



A Kinetics and Mechanistic study of Permanganatic Oxidation of Ranitidine in Acidic Medium

Sandipsingh Gour¹, Bhagawasingh Dobhal² and Mazahar Farooqui³

¹Sant Ramdas College, Ghansawangi, Dist Jalna(MS) India

²Barwale College, Jalna.(MS) India

³Dr Rafiq Zakaria College for Women, Aurangabad(MS) India.

ARTICLE INFO

Article history:

Received: 6 October 2011;

Received in revised form:

14 November 2011;

Accepted: 25 November 2011;

Keywords

Kinetics and Mechanistic Study,
Permanganatic Oxidation,
Ranitidine

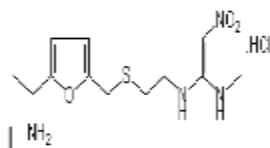
ABSTRACT

The oxidation of pyrazinamide in acidic media is carried out using potassium permanganate as a oxidizing agent. The reaction was monitored using UV-Visible spectrophotometer at 525 nm. It was found to be first order with respect to oxidant,, fractional order with respect to hydrogen ion concentration and first order with respect to substrate. The thermodynamic parameters (were determined . The average (ΔG^\ddagger) was found to be 87.91 KJ/mol. The values ΔS^\ddagger was found to be -0.1888 KJ/mole and energy of activation was found to be 31.36 KJ/mole. A suitable mechanism is proposed based on the experimental conditions.

© 2011 Elixir All rights reserved.

Introduction

Ranitidine is widely used effective treatment of gastric and duodenal ulcers. It is known to inhibit the hepatic cytochrome P450 (CYP450) metabolism of a number of concurrently administered drugs [1]. The structure of ranitidine hydrochloride is



The physical properties of ranitidine is given in the table number 1

Ranitidine has become the most frequently used H_2 -receptor antagonist. It inhibits gastric alcohol dehydrogenase (ADH) activity in vitro [2]. The interaction of ranitidine with other drug depends on pH of gastric juice [3].It is also reported that ranitidine does not interact with nifedipine drug [4].

Ranitidine, (N-(2-((S-dimethylamino-methyl)-2-furanil)-methyl thioethyl) N-ethyl-nitro-1, 1 diaminoethane) was introduced to market in 1981. It is extensively used in the treatment of active duodenal ulcer, active and benign gastric ulcer, pathogenic gastrointestinal hypersecretory conditions and symptomatic relief of gastro esophageal refluxes. It is metabolized in liver to ranitidine N-oxide, desmethyl ranitidine and ranitidine S-oxide [5]. The literature survey indicates very few papers on kinetics of reactions of ranitidine. Dash et al [6] studied kinetics of reaction of ranitidine with hexa aqua chromium with trans-(diaqua) (N, N'-ethylene-bis-salicylamide). The oxidation of ranitidine was also reported by diperiodocuprate (III) in aqueous alkaline medium [7]. A titometric method based on the oxidation of the ranitidine by a known excess of iodate in acidic conditions followed by the iodometric back titration of the surplus oxidant was reported by

Basavaiah and Nagegowda [8]. The ranitidine undergo photoderivatization to give product. These photoproducts cause inhibition of growth population on rotifers and crustaceans. The ranitidine did not show any acute toxicity at the highest concentration (100mg/L) for above organisms [9].

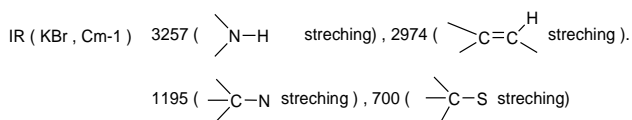
Kinetic procedure: The reactions were allowed to occur in glass stopper Erlenmeyer flask of coming make. These flasks were suspended in a water bath with temperature sensitivity of 0.1° C. The reaction mixture except substrate was prepared by taking all reaction ingredients.

The temperature preequilibrated solution of substrate was added into the reaction mixture and the time of initiation of the reaction was recorded when half of the contents of pipette were released. The reaction mixtures were shaken and aliquot (1ml) was taken out at different time intervals and absorbance of remaining $KMnO_4$ was noted at $\lambda_{max} = 525$ nm. The reaction rates were calculated by drawing pseudo first order plot, $[substrate] > [KMnO_4]$ condition. Good straight lines were obtained and pseudo first rate constant were calculated in the usual manner. These rate constants exhibit reproducibility within to 5%. These results are given in the tables 5.2 to 5.14.

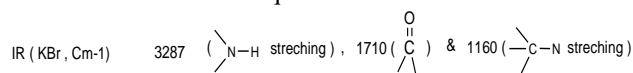
Product Analysis

Known volume of 0.1 M substrate and 0.01M $KMnO_4$ in 1 M H_2SO_4 solution were taken in 250ml beaker and kept the reaction mixture for 4-5 days for completion of the reaction. The diethyl ether was added into the reaction mixture and then it was shaken for an hour before separating two layers ether and water by employing separating funnel.

The ethereal layer was taken on the watch glass; latter was left for some time for evaporation of ether. The residue left on the watch glass was air drying before identification. The solid mass was identified by M.P. and IR Spectra. The IR spectra of RTD and the product obtained was compared. It gives values for RTD



The product obtained was 1-(2-((2-aminopropan-2-yl) furan-2-yl) methylthio ethyl)-3-methylurea with melting point is 357°C and shows IR frequencies



Experimental kinetic results

Dependence of permanganate concentration

To study the effect of dependence of permanganate concentration, the concentration of KMnO_4 was varied from 1×10^{-4} to 9×10^{-4} M, keeping constant concentration of other reaction ingredients such as substrate and acid. Since reaction has been studied under pseudo first order condition a plot of $\log [\text{MnO}_4^-]$ versus time was made and pseudo first order rate constant were calculated. These results are given in the tables 2 From the perusal of the results, it is clear that pseudo first rate constant do not change with change in concentration of permanganate confirming the first order dependence with respect to oxidant.

The rate constant values found to be decreases regularly with increase in the concentration of KMnO_4 with few exceptions but there was no regular trend obtained for initial rate. When double log plot of k_{obs} versus $[\text{KMnO}_4]$ was taken, the order was found to be in fraction and negative. The average rate was calculated as earlier

Dependence of substrate concentration

The concentration of substrate was varied from 1×10^{-3} to 9×10^{-3} M and fixed concentration of $[\text{MnO}_4^-] = 1 \times 10^{-4}$ M and $[\text{H}_2\text{SO}_4] = 1$ M. The pseudo first order rate constants were calculated. This shows that order with respect to substrate is also one.

It was observed that k_{obs} increases with increase in concentration of substrate upto 6×10^{-4} M then it decreases. Similarly the initial rate first decreases and then increases finally again decreases.

The experimental data was converted into double reciprocal plot of initial rate at varying content.

$$[\text{RTD}] = 5 \times 10^{-4} \text{ M} \quad [\text{KMnO}_4] = 1 \times 10^{-4} \text{ M} \quad [\text{H}_2\text{SO}_4] = 1 \text{ M}$$

The order of reaction was determined from the slopes of $\log k_{\text{obs}}$ versus $\log [\text{concentration}]$

Considering the equation

$$\text{Rate} = k [\text{C}]^n$$

Where k is the pseudo order rate constant and n is the order of reaction. The rate of reactions could be estimated as $\Delta A / \Delta t$, where A is the absorbance and t is the time in second. Taking logarithm, the equation (1) becomes

$$\log \text{Rate} = \log (\Delta A / \Delta t) = \log k + n \log C$$

The nonlinearity of k_{obs} with substrate indicates a complex mechanism for the oxidation reaction [10].

Dependence of acid concentration

The hydrogen ion concentration dependence was studied by employing H_2SO_4 at fixed $[\text{MnO}_4^-]$ and $[\text{substrate}]$ respectively. The pseudo first plot were made and the plot of these rate constant against $[\text{H}^+]$ shows fractional order with respect to acid. Since rate decrease with increase in $[\text{H}^+]$ ion, the deprotonated

species of oxidant or substrate must involve in the reaction mechanism. The results are given in the table 4.

Using least square method double log plot of k_{obs} verses $[\text{H}_2\text{SO}_4]$ gives fractional order [11] with negative slope.

The pH effect on oxidation process is arising when one of the reagents has acid-base property, affecting the reactivity of that reagent. Although the observed rate constant is a function of several parameters [12].

Using least square method the relation between k_{obs} and $[\text{H}_2\text{SO}_4]$ was checked for linear fit.

The correlation coefficient is very less (0.07914), which indicate almost no relation between k_{obs} and $[\text{H}_2\text{SO}_4]$. Hence the reaction is not catalysed by acid. Generally, the investigations of reactions catalysed by general acids or bases are preferably carried out using buffer solution i.e. at constant pH.

Effect of added salts

When the salts of different anions are added MX (KCl , KBr , KI), it was observed that for KCl , no regular trend in the initial rate but in case of KBr and KI , the initial rate increases with increase in concentration of salt. Secondly the initial rate for KI is greater than KBr .

The effect of anion on the rate constant has no regular trend. When different salts with cations (K^+ , Ca^{2+} , Al^{3+}) and anions (SO_4^{2-} , NO_3^-) are taken, the rate constant values are within the same range.

This indicates there is no effect of added salt on oxidation process [13].

During kinetic studies, on the oxidation of substituted cinnamonic acid, it was reported that the addition of Mn^{2+} ions, increases the rate of oxidation and addition of Al^{3+} thus affect the oxidation rate due to the formation of complex [14].

There was no regular trend observed for any of the added salts. But among these salts the rate constant for the oxidation of ranitidine in presence of Al salt was more and the trend will be $\text{KI} < \text{KBr} < \text{KCl} < \text{K}_2\text{SO}_4 < \text{Ca}(\text{NO}_3)_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{Al}(\text{NO}_3)_3 < \text{AlCl}_3$

Effect of temperature

The effect of temperature was also studied keeping constant concentration of all other reaction ingredients such as $[\text{MnO}_4^-]$, $[\text{substrate}]$ and $[\text{H}^+]$. The temperature variation was at 25 to 60°C. The energy of activation was calculated by plotting graph between $\log k$ verses $1/T$, a straight line was obtained.

From the linear Arrhenius plot of $\log k$ verses $1/T$, activation energy and other thermodynamic parameters were found to be $E_a = 31.36774788 \text{ KJmol}^{-1}$. The activation enthalpy ΔH^\ddagger and activation entropy ΔS^\ddagger can be calculated by

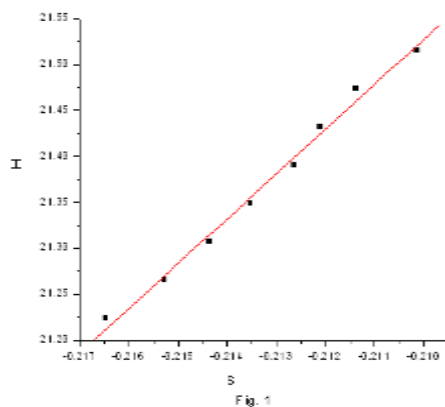
$$\ln k_{\text{obs}} = \ln \frac{k_B T}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}$$

Where $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$, $h = \text{Plank's constant} = 6.626 \times 10^{-34} \text{ JS}$. This equation can be rearrange in such away that plot of $\ln(k_{\text{obs}}/T)$ verses $1/T$ allows to determine ΔH^\ddagger and ΔS^\ddagger from the intercept and slope respectively.

The values of ΔS^\ddagger has been ascribed to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom formerly available to the reactants upon the formation of rigid transition state [15].

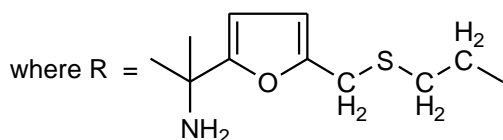
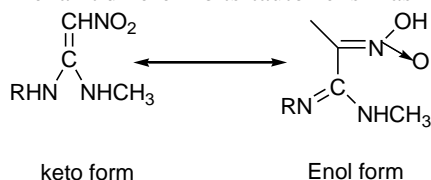
The negative values or very small values of indicate multistep reaction.

A plot of (ΔH^\ddagger) verses (ΔS^\ddagger) is linear with slope $\beta = 0.00848$. The nature of graph was shown in figure. 1

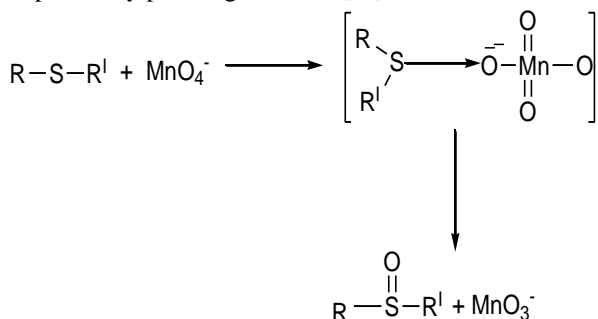


Mechanism

The ranitidine exhibits tautomerism as keto-enol form [16]



While oxidation process, ranitidine undergoes enolization also. It was also reported earlier that the rate of enolization is higher compared to the rate of oxidation in case of substituted 4-oxy acids. Hence step involving enol formation can not be considered as the rate determining step since it is a fast step [17]. There are two possibilities or probable site where oxidation by permanganate can take place. It is reported that the transfer of electrophilic oxygen from permanganate ion to the sulphide is the rate determining step in the oxidation of divalent organic sulphides by permanganate ion [18].



For the redox reaction, involving transfer of electron, there are two types of mechanisms possible i.e. inner sphere and outer sphere.

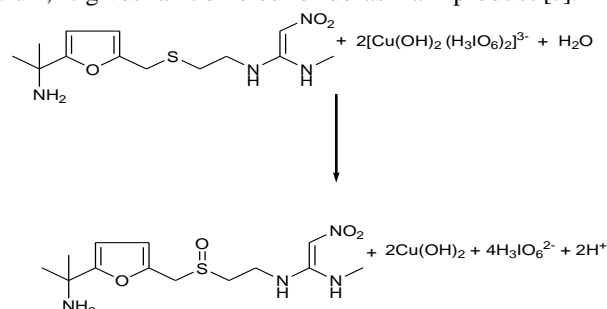
In principle, an outer sphere mechanism can be recognized if (i) the rate law is first order in each reactant. (ii) if both the reactants are inert to substitution. On the other hand, if electron transfer takes place via bridging group, it is an inner transfer reaction.

As far as reactive intermediates of Mn are concerned, different species ranging from Mn (III) to Mn (VII) may involve in oxidation process. These can be confirmed on spectroscopic data only.

Since in our experiment no precipitate or colloidal solution was observed hence the possibility of formation of MnO_2 is

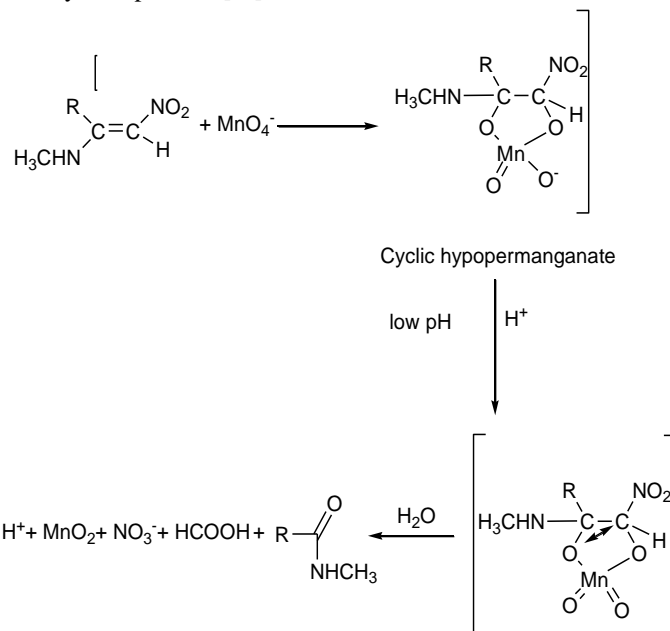
ruled conditions out. The formation of MnO_2 particles depends on concentration and reaction conditions [19]. The MnO_4^- may oxidize compound by different ways which include electron transfer, hydrogen abstraction, hydride ion abstraction and oxygen donation. The pathway totally depends on reaction condition that is pH and concentration of the oxidant.

In RNH, there are two probable sites at which oxidation may take place. The first one is sulphur, it was reported that when RNH is oxidized by diperiodocuprate (III) in aqueous alkaline medium, it gives ranitidine sulfoxide as main product [7].



But the reaction is carried out in acidic medium and hence this possibility is ruled out. The second site is carbon double bond carbon. In double bond, oxidation product varies with reaction condition again.

In alkaline condition alkenes are converted to cis-diol, in neutral or slightly basic solutions α -hydroxyl ketones are the predominant products and in acidic condition alkenes give carbonyl compounds [20].



For any bimolecular reaction, the kinetic rate law is given by $r_c = dC/dt = -k_c [\text{sub}]^\alpha [\text{KMnO}_4]^\beta$

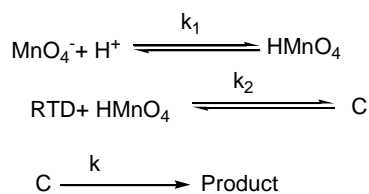
Where r_c is the oxidation rate, [sub] is the RNH, k_c is the second order reaction coefficient and α and β are the reaction order with respect to [sub] and $[\text{KMnO}_4]$.

Since substrate concentration is 10 times more than oxidant concentration, [sub] does not change significantly and hence, we can write

$$\text{R} = k_{\text{obs}} [\text{KMnO}_4]^\beta$$

where $k_{\text{obs}} = k_c [\text{sub}]^\alpha$

The plot of $\log k_{\text{obs}}$ versus $\log [\text{sub}]$ gives the value of k_c , which was found to be The order was found to be fraction.



$$\begin{aligned} [\text{MnO}_4^-]_T &= [\text{MnO}_4^-] + [\text{HMnO}_4] \\ &= [\text{MnO}_4^-] + k_1 [\text{MnO}_4^-] [\text{H}^+] \\ &= [\text{MnO}_4^-] \{1 + k_1 [\text{H}^+]\} \end{aligned}$$

$$\text{Rate} = \frac{k k_2 [\text{MnO}_4^-] [\text{PZA}]}{1 + k_1 [\text{H}^+]}$$

$$\frac{\text{Rate}}{[\text{MnO}_4^-] [\text{RTD}]} = \frac{k k_2}{1 + k_1 [\text{H}^+]}$$

$$k_{\text{obs}} = \frac{k k_2}{1 + k_1 [\text{H}^+]}$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k k_2} + \frac{k_1 [\text{H}^+]}{k k_2}$$

References

- [1]. G A Ford and E Snoeck; A pharmacokinetic and Pharmacodynamics interaction study between nebivolol and the H₂ -receptor antagonists Cimetidine and Ranitidine; Br J Clin Pharmacol 43, 1997 ,201-204.
- [2]. Carlo Di Padova, Risto Roine, Mario Frezza, R Thomas Gentry; Effect of ranitidine on blood alcohol levels after ethanol ingestion; JAMA, 267(1), 1992 ,83-86.
- [3]. S Toon, K J Hopkins, F M Garstang and Rowland; Comparative effects of ranitidine and Cimetidine on the pharmacokinetics and pharmacodynamics of Warfarin in Man; Eur J Clin Pharmacol; 32, 1987 ,165-172.
- [4]. S R Smith, M J Kendall, J Lobo, A Beerah, D B Jack, M R Wikins; Ranitidine and Cimetidine; drug interactions with single dose and steady state nifedipine administration; Br J Clin Pharmacol ,23, 1987 ,311-315.
- [5]. Javier Rivas, Olga Gimeno, Angel Encinas, Fernando Beltran; Ozonation of the pharmaceutical compound ranitidine; reactivity and kinetic aspect; Chemosphere, 76, 2009, 651-656.
- [6]. S C Dash, N N Das and P Mohanty; Kinetics and mechanism of the reaction of ranitidine hydrochloride with trans-(diaqua) (N,N-ethylene-bis-salicylamide) chromium(III) and hexa-aquachromium(III) ion ; A comparative study; Ind J of chemical technology 18, 2011, 132-136.
- [7]. T M Veeresh, R K Patil and Sharanappa T Nandibewoor; Thermodynamic quantities for the oxidation of ranitidine by

diperiodotocuprate (III) in aqueous alkaline medium; Transition Met Chem 33, 2008, 981-988.

[8]. K Basavaih and Nagegowda; Determination of ranitidine using potassium iodate and dichlorofluorescein; Indian J Chem Tech, 11, 11-16, 2004.

[9]. Marina Isidori Alfredo Parrella, Paola Pistillo Fabio Temussi; Effect of ranitidine and its photo derivatives in the aquatic environment; Environ International; 35, 2009, 821-825.

[10]. Prangya Rani Sahoo, Sandhyamayee Sahu, Sabita Patel and B K Mishra; Oxidation kinetics of arylthiourea by cetyltrimethylammonium dichromate; Indian J Chem 49A, 2010, 1483-1487.

[11]. Mohd Akram, Mohammad Altaf and Kabir-ud-Din; Oxidation of aspartic acid by water soluble colloidal MnO₂ in absence and presence of ionic and non-ionic surfactant; Indian J Chem; 46A, 2007, 1427-1431.

[12]. M K Ei Rifai and M M Ei Jamal; Kinetics of the oxidation of HCOOH with KMnO₄ over a wide range of pH; J Uni Chem Tech Metall; 44(3), 2009, 275-280.

[13]. Mohammed M, Al Subu; Kinetics and mechanism of Osmium (VIII) - catalysed oxidation of thiomorpholine by alkaline hexacyanoferrate (III); Pak J Appl Sci.2 (7), 2002, 742-746.

[14]. G Vanangamudi and S Srinivasan; Kinetics studies on the oxidation of some para and meta substituted cinnamic acids by pyridinium Bromochromate in the presence of oxalic acid (A co-oxidation on study); EJ Chem 6(3), 2009, 920-927.

[15]. S A Chimatadar, s v Madawale, K A Thabai and S T Nandibewoor; Oxidation of hexacyanoferrate(II) by peroxodisulphate in aqueous perchloric acid ; A Kinetic and mechanistic study; Indian J Chem 46A, 2007 1090-1094.

[16]. S C Dash, N N Das and P Mohanty; Kinetics and mechanism of the reaction of ranitidine hydrochloride with trans-(diaqua) -(N N1- ethylene- bis -salicylamide) chromium (III) and hexa- aquachromium (III) ion- a comparative study; Indian J Chem Tech; 18, 2011, 132-136.

[17]. Cherkupally Sanjeeva Reddy and Padma Sunitha Manjari; Kinetics and mechanism of acid bromate oxidation of substituted 4-oxoacids; Indian J Chem 49A, 2010, 418-424.

[18]. S Rajagopal, geetha Sivasubramanian, R Suthakaran and C Srinivasan; Mechanism of permanganate ion oxidation of diaryl sulphoxides- A kinetic study ; Proc Indian Acad Sci (Chem Sci); 103(5), 1991, 637-643.

[19]. Michelle Crimi, Saebom Ko; Control of manganese dioxide particles resulting from in situ chemical oxidation using permanganate; Chemosphere; 74, 847-853, 2009.

[20]. Kun -Chang Huang, George E Hoag, Pradeep Chheda, Bernaad A Woody, Gregory M Dobbs; Kinetics and mechanism of oxidation of tetrachloroethylene with permanganate; Chemosphere; 46, 2002, 815-825.

The physical properties of ranitidine is given in the table number 1

Table 1 Physical properties of ranitidine

S.No.	Name of property	Value
1	Mol. Formula	C ₁₃ H ₂₃ N ₄ O ₃ SCl
2	Mol. Weight	350.87 g/mol
3	R.I	1.558
4	Molar Refractivity	85.64 cm ³
5	Molar volume	265.4 cm ³
6	Boiling point	437.4 ^o 760 mm of Hg
7	Surface tension	45 dyne/cm
8	Density	1.184 g/cm ³
9	Flash Point	218.2 ^o C
10	Enthalpy of vaporizations	69.37 KJ/mol
11	M.P.	69-70 ^o C
12	solubility	Water soluble

Table 2 first order rate constant

S.No.	[TRD]	[KMnO ₄]	[H ₂ SO ₄]	k(s ⁻¹)
1	1x10 ⁻³	1 x10 ⁻⁴	1	0.0441
2	1x10 ⁻³	2 x10 ⁻⁴	1	0.0397
3	1x10 ⁻³	3 x10 ⁻⁴	1	0.0278
4	1x10 ⁻³	4 x10 ⁻⁴	1	0.0236
5	1x10 ⁻³	5 x10 ⁻⁴	1	0.0269
6	1x10 ⁻³	6 x10 ⁻⁴	1	0.0204
7	1x10 ⁻³	7 x10 ⁻⁴	1	0.0184
8	1x10 ⁻³	8 x10 ⁻⁴	1	0.0254
9	1x10 ⁻³	9 x10 ⁻⁴	1	0.0167

Table 3 First order rate constant

S.No.	[RTD]	[KMnO ₄]	[H ₂ SO ₄]	k(s ⁻¹)
1	1 x10 ⁻⁴	1x10 ⁻⁴	1	0.0201
2	2 x10 ⁻⁴	1x10 ⁻⁴	1	0.0267
3	3 x10 ⁻⁴	1x10 ⁻⁴	1	0.0272
4	4 x10 ⁻⁴	1x10 ⁻⁴	1	0.0411
5	5 x10 ⁻⁴	1x10 ⁻⁴	1	0.0535
6	6 x10 ⁻⁴	1x10 ⁻⁴	1	0.0475
7	7 x10 ⁻⁴	1x10 ⁻⁴	1	0.0436
8	8 x10 ⁻⁴	1x10 ⁻⁴	1	0.0301
9	9 x10 ⁻⁴	1x10 ⁻⁴	1	0.0287

Table 4 First order rate constant

S.No.	[RTD]	[KMnO ₄]	[H ₂ SO ₄]	k(s ⁻¹)
1	1x10 ⁻³	1x10 ⁻⁴	0.1	0.0281
2	1x10 ⁻³	1x10 ⁻⁴	0.2	0.0177
3	1x10 ⁻³	1x10 ⁻⁴	0.3	0.0107
4	1x10 ⁻³	1x10 ⁻⁴	0.4	0.0092
5	1x10 ⁻³	1x10 ⁻⁴	0.5	0.029
6	1x10 ⁻³	1x10 ⁻⁴	0.6	0.0208
7	1x10 ⁻³	1x10 ⁻⁴	0.7	0.0126
8	1x10 ⁻³	1x10 ⁻⁴	0.8	0.0084
9	1x10 ⁻³	1x10 ⁻⁴	0.9	0.0355

Table 5 Effect of added salt on first order rate constant

Conc. of salt	Rate constants (S ⁻¹)								
	KCl	KBr	KI	K ₂ SO ₄	CaCl ₂	Ca(NO ₃) ₂	MgCl ₂	AlCl ₃	Al(NO ₃) ₃
1x10 ⁻²	0.0237	0.0236	0.0332	0.0256	0.0158	0.0332	0.0262	0.0246	0.0288
2x10 ⁻²	0.0345	0.0161	0.0242	0.029	0.0256	0.0199	0.0211	0.0223	0.0208
3x10 ⁻²	0.0275	0.0138	0.0451	0.0245	0.0212	0.0273	0.0236	0.0224	0.0225
4x10 ⁻²	0.054	0.0291	0.03	0.0124	0.0213	0.0251	0.0272	0.0268	0.016
5x10 ⁻²	0.0095	0.0226	0.0257	0.0198	0.0177	0.0182	0.0311	0.0249	0.0186
6x10 ⁻²	0.0136	0.017	0.0225	0.0232	0.0185	0.0169	0.0365	0.0231	0.0186
7x10 ⁻²	0.0289	0.0364	0.0182	0.0197	0.0272	0.0277	0.0365	0.0356	0.0277
8x10 ⁻²	0.0227	0.0185	0.0153	0.0165	0.0216	0.0171	0.0356	0.0236	0.0151
9x10 ⁻²	0.0215	0.0148	0.0186	0.0274	0.0179	0.0172	0.0249	0.0365	0.0295

Table 6 Thermodynamic parameter

S.No.	Temp.(K)	ΔH [#] (KJmol ⁻¹)	ΔS [#] (KJmol ⁻¹)	ΔG [#] (KJmol ⁻¹)
1	295	28.91511788	-0.188795976	84.60993088
2	298	28.89017588	-0.186843734	84.56960874
3	303	28.84860588	-0.187399055	85.63051952
4	308	28.80703588	-0.188916085	86.99319012
5	313	28.76546588	-0.188433544	87.7451652
6	318	28.72389588	-0.189237148	88.90130888
7	323	28.68232588	-0.190356814	90.16757773
8	328	28.64075588	-0.19026266	91.04690823
9	332	28.60749988	-0.189599081	91.55439469