Chapter IV

KINETICS OF UNCATALYSED OXIDATION OF S(IV) IN AQUEOUS PHASE BY DISSOLVED OXYGEN
The aqueous phase oxidation of S(IV) by dissolved oxygen either uncatalysed or catalysed is a classic process which has been studied over past fifty years. The solution of sodium sulphite oxidises slowly in the presence of molecular oxygen. Whether, it is due to true uncatalysed or due to the presence of extremely small amount of catalyst in the form of impurities either in distilled water or in the sodium sulphite itself is a controversial subject. Various researchers have studied the uncatalysed aqueous phase oxidation but obtained different results and rate expressions (Fuller and Crist, 1941; Schroeter, 1963; Scot and Hobbs, 1967; McKay, 1971; Beilke et. al., 1975; Larson et. al., 1978; Brimblecombe and Spedding, 1978; Redojevic, 1984). They not only disagree on the rate constant but also on the direction of pH dependence.

The uncertainty over the rate expression and its pH dependence for the uncatalysed oxidation of S(IV) prompted the work presented in this section. Initially, the experiments were conducted to ascertain The principal aim of this section of the research is to determine a general form of rate expression for the uncatalysed oxidation in the atmospheric pH range.

The first and foremost task of this section of the study was to ascertain, whether, the uncatalysed oxidation by dissolved oxygen takes place or not. Having established that the uncatalysed oxidation does indeed take place, the rate expression for the uncatalysed oxidation in the atmospheric pH range are determined.
4.1. VARIATION OF REACTION RATE WITH S(IV) CONCENTRATION

Figure 4.1 shows the reaction profiles of the uncatalysed oxidation of S(IV) in aqueous phase at constant pH (5.00). Experiments were performed at seven different initial concentrations ranging from $2 \times 10^{-3}$ to $8 \times 10^{-3}$ mol/l. The pH of the reaction was maintained by sodium acetate/acetic acid buffer solution. The rate of decrease in concentration of S(IV) with time implies the rate of increase in oxidation of S(IV). When the initial concentration is $2 \times 10^{-3}$ mol/l the rate of reaction is very slow. The relative increase in the rate of reaction is very small. For higher concentrations, the rate of reaction increases quite steeply as a function of time up to 30-35 minutes. Thereafter, the rate of increase in the oxidation is moderate to slow.

The log-log plot of initial concentrations versus initial rates of the oxidation has been presented in figure 4.2. From the slope and the intercept of the regression line the order and the rate constant of the reaction are inferred. The slope is the order ($n_1$) of the reaction and the intercept is $-\log (k_1)$, where $k$ is the rate constant. The rate expression can be written as

$$\frac{d[S(IV)]}{dt} = k_1 [S(IV)]^{n_1}$$  \hspace{1cm} (4.1)

Where, $n_1 = 0.3732$

$$k_1 = 3.265 \times 10^{-3} \text{ (M)}^{0.6268} \text{ s}^{-1}$$

From this rate expression it is clear that the order of reaction is 0.3732 with respect to S(IV) concentration.
Fig. 4.1: Concentration-time profiles of the uncatalysed oxidation of S(IV) in aqueous phase

Fig. 4.2: Log-log plot of initial rate vs. concentration for the uncatalysed oxidation of S(IV)
4.2. VARIATION OF REACTION RATE WITH pH

The reaction profiles of the oxidation of S(IV) at different pH and constant initial concentration of S(IV) are given in figures 4.3 and 4.4. From these figures it is clear that the initial rate of oxidation is lowest at pH 4.50 followed by that at pH 4.00. The highest rate of oxidation is associated with pH 6.00 followed by that with 5.5. These concentration-time profiles indicate a complex pattern of dependence of rate of reaction on pH.

The log-log plot of initial rate of reaction versus $[H^+]$ concentration in the pH range 3.50-7.00 has been given in figure 4.5. This figure illustrates that the rate of reaction increases with increase in pH value from 4.00 to 6.00, but from 6.00 to 7.00 it decreases with increase in pH. This indicates that there are two trends of variation associated with rate of reaction with pH. Here, it is not possible to provide a single rate expression for the entire pH range with accuracy. Figure 4.6 shows the linear best fit line of the log-log plot of the rate versus $[H^+]$ concentration in the pH range 4.00-6.00. In this pH range the rate expression at 25°C tempt. and constant initial S(IV) concentration (5x10^{-3} mol/l) is

$$\frac{d[S(IV)]}{dt} = k_2 [H^+]^{n_2}$$  \hspace{1cm} (4.2)

Where, $n_2 = -0.8781$

$$k_2 = 2.234 \times 10^{-11} (M)^{0.1219} \text{s}^{-1}$$

The order of reaction in this pH range with respect to $[H^+]$ concentration is -0.8781.

The linear best fit line of the log-log plot of the rate of oxidation of S(IV) versus $[H^+]$ concentration in the pH range 6.00-7.00 has been given in Figure 4.7. The slope of
Fig. 4.3: Reaction profiles for the oxidation of S(IV) at different pH

Fig. 4.4: Reaction profiles for the oxidation of S(IV) at different pH.
Fig. 4.5: Log-log plot of rate vs. [H+] concentration for the uncatalysed oxidation of S(IV).

Fig. 4.6: Log-log plot of rate vs. [H+] concentration for the uncatalysed oxidation of S(IV).
the line gives the order of reaction with respect to [H⁺] concentration in this pH range.
The rate expression in the pH range 6.00-7.00 is found to be

\[ \frac{d[S(IV)]}{dt} = k_3 [H^+]^{n_3} \]  \hspace{1cm} (4.3)

Where, \( n_3 = 0.4277 \) and 
\[ k_3 = 8.235 \times 10^{-4} \text{ (M)}^{0.5723} \text{ s}^{-1} \]

In this pH range, the order of reaction is 0.4277.

**4.3. GENERAL RATE EXPRESSION**

The general rate expression is obtained by incorporating [H⁺] dependence in the rate equation (4.1). In the pH range 4.00-6.00, the modified rate law becomes

\[ \frac{d[S(IV)]}{dt} = k [S(IV)]^n[H^+]^m \]  \hspace{1cm} (4.4)

Where, \( n = 0.3732 \),
\[ m = -0.8781, \text{ and} \]
\[ k = 1.85 \times 10^{-10} \text{ (M)}^{0.5049} \text{ s}^{-1} \]

and in the pH range 6.00-7.00, it becomes

\[ \frac{d[S(IV)]}{dt} = k' [S(IV)]^{n'}[H^+]^{m'} \]  \hspace{1cm} (4.5)

Where, \( n' = 0.3732 \),
\[ m' = 0.4277, \text{ and} \]
\[ k' = 1.998 \times 10^{-5} \text{ (M)}^{0.1991} \text{ s}^{-1} \]
Fig. 4.7: Log-log plot of rate vs. [H+] concentration for the uncatalysed oxidation of S(IV)

Fig. 4.8: Plot of the rate of oxidation (uncatalysed) vs. Na-Acetate conc. in the buffer solution
Thus our study yields two different rate expressions in different pH ranges. This is not very surprising in view previous studies on the uncatalysed oxidation of S(IV) which disagree not only on the rate expressions but also on the order of reaction, rate constants and the directions of pH dependency. For example, some of the studies on the uncatalysed oxidation of S(IV), though conducted in different reaction conditions, show a negative correlation between rate constant and pH for a pseudo first order reaction (Fuller and Crist, 1941; Schroeter, 1963; Larson et. al., 1978), while, Beilke et. al. (1975) have reported that the rate constant increases with increasing pH (Beilke et. al., 1975). The appreciable variation in the value of rate constants in different pH ranges points towards the existence of some other factor(s) which influence(s) the rate of reaction. One possible factor may be the concentration of dissolved oxygen. Larson et. al.(1978) on the basis of his study on the uncatalysed oxidation of SO₂ in aqueous system bubbling O₂ from outside at different rates found zero order O₂ dependence in acidic solution.

4.4. EFFECT OF BUFFER CONCENTRATION ON REACTION RATE

The influence of buffer concentration on the reaction rates has been examined by conducting the kinetic runs with different buffer concentration, but keeping the buffer ratio constant, so that the pH of the solution remained constant. Figure 4.8 shows the variation of initial rate with Na-acetate concentration of the buffer solution. This figure illustrates that an increase in buffer concentration (Na-acetate) decreases the rate of reaction. The decrease in rate is quite appreciable up to the Na-acetate concentration 4.5 x 10⁻² mol/l after that the rate is nearly constant. Considering this
dependence of reaction rate, it would desirable in principle to study the rate without buffering. But, the rate reaction is highly dependent on the pH and the pH of the reaction decreases on the advancement of reaction, and there is no other simple means for keeping the pH constant through out the reaction except the addition of NaOH. However, there is practical difficulty in adopting this procedure, as the addition of a concentrated NaOH would raise the pH high enough and a diluted one would raise the volume of the reaction solution resulting in reduction of S(IV) concentration. In view of the above facts, it is easier to use a buffer solution to maintain a constant pH through out the reaction, provided the buffer concentration is not high enough to have an appreciable effect on the reaction rates. The buffer concentration that was used during this study (1.5 x 10^{-2} \text{ mol/l}) does not have major influence over the rate of reaction as evident from the Figure 4.8.

4.5. INFLUENCE OF EDTA ON THE REACTION RATE

The influence of metal ion complexing agent, EDTA on the uncatalysed oxidation of S(IV) in aqueous phase has been studied by taking different concentration of EDTA in the reaction vessel in different kinetic runs. The results of this study have been shown in Figure 4.9 by plotting the rate of oxidation against the molar concentration of EDTA. This diagram shows that the rate of oxidation strongly depends on the EDTA concentration. The rate decreases on increasing EDTA concentration and follows an exponential profile. Since EDTA is a strong hexadentate ligand and it forms stable complexes with transition metal ions, even small concentration of EDTA in reaction solution is likely to convert all metal ions present as impurities in the reaction solution into unreactive species. It has been argued that the complexing agents are good inhibitors of the reaction (Counterman and Altwicker, 1972; Martin, 1984). Following this argument the observed decreasing trend (Figure 4.9) is possibly
Fig. 4.9: Plot of rate of oxidation of S(IV) vs. EDTA concentration
supposed to be due to the inhibition of reaction by the complexing agent, EDTA. Tasunogai (1971) has shown that small amount of EDTA cause the reaction to cease. In our experiments inspite of increasing concentration of EDTA the reaction did not cease. This indicates towards the uncatalyed oxidation of S(IV). Larson et. al. (1978) have also reported the uncatalysed oxidation of SO₂.

The above study on the kinetics of oxidation of S(IV) in aqueous phase by dissolved oxygen concludes that uncatalysed oxidation does indeed take place. The order of reaction in S(IV) concentration is less than 1/2. The order of reaction in [H⁺] concentration it is approximately ≈-1 in the pH range 4.00-6.00 and approximately ≈ 1/2 in the pH range 6.00-7.00. The orders of reaction in [H⁺] concentration being of different signs indicate opposite trends in variation of reaction rates with pH in the two ranges. The rate constants are found to be $1.85 \times 10^{10} \ (M)^{0.5049} \ s^{-1}$ and $1.998 \times 10^{-5} \ (M)^{0.1991} \ s^{-1}$ respectively.