KINETICS AND MECHANISM OF THE AQUEOUS PHASE OXIDATION OF HYDROGEN SULFIDE BY OXYGEN: CATALYZED BY HYDROQUINONE

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ABSTRACT

Hydroquinone, which is a trace atmospheric constituent, catalyzes the oxidation of hydrogen sulfide in aqueous phase strongly. The reaction was followed by measuring the disappearance of oxygen with the help of DO meter in a reactor. The reaction obeys the kinetics rate law:

$$-d[O_2]/dt = k_2 K_1 K_3 K_4 [M^{n+}][O_2][H_2Q][S][H^+] / \{ [H^+]^2 + K_1[H^+] + K_1 K_2 \}$$

This work shows hydroquinone to be a strong catalyst for the oxidation of H₂S by O₂ and therefore it will catalyze the oxidation of aqueous H₂S into H₂SO₄ and contribute the acidification of atmospheric water.

Keywords: Hydrogen sulfide, Hydroquinone, Oxygen, Oxidation, Catalysis.

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INTRODUCTION

Hydroquinone is an important organic compound and has several applications as an antioxidant in industry. Production and applications of hydroquinone(H₂Q) in the industry are its major atmospheric sources. Its use in photographic processes and coal gasification results in its releasing effluents.¹⁻² It is a toxic and hazardous chemical. Its inhalation may cause cyanosis, vomiting, nausea, headache, convulsions, dizziness etc. Hydroquinone causes skin irritation in humans.

The oxidation of hydroquinone(H₂Q) by oxygen is well known and has been the subject of several studies and its chemistry is well documented due to its many biological, chemical and clinical functions. It works as an electron transfer reagent in the systems. Quinone chemistry has been the subject of several books³⁻⁶ and many excellent reviews.⁷⁻¹³ The role of different metals in catalyzing the reactions of hydroquinone with oxygen is well known.¹⁴ Transition metal ion catalysis by overcomes the spin restriction and lowers the free energy of activation. The metal ions favor the formation of a ternary complex- metal -reductant-oxygen. The ternary metal – O₂ – H₂Q complex provides several alternative pathways for the reduction of oxygen by hydroquinones.¹⁵

The H₂Q-O₂ reaction generates intermediates such as superoxide ion, O₂⁻, hydrogen peroxide, etc. The reaction in the absence of metal catalyst is proposed to occur as follows.¹⁴

Metal catalyzed oxidation may proceed by the following pathway.

Initiation

Propagation

The accumulation of quinone products leads to the propagation reaction of quinone with oxygen by co-proportionation.

The hydroquinone and the metal catalysts decide the contribution of each of the pathways(4-10). Metal-binding ligands and radical and scavengers also influence these contributions.¹⁴

The aqueous phase atmospheric oxidation of H₂S by oxygen is an important acid rain formation in the atmosphere. H₂S is reported to be oxidized by active oxygen species such as H₂O₂, O₂^{·-}, OH[·].¹⁶⁻¹⁷ The effect of some VOCs on H₂S autoxidation has been studied and while examining the effect of hydroquinone it was found to catalyze the H₂S autoxidation.¹⁸ Since both H₂S and H₂Q are oxidized by O₂, H₂Q is most likely intervenes in the oxidation of H₂S and accelerate the H₂S reaction. This led us to investigate the role of hydroquinone, which is found in the atmosphere in trace amount, in aqueous phase oxidation of H₂S by O₂ in presence of catalytic concentrations of H₂Q(2×10⁻⁶ -1×10⁻⁵ mol L⁻¹).

EXPERIMENTAL

Hydroquinone was of SISCO(98%) make. In this study, the chemicals of only reagent grade were used. The solutions of these chemicals were prepared always in double-distilled water. The only afresh aqueous solution of sodium sulfide was used. H₂Q-H₂S-O₂ reactions were carried out in an air-tight sealed vessel. It was a three-necked glass reactor of 250 ml capacity. It was immersed in a thermo-stated water bath, which was maintained at 30 ± 0.1 °C. One neck was used for fitting the dissolved oxygen probe. Through the other neck, the oxygen was passed from an O₂-cylinder. Sodium sulfide solution was added through the third neck. The following procedure was used for studying kinetics. To begin with, O₂ was bubbled in the reactor until the achievement of desired [O₂]. Now the desired amount of aqueous solution of H₂Q was added followed by the addition of Na₂S solution. The reactor was now sealed and the measurement started. The kinetics was followed by recording a decrease in O₂ concentration by dissolved oxygen(DO) meter.¹⁹ To check the reproducibility of the kinetics runs, each experiment was performed at least three times. Such replicate rate determinations were found to be reproducible within ± 10%. MS Excel 2007 software was used for all calculations.

RESULTS AND DISCUSSION

Preliminary Investigation

Kinetics was studied under pseudo-first-order conditions. The oxygen concentration was in deficit. The concentration of sulfide was in excess at least ten times over oxygen concentration. The catalytic amounts of H₂Q were used in the range 1×10⁻⁶ -1×10⁻⁵ mol L⁻¹. Sodium sulfide, Na₂S has been used as a source of H₂S. Hereafter the analytical concentration of H₂S has been denoted by [S]. The rate of reaction was measured by following the disappearance of [O₂]. The oxidation of both H₂S and H₂Q is strongly affected by trace metal ion and hence a buffered was not used to avoid the introduction of trace metal impurities present in buffered reagents. In many previous studies, buffers have not used for this reason²⁰. Since the buffered was not used, the pH of the reaction mixture varied slightly with the progress of the reaction.

The reaction obeyed first order kinetics in [O₂] disappearance both in presence and absence H₂Q as shown in some representative first-order plots are in Fig.-1. Values of pseudo first-order rate constants, k_{obs}, were obtained from log [O₂]_t versus time, t, plots defined by Eq.(11).

$$-d[O_2]/dt = k_{obs} [O_2]_t \quad (11)$$

Where [O₂]_t is the concentration of oxygen at time t.

Kinetics in Uncatalyzed Reaction

At first, the rate law was determined for the uncatalyzed reaction in the absence of H₂Q. The effect of H₂S concentration was studied by varying Na₂S (2×10^{-3} - 8×10^{-3} mol L⁻¹) in the unbuffered medium. Kinetics order in [S] was determined from the plot of log k_{obs} versus log[S] and found to be 0.97 ± 0.14 , which can be taken as unity. Thus, the rate law for the uncatalyzed reaction at a fixed pH in the absence of hydroquinone is:

$$-d[\text{O}_2]/dt = k[\text{S}][\text{O}_2]_t \quad (12)$$

A comparison of Eqs. (11) and (12) shows

$$k_{\text{obs}} = k[\text{S}] \quad (13)$$

In accordance with Eq. (13), the plot of k_{obs} versus [S] is linear (Fig.-2). The values of k_{obs} at different [S] and [O₂] are in Table-1.

Table-1: The Selected Values of Rate Constants, k_{obs} at Different [S], mol L⁻¹ and $t = 30^\circ\text{C}$

Initial pH	[O ₂], mg/L	[S], mol L ⁻¹	k_{obs} , s ⁻¹
10.77	5.71	2×10^{-3}	1.09×10^{-4}
11.06	5.60	4×10^{-3}	2.74×10^{-4}
11.23	5.70	6×10^{-3}	3.22×10^{-4}
11.32	5.67	8×10^{-3}	4.37×10^{-4}

Fig.-1: The Plot of log [O₂]_t Versus Time at [S] = 2×10^{-3} mol L⁻¹, pH = 10.84 and $t = 30^\circ\text{C}$

Fig.-2: The Plots of k_{obs} Versus [S] at pH = 10.77-11.32 and $t = 30^\circ\text{C}$

Kinetics of Hydroquinone Catalyzed Reaction

The effect of H_2S concentration in the presence of H_2Q (Table-2) was studied by varying Na_2S (1×10^{-3} - 9×10^{-3} mol L^{-1}). Kinetics order in $[\text{S}]$ was determined from the plot of $\log k_{\text{H}_2\text{Q}}$ versus $\log [\text{S}]$ and found to be 0.84 ± 0.1 , which can be taken as unity. The rate law for the catalyzed reaction at a fixed pH in the presence of hydroquinone is:

$$-d[\text{O}_2]/dt = k_{\text{H}_2\text{Q}} [\text{O}_2]_t \quad (14)$$

The effect of $[\text{H}_2\text{Q}]$ at a fixed pH was found to be governed by the rate law (15).

$$k_{\text{H}_2\text{Q}} = k[\text{S}] + k_{\text{cat}} [\text{S}][\text{H}_2\text{Q}] \quad (15)$$

Where, k_{cat} is rate constant for H_2Q -catalyzed reaction.

Table-2: The Selected Value of $k_{\text{H}_2\text{Q}}$ at $[\text{H}_2\text{Q}] = 3 \times 10^{-6}$ mol L^{-1} and $t = 30^\circ\text{C}$

$[\text{O}_2]$, mg/L	pH	[Hydroquinone], mol L^{-1}	$[\text{S}]$, mol L^{-1}	$k_{\text{H}_2\text{Q}}$, s^{-1}
5.11	10.13	3×10^{-6}	1×10^{-3}	5.79×10^{-4}
4.86	10.67	3×10^{-6}	2×10^{-3}	1.42×10^{-3}
4.82	10.97	3×10^{-6}	3×10^{-3}	2.14×10^{-3}
4.79	11.11	3×10^{-6}	4×10^{-3}	2.45×10^{-3}
4.91	11.21	3×10^{-6}	7×10^{-3}	3.23×10^{-3}
4.82	11.30	3×10^{-6}	9×10^{-3}	4.14×10^{-3}

The variation of $k_{\text{H}_2\text{Q}}$ was first order in $[\text{S}]$ (Fig.-3). The plot of $k_{\text{H}_2\text{Q}}$ versus $[\text{H}_2\text{Q}]$, mol L^{-1} was linear as shown in Fig.-4. The values of $k_{\text{H}_2\text{Q}}$ at different $[\text{H}_2\text{Q}]$ and $[\text{O}_2]$ in the presence of $[\text{S}] = 2 \times 10^{-3}$ mol L^{-1} are in Table-3. The value of intercept ($= k[\text{S}]$) and the slope ($= k_{\text{cat}}[\text{S}]$) were found to be 4.74×10^{-4} and $4.3 \times 10^2 \pm 30$ respectively at $[\text{S}] = 2 \times 10^{-3}$ mol L^{-1} , pH = ~ 10.8 and $t = 30^\circ\text{C}$. From these $k[\text{S}]$ and $k_{\text{cat}}[\text{S}]$ values, k and k_{cat} found to be $0.24 \text{ L mol}^{-1} \text{ s}^{-1}$ and 2.13×10^5 respectively at pH = ~ 10.8 and $t = 30^\circ\text{C}$. The k value of $0.14 \text{ L mol}^{-1} \text{ s}^{-1}$ determined in the absence of hydroquinone compares favorably with the value of $0.24 \text{ L mol}^{-1} \text{ s}^{-1}$ under similar reaction conditions.

Table-3: The Selected Value of $k_{\text{H}_2\text{Q}}$ at $[\text{S}] = 2 \times 10^{-3}$ mol L^{-1} and $t = 30^\circ\text{C}$

$[\text{O}_2]$, mg/L	pH	$[\text{S}]$, mol L^{-1}	[Hydroquinone], mol L^{-1}	$k_{\text{H}_2\text{Q}}$, s^{-1}
5.1	10.82	2×10^{-3}	0.0	2.87×10^{-4}
5.03	10.83	2×10^{-3}	2×10^{-6}	1.65×10^{-3}
4.84	10.84	2×10^{-3}	3×10^{-6}	1.92×10^{-3}
4.81	10.83	2×10^{-3}	4×10^{-6}	2.24×10^{-3}
4.86	10.74	2×10^{-3}	5×10^{-6}	2.25×10^{-3}
4.53	10.78	2×10^{-3}	6×10^{-6}	2.85×10^{-3}
4.51	10.83	2×10^{-3}	8×10^{-6}	4.02×10^{-3}
4.66	10.78	2×10^{-3}	1×10^{-5}	4.78×10^{-3}

pH- Dependence

Since in this reaction, multiple hydrogen sulfide species are involved, the H^+ ion dependence is an important parameter in deciding the nature of reactive species and the mechanism. The rate of reaction increases with an increase in pH, i.e., decrease in $[\text{H}^+]$ (Table-4). The order of reaction with respect to $[\text{H}^+]$ was determined from the plot of $\log k_{\text{H}_2\text{Q}}$ versus $\log [\text{H}^+]$ and found to be -0.35 ± 0.04 . The nature of the effect of pH on $k_{\text{H}_2\text{Q}}$ is shown in Fig.-5.

Fig.3-: The Plot of k_{H_2Q} Versus $[S]$ at $[H_2Q] = 3 \times 10^{-6} \text{ mol L}^{-1}$, pH = 10.13- 11.30 and $t = 30^\circ\text{C}$

Fig.4-: The Plot of k_{H_2Q} Versus $[H_2Q]$ at $[S] = 2 \times 10^{-3} \text{ mol L}^{-1}$, pH = 10.82 and $t = 30^\circ\text{C}$

In aqueous solution hydrogen sulfide exists as undissociated H_2S and HS^- and S^{2-} ions governed by the equilibria(16-17) :

Where K_1 and K_2 are first and second dissociation constants of H_2S . The kinetics in this work was investigated in the pH range 6.4- 10.8 and $K_1 = 9.63 \times 10^{-8}$ and $K_2 = 1.34 \times 10^{-13}$ were used.²¹ In the range of pH studied(7.89 - 10.18), the dominant form is HS^- and it is more than 90%²²⁻²³ and our calculations were in confirmative with the calculations of Chen and Morris²². A detailed analysis of $[H^+]$ - dependence of the reaction rate showed HS^- to be not only dominant but also the reactive species.

Effect of EDTA

EDTA is known to complex the metal ions and inhibits the reactions in which the metal ions catalyzed the reaction by forming one or more complexes with the reactant. It is known to inhibit the aqueous H_2S ¹⁸ and SO_2 ²⁴ autoxidation. In view of this, we examined its effect. Its addition led to strong inhibition as shown in Fig.-6.

Mechanism of the Reaction

The hydroquinone is well known to be oxidized into quinone and metals are known to play a catalytic role.²⁵⁻²⁶ The kinetics results of this study can be explained in terms of the following simple mechanism.

K_3 and K_4 are the equilibrium constants for the formation of intermediates $[MH_2Q]^{n+}$ and $[MH_2Q.O_2]^{n+}$ respectively and k_2 is the rate constant for rate-determining step(20).

Table-4: The Selected Value of k_{H_2Q} at $[S] = 2 \times 10^{-3} \text{ mol L}^{-1}$, $[H_2Q] = 5 \times 10^{-6} \text{ mol L}^{-1}$ and $t = 30^\circ\text{C}$

$[O_2]$, mg L^{-1}	pH	k_{H_2Q} , s^{-1}	$[H^+]^2 + K_1[H^+] + K_1K_2$	$k_{H_2Q}\{[H^+]^2 + K_1[H^+] + K_1K_2\}$	$k_{H_2Q}\{[H^+]^2 + K_1[H^+] + K_1K_2\} / [S]$
4.80	10.18	1.05×10^{-3}	6.38×10^{-18}	6.67×10^{-21}	3.33×10^{-18}
5.10	10.04	8.44×10^{-4}	8.80×10^{-18}	7.43×10^{-21}	3.71×10^{-18}
4.81	9.91	1.55×10^{-3}	1.19×10^{-17}	1.84×10^{-20}	9.18×10^{-18}
4.93	9.78	1.42×10^{-3}	1.60×10^{-17}	2.28×10^{-20}	1.14×10^{-17}
4.84	9.71	4.75×10^{-4}	1.88×10^{-17}	8.95×10^{-21}	4.47×10^{-18}
4.80	9.57	1.95×10^{-4}	2.60×10^{-17}	5.07×10^{-21}	2.54×10^{-18}
4.80	9.50	1.41×10^{-3}	3.06×10^{-17}	4.30×10^{-20}	2.15×10^{-17}
4.86	9.11	2.38×10^{-4}	7.54×10^{-17}	1.79×10^{-20}	8.95×10^{-18}
4.91	8.72	1.00×10^{-3}	1.87×10^{-16}	1.87×10^{-19}	9.36×10^{-17}
5.18	8.22	1.04×10^{-4}	6.17×10^{-16}	6.41×10^{-20}	3.21×10^{-17}
4.83	8.19	3.29×10^{-4}	6.63×10^{-16}	2.18×10^{-19}	1.09×10^{-16}
4.68	8.03	3.07×10^{-4}	8.92×10^{-16}	2.74×10^{-19}	1.37×10^{-16}
5.60	7.89	2.03×10^{-4}	1.41×10^{-15}	2.86×10^{-19}	1.43×10^{-16}
4.75	7.76	1.77×10^{-4}	1.98×10^{-15}	3.50×10^{-19}	1.75×10^{-16}
4.85	7.56	9.29×10^{-5}	3.41×10^{-15}	3.17×10^{-19}	1.58×10^{-16}
4.78	7.35	8.56×10^{-5}	6.30×10^{-15}	5.39×10^{-19}	2.69×10^{-16}
4.71	7.27	1.36×10^{-4}	8.06×10^{-15}	1.10×10^{-18}	5.49×10^{-16}
4.83	7.23	1.24×10^{-4}	9.14×10^{-15}	1.13×10^{-18}	5.66×10^{-16}
5.08	7.19	6.64×10^{-5}	1.04×10^{-14}	6.90×10^{-19}	3.45×10^{-16}
5.30	7.12	1.47×10^{-4}	1.31×10^{-14}	1.92×10^{-18}	9.62×10^{-16}
5.26	7.03	1.00×10^{-4}	1.54×10^{-14}	1.55×10^{-18}	7.73×10^{-16}
4.71	6.93	9.98×10^{-5}	2.51×10^{-14}	2.51×10^{-18}	1.25×10^{-15}
4.91	6.58	3.88×10^{-5}	9.45×10^{-14}	3.66×10^{-18}	1.83×10^{-15}
5.01	6.46	4.72×10^{-5}	1.54×10^{-13}	7.25×10^{-18}	3.63×10^{-15}

This mechanism leads to rate law(22) :

$$-d[O_2]/dt = k_2 K_3 K_4 [M^{n+}] [O_2] [H_2Q] [HS^-] \quad (22)$$

From the equilibria(16-17) it can be shown that the equilibrium concentration of HS^- species is given by Eq.(23):

$$[HS^-] = K_1 [S] [H^+] / ([H^+]^2 + K_1 [H^+] + K_1 K_2) \quad (23)$$

On substituting the value of $[HS^-]$ in Eq.(22) we get the complete rate law(24):

$$-d[O_2]/dt = k_2 K_1 K_3 K_4 [M^{n+}] [O_2] [H_2Q] [S] [H^+] / ([H^+]^2 + K_1 [H^+] + K_1 K_2) \quad (24)$$

$$\text{or } k_{H_2Q} = k_2 K_1 K_3 K_4 [M^{n+}] [H_2Q] [S] [H^+] / ([H^+]^2 + K_1 [H^+] + K_1 K_2) \quad (25)$$

$$k_{H_2Q} ([H^+]^2 + K_1 [H^+] + K_1 K_2) / [S] = k_2 K_1 K_3 K_4 [M^{n+}] [H_2Q] [H^+] \quad (26)$$

As required by Eq.(26) the plot of $k_{H_2Q} ([H^+]^2 + K_1 [H^+] + K_1 K_2) / [S]$ versus $[H^+]$ is a straight line passing through origin (Fig.-7). The slope of this plot is equal to $k_2 K_1 K_3 K_4 [M^{n+}] [H_2Q]$. By dividing the value of slope by $[H_2Q]$ the value of $k_2 K_1 K_3 K_4 [M^{n+}] = 1.86 \times 10^{-3}$ at 30°C .

Fig.5:- The Plot of k_{H_2Q} Versus pH at $[S] = 2 \times 10^{-3} \text{ mol L}^{-1}$, $[H_2Q] = 5 \times 10^{-6} \text{ mol L}^{-1}$ and $t = 30^\circ\text{C}$

Fig.6:- The Plot of k_{H_2Q} Versus [EDTA] at $[S] = 2 \times 10^{-3} \text{ mol L}^{-1}$, $[H_2Q] = 2 \times 10^{-6} \text{ mol L}^{-1}$, pH = 10.68 and $t = 30^\circ\text{C}$

Fig.7:- The Plot of $k_{H_2Q} ([H^+]^2 + K_1 [H^+] + K_1 K_2) / [S]$ Versus $[H^+]$ at $[S] = 2 \times 10^{-3} \text{ mol L}^{-1}$, $[H_2Q] = 2 \times 10^{-6} \text{ mol L}^{-1}$ and $t = 30^\circ\text{C}$

The mechanism (18-21) is not unique and several alternative mechanisms that will lead to the same rate law as observed experimentally. It is interesting to point out that the transition metal catalysis and the formation of the ternary complex, metal-reductant-oxidant, have been proposed earlier.²⁷⁻²⁹

This work shows hydroquinone to be a strong catalyst for the oxidation of H₂S by O₂ and therefore it will catalyze the oxidation of aqueous H₂S into H₂SO₄ and contribute the acidification of atmospheric water.

CONCLUSION

The oxidation of aqueous H₂S by oxygen is strongly catalyzed by hydroquinone. It obeys the rate law: $d[O_2]/dt = k_2 K_1 K_3 K_4 [M^{n+}][O_2][H_2Q][S][H^+] / ([H^+]^2 + K_1[H^+] + K_1 K_2)$. The addition of EDTA strongly inhibited the rate of oxidation. Hydroquinone which is a trace atmospheric constituent will strongly catalyze the oxidation of H₂S by oxygen in atmospheric water and contributes to acid rain.

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[RJC-5612/2019]