]	10.4–5[b]	0.010	0.043	1160 ± 20	2.39 ± 0.04
15[d]	5.0	8.4[l]	10.4[b]	0.010	0.043	858 ± 12	3.23 ± 0.03
16[d]	5.0	12.5[l]	10.2[b]	0.010	0.043	558 ± 9	4.97 ± 0.08
17[d]	5.0	16.5[l]	10.5[b]	0.010	0.043	344 ± 9	8.07 ± 0.02

[a] Refers to initial concentration. [b] 5.0 × 10^{-4} M in added KOH. [c] No KOH added. High pH resulted from decomposition. [d] Less than 6% decomposition during run. [e] Approximately 13% decomposition during run. [f] Errors represent one standard deviation. [g] 6.7 × 10^{-4} M in added KOH. [h] Isotopic analysis using thermal method except for this run (used $Hg(CN)_2$ method). [i] Samples washed with water. [j] KNO_3 added. [k] Average of runs 3, 9, 11, 12, 13, 18, and 19. [l] ±0.05°.

only slightly (Table I). The slight decrease in 1 M may be due to medium effects or to the somewhat larger rate of reduction by water which may utilize a common activated intermediate. Table II contains the results of experiments designed to determine the order with respect to [FeO_4^{2-}]. The order observed was 0.88 × 0.04, a value somewhat less than unity. Again, the rate of reduction may be responsible for the slower-than-expected value of R at high [FeO_4^{2-}]. Since the rate of reduction is dependent on $[FeO_4^{2-}]^{3/2}$ (approximately), the fraction of FeO_4^{2-} reduced during the isotopic exchange study would be related to the initial [FeO_4^{2-}]. Thus, these results are taken to imply a first-order dependence on [FeO_4^{2-}] and independence of [OH^-]. A similar term has been observed in the isotopic water exchange with chromate,[29] permanganate,[30] and perrhenate[31] ions in neutral or basic media. The effect of ionic media is illustrated in Table II. The exchange is little affected by a change in ionic strength or by switching from KNO_3 to $KClO_4$. The temperature dependence is shown in Table II. The Arrhenius activation energy from a least-squares analysis gave E_a = 15.4 ± 1.0 kcal/mol. Similar activation energies for MnO_4 and ReO_4 (same kinetic term) are 14.1 and 15.44 ± 0.05 kcal/mol, respectively, suggesting that the activated states are basically similar.

From the results tabulated in Table III the rate of exchange is insensitive to the presence of the iron hydroxide impurity in the reactant or that produced due to decomposition. Further, the rate is not modified by changing the container surface from glass to Teflon. An attempt was made to find out if the reaction or a portion of it was carried by traces of Fe^{IV} or Fe^V formed by reduction. Both are expected to react rapidly with OCl^- in basic media regenerating FeO_4^{2-}. If a significant portion of the exchange is carried by a lower oxidation state of iron, the presence of OCl^- should lower the observed rate constant. In fact, the experimental rate increases significantly. Thus, lower oxidation states of iron are probably not responsible for a major portion of the exchange. The rate increase is likely due to the

Table III. Possible Effects of Iron Species in Lower Oxidation State[a]

Run	pH	$t_{1/2}$, sec[b]	$10^3k'$, sec^{-1} [b]
3[c]	10.4[g]	1850 ± 20	1.50 ± 0.02
18[c,e]	10.1[g]	1770 ± 20	1.57 ± 0.02
19[d,f]	10.2–10.4[h]	1860 ± 70	1.49 ± 0.05
20[c,f,i]	10.4	1520 ± 30	1.82 ± 0.03

[a] 5 × 10^{-3} M K_2FeO_4, 0.0°, isotopic analysis using thermal decomposition. [b] Errors represent one standard deviation. [c] Less than 6% decomposition occurred during the reaction. [d] Approximately 6% decomposition occurred during the reaction. [e] Carried out in a Teflon beaker. Some CO_2 was probably absorbed since the reaction was not run under nitrogen. [f] Iron hydroxide was removed by centrifuging before reaction carried out. [g] 5.0 × 10^{-4} M in added KOH. [h] 3.8 × 10^{-4} M in added KOH. [i] 2.5 × 10^{-4} M in added KOH and 0.05 M in NaOCl. Samples washed with normal water.

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(29) R. H. Holyer and H. W. Baldwin, *Can. J. Chem.*, **45**, 413 (1967).

(30) K. H. Heckner and R. Landsberg, *J. Inorg. Nucl. Chem.*, **29**, 413 (1967).

(31) R. K. Murmann, *J. Phys. Chem.*, 71, 974 (1967).

generation of exchanged FeO_4^{2-} from the OCl^- oxidation of Fe^{III} to Fe^{IV} to Fe^V. Thus, the equation $R = k[FeO_4^{2-}]$ describes the isotopic oxygen exchange basic media with $k = 1.62 \times 10^{-2}$ sec^{-1} at 25° and Arrhenius parameters log $A = 9.51 \pm 0.79$ sec^{-1} and $E_a = 15.4 \pm 1$ kcal/mol.

The mechanism of exchange by this path may be described by: (a) an SN2 reaction utilizing H_2O as a reactant, (b) a nonspecific solvent assisted dissociation, or (c) the formation of symmetrical (HO–Fe(O_3)–OH) from $HFeO_4^-$ and OH^-.

On the basis of recent studies[31,32] on water exchange with ReO_4^- in methanol, (a) seems improbable, but no means of differentiating between the latter two possibilities exists.

Measurement of the rate of exchange in more acidic media is virtually impossible due to the rapid rate of water oxidation by FeO_4^{2-}.

$$10H_2O + 4FeO_4^{2-} \longrightarrow 4Fe_{aq}^{3+} + 3O_2 + 20(OH^-)$$

Some information about the H_{aq}^+ susceptibility of the exchange rate may be obtained under favorable circumstances from the kinetics of decomposition and the isotopic composition of the oxygen generated from FeO_4^{2-} and H_2O of different oxygen isotope composition.

Previous work[12] suggested that the rate of decomposition was proportional to $[FeO_4^{2-}]^2[H^+]$. Preliminary work suggested that this was approximately true, but quantitative results could not be obtained owing to large pH changes and $Fe(OH)_3$ precipitation during reaction. The addition of phosphate ion buffers eliminated both problems. However, the observed rate was a function of $[PO_4^{3-}]$.[33] The rate of FeO_4^{2-} oxidation of water was, within experimental error, equally well fitted with first- and second-order terms in $[FeO_4^{2-}]$ or to an equation to the $^3/_2$ order in $[FeO_4^{2-}]$. The values of these constants evaluated by a least-squares analysis of absorbance *vs.* time data are given in Table IV. In an effort to distinguish between these rate equations, the initial concentration of reactant was lowered by a factor of 10 by using 10-cm cells. From Table IV it can be seen that $k_{3/2}$ is not constant, but neither is the value for k_1 (k_2 is constant). The fact that the value for k_1 but not for k_2 is dependent on [products] suggests that the correct rate equation involves a first- and second-order term in FeO_4^{2-} with k_1 being sensitive to the presence of products. The results of the pH dependence study are shown in Table V.

Table IV. Concentration Dependence on Ferrate ion Reduction Rate[o]

Expt	Initial $[FeO_4^{2-}]$	10^3k_1, sec^{-1} [b]	k_2, M^{-1} sec^{-1}	$k_{3/2}$, $M^{-1/2}$ sec^{-1}
1	3.8×10^{-5}	1.1 ± 0.1	98 ± 7	0.70 ± 0.01
2	3.7×10^{-4}	4.9 ± 0.5	$100 + 5$	1.45 ± 0.08
3[c]	3.7×10^{-4}	8.1 ± 0.7	101 ± 8	1.87 ± 0.02

[o] 25.0°, 5050 Å, 0.01 M K_2HPO_4 (total concentration of all phosphate species), pH 7.60. [b] Values are the average of at least three determinations, and the errors are the average deviation from the mean. [c] Initially 8.6×10^{-4} M in Fe(III).

Table V. Hydrogen Ion Dependence on Ferrate Ion Reduction Rate[a]

pH	10^3k_1, sec^{-1} [b]	k_2, M^{-1} sec^{-1}	$k_{3/2}$, $M^{-1/2}$ sec^{-1}
7.21	10.6 ± 3.0	350 ± 40	4.10 ± 0.10
7.41	8.7 ± 0.7	195 ± 8	2.70 ± 0.07
7.60	4.9 ± 0.5	100 ± 5	1.45 ± 0.08
7.76	4.8 ± 0.3	62 ± 2	1.12 ± 0.02
7.90	2.5 ± 0.1	39 ± 1	0.67 ± 0.01

[a] 25.0°, 5050 Å, 0.10 M K_2HPO_4 (total concentration of all phosphate species), $[FeO_4^{2-}]_0 = 3.7 \times 10^{-4}$ M. [b] Values are the average of three to five determinations and the errors are the average deviation from the mean.

The following orders with respect to $[H^+]$ were revealed: k_1, 0.87 ± 0.18; k_2, 1.39 ± 0.03. The nonintegral terms may reflect general acid catalysis by phosphate species. For a 0.05 M phosphate ion solution $\sim 1 \times 10^{-3}$ M FeO_4^{2-} at pH 7.20, the apparent values of k_1 and k_2 at 25° are $6.0 \pm 0.5 \times 10^{-3}$ sec^{-1} and 163 ± 10 M^{-1} sec^{-1}, respectively.

H_2O Oxidation by FeO_4^{2-}. Tracer Studies. Table VI shows the results of studies conducted using normal FeO_4^{2-} and enriched H_2O. The fraction of oxygen derived from the solvent, F, was calculated using $N_{O_2} = (N_{H_2O})F + (N_{FeO_4^{2-}})(1 - F)$. The quantities N_{O_2}, N_{H_2O}, and $N_{FeO_4^{2-}}$ refer to relative ^{18}O abundances in these materials at the time of mixing. An obvious conclusion is that in the most basic region over half of the oxygen comes from FeO_4^{2-}, with the rest from the

Table VI. Tracer Studies on the Acid Reduction of Ferrate Ion

Acid or buffer[a]	pH[b]	N_{H_2O}[c]	N_{O_2}[c]	% O_2 from solvent
$HClO_4$	0.5[d]	3.445	3.223	90.9
$HClO_4$	0.5[d]	3.427	3.067	85.2
$HClO_4$	0.92[d]	3.652	3.519	95.0
H_3PO_4	1.32[d]	3.428	3.329	95.9
$HClO_4$	1.48[d]	3.438	3.233	91.6
H_3PO_4–KH_2PO_4	2.25–2.40	3.483	3.376	95.7
HOAc–KOAc	4.0–4.3	3.491	2.917	77.0
HOAc–KOAc	4.0–4.3	3.514	2.700	67.6
KHP	4.1–4.9	3.438	2.787	73.3
KH_2PO_4–K_2HPO_4	6.8–7.3	3.503	2.492	59.4
KH_2PO_4–K_2HPO_4	6.8–7.5	3.504	2.401	56.0
KH_2PO_4–K_2HPO_4	7.3–8.3	3.421	2.040	43.0
$HClO_4$	1.0	3.361	2.614	68.4[e]
H_3PO_4–KH_2PO_4	2.25–2.50	3.3457	1.843	34.3[e]
KH_2PO_4–K_2HPO_4	7.3–8.8	3.451	1.948	38.7

[a] Buffers were 0.03–0.2 M (25°). [b] pH of the reaction mixture (range beginning to end). [c] Enrichments, where the enrichment of the K_2FeO_4 was arbitrarily assigned a value of 1.000. [d] Calculated pH values from the amount of acid added. [e] Reactions with solid K_2FeO_4.

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(32) R. K. Murmann, *J. Amer. Chem. Soc.*, **93**, 4184 (1971).
(33) M. Wronska, *Rocz. Chem.*, **36**, 789 (1962).

solvent. Using solid K_2FeO_4 instead of a solution increases this value. In the acid region, the solvent contribution increases until at *ca.* 1 *M* acid the O_2 has essentially the same ^{18}O composition as the solvent.

One may conclude that either the exchange rate is not acid dependent and the mechanism of water oxidation changes in acid such that no FeO_4^{2-} oxygen is transferred to the O_2, or that the rate of FeO_4^{2-}–H_2O exchange has a $[H^+]^n$ term which causes the exchange to become more competitive with water oxidation at the higher acidities. In view of the fact that all oxyanions which have been studied show a $[H^+]^n$ term in the exchange rate law, the latter explanation is the most likely. Further, since the decomposition is about first order with respect to $[H^+]$ and the exchange becomes essentially complete at high [acid], the order with respect to $[H^+]$ must be greater than one. By analogy with other systems it is likely that the FeO_4^{2-}–H_2O exchange contains a term which is second order in $[H^+]$.

The FeO_4^{2-}–SO_3^{2-} Reaction. The stoichiometry with excess FeO_4^{2-}

$$2FeO_4^{2-} + 3SO_3^{2-} \longrightarrow 2Fe(III) + 3SO_4^{2-}$$

was determined by gravimetric analysis of the sulfate ion produced. The amounts of $BaSO_4$ were found to be 92.21 and 94.39 mg, while the amounts expected were 94.88 and 97.52 mg, respectively. The results have been corrected for the small SO_4^{2-} contamination in Na_2SO_3. From this, 1.55 mol of SO_3^{2-} is consumed per mole of FeO_4^{2-}. With excess SO_3^{2-}, the following results were obtained: SO_3^{2-}:FeO_4^{2-} (molar ratio consumed) = 1.57, 1.59, 1.59, 1.54 (average = 1.57 ± 0.02). Within experimental error, this implies that 1.5 mol of SO_3^{2-} reacts with 1.0 mol of FeO_4^{2-}. The somewhat high value under both conditions could be due to the formation of dithionate ion, but tests for it were essentially negative.

Table VII. Apparent Rates of the Reaction[a] $FeO_4^{2-} + SO_3^{-2} \rightarrow Fe^{111} + SO_4^{-2}$

$[SO_3^{2-}]$	Temp, °C	k, sec^{-1}	$[SO_3^{2-}]$	Temp, °C	k, sec^{-1}
0.002[b]	9	0.005	0.008[c]	9	0.017
0.004[b]	9	0.014	0.005[c]	9	0.010
0.005[b]	9	0.020	0.008[b]	8	0.035
0.006[b]	9	0.026	0.008[b]	13	0.038
0.008[b]	9	0.039	0.008[b]	20	0.037
0.010[b]	9	0.062			
0.012[b]	9	0.081			

[a] 0.10 *M* sodium buffer solutions used. $[FeO_4^{2-}]$ 3 × 10^{-4} *M*. k is the pseudo-first-order rate constant (excess SO_3^{2-}). [b] HPO_4^{2-}:PO_4^{3-} = 3, pH(measured) 10.92. [c] HPO_4^{2-}:PO_4^{3-} = 1, pH(measured) 11.92.

The kinetic results for the reaction between FeO_4^{2-} and SO_3^{2-} are given in Table VII. The rate law is $-d[FeO_4^{2-}]/dt = k[FeO_4^{2-}][SO_3^{2-}]^2$ to the precision expected on the basis of the reliability of each run. There appears to be a $[SO_3^{2-}]$-independent term which is of the same magnitude as, and is probably due to, FeO_4^{2-} reaction with water. The reaction rate increases with acidity and with ionic strength. The acid dependence interpretation is complicated by the concurrent change in phosphate ion forms. The temperature dependence is small. A much more complete study is needed before a mechanism can be suggested.

Table VIII. Tracer Studies of the FeO_4^{2-}–SO_3^{2-} Reaction[a]

Excess reagent	N_{H_2O}[b]	N_{PbSO_4}[b]	% oxygen from solvent[c]
	Normal FeO_4^{2-}		
FeO_4^{2-}	3.060	1.174	34
FeO_4^{2-}	3.060	1.181	35
FeO_4^{2-}	2.979	1.165	33[d]
FeO_4^{2-}	2.979	1.183	37[e]
SO_3^{2-}	3.060	1.170	33
SO_3^{2-}	3.060	1.166	32
SO_3^{2-}	2.979	1.164	33
	Enriched FeO_4^{2-}		
			% oxygen from solvent FeO_4^{2-}[c]
FeO_4^{2-}	3.060	1.395	77[f]
SO_8^{2-}	3.060	1.366	71[f]
FeO_4^{2-}	2.979	1.436	88[e]
FeO_4^{2-}	2.979	1.434	88[e]

[a] 5.0 × 10^{-4} *M* KOH, 0°. [b] The numbers refer to enrichment, where the enrichment of Na_2SO_3 was arbitrarily set as 1.000. [c] The value would be 100% if one SO_4^{2-} oxygen in four was of solvent enrichment. [d] Reaction allowed to stand 60 min. [e] Carried out with deaerated solutions and reactions run under nitrogen. [f] Results of doubtful significance since air oxidation probably occurred.

The results of ^{18}O tracer studies are shown in Table VIII. The fraction of the fourth sulfate oxygen, F, derived from the solvent (and FeO_4^{2-} in experiments 8–11) was calculated using

$$4N_{PbSO_4} = (N_{H_2O})F + (N_{SO_3^{2-}})(4 - F)$$

where N refers to the relative ^{18}O abundance in the substances specified. Some corrections which would slightly modify the values in Table VIII include accounting for the initial SO_4^{2-} impurity in Na_2SO_3, correcting for FeO_4^{2-} exchange during reaction, air oxidation of SO_3^{2-}, and systematic errors in the $PbSO_4$ isotropic analysis. In the first set, a value of 35 × 5% is a reliable estimate of the amount of the fourth oxygen derived from the solvent. The second set shows the importance of SO_3^{2-} air oxidation. Applying the measured systematic error in $PbSO_4$ ^{18}O measurement at high $[^{18}O]$ gives 97% of the fourth oxygen derived from the solvent and FeO_4^{2-}.

The combination of both tracer experiments shows that 65 × 5% of one sulfate ion oxygen is obtained from FeO_4^{2-}. This and the kinetic data can be rationalized by the following set of equations

$$FeO_4^{2-} + SO_3^{2-} \rightleftarrows [O_3Fe\text{–}O\text{–}SO_3]^{4-}$$

$$[O_3Fe\text{–}O\text{–}SO_3]^{4-} + SO_3^{2-} \xrightarrow{k} Fe(II) + 2SO_4^{2-}$$

$$Fe(II) + FeO_4^{2-} \xrightarrow{\text{fast}} 2Fe(IV)$$

$$2Fe(IV) + SO_3^{2-} \xrightarrow{\text{fast}} 2Fe(III) + SO_4^{2-}$$

which would produce 66.6% oxygen transfer.

Table IX. $FeO_4^{2-} + H_2O_2 \rightarrow Fe(III) + O_2 + H_2O$ Kinetic Results

$10^4[FeO_4^{2-}]$	$10^4[H_2O_2]$	$[Na_2HPO_4]$	Temp, °C	k, sec^{-1} M^{-1} [a]
3.64	6.66	0.01	15.0	77.0
7.18	18.99	0.01	15.0	78.8
4.91	12.90	0.01	15.0	75.9
5.18	12.90	0.01	15.0	82.1
4.92[b]	6.56	0.01	15.0	75.9
4.83[b]	4.22	0.01	15.0	78.3
2.95	10.38	0.10	15.0	36.3
3.83	8.67	0.10	15.0	35.2
2.25	25.19	0.10	15.0	36.7
5.87	29.98	0.10	15.0	36.2
2.95	20.35	0.10	15.0	37.1
5.98	17.07	0.10	15.0	36.4
4.36	17.07	0.05	15.0	47.7
2.93	6.28	0.10	15.0	37.1
4.28	12.32	0.10	15.0	38.1
4.33[b]	4.13	0.10	15.0	37.6
3.62	12.32	0.05	15.0	48.2
2.45	12.32	0.025	15.0	56.2
3.10	12.32	0.013	15.0	68.6
4.36	12.32	0.006	15.0	94.1
3.35	8.04	0.10	25.0	66.53
3.99	8.04	0.10	20.3	53.76
2.71	8.04	0.10	15.5	38.67
3.96	8.04	0.10	11.5	32.98

[a] k defined by $-d[FeO_4^{2-}]/dt = k[FeO_4^{2-}][H_2O_2]$. [b] Excess FeO_4^{2-}.

FeO_4^{2-}–H_2O_2 Reaction. The results of six experiments to determine the reactant ratio $H_2O_2:FeO_4^{2-}$ gave a value of 1.48 ± 0.03 (average deviation) in the presence of 0.1 M HPO_4^{2-}. The kinetic results are shown in Table IX. From these, the reaction follows the equation $-d[FeO_4^{2-}]/dt = k[FeO_4^{2-}][H_2O_2]$ with either reactant in excess. As $[Na_2HPO_4]$ increases, the rate decreases. The observed rate constant is a linear function of the relative $[H^+]$ calculated at the different phosphate salt concentrations. However, such a graph gives a negative intercept at $[H^+] = 0$, indicating an ionic strength or specific phosphate species effect. At pH 9.2 (0.10 M Na_2HPO_4), the data give values for the Arrhenius parameters of $\log A = 8.64 \pm 0.22$ sec^{-1} and $E_a = 9.29 \pm 0.20$ kcal/mol.

The ^{18}O transfer experiments are listed in Table X. Runs 1, 2, and 4 show that essentially all the O_2 comes from H_2O_2 or FeO_4^{2-}. Runs 5 and 8 show that essentially all the O_2 comes from H_2O_2 molecules. The slight enrichment in 5, 7, and 8 comes from the decomposition of FeO_4^{2-} (partially enriched) before the H_2O_2 was added. In run 6 the slight enrichment is caused by a competition between the FeO_4^{2-}–H_2O_2 reaction and FeO_4^{2-} decomposition when $[H_2O_2]$ becomes low. This result is in agreement with many other oxidations of H_2O_2[34] where the O–O bond is usually retained.

Table X. Oxygen Composition from FeO_4^{2-}–H_2O_2 Reaction[a]

Run no.	$10^3R_n(O_2)$[b]	10^3R_n(reactants)
1	4.16[c]	H_2O (normal) 4.22
2	4.16[c]	H_2O_2 4.12
3	4.50[c,f]	FeO_4^{2-} (oxygen) 4.25
4	4.17[c]	H_2O (solvent) 10.15
5	4.30[e]	
6	4.24[g]	
7	4.38[d]	
8	4.22[e]	
9	4.21[e]	

[a] 25°, 0.05 M $NaHPO_4$. [b] $R_n = 34/(32 + 33)$, mass:charge ratio for O_2. [c] Excess H_2O_2. [d] Large excess of FeO_4^{2-}. [e] K_2FeO_4 equilibrated with enriched H_2O for $3t_{1/2}$ before reaction with H_2O_2. [f] Some enriched solvent condensed on K_2FeO_4 by error. [g] Stoichiometric amounts of reactants.

Summary

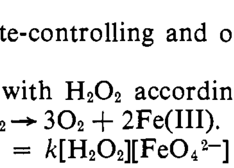
The formula of the negative ion obtained when K_2FeO_4 is placed in dilute alkaline media is FeO_4^{2-}, which has equivalent oxygens which exchange slowly with the solvent. The isotopic oxygen exchange follows the rate law $R = k[FeO_4^{2-}]$, with no appreciable $[OH^-]$ dependence from pH 9.6 to 1 M OH^-. Indirect experiments suggest a higher than first-order term in $[H^+]$ in the acidic region (most likely second order).

The reduction of FeO_4^{2-} by nearly neutral water proceeds by either first + second-order terms or a $^3/_2$-order term in $[FeO_4^{2-}]$ and is approximately first order in $[H^+]$. A large portion of the evolved O_2 comes from FeO_4^{2-}, but in 1 M acid the O_2 released is in isotopic equilibrium with the solvent.

The FeO_4^{2-}–SO_3^{2-} reaction proceeds by the rate equation

$$-d[FeO_4^{2-}]/dt = k[FeO_4^{2-}][SO_3^{2-}]^2$$

With either reagent in excess, the reaction $3SO_3^{2-} + 2FeO_4^{2-} \rightarrow 3SO_4^{2-} + Fe(III)$ is followed. Two-thirds of one oxygen appearing in the SO_4^{2-} comes from FeO_4^{2-}, suggesting an intermediate of the form



$$\left[\begin{array}{ccccc} & O & & O & \\ & | & & | & \\ O- & Fe & -O- & S & -O \\ & | & & | & \\ & O & & O & \end{array}\right]^{4-}$$

as part of the rate-controlling and oxygen-transferring step.

FeO_4^{2-} reacts with H_2O_2 according to the equation $2FeO_4^{2-} + 3H_2O_2 \rightarrow 3O_2 + 2Fe(III)$. The rate equation is $-d[FeO_4^{2-}]/dt = k[H_2O_2][FeO_4^{2-}]$ and is accelerated by base. The oxygen produced has the same isotopic composition as the H_2O_2, in agreement with the results of most other oxidations of H_2O_2.

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(34) A. E. Cahill and H. Taube, *J. Amer. Chem. Soc.*, **74**, 2312 (1952).