CHAPTER 3

KINETICS OF REDUCTION OF DIMETHYLGLYOXIME, FURFURALDOXIME AND α-FURIL DIOXIME BY TITANIUM(III)SULPHATE IN AQUEOUS SULPHURIC ACID - ETHANOL MEDIUM
SECTION A: TITANIUM(III) REDUCTION OF DIMETHYLGLYOXIME: ELECTROCHEMICAL AND KINETIC STUDY

3.1.1 Introduction

Section A, gives an overview of chemical kinetics and review of kinetic features of titanium(III) reductions and kinetic features of titanium(III) reduction of dimethylglyoxime. Kinetic investigations are carried out under nitrogen atmosphere. The reduction product is isolated and characterised as Schiff’s base of 2,3- butane diamine with salicylaldehyde. The stoichiometry of the reduction of dimethylglyoxime by titanium(III)sulphate solution is established by back titration method using 10 % ammonium thiocyanate indicator. Kinetic investigations have been carried out under stoichiometric and non-stoichiometric conditions in aqueous sulphuric acid–ethanol medium by spectrophotometric method. The reaction follows overall second order kinetics, first order each in [Ti(III)] and [oxime] and fractional order in [H2SO4]. The effect of varying concentrations of Ti(III), DMG, H2SO4, ionic strength and solvent composition has been studied and effect of temperature has also been studied and activation parameters have been computed from Arrhenius and Eyring plots. A suitable kinetic scheme consistent with the observed results is suggested and discussed.

3.1.2 An Overview of Chemical Kinetics

The subject of chemical kinetics is concerned with detailed study of the rate of chemical reactions1-16. The experimental part of the subject deals with ways of measuring precisely the rates of reactions at various varying conditions of experiments. The interpretation of results leads to an understanding of the mechanism of reaction. The combination of the results of a large number of experiments gives rise to general theories of chemical reactivity. The important steps in any kinetic investigations are:

i) collection of kinetic data
ii) establishment of relationships between the rate and reaction composition
iii) study of structural effects and
iv) interpretation of the collected data to arrive at reaction mechanism

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The study of reaction kinetics gives wealth of information about the nature and course of reactions. The order of a reaction can be used to interpret the reaction on molecular level. For example, the chemists by considering the order of a reaction with respect to different reactive species, predict the sequence in which bonds break and atoms rearrange during the reaction and hence proposed the reaction mechanism.

Thus, the kinetic data will be the source of a great deal of detailed insight into the mechanism of a reaction. Although other types of experimental evidences are also sought for purpose of formulating a reaction mechanism, the study of reaction kinetics generally forms the back bone of a thorough mechanistic investigation.

Terminology: The rate of reaction is expressed in terms of the concentration of any reactant or product of the reaction. It is defined as the rate of disappearance of a reactant or the rate of appearance of a product of the reaction. For a general reaction of the type,

\[ aA + bB \rightarrow cC + dD \]  \hspace{1cm} (3.1)

rate of the reaction is written as

\[ \text{rate} = \frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \]  \hspace{1cm} (3.2)

where \([A], [B], [C] \text{ and } [D]\) denote the concentrations in \(\text{mol dm}^{-3}\) of species \(A,B,C\) and \(D\) respectively, 't' represents the time and \(a,b,c \text{ and } d\) are the stoichiometric coefficients. Depending on whether the concentration change of the product or reactant is measured, \(dt\) is denoted as positive or negative so that rate will always be a positive quantity. Rate of reaction is an intensive quantity. The rate of reaction can also be expressed in general terms \(dx/dt\), if reaction variable 'x' is introduced in place of concentration of an individual component, then 'x' is equal to the number of equivalent per \(\text{dm}^{-3}\), which reacted between
the initiation of the reaction and time, t. The rate depends on concentrations of the starting material.

Equation 3.2 is referred to as the rate law. Exponents m and n define the order of dependence of the rate on [A] and [B] respectively, 'k' is the proportionality constant referred to as the reaction rate constant or the specific rate constant. The order of a reaction is the algebraic sum of all the concentration terms which appear in the rate law. For complicated reactions the overall order has not much significance. The order of the reaction is determined by kinetic methods and the rate law is established experimentally. Hence the rate law is the experimentally found relationship between the rate and concentration of participating species. The integrated equations are widely used for analysing the kinetic data. They are applied to kinetic data by graphical means or otherwise. In multistep reactions there is one step which is very much slower than all other steps, all of which are rapid compared to the last slow step. Such a last step is termed as the rate determining step of the reaction. The stoichiometry of reaction is empirical molar ratio of reactants and products as indicated in the overall reaction equation. The reaction order and stoichiometry are empirical factors on experimental facts. The interpretation of kinetic data with respect to the mechanism of reaction studied requires the knowledge of the products and the stoichiometric ratios. Thus the first stage of kinetic investigation should be an unequivocal establishment of the stoichiometry of the reaction to be investigated and identification and determination of the products formed. In addition to the above information, the detection of intermediates is an important contribution to the understanding of the reaction mechanism. The knowledge of the existence of an intermediate aids the choice of a proper reaction rate equation and serve as a model for the structure of the transition state. In reaction kinetics major part of efforts is devoted to explain why certain reactions occur faster than others on the basis of the rate constants. Two alternate theories, collision and transition state theories, based on two different theoretical approaches have been developed to correlate the properties of molecules and the magnitudes of the rate constants.
The success of reaction kinetics depends on the accuracy with which the complex quantity, the rate constant can be determined. The accuracy of the latter in turn depends on the accuracy of measurement of all the concentration involved, accurate measurement of time and the manner in which experimental data are handled to obtain the rate constants.

Accuracy of measurement: The techniques employed for the measurement of concentrations include physical and chemical methods. These techniques either measure concentration directly or a quantity that is proportional to it, such as absorbance, conductivity, optical rotation etc. The measurements have to be carried out at suitable time intervals, depending upon the half life of the reaction. The accuracy of measurements depends on the technique used on the degree of sophistication in the application of a given technique. The choice of the technique depends on the kind of the reaction. It is therefore of primary importance to state always the exact conditions of kinetic measurements. Frequently, the study of effects of various factors on the values of rate constants is of much greater interest and importance that an accurate measurement of the value of a single rate constant. It is important to control other factors such as temperature, pressure etc., that effects the reaction rate. It is necessary to keep these factors constant.

Calculation of rate constant: After the best fitting reaction rate equation is found and the reaction order in individual component is determined, the next task is to find the best value of the rate constant. Generally the rate constants are determined by the graphical method. The later are usually based on the determination of the slope of a linear plot. One can also use regression analysis to find the best linear plot fitting the experimental results. Recently, the application of computers for the calculation of rate constant has increased considerably. For first order reactions, the most accurate values of rate constants are obtained after reaching about 60 % conversion, for the second order reactions about 50 % conversion, provided that the error in the measurement of time is small when compared with the accuracy in concentration measurement. Thus in numerical as well as graphical treatments less weightage should be given.
to data obtained at the very beginning of the reaction and at conversions higher than 70–90%.

Analysis of kinetic data: An important task in reaction kinetics is to determine, how rates depend on the concentration of reacting substances and show how rates are affected by the products of reaction, changes in solution composition or by added substances which may catalyse or inhibit reaction. The rates of reactions are also affected by the nature of the solvent used and nature and concentration of neutral salts added to the reaction mixture. The study of the effects of pH, solvent, ionic strength and temperature on rate constants offers further diagnostic tools, as they offer information on the nature of the reactive forms of the species participating in the reaction.

Effect of pH on reaction rates: The rate of numerous chemical action in solutions are affected by the change in acidity, where the rate constant depends on pH or analogous functions. Such change in the value of the rate constant can be observed when,

i) the rate determining step (rds) is preceded by a rapidly established acid–base equilibrium, which causes a change in the actual concentration of the reactive form of one of the participating reactions.

ii) the rds is the formation of an acid or a base

iii) the rds involves addition of hydroxide ion as a nucleophilic or a proton transfer. The solvent base or acid form is consumed or transformed in the course of the reaction and is not regenerated and

iv) the reaction is general acid-base catalysed. The first and third cases are sometimes described as specifically catalysed.

Salt and solvent effects: Effect of solvent on reaction is described by grouping the reactions into three categories. Reaction between (i) two iones, (ii) an ion and a neutral molecule and (iii) two neutral dipolar molecules. The resistance of salt effects indicates the necessity for adequate control of the ionic strength in a kinetic investigation. Either the ionic strength must be kept low so that the effects are small or a series of measurements have to be made and extrapolated to zero
ionic concentrations. A different technique which is often useful is to keep the ionic strength constant at some large value which does not change significantly during the course of an investigation.

**Effect of temperature and activation parameters:** Rates of reactions are sensitive to temperature changes. An often quoted rule-of-thumb in chemistry states that raising the temperature by 10°C results in doubling of the reaction rate. The rate constant ($k$) increases exponentially with temperature according to the Arrhenius equation,

$$k = A \exp \left( \frac{-E_a}{RT} \right)$$  \hspace{1cm} (3.3)

where $A$ is the pre-exponential factor called Arrhenius factor. The values of empirical constant $E_a$ and $A$ are usually evaluated graphically from the logarithmic form of the Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303 RT}$$  \hspace{1cm} (3.4)

A graph of $\log k$ versus $1/T$ gives a straight line with slope $= E_a / 2.303 R$ and $\log A$ as the intercept. The accuracy of the values of activation parameters depends predominantly on the accuracy of temperature control. The transition state theory may be summarised in the form,

$$k = \left( k_b T / h \right) K^*$$  \hspace{1cm} (3.5)

This equation predicts that for any elementary reaction the rate constant is an equilibrium constant multiplied by a universal frequency factor $k_b T / h$, which varies only with with the temperature and has dimension of reciprocal time. $K^*$ is not only exactly an equilibrium constant but is only similar to one. Analogous to classical thermodynamics, $K^*$ can be related to the free energy of activation ($\Delta G^*$) by the relationship:

$$\Delta G^* = -RT \ln K^* \quad \text{or} \quad K^* = \exp \left( -\frac{\Delta G^*}{RT} \right)$$  \hspace{1cm} (3.6)
Equation (3.6) takes the form

\[
K^* = \exp\left(\frac{-\Delta H^*}{RT}\right) \exp\left(\frac{\Delta S^*}{R}\right)
\]  
(3.7)

as \[\Delta G^* = \Delta H^* - T \Delta S^*\]  
(3.8)

On substitution for \(K^*\) from equations (3.6) and (3.7) we have,

\[
k = \left(\frac{k_B T}{h}\right) \exp\left(\frac{-\Delta G^*}{RT}\right) = \left(\frac{k_B T}{h}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \exp\left(\frac{\Delta S^*}{R}\right)
\]  
(3.9)

and equation (3.9) can be rearranged as

\[
\log\left(\frac{k}{T}\right) = \log\left(\frac{k_B}{T}\right) + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT}
\]  
(3.10)

Thus the rate constant \(k\) can be expressed in terms of thermodynamic and activation parameters.

For most reactions in solutions \(\Delta V^*\) the volume of activation is small and equation (3.11) reduces to equation (3.12)

\[
\Delta H^* = E_a - RT + P \Delta V^*/ \Delta H^* = E_a - RT
\]  
(3.11)  
(3.12)

Equation (3.10), therefore takes the form,

\[
k = \exp\left(\frac{k_B T}{h}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{E_a}{RT}\right)
\]  
(3.13)

and this equation applies to a good approximation to any reaction in solution. \(\Delta H^*\) and \(\Delta S^*\) are evaluated from the slope, \(\Delta H^*/2.303R\) and intercept \([\log k_B / h + \Delta S^*/2.303R]\) of the linear plot of \(\log(k/T)\) versus \(1/T\). \(\Delta G^*\) is then calculated from equation (3.8). \(\Delta S^*\) can also be evaluated as follows:
Comparison of equation (3.13) with equation (3.3) gives,

\[ A = \exp \left( \frac{k_B T}{h} \right) \exp \left( \frac{\Delta S^*}{R} \right) \]  \hspace{1cm} (3.14)

or \[ \Delta S^* = 2.303 R \log (A \ 10^{-13}) \]  \hspace{1cm} (3.15)

\exp(k_B T/h) \approx 10^{13} \text{ around } 300 \text{ K. Thus } \Delta S^* \text{ is positive or negative depending on whether } A > 10^{13} \text{ or } A < 10^{13} \text{ or } A = 10^{13}. \text{ Equation (3.14) may also be simplified as,}

\[ \Delta S^* = 4.58 \log A - 46.2 - 4.58 \log T \]  \hspace{1cm} (3.16)

**Entropy of activation and mechanism**: Entropy is a measure of the randomness of a system. Since all systems tend to attain a state of randomness, the increase in entropy means much disorder. The difference in entropy between the reactants and the transition state is known as entropy of activation. It can be evaluated by substituting appropriate data in equation (3.14). The entropy of \( \Delta S^* \) in conjunction with other experimental data give a good indication about the transition state and is used in the mechanistic interpretation. The value of \( \Delta S^* \) indicates the changes in the relative orderedness of the structure of the activated complex and the reactants, including the solvent molecules. The negative value of entropy of activation \( \Delta S^* \) indicates that the transition state is more ordered than the state of the separated reactants. The entropy factor turns out to be dominant one in ionic reactions. On the other hand, solvent effects involve a significant change in polarity or charge separation.

**3.1.3 Review of Kinetics of Titanium(III) Reductions**

Titanous salts in acid solutions are well known reducing agents for the reduction of nitro, nitroso and azo groups in organic compounds. Titanium(III)sulphate for the rapid determination of nitroso and azo groups in micro, semi micro and macro scale has been reported\(^{17-18}\). These groups are reduced to the corresponding primary base, each of them requiring four equivalents of the reducing agent for quantitative reduction as follows:
\[-\text{NO} + 4 \text{Ti}^{3+} + 4 \text{H}^+ \rightarrow -\text{NH}_2 + 4 \text{Ti}^{4+} + \text{H}_2\text{O} \quad (3.17)\]
\[-\text{N=N-} + 4 \text{Ti}^{3+} + 4 \text{H}^+ \rightarrow 2 -\text{NH}_2 + 4 \text{Ti}^{4+} \quad (3.18)\]

It has been found that the reduction of nitroso and azo compounds is easier than that of nitro compounds and a large excess of the reagent is not necessary.

The kinetics of reduction of nitro benzene and substituted nitro benzene by titanium(III)chloride has been studied by Newton and coworkers\(^\text{19}\) in an aqueous hydrochloric acid medium. The reaction was found to be proportional to [Ti(III)], [NB] and inversely proportional to [H\(_2\)SO\(_4\)]. Further, the kinetics of reduction of azo benzene and substituted azo benzene by titanium(III)chloride was reported by same group of workers\(^\text{20-21}\). The reduction reactions was found to be first order with respect to each components. The rate determining step being the transfer of an electron from titanium(III) species to the azo compounds, which has taken up protons.

The kinetics of the reduction of azoxy benzene and some derivatives by titanium(III)chloride has been reported\(^\text{22}\). The initial rate of reduction was proportional to [TiCl\(_3\)] and to [Ph NO NPh] and the whole system was an example of second order consecutive reaction and the initial rate was approximately proportional to 1/[H\(^+\)].

Imoto et al.\(^\text{23-24}\) reported the kinetics of reduction of nitrobenzene by titanium(III)chloride in aqueous hydrochloric acid.

The kinetics of titanium(III) reduction of ortho, meta, and para-substituted phenyl methyl sulfoxides with titanium(III)chloride in aqueous ethanol has been studied\(^\text{25}\). The reaction was second order, first order each in sulphoxide and titanium(III).
Kinetics of reactions between azidothiocyanato and isothiocyanato penta cyanocobaltate(III) by titanium(III) chloride in aqueous hydrochloric acid has been studied.

Johnson and Winstein studied the kinetics of the reduction of sodium anthraquinone sulphonate by titanium(III) chloride spectroscopically.

Shaffer has reported the catalysis of the titanium(III) chloride-iodine reaction by phenazines, pyocyanine, anthraquinone etc. Quantitative and kinetic work of the same has been carried out latter.

The kinetics of the oxidation of trivalent titanium(III) compounds with perchloric acid in aqueous sulphuric acid and hydrochloric acid solutions as well as the rate of reaction of perchloric acid with Cr(II) and Mo(II) compounds was studied by Bredig and Michel. Further, Duke and Quinelly have studied the reduction of perchlorate and showed that reduction has $[H^+]$ dependent as well as $[H^+]$ independent paths. The reaction was linear in $[\text{ClO}_4^-]$ at concentrations below about 1.0 mol dm$^{-3}$. Above this concentration the reaction rate increases. This is probably due to the increased activity coefficient of the perchlorate ion at higher concentrations. The activation energies for the various reactions were calculated and a mechanism was proposed.

The kinetic investigations of the reaction between $[\text{Ti(H}_2\text{O)}_6]^{3+}$ and $\text{Cl}_2$(aq) has been reported. Such studies has also been extended to the oxidation of Ti(III)-EDTA by $\text{I}_2$(aq) and $\text{O}_2$. The kinetics of oxidation of Ti(III) (aq) and Ti(III)-EDTA by aqueous bromine solutions have also been reported.

Reductive chlorinating kinetics of tetrachloroethylene to ethylene catalysed by vitamin B$_{12}$ using titanium(III)citrate as the bulk reductant is examined by David et al. in a vapor/ water batch system. The kinetics of the oxidation-reduction reaction between uranium(VI) and titanium(III) in hydrochloric acid medium has been reported.
Marco et al.\textsuperscript{40} studied the reductive transformation of acetylene, chloroacetylene, 1,1-dichloroethene and cis- and trans-dichloroethene mediated by cobalamine in the presence of titanium(III)citrate. Acetylene quantitatively reacted to ethene via vinylcobalamine as the proposed intermediate. Chloroacetylene reacted to acetylene and vinyl chloride through the proposed intermediates ethynylcobalamine and vinylcobalamine, respectively. Kinetic modeling suggests half-lives for ethynylcobalamine and vinylcobalamine of 1.4 hours and 251 hours, respectively.

Electrode kinetics of the Ti(IV)/Ti(III) system in water and in water-dimethyl formamide and water-dimethyl sulfoxide mixed solvents have been studied\textsuperscript{41} and the electron transfer rate constants of in the reduction of titanium(IV) and oxidation of titanium(III) were determined by square-wave, d.c. and pulse polarograms.

3.1.4 Materials and Method

Dimethylglyoxime(GSC), ferric ammonium sulphate (Sisco-Chem. India), acetic acid(GSC), sodium acetate(Sisco-Chem. India), 1,10-phenanthroline(s.d.fine), sodium sulphate(GSC) are of analar grade and are used without further purification.

The stock solution of titanium(IV) is prepared by the gradual addition of TiO\textsubscript{2} (Glaxo special quality) to hot concentrated sulphuric acid as reported in section 2.2.1. Aqueous stock solution of titanium(III)sulphate solution is prepared by electrolytic reduction of an appropriate titanium(IV)sulphate solution and standardised against ferric ammonium sulphate using 10 \% ammonium thiocyanate as indicator\textsuperscript{42} as described in sections 2.3 and 2.4. Standard solution of ferric ammonium sulphate (0.1 mol dm\textsuperscript{-3}), 1,10-phenanthroline(0.25 \%), sodium acetate-acetic acid buffer and dimethylglyoxime(DMG) solution (0.1 mol dm\textsuperscript{-3}) are prepared.

Double distilled water is used throughout the experiment. Pure nitrogen is used for the deaeration of all experimental systems.
Electrolytic cell: The electrolytic cell consisted of a divided cell, comprising a cation exchange membrane. Catholyte is sulphuric acid (0.75 mol dm$^{-3}$) containing titanium(IV)sulphate (0.20 mol dm$^{-3}$) and dimethylglyoxime (1.0 g). Copper and lead are used as cathode and anode respectively at a distance of 2.0 cm. The electrolysis is monitored with the help of an electrolytically stabilised dc power supply. The electrolytic cell is mounted on a magnetic stirrer and the medium is adequately stirred. The electrolysis is carried out under the galvanostatic conditions using current 10 % higher than that theoretically required. Completion of reduction is indicated by the appearance of permanent violet colour of titanium(III) species. Time taken for the complete reduction is noted and accordingly percentage current efficiency (% CE) is calculated using equation 3.19

$$\text{% CE} = \frac{\text{theoretical time required for complete reduction}}{\text{actual time taken for complete reduction}} \times \frac{100}{W} \quad (3.19)$$

where 'W' is the weight of dimethylglyoxime

Effect of concentrations of titanium(IV)sulphate, sulphuric acid and temperature on the current efficiency is also studied and results are computed (Table 3.1-3.3).

Product recovery and characterisation: Dimethylglyoxime is expected to give 2,3-butane diamine. Repeated attempts by various methods to isolate it is not successful. This is probably because of low boiling point and high solubility of the same in water. Therefore the product, 2,3- butane diamine, is isolated as Schiff's base of salicylaldehyde and characterised by its melting point (182°C) and IR spectra. IR spectrum (Fig.3.8) showed absorption frequencies at 1640 cm$^{-1}$ (C=N stretching), 1460 cm$^{-1}$ (C-H bending in CH$_3$), 1150 cm$^{-1}$ (C-O stretching and O-H bending of the phenol group) and 760 cm$^{-1}$ (aromatic ring with four adjacent hydrogen atoms).
3.1.6 Results and Discussion

Stoichiometry

Stoichiometry for the reduction of dimethylglyoxime by titanium(III) is established by back titration method. To a known volume ($v_1$) of substrate in aqueous medium ($5 \text{ cm}^3$ of $0.001 \text{ mol dm}^{-3}$), titanium(III)sulphate ($5.0 \text{ cm}^3$ of $0.01 \text{ mol dm}^{-3}$) solution ($v_2$) is added under deaerated condition. To this, ammonium iron (III) sulphate solution ($5 \text{ cm}^3$ of $0.025 \text{ mol dm}^{-3}$) is added. The resulting solution is back-titrated against standard titanium(III)sulphate ($0.05 \text{ mol dm}^{-3}$) stored under nitrogen atmosphere using 10% ammonium thiocyanate indicator ($v_3$). A blank titration is carried out by taking same amount of titanium(III)sulphate and ammonium iron(III)sulphate solutions. Titration volume is $v_4$. The number of electrons ($n$) is given by the equation 3.20

$$n = \frac{[v_2 - (v_4 - v_3) \times M_2]}{v_1 \times M_1} \quad (3.20)$$

where $M_1$ and $M_2$ are the molarities of sample solution and titanium(III)sulphate solution respectively. Stoichiometry of dimethylglyoxime by titanium(III) is found to be 1:8 as shown below,

$$\text{C}_4\text{H}_8\text{O}_2\text{N}_2 + 8 \text{Ti}^{4+} + 8 \text{H}^+ \rightarrow \text{C}_4\text{H}_{12}\text{N}_2 + 8\text{Ti}^{3+} + 2 \text{H}_2\text{O} \quad (3.21)$$

(3.21)

The electrochemical reduction of dimethylglyoxime in sulphuric acid medium is found to give irreversible cyclic voltammogram with a well defined cathodic peak (Fig. 2.9, chapter 2). The cathodic peak potential is found to decrease from $-608$ to $-488$ mV as the concentration of the sulphuric acid is varied from 4 to 72mM, thereby showing the involvement of $\text{H}^+$ ion (proton) during the reduction process.
The initial rates are obtained from the slopes of concentration versus time curves at the initial stages of the reaction by the plane mirror method, reproducible to ± 3%.

The order of the reaction is found by log(rate) versus log(concentration) plots (Fig. 3.1 and 3.2). The order is found by varying the concentrations of the oxidant, reductant and sulphuric acid in turn, while keeping others constant and the results are computed (Table 3.5). The order with respect to reductant (Ti(III) and oxidant (DMG) is nearly unity and the order with respect to sulphuric acid is about 0.5. Therefore,

$$rate = k [\text{Ti(III)}]^{1.0} [\text{DMG}]^{1.0} [H^+]^{0.5}$$ (3.22)

In a typical standard run, kinetics of dimethylglyoxime are studied at $[\text{Ti(III)}] = 0.05 \text{ mol dm}^{-3}$, $[\text{DMG}] = 0.00625 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.4 \text{ mol dm}^{-3}$, ionic strength = 3.0 mol dm$^{-3}$ and temperature = 306 K in 25 % ethanol-water medium.

### 3.1.7 Kinetic Scheme

The mechanism for the observed kinetics is as shown in scheme 3.1

$$\text{S} + H^+ \xrightarrow{K_1} \text{SH}^+$$

(DMG) fast

$$\text{SH}^+ + \text{Ti}^{3+} \rightarrow \text{SH}^0 + \text{Ti}^{4+} \text{ (slow & rds)}$$

$$\text{SH}^0 + 7 \text{Ti}^{3+} + 7 H^+ \rightarrow 2,3\text{-butane diamine} + 2 H_2O + 7 \text{Ti}^{4+} \text{ fast}$$

**Scheme 3.1**

In the above scheme 3.1, $[S] = \{[S]_0 - [SH^+]\}$

$$[SH^+] = k_1 [S]_0 [H^+] / \{ k_{-1} + k_1 [H^+] + k_2 [\text{Ti}^{3+}]\}$$
Overall rate of the reaction = \( k_2 [\text{SH}^+] [\text{Ti}^{3+}] \)

rate = \( k_1 k_2 [S]_o [\text{Ti}^{3+}] [\text{H}^+] / \{k_{-1} + k_1 [\text{H}^+] + k_2 [\text{Ti}^{3+}]\} \)

Assuming that \( k_2 \) is negligible as compared to other terms in the denominator,

\[
\text{rate} = K_1 k_2 [S]_o [\text{Ti}^{3+}] [\text{H}^+] / \{1 + K_1 [\text{H}^+]\} \tag{3.23}
\]

where \( K_1 = k_1 / k_{-1} \)

Rate law (3.23) takes the form,

\[
1/\text{rate} = 1/ K_1 k_2 [S]_o [\text{Ti}^{3+}] [\text{H}^+] + 1/ k_2 [S]_o [\text{Ti}^{3+}] \tag{3.24}
\]

The plots of \( 1/\text{rate} \) versus \( 1/[\text{H}^+] \) are linear (Fig. 3.3) with intercept on the ordinate in accordance with rate law (3.24) and scheme 3.1. The second order rate constant \( k_2 \) (4.00 mol dm\(^{-3}\) s\(^{-1}\)) and formation equilibrium constant, \( K_1 \) (4.80 dm\(^{-2}\) mol\(^{-1}\)) are calculated from the intercept and slopes of the double reciprocal plot (Fig. 3.3).

The protonated substrate, \( \text{SH}^+ \) reacts with \( \text{Ti}^{3+} \) in the slow step to give a free radical. The free radical further reacts with additional \( \text{Ti}^{3+} \) ions in fast steps to give the products. The observed decrease in dielectric constant of the medium is in accordance with Laidler and Eyring equation\(^a\) as applicable to reaction between ions of equal charge. Decrease in rate of the reaction with increase in ionic strength (Table 3.4) due to the added \( \text{SO}_4^{2-} \) could be due to the equilibrium,

\[
\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^- \tag{3.25}
\]

resulting in lowering of \( \text{H}^+ \) and hence decrease in rate.
The detailed mechanism of reduction is shown in scheme 3.2

\[
\begin{align*}
H_3C-C=N-OH + H^+ & \xrightarrow{K_1} H_3C-C=N'H-OH \\
H_3C-C=N-OH & \xrightarrow{k_2} H_3C-C=N-OH \\
H_3C-C=N'H-OH + Ti^{3+} & \xrightarrow{\text{slow}} H_3C-C'^-NH-OH + Ti^{4+} \\
H_3C-C=N-OH + 7Ti^{3+} + 7H^+ & \rightarrow H_3C-CH-NH_2 + 7Ti^{4+} + 2H_2O
\end{align*}
\]

Scheme 3.2

It is found that the reaction mixtures initiate polymerisation of monomers like acrylonitrile or methyl methacrylate in an hour. As neither of the reacting species, Ti(III) or DMG, initiate polymerisation when added separately to an aqueous mixture of the two monomers, it can be assumed that the reduction steps produce free radicals which induce polymerisation.

The effect of temperature on the initial rate of the reaction is studied at 296, 301, 306, and 311K and 10^4 x initial rate obtained are 3.75, 5.00, 7.04, and 10.29 mol dm^{-3} s^{-1} respectively giving the activation parameters, \(E_a=46.07\pm5kJ \text{ mol}^{-1}\), \(\Delta H^* = 44.18 \pm 5 \text{ kJ mol}^{-1}\), \(\Delta G^* = 2.78 \pm 0.9 \text{ kJ mol}^{-1}\) and \(\Delta S^* = -160.10 \pm 16 \text{ JK}^{-1} \text{ mol}^{-1}\) and \(\log A = 4.83 \pm 0.8\)

The relative low energy of activation energy or enthalpy of activation for the overall reaction support the free radical mechanism. Negative entropies of activation and high positive free energy of activation suggest the role of bond breaking in the formation of reduction product.
SECTION B. KINETICS AND MECHANISM OF TITANIUM(III) REDUCTION OF FURFURALDOXIME AND \(\alpha\)-FURIL DIOXIME

3.2.1 Introduction

Section B, describes the kinetics and mechanism of titanium(III) reduction of heterocyclic aromatic monoxime and dioxime viz. fufuraldoxime and \(\alpha\)-furil dioxime, under nitrogen atmosphere, in the temperature range of 298-313 K. The reduction products are isolated and characterised as Schiff's base of furfurylamine or \(\alpha\)-furil diamine with salicylaldehyde. The stoichiometry of the reduction of fufuraldoxime and \(\alpha\)-furil dioxime by titanium(III)sulphate solution is established by back titration method using 10% ammonium thiocyanate indicator. Kinetic investigations have been carried out under stoichiometric and non-stoichiometric conditions in aqueous sulphuric acid–ethanol medium by spectrophotometric method. The reaction follows overall second order kinetics, first order each in \([\text{Ti(III)}]\) and \([\text{oxime}]\) and fractional order in \([\text{H}_2\text{SO}_4]\). The effect of varying concentrations of \(\text{Ti(III)}\), oxime, \(\text{H}_2\text{SO}_4\), ionic strength and solvent composition has been studied and effect of temperature has also been studied and activation parameters are computed from Arrhenius and Eyring plots. A suitable kinetic scheme consistent with the observed results is suggested and discussed.

3.2.2 Materials and Method

\(\alpha\)-Furil dioxime, ferric ammonium sulphate(Sisco Chem), acetic acid(GSC), sodium acetate(Sisco Chem.), 1, 10-phenanthroline(s.d.fine), sodium sulphate(GSC) are of analar grade and are used without further purification.
Furfuraldoxime is prepared by literature method and characterised by determining its melting point (85°). The stock solution of titanium(IV) is prepared as reported as in section 2.2.1, chapter 2.

Aqueous stock solution of titanium(III) sulphate solution is prepared by electrolytic reduction of an appropriate titanium(IV)sulphate solution and standardised against ferric ammonium sulphate using 10 % ammonium thiocyanate as indicator as described in sections 2.3 and 2.4. Standard solution of ferric ammonium sulphate (0.1 mol dm$^{-3}$), 1,10-phenanthroline(0.25 %), sodium acetate-acetic acid buffer, oxime solution(0.1 mol dm$^{-3}$, absolute alcohol) are prepared.

Doubly distilled water is used throughout the experiment. Pure nitrogen is used for the deaeration of all experimental systems.

3.2.3 Kinetic Measurements

The kinetic measurements are performed as described in section 3.1.5

3.2.4. Results and Discussion

Stoichiometry for the reduction of furfuraldoxime and $\alpha$-furil dioxime by titanium(III) is established by back titration method as described in section 3.1.6

Stoichiometry of reduction of furfuraldoxime by titanium(III) is found to be 1:4 as shown below,

$$C_5H_5O_2N + 4 Ti^{4+} + 4H^+ \rightarrow C_5H_7NO + 4 Ti^{4+} + H_2O$$

(FAO) (furfurylamine)

Similarly stoichiometry of reduction of $\alpha$-furil dioxime by titanium(III) is found to be 1:8 as shown in equation 3.27

$$C_{10}H_8N_2O_4 + 8 Ti^{3+} + 8 H^+ \rightarrow C_{10}H_{12}O_2N_2 + 8 Ti^{4+} + 2 H_2O$$

($\alpha$- FDO) ($\alpha$-furil diamine)
The electrochemical reduction of furfuraldoxime in sulphuric acid medium is found to give irreversible cyclic voltammogram with a well defined cathodic peak (as shown in Fig. 2.10, chapter 2). The cathodic peak potential is found to decrease from -524 to -675 mV as the concentration of the sulphuric acid is varied from 4 to 72 mM, thereby showing the involvement of H\(^+\) ion (proton) during the reduction process.

The initial rates are obtained from the slopes of concentration versus time curves at the initial stages of the reaction by the plane mirror method\(^5\), reproducible to ± 3%.

The order of the reaction is found by log(rate) versus log(concentration) plots (Fig. 3.4-3.6). The order is found by varying the concentration of the oxidant, reductant, sulphuric acid in turn, while keeping others constant and the results are computed(Table 3.6 and 3.8). The concentration of the oxidant, reductant, sulphuric acid in turn, while keeping others constant. The order with respect to reductant and oxidant is nearly unity and the order with respect to sulphuric acid is about 0.5 in case of both the oximes. Therefore,

\[
\text{rate} = k \ [\text{[Ti(III)]} \ ^{1.0}\ [\text{Substrate}] \ ^{1.0}\ [\text{H}^+] \ ^{0.5}\]
\]  \hspace{1cm} (3.28)

In a typical standard run, kinetics of furfuraldoxime are studied at [Ti(III)]= 0.03 mol dm\(^{-3}\), [FAO] = 0.0075 mol dm\(^{-3}\), [H\(_2\)SO\(_4\)] = 0.4 mol dm\(^{-3}\), ionic strength= 2.0 mol dm\(^{-3}\) and temperature = 310 K in 25% ethanol-water system. Similar kinetics of \(\alpha\)-furil dioxime are performed at [\(\alpha\)-FDO] = 0.00375 mol dm\(^{-3}\) (to obey the stoichiometry) while keeping all the parameters same as in case of furfuraldoxime.
3.2.5 Kinetic Scheme

The mechanism for the observed kinetics is as shown in scheme 3.3 and 3.4 for furfuralaldoxime and \(\alpha\)-furil dioxime respectively,

\[
S + H^+ \xrightarrow{K_1, (FAO)} SH^+ \quad \text{fast}
\]

\[
SH^+ + Ti^{3+} \xrightarrow{k_2} SH^o + Ti^{4+} \quad \text{slow & rds}
\]

\[
SH^o + 3 Ti^{3+} + 3 H^+ \rightarrow \text{amine product} + H_2O + 3Ti^{4+} \quad \text{fast}
\]

Scheme 3.3

\[
S + H^+ \xrightarrow{K_1, (\alpha-FDO)} SH^+ \quad \text{fast}
\]

\[
SH^+ + Ti^{3+} \xrightarrow{k_2} SH^o + Ti^{4+} \quad \text{slow & rds}
\]

\[
SH^o + 7 Ti^{3+} + 7 H^+ \rightarrow \text{diamine product} + 2 H_2O + 7 Ti^{4+} \quad \text{fast}
\]

Scheme 3.4

Here both the schemes follow same path except the stoichiometry difference.

In the above schemes, \([S] = \{[S]_0 - [SH^+]\}\)

\[
[SH^+] = k_1 [S]_0 [H^+] / \{k_{-1} + k_1[H^+] + k_2[Ti^{3+}]\}
\]

Overall rate of the reaction \(= k_2[SH^+][Ti^{3+}]\)

Substituting the value of \(SH^+\),

\[
\text{rate} = \frac{k_1k_2[S]_o[Ti^{3+}][H^+]}{k_{-1} + k_1[H^+] + k_2[Ti^{3+}]} \quad (3.29)
\]
Assuming that \( k_2 \) is negligible as compared to other terms in the denominator,

\[
\text{rate} = \frac{K_i k_2 [S]_o [Ti^{3+}] [H^+]}{1 + K_i [H^+]} \tag{3.30}
\]

where \( K_i = \frac{k_i}{k_{-1}} \)

Rate law (3.30) takes the form,

\[
1/\text{rate} = 1/ K_i k_2 [S]_o [Ti^{3+}] [H^+] + 1/ k_2 [S]_o [Ti^{3+}] \tag{3.31}
\]

The plots of \( 1/\text{rate} \) versus \( 1/[H^+] \) are linear with intercept on the ordinate in accordance with rate law (3.31) and scheme 3.3 and 3.4. The second order rate constant \( k_2 (1.62 \text{ and } 2.57 \text{ mol dm}^{-3} \text{ s}^{-1}) \) and formation equilibrium constant \( K_i (7.62 \text{ and } 10.74 \text{ dm}^3 \text{ mol}^{-1}) \) of the reduction process of furfuraldoxime and \( \alpha \)-furil dioxime respectively are calculated from the intercept and slopes of the double reciprocal plot (Fig. 3.7).

The protonated substrate, \( \text{SH}^+ \) reacts with \( \text{Ti}^{3+} \) in the slow step to give a free radical. The free radical further reacts with additional \( \text{Ti}^{3+} \) ions in fast steps to give the products. The observed decrease in dielectric constant of the medium is in accordance with Laidler and Eyring equation\(^{43} \) as applicable to reaction between ions of equal charge. Decrease in rate of the reaction with increase in ionic strength (Table 3.7 and 3.9) due to the added \( \text{SO}_4^{2-} \) could be due to the equilibrium,

\[
\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^- \tag{3.32}
\]

resulting in lowering of \( \text{H}^+ \) and hence decrease in rate.

It is found that the reaction mixture initiates, polymerisation of monomers like acrylonitrile or methyl methacrylate in an hour. As neither of the reacting species, titanium(III) or furfuraldoxime or \( \alpha \)-furil dioxime, initiate polymerisation when added separately to an aqueous mixture of the two monomers, it can be assumed that the reduction steps produce free radicals which induce polymerisation as reported earlier.
The detailed mechanism of reduction is shown in schemes 3.5 and 3.6 for furfuraldoxime and furil dioixime respectively.

Scheme 3.5

Scheme 3.6
The effect of temperature on the initial rate of the reaction is studied at 298, 303, 310, and 313 K, and $10^4 \times$ initial rate obtained are 0.83, 1.05, 2.52, and 3.16 mol dm$^{-3}$ s$^{-1}$ respectively for furfuraldoxime giving the activation parameters, $E_a = 68.17 \pm 2.9$ kJ mol$^{-1}$, $\Delta H^\circ = 65.62 \pm 3$ kJ mol$^{-1}$, $\Delta G^\circ = 73.76 \pm 0.2$ kJ mol$^{-1}$, and $\Delta S^\circ = -26.41 \pm 9$ JK$^{-1}$ mol$^{-1}$.

Similar effect of temperature on the initial rate of the reaction is also studied for $\alpha$-furil dioxime at 298, 303, 310 and 313 K and $10^4 \times$ initial rates obtained are 0.82, 1.27, 2.21, and 2.78 mol dm$^{-3}$ s$^{-1}$ respectively, giving the activation parameters, $E_a = 63.0 \pm 1.0$ kJ mol$^{-1}$, $\Delta H^\circ = 60.4 \pm 1.1$ kJ mol$^{-1}$, $\Delta G^\circ = 73.82 \pm 0.2$ kJ mol$^{-1}$, and $\Delta S^\circ = 41.26 \pm 3$ JK$^{-1}$ mol$^{-1}$.

The relative low energy of activation energy or enthalpy activation for the overall reaction support the free radical mechanism. Negative entropies of activation and high positive free energy of activation suggest the role of bond breaking in the formation of reduction product.

Product isolation and characterisation

It has been found that the reduction products (primary amines) are highly soluble in water and they have low boiling point also. Repeated attempts by various methods to isolate the reduction products are not successful, therefore, the macro quantities of products, furfurylamine and $\alpha$-furil diamine are produced by titanium(III) mediated electroreduction process and isolated as their Schiff's bases of salicylaldehyde as follows:

The electrolytic cell consists of two cylindrical glass tubes fused to two halves of square shaped steel frames, having a circular opening at the centre. These steel frames are tightened together with the help of screws provided for this purpose by placing an anionic exchange membrane in between which acts as diaphragm. One glass tube is used as anodic compartment and another as cathodic compartment. Sulphuric acid (25 cm$^3$ of 0.75 mol dm$^{-3}$) is used as anolyte. Catholyte is sulphuric acid (25 cm$^3$ of 0.75 mol dm$^{-3}$) containing 3-4%
titanium(IV)sulphate solution and 1.0 g of furfuraldoxime or α-furil dioxime. Pure copper (2x 6 cm) is used as cathode and bright platinum foil as anode. Electrodes are separated by a distance of 2.0 cm. The electrolysis is carried out under galvanostatic conditions using 10 % more current than theoretically required. Completion of the reduction is indicated by the appearance of permanent violet colour of titanium(III) species.

Catholyte is neutralised with sodium carbonate. Titanium hydroxide which precipitated out is filtered and washed well with water. It is then ignited at high temperature to recover titanium dioxide. The filtrate is diluted to 150 cm$^3$. To this 50 cm$^3$ freshly prepared solution of basic salicylaldehyde (10 cm$^3$ of salicylaldehyde is added to 200 cm$^3$ of water containing 5.0 g of sodium hydroxide and stirred rapidly on a magnetic stirrer until all oil is dissolved) is added with vigorous stirring. Solution turns turbid immediately and on cooling it for about 15 minutes. Precipitate is settling down at the bottom. It is filtered in sintered glass crucible of required specifications, dried at 70° C and characterised by its melting point (> 295°C) and IR spectra. The IR spectrum(Fig.3.9), showed sharp absorption frequencies at 3464 cm$^{-1}$ (O-H stretching), 2932 cm$^{-1}$ (C-H stretching), 1626 cm$^{-1}$ (C=N stretching), 1460 cm$^{-1}$ (C-H bending in $-\text{CH}_2$), 1150 cm$^{-1}$ (C-O stretching and O-H bending of the phenol group) and 760 cm$^{-1}$ and 850 cm$^{-1}$ (C-H bending frequencies for aromatic ring with adjacent hydrogen atoms).

3.2.6 Conclusion

The reported work has shown that electrolytically generated titanium(III) can be used for the reduction of several aliphatic and aromatic monoximes, dioximes, heterocyclic oximes to corresponding amines having important applications in organic synthesis. Moreover, a detailed kinetic study enables mechanistic features of the reduction process. The free radicals formed 'in situ', in the titanium(III)-oxime redox reaction initiate the polymerisation of vinyl monomers.
Table 3.1

Effect of concentration of titanium(IV)sulphate on the current efficiency of reduction of dimethyglyoxime, \([\text{H}_2\text{SO}_4]\) : 0.75 mol dm\(^{-3}\); cathode: copper; anode: lead; diaphragm: cationic exchange membrane and temperature: 298 K

<table>
<thead>
<tr>
<th>([\text{Ti(SO}_4)_2]) (mol dm(^{-3}))</th>
<th>Time taken for complete reduction (in minutes)</th>
<th>Current efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
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<td>120</td>
<td>255</td>
</tr>
<tr>
<td>0.20</td>
<td>120</td>
<td>200</td>
</tr>
<tr>
<td>0.10</td>
<td>120</td>
<td>180</td>
</tr>
<tr>
<td>0.05</td>
<td>120</td>
<td>160</td>
</tr>
</tbody>
</table>

Table 3.2

Effect of concentration of sulphuric acid on the current efficiency of reduction of dimethyglyoxime, \([\text{Ti(SO}_4)_2]\) : 0.2 mol dm\(^{-3}\); cathode: copper; anode: lead; diaphragm: cationic exchange membrane and temperature: 298 K

<table>
<thead>
<tr>
<th>([\text{H}_2\text{SO}_4]) (mol dm(^{-3}))</th>
<th>Time taken for complete reduction (in minutes)</th>
<th>Current efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
<td>0.50</td>
<td>120</td>
<td>255</td>
</tr>
<tr>
<td>0.75</td>
<td>120</td>
<td>200</td>
</tr>
<tr>
<td>1.50</td>
<td>120</td>
<td>155</td>
</tr>
<tr>
<td>2.25</td>
<td>120</td>
<td>147</td>
</tr>
</tbody>
</table>
### Table 3.3

Effect of temperature on the current efficiency of reduction of dimethylglyoxime, 
\([\text{Ti(SO}_4\text{)}_2] : 0.2 \text{ mol dm}^{-3} ; [\text{H}_2\text{SO}_4] : 0.75 \text{ mol dm}^{-3} ; \text{cathode} : \text{copper} ; \text{anode} : \text{lead} ; \text{diaphragm} : \text{cationic exchange membrane} \) and temperature : 298 K

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Time taken for complete reduction (in minutes)</th>
<th>Current efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc Found</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>120 200</td>
<td>60.12</td>
</tr>
<tr>
<td>303</td>
<td>120 190</td>
<td>63.15</td>
</tr>
<tr>
<td>308</td>
<td>120 175</td>
<td>68.57</td>
</tr>
<tr>
<td>313</td>
<td>120 160</td>
<td>75.12</td>
</tr>
</tbody>
</table>

### Table 3.4

Effect of ionic strength and solvent composition on the initial rate of the reaction 
\(\{\text{Temp} = 310; [\text{Ti(III)}] = 0.03 \text{ mol dm}^{-3} ; [\text{DMG}] = 0.00625 \text{ mol dm}^{-3} \) and \([\text{H}_2\text{SO}_4] = 0.4 \text{ mol dm}^{-3}\) \)

<table>
<thead>
<tr>
<th>Ionic strength(l) (mol dm⁻³)</th>
<th>Initial rate x 10⁴ (mol dm⁻³ s⁻¹)</th>
<th>Alcohol (%)</th>
<th>Initial rate x 10⁴ (mol dm⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>11.75</td>
<td>22</td>
<td>9.00</td>
</tr>
<tr>
<td>2.75</td>
<td>10.50</td>
<td>25</td>
<td>7.94</td>
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<tr>
<td>3.00</td>
<td>7.94</td>
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<td>6.36</td>
</tr>
<tr>
<td>3.50</td>
<td>5.44</td>
<td>35</td>
<td>5.65</td>
</tr>
</tbody>
</table>
Table 3.5

Effect of varying concentrations of titanium(III), dimethylglyoxime (DMG) and sulphuric acid on initial rate of the reaction [Temp=306 K and I = 3.0 mol dm\(^{-3}\)]

<table>
<thead>
<tr>
<th>[Ti(III)] x 10^2 (mol dm(^{-3}))</th>
<th>[DMG] x 10^3 (mol dm(^{-3}))</th>
<th>[H(_2)SO(_4)] x 10 (mol dm(^{-3}))</th>
<th>Initial rate x 10^4 (mol dm(^{-3}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.15</td>
<td>6.25</td>
<td>4.0</td>
<td>4.69</td>
</tr>
<tr>
<td>4.06</td>
<td>6.25</td>
<td>4.0</td>
<td>6.19</td>
</tr>
<tr>
<td>4.55</td>
<td>6.25</td>
<td>4.0</td>
<td>7.50</td>
</tr>
<tr>
<td>5.00</td>
<td>6.25</td>
<td>4.0</td>
<td>7.94</td>
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<tr>
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<td>3.25</td>
<td>4.0</td>
<td>3.95</td>
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<td>4.25</td>
<td>4.0</td>
<td>5.21</td>
</tr>
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<td>5.00</td>
<td>5.25</td>
<td>4.0</td>
<td>6.40</td>
</tr>
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<td>5.00</td>
<td>6.25</td>
<td>1.0</td>
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<td>6.25</td>
<td>2.0</td>
<td>5.59</td>
</tr>
<tr>
<td>5.00</td>
<td>6.25</td>
<td>7.5</td>
<td>10.00</td>
</tr>
</tbody>
</table>
Table 3.6

Effect of varying concentrations of titanium(III), furfuraldoxime (FAO) and sulphuric acid on initial rate of the reaction [Temp=310 K and I = 2.0 mol dm\(^{-3}\)]

<table>
<thead>
<tr>
<th>[Ti(III)] (\times 10^2) (mol dm(^{-3}))</th>
<th>[FAO] (\times 10^3) (mol dm(^{-3}))</th>
<th>[H(_2)SO(_4)] (\times 10) (mol dm(^{-3}))</th>
<th>Initial rate (\times 10^4) (mol dm(^{-3}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>7.5</td>
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<td>1.60</td>
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<tr>
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<td>7.5</td>
<td>4.0</td>
<td>2.50</td>
</tr>
<tr>
<td>4.5</td>
<td>7.5</td>
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<td>3.66</td>
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<tr>
<td>5.3</td>
<td>7.5</td>
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<td>4.36</td>
</tr>
<tr>
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<td>3.03</td>
</tr>
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Table 3.7

Effect of ionic strength and solvent composition on the initial rate of the reaction { Temp = 310 K ; [Ti(III)] = 0.03 mol dm\(^{-3}\); [FAO] = 0.0075 mol dm\(^{-3}\) and [H\(_2\)SO\(_4\)] = 0.4 mol dm\(^{-3}\)}

<table>
<thead>
<tr>
<th>Ionic strength (I) (mol dm(^{-3}))</th>
<th>Initial rate (\times 10^4) (mol dm(^{-3}) s(^{-1}))</th>
<th>Alcohol (%)</th>
<th>Initial rate (\times 10^4) (mol dm(^{-3}) s(^{-1}))</th>
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<td>1.31</td>
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Table 3.8
Effect of varying concentrations of titanium(III), α-furil dioxime(α-FDO) and sulphuric acid on initial rate of the reaction (Temp = 310 K and I = 2.0 mol dm⁻³)

<table>
<thead>
<tr>
<th>[Ti(III)] x 10² (mol dm⁻³)</th>
<th>[α-FDO] x 10³ (mol dm⁻³)</th>
<th>[H₂SO₄] x 10 (mol dm⁻³)</th>
<th>Initial rate x 10⁴ (mol dm⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.75</td>
<td>4.0</td>
<td>1.27</td>
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Table 3.9
Effect of ionic strength and solvent composition on the initial rate of the reaction (Temp = 310 K; [Ti(III)] = 0.03 mol dm⁻³; [α-FDO] = 0.00375 mol dm⁻³ and [H₂SO₄] = 0.4 mol dm⁻³)

<table>
<thead>
<tr>
<th>Ionic strength(I) (mol dm⁻³)</th>
<th>Initial rate x 10⁴ (mol dm⁻³ s⁻¹)</th>
<th>Alcohol (%)</th>
<th>Initial rate x 10⁴ (mol dm⁻³ s⁻¹)</th>
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</tr>
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<td>2.75</td>
<td>0.60</td>
<td>35</td>
<td>1.16</td>
</tr>
</tbody>
</table>
Fig. 3.1. Plots of log(concentration) versus log(initial rate, R)

(A) = Plot of $4 + \log R$ vs $3 + \log[\text{DMG}]$ at 306 K; $\text{Ti(III)}$ : 0.05 mol dm$^{-3}$; $[\text{H}_2\text{SO}_4]$ : 0.4 mol dm$^{-3}$; ionic strength : 3.0 mol dm$^{-3}$; ethanol : 25% (v/v) and $[\text{DMG}]$ : $3.25 \times 10^{-3}$, $4.25 \times 10^{-3}$, $5.25 \times 10^{-3}$, and $6.25 \times 10^{-3}$ mol dm$^{-3}$.

(B) = Plot of $4 + \log R$ vs $2 + \log[\text{Ti(III)}]$ at 306 K; $[\text{DMG}]$ : $0.00625$ mol dm$^{-3}$; $[\text{H}_2\text{SO}_4]$ : 0.4 mol dm$^{-3}$; ionic strength : 3.0 mol dm$^{-3}$; ethanol : 25% (v/v) and $[\text{Ti(III)}]$ : $3.15 \times 10^{-2}$, $4.06 \times 10^{-2}$, $4.55 \times 10^{-2}$, and $5.53 \times 10^{-2}$ mol dm$^{-3}$.
Fig. 3.2. Plots of 4+ log R versus 2+ log[H+] at 306 K; Ti(III) : 0.05 mol dm⁻³; [DMG] : 0.00625 mol dm⁻³; ionic strength : 3.0 mol dm⁻³; ethanol : 25% (v/v) and [H₂SO₄] : 0.1, 0.2, 0.4, and 0.75 mol dm⁻³.
Fig. 3.3. The plot of 1/rate versus 1/[H⁺] at 306 K; Ti(III): 0.05 mol dm³; [DMG]: 0.00625 mol dm³; ionic strength: 3.0 mol dm³; ethanol: 25% (v/v) and [H₂SO₄]: 0.1, 0.2, 0.4 and 0.75 mol dm³.
Fig. 3.4. Plots of log (initial rate, R) versus log(concentration).

(A) = Plot of \(5+ \log R\) versus \(3+ \log [\text{FAO}]\), at 310 K; [Ti(III)]: 0.03 mol dm\(^{-3}\); [H\(_2\)SO\(_4\)]: 0.4 mol dm\(^{-3}\); Ionic strength: 2.0 mol dm\(^{-3}\); ethanol: 25% (v/v) and [FAO]: 5 x 10\(^{-3}\), 7.5 x 10\(^{-3}\), 10 x 10\(^{-3}\) and 12 x 10\(^{-3}\) mol dm\(^{-3}\).

(B) = Plot of \(4+ \log R\) versus \(2+ \log [\text{H}^+]\) at 310 K; [FAO]: 7.5 x 10\(^{-3}\) mol dm\(^{-3}\); [Ti(III)]: 0.03 mol dm\(^{-3}\); Ionic strength: 2.0 mol dm\(^{-3}\); ethanol: 25% (v/v) and [H\(_2\)SO\(_4\)]: 0.2, 0.3, 0.4 and 0.5 mol dm\(^{-3}\).
Fig. 3.5. Plots of log(concentration) versus log (initial rate, R).

(A) = Plot of $4 + \log R$ vs $2 + \log [\text{Ti(III)}]$ at 310 K; [FAO] : 0.0075 mol dm$^{-3}$; \([\text{H}_2\text{SO}_4]\) : 0.4 mol dm$^{-3}$; ionic strength : 2.0 mol dm$^{-3}$; ethanol: 25% (v/v) and \([\text{Ti(III)}] : 2.0 \times 10^{-2}, 3.0 \times 10^{-2}, 4.55 \times 10^{-2} \text{ and } 5.3 \times 10^{-2}$ mol dm$^{-3}$.

(B) = Plot of Plot of $4 + \log R$ vs $2 + \log [\text{Ti(III)}]$ at 310 K; [FDO] : 0.00375 mol dm$^{-3}$; \([\text{H}_2\text{SO}_4]\) : 0.4 mol dm$^{-3}$; ionic strength : 2.0 mol dm$^{-3}$; ethanol: 25% (v/v) and \([\text{Ti(III)}] : 2.0 \times 10^{-2}, 3.0 \times 10^{-2}, 4.0 \times 10^{-2} \text{ and } 4.9 \times 10^{-2}$ mol dm$^{-3}$. 

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Fig. 3.6. Plots of \( \log(\text{initial rate, } R) \) versus \( \log(\text{concentration}) \).

(A) = Plot of \( 5 + \log R \) versus \( 3 + \log[\text{FDO}] \), at 310 K; [Ti(III)]: 0.03 mol dm\(^{-3}\); \( [\text{H}_2\text{SO}_4] \): 0.4 mol dm\(^{-3}\); Ionic strength: 2.0 mol dm\(^{-3}\); ethanol: 25 % (v/v) and [FDO] : \( 1.75 \times 10^{-3} \), \( 2.75 \times 10^{-3} \), \( 3.75 \times 10^{-3} \) and \( 4.75 \times 10^{-3} \) mol dm\(^{3}\).

(B) = Plot of \( 4 + \log R \) versus \( 1 + \log[H^+] \) at 310 K; [FDO]: \( 3.75 \times 10^{-3} \) mol dm\(^{-3}\); [Ti(III)]: 0.03 mol dm\(^{-3}\); Ionic strength: 2.0 mol dm\(^{-3}\); ethanol: 25 % (v/v) and \( [\text{H}_2\text{SO}_4] \) mol dm\(^{-3}\): 0.2, 0.3, 0.4 and 0.5 mol dm\(^{3}\).
Fig. 3.7. The plots of $1/\text{rate}$ versus $[1/\text{H}^+]$.

(A) = Plot of $1/\text{rate}$ versus $[1/\text{H}^+]$ at 310 K; Ti(III) : 0.03 mol dm$^{-3}$; [FAO] : 0.0075 mol dm$^{-3}$; ionic strength : 2.0 mol dm$^{-3}$; ethanol : 25% (v/v) and $[\text{H}_2\text{SO}_4] = 0.2, 0.3, 0.4$ and 0.5 mol dm$^{-3}$.

(B) = Plot of $1/\text{rate}$ versus $[1/\text{H}^+]$ at 310 K; Ti(III) : 0.03 mol dm$^{-3}$; [FAO] : 0.00375 mol dm$^{-3}$; ionic strength : 2.0 mol dm$^{-3}$; ethanol: 25% (v/v) and $[\text{H}_2\text{SO}_4] = 0.2, 0.3, 0.4$ and 0.5 mol dm$^{-3}$. 
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