INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

OXIDATION OF HYDROQUINONE BY N-CHLOROPIPERAZINE-2,5-DIONE- KINETIC AND MECHANISTIC STUDY

Chemistry

K.Rajalakshmi Associate Professor, PG Department of Chemistry, Srimad Andavan Arts & Science College, Trichy-05

ABSTRACT

The kinetics and mechanism of oxidation of Hydroquinone, 8-Hydroxyquinoline and Hydroxylamine was studied by N-Chloropiperazine-2, 5-dione in acetic acid-water medium. The reaction was found in Hydroquinone and 8-Hydroxyquinoline to be one with respect to [oxidant] and fractional order with respect to [substrate]. The reactions are studied at five different temperatures. The enthalpy of activation and entropy of activation are calculated. Based on the above kinetic facts, a suitable mechanism was proposed for each substrate.

KEYWORDS

Substrate, Oxidation, Hydrogen ion Concentration, enthalpy of activation, entropy of activation

INTRODUCTION

When a reaction occurs in steps, intermediate species are probably formed and they may not be detectable, because they may be promptly used up in a subsequent step1,2. However by investigating the influence that various factors on the rate at which the net change occurs, it is sometimes possible to elucidate what the intermediates are and how they are involved in the mechanism of the reaction.

Among oxidation and reduction reactions, oxidation is the most commonly studied reaction. A large amount of kinetic study is concentrated on oxidation reactions. An interesting fact is that many oxidations are accompanied by the release of energy. Such released energy is the source of work in biological systems including the human system and also in man-made machines. Hence the knowledge of oxidative pathways may be very useful in understanding processes in nature and synthetic situations.N-chloropiperazine-2, 5-dione (NCDP) was introduced in the series of N-halo compounds3,4. NCDP is proved to be a mild oxidizing agent .It liberates iodine from acidified potassium iodide solution. A survey of literature provides much information on the mechanism of reactions involving N-halo compounds.

EXPERIMENTAL METHODS

100g (1.33mol) of glycine and 500ml of ethylene glycol were placed in a one liter three necked flask, fitted with an air-cooled reflux condenser and a sealed mechanical stirrer. A thermometer was fitted so that the bulb was inside the liquid. The mixture was heated in the fume cupboard to 175o C and that level was maintained with continuous stirring for one hour. The dark brown reaction product was cooled to room temperature and left overnight in refrigerator. The resulting suspension was centrifuged and the mother liquor was decanted. The solid was transferred to a Buckner funnel with the aid of cold methanol and the solid was washed with more methanol, using about 200ml in all. The product was crystallized from 300ml of boiling water but no attempt was made to filter the hot solution at the stage. The light brown crystals were collected which separated on cooling in ice. The crude material was dissolved in 350 ml of water; 4g of decolorizing carbon was added and boiled for three minutes. The hot suspension was filtered through a preheated Buckner funnel and the filtrates were cooled in ice. The colorless crystals of pure piperazine-2, 5-dione was collected, washed with ice water and dried in the oven at 50o C. piperazine-2, 5-dione has melting point of 310 – 312o C.

Preparation of N-chloropiperazine-2, 5-Dione

1g of piperazine-2, 5-dione was taken in a 50ml conical flask and 10 ml of water was added to it. Then chlorine gas passed for about 15-20 minutes. Then 0.8g of sodium bicarbonate was also added to it. The resulting white precipitate was filtered and dried.

KINETIC AND MEASUREMENT FOR THE OXIDATION OF HYDROQUINONE BY NCDP

Measurement were made at 40oC and the temperature was controlled using a thermostat to an accuracy of +-0.1oC.the following solutions of the desired concentrations were prepared and used.

1. Hydroquinone in acetic acid
2. NCDP in acetic acid
3. Other reagents in doubly distilled water

Known volumes of substrate, water, perchloric acid and acetic acid were mixed to bring the percentage of acetic acid to the desired value and thermostated.the reaction was started by adding the oxidant to the mixture5. a stop watch was started when half of the oxidant solution had been delivered. aliquots (2ml)were removed at definite intervals and the unreacted NCDP was estimated iodometrically by draining 10ml of 3N sulphuric acid and 10ml of 5%potassium iodide solution and the liberated iodine was titrated against standard sodium thiosulphate solution using starch as indicator.

Reactions were generally followed to 60-75% completion. The kinetic investigations were carried out under pseudo-first order conditions, keeping the substrate concentrations always in excess. The pseudo-first order rate constants(k1)were calculated from the slope of linear plots of log (titre) against time by the method of least squares[6,7].

Throughout the kinetic studies hydroquinone concentration was kept ten times greater than that of the N-chloro compound

Evaluation of rate constants[8]

The pseudo-first order rate constant of each kinetic run was evaluated from the slope of the linear plot of log (a-x) Vs time, according to the first order rate equation by the method of least squares.

The linearity of each fit is given in terms of the correlation coefficient (r)

$$k1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$t = \frac{2.303}{k1} \log \frac{a}{a-x}$$

where k1 is the pseudo-first order rate constants 't' is the time in second and 'a' and (a-x) denote the initial concentration and concentration at time 't' respectively of N-chloropiperazine-2,5-dione.the specific reaction rate is evaluated by dividing the k1 by substrate raise to the power of its order.

Activation parameters

The activation parameters were calculated by the least square analysis of linear plot of ln(k2/T) Vs 1/T of Eyring's equation. ΔH# and ΔS# were calculated from the slope and the intercept of the plot respectively as per the following equation[9].

$K = kB\,T / h.e\text{-}\ \Delta H\# / RT.e\ \ \Delta S\# / R$

Where,

K = Rate constant

kB = Boltzman constant

h = Planck's constant

T = Temperature in Kelvin

The logarithmic form of eyring's equation can be rearranged in the form of a linear equation as shown below.

$$\ln \frac{k1}{T} = \ln \frac{kB}{h} + \frac{S\#}{R} - \frac{H\#}{RT}$$

ΔS# , ΔH# and ΔG# were calculated using the following relationships

ΔH# = (-slope) * 0.008318kJ mol-1

Δ S# = (intercept – 23.7604) * 8.318 J K-1 mol-1

ΔG# = ΔH# - T ΔS# kJ mol-1

all the calculations, graphs and correlation coefficients were computed.10,11

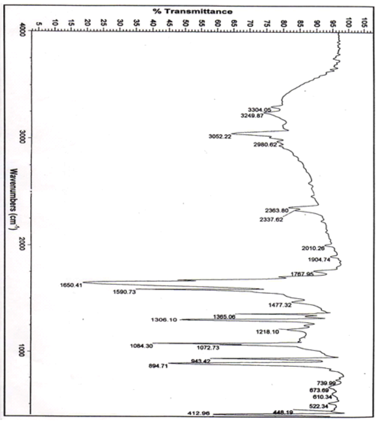
Stoichiometry

Reaction mixture containing an excess of oxidant (NCDP) 0.01M over hydroquinone (0.01M) in the presence of perchloric acid were kept at room temperature for a sufficient length of time under the conditions employed for the kinetic runs. Estimation of unchanged oxidant showed that one mole of hydroquinone consumed one mole of N-chloropiperazine-2, 5-dione.Thus the stoichiometry of the reaction was found to be 1:1 mole ratio of the substrate and oxidant respectively.

Product analysis

Hydroquinone (0.1M) and NCDP (0.1M) were mixed in 80% acetic acid water medium and kept at room temperature for two days under the conditions employed for the kinetic runs. Then the product was extracted with chloroform. The extract was dried over anhydrous sodium sulphate and chloroform layer was evaporated13. The product obtained was p-benzoquinone (pic.-1).

(pic-1)FT-IR Spectra



RESULTS AND DISCUSSION

KINETICS AND MECHANISM OF OXIDATION OF HYDROQUINONE

Effect of varying the [oxidant]

The oxidation of hydroquinone by NCPD was investigated at several initial concentrations of the oxidant [NCPD] (table-1). At constant temperature and the [substrate] in excess, the plot of log (titre) Vs time was linear indicating first order dependence of the reaction of [NCPD]. The values of the pseudo-first order rate constants (k1) were evaluated from the plots, according to the first order equation by the methods of least square[14.]

Table-1

[Hydroquinone] = 3.0 x 10-2 mol dm-3

[HClO$_4$] = 1.5 mol dm-3

Solvent = 80%(v\v) acetic acid-water

Temperature = 40oC

[NCDP] x 103	k1 x 104s-1
0.5	4.2913
1.0	4.3304
1.5	4.5774
2.0	4.6235
2.5	4.4569

Effect of varying the [substrate]

The reactions were carried out at 40oC with varying concentrations of hydroquinone while keeping the concentration of all other factors constant. The rate constants were found to slightly increase in substrate concentration (table- 2). A plot of log [substrate] Vs log k1 was linear with a slope of 0.285 (r = 0.997) for hydroquinone .

Table - 2

[NCPD] = 1.0 x 10-3 mol dm-3

[HClO4] = 1.5 mol dm-3

Solvent = 80%(v\v) acetic acid-water

Temperature = 40oC

[Hydroquinone] x 102 mol dm-3	k1 x 104s-1
2.0	3.9080
2.5	4.1213
3.0	4.3304
3.5	4.5578
4.0	4.7648

Effect of varying the ionic strength

The reactions were carried out at various concentrations of sodium perchlorate while keeping all other variables constant5. The results indicate that there was no appreciable change in the rate of the reaction (table-3).

Table - 3

[Hydroquinone] = 3.0 x 10-2 mol dm-3

[NCPD] = 1.0 x 10-3 mol dm-3

[HClO4] = 1.5 mol dm-3

Solvent = 80%(v\v) acetic acid-water

Temperature = 40oC

[NaClO4] x 10^2 mol dm-^{3}	k1 x 10^{4}s^{-1}
0.25	4.4799
0.50	4.1420
1.00	4.1559
1.50	4.2879
2.00	4.1829

Effect of varying the [H+] ion

The reactions were carried out at five different pH while keeping the other factors constant. The pH of the medium was measured using I.T.L. Digital pH meter. The rate constant was found to increase as the pH was increased (table - 4). For hydroquinone the plot of log k1 Vs log [H+] was linear with a negative slope indicating the inverse order of dependence in [H+]8.

Table - 4

[Hydroquinone] = 3.0 x 10-2 mol dm-3

[NCPD] = 1.0 x 10-3 mol dm-3

Solvent = 80% (v\v) acetic acid-water

Temperature = 40oC

pH	[H+] x 10^{-3} mol dm^{-3}	k1 x 10^{4}s^{-1}
1.95	11.220	0.6069
2.17	6.761	1.6697
2.39	4.074	4.3304
2.64	2.291	8.5211
2.80	1.585	12.5361

Effect of varying the dielectric constant[9]

The reaction were carried out at different percentage acetic acid –water (v/v) mixture containing 65,70,75,80 and 85% and the rate constants were found to increase with increase in the percentage of acetic acid (Table - 5).

Table - 5

[Hydroquinone] = 3.0 x 10-2 mol dm-3

[NCPD] = 1.0 x 10-3 mol dm-3

[HClO4] = 1.5 mol dm-3

Temperature = 40oC

Acetic acid %(v\v)	k1 x 10^{4}s^{-1}
65	0.3153
70	0.4581
75	1.1687
80	4.3304
85	7.8498

Effect of varying the temperature

The reactions have been studied at five different temperatures keeping the other factors constant11. The following thermodynamic parameters have been computed from the linear plot of (ln k2/T) Vs (1/T) of Eyring's equation(Table - 6).

Table - 6

ΔH# = 71.06kJ mol-1
ΔS# = -75.37 J K-1 mol-1
ΔG # = 94.65 kJ mol-1
[Hydroquinone] = 3.0 x 10-2 mol dm-3
[NCPD] = 1.0 x 10-3 mol dm-3
[HClO4] = 1.5 mol dm-3
Temperature = 40oC
The specific reaction rate k2 was calculated using k1/[S]0.285

Temperature	k1 x 104 s-1	K2 x 10^4 mol-1 dm^3 s^{-1}
30	1.4118	3.8352
35	2.6134	7.0995
40	4.3304	11.7638
45	5.8208	15.8126
50	8.9871	24.4141

MECHANISM OF HYDROQUINONE

From the above observations it is clear that the reaction is showing first order dependence with respect to [oxidant] and fractional order with respect to[substrate].The rate is showing inverse order of dependence with respect to the [H+] ions.

The rate shows no appreciable change on changing the ionic strength of the medium. But the rate increase with increase of percentage of acetic acid.

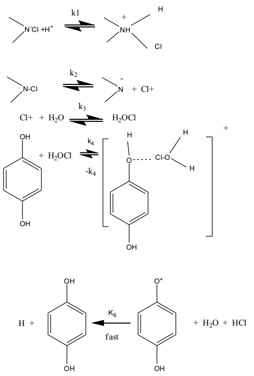
The N-Cl bond in N-chloropiperazine-2,5-dione is partially polar similar to N-Br bond in N-bromosuccinimide. Various possible oxidizing species in acidified solution are the molecular NCPD, protonated NCPD i.e. NCPDH+, solved chlorocation [H2OC1] and HOC1.

As the reaction rate is not inhibited by inhibited by acylonitrile, the chlorine is not the reacting species. As the protonation and deprotonation are said to be fast, at this higher acidic solution both NCPD and NCPDH+ are less likely to be the reactive species. Moreover, as the reaction rate increase with the decrease of acidity, NCPDH+ is not considered as the reactive species.

At low pH, among HOCl, H2O and Cl+, the protonated form is predominating, also this is a strong electrophile and a more potent reactive species.

Moreover, as the reaction rate increase with the decrease of acidity, NCPDH+ is not considered as the reactive species.

At low pH, among HOCl, H_2O and Cl^+, the protonated form is predominating, also this is a strong electrophile and a more potent reactive species.



Rate of the reaction = ks[complex]

Applying the steady state approximation for the complex formed we will get,

$k_4[S]\,[H_2O+Cl] - k_{-4}\,[C_1]\,-k5\,[C_1] = 0$

$$[Complex = \frac{k_4[S]\,[H_2O+Cl]}{\frac{k_{-4}\ -k5}{k_4} + [S]}$$

But

$H_2O + Cl = k_3\ k_2\ [NCPD]_f\ [H_2O]$

$$[NCPD]_f = \frac{[NCPD]_t}{1+k_1[H^+]}$$

$$\text{Rate} = \frac{k_5k_4[S]\ [NCPD]_t}{\left\{\frac{k_{-4}+k_5}{k_1} + [S]\right\}\left\{1+k_1[H^+]\right\}}$$

This rate law is in accordance with the proposed mechanism.

CONCLUSION

The kinetics of oxidation of hydroxyquinone by N-chloropiperazine-2,5-dione was studied in 80% (v/v) acetic acid-water medium. The order of the reaction was found to be one with respect to the [oxidant], fractional order with respect to the [substrate].The reaction showed inverse order of dependence with respect to hydrogen ion concentration. Variation in the ionic strength of the medium has no appreciable change in the rate of the reaction. As the percentage of the acetic acid increases, the rate of the reaction increases. The reactions were studied at five different temperatures. The enthalpy of activation and entropy of activation are computed as 71.06KJmol-1 and -75.37JK-1mol-1 for hydroquinone.

REFERENCES

1. Ganapathy K and Vijayan B J.Indian Chem.Soc.,1974, 55:957
2. Subramaniyan S P Indian J.Chem.,1987,20:429
3. Palaniappan A N J.Indian Chem. Soc.,1986,56:1102
4. Iyanar K J.Indian Chem.Soc.,1986,67:1108
5. Saradamani P N and Jaganadhan V Indian Chem., 1990, 29A:700
6. Bachhawat J M,.Mathur N K Indian J.Chem.,1971,9:1335
7. Mahadevappa D S and .Naidu H M K Aust.J.Chem,1974, 27:1203
8. Kalyan K.Banerji Indian J.Chem.,1997,15A:615
9. Gomathi R J.Indian Chem.Soc.,2001,38:987
10. Natarajan M M and Thiagaran V Ibid Perkin II,1975,1590
11. Rajalakshmi K and Ramachandramoorthy T, Journal of Chemical and Pharmaceutical Research, 2012, 4(1):894-900
12. Morris D F C and Ritter T J J.Less-common Met.,1979,65(2):49
13. D.Sazou,I.Poulios and g.Kokkinidis,Synth.Met.,1989,32(1):113
14. Rajalakshmi K and Ramachandramoorthy T,Der Chemica Sinica, 2012, 3(2):336-342.