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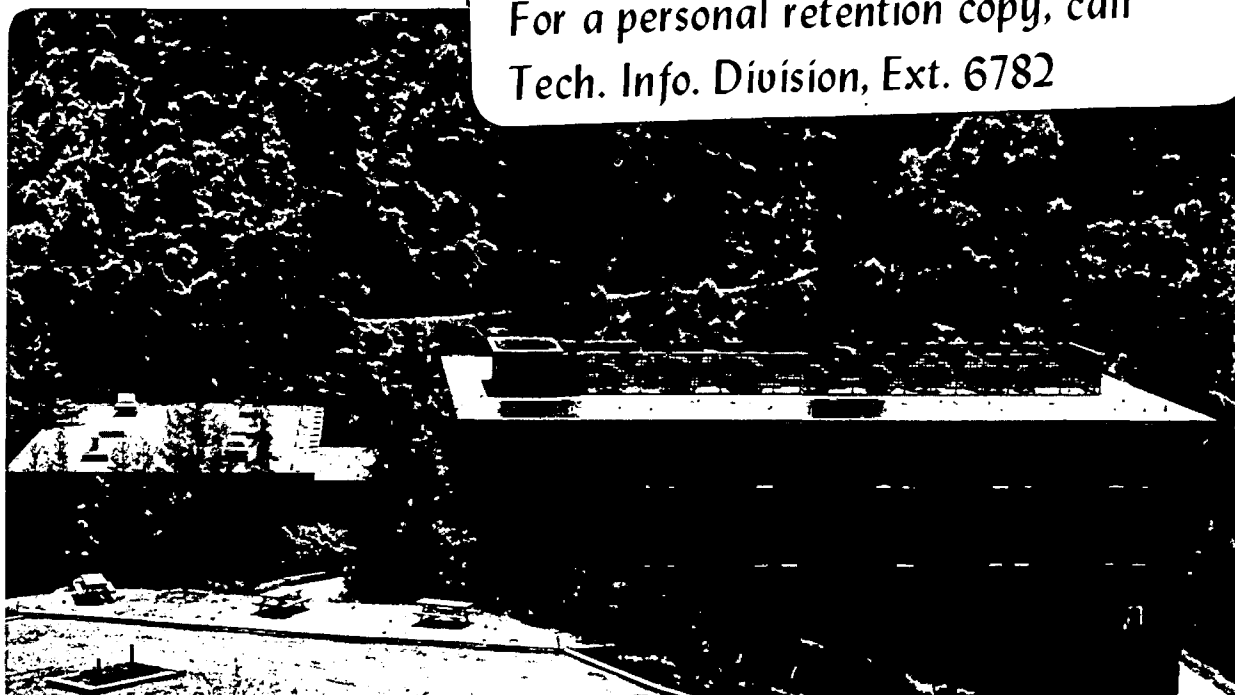
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July 1981

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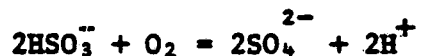
KINETICS OF THE OXIDATION OF BISULFITE ION BY OXYGEN

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The chain reaction between sulfur (IV) and oxygen has been studied in the pH region of 3.0 and 4.7 where bisulfite ion, HSO_3^- , is the principal species. Preliminary measurements were made with a two-phase gas-aqueous system. To avoid mass-transfer problems, the remaining studies were done on a single aqueous phase with no gas phase present and using an oxygen meter to follow the concentration of dissolved oxygen as a function of time. Empirical rate laws were determined for a variety of conditions, including the presence of ethanol, manganous ion and ultra violet light. Without additives the chain appears to be terminated by a bimolecular reaction of chain carriers, since the rate law contains powers of multiples of 1/2. Ethanol inhibits the reaction by chain termination involving a single chain carrier. Manganous ion is a strong catalyst, apparently through the introduction of a new propagating path as well as participation in the initiation. Ultra violet light presumably initiates the chain. The "simplest" resolution of the rate laws into the three components: initiation, propagation and termination is suggested. The data do not establish the identity of the intermediates; other information will be necessary to fix mechanisms of the reaction.

The oxidation of bisulfite ion by oxygen:



is of importance in the lime/limestone processes for removing sulfur dioxide from stack gases of coal-burning power plants as well as in the conversion of atmospheric SO_2 to sulfuric acid, the principal component of acid rain. In the various Flue Gas Desul-

purification processes, there are advantages to be gained in accelerating this oxidation in some cases and in slowing it down in others. Thus a basic understanding of the kinetics of the reaction is a desirable goal.

Since Bäckström (1,2) reported studies of the thermal and photo-oxidation of sodium sulfite solutions, the oxidation of S(IV) species by oxygen has been known to proceed by a chain mechanism. The details of the mechanism, however, are still a matter of much controversy.

A review of the extensive literature (3,4) shows considerable disagreement concerning the rate law and rate constants. Most of the studies were done on sulfite solutions around pH 9. The rate law appears to vary depending on the experimental conditions, and no consistent law has been obtained. The rate has been reported to be proportional to the sulfite concentration and independent of the oxygen concentration (5-7) as well as proportional to both the sulfite and oxygen concentrations (8-10). Although some reports (11) distinguish between the rate laws at sulfite concentrations less than or greater than 0.01 M, both expressions have been reported for both ranges. Dramatic effects of many metal ions (12-14) and organic molecules (15-16) have been cited, however in many cases the role of these additives has not been determined.

The effects of impurities have been well documented, with investigators reporting that consistent results could only be approached after extensive purification (7,9), although even then the rate may have been controlled by impurities. This sensitivity is not surprising since, as a chain reaction, the process involves highly reactive chain carriers.

We have chosen to attack the control of this reaction not by exhaustive purification, which has proven to be a difficult task owing to the large effects produced by some catalysts even in trace amounts, but by attempting to control or define the chain processes by the introduction of known catalysts and inhibitors.

The present studies were carried out at acidities where HSO_3^- is the principal S(IV) species. The dependences of the oxidation rate on the concentration of bisulfite, oxygen and H^+ were studied in the pH range of 3.0 to 4.7. The effects of ethanol, manganese ion and ultraviolet radiation on the rate and above dependences were investigated in order to gain information concerning the feasibility of controlling the oxidation reaction through their presence.

Experimental.

Two Phase Experiments. The rate of O_2 uptake by bisulfite solutions was measured by following the change in the volume of oxygen gas at one atmosphere pressure in a closed, thermostated system at 25°C . The solution was violently agitated using a Vibro Mischer (Ag. für Chemie-Apparatebau, Zürich, Switzerland) which vibrated a perforated plate vertically about 5 mm below the

surface of the liquid at 7200 rpm with ca. 2 mm amplitude. This action forces many small gas bubbles into the solution below the plate and produces almost a froth above the plate. The mixing was further enhanced by a magnetic stirring bar operating on the bottom of the vessel at its maximum speed.

Aliquots of HSO_3^- solution were introduced into the system by means of a pressure equalizing buret.

Single Phase Experiments. In order to eliminate the possibility of gas-liquid mass transfer control, the rate of the disappearance of dissolved oxygen in bisulfite solutions was determined in the liquid phase in the absence of a gas phase using the vessel shown in Figure 1. Concentrations were varied by introducing aliquots of the reagents through the port of the vessel both at the beginning and sometimes during a kinetic run. The initial oxygen concentration was usually 2.6×10^{-4} M but in a few cases was as high as 4.3×10^{-4} M. The direct measurement of the change in the concentration of oxygen with time was achieved by using a Yellow Springs Instrument model 57 oxygen meter and model 5739 probe. This probe consists of a Clark-type membrane covering a gold and AgCl electrode system. Output was recorded on a Leeds and Northrup Speedomax strip chart recorder.

The response time of the oxygen probe was determined by measuring the response of the probe to a sudden change in oxygen concentration. This was accomplished by physically transferring the probe from air saturated water to deoxygenated water. Analyzing these data in terms of a two layer diffusion model (17) indicated that a zero order rate of O_2 disappearance of less than $\sim 3 \times 10^{-6}$ M sec^{-1} could be determined without applying any corrections due to diffusional processes. Larger zero order rates were determined by graphically fitting the decay to a series of plots calculated using a mathematical treatment analogous to that of Benedek and Heideger (17) for the oxygen probe. Rates less than $\sim 2 \times 10^{-5}$ M sec^{-1} were measurable, i.e., appreciably slower than the diffusion control limit.

The pH of the solution was measured with an Orion Research model 601A digital meter and a Markson model 788 combination electrode.

Ultraviolet radiation was produced by a General Electric H100A4/T bulb, with the glass outer casing removed, located approximately 6 cm above the upper solution. The UV light was allowed to shine into the solution through the quartz tube indicated (Figure 1). The intensity of the light on the solution was varied by masking the cross sectional area of the tube close to the light source with a foil perforated with holes. All experiments were at 25°C.

Results

Two Phase Experiments. Figure 2 shows typical data for the

absorption of gaseous O_2 into a bisulfite solution. To maintain pH control, an acetic acid-sodium acetate buffer (pH = 3.7 to 4.7) was used. Since the solution was prepared from oxygen depleted water, the initial rapid drop in volume of oxygen occurs as the solution is quickly being saturated, followed by the slower decrease in volume as the oxidation proceeds. When the data for the first few minutes have subtracted from them values of the smoothly extrapolated remainder of the curve, it is found that the first order rate agrees closely with the rate at which $O_2(g)$ goes into water under the same mixing conditions (insert, Figure 2). The rate of reaction between HSO_3^- and O_2 is shown to be much slower than the mass transfer rate and therefore is kinetically controlled. This rate, on analysis, is found to be 3/2 order in bisulfite concentration during a single experiment (Figure 3).

Rates were not reproducible between runs, varying usually 10 to 20 percent but sometimes much more. Varying the source and purity of the water and the source of bisulfite failed to eliminate the problem. However, comparison of rates between experiments seemed consistent with 3/2 order for HSO_3^- and indicated the rate was inverse first order in H^+ concentration. The oxygen dependence was not tested.

Single Phase Experiments.

Buffered Solutions. Single phase experiments in 0.5 M acetic acid-0.5 M sodium acetate buffer solutions, with HSO_3^- (0.01 to 0.04 M) in large excess over oxygen, gave approximately a zero order dependence on oxygen. The data actually indicated a somewhat less than zero order initially which gradually became zero order as the reaction approached completion. The complete rate law for these buffered solutions at pH ~4.7 appears to be

$$\frac{-d[O_2]}{dt} = \text{Rate} = \frac{k[HSO_3^-]^{3/2}[O_2]^0}{[H^+]} \quad (2)$$

with $k \approx 3 \times 10^{-8} \text{ M}^{1/2} \text{ s}^{-1}$. The addition of 0.2 M $CuSO_4$ increased the rate by a factor of 3 for 0.016 M HSO_3^- in the equimolar buffer.

Buffered Solutions with $MnSO_4$ and Ethanol. A series of experiments at constant $[HSO_3^-]$, buffer and initial $[O_2]$ showed a first order dependence of the rate on concentration of manganous ion (Figure 4, curve A).

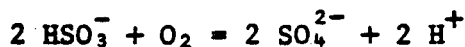
A series of experiments at constant $[HSO_3^-]$, buffer and initial $[O_2]$ gave an inverse dependence of the rate on ethanol concentration as shown in Figure 5 where the reciprocal of the rate, normalized to the value at zero ethanol is plotted. For sulfite solutions Bäckström (1) found an alcohol dependence of the form

$$\text{Rate} \propto \frac{1}{1 + k [\text{EtOH}]} \quad (3)$$

The present results at low ethanol concentrations are probably consistent with this relationship. At higher ethanol, a new reaction path becomes observable (Figure 5). This path is roughly 100 fold slower than the original path and is independent of the ethanol concentration. Further experiments showed that the new path had a 3/2 order dependence on oxygen and increased in rate as the buffer concentration was increased.

Experiments were attempted with both ethanol and manganous ion present. The results conformed to no simple rate law and seemed only understandable if it was assumed that the manganous ion (at $<4 \times 10^{-4}$ M) was being complexed by an impurity in the ethanol. Purification of the ethanol by distillation increased the rate ca. 4 fold but did not eliminate the effect. Because of the apparent participation of the buffer in the rate law, work on buffered systems was discontinued.

Non-buffered Solutions. The net reaction



produces one H^+ per HSO_3^- consumed so it is necessary to add base to the reacting system if the pH is to be kept constant. This was done by addition of NaHCO_3 solution by means of a finely-tipped buret inserted into the solution in the cell (Figure 1). The addition was done manually using the pH meter as an indicator of acidity.

As in the buffered solutions, the rate was initially less than zero order in $[\text{O}_2]$. It was discovered, however, that the rate increased somewhat and became zero order if the reaction was repeated several times by introducing fresh oxygen. For this reason, the following procedure was adopted. After an aliquot of a HSO_3^- solution was injected into the reaction vessel, the $[\text{O}_2]$ was recorded until the oxygen was completely depleted. The solution was then re-oxygenated by bubbling O_2 through it. After the removal of all bubbles, the time dependence of the $[\text{O}_2]$ was again recorded. This procedure was continued until the rate became constant. Usually two complete reactions sufficed.

As the rate was generally zero order in $[\text{O}_2]$ with HSO_3^- in large excess, the constant slope of the $[\text{O}_2]$ vs. time plot made it easy to determine the rate. Because of this circumstance and in order to minimize changes in the solution that could lead to irreproducibility, many of the experiments on the order with respect to HSO_3^- , Mn^{2+} , ethanol and light intensity were done by following the O_2 disappearance long enough to establish the rate, adding a small volume of the species whose order was being determined, following long enough to get the new rate, adding more of

the species, etc. In this way changes in the reaction solution were kept to a minimum and hopefully irreproducibility was minimized.

Figure 6, curve A, and Figure 7, curve A, show the dependence of the rate on the concentrations of bisulfite and hydrogen ion for the oxidation where the pH was controlled by the addition of NaHCO_3 . These data indicate that under the described conditions, the rate is 3/2 order with respect to $[\text{HSO}_3^-]$ and approximately inverse 3/2 order with respect to $[\text{H}^+]$. Also, since the concentration of O_2 was observed to decrease linearly with time, the rate is independent of $[\text{O}_2]$, as in the buffered systems.

An earlier series of experiments using different distilled water, bisulfite and sodium bicarbonate solutions gave a second order dependence on bisulfite concentration and an inverse second order dependence on $[\text{H}^+]$. The rate of reaction was approximately 3 fold less. Since these inconsistencies could possibly be attributed to the introduction of impurities, another method of varying the $[\text{HSO}_3^-]$ was tried. After making a run with a given HSO_3^- concentration, a small volume of ca. 2 M H_2O_2 (prepared from 30% H_2O_2 Mallinckrodt Superoxol) was added to reduce the HSO_3^- concentration by oxidation of a part of it to SO_4^{2-} . The solution was then reoxygenated and run again, etc. These experiments gave a 3/2 order with respect to bisulfite, thus adding support to the first cited rate law, although, as in other cases, it was still not possible to rule out contributions from impurities.

Non-buffered Solution with Ethanol. The effect of ethanol on the non-buffered solutions at constant $[\text{HSO}_3^-]$ is shown in Figure 8, curve A. These data indicate that the effect of ethanol under these conditions is qualitatively the same as in the buffered solutions and is described by equation 3 at low alcohol.

The dependence of the reaction on $[\text{HSO}_3^-]$ and pH in the presence of ethanol were investigated under the conditions shown in Figure 6, curve B, and Figure 7, curve B. The reaction is shown to be second order in $[\text{HSO}_3^-]$ and inverse second order in $[\text{H}^+]$. In all cases the rate was still independent of $[\text{O}_2]$.

Non-buffered Solution with MnSO_4 . The effect of the addition of Mn^{2+} on the non-buffered rate is shown in Figure 4, curve B, where rates corrected for the rate for zero manganous concentration are plotted. This treatment suggests that the manganous catalyzed rate is dependent on $[\text{Mn}^{2+}]^{3/2}$.

In the presence of manganous, the rate is shown to be independent of $[\text{HSO}_3^-]$ (Table I) and inversely proportional to $[\text{H}^+]$ (Figure 7, curve C), while still independent of $[\text{O}_2]$. Therefore, it appears that the rate law for the path catalyzed by Mn^{2+} under these conditions is of the form

$$\text{Rate} = \frac{k[\text{Mn}^{2+}]^{3/2} [\text{HSO}_3^-]^0 [\text{O}_2]^0}{[\text{H}^+]} \quad (4)$$

Non-buffered Solutions with Ultraviolet Light. Analysis of the photooxidation data was made with the assumption that although only part of the solution was illuminated (<50%), a correction for the dark reaction could be made by subtracting the dark rate from the observed rate.

The rate of the oxidation under these conditions was shown to be dependent on $[\text{HSO}_3^-]^{3/2}$ (Figure 6, curve C). Also, it is independent of both $[\text{O}_2]$ and pH over the pH range of 3.0 - 4.2.

Rough measurements with variable intensity of light suggest that the rate depends on the square root of the light intensity (Figure 9, curve A).

Non-buffered Solutions with Ultraviolet Light and Ethanol. As in the case of the thermal oxidation, the rate expression for the photooxidation with ethanol is initially of the form of equation 3. At higher ethanol concentrations, however, the rate is becoming independent of ethanol, as was the case of the buffered solution experiments, indicating the contribution of a new pathway (Figure 8, curve B). Under conditions where the rate was inversely proportional to the ethanol concentration, the rate was independent of pH (3.0 - 4.2) and $[\text{O}_2]$, was second order in $[\text{HSO}_3^-]$ (Figure 6, curve D), and was proportional to the intensity of light (Figure 9, curve B).

Non-buffered Solutions with Ultraviolet Light and MnSO_4 . The photooxidation rate was found to be proportional to the concentration of Mn^{2+} (Figure 4, curve C), independent of $[\text{O}_2]$ and hydrogen ion concentration, and proportional to the intensity of light to the 0.5 power (Figure 9, curve C). The order with respect to HSO_3^- is somewhat greater than 0.5 but less than 1.0 (Figure 10).

Reproducibility. As all other investigators have found, the rate of the reaction is not reproducible within the experimental accuracy, even when careful precautions are taken to use the same chemicals and containers. No satisfactory explanation has been advanced other than the presence of variable amounts of unknown impurities. In our experience, experiments done under as identical conditions as possible usually gave rates within 10% of each, but sometimes varied as much as 20% and infrequently more. Experiments with different solutions of reagents gave greater variations, sometimes as much as several fold. Within a single run in the one-phase system the $[\text{O}_2]$ vs. time plot was quite linear, within the experimental accuracy. The two-phase system showed some irreproducibility in a single run. The use of ethanol as a

terminator and manganous ion as a presumed propagator did not eliminate the irreproducibility. Therefore it is suspected that it arises at least in part in the initiation. The experiments with UV light were not sufficiently well controlled to determine whether the reproducibility was improved.

Discussion. The rate of a chain reaction of long chain length may be represented symbolically by a chain initiating step I, a chain propagating step P, and a chain terminating step T:

$$\text{Rate} = P \left(\frac{I}{T} \right)^{\frac{1}{n}} \quad (5)$$

where n is a small integer, usually 1 or 2. The rates of initiation and termination are equal, i.e., $I = T$. The factor I/T is introduced to cancel from the rate law the concentration(s) of chain carrier(s) which appear in P and T. If the termination involves one chain carrier, n will be unity; if it involves two chain carriers, n will be two. Analysis of rate expressions in terms of equation 5 can help in the determination of the role of catalysts or inhibitors in the chain process.

In the treatment of the data, the effects of Mn^{2+} and ultra-violet light were assumed to be separable from the processes without these additives. Therefore, the rates of the catalyzed reaction paths were determined by correcting the observed rate for contributions from the rate without the additives. It must be understood, however, that this assumption is exact only when the catalyzed reaction is independent of the non-catalyzed reaction or when the catalyst only affects one process (i.e., initiation or propagation) additively while the other processes are unchanged. However, the assumption yields a first order correction if the catalyst is involved in more than one process.

The order of the reaction with respect to a particular reagent was generally determined by changing the concentration through additions of the reagent. Exceptions were HSO_3^- in the two-phase experiments and O_2 in the single-phase experiments, where the order could be determined from the change in concentration during a single run. For the usual case, i.e., where reagent was added, there was always the possibility of the presence in the reagent of an impurity which entered into the rate, with the consequence that a false order for the reagent would be obtained. In an attempt to guard against this possibility different sources of each reagent were tried with no evidence of a significant effect within the general level of reproducibility of the rate, except for the case of ethanol in the presence of Mn^{2+} cited earlier. Yet the possibility that the orders might be flawed by impurities must be kept in mind. Accepting these assumptions in the treatment of the data, a qualitative explanation of the results can be obtained by analyzing the rate laws for the various conditions in terms of equation 5. A possible analysis which

utilizes the minimum number of paths is shown in Table II.

The discerning reader will notice that the alcohol dependence given in equation (3) is not that predicted from the proper combination of the second and third rate laws of Table II. The difference is small, however, and probably not detectable within the reproducibility of the experiments. The inability of the analysis to explain completely the bisulfite dependence shown in rate law 7 may be due to over-simplification. A contribution of another term in the propagation process which is proportional to $[\text{HSO}_3^-][\text{X}]$ (i.e., the propagation term for the rate laws without the presence of Mn^{2+}), may not be negligible. The addition of this term would produce a gradual increase in the order of the rate with respect to $[\text{HSO}_3^-]$ from 0.5 to 1.5 with increasing $[\text{HSO}_3^-]$. This is not unlike the effect shown in Figure 10.

The most serious discrepancy in Table II occurs in rate law 2 where the $[\text{H}^+]$ dependence measured is $-3/2$ while that predicted is -1 , as found in rate law 1. Unless the results are in error, the system is more complex than pictured.

The suggested breakdown of the rate laws in Table II into initiation, propagation and termination is of course not unique, but rather the simplest interpretation for a chain mechanism. For example, wherever an $[\text{X}][\text{X}]$ termination was used, it could equally well be an $[\text{X}][\text{Y}]$ termination involving two intermediates. The propagation term would then be the square root of the product of two of the propagating steps - one involving $[\text{X}]$ and the other $[\text{Y}]$. Further, the concentration terms in the rate law that are to be attributed to each of the three terms is not unique, but the choice given seems the most reasonable of the possibilities. The selection of a termination step involving two chain carriers is strongly suggested whenever the rate law contains an odd multiple of one half order, corresponding to $n = 2$, although other sources of such orders are possible in principle. If there are no half orders in the rate law it is likely, although not necessary, that the termination involves only a single chain carrier.

These results suggest the following:

Ultraviolet light appears to affect only the initiation. This is indicated by the change in the dependence on the intensity of light from 0.5 to 1.0 order upon the addition of ethanol, a known terminator (1) which switches the termination from $[\text{X}][\text{X}]$ to $[\text{EtOH}][\text{X}]$ and n from 1 to 2.

The $3/2$ order in $[\text{Mn}^{2+}]$ suggests that manganous is involved in both the initiation and propagation, although other explanations involving more complex mechanisms and higher order terms are possible.

In the resolution of the rate laws of Table II into their component parts, intermediates (chain carriers) have always been symbolized by X. The simplest interpretation would have X the same species for all of the rate laws. Assuming this to be the case, it is possible to combine the rate laws of Table II into a single master rate law that allows comparison of a calculated

rate with the experimental rate for each data set. The irreproducibility of the experiments, however, makes such a procedure questionable. The results are generally consistent qualitatively with such an analysis, but there is not perfect quantitative agreement.

Of course there may be impurities involved in some of the steps in Table II, and in particular it seems likely that some impurity participates in the initiation step of the first three rate laws.

From the analysis of the rate laws in Table II one can write plausible mechanisms for the reaction, but always more than one. The chain initiation reaction is in no case defined by the rate law, and the chain carriers cannot be uniquely fixed from the rate law. Therefore no attempt will be made to give mechanisms until further information is available to limit the possibilities.

Acknowledgement

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Literature Cited

1. Bäckström, H. L. J. Am. Chem. Soc. 1927, 49, 1460.
2. Alyea, H. N.; Bäckström, H. L. J. Ibid 1929, 51, 90.
3. The older literature, up to 1949, is analyzed in Gmelins Handbuch Der Anorganischen Chemie 1963, 9, 1293-1514.
4. Most of the recent literature is cited by J. L. Hudson in "Sulfur Dioxide Oxidation in Scrubber Systems," EPA-600/7-80-083, April, 1980.
5. Reinders, W.; Dingemans, P. Rec. Trav. Chim. 1934, 53, 231.
6. Titoff, A. Z. Physik. Chem. 1903, 45, 641.
7. Winkelmann, V. D. Z. Elektrochem. 1955, 59, 891.
8. Schultz, J. S.; Gaden, E. L. Ind. Eng. Chem. 1956, 48, 2209.
9. Fuller, E. C.; Crist, R. H. J. Am. Chem. Soc. 1941, 63, 1644.
10. Yagi, S.; Inoue, H. Chem. Eng. Sci. 1962, 17, 411.
11. Srivastava, R. D.; McMillan, A. F.; Harris, I. J. Can. J. Chem. Eng. 1968, 46, 181.
12. Hoather, R. C.; Goodeve, C. F. Trans. Faraday Soc. 1934, 30, 626, 1149.
13. Chen, T-I.; Barron, C. H. Ind. Eng. Chem. Fundam. 1972, 11(4), 466.
14. Alper, E. Trans. Inst. Chem. Eng. 1973, 51(2), 159.
15. Altwicker, E. R. Trans. Inst. Chem. Eng. 1977, 55, 281.
16. Mathews, J. H.; Weeks, M. E. J. Am. Chem. Soc. 1917, 39, 635.
17. Benedek, A. A.; Heideger, W. J. Water Res. 1970, 4, 627.

Table I

Dependence of Rate on $[\text{HSO}_3^-]$ with $[\text{Mn}^{2+}] = 9.14 \times 10^{-6}$ M.

$[\text{HSO}_3^-] \times 10^3$ M	Rate(observed) $\times 10^7$ M sec $^{-1}$	Rate(without Mn^{2+}) $\times 10^8$ M sec $^{-1}$	Rate(with Mn^{2+}) $\times 10^7$ M sec $^{-1}$
3.47	1.50	0.85	1.41
4.65	1.48	1.30	1.35
8.47	1.95	4.50	1.50
8.96	1.95	5.70	1.38

Table II

Possible Interpretation of the Rate Laws

Conditions	Rate Law	Analysis
1) Buffered solutions	$\text{Rate} \propto \frac{[\text{HSO}_3^-]^{3/2} [\text{O}_2]^0}{[\text{H}^+]}$	$\begin{aligned} I &\propto [\text{HSO}_3^-][\text{H}^+]^{-2} \\ P &\propto [\text{HSO}_3^-][\text{X}] \\ T &\propto [\text{X}][\text{X}] \end{aligned}$
2) Non-buffered solutions	$\text{Rate} \propto \frac{[\text{HSO}_3^-]^{3/2} [\text{O}_2]^0}{[\text{H}^+]^{3/2}}$	$\begin{aligned} I &\propto [\text{HSO}_3^-][\text{H}^+]^{-2} \\ P &\propto [\text{HSO}_3^-][\text{X}] \\ T &\propto [\text{X}][\text{X}] \end{aligned}$
3) Non-buffered solutions with ethanol	$\text{Rate} \propto \frac{[\text{HSO}_3^-]^2 [\text{O}_2]^0}{[\text{H}^+]^2 [\text{EtOH}]}$	$\begin{aligned} I &\propto [\text{HSO}_3^-][\text{H}^+]^{-2} \\ P &\propto [\text{HSO}_3^-][\text{X}] \\ T &\propto [\text{EtOH}][\text{X}] \end{aligned}$
4) Non-buffered solutions with MnSO_4	$\text{Rate} \propto \frac{[\text{Mn}^{2+}]^{3/2} [\text{HSO}_3^-]^0 [\text{O}_2]^0}{[\text{H}^+]}$	$\begin{aligned} I &\propto [\text{Mn}^{2+}][\text{H}^+]^{-2} \\ P &\propto [\text{Mn}^{2+}][\text{X}] \\ T &\propto [\text{X}][\text{X}] \end{aligned}$
5) Non-buffered solutions with UV light	$\text{Rate} \propto I_{\text{hv}}^{1/2} [\text{HSO}_3^-]^{3/2} [\text{O}_2]^0$	$\begin{aligned} I &\propto I_{\text{hv}} [\text{HSO}_3^-] \\ P &\propto [\text{HSO}_3^-][\text{X}] \\ T &\propto [\text{X}][\text{X}] \end{aligned}$
6) Non-buffered solutions with UV light and ethanol	$\text{Rate} \propto \frac{I_{\text{hv}} [\text{HSO}_3^-]^2 [\text{O}_2]^0}{[\text{EtOH}]}$	$\begin{aligned} I &\propto I_{\text{hv}} [\text{HSO}_3^-] \\ P &\propto [\text{HSO}_3^-][\text{X}] \\ T &\propto [\text{EtOH}][\text{X}] \end{aligned}$
7) Non-buffered solutions with UV light and MnSO_4	$\text{Rate} \propto I_{\text{hv}}^{1/2} [\text{Mn}^{2+}] [\text{HSO}_3^-]^{0.8} [\text{O}_2]^0$	$\begin{aligned} I &\propto I_{\text{hv}} [\text{HSO}_3^-] \\ P &\propto [\text{Mn}^{2+}][\text{X}] \\ T &\propto [\text{X}][\text{X}] \end{aligned}$

Figure 1

Reaction vessel used for single phase experiments.

Figure 2

Typical gas volume data for the absorption of gaseous O_2 into a bisulfite solution. Sodium acetate-acetic acid buffer at 0.5 M; initial $[HSO_3^-] = 0.012$ M; $[O_2] = 1.23 \times 10^{-3}$ M. Insert \circ - O_2 absorption into H_2O , \bullet -initial O_2 absorption into HSO_3^- solution.

Figure 3

Plot indicating $3/2$ order dependence of rate on $[HSO_3^-]$ for the reaction: $HSO_3^- + O_2$ in 0.5 M acetic acid-sodium acetate buffer. Initial $[HSO_3^-] = 0.012$ M; $[O_2] = 1.23 \times 10^{-3}$ M.

Figure 4

Effect of Mn^{2+} on the rate of oxidation of HSO_3^- . Curve A: 0.25 M acetic acid - 0.25 M sodium acetate buffer, 0.02 M HSO_3^- , 1.8×10^{-4} M O_2 , rate without Mn^{2+} (R_0) = 9.6×10^{-7} M s $^{-1}$. Line of slope 1.0 indicated. Curve B: 9.0×10^{-3} M HSO_3^- , pH 4.2, $R_0 = 5.70 \times 10^{-8}$ M s $^{-1}$. Line of slope 1.5 indicated. Curve C: 1.04×10^{-2} M HSO_3^- , pH 3.00, $R_0 = 2.40 \times 10^{-7}$ M s $^{-1}$. Line of slope 1.0 indicated.

Figure 5

Effect of ethanol on the rate of the oxidation of HSO_3^- in a 0.25 M acetic acid-0.25 sodium acetate buffer. $[HSO_3^-] = 0.02$ M; $[O_2] = 1.8 \times 10^{-4}$ M. Rate without ethanol (R_0) = 8.7×10^{-7} M s $^{-1}$.

Figure 6

Dependence of the rate of oxidation on $[\text{HSO}_3^-]$. Curve A - O: pH 4.2, line of slope 3/2 indicated. Curve B: pH 4.2, 1.28×10^{-3} M EtOH, line of slope 2.0 indicated. Curve C - \square : pH 3.90, line of slope 1.5 indicated. Dark reaction negligible. Curve D: pH 3.90, 5.84×10^{-3} M EtOH, line of slope 2.0 indicated. Dark reaction negligible.

Figure 7

Dependence on pH of the rate of oxidation of HSO_3^- . Curve A: 8.7×10^{-3} M HSO_3^- , line for $[\text{H}^+]^{-1.5}$ dependence indicated. Curve B: 6.94×10^{-2} M HSO_3^- , 2.51×10^{-3} M EtOH, line for $[\text{H}^+]^{-2}$ dependence indicated. Curve C: 8.47×10^{-3} M HSO_3^- , 8.80×10^{-6} M Mn^{2+} , line for $[\text{H}^+]^{-1}$ dependence indicated. Ordinate is rate minus rate without Mn^{2+} (R_0) where $R_0 = 2.8 \times 10^{-14} [\text{H}^+]^{-3/2}$.

Figure 8

Effect of ethanol on the rate of oxidation of HSO_3^- . Curve A: 3.76×10^{-2} M HSO_3^- , pH 4.2, line of slope 1.0 indicated. Rate without ethanol (R_0) = 4.65×10^{-7} M s⁻¹. Curve B: 1.97×10^{-2} M HSO_3^- , pH 3.90, line of slope 1.0 indicated, $R_0 = 8.7 \times 10^{-7}$ M s⁻¹.

Figure 9

Dependence of the rate of photooxidation of HSO_3^- on the intensity of ultraviolet light. Curve A: 3.20×10^{-2} M HSO_3^- , pH 3.90, line of slope 0.5 indicated. Dark reaction negligible.

Curve B: 5.84×10^{-3} M EtOH, 4.36×10^{-2} M HSO_3^- , pH 3.90, rate without ethanol (R_0) = 2.0×10^{-6} M s⁻¹, line of slope 1.0 indicated. Dark reaction negligible. Ordinate is $10^7 (1/R - 1/R_0)^{-1}$.

Curve C: 6.7×10^{-6} M Mn^{2+} , 1.00×10^{-2} M HSO_3^- , pH 3.00, dark rate = 2.83×10^{-7} M s⁻¹, slope of 0.5 indicated. Ordinate is 10^7 (rate - dark rate).

Figure 10

Dependence on $[\text{HSO}_3^-]$ of the rate of photooxidation in the presence of Mn^{2+} . $[\text{Mn}^{2+}] = 6.7 \times 10^{-6}$ M; pH = 3.00. Slope is equal to 0.8.

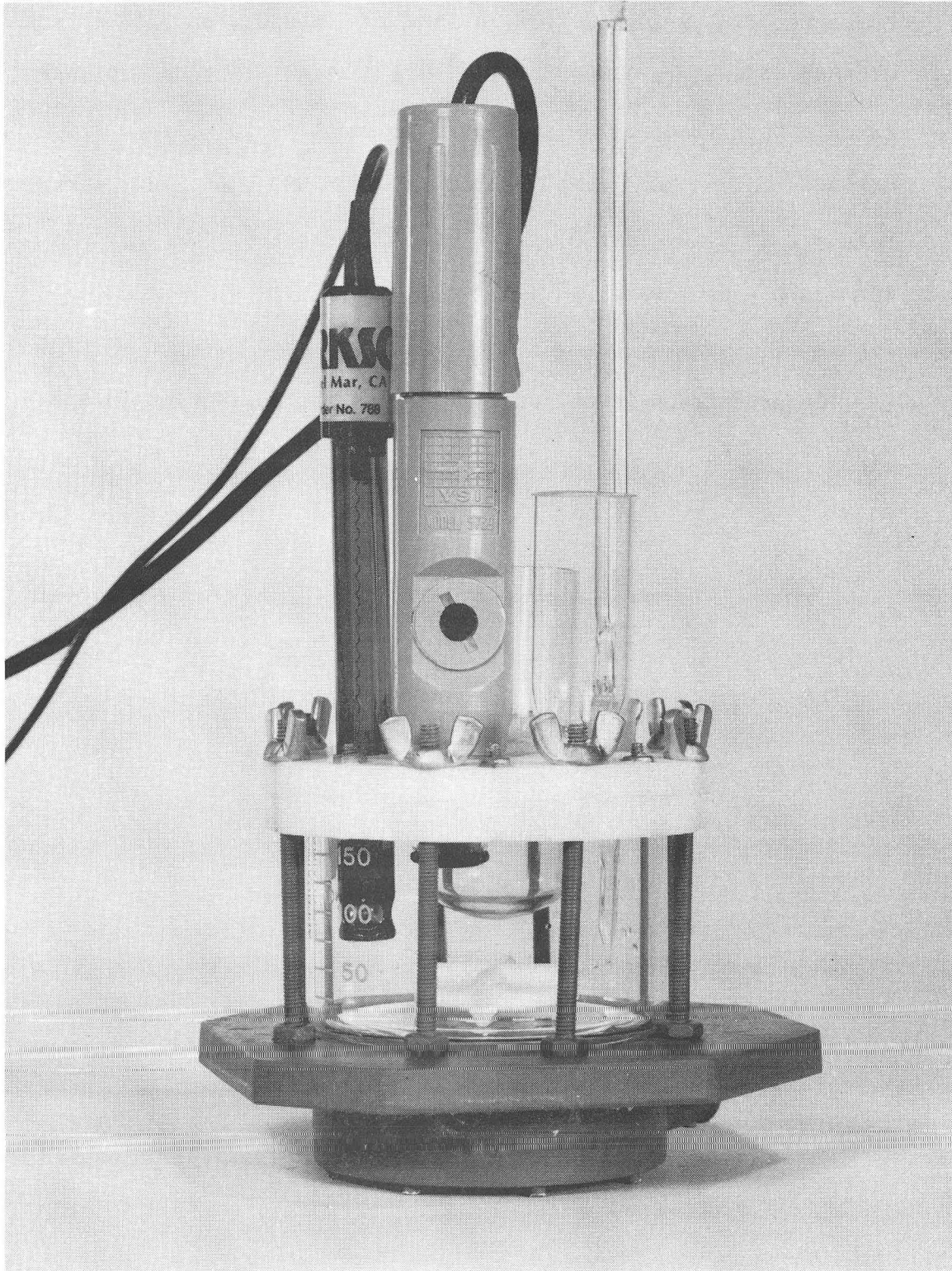


Figure 1

CBB 813-2787

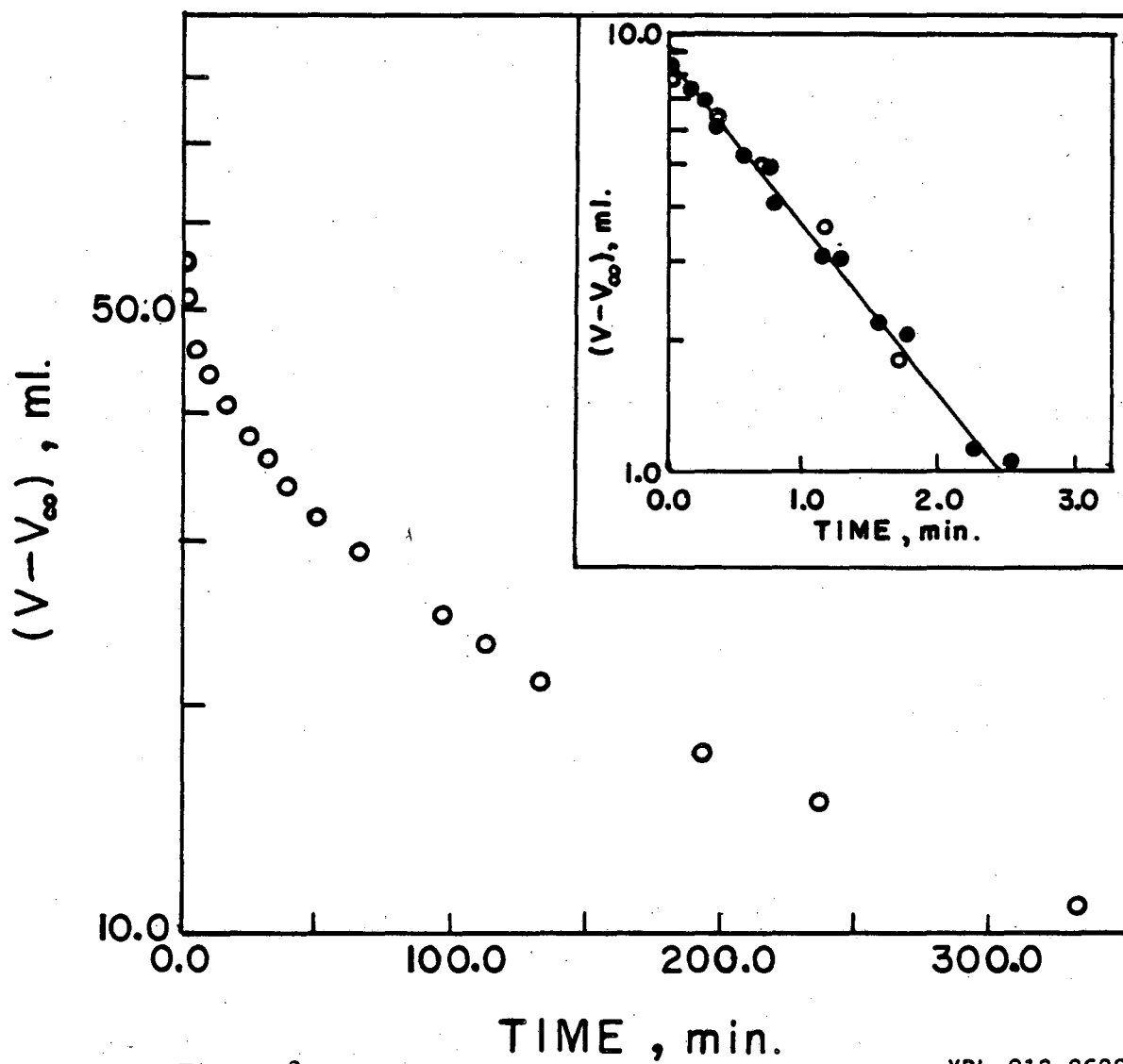


Figure 2

XBL 813-8698

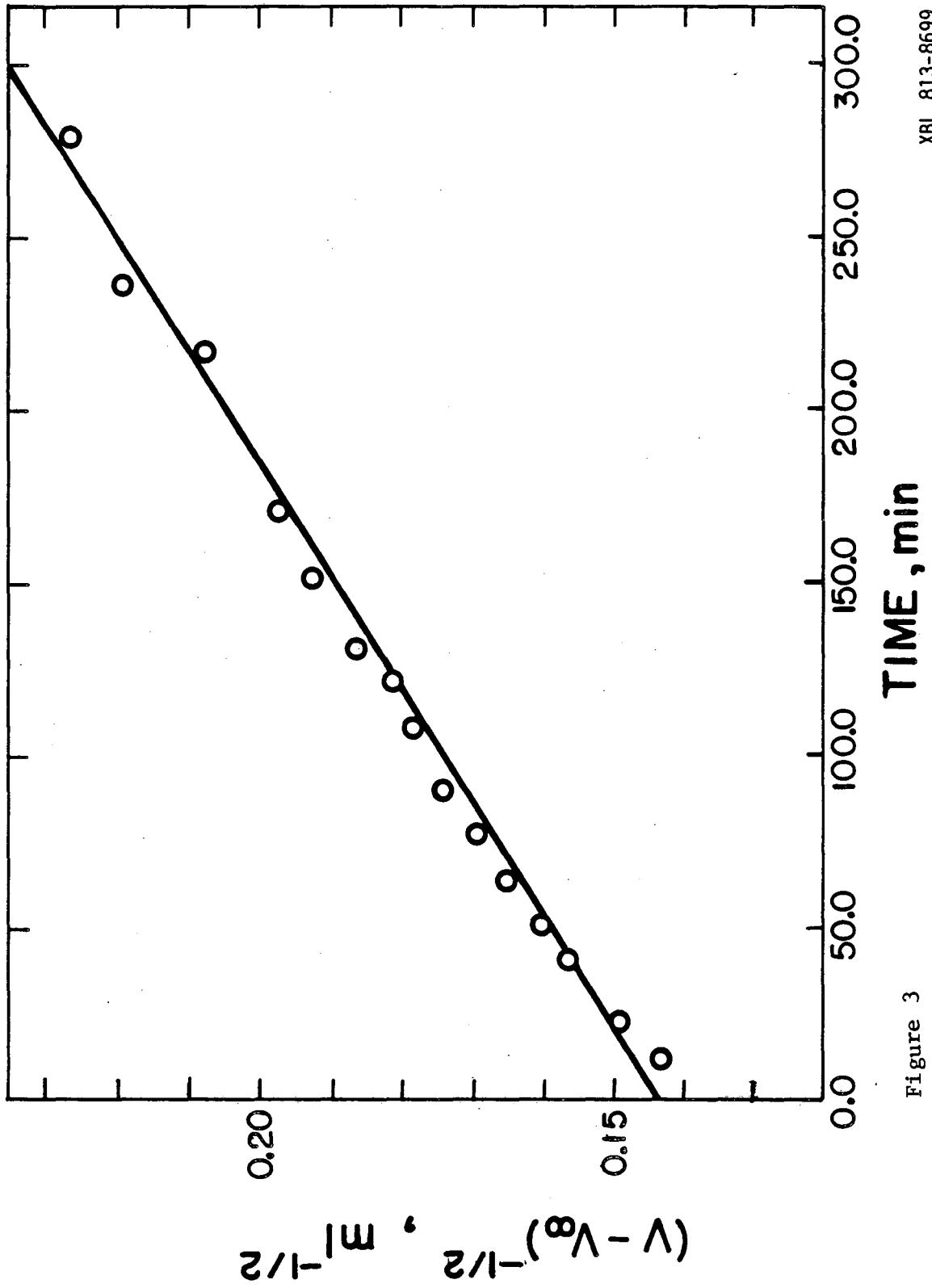


Figure 3

XBL 813-8699

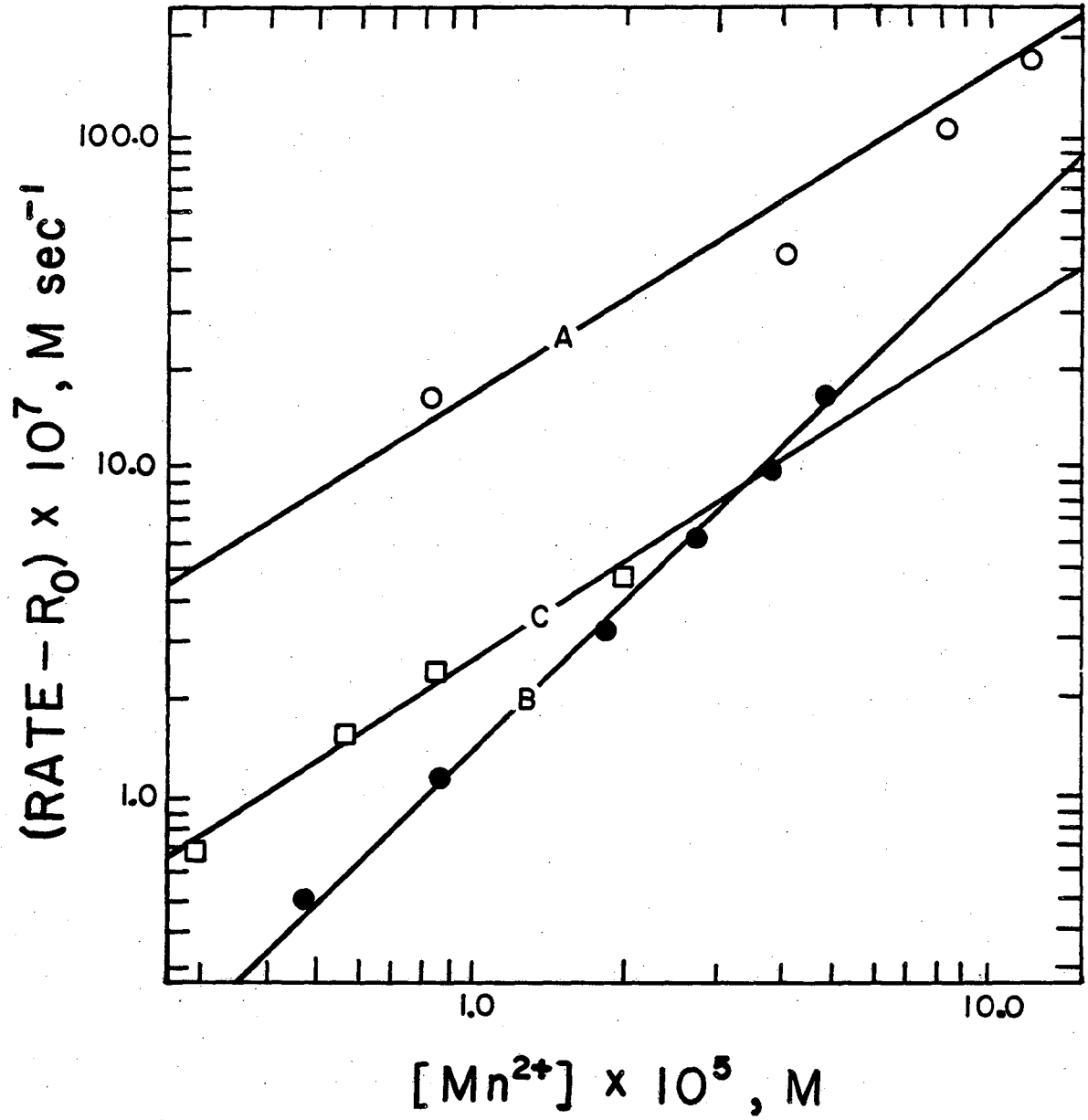


Figure 4

XBL 8112-12933

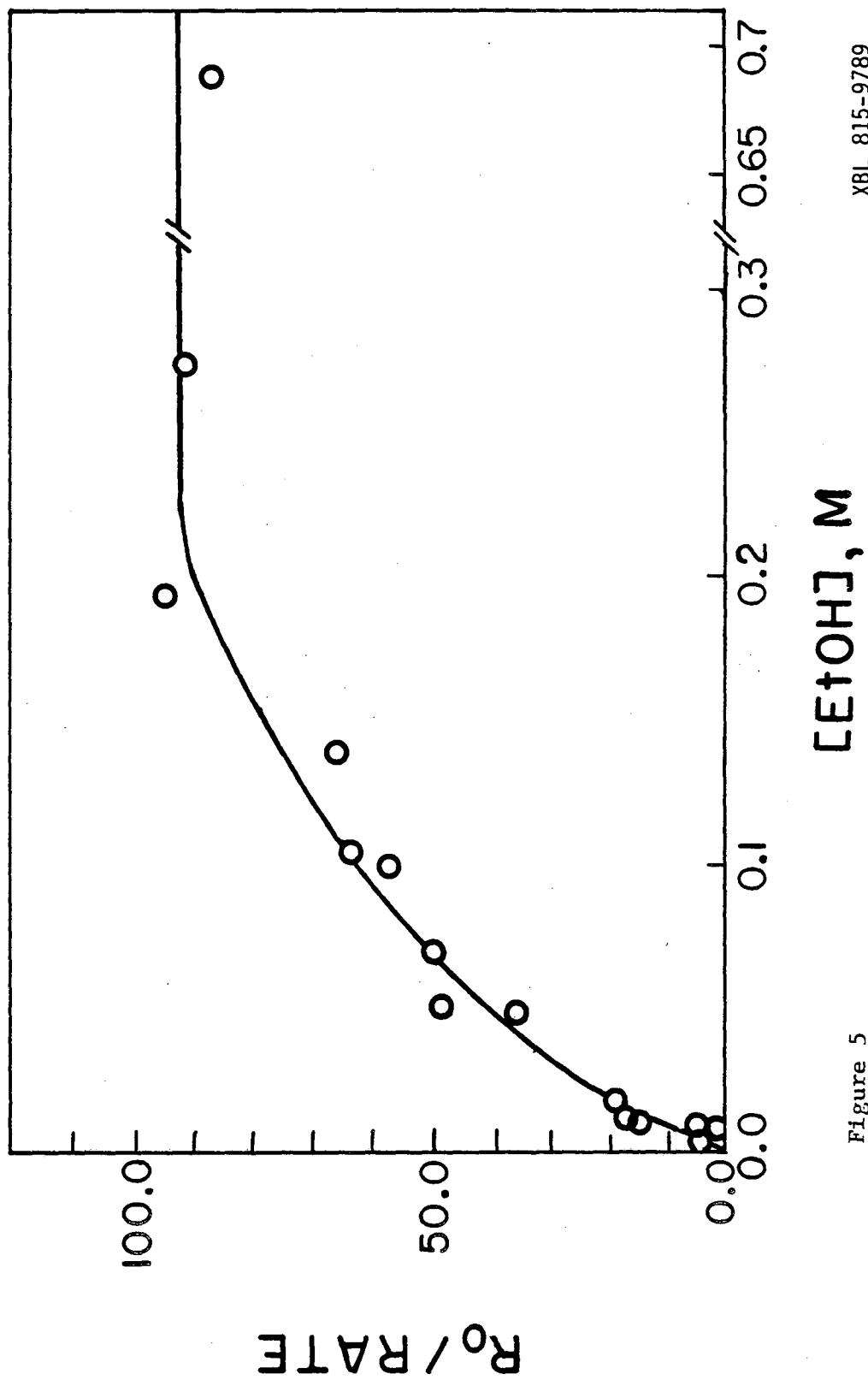


Figure 5

XBL 815-9789

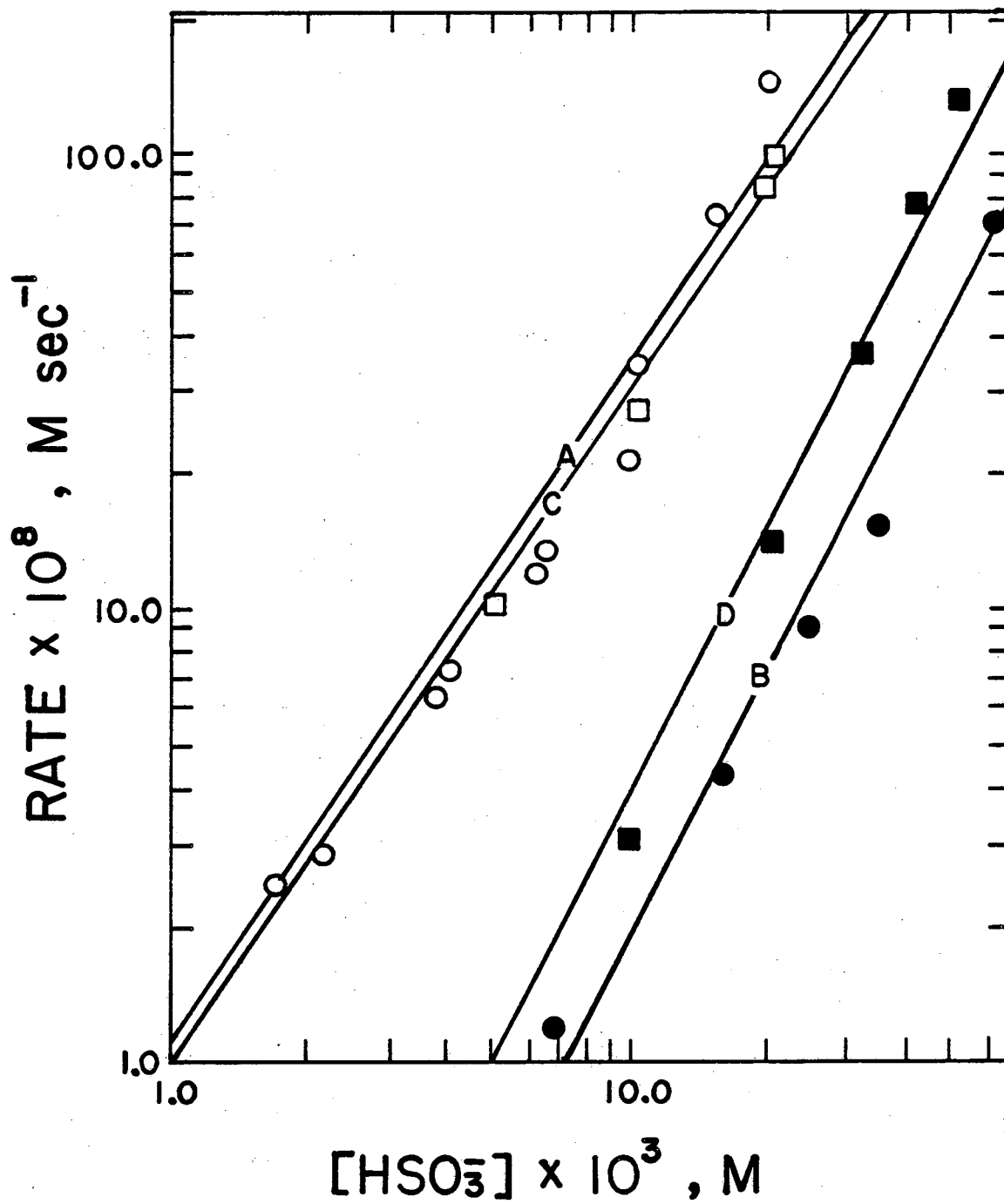


Figure 6

XBL 8112-12934

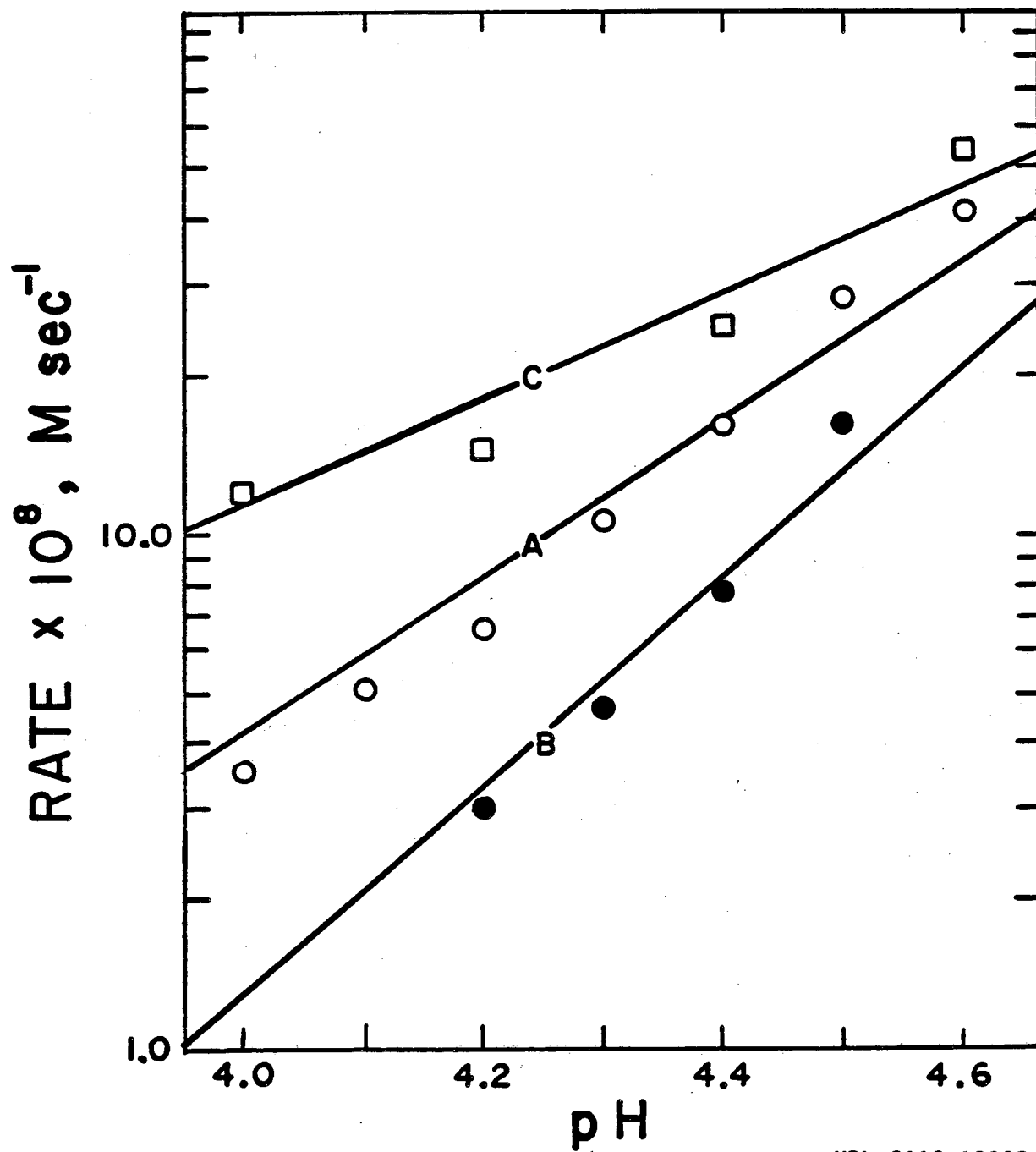


Figure 7

XBL 8112-12935A

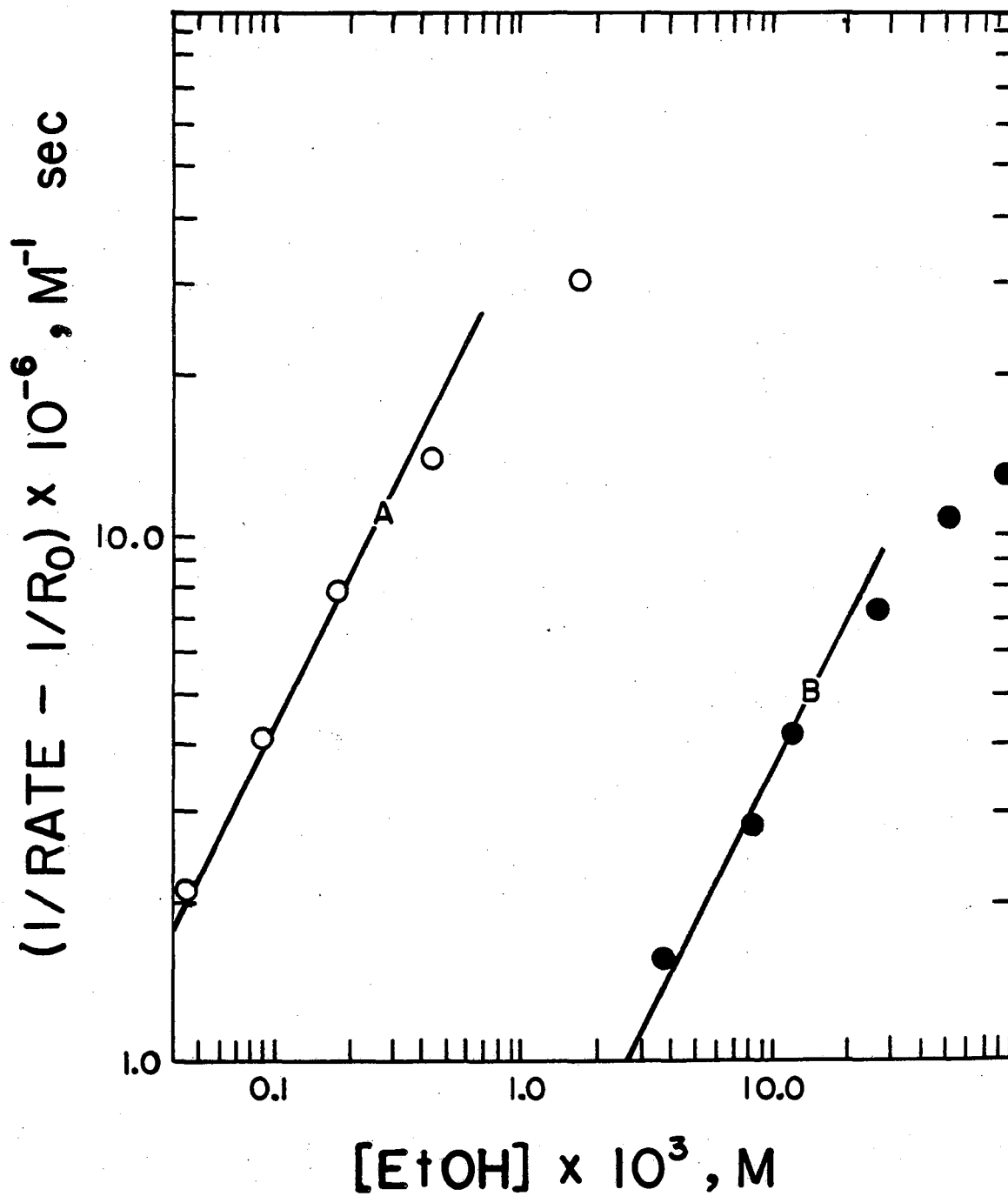


Figure 8

XBL 8112-12936

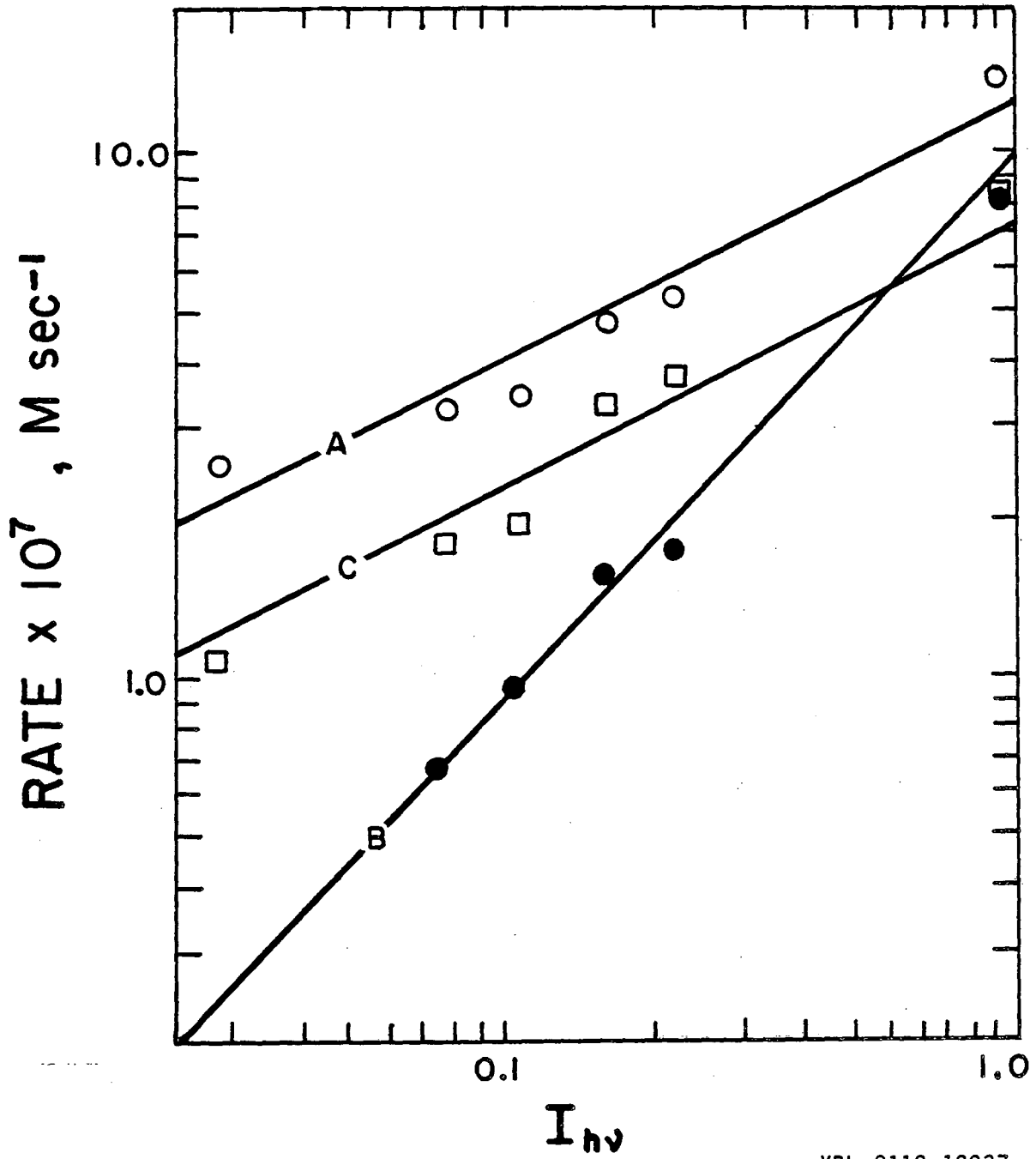


Figure 9

XBL 8112-12937

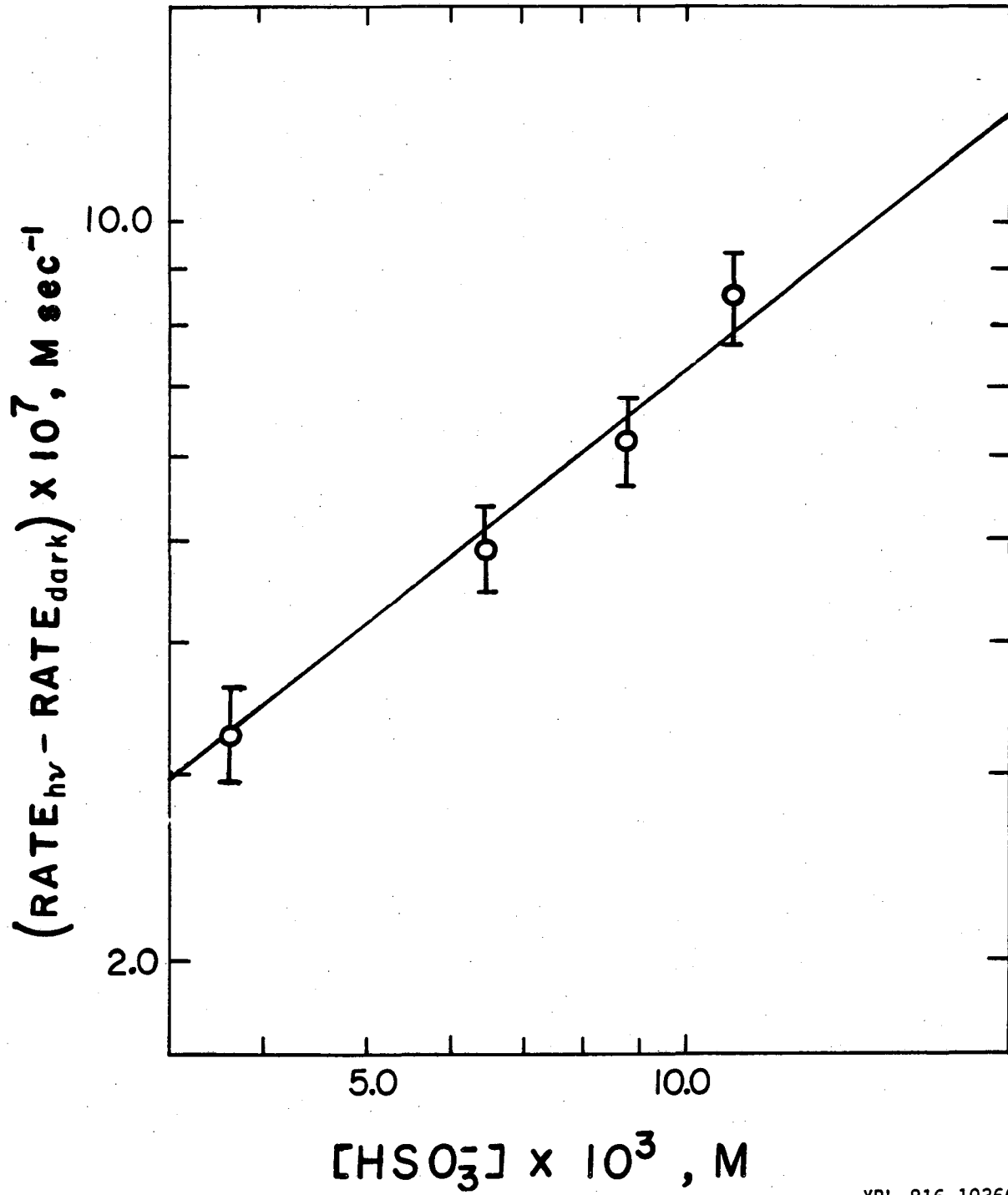


Figure 10

XBL 816-10366

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