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:

\[-d[O_2]/dt = k_k_1 k_2 k_3 k_4 [M^{n+}][O_2][H_2Q][S][H^+] / \{ [H^+]^2 + k_1[H^+] + k_2 \}\]

This work shows hydroquinone to be a strong catalyst for the oxidation of H_2S by O_2 and therefore it will catalyze the oxidation of aqueous H_2S into H_2SO_4 and contribute the acidification of atmospheric water.

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

INTRODUCTION
Hydroquinone is an important organic compound and has several applications as an antioxidant in industry. Production and applications of hydroquinone(H_2Q) 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(H_2Q) 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 – O_2 – H_2Q complex provides several alternative pathways for the reduction of oxygen by hydroquinones.15 The H_2Q-O_2 reaction generates intermediates such as superoxide ion, O_2-, hydrogen peroxide, etc. The reaction in the absence of metal catalyst is proposed to occur as follows.14

\[
\begin{align*}
QH_2 + O_2 & \rightleftharpoons Q^- + O_2^- + 2H^+ \\
2O_2^- + 2H^+ & \rightarrow H_2O_2 + O_2 \\
2Q^- + 2H^+ & \rightarrow QH_2 + Q
\end{align*}
\]

Metal catalyzed oxidation may proceed by the following pathway.

Initiation
\[QH_2 + M^{n+} \rightleftharpoons Q^- + M^{(n-1)+} + 2H^+\]

Propagation
\[Q^- + O_2 \rightarrow Q + O_2^-\]

Rasayan J. Chem., 13(1), 112-120(2020)
http://dx.doi.org/10.31788/RJC.2020.1315612
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M^{(n-1)+} + 2H^+ + O_2^- \rightarrow M^{n+} + H_2O_2 \quad (6)

QH_2 + O_2^- \rightarrow Q^- + H_2O_2 \quad (7)

QH_2 + H_2O_2 \rightarrow Q^- + 'OH + OH^- \quad (8)

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

QH_2 + Q \rightarrow 2Q^- + 2H^+ \quad (9)

Q^- + O_2 \rightarrow Q + O_2^- \quad (10)

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 H_2S by oxygen is an important acid rain formation in the atmosphere. H_2S is reported to be oxidized by active oxygen species such as H_2O_2, O_2^-, OH^-16-17. The effect of some VOCs on H_2S autoxidation has been studied and while examining the effect of hydroquinone it was found to catalyze the H_2S autoxidation.18 Since both H_2S and H_2Q are oxidized by O_2, H_2Q is most likely intervenes in the oxidation of H_2S and accelerate the H_2S reaction. This led us to investigate the role of hydroquinone, which is found in the atmosphere in trace amount, in aqueous phase oxidation of H_2S by O_2 in presence of catalytic concentrations of H_2Q(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. H_2Q-H_2S-O_2 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-tight 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 O_2-cylinder. Sodium sulfide solution was added through the third neck. The following procedure was used for studying kinetics. To begin with, O_2 was bubbled in the reactor until the achievement of desired [O_2]. Now the desired amount of aqueous solution of H_2Q was added followed by the addition of Na_2S solution. The reactor was now sealed and the measurement started. The kinetics was followed by recording a decrease in O_2 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 H_2Q were used in the range 1×10^{-6}-1×10^{-5} mol L^{-1}. Sodium sulfide, Na_2S has been used as a source of H_2S. Hereafter the analytical concentration of H_2S has been denoted by [S]. The rate of reaction was measured by following the disappearance of [O_2]. The oxidation of both H_2S and H_2Q 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 reason.50. 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 [O_2] disappearance both in presence and absence H_2Q 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 [O_2] versus time, t, plots defined by Eq.(11).

\[ -d[O_2]/dt = k_{obs} [O_2]_0 \quad (11) \]

Where [O_2]_0 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 H$_2$Q. The effect of H$_2$S concentration was studied by varying Na$_2$S (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:

$$-d[O_2]/dt = k[S][O_2]$$

(12)

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

$$k_{obs} = k[S]$$

(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 [O$_2$] are in Table-1.

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

| Initial pH | [O$_2$], mg/L | [S], mol L$^{-1}$ | $k_{obs}$, s$^{-1}$ |
|------------|--------------|-----------------|-----------------|
| 10.77      | 5.71         | 2 $\times$ 10$^{-3}$ | 1.09 $\times$ 10$^{-4}$ |
| 11.06      | 5.60         | 4 $\times$ 10$^{-3}$ | 2.74 $\times$ 10$^{-4}$ |
| 11.23      | 5.70         | 6 $\times$ 10$^{-3}$ | 3.22 $\times$ 10$^{-4}$ |
| 11.32      | 5.67         | 8 $\times$ 10$^{-3}$ | 4.37 $\times$ 10$^{-4}$ |

Fig.-1: The Plot of log [O$_2$] Versus Time at [S] = 2 $\times$ 10$^{-3}$ mol L$^{-1}$, pH = 10.84 and t = 30°C

Fig.-2: The Plots of $k_{obs}$ Versus [S] at pH = 10.77-11.32 and t = 30°C
Kinetics of Hydroquinone Catalyzed Reaction
The effect of H\(_2\)S concentration in the presence of H\(_2\)Q(Table-2) was studied by varying Na\(_2\)S (1\(\times\)10\(^{-3}\) - 9\(\times\)10\(^{-3}\) mol L\(^{-1}\)). Kinetics order in [S] was determined from the plot of log \(k_{H2O}\) versus log[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:

\[
-d[O_2]/dt = k_{H2Q}[O_2],
\]

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

\[
k_{H2Q} = k[S] + k_{cat}[S][H_2Q]
\]

Where, \(k_{cat}\) is rate constant for H\(_2\)Q-catalyzed reaction.

### Table-2: The Selected Value of \(k_{H2Q}\) at [H\(_2\)Q] = 3\(\times\)10\(^{-6}\) mol L\(^{-1}\) and t = 30°C

| [O\(_2\)], mg/L | pH  | [Hydroquinone], mol L\(^{-1}\) | [S], mol L\(^{-1}\) | \(k_{H2O}\), s\(^{-1}\) |
|----------------|-----|-------------------------------|-----------------|------------------|
| 5.11           | 10.13 | 3\(\times\)10\(^{-6}\)             | 1\(\times\)10\(^{-3}\)       | 5.79\(\times\)10\(^{-4}\) |
| 4.86           | 10.67 | 3\(\times\)10\(^{-6}\)             | 2\(\times\)10\(^{-3}\)       | 1.42\(\times\)10\(^{-4}\) |
| 4.82           | 10.97 | 3\(\times\)10\(^{-6}\)             | 3\(\times\)10\(^{-3}\)       | 2.14\(\times\)10\(^{-4}\) |
| 4.79           | 11.11 | 3\(\times\)10\(^{-6}\)             | 4\(\times\)10\(^{-3}\)       | 2.45\(\times\)10\(^{-4}\) |
| 4.91           | 11.21 | 3\(\times\)10\(^{-6}\)             | 7\(\times\)10\(^{-3}\)       | 3.23\(\times\)10\(^{-4}\) |
| 4.82           | 11.30 | 3\(\times\)10\(^{-6}\)             | 9\(\times\)10\(^{-3}\)       | 4.14\(\times\)10\(^{-4}\) |

The variation of \(k_{H2O}\) was first order in [S](Fig.-3). The plot of \(k_{H2O}\) versus [H\(_2\)Q], mol L\(^{-1}\) was linear as shown in Fig.-4. The values of \(k_{H2O}\) at different [H\(_2\)Q] and [O\(_2\)] in the presence of [S] = 2\(\times\)10\(^{-3}\) mol L\(^{-1}\) are in Table-3. The value of intercept(= k[S]) and the slope (=k\(_{cat}\)[S]) were found to be 0.24 L mol\(^{-1}\) s\(^{-1}\) and 2.13\(\times\)10\(^5\) respectively at pH = ~ 10.8 and t = 30°C. From these k[S] and k\(_{cat}\)[S] values, k and k\(_{cat}\) found to be 0.14 L mol\(^{-1}\) s\(^{-1}\) and 2.13\(\times\)10\(^5\) respectively at pH = ~ 10.8 and t = 30°C. The k value of 0.14 L mol\(^{-1}\) s\(^{-1}\) determined in the absence of hydroquinone compares favorably with the value of 0.24 L mol\(^{-1}\) s\(^{-1}\) under similar reaction conditions.

### Table-3: The Selected Value of \(k_{H2O}\) at [S] = 2\(\times\)10\(^{-3}\) mol L\(^{-1}\) and t = 30°C

| [O\(_2\)], mg/L | pH   | [S], mol L\(^{-1}\) | [Hydroquinone], mol L\(^{-1}\) | \(k_{H2O}\), s\(^{-1}\) |
|----------------|------|--------------------|-------------------------------|------------------|
| 5.1            | 10.82 | 2\(\times\)10\(^{-3}\)       | 0.0                            | 2.87\(\times\)10\(^{-4}\) |
| 5.03           | 10.83 | 2\(\times\)10\(^{-3}\)       | 2\(\times\)10\(^{-6}\)        | 1.65\(\times\)10\(^{-3}\) |
| 4.84           | 10.84 | 2\(\times\)10\(^{-3}\)       | 3\(\times\)10\(^{-6}\)        | 1.92\(\times\)10\(^{-3}\) |
| 4.81           | 10.83 | 2\(\times\)10\(^{-3}\)       | 4\(\times\)10\(^{-6}\)        | 2.24\(\times\)10\(^{-3}\) |
| 4.86           | 10.74 | 2\(\times\)10\(^{-3}\)       | 5\(\times\)10\(^{-6}\)        | 2.25\(\times\)10\(^{-3}\) |
| 4.53           | 10.78 | 2\(\times\)10\(^{-3}\)       | 6\(\times\)10\(^{-6}\)        | 2.85\(\times\)10\(^{-3}\) |
| 4.51           | 10.83 | 2\(\times\)10\(^{-3}\)       | 8\(\times\)10\(^{-6}\)        | 4.02\(\times\)10\(^{-3}\) |
| 4.66           | 10.78 | 2\(\times\)10\(^{-3}\)       | 1\(\times\)10\(^{-5}\)        | 4.78\(\times\)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 [H\(^+\)](Table-4). The order of reaction with respect to [H\(^+\)] was determined from the plot of log \(k_{H2O}\) versus log[H\(^+\)] and found to be -0.35 ± 0.04. The nature of the effect of pH on \(k_{H2O}\) is shown in Fig.-5.
In aqueous solution hydrogen sulfide exists as undisassociated \( \text{H}_2\text{S} \) and \( \text{HS}^- \) and \( \text{S}^{2-} \) ions governed by the equilibria (16-17):

\[
\begin{align*}
\text{H}_2\text{S} & \rightleftharpoons \text{K}_1 \quad \text{HS}^- + \text{H}^+ \quad (16) \\
\text{HS}^- & \rightleftharpoons \text{K}_2 \quad \text{S}^{2-} + \text{H}^+ \quad (17)
\end{align*}
\]

Where \( \text{K}_1 \) and \( \text{K}_2 \) are first and second dissociation constants of \( \text{H}_2\text{S} \). The kinetics in this work was investigated in the pH range 6.4-10.8 and \( \text{K}_1 = 9.63 \times 10^{-8} \) and \( \text{K}_2 = 1.34 \times 10^{-13} \) were used.\(^{21}\) In the range of pH studied (7.89-10.18), the dominant form is \( \text{HS}^- \) and it is more than 90\%\(^{22,23}\) and our calculations were in confirmative with the calculations of Chen and Morris\(^{22}\). A detailed analysis of \([\text{H}^+]\)-dependence of the reaction rate showed \( \text{HS}^- \) 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 \( \text{H}_2\text{S} \)\(^{18}\) and \( \text{SO}_2^{24} \) 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.
This mechanism leads to rate law (22):

\[ \frac{d[O_2]}{dt} = k_2 K_3 K_4 [M^{n+}][O_2][H_2Q][HS^-] \]  

(22)

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

\[ [HS^-] = K_1 [S][H^+] / ( [H^+]^2 + K_1[H^+] + K_1K_2) \]  

(23)

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

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\[ [HS^-] = K_1 [S][H^+] / ( [H^+]^2 + K_1[H^+] + K_1K_2) \]  

(23)

On substituting the value of [HS\(^{-}\)] in Eq. (22) we get the complete rate law (24):
-d[O₂]/dt = k₂K₁K₃K₄[Mⁿ⁺][O₂][H₂Q][S][H⁺] / ( [H⁺]² + K₁[H⁺] + K₁K₂ )

or \( k_{H_{2}Q} = k_2K_1K_3K_4[H_2Q][S][H^+] / ([H^+]^2 + K_1[H^+] + K_1K_2) \)  \( (24) \)

\( k_{H_{2}Q} \frac{([H^+]^2 + K_1[H^+] + K_1K_2)}{[S]} = K_2K_1K_3K_4[H_2Q][H^+] \)  \( (25) \)

\( k_{H_{2}Q} \frac{([H^+]^2 + K_1[H^+] + K_1K_2)}{[S]} = k_2K_1K_3K_4[M^{n⁺}][H_2Q][H^+] \)  \( (26) \)

As required by Eq.(26) the plot of \( k_{H_{2}Q} \frac{([H^+]^2 + K_1[H^+] + K_1K_2)}{[S]} \) versus \([H^+]\) is a straight line passing through origin(Fig.-7). The slope of this plot is equal to \( k_2K_1K_3K_4[M^{n⁺}][H_2Q] \). By dividing the value of slope by \([H_2Q]\) the value of \( k_2K_1K_3K_4[M^{n⁺}] = 1.86 \times 10^{-3} \) at 30°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. This work shows hydroquinone to be a strong catalyst for the oxidation of H$_2$S by O$_2$ and therefore it will catalyze the oxidation of aqueous H$_2$S into H$_2$SO$_4$ and contribute the acidification of atmospheric water.

**CONCLUSION**

The oxidation of aqueous H$_2$S by oxygen is strongly catalyzed by hydroquinone. It obeys the rate law:

$$\frac{d[O_2]}{dt} = k_2K_1K_3[M^{n+}][O_2][H_2Q][H^+] / (\text{[H}^+\text{]}^2 + K_1\text{[H}^+\text{]} + K_2).$$

The addition of EDTA strongly inhibited the rate of oxidation. Hydroquinone which is a trace atmospheric constituent will strongly catalyze the oxidation of H$_2$S by oxygen in atmospheric water and contributes to acid rain.

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[RJC-5612/2019]