Titanium (III) reduction of dimethylglyoxime: Electrochemical and kinetic studies

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Titanium (III) mediated electroreduction of dimethylglyoxime has been carried out in aqueous sulphuric acid medium and the reduction product has been isolated and characterised. The kinetic investigations have been carried out under stoichiometric and non-stoichiometric conditions at 306K. It has been found that the reaction follows overall second order kinetics, first order each in \([\text{Ti(III)}]\) and \([\text{DMG}]\) and fractional order in sulphuric acid. The effect of varying concentrations of \([\text{Ti(III)}], \text{DMG}, \text{H}_2\text{SO}_4, \text{ionic strength, and solvent composition has been studied. Effect of temperature has also been studied and activation parameters have been computed from Arrhenius and Eyring plots.}

Titanium (III) in aqueous acid media has been found to be an efficient reducing agent for a variety of organic as well as inorganic compounds. The kinetics of reduction of nitro, nitroso, azo and azoxy compounds and its substituted products by titanium(III) chloride was studied by Hinshelwood and co-workers\(^1\). Titanium(III)-mediated electrode-reduction of nitro compounds has been reported earlier\(^2\). Dimethyl glyoxime is mainly used in quantitative analysis as a complexing agent. On reduction, dimethyl glyoxime is expected to give the corresponding diamine\(^3\). In recent years the production of diamines by reduction methods has become increasingly important due to their importance in organic synthesis. To understand the reductive capability of titanium(III), we have studied the kinetics of reduction of dimethyl glyoxime in aqueous sulphuric acid medium.

Experimental

All chemicals used were of analytical grade. Doubly distilled water was used throughout. The stock solution of titanium(IV) was prepared as reported elsewhere\(^4\). Standard solutions of ferric ammonium sulphate (0.1 mol dm\(^{-3}\)), 1,10-phenanthroline (0.25%), sodium acetate-acetic acid buffer, dimethyl glyoxime (0.1 mol dm\(^{-3}\)) in ethanol and sodium sulphate (1.5 mol dm\(^{-3}\)) were prepared.

The electrolytic cell consisted of a divided cell, comprising cationic exchange membrane. Catholyte was sulphuric acid (0.75 mol dm\(^{-3}\)) containing titanium(IV) sulphate (0.20 mol dm\(^{-3}\)) and dimethyl glyoxime (1.0 g). Copper and lead were used as cathode and anode respectively at a distance of 2.0 cm. The electrolysis was monitored with the help of an electrolytically stabilised dc power supply. The electrolytic cell was mounted on a magnetic stirrer and the medium was adequately stirred. The electrolysis was carried out under galvanostatic conditions using current 10% higher than that theoretically required. Completion of reduction was indicated by the appearance of permanent violet colour of titanium(III) species. Time taken for the complete reduction was noted and accordingly percentage current efficiency (% CE) was calculated using Eq. (1).

\[
\% \text{CE} = \frac{\text{Theoretical time required for complete reduction}}{\text{Actual time taken for complete reduction}} \times 100
\]

where \(W\) is the weight of dimethyl glyoxime.

Effect of concentrations of titanium(IV) sulphate, sulphuric acid and temperature on the current efficiency was also studied. Repeated attempts by various method to isolate the corresponding diamine were not successful, therefore the product, 2,3-butane diamine, was isolated as Schiff’s base of salicylaldehyde and characterised by its melting point (182°C) and IR spectra. IR spectrum showed absorption frequencies at 1640 cm\(^{-1}\) (C=\(\equiv\)N stretching), 1460 cm\(^{-1}\) (C=\(\equiv\)N bending in CH\(_2\)), 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).

Kinetic procedure

Kinetics of titanium(III) reduction of dimethyl glyoxime was studied under stoichiometric and non-stoichiometric conditions. The reaction mixture consisted
of organic substrate, sulphuric acid (to maintain acid concentration), titanium(IV) sulphate (to nullify the product effect), sodium sulphate solution (to maintain ionic strength), ethyl alcohol (to keep the organic substrate in homogeneous phase) and water (to keep the overall volume constant).

Kinetic runs were initiated by mixing the previously thermostated reactant solutions. A stream of nitrogen was passed over the reaction mixture. A known amount of titanium(III) sulphate solution, maintained at the same temperature under deaerated conditions, was added and homogenised. The progress of the reaction was monitored spectrophotometrically as follows:

At regular intervals of time, a known amount of reaction mixture was pipetted out into known excess of previously deaerated ammonium iron(III) sulphate taken in a 50.0 cm$^3$ standard flask. The volume was made up to the mark. Titanium(III) present in the reaction mixture quantitatively reduces iron(III) to iron(II). From this, 1.0 cm$^3$ of the solution was added to 4.0 cm$^3$ of 1.0-phenanthroline indicator (0.25%) and 12.0 cm$^3$ of sodium acetate-acetic acid buffer (to maintain the pH(II) taken in a 50.0 cm$^3$ standard flask. The solution was made up to the mark and the absorbance of the iron(II)-1,10-phenanthroline complex was measured at 515 nm using Shimadzu UV-vis spectrophotometer provided with a 1.0 cm quartz cell. Concentration of iron(II) obtained from the calibration plot was used to compute the concentration of titanium(III). Separate calibration plots were obtained for variation of [Ti(III)], [DMG], [H$_2$SO$_4$], ionic strength and solvent composition.

Results and discussion

The effect of variation in concentrations of titanium(IV) sulphate, sulphuric acid and temperature on the percentage of current efficiency ( %CE) was studied at 298K. It was found that the % CE steadily increased from 47.0-75.0 as the concentration of titanium(IV)sulphate varied from 0.40-0.05 mol dm$^{-3}$ at 0.75 mol dm$^{-3}$ [H$_2$SO$_4$]. Similarly, as [H$_2$SO$_4$] was varied from 0.50-2.25 mol dm$^{-3}$, % CE increased steadily from 47.0-82.0 at 0.20 mol dm$^{-3}$ titanium(IV) sulphate. Also, the % CE increased from 60.0-75.0 with rise in temperature from 298-313K at 0.20 mol dm$^{-3}$ [titanium(IV)sulphate] and 0.75 mol dm$^{-3}$ [H$_2$SO$_4$]. In all the above cases the amount of dimethyl glyoxime (1.0 g) and cathode current (200 mA) was kept constant.

Stoichiometry for the reduction of dimethyl glyoxime by titanium(III) was established by back-titration method. To a known volume ($V_1$) of substrate in aqueous ethanol (5 cm$^3$, 0.001 mol dm$^{-3}$), titanium(III)sulphate (5.0 cm$^3$, 0.01 mol dm$^{-3}$) solution ($V_2$) was added under deaerated condition. To this, ammonium iron(III)sulphate solution (5 cm$^3$, 0.025 mol dm$^{-3}$) was added. The resulting solution was back-titrated against standard titanium(III)sulphate (0.05 mol dm$^{-3}$) stored under nitrogen atmosphere using 10% ammonium thiocyanate as indicator ($V_3$).

A blank titration was carried out by taking the same amounts of titanium(III)sulphate and ammonium iron(III)sulphate solutions. Titration volume was $V_3$. The number of electrons is given by the Eq. (2).

$$n = [V_2 - (V_3 - V_1)] 	imes M_1/2V_1 	imes M_2$$

where $M_1$ and $M_2$ are the molarities of sample solution and titanium(III)sulphate solution respectively.

Stoichiometry of reduction of dimethyl glyoxime by titanium(III) was found to be 1:8 as shown below,

$$\text{C}_4\text{H}_5\text{N}_2\text{O}_2 + 8\text{Ti}^{3+} + 8\text{H}^+ \rightarrow \text{C}_4\text{H}_5\text{N}_2\text{H}_2\text{O} + 8\text{Ti}^{2+} + 2\text{H}_2\text{O}$$

(2,3-butane diamine)

The initial rates were obtained from the slopes of concentration versus time curves at the initial stages of the reaction by the plane mirror method reproducible to ±5%.

The order of the reaction was found by log[rate] versus log[concentration] plots. The order was found by varying the concentration of oxidant, reductant, sulphuric acid in turn, while keeping others constant (Table 1). The order with respect to oxidant and reductant was nearly unity and the order with respect to sulphuric acid was about 0.5 (Eq. 4).

$$\text{Rate} = k \left[\text{Ti}(\text{III})\right]^{1.0} \left[\text{DMG}\right]^{1.0} \left[\text{H}^+\right]^{0.5}$$

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

The mechanism as shown in Scheme I for the observed kinetics:

The rate law was derived by applying steady state approximation to the intermediate SH$^-$.

$$d[\text{SH}^-]/dt = k_1 [\text{S}][\text{SH}^-][\text{H}^+] - k_2 [\text{SH}^-][\text{Ti}^{3+}] = 0$$
Table 1—Effect of varying concentration of Ti(III), DMG and 
\(\text{H}_2\text{SO}_4\) on initial rate of the reaction. [Temp. = 306K; \(\rho = 3.0 \text{ mol dm}^{-3}\)]

<table>
<thead>
<tr>
<th>[Ti(III)] (10^2) (mol dm(^{-3}))</th>
<th>[DMG] (10^2) (mol dm(^{-3}))</th>
<th>[(\text{H}_2\text{SO}_4)] (10^3) (mol dm(^{-3}))</th>
<th>Initial rate ((\text{mol dm}^{-3} \text{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>
</tr>
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</tr>
<tr>
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<td>2.0</td>
<td>5.59</td>
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<tr>
<td>5.00</td>
<td>6.25</td>
<td>7.5</td>
<td>10.00</td>
</tr>
</tbody>
</table>

Table 2—Effect of ionic strength and solvent composition on the 
initial rate of the reaction

<table>
<thead>
<tr>
<th>Ionic strength (mol dm(^{-3}))</th>
<th>Initial rate (\times 10^5) (mol dm(^{-3}) s(^{-1}))</th>
<th>Alcohol (%)</th>
<th>Initial rate (mol dm(^{-3}) s(^{-1}))</th>
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<tr>
<td>2.50</td>
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<td>9.00</td>
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<tr>
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</tr>
<tr>
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<td>7.94</td>
<td>30</td>
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<tr>
<td>3.50</td>
<td>5.44</td>
<td>35</td>
<td>5.65</td>
</tr>
</tbody>
</table>

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 rate (Table 2) with decrease in dielectric constant of the medium is in accordance with Laidler and Eyring equation applicable to reaction between ions of equal charge. Decrease in rate of the reaction with increase in ionic strength due to the added \(\text{SO}_4^{2-}\) could be due to the equilibrium.

\(\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{HSO}_4^-\),

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

It was 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 IR spectrum of the polymer product shows absorption frequencies at 3468 cm\(^{-1}\) (\(-\text{N-H}\) and \(\text{O-H}\) stretching), 2939 cm\(^{-1}\) (\(-\text{C-H}\) stretching), 2250 cm\(^{-1}\) (\(-\text{C=N}\) stretching) and 1650 cm\(^{-1}\) (\(-\text{N-H}\) bending and \(-\text{C=N}\) stretching).
indicating the dimethyl glyoxime moiety as end group of the polyacrylonitrile macromolecule. The investigation on kinetics of titanium(III)-dimethyl glyoxime mediated electro-polymerisation of acrylonitrile is under progress.

The effect of temperature on the initial rate of the reaction was also studied at 296, 301, 306 and 311K, and 10^4 x initial rate obtained were 3.75, 5.00, 7.04 and 10.29 mol dm$^{-3}$ s$^{-1}$ respectively giving the activation parameters $E_a$ = 46.70 ± 5 kJ mol$^{-1}$, $\Delta H^*$ = 44.18 ± 5 kJ mol$^{-1}$, $\Delta G^*$ = 92.78 ± 0.9 kJ mol$^{-1}$, $\Delta S^*$ = 160.10 ± 16 JK$^{-1}$ mol$^{-1}$ and log $A$ = 4.83 ± 0.8.

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

Acknowledgement

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References