Kinetics of Oxidation of Sodium Dithionite by Flow Thermal Method

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The homogeneous kinetics and inhibition of sodium dithionite oxidation in an aqueous solution were studied by means of a flow thermal method. Results on the oxidation study of dithionite solutions at 30°C show that the reaction is first order with respect to dithionite and zero order with respect to oxygen. An activation energy of 17.5 kcal/g-mole has been calculated for this reaction. The inhibiting effects of manganese chloride, manganese sulfate, and triethanolamine were inversely proportional to 0.8, 0.9, and 0.2 power, respectively.

A free radical chain mechanism has been proposed, and the rate expressions derived are in good agreement with the experimental data.

SCOPE

Solutions of sodium dithionite are used as powerful and rapid reducing agents for vat dyeing, bleaching, and for manufacture of various chemicals. The inherent instability of this compound with respect to atmospheric oxidation in aqueous solutions, however, lowers the efficiency of the solutions after prolonged storage. Therefore, a considerable excess of sodium dithionite over stoichiometric amounts must be used. It would be very desirable to minimize the excess consumption of sodium dithionite in industrial applications, and it is essentially in regard to this problem that the kinetics of sodium dithionite oxidation in aqueous solutions has been studied in some detail. The resulting information, however, is contradictory in many ways and thus remains inconclusive. The earliest oxidation study of dithionite was probably conducted by Meyer (1903); he computed first-order rate constants which drifted over a wide range. Nicloux (1933) and Lynn (1954) proposed an overall stoichiometry for the reaction. Lynn (1954) reported that the rate of atmospheric oxidation was first order, involving dithionite in solutions of 0.1M. Morello et al. (1964) reported that the reaction is first order with respect to dithionite and zero order with respect to molecular oxygen at operating concentrations between 8×10^{-5} M and 47.5×10^{-5} M dithionite and 10×10^{-5} for oxygen. In contrast, Rinker et al. (1960) observed that the reaction is half order with respect to dithionite and first order with respect to oxygen. The *p*H of the reacting medium was held approximately at the value used by Morello et al. Jhaveri and Sharma (1968) found the reaction to be first order with respect to dithionite for concentrations below 0.08 M/l and second order for concentrations above 0.08 M/l. In the case of oxygen, the reaction was observed to proceed with zero order.

The kinetic analysis has not been projected as a focal point because of the existing controversy in the experimental results. It should also be noted that substances such as manganese compounds, trialkanolamines, sodium phosphate, ammonium thiocyanate, etc. are known to inhibit the oxidation of sodium dithionite solutions; however, there seems to be no reported data on kinetics and inhibition. In the present investigation, the reaction rate of homogeneous liquid-phase oxidation of sodium dithionite solutions was studied by a flow-thermal method similar to that employed by Hartridge and Roughton (1923) and by Roughton (1963), in wide ranges of temperature, *p*H, and reactant concentrations. Experiments were also conducted to study the inhibiting effects of manganese compounds and triethanolamine. It was hoped that the present work would lead to a plausible mechanism of dithionite oxidation with and without inhibition.

CONCLUSIONS AND SIGNIFICANCE

Results on the oxidation study of dithionite solutions show that the reaction is first order with respect to dithionite and zero order with respect to molecular oxygen. The overall stoichiometry conforms to that reported by Nicloux (1933) and Lynn (1954).

A free radical chain mechanism has been proposed, and the rate expressions derived satisfactorily account for the kinetics of the oxidation of dithionite solutions. An activation energy of 17.5 kcal/g-mole has been calculated for the reaction. The inhibition step is believed to follow a different termination path. It is proposed that the inhibiting role of manganese compounds has been due to direct termination of active radicals, whereas for triethanolamine it is due to biradical termination in addition to the direct one.

Parametric dependence of the *p*H of the reacting medium upon the reaction rate has also been followed. It has been observed that the rate decreases in a regular pattern with the increase of *p*H. This may be attributed to the possibility that dithionite undergoes hydrolysis, resulting in reduction of the dithionite concentration available for oxidation.

It is expected that the present results will contribute to the understanding of the kinetics and mechanism of this reaction.

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TABLE 1. PROPOSED ORDERS OF REACTION

Dithionite	Oxygen	Reference
One	—	Lynn (1954)
Half	One	Rinker et al. (1960)
One	Zero	Morello et al. (1964)
One <0.08 M	Zero	Jhaveri and Sharma (1968)
Two >0.08 M		

The kinetics of the homogeneous liquid-phase oxidation of sodium dithionite reported here is the third in a series of investigations of the kinetics of some fast homogeneous reactions. The results of the oxidations of ammonium and potassium sulfites have been published previously (Mishra and Srivastava, 1975, 1976).

Solutions of $Na_2S_2O_4$ are used in the textile industry for the reduction of vat dyes. The inherent instability of this compound with respect to atmospheric oxidation in aqueous solutions, however, lowers the efficiency of the solutions after prolonged storage. While experimental studies of the oxidation of $Na_2S_2O_4$ have been made for some time, kinetic analyses have been slow to develop. There is wide disagreement in the reported data, and the kinetics of the reaction are still not well understood.

Morello et al. (1964) studied the rate of removal of oxygen from aqueous solutions of sodium dithionite. Working with extremely low concentrations of dithionite and oxygen, they reported a first-order reaction with respect to dithionite and zero order with respect to oxygen. In the temperature range of 30° to 60°C, Rinker et al. (1960) found that the oxidation was half order in terms of dithionite and first order with respect to oxygen. The results of Lynn (1954) suggested that the atmospheric oxidation of $Na_2S_2O_4$ proceeded according to a first-order mechanism with respect to dithionite. From an examination of these data, it appears that in the heterogeneous reaction between oxygen and dithionite, diffusion is likely to be a contributing factor.

The absorption of oxygen by sodium thionite solutions has also been used to study the characteristics of mass transfer with simultaneous reaction (Jhaveri and Sharma, 1968). The reaction was found to be first order with respect to dithionite for concentrations below 0.08 g mole/l and second order with respect to concentrations above 0.08 g mole/l. They reported the reaction to be zero order with respect to oxygen for all dithionite concentrations. Interpretation of the experimental data for simultaneous diffusion and reaction requires a knowledge of homogeneous reaction rates. Proposed orders of reaction are summarized in Table 1.

A variety of substances, such as manganese compounds (Mecco, 1954) and trialkanolamines (Mecco, 1954; Klemin, 1958), has been claimed to inhibit this reaction. A careful examination of the literature reveals that there is no prior kinetic study where the oxidation of sodium dithionite was inhibited by these compounds. In commercial practice, it is very desirable to find methods for decreasing the rate of dithionite oxidation.

The objective of this study has therefore been to determine the rate data of the homogeneous liquid-phase oxidation of sodium dithionite in a wide range of reactant concentrations; the effects of *p*H and temperature; the effect of inhibitor concentration using manganese compounds such as manganese chloride and manganese sulfate, and triethanolamine, $(OHCH_2CH_2)_3N$ as inhibitors; and to establish the mechanism of dithionite oxidation.

In this investigation, measurements of the homogeneous reaction rate were made by a flow-thermal method (Hartridge and Roughton, 1923; Roughton, 1963). The temperature change of the solution as a result of the heat of reaction at a particular point along the reactor is a measure of the amount of reaction occurring at that point.

EXPERIMENTAL

The flow-thermal method employed an adiabatic plug flow tubular reactor. The details of the apparatus and procedure have been described previously (Mishra and Srivastava, 1975). The mixing chamber and the reactor were constructed from plastic, so that the reactant solution did not come into contact with metal in that part of the apparatus where the rate measurements were made. The mixing chamber was simular to that used by Srivastava et al. (1968). The reactor consisted of lengths of 1/4 in. OD by 1/8 in. ID Plexiglas tubing with Zytel Swagelok fittings to permit insertion of thermocouples in the tube. Measurements of the potential difference were made between the mixing point and various points along the reactor by means of a Keithley model 149 microvoltmeter. The thermocouples were calibrated against a 25 ohm Leeds and Northrup platinum resistance thermometer and a Mueller bridge.

Analysis of the sodium dithionite concentration in the feed solution was made by the method described by Committee on Analytical Methods (1957). The oxygen solution was prepared by bubbling oxygen into the feed tank containing distilled water under pressure, and its concentration was determined by Winkler's method. Flow rates were adjusted to provide the desired ratio of the two reactant streams. The average initial concentrations of $Na_2S_2O_4$ and oxygen were calculated from the concentrations and respective rates of flow of the charged solutions. The *p*H was maintained at a constant value by addition of small amounts of alkali. For the anticatalytic runs, inhibitors were added in equal strength to both storage tanks from the stock solutions.

The oxidation of dithionite is an exothermic reaction. The energy liberated by reaction raised the temperature of the solution and the temperature rise was measured. The oxygen concentration M was determined by the energy balance $\Delta H_R \times M = \Delta T \times Cp$. The mean heat capacity Cp of the solution was approximated as that of water, since the dithionite concentration was low. The experimental data were obtained as potential differences along the observation tube with respect to mixing point. Plotting potential difference vs. residence time indicated various straight lines rising to a plateau. The rate of oxygen consumption was calculated from the slope of such lines.

The reliability of the equipment was checked using the sodium hydroxide-carbon dioxide system. The average of the second-order rate constant agreed within 5% with the value reported by Pinsent et al. (1956).

RESULTS AND DISCUSSION

The overall stoichiometry for the oxidation of dithionite has been described by the equation (Lynn, 1954; Nicloux, 1933; Jhaveri and Sharma, 1968)

$$Na_2S_2O_4 + O_2 + H_2O \rightarrow NaHSO_3 + NaHSO_4 \quad (1)$$

The standard enthalpy of reaction is -135.1 kcal/g-mole of oxygen reacted (Dean, 1973; Washburn, 1929).

Typical examples of the change in temperature as a function of residence time are shown in Figure 1. Such plots always showed straight lines with different slopes up to the point where dithionite was completely consumed. The temperature corresponding to this point resulted in the heat of reaction, which approximately corresponded to the enthalpy of the overall reaction given by Equation (1). The present results clearly establish the stoichiometric Equation (1).

It has been reported by several authors (Rinker et al., 1960; Morello et al., 1964) that the reaction in the low *p*H range was very fast. It was, therefore, very difficult to measure these rates. In an alkaline medium, however, it was found that the rates were measurable, and that is

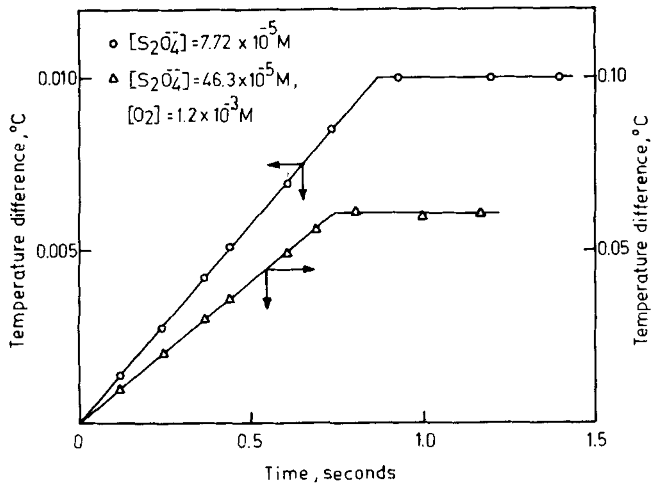


Fig. 1. Typical temperature profiles as a function of time of reaction rate at 30°C; $pH = 11$.

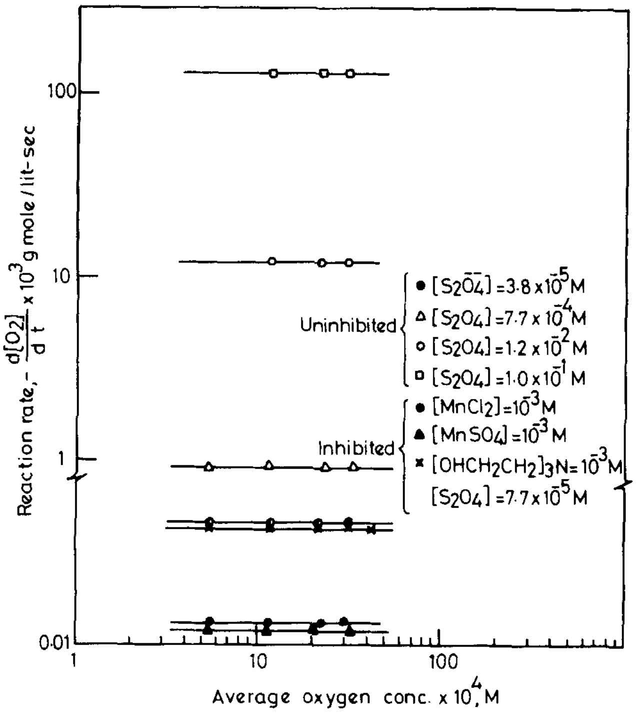


Fig. 3. Effect of oxygen concentration on reaction rate at 30°C; $pH \simeq 11$.

why most of these authors conducted their experiments in that medium. However, no detailed study of the variation of pH was made for the oxidation of dithionite. In the present investigation, the effect of pH on the reaction rate was studied in the range $p\text{H} = 8$ to 11. The results are shown in Figure 2. Evidently, at constant concentrations of dithionite and oxygen, the rate decreases with the increase in pH values. The effect of pH is discussed later in the text.

Rate Studies

In order to study the effect of oxygen concentration on the rate of reaction, rate data were obtained at 30°C and at a pH of 11. The relation of rate vs. oxygen concentration is shown in Figure 3. The dithionite concentration was held constant at values ranging from 3.8×10^{-5} to 1.0×10^{-1} M. Over a wide range of oxygen concentration, the reaction rate was found to be independent of oxygen concentration in both the uninhibited and inhibited runs.

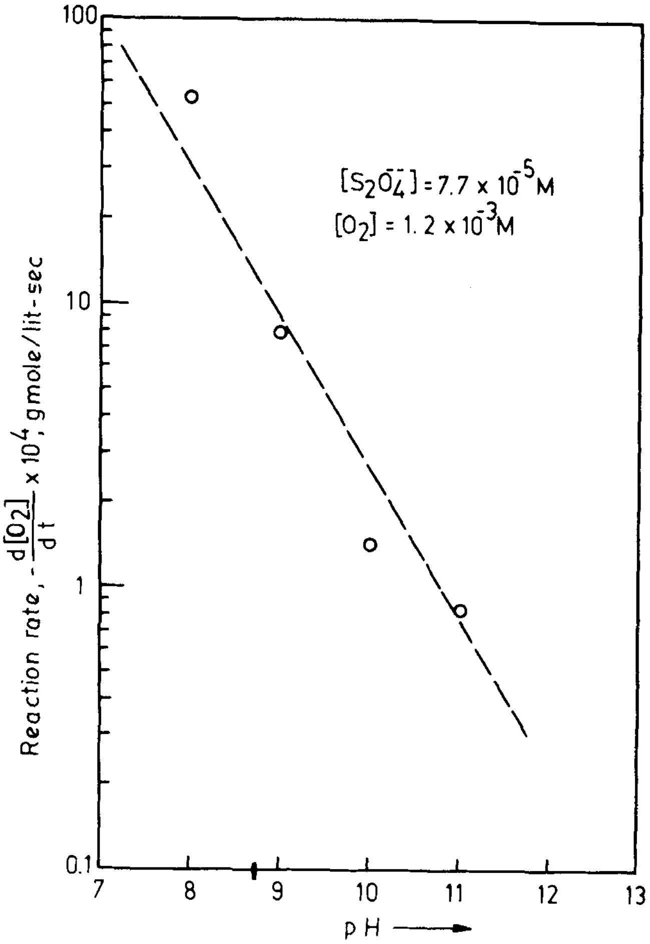


Fig. 2. Effect of pH on reaction rate at 30°C.

In the determination of the order of the reaction with respect to dithionite, the oxygen concentration was held constant. The concentrations of dithionite ranged from 3.8×10^{-5} to 1.0×10^{-1} M. The rate of oxygen consumption is shown as a function of average dithionite concentration in Figure 4. All the data shown in this figure correspond to an average oxygen concentration of 0.0012 M. Rates were different with and without 10^{-3} M inhibitors added, but in all cases the rate against dithionite concentration resulted in one power relation.

As part of physiological studies in terms of oxygen absorption in haemoglobin, Morello et al. (1964) studied the rate of reaction of the dithionite ion with oxygen in aqueous solutions employing the rapid mixing apparatus. The oxygen concentrations during the course of reaction were measured by a polarographic technique. The initial range of dithionite concentrations were from 8×10^{-5} to 4.7×10^{-4} M, while the oxygen concentration was 10×10^{-5} M. They reported that the reaction was first order with respect to dithionite and zero order with respect to molecular oxygen. This is in complete agreement with the results of the present study. Morello et al. (1964) further indicate that the first-order rate constant would have an initial value greater than 42 s^{-1} at a pH of 7 or 8. The rate constant calculated on the basis of the present experiments at a pH of 8 is 69 s^{-1}.

Rinker et al. (1960) studied the air oxidation of sodium dithionite in aqueous solutions, which was 0.1 M in sodium hydroxide. The initial concentrations of dithionite varied from 5×10^{-3} to 20×10^{-3} M. Under conditions in which diffusion of air was not controlling the rate, the authors observed that the oxidation was half order with respect

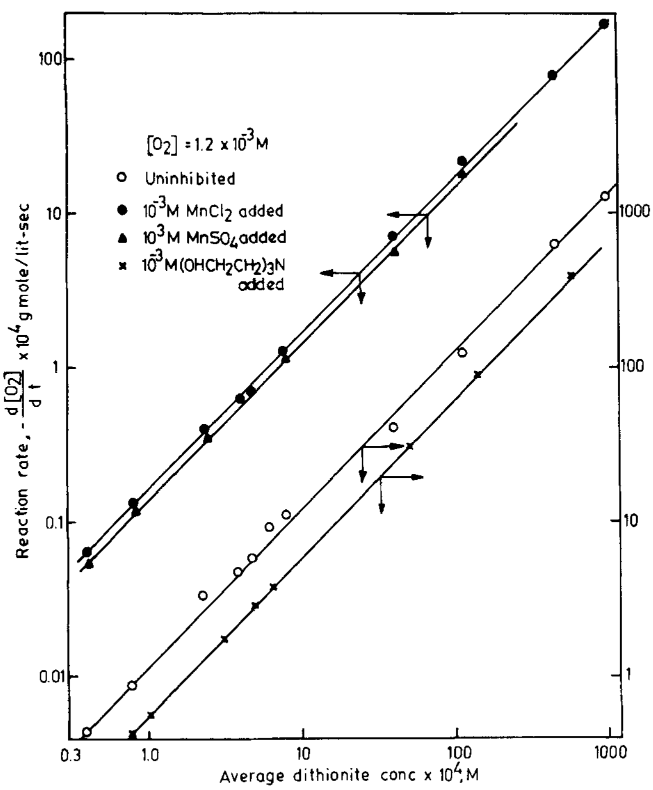


Fig. 4. Effect of dithionite concentration on reaction rate at 30°C; pH = 11.

to dithionite. These results are in disagreement with the present findings. It is interesting, however, to compare the reaction rates at compatible dithionite concentrations and *p*H values with the assumption that oxygen concentration does not affect the reaction rate. The interpolated value of the reaction rate at a dithionite concentration of 7.7×10^{-5} M from the data of Rinkers et al. (1960) is approximately 4×10^{-6} M/s. This would be at 0.1 M sodium hydroxide, or at a *p*H of 13. The extrapolated value of reaction rate at the dithionite concentration of 7.7×10^{-5} M from the curve of *p*H vs. reaction rates (Figure 2) reads approximately 6×10^{-6} M/s, which is in good agreement with the value of Rinker et al. (1960). It should, however, be noted that the extrapolated value of the reaction rate at the specified concentration for a *p*H of 13 is only approximate, since a linear dependence is assumed, whereas, seemingly, it might be a complex reaction. The idea is mainly to compare the reported rate of Rinker et al. (1960) with the findings of the present experiments.

Reactions were carried out over the temperature range 30° to 90°C. The logarithm of the initial rate of reaction was plotted with the inverse of the absolute temperature at temperatures of 30°, 45°, 60°, 75°, and 90°C (Figure 5). The apparent activation energy for the overall oxidation was calculated to be 17.5 kcal/mole.

Effect of Inhibitor Concentration

The most significant feature of dithionite oxidation is marked sensitivity to inhibitors (Mecco, 1954; Klemin, 1958). The rate in the presence of the inhibitors is shown in Figures 3 and 4.

To clarify the dependencies of manganese chloride, manganese sulfate, and triethanolamine on the rate of dithionite oxidation, experiments were performed at constant average dithionite and oxygen concentrations of 7.7×10^{-5} M and 1.2×10^{-3} M, respectively. The concentration of inhibitors varied 1.0×10^{-4} to 1.0×10^{-2} M. Figure 6 shows a plot of reaction rate vs. inhibitor concentration. From the figure, it is evident that the reaction rate is inversely proportional to 0.8, 0.9, and 0.2 powers of manganese chloride, manganese sulfate, and $(OHCH_2CH_2)_3N$, respectively.

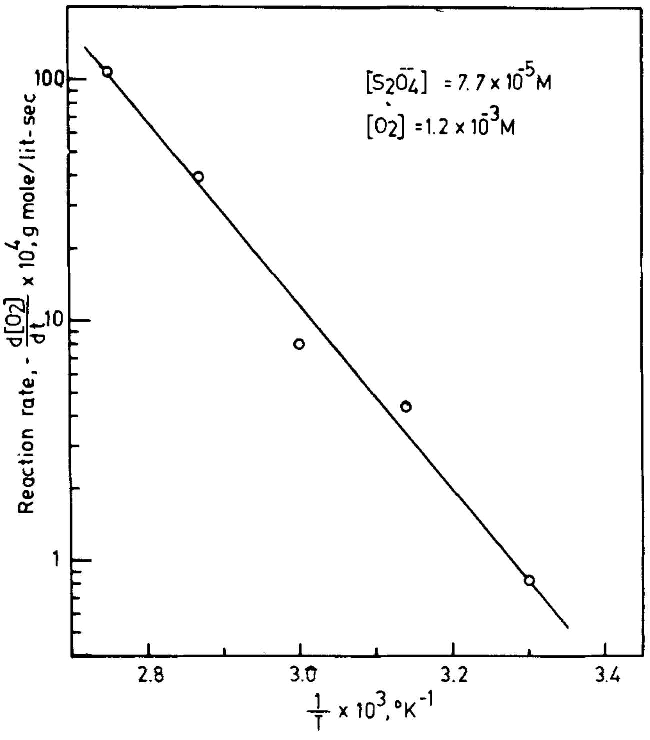


Fig. 5. Effect of temperature on initial reaction rate; pH = 11.

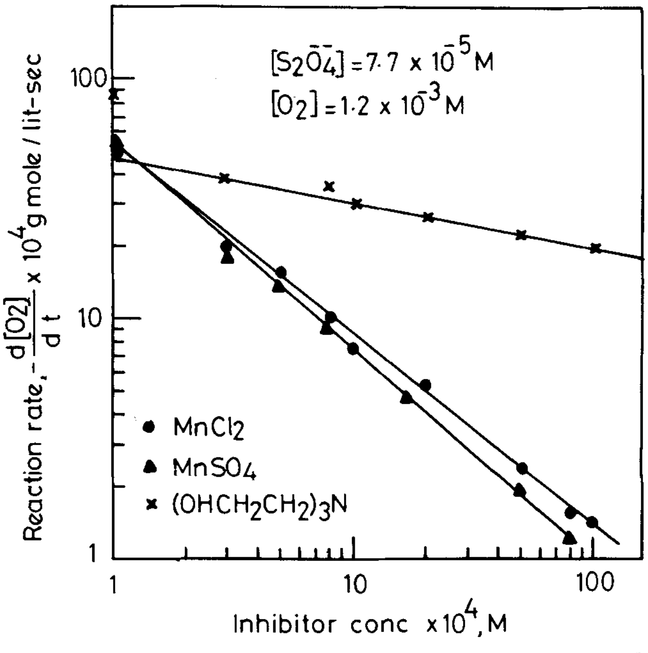
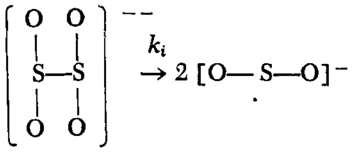


Fig. 6. Effect of inhibitor concentration on reaction rate at 30°C; pH = 8.

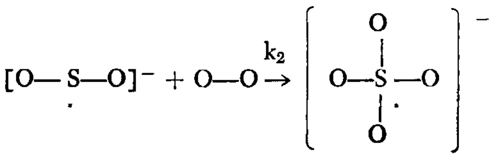
Reaction Mechanism

The results of inhibited study presented above have convincingly shown that the reaction rates of dithionite oxidation are independent of oxygen concentrations, that the reaction order is one power with respect to dithionite concentration, and that the reaction rate follows close to one power relation with respect to manganese compounds and approximately zero power relation with respect to triethanolamine. The results of uninhibited study have shown similar dependencies on oxygen and dithionite.

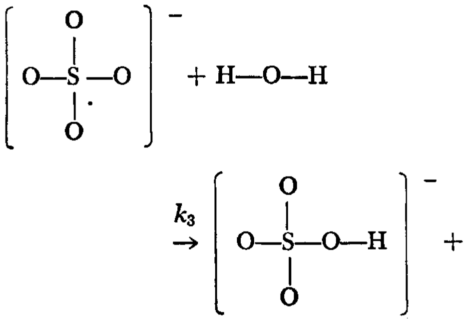
The oxidation of dithionite has all the characteristics of proceeding by radical chains. A mechanism which satisfies established order of reaction with respect to dithionite and oxygen, and in which the initial step was dissociation of dithionite to produce a free radical, is given as



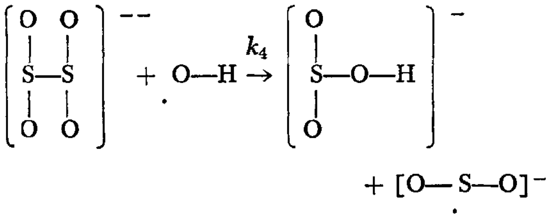
$$\left[\begin{array}{cc} O & O \\ | & | \\ S & \!\!-\!S \\ | & | \\ O & O \end{array}\right]^{--} \xrightarrow{k_i} 2\,[O-\underset{\cdot}{S}-O]^- \qquad \text{(i)}$$



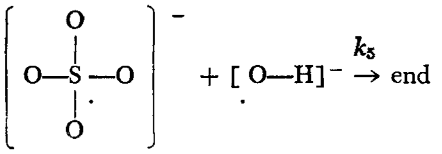
$$[O-\underset{\cdot}{S}-O]^- + O-O \xrightarrow{k_2} \left[\begin{array}{c} O \\ | \\ O-S-O \\ |\cdot \\ O \end{array}\right]^- \qquad \text{(ii)}$$



$$\left[\begin{array}{c} O \\ | \\ O-S-O \\ |\cdot \\ O \end{array}\right]^- + H-O-H \xrightarrow{k_3} \left[\begin{array}{c} O \\ | \\ O-S-O-H \\ | \\ O \end{array}\right]^- + \underset{\cdot}{O}-H \qquad \text{(iii)}$$



$$\left[\begin{array}{cc} O & O \\ | & | \\ S & \!\!-\!S \\ | & | \\ O & O \end{array}\right]^{--} + \underset{\cdot}{O}-H \xrightarrow{k_4} \left[\begin{array}{l} O \\ | \\ S-O-H \\ | \\ O \end{array}\right]^- + [O-\underset{\cdot}{S}-O]^- \qquad \text{(iv)}$$



$$\left[\begin{array}{c} O \\ | \\ O-S-O \\ |\cdot \\ O \end{array}\right]^- + [\underset{\cdot}{O}-H]^- \xrightarrow{k_5} \text{end} \qquad \text{(v)}$$

The formation of $\underset{\cdot}{S}O_2^-$ in solutions of sodium dithionite has been shown from electron paramagnetic resonance signal intensity measurements (Burlamacchi et al., 1969).

The above steps represent a typical chain reaction. The first reaction in an initiation step in which the $\underset{\cdot}{S}O_2^-$ produced acts as active centers (Rinker et al., 1959, 1960; Lynn et al., 1964). Then the propagation step produces another active center $\underset{\cdot}{S}\bar{O}_4$ .The sulfate ion radicals react with water to form $HS\bar{O}_4$ .The OH radical produced reacts with dithionite to produce HSO_3^- ions. These steps have ample precedent in the literature (Bailar et al., 1973; Uri, 1952; Ashmore, 1963). Since the rate of reaction is independent of oxygen concentration, the oxygen addition step is the most rapid and therefore does not limit the overall rate. In aqueous medium, the probability of water influencing the overall rate seems to be remote, thus excluding step (iii) as the controlling step. The active center $\underset{\cdot}{S}O_2^-$ is thus present in low concentration compared to $\underset{\cdot}{O}H$ and $\underset{\cdot}{S}O_4^-$. It may therefore be assumed that the active centers $\underset{\cdot}{S}O_4^-$ and OH are rate limiting, and in in the present scheme, obviously, the only significant termination step is (v). An application of the steady state assumption to radical ion concentrations then leads to

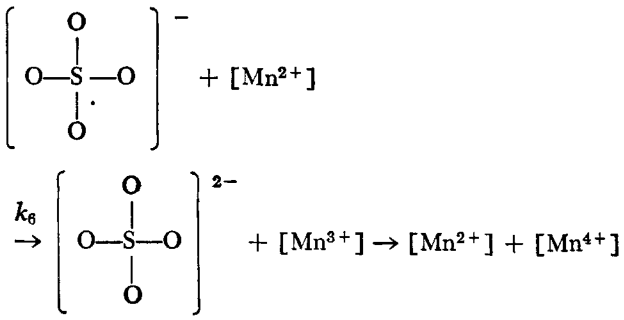
$$-\frac{d[O_2]}{dt} = k\,[S_2O_4^{--}] \qquad (2)$$

where

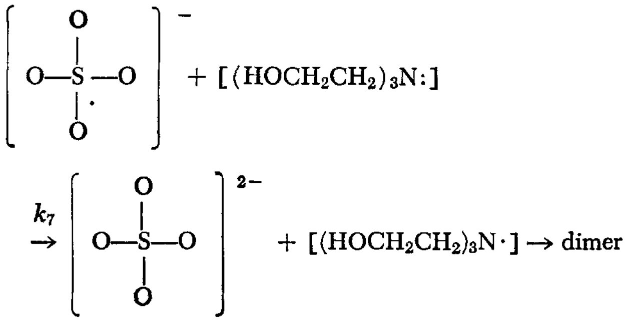
$$k = \frac{k_3k_4}{k_5}\,[H_2O]$$

The reaction of this equation is consistent with the experimental order.

The inhibiting effect of manganese (II) salts or triethanolamine could be visualized by transfer of electron from these species to $\underset{\cdot}{S}O_4^-$ to form inactive SO_4^{--} species, since the $\underset{\cdot}{S}O_4^-$ radical is present in high concentration. Therefore, it is fair to assume that the chain termination proceeds according to



$$\left[\begin{array}{c} O \\ | \\ O-S-O \\ |\cdot \\ O \end{array}\right]^- + [Mn^{2+}] \xrightarrow{k_6} \left[\begin{array}{c} O \\ | \\ O-S-O \\ | \\ O \end{array}\right]^{2-} + [Mn^{3+}] \rightarrow [Mn^{2+}] + [Mn^{4+}] \qquad \text{(vi)}$$



$$\left[\begin{array}{c} O \\ | \\ O-S-O \\ |\cdot \\ O \end{array}\right]^- + [(HOCH_2CH_2)_3N:] \xrightarrow{k_7} \left[\begin{array}{c} O \\ | \\ O-S-O \\ | \\ O \end{array}\right]^{2-} + [(HOCH_2CH_2)_3N\cdot] \rightarrow \text{dimer} \qquad \text{(vii)}$$

Indeed, the chain termination by the inhibitors may be competitive with the reaction (v).

If the chain termination is assumed to be reaction (vi), then the rate expression is given by

$$-\frac{d[O_2]}{dt} = \frac{k'\,[S_2O_4^{--}]}{[I]} \qquad (3)$$

where

$$k' = \frac{k_3k_i}{k_6}\,[H_2O]$$

and $[I]$ = inhibitor concentration.

If we consider both the termination steps (v and vii) to be significant, the rate expression obtained is

$$-\frac{d[O_2]}{dt} = \frac{k_ik_3k_4\,[H_2O]}{k_5k_i + k_4k_7\,[I]} \cdot [S_2O_4^{--}] \qquad (4)$$

It can be assumed that $k_4k_7\,[I] << k_5k_i$, since k_4 is the rate constant for the rate determining step, and $[I]$ is in extremely low concentrations. Therefore

$$-\frac{d[O_2]}{dt} = k''\,[S_2O_4^{--}] \qquad (5)$$

where

$$k' = \frac{k_3 k_4}{k_5}[H_2O]$$

The derived rate expression (3) is in good agreement with the experimental results for manganese chloride and manganese sulfate inhibitors. Rate expression (5) satisfies the experimental findings of triethanolamine inhibited runs. From the results shown in Figure 6, we can conclude that the concentration of $[I]$ is directly proportional to the total concentration of the inhibitor present in the reacting solution. Of the two inhibitors, manganese (II) seems to be a better electron transfer reagent in bringing about this inhibition.

The experimental results have shown that the rate decreases with the increase in pH values. It is possible that dithionite undergoes hydrolysis (Bailar et al., 1973) which would partially remove the dithionite ion from the reaction medium, thereby reducing its effective concentration available for oxidation reaction. The higher the concentration of OH ions, that is, increased values of pH ,the greater would be the extent of hydrolysis reaction, resulting in increased depletion of dithionite concentrations and thus decreasing the rate of oxidation effectively.

NOTATION

$[I]$ = inhibitor concentration, mole/l
k_1, k_2, etc. = rate constants for reaction steps
M = concentration, mole/l
$[O_2]$ = average oxygen concentration, mole/l
r = rates, mole/(l)(s), $-d[O_2]/dt$
$[S_2O_4^{--}]$ = average dithionite concentration, mole/l
t = time, s
T = absolute temperature, °K

LITERATURE CITED

Ashmore, P. G., *Catalysis and Inhibition of Chemical Reactions*, Butterworths, London, England (1963).

Bailar, J. C., H. J. Emelus, S. R. Nyholm, and A. F. Trotman Dickeson, "Comprehensive Inorganic Chemistry," Pergamon Press, Oxford, England (1973).

Burlamacchi, L., G. Guarini, and E. Tiezzi, *Trans. Faraday Soc.*, **65**, 496 (1969).

Committee on Analytical Methods Report, "Essay of Sodium Hydrosulfite," *Am. Dye Stuff. Reptr.*, **46**, 443 (1957).

Dean, J. A., *Langas Hand Book of Chemistry*, 11 ed., McGraw-Hill, New York (1973).

Hartridge, H., and F. J. W. Roughton, "Rate of Oxidation and Reduction of Hemoglobin," *Proc. Roy. Soc. (London)*, **A104**, 376 (1923).

Jhaveri, A. S., and M. M. Sharma, "Absorption of Oxygen in Aqueous Alkaline Solutions of Sodium Dithionite," *Chem. Eng. Sci.*, **23**, 1 (1968).

Klemin, N. G., and P. V. Moriganov, "Stability of Solutions of Sodium Hydrosulfite and Leuco Compounds or Brilliant Violet K in Different Media," *Chem. Abs.*, **55**, 9881a (1958).

Lynn, S., Ph.D. thesis, Calif. Inst. Technol. (1954).

———, R. G. Rinker, and W. H. Corcoran, "The Monomerization Rate of Dithionite Ion in Aqueous Solution," *J. Phys. Chem.*, **68**, 2363 (1964).

Mecco, J. M., "High Temperature Vat Dyeing Baths," *Chem. Abs.*, **48**, 11801 (1954).

Meyer, J., *Z. Anorg. Chem.*, **34**, 43 (1903); cited in Rinker et al. (1960).

Mishra, G. C., and R. D. Srivastava, "Kinetics of Oxidation of Ammonium Sulfite by Rapid Mixing Method," *Chem. Eng. Sci.*, **30**, 1387 (1975).

———, "Homogeneous Kinetics of Potassium Sulfite Oxidation," *ibid.*, **31**, 969 (1976).

Morello, J. A., M. R. Craw, H. P. Constantine, and R. E. Forster, "Rate of Reaction of Dithionite Ion with O_2 in Aqueous Solution," *J. Appl. Physiol.*, **19**, 522 (1964).

Nicloux, M., "Oxidation of Sodium Hyposulfite with Free Oxygen," *Chem. Abs.*, **27**, 3160 (1933).

Pinsent, B. R. W., L. Pearson, and F. J. W. Roughton, "The Kinetics of Combination of Carbon Dioxide with Hydroxide Ion," *Trans. Faraday Soc.*, **52**, 1512 (1956).

Rinker, R. G., T. P. Gordon, D. M. Mason, and W. H. Corcoran, "The Presence of SO_2^- Radical Ion in Aqueous Solution of Sodium Dithionite," *J. Phys. Chem.*, **63**, 302 (1959).

———, and R. R. Sakadia, "Kinetics and Mechanism of the Oxidation of the Dithionite Ion ($S_2O_4^{--}$) in Aqueous Solution," *ibid.*, **64**, 573 (1950).

Roughton, F. J. W., *Techniques of Organic Chemistry*, Vol. VIII, Interscience, New York (1963).

Srivastava, R. D., A. F. McMillan, and I. J. Harris, "The Kinetics of Oxidation of Sodium Sulfite," *Can. J. Chem. Eng.*, **46**, 181 (1968).

Uri, N., "Inorganic Free Radicals in Solution," *Chem. Rev.*, **50**, 375 (1952).

Washburn, *International Critical Tables of Numerical Data*, Vol. V, p. 201, McGraw Hill, New York (1929).

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Adsorption Rate on Molecular Sieving Carbon by Chromatography

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Diffusivities in the micropore and adsorption equilibrium constants were determined for neon, argon, krypton, xenon, nitrogen, methane, ethylene, ethane, propylene, propane, n-butane, and benzene on molecular sieving carbon by chromatographic measurement and moment analysis. Isosteric heat of adsorption was found to be 2.6 times heat of vaporization for the gases examined here. Two separate linear relations were obtained between activation energies of diffusion in micropore and isosteric heats of adsorption for rare gases, methane, and benzene, and for *n*-paraffin and *n*-olefin except methane.

SCOPE

Diffusion as well as adsorption equilibrium in adsorbent particles is important in designing adsorption processes. The possible mechanisms of diffusion in adsorbent particles are classified into three groups in the case of gaseous adsorption. They are diffusion in gas phase of macropores

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