THE EFFECT OF SULPHATE IONS ON THE KINETICS OF THE REACTION OF IRON (III) WITH SULPHIDE ION IN PERCHLORATE MEDIA

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The Kinetics of reduction of Fe(III) ions by sulphide ion have been investigated in perchlorate medium. In all cases the reaction is first order in sulphide ion and second order in ferric ion. Over all the reaction is found to be third order.

The decrease in the third order rate constant k_o for the reaction of iron (III) with sulphide ion found with added sulphate ions. k_o decreases to a very low insignificant value.

This is interpreted in terms of complex formation between ferric ions and sulphate ions, the complex not reacting with sulphide ions. From the variations of k_o with concentration of sulphate ions the type of complex is distinguished. Formation constant are determined for the complex under experimental conditions.

INTRODUCTION

The kinetics of the reduction of Fe(III) ion by sulphide ion have been investigated in perchlorate medium. The reaction has been found to be a third order one under experimental conditions with consumption ratio.

$$\Delta [Fe(III)] / \Delta [Na_2 S] \text{ is } 2 : 1$$

The reaction appears to be first order in sulphide and second order in ferric ion.

The rate of the reaction is retarded when the perchlorate ions are replaced by sulphate ions, in analogy to Sykes' observation [1] for ferric-iodide reaction. This effect is interpreted in terms of the association between the sulphate and ferric ions to form an inactive complex. The nature and Association constant of the complex is determined.

EXPERIMENTAL

Materials. Ferric perchlorate solution was prepared by substitution reaction of stoichiometric amounts of ferric sulphate and barium perchlorate was made acidic by adding perchloric acid. Sodium perchlorate and barium perchlorate were prepared by dissolving A.R. anhydrous sodium carbonate and barium carbonate in calculated quantities of perchloric acid. pH was adjusted by adding sodium carbontae or perchloric acid. Ionic strength was adjusted by the addition of sodium perchlorate. The acid used was A.R. perchloric acid. Sulphate ions were added as A.R. sodium sulphate solution. Water was double — distilled from an all glass still. The sulphate ions cannot be added alone because the equilibrium between H^+, sulphate and bisulphate ions will affect the sulphate ion concentration. The acidity is low, pH is about 5 in these experiments. The concentration of bisulphate ions is very low and it is unlikely that low amount of HSO_4^- ions will compete appreciably with the more highly charged SO_4^- ion for association with ferric ions.[2]

Correction of $[SO_4^-]$ for the small amount of $[H_2SO_4^-]$ at $\mu 0.006$ by the use of the data of Reynolds and Fukushima [3] produced no significant change in $[SO_4^-]$.

Procedure.

The reaction vessel consisted of a wide tube fitted with a B-34 ground glass stopper and a side arm.

Solutions of ferric perchlorate, perchloric acid and sodium perchlorate were placed in the tube and sodium sulphide solution in the side arm. Several reaction vessels were filled with the same amounts of reagents in a similar manner for each kinetic run.

The reaction was started by mixing the reactants and the reaction was quenched at a known time by addition of a mixture of 0.1 M NaF solution 1M NaAc solution and 0.1% 2,2;-dipyridyl solution in water. Each vessel gave only one reading at a particular time and optical density

at 522 nm was measured. F^- ions were used to complex Fe^{3+} and acetate solution as buffer. The (Fe(II)) formed as determined spectrophotometrically [5] at 522nm as tris-2,2'-bipyridyl complex $\epsilon = 8.5 \times 10^3$).

RESULT AND DISCUSSION

In all cases linear trimolecular plots were obtained by plotting $\frac{2 \times (2b-a)}{a \ (a-2x)} + 2.303 \log \frac{b(a-2x)}{a(b-x)}$ against time in minutes. Some results summarized in Table 1, give the rate constant of the third order plots. Then, the trimolecular rate constant was calculated using $K_O = \dfrac{\text{slope}}{(2b-a)\times60}$. In Table 1, k=$4.10^{-6}$ 1^2 moles^{-2} S^{-1} at 25°C and the ionic strength $\mu = 0.006$ is independent of changes in the initial ratio $\Delta[Fe(III)] / \Delta[Na_2S]$ between 0.46 to 5.80. In all cases, the consumption ratio was found to be $[Fe(III)]/[Na_2S] = 2:1$. In order to investigate the reaction further, ferric ions were taken in large excess so that the ratio $[Fe(III)]/[Na_2S]$ were varied between 66 to 3.8×10^3. The reaction appears to obey first order kinetics. The value of k (first order rate constant) obtained from the value of slope at 25°C, 3.84×10^{-3} sec^{-1} was found to be independent of the initial ratio of $[Fe(III)]/[Na_2S]$ similarly in this range by changing the initial ratio $Fe(III)/(Na_2S)$ from 0.04 to 0.004 the reaction was found to be second order and rate constant is 0.25 1 mol^{-1} sec^{-1}. In each case the consumption ratio was found to $\Delta[Fe^{3+}] / \Delta[Na_2S] : 2:1$.

Influence of Sulphate Ions. The runs were repeated in the presence of sodium sulphate solution. The plots obtained, computing third order kinetics, were found to be straight lines but not passing through the origin (Fig. 2).

The slopes of these lines were calculted from the graph

Table 1. Showing 3rd order rate constant at temperature 25°C and ionic strength $\mu = 0.006$.

$[Fe^{3+}]/[Na_2S]$	$K_O \times 10^6$	$\Delta[Fe^{3+}]/\Delta[Na_2S]$
4.22	4.3	1.98
0.46	4.8	2.01
5.80	4.0	2.00
5.80	4.4	1.97
2.80	4.0	1.97
2.50	3.9	2.02

and they were computed in the equation slope/$(2b-a'^2) = 4 \times 10^6$, knowing b the initial concentration of sulphide the value of á. was claculated. The new value of a', thus obtained, may be the amount of free ferric ions i.e. uncomplexed ferric ions. This value of a' is computed and plotted, now the straight lines, thus obtained, passed through the origin (Fig. 1). The value of K'' obtained from these new value of a' was found to be in agreement with 4×10^{-6} 1^2. mole^{-2} sec^{-1}. Knowing the amount of uncomplexed ferric ions, the equilibrium constant of the following reaction was determined:

$$Fe_3 + SO_4^{-2} \rightleftharpoons FeSO_4^+$$
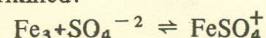
In order to investigate the nature of complex ions for the reaction

$$Fe^{3+} + nSO_4^{2-} \rightleftharpoons Fe(SO_4)_n^{3-2n}$$
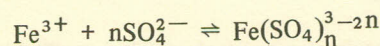
$$\frac{Fe(SO_4)_n^{3-2n}}{[Fe^{3+}]} = K. [(SO_4^{2-})]^n$$

the ratio of complexed to uncomplexed ferric ions was plotted against $[SO_4^{2-}]^n$, keeping n = 1/2, 1/3, 1/4 and n=1,2,3,4. Straight line passing through the origin was obtained only when n = 1. Hence, showing that the equilibrium at $\mu=0.0006$ and 25°C is as follows (Fig.2)

$$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+$$
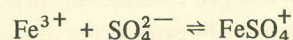
The values of K at the two ionic strengths studied and at 25° were found to be $1.285 \times 10^{+4}$ and $2.75 \times 10^{+3}$. The association of ferric and sulphate ions has been studied by Sykes [1] at 18° at an ionic strength of 0.66 which is much higher than the ionic strength used in the present work.
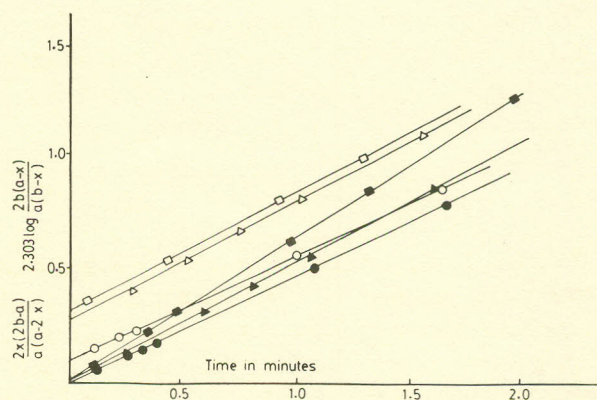

Fig. 1. Third order plots. ○,□,△, using ferric concentration without consideration of complex formation ●,□,△, using ferric ion concentration after correction for complex formation.

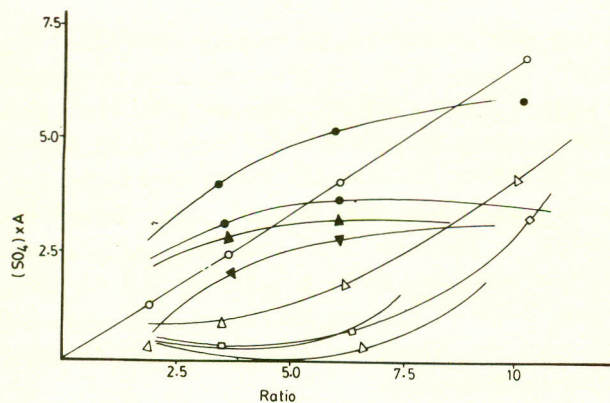Fig. 2. Plots, of ratio between complex and uncomplexed ferric versus $(SO_4^{-2})n$ $\bigcirc n=1$, $A=10^4$, $\triangle n=2$, $A=10^7$, $\square n=3$, $A=10^{10}$. $\blacktriangle 10^{-2}$, $\bullet n=1/4$ $A=10$, $\ominus n=1/3$ $A50$, $\bullet n=2/3$ $A=10^3$ $\triangledown n=1/6$ $A=10$ $\triangledown n=4$ $A-10^{13}$.

On the basis of empirical activity coefficient equation

$$- \log_{10} \ f = A \, z^2 \sqrt{\mu}$$

the product of $f_{FeSO_4}/f_{Fe} \times f_{SO_4^{-2}}$ is found to be 3 at the experimental ionic strength. The thermodynamic equilibrium constant is thus calculated to be approximately 3.95×10^4 at $18°$ which is of the same order of magnitude as that now obtained. Moreover Davies [6] has given the value of equilibrium constant for the formation of $LaSO_4^+$ as 0.36×10^4 derived from his solubility and conductivity data. La is also a triply charged metallic ion like ferric ion. The value given by him is of the same order of magnitude.

The experimental evidence gives the assumption that only free (uncomplexed) ferric ions are reactive towards sulphide ion under the experimental conditions and that complexed ferric ion does not react with sulphide ion. This conclusion supports the view of Sykes[1] who studied the reduction of Fe^3 ions with iodide ions.

The presence of a ligand in an ionic reaction if one of the reactants associates specifically with it may produce large changes in the rate of reaction. This work describes the important part of the sulphate ion which it plays in ferric — sulphide reaction. Bell indicated the facts and interpretted in terms of difference in electrical charge in magnitude and in distribution. Fe^{3+} bears a triple positive charge while the transition complex probably has the composition FeS_2^+. It is expected that SO_4^{2-} will associate more strongly with the reactant than with the transition state. The ferric complex more stable for reaction has to pass through the same transition state, so it seems to be unreactive.

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