

A KINETIC STUDY OF OXIDATION OF HYDROGEN PEROXIDE BY DIETHYLENETRIAMINEPENTAACETIC ACID – IRON (III) DISODIUM, DIHYDRATE COMPLEX

PRAVEEN KUMAR SANSANWAL

Department of Chemistry, CCS Haryana Agricultural University, HISAR–125004 (Haryana) INDIA
E-mail: sansanwalpk@hau.nic.in

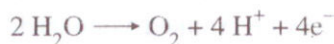
ABSTRACT

Kinetics of oxidation of hydrogen peroxide of diethylenetriaminepentaacetic acid–iron (III) disodium, dihydrate, $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$ has been investigated spectrophotometrically at 382 nm as a function of pH, ionic strength and inert electrolyte. The rate data indicates first order dependence on $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$, independent of $[\text{H}_2\text{O}_2]$ and inverse order with $[\text{H}^+]$. The rate constant enhanced with the increase in ionic strength and its magnitude depends upon the nature of inert electrolyte. A suitable mechanism has been proposed for the overall chemical reaction.

Key words : Kinetic, Oxidation, Hydrogen peroxide, Iron (III)–DTPA Complex

INTRODUCTION

Formation of molecular oxygen from the oxidation of water involves the overall transfer of four electrons and four protons.



This reaction represents the net oxidation process in green plant photosynthesis¹ and is important in transfer and storage of energy in many chemical and biochemical systems. The successive addition of electrons to molecular oxygen generates dioxygen intermediates such as superoxide, $\text{H}_n\text{O}_2(n-1)^+$, peroxide, $\text{H}_n\text{O}_2(n-1)^+$, radicals and ions. The interconversions of various dioxygen species and their affinities for metal complexes have been earlier studied in considerable detail²⁻⁴.

Hydrogen peroxide has attracted interest for years and has played an important role in many research areas such as atmospheric chemistry^{5,6} oxidation reactions^{7,8} and biological processes⁹. Hydrogen peroxide is usually considered as an oxidant but may itself be oxidized by species such as MnO_4^- and Cl_2 and with metal aquo ions such as $\text{Fe}^{\text{III}}(\text{aq})$ ^{10,12}, $\text{Ce}^{\text{IV}}(\text{aq})$ ^{13,14}, $\text{Mn}^{\text{III}}(\text{aq})$ ^{13,15}, $\text{Co}^{\text{III}}(\text{aq})$ ^{13,16}, and $\text{Ag}^{\text{II}}(\text{aq})$ ^{13,17}. There have been reports^{18,19} that many complexes of transition metals are more effective catalysts than their aquo metal ions in catalyzing the decomposition of H_2O_2 . The catalytic activity of iron (III) complexes of some negatively charged ligands, viz. nitrotriacetate ion (NTA), ethylenediaminediacetate ion

(EDDA), ethylenediaminetetraacetate ion (EDTA) and triethylenetetraamine (TETA) has earlier been investigated^{18, 19, 20}.

The complex diethylenetriaminepentaacetic acid iron (III) disodium, dihydrate $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$ was chosen because in its presence, the catalysed decomposition of H_2O_2 occurs at reasonable rate and the complex has earlier been partially characterised²¹.

This paper reports the kinetics of hydrogen peroxide in the presence of $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$ from spectrophotometric observations. Effects of pH, ionic strength (μ) and inert electrolyte on the kinetics of this system have been investigated.

EXPERIMENTAL

$\text{Na}_2[\text{FeDTPA}] \cdot 2\text{H}_2\text{O}$ (Aldrich), H_2O_2 (E. Merck), NaOH (BDH), HCl (BDH), KCl (BDH), NaCl (Ranbaxy), NaNO_3 (BDH), KMnO_4 (BDH) NaClO_4 (E. Merck) and Na_2SO_4 (BDH) were of analytical grade. Double-distilled water was used throughout. The ionic strength was maintained using KCl .

A Systronic digital pH meter-335 was used for pH measurements. It was standardized before use using standard buffers (BDH). The temperature around the reactants was maintained using an automatic high precision Scientronic, NSW-129 thermostatic water bath. An automatic spectrometer (Spekol 1200, AJ Analytical system) coupled with printer was used for the optical measurements. The reaction was carried out in a stoppered volumetric flask and the temperature of each substrate was equilibrated for at least 30 minutes before mixing. The progress of reaction was followed by decrease in absorbance at 382 nm as a function of time. The reaction was followed under pseudo-first order condition by taking large concentration of hydrogen peroxide. H_2O_2 concentration was determined volumetrically by titrating against standard solutions of KMnO_4 .

The complex, $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$ was reduced to $[\text{Fe}^{\text{III}} \text{DTPA}]^{3-}$ as indicated by spectral changes. The reaction is moderately fast. Therefore, absorbance changes were recorded at initial stage of reaction as the product interfered with spectrophotometric measurements. Absorbance versus time data was fitted in a first order kinetic equation using a linear least squares fitting routine.

Determination of the stoichiometries

The stoichiometry of the oxidation of hydrogen peroxide by $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$ was determined by the following method. To a hydrogen peroxide solution, the concentration of which was determined volumetrically, was added a weighed amount of solid $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$. After the reaction was complete (up to 30 minute) the amount of excess of hydrogen peroxide was determined. This procedure was repeated three times and the stoichiometry determined as $2.01 \pm 0.01:1$ for $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-} : \text{H}_2\text{O}_2$.

Identification of product

The product formed in the reaction for the oxidation of H_2O_2 by $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$ was appeared in the form of precipitate which was brown in colour. It was analysed qualitatively for nitrogen, which gave positive test for nitrogen, indicating that nitrogen of DTPA is still present in the product. The complex $[\text{Fe}^{\text{II}} \text{DTPA}]^{3-}$ was prepared by mixing equimolar solution of ferrous sulphate and disodium salt of DTPA at pH 6.0. The resulting complex is also brown in colour. It was mixed with water and slightly heated on a water bath. The oxidised compound $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$ is yellow in colour and soluble in water. When it was treated with H_2O_2 , it gave a brown precipitate of $[\text{Fe}^{\text{II}} \text{DTPA}]^{3-}$.

RESULTS AND DISCUSSION

Pseudo first order rate constant (k_{obs}) values were obtained using different $[\text{Fe}^{\text{II}} \text{DTPA}^{2-}]$ ($= 2.05, 4.27, 5.70, 7.12$ and 8.55) $\times 10^{-3}$ M but at fixed $[\text{H}_2\text{O}_2] = 0.16$ M; pH (4.0, 5.0, 6.0 and 7.0); $\mu = 0.01$ M and temperature 303.15 K. The reaction follows first order kinetics with respect to $[\text{Fe}^{\text{III}} \text{DTPA}^{2-}]$ as the plot of log absorbance (absorbance $= [\text{Fe}^{\text{III}} \text{DTPA}^{2-}]$) versus time was found to be linear in each case. The observed rate constant (k_{obs}) increases with increase of the initial concentration. The data has been condensed in Table 1.

Table 1. Effect of $[\text{Fe}^{\text{III}} \text{DTPA}^{2-}]$ concentration on the first order rate constant for the oxidation of H_2O_2 by $[\text{Fe}^{\text{III}} \text{DTPA}^{2-}]$

$[\text{H}_2\text{O}_2] = 0.08$ M ($\mu = 0.01$ M, KCl);

Temperature = 303.15 K; $\lambda_{\text{max}} = 382$ nm

$[\text{Fe}^{\text{III}} \text{DTPA}^{2-}] \times 10^3$ M	$k_{\text{obs}} \times 10^3$ (s ⁻¹)			
	pH = 4.0	5.0	6.0	7.0
2.05	0.422	0.737	1.214	1.602
4.27	0.842	1.149	1.996	2.982
5.70	1.072	1.810	2.876	3.799
7.12	1.350	2.379	3.954	4.876
8.55	1.742	3.076	4.697	5.999

The k_{obs} values were also calculated at different $[\text{H}_2\text{O}_2]$ (0.08, 0.16, 0.24, 0.32, 0.40, 0.48) M but at fixed $[\text{Fe}^{\text{III}} \text{DTPA}^{2-}]$ ($= 5.70 \times 10^{-3}$ M) at four different pH (= 4.0, 5.0, 6.0 and 7.0) $\mu = 0.01$ M and temperature 303.15 K. The k_{obs} values (Table 2) indicates that the rate of reaction is independent of $[\text{H}_2\text{O}_2]$. The effect of ionic strength (μ) was studied at different ionic strength (= 0.01, 0.02, 0.04, 0.06, 0.08, 0.10 and 0.12) M maintained using KCl and at fixed

Table 2. Effect of [H₂O₂] concentration on the first order rate constant for the oxidation of H₂O₂ by [Fe^{III} DTPA]²⁻

[Fe^{III} DTPA]²⁻ = 5.70 x 10⁻³ M

(μ = 0.01 M, KCl);

λ_{max} = 382 nm

Temperature = 303.15 K

[H ₂ O ₂]M	k _{obs} x 10 ³ (S ⁻¹)			
	pH = 4.0	5.0	6.0	7.0
0.08	1.072	1.810	2.876	3.799
0.16	1.089	1.816	2.884	3.791
0.24	1.093	1.807	2.869	3.790
0.32	1.069	1.805	2.873	3.806
0.40	1.077	1.813	2.871	3.810
0.48	1.081	1.819	2.879	3.802

[Fe^{III} DTPA²⁻] (= 5.70 x 10⁻³)M, [H₂O₂] = 0.16M at four different pH (4.0, 5.0, 6.0 and 7.0) and temperature 303.15 K. It was found that rate constant (k_{obs}) enhanced with increase in ionic strength (Table 3) and plots of log k_{obs} versus μ^{1/2} was linear with positive slope (Fig. 1).

Table 3. Effect of ionic strength on the first order rate constant for the oxidation of H₂O₂ by [Fe^{III} DTPA]²⁻

[Fe^{III} DTPA]²⁻ = 5.70 x 10⁻³ M

[H₂O₂] = 0.08M

λ_{max} = 382 nm

Temperature = 303.15 K

Ionic strength (μ) M	k _{obs} x 10 ³ (s ⁻¹)			
	pH = 4.0	5.0	6.0	7.0
0.01	1.072	1.810	2.876	3.799
0.02	1.781	2.590	3.456	4.452
0.04	2.398	3.127	4.002	5.111
0.06	2.967	3.989	4.834	5.893
0.08	3.779	4.887	5.782	6.893
0.10	4.671	5.962	6.978	7.854
0.12	5.678	6.878	7.795	8.978

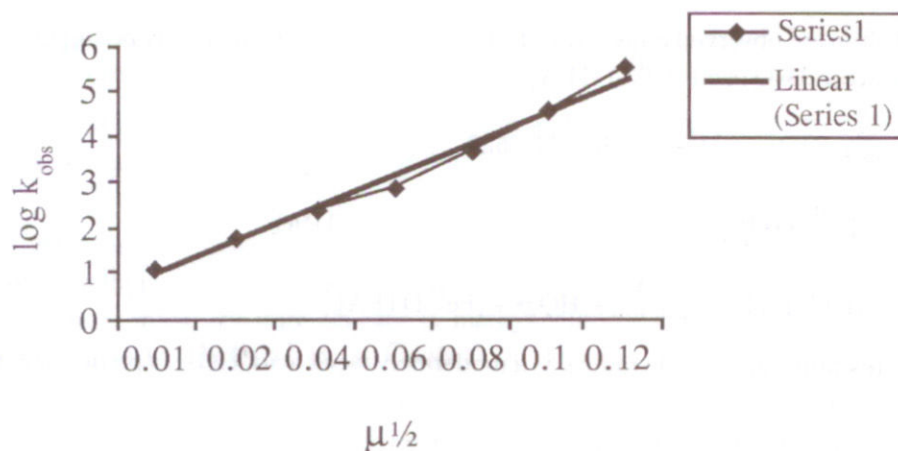


Fig. 1. Plot of $\log K_{obs}$ versus $\mu^{1/2}$ at pH 4.0 showing the effect of ionic strength

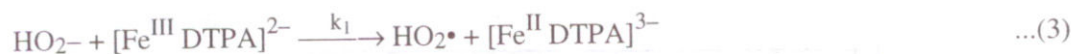
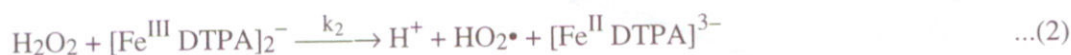
To determine specific salts effect (using inert salts NaCl, KCl, NaNO₃ and NaClO₄) on the k_{obs} values at fixed $[Fe^{III} DTPA^{2-}] (= 5.70 \times 10^{-4} M)$, $[H_2O_2] = 0.16 M$, $\mu = 0.01 M$, pH 6.0 and temperature 303.15 K, a series of observations have been made. The data (Table 4) indicates that k_{obs} increases with increasing size of cation i.e. Na⁺ to K⁺ (keeping same anion) as well as on increasing size of anions i.e. Cl⁻ to ClO₄⁻ (keeping same cation). This may be due to more hydration of smaller Na⁺ ion as compared to K⁺. Therefore, the effective ionic size of Na⁺. $x H_2O$ is more than K⁺. $y H_2O$ ($x > y$). The larger hydrated sodium ion being less mobile/active, is responsible for its lower k_{obs} compared to hydrated potassium ion. Similar explanation stands for the higher k_{obs} for NaClO₄ over NaCl when Cl⁻ being smaller is hydrated to larger extent than ClO₄⁻.

Table 4. Effect of inert electrolytes on the first order rate constant for the oxidation of H₂O₂ by $[Fe^{III} DTPA]^{2-}$ at pH = 6.0 and $\mu = 0.01 M$ for each electrolyte

$[Fe^{III} DTPA]^{2-} = 5.70 \times 10^{-3} M$	$[H_2O_2] = 0.08 M$
Temperature = 303.15 K	$\lambda_{max} = 382 \text{ nm}$
Electrolyte	$k_{obs} \times 10^3 (s^{-1})$
NaCl	2.213
KCl	2.876
NaNO ₃	3.314
NaClO ₄	3.719

The entire reaction system was studied using the pH range 4.0 – 7.0 (Table 1–3) which suggests that the first order rate constant varies inversely with $[H^+]$.

Based upon the observed kinetic results, the following mechanism may be suggested for the reaction between H_2O_2 and $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$.



As the resulting superoxide radical is a moderately weak acid, HO_2^\bullet is predominant species under experimental conditions.



Superoxide formed by reaction (2) and (3) are then consumed by the disproportionation reaction (5).



On adding up the reactions (1), (2) (3) and (5), the overall reaction may be expressed as:



As the reactivity of superoxide radical is very high, reaction (2) and (3) are the rate determining steps and the rate law is given in equation (7).

The equation–

$$\frac{-d [\text{Fe}^{\text{III}} \text{DTPA}]_2^{2-}}{dt} = 2 \left(\frac{k_1 K}{[\text{H}^+]} + k_2 \right) [\text{Fe}^{\text{III}} \text{DTPA}]_2^{2-} [\text{H}_2\text{O}_2] \quad \dots(7)$$

Under pseudo condition at higher concentration of H_2O_2 , the rate law becomes:

$$\frac{-d [\text{Fe}^{\text{III}} \text{DTPA}]_2^{2-}}{dt} = 2 \left(\frac{k_1 K}{[\text{H}^+]} + k_2 \right) [\text{Fe}^{\text{III}} \text{DTPA}]_2^{2-}$$

Where,

$$k_{\text{obs}} = 2 \left(\frac{k_1 K}{[\text{H}^+]} + k_2 \right) [\text{H}_2\text{O}_2]_0$$

The observed kinetic results also support the rate law equation (7) in respect – (a) the rate of reaction increases with decrease of $[\text{H}^+]$ (increase of pH); (b) reaction rate constant (k_{obs}) show first order dependence on $[\text{Fe}^{\text{III}} \text{DTPA}]_2^{2-}$ and (c) k_{obs} increases with increasing ionic

strength due to reaction between similar charges as in one of the rate determining step (equation 3) both the reactants; HO_2^- and $[\text{Fe}^{\text{III}} \text{DTPA}]^{2-}$ possess similar charge and $Z_A Z_B > 0$.

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