

POLAROGRAPHIC REDUCTION OF IRON(III) IN PRESENCE OF PEROXODIPHOSPHATE IN ALKALINE MEDIUM

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In the presence of peroxodiphosphate in alkaline medium, the reduction wave of Fe(III) has a kinetic character. The depolarizer is regenerated by a chemical reaction with peroxide at the electrode. The reoxidation was studied at pH 8–14 both with a hydroxo complex and with a mixed hydroxotriethanolamine complex of Fe(III). A mechanism of the reoxidation process was proposed and the rate constant of reoxidation was calculated from the polarographic limiting currents as $k \approx 10^{12} \text{ l mol}^{-1} \text{ s}^{-1}$ for the hydroxo complex and $k = 2.8 \cdot 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for the triethanolamine complex.

It was found¹ that peroxodiphosphate is reduced on the dropping mercury electrode in two waves. The first one is formed in the region of positive potentials and is limited (except for strongly acidic solutions) by the rate of protonation; it can be observed in alkaline medium only at small ionic strengths where it has the form of a maximum. The second one (in alkaline medium at -1.5 V against s.c.e) has the form corresponding to an irreversible two-electron reduction. Between these two waves, the current drops practically to zero. If sodium hydroxide of reagent grade is used as a supporting electrolyte, another wave appears before the more negative reduction wave of peroxodiphosphate. Its limiting current is kinetic in nature and corresponds to reduction of Fe(III) present as a trace impurity in the hydroxide. This wave is in the presence of peroxodiphosphate several times higher than would correspond to the diffusion current due to reduction of Fe(III). The depolarizer is regenerated by a chemical reaction with peroxide at the electrode, hence the current is kinetic in nature.

It was the aim of the present work to study the kinetics of this reaction and to compare the results with other catalytic reactions of iron studied under similar experimental conditions.

EXPERIMENTAL

Measurements were performed on an OH 102 type polarograph (Radelkis, Budapest) in a Kalousek cell with a saturated calomel reference electrode. The capillary had a rate of flow of 0.74 mg/s and drop time 10.0 s at a height of mercury column of 60 cm . The drop time was adjusted during measurement with an electromagnetic drop time controller to 3.9 s . Nitrogen used to remove oxygen was led through a copper catalyst column heated to 150°C . The pH value of solutions with $\text{pH} < 12$ was measured with an OP-205 type pH meter (Radelkis, Budapest) connected with a glass electrode. The concentration of OH^- ions in strongly alkaline solutions was determined by titration.

The chemicals used were of reagent grade except for the peroxodiphosphate salts which were prepared in the Department of Inorganic Chemistry of this University as 99.9% $\text{Na}_4\text{P}_2\text{O}_8 \cdot 6\text{H}_2\text{O}$ and 99.9% $\text{K}_4\text{P}_2\text{O}_8$ (ref.²). Triethanolamine was in the form of its hydrochloride, TEA · HCl. Sodium and potassium hydroxides were purified by a several-day electrolysis at constant voltage prior to use. The cathode was mercury pool, anode smooth platinum, voltage -1.7 V and current several tens mA. The TEA-iron complex was prepared by mixing solutions in the order: NaOH, TEA, FeSO_4 . The ratio of Fe(III) to TEA was 1 : 2000. The decrease of the TEA concentration as a result of the formation of TEAH^+ cations is manifested at pH close³ to 8 ($\text{p}K_{\text{TEAH}^+} = 8.04$). The ionic strength was adjusted by the addition of NaClO_4 or KCl. The stock solution of the perchlorate was standardized by titration with the use of a cation exchanger. The temperature of measurement was 22°C .

RESULTS AND DISCUSSION

The assumption that the catalysis is due to ferric ions was evidenced as follows. If a $10^{-6}\text{M-Fe}_2(\text{SO}_4)_3$ solution was added to an electrolytically purified sodium hydroxide solution, the catalytic wave appeared at the same potential (about -1.0 V) as in the nonpurified solution (Fig. 1). The catalytic current decreases at potentials more negative than -1.4 V owing to reduction of Fe(II) to metal, which becomes more rapid than the reoxidation, hence the catalysis ceases to proceed. The current drops to the diffusion current corresponding to reduction of Fe(III) to metal without reoxidation. Since, however, in this region at a higher ionic strength direct reduction of peroxodiphosphate takes place, the mentioned current drop can be masked by this reduction wave.

Reduction of Fe(III) in Absence of Peroxide

Polarographic reduction of trivalent iron in alkaline medium proceeds in two steps, a one-electron and a two-electron one. The shape of the first wave corresponds to a reversible electrode reaction. The half-wave potential shifts with increasing concentration of OH^- ions to negative values, namely by 50 mV per pH unit suggesting a loss of one OH^- ligand during the conversion of the oxidized form to the reduced one. The concentration of OH^- ions influences also the limiting diffusion current i_d^+ whose decrease with decreasing pH corresponds roughly to the decrease in solubility of the $\text{Fe}(\text{OH})_4^-$ anion⁴. Hence it seems that only this anion is directly reducible in contrast to $\text{Fe}(\text{OH})_3$ which forms a colloid. The formation of bi- or polynuclear hydroxo complexes is improbable in view of the low concentrations used. It follows from the solubility diagram of $\text{Fe}(\text{OH})_3$ and from the corresponding equilibrium constant⁴ that $\text{Fe}(\text{OH})_4^-$ reaches a suitable polarographic concentration at $\text{pH} > 12$ although it does not exceed 10^{-5}M at $\text{pH} 12-14$ and so the measurement of i_d^+ is subject to a certain error. To calculate the rate constant of reoxidation, an average value of i_d^+ from several measurements was taken.

The solubility of the colloidal $\text{Fe}(\text{OH})_3$ can be increased also by addition of TEA, which forms a complex with divalent and trivalent iron. This enables to study the catalysis even at pH 8–12, however the exact composition of the complex which participates in the electrode process is not known. It follows from the study of the $\text{Fe}(\text{II})$ -TEA complex³ that at pH < 9 one or two TEA ligands are bound with $\text{Fe}(\text{II})$ and the corresponding instability constants are $\text{p}K_1$ 2.27 and $\text{p}K_2$ 1.32. At pH > 9 there exist mixed TEA hydroxo complexes, $[\text{Fe}^{\text{II}}(\text{TEA})_x(\text{OH})_y]^{2-y}$, where the values of x and y are not known. The reduction of the $\text{Fe}(\text{III})$ -TEA complex⁵ proceeds similarly as with $\text{Fe}(\text{OH})_4^-$. From the independence of the half-wave potential of the TEA concentration it follows that the number of ligands does not change during the reduction.

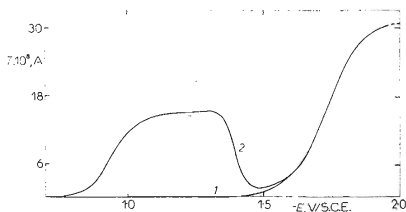


FIG. 1

Polarographic Waves for Peroxodiphosphate in 0.01M-NaOH

1 $10^{-4}\text{M-Na}_4\text{P}_2\text{O}_8 + 0.08\text{M-NaClO}_4 + 0.01\text{M-NaOH}$; 2 same as 1 but in the presence of $10^{-6}\text{M-Fe}_2(\text{SO}_4)_3$. In both cases I 0.09.

TABLE I

Rate Constants of Reoxidation of $\text{Fe}(\text{II})$

Oxidation agent	Compl. agent	Medium	k $l \text{ mol}^{-1} \text{ s}^{-1}$	Ref.
H_2O_2	KOH	0.5M-KOH	$6.1 \cdot 10^8$	4
H_2O_2	TEA	1.0M-NaOH	$3 \cdot 10^6$	9
H_2O_2	EDTA	pH 4.7	$7 \cdot 10^3$	10
H_2O_2	—	0.5M- H_2SO_4	60	11
NH_2OH	TEA	0.01–1.0M-NaOH	1 to $5 \cdot 10^2$	5
$\text{Na}_4\text{P}_2\text{O}_8$	NaOH	0.01–2.0M-NaOH	10^{12}	^a
$\text{Na}_4\text{P}_2\text{O}_8$	TEA	pH 8–14	$3 \cdot 10^9$	^a

^a Present work.

Reduction of Fe(III) in Presence of Peroxodiphosphate

The concentration of peroxodiphosphate was chosen 10–100 times higher than that of Fe(III) in order that the following simple equation for a reoxidation reaction of first order might be used:

$$i_1/i_d^+ = 0.81[2kt_1c(1 - i_1/i_d)]^{1/2}. \quad (1)$$

It is assumed that one molecule of the oxidation agent regenerates two depolarizer molecules⁶. The validity of this equation was checked by the dependence of the

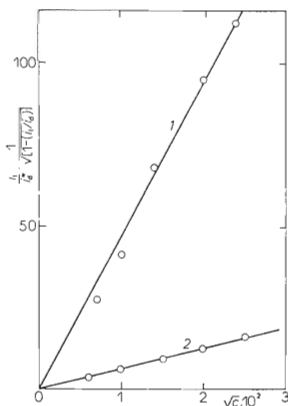


FIG. 2

Dependence of Corrected Ratio of Limiting Catalytic and Limiting Diffusion Currents on Square Root of Analytical Concentration of $K_4P_2O_8$

1 $0.5M\text{-KOH} + 5 \cdot 10^{-5} - 6 \cdot 10^{-4}M\text{-K}_4P_2O_8$; concentration of iron about $10^{-6}M$ present as impurity in KOH. 2 $0.01M\text{-NaOH} + 1.0M\text{-NaClO}_4 + 0.01M\text{-TEA} + 2.5 \cdot 10^{-6}M\text{-Fe}_2(SO_4)_3 + 3.6 \cdot 10^{-5} - 6.25 \cdot 10^{-4}M\text{-Na}_4P_2O_8$; pH 12.0.

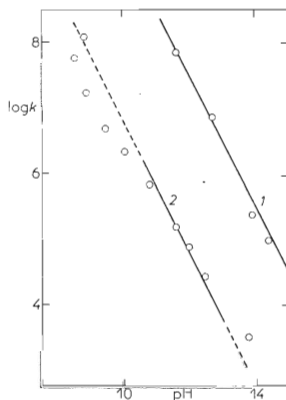


FIG. 3

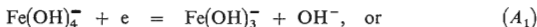
Dependence of the Logarithm of Reoxidation Rate Constant on pH

1 $10^{-6}M\text{-Fe}_2(SO_4)_3 + 10^{-4}M\text{-Na}_4P_2O_8 + 0.01 - 2.0M\text{-NaOH}$; I 2.0 (addition of $NaClO_4$); 2 $2.5 \cdot 10^{-6}M\text{-Fe}_2(SO_4)_3 + 10^{-4}M\text{-Na}_4P_2O_8 + 0.01M\text{-TEA} + 0.02M$ Britton-Robinson buffer or $0.01 - 1.0M\text{-NaOH}$; I 1.0 (addition of $NaClO_4$).

expression $(i_1/i_d^+)/(1 - i_1/i_d)^{1/2}$ on the square root of the peroxodisulphate concentration. At pH 12 this dependence is linear both in the presence and in the absence of TEA (Fig. 2). The slope of the straight lines suggests that the reoxidation of the TEA complex proceeds more slowly. However, the dependence obtained at pH 10 is somewhat curved. Since the reoxidation becomes considerably accelerated towards lower pH values (the dependence of the rate constant on pH see below), the correction for the exhaustion of peroxide at the electrode is apparently insufficient. It is also possible that the reaction mechanism changes and the mentioned relation ceases to be valid. Eq. (1) was used to calculate the rate constant in the whole studied pH region; the error of the calculation increases with decreasing pH.

Fig. 3 shows the dependence of the logarithm of the rate constant on pH. It was calculated under the assumption that divalent iron reacts with any form of peroxodiphosphate, i.e. that the concentration of the oxidizing agent in Eq. (1) is equal to the analytical concentration of peroxodiphosphate. The straight lines are theoretical with a slope of -1 and represent the dependence of the rate constant on concentration of hydrogen ions. The experimental points are more or less in agreement with this dependence, which is analogous for the hydroxo complex as well as for the TEA-iron complex. It can be therefore concluded that the reoxidation mechanism is the same in both cases. The dependence of the rate constants on ionic strength (Fig. 4) shows, however, that the charges of the reacting particles in reoxidation of the hydroxo complex and TEA complex are probably different. At sufficiently low values of the ionic strength the slope of the curve 1 is $d \log k/dI^{1/2} = +2$. It is probable that the reacting particles have charges -1 and -2 (ref.⁷). In the presence of TEA the slope of -2 indicates particle charges $+1$ and -2 . The charge of -2 in both cases can be ascribed to an associate of the partially protonated anion, $\text{NaHP}_2\text{O}_8^{3-}$.

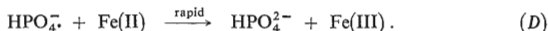
In proposing a mechanism of the whole catalytic process it should be considered that (1) one OH^- ligand is lost during the electrode reaction (in both cases), (2) one proton is consumed in or before the rate-determining step in the chemical reaction, and (3) the charges of the Fe(II) complexes in the chemical step are -1 and $+1$, and the peroxidic particle has the charge -2 . Thus, we have the electrode reaction:



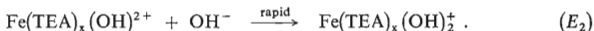
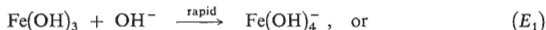
In the subsequent step we assume the formation of an associate and the acceptance of a proton by the $\text{NaP}_2\text{O}_8^{3-}$ anion:



The reoxidation proceeds in two steps:



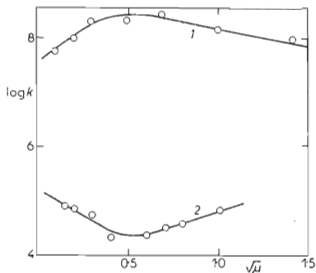
The last phase of the mechanism is a rapid conversion of the Fe(III) compounds to the original depolarizer:



If the quantity c in Eq. (1) is set equal to the equilibrium concentration of the $\text{HP}_2\text{O}_8^{3-}$ anion calculated on the basis of the known dissociation constant⁸, $K_4 = 4.5 \cdot 10^{-8}$ for $I = 1.0$, we obtain the rate constant independent of pH, but its value is too large and differs considerably from the constants found for other reoxidations of Fe(II) (Table I). If the rate constants for the hydroxo complex and for the TEA complex were the same, it could be concluded that the reoxidation process is controlled in both cases by the rate of the same reaction, possibly protonation. Since the rate constants are different, it follows that at least in the case of the TEA complex the overall process is controlled by the rate of the reoxidation proper. The rate constant of reoxidation of the hydroxo complex is, however, very close to the rate constants of recombination of protons with acid anions¹², therefore it is not possible to decide reliably which reaction is rate-limiting. The resulting value of the rate constant should be corrected for changes in the concentrations of reactants due

FIG. 4
Dependence of the Logarithm of Reoxidation Rate Constant on Square Root of Ionic Strength

1 $0.01\text{M-NaOH} + 10^{-6}\text{M-Fe}_2(\text{SO}_4)_3 + 10^{-4}\text{M-Na}_4\text{P}_2\text{O}_8$; pH 12; 2 $0.01\text{M-NaOH} + 2.5 \cdot 10^{-6}\text{M-Fe}_2(\text{SO}_4)_3 + 0.01\text{M-TEA} + 10^{-4}\text{M-Na}_4\text{P}_2\text{O}_8$. Ionic strength adjusted by addition of NaClO_4 .



to the influence of the potential of the outer Helmholtz plane. The calculation would be, however, very difficult in view of the fact that polyvalent ions are present in the Helmholtz double layer.

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