

Kinetics and Mechanism of the Oxidation of HSO_3^- by O_2 . 1. The Uncatalyzed Reaction

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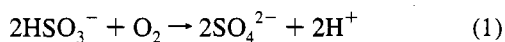
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The reaction between S(IV) and O_2 in aqueous solution is of importance because of its involvement in flue gas desulfurization processes and in acid rain formation. Despite considerable research, a complete mechanism for the reaction has not been established. In this work a detailed study of the uncatalyzed reaction in the region of pH 4.5 has been carried out. The overall rate law was found to be $-\text{d}[\text{O}_2]/\text{dt} = k_{\text{obs}} [\text{HSO}_3^-]^2 [\text{H}^+]^{-2} [\text{O}_2]^0$ with k_{obs} of $3.6 \times 10^6 \text{ M s}^{-1}$ at 25 °C and ionic strength 0.05 M. The yield of the intermediate $\text{S}_2\text{O}_7^{2-}$ formed during the reaction has been determined over the pH range 4.1–6.3. By comparison with the yield of $\text{S}_2\text{O}_7^{2-}$ produced in the reaction of HSO_3^- with HSO_5^- , it is concluded that $\text{S}_2\text{O}_7^{2-}$ formed in the HSO_3^- – O_2 reaction comes from the reaction between HSO_5^- and HSO_3^- , and therefore HSO_5^- must be an intermediate in the HSO_3^- – O_2 reaction in this pH region. From the above yields it is concluded that 60% of the reaction proceeds through the intermediate HSO_5^- . A detailed mechanism consistent with the overall rate law of the reaction has been proposed. A key feature is the proposal that the chain initiation occurs through the reaction of HSO_5^- with HSO_3^- to form $\text{SO}_3^{\cdot-}$ and $\text{SO}_4^{\cdot-}$. In order to study the individual rate laws for the initiation, propagation and termination reactions, a relaxation technique was applied. In these experiments, the reaction at a steady state rate was perturbed by suddenly introducing a change in the concentration of HSO_3^- or H^+ , and the relaxation of the reaction to the new steady state was recorded. Treatment of these experimental data not only confirmed the HSO_3^- dependence of the rates of initiation, propagation, and termination in the proposed mechanism but also gave the pH dependence of these reactions. A study of the remarkable inhibitory effect of methanol produced strong support for the proposed initiation reaction. The effect of the introduction of chain initiator $\text{S}_2\text{O}_8^{2-}$ was also found to be consistent with the mechanism. Relative values of rate constants of reactions in the proposed mechanism have been evaluated from the present experimental data. Evaluation of absolute values of these rate constants requires one additional piece of experimental information, which, depending on the choice, yields a range of values. An arbitrary choice is used to give rough values of the rate constants for initiation, propagation and termination and typical values for the steady state concentrations of chain carriers. The chain length appears to be about one thousand at pH 4.5, independent of the bisulfite concentration.

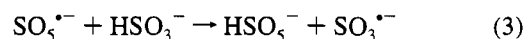
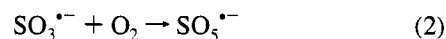
Introduction

The oxidation of aqueous S(IV) by oxygen has been investigated for nearly 100 years, but a complete understanding of the mechanisms of the reaction has not been achieved. Westley¹ has compiled a bibliography of some 320 papers and reports dealing with the reaction extending from 1897 through 1981. The reaction is of importance in flue gas desulfurization² and acid rain^{3–5} as well as in photography, polarography, etc. At moderate pH the stoichiometry corresponds closely to



The present paper is concerned with the mechanism of the uncatalyzed reaction in the pH region where bisulfite ion is the predominant S(IV) species in aqueous solution. No attempt will be made to review the vast literature, but reference will be made to studies that have contributed importantly to the elucidation of the mechanism of the reaction.

The first serious mechanistic study was done by Bäckström and co-workers.^{6–10} On the basis of the strong effect of many inhibitors, Bäckström⁶ suggested that the reaction was a chain process. In addition he suggested,¹⁰ without proof, that the reaction goes through the peroxy intermediate HSO_5^- (peroxy-monosulfate ion). In a classic study, he and Alyea⁸ determined a minimum value of 54 000 for the chain length at pH ~8.8 where sulfite ion is the dominant S(IV) species. Bäckström⁹ hypothesized the following mechanism for the chain propagation part of the reaction:



By analogy to hydrogen peroxide, he suggested that HSO_5^- would react rapidly with HSO_3^- to give sulfate and hydrogen ions. From the square root dependence of the photochemical rate on light intensity, he concluded that the termination reaction was between two chain carriers.⁹

It was shown by Halperin and Taube¹¹ using ¹⁸O tracer that the great majority, if not all, of the oxygen atoms of the O_2 end up in sulfate ions.

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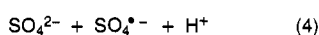
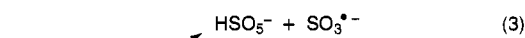
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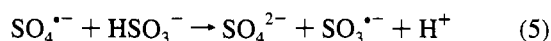
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Many mechanisms or partial mechanisms have been proposed for the reaction, mostly with little experimental evidence. With the advent of pulse radiolysis and flash photolysis techniques it became possible to obtain direct evidence on the formulas of the chain carriers. Dogliotti and Hayon¹² using flash photolysis showed that $\text{SO}_3^{\bullet-}$ could be produced from sulfite solutions and measured the rate of reaction of $\text{SO}_3^{\bullet-}$ with itself. Hayon, Treinin, and Wilf¹³ then showed that $\text{SO}_3^{\bullet-}$ combines rapidly with O_2 , presumably to form $\text{SO}_5^{\bullet-}$.

The $\text{SO}_5^{\bullet-}$ might react in either of two ways with S(IV):



The $\text{SO}_4^{\bullet-}$ was known¹³ to react rapidly with S(IV) to form $\text{SO}_3^{\bullet-}$.

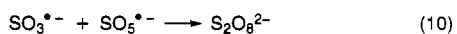
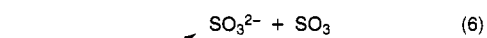


The problem with reaction 3 is that it does not account for the inhibitory effect of alcohols since Dogliotti and Hayon¹² had shown that neither $\text{SO}_5^{\bullet-}$ nor $\text{SO}_3^{\bullet-}$ reacts readily with alcohols. Because $\text{SO}_4^{\bullet-}$ is rapidly scavenged by alcohols, Hayon et al.¹³ chose to replace Bäckström's second step (eq 3) with reactions 4 and 5.

The question of whether $\text{SO}_5^{\bullet-}$ reacts with S(IV) according to reaction 3 or reaction 4 remained unsettled. Devuyt, Ettl, and Mosoiu¹⁴ gave experimental evidence that in alkaline solution considerable SO_5^{2-} was formed, as would be expected from eq 3. Connick and Braga¹⁵ observed in this laboratory that, at moderate pH, the reaction produces an intermediate that continues to form hydrogen ions after all of the oxygen is consumed. This intermediate was shown by Chang, Littlejohn, and Hu¹⁶ to be disulfate ion, $\text{S}_2\text{O}_7^{2-}$. It was then shown by Connick, Lee, and Adamic¹⁷ that peroxymonosulfate ion reacts with bisulfite ion to form $\text{S}_2\text{O}_7^{2-}$, thus adding strong evidence for reaction 3.

The solution to these apparently contradictory pieces of evidence is of course to assume that both reaction 3 and reaction 4 are taking place, as proposed by Huie and Neta,¹⁸ who for purpose of modeling assumed arbitrarily that the rate of (3) was three times that of (4).

The chain termination could occur through reaction of either chain carrier with itself or with each other. Possible reactions are



Reaction 9 is not a chain termination reaction but is included for the following discussion. The disappearance of $\text{SO}_3^{\bullet-}$ and

$\text{SO}_5^{\bullet-}$ have been shown by Huie et al.¹⁹ to be very fast. The rate of reaction 10 has not been measured. Thompson,²⁰ in a study of the decomposition of HSO_5^- , catalyzed by Ag^+ and $\text{S}_2\text{O}_8^{2-}$, inferred a value for the ratio of the rate of reaction 8 to reaction 9 of 1:10. Huie and Neta¹⁸ in making calculations adopted a value of the ratio of 1:4.3; Huie et al.¹⁹ later concluded that they could not determine the ratio. In the most recent work Yermakov et al.²¹ found a ratio of 1:7 which we will adopt. Huie et al.¹⁹ reported a value of $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the overall rate constant, $k_8 + k_9$, with only one significant figure given. An earlier value of $\sim 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was given by Hayon et al.¹³ Of course other possibilities also exist for chain termination, for example, reaction of a chain carrier with a non free radical to give a species incapable of propagating the chain.

The initiation of the chain in the noncatalyzed reaction has remained obscure. The fact that initiation can be achieved photochemically sheds little light on the thermal initiation. There are those who believe there is no noncatalyzed reaction and that initiation always occurs from impurities, such as metal ions. If so, one would expect much greater irreproducibility than is observed. No convincing suggestion for the initiation reaction has been put forward, however.

Experimental Section

The following chemicals were used: SO_2 and NH_3 gases (Matheson), NaOH solid (Fisher), hydrochloric acid (Fisher), potassium nitrate (Fisher), sodium thiosulfate (Mallinkrodt), ethyl alcohol and methanol (Fisher), and sodium bicarbonate (Baker Analyzed Reagent). House deionized water was distilled, and the middle 60% of the distillate was used as solvent in all experiments. Bisulfite was generated by bubbling gaseous SO_2 into an aqueous NH_3 solution prepared from the gas. A Pyrex glass reactor with a water jacket was used throughout the experiments. The volume of the reactor is 640 mL. The ground glass joints on top of the reactor allow the insertion of a microburet, an oxygen probe, and a glass electrode. The vessel was completely filled with reaction solution to eliminate the gas phase but with a small capillary opening to the outside to maintain a constant pressure in the vessel and to allow a small amount of solution to overflow when base was added from the buret to adjust the pH of the solution. Constant stirring of the solution was provided by a magnetic stirrer. The temperature of the reaction solution was maintained at $25 \pm 0.1^\circ \text{C}$. An Orion Research Model 601A Ionanalyzer was used to measure the pH and a Yellow Springs YSI57 oxygen meter and a YSI 5739 oxygen probe were used to monitor the oxygen concentration. Both the pH meter and the oxygen meter were connected to a HP 17501A chart recorder.

The kinetics of the reaction of bisulfite ion with oxygen was followed in two ways: by measuring the oxygen concentration change with the oxygen probe and by monitoring the amount of base added to keep the pH constant. Buffer solutions were avoided because they may affect the rate of the reaction. Ionic strength was usually maintained at $\mu = 0.050 \text{ M}$ with NH_4Cl or KNO_3 . The reaction was initiated either by raising the pH of an aerated solution containing bisulfite ion to the desired value or by bubbling oxygen through a deaerated bisulfite solution already adjusted to the correct pH. In some experiments reactions were started by injecting a small amount of freshly prepared HSO_3^- stock solution into an air-saturated solution containing all other chemicals. The pH was kept constant by manual addition of NH_3 , NaOH, Na_2CO_3 , or NaHCO_3 solutions. In all calculations it was assumed that pH meter readings gave minus the logarithm of the activity of hydrogen ion.

Results and Discussion

A. Oxygen, Bisulfite Ion, and Acid Dependence. When a bisulfite solution is added to an aqueous solution containing

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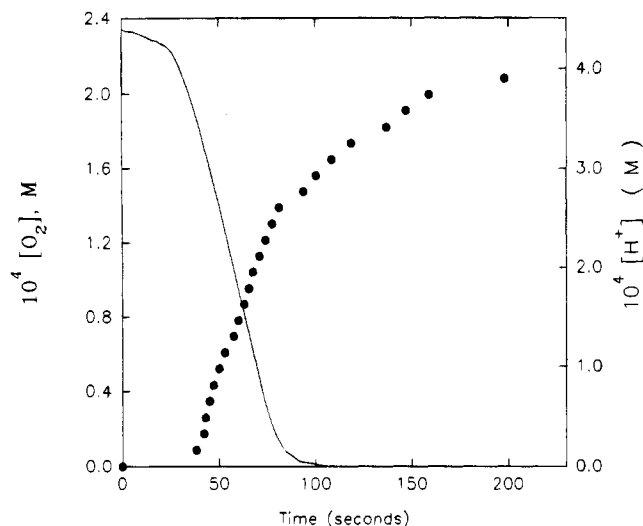


Figure 1. Typical kinetic data for the HSO_3^- - O_2 reaction. Key: solid line, oxygen concentration; filled circles, moles per liter of H^+ released during the reaction. Initial conditions: $[\text{HSO}_3^-] = 0.0236 \text{ M}$, $[\text{O}_2]_0 = 2.34 \times 10^{-4} \text{ M}$, 25°C , ionic strength 0.050 M . The pH was maintained at 4.50 throughout the reaction.

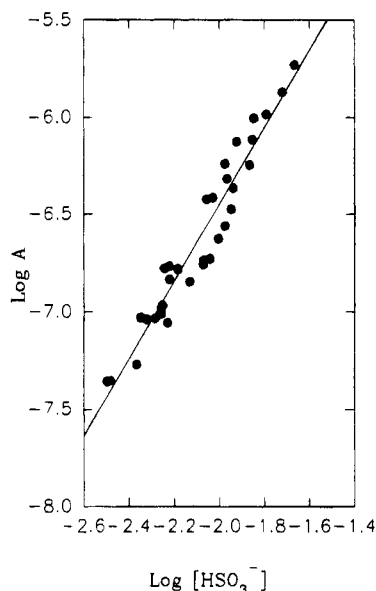


Figure 2. Dependence of the rate of the HSO_3^- - O_2 reaction on the HSO_3^- concentration at pH 4.50, 25°C , and ionic strength 0.050 M . The symbol A on the ordinate axis representing the steady state rate of the reaction, $-\text{d}[\text{O}_2]/\text{dt}$, was obtained either from the slope of the $[\text{O}_2]$ vs time curve from a single run or from fitting the relaxation experimental data with eq 25. Filled circles are experimental data, and the solid line is from the least-squares fit of the data.

O_2 , the reaction builds up rather quickly to reach a steady state rate which it then maintains constant until the oxygen is all consumed (Figure 1). The apparent toe on the curve as zero oxygen is approached is caused by the slowness of the response of the oxygen probe. The constancy of the rate as the oxygen is consumed shows the rate of the reaction to be independent of the oxygen concentration. The rate is, however, sensitive to the bisulfite concentration as shown in Figure 2 for a number of experiments at pH 4.50. In some cases where the experiment was run at a slightly lower or higher pH the data were corrected to pH 4.50 using acidity dependence data. The quantity $\log A$ plotted as ordinate is the logarithm of the rate of oxygen disappearance, $-\text{d}[\text{O}_2]/\text{dt}$. The range of bisulfite ion concentration studied was limited because the reaction becomes too fast to measure (slow O_2 probe response) at high HSO_3^- concentra-

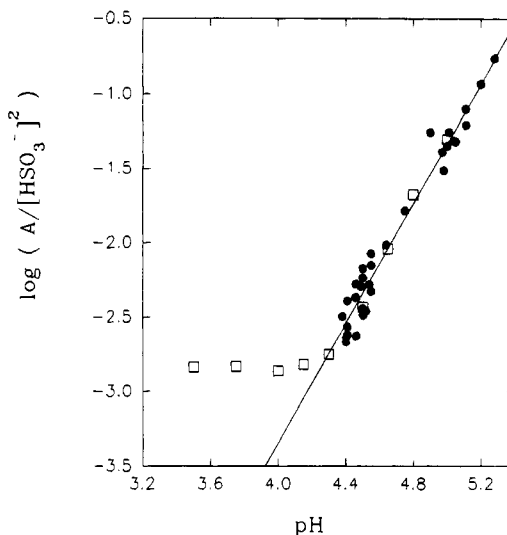


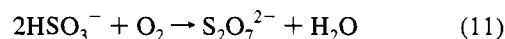
Figure 3. Dependence of the rate of the HSO_3^- - O_2 reaction on pH at 25°C and ionic strength 0.050 M . The symbol A on the ordinate axis represents the steady state rate of the reaction, $-\text{d}[\text{O}_2]/\text{dt}$. Filled circles are experimental results from separate runs of experiments. The squares are from a single run made by successively adding NaHCO_3 solution to the reaction mixture to increase the pH of the solution. The solid line is from the least squares fit of the data.

tion and too slow to measure (slow O_2 leakage into the apparatus) at low concentrations.

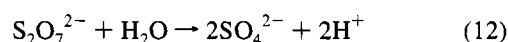
Examination of Figure 2 shows the experimental measurements are not as reproducible as the expected experimental error. We have been unable to determine the source of this irreproducibility. A least squares fit of the data of Figure 2 yields a slope of 1.98 ± 0.09 corresponding closely to a second-order dependence on bisulfite ion concentration. As might be expected, for a rate of reaction which is a combination of at least three separate rates of reactions (initiation, propagation, and termination), it is possible to write more than one plausible mechanism that fits this rate law.

For reasons discussed later the acidity dependence was studied in experiments where the steady state was reached at one acidity, the acidity then suddenly changed, and the steady state allowed to be established at the new acidity. In the one exception, indicated by the square symbols in Figure 3, the steady state rate of a single solution was measured at nine acidities by successively raising the pH. The data for the acidity dependence at the steady state are shown in Figure 3, where $\log (A/[\text{HSO}_3^-]^2)$ is plotted versus pH. The least squares fit gave a slope of 2.01 ± 0.07 for the pH 4.4–5.3 region corresponding to a -2 power for the hydrogen ion dependence. At lower pH the dependence on the hydrogen ion concentration becomes much less negative, indicating a change in rate law. To avoid this complication, most of the experiments were conducted at pH 4.5 or higher. As will be discussed later, the -2 power hydrogen ion concentration dependence is probably more complex than it appears to be.

B. Formation of $\text{S}_2\text{O}_7^{2-}$. As noted in the introduction the intermediate $\text{S}_2\text{O}_7^{2-}$ is formed in the reaction around pH 4.5 according to the net reaction



and it hydrolyzes by the reaction



Since the first order rate constant for reaction 12 was measured¹⁷ to be 0.0128 s^{-1} at 25°C , an appreciable concentration of

$S_2O_7^{2-}$ can be present at the time all of the O_2 is consumed. This is illustrated in Figure 1 where the circles indicate the concentration of H^+ produced during the reaction, which is equivalent to the moles per liter of base that had to be added to maintain constant pH. It was shown experimentally that the acid produced subsequent to the disappearance of the oxygen followed a first-order rate law from pH 4.35 to 10.90 with an acid-independent rate constant of $\sim 1.28 \times 10^{-2} \text{ s}^{-1}$ at 25 °C, as expected¹⁷ for $S_2O_7^{2-}$.

To determine what fraction of the O_2 - HSO_3^- reaction formed $S_2O_7^{2-}$, it was necessary to measure the amount of base consumed after the O_2 was all gone and then correct this quantity for the $S_2O_7^{2-}$ that had already hydrolyzed. The rate of change of $S_2O_7^{2-}$ concentration is given by

$$\frac{d[S_2O_7^{2-}]}{dt} = nR - k_{12}[S_2O_7^{2-}] \quad (13)$$

where R is the rate of disappearance of O_2 , $-d[O_2]/dt$, and n is the number of $S_2O_7^{2-}$ ions formed per molecule of O_2 reacted. Assuming n and R are constant, integration yields

$$\frac{[S_2O_7^{2-}]_e}{[S_2O_7^{2-}]_i} = \{1 - \exp(-k_{12}t_e)\} \frac{R}{k_{12}[O_2]_i} = g \quad (14)$$

where the subscripts e, t, and i refer to end of O_2 consumption, total, and initial respectively. In determining time zero and t_e , correction must be made for the slowness of the oxygen meter response. If significant, correction can be made for the fact that R is not the steady state rate near the start of the reaction by using the actual value of R in the integration.

The left side of eq 14 is equal to the ratio of the molecules of hydrogen ion formed after the O_2 disappeared to the total moles of hydrogen ion formed by hydrolysis of all $S_2O_7^{2-}$ produced during the course of the reaction. Therefore dividing the moles of base added subsequent to the disappearance of the O_2 by g yields the total moles of hydrogen ion formed through $S_2O_7^{2-}$ hydrolysis. Dividing this quantity by 2 times the initial moles of O_2 gives the moles of $S_2O_7^{2-}$ produced per mole of O_2 reacted. The results over a wide pH range are shown as the points in Figure 4. It should be pointed out that for a fixed pH the yield of $S_2O_7^{2-}$ was found to be independent of bisulfite concentration.

As mentioned earlier, the formation of $S_2O_7^{2-}$ is strong evidence that HSO_5^- is produced in the reaction since HSO_5^- is known to react with bisulfite ion to produce $S_2O_7^{2-}$ at moderate pH.¹⁷ This evidence is made almost certain by comparison of the pH dependence of the yield of $S_2O_7^{2-}$ of the HSO_3^- - O_2 reaction with that of the HSO_3^- - HSO_5^- reaction.¹⁷ The curve in Figure 4 is the yield of $S_2O_7^{2-}$ per HSO_5^- consumed in the HSO_3^- - HSO_5^- reaction, but shifted vertically to fit the HSO_3^- - O_2 data. Corrections have been made to the original curve¹⁷ to correct it from ionic strength 0.0050 M to the present ionic strength of 0.050 M. This introduces appreciable uncertainty in the points of the curve at the higher pH end. The agreement, however, between the experimental data and the fitted curve is apparent.

At low pH the solid line of Figure 4 approaches a limiting value of 0.54 $S_2O_7^{2-}$ ions formed per molecule of O_2 consumed. The yield of $S_2O_7^{2-}$ ions per HSO_5^- ion consumed in the HSO_3^- - HSO_5^- reaction in this pH region is 0.90.¹⁷ Therefore the HSO_3^- - O_2 reaction must form 0.60 HSO_5^- ions per O_2 molecule consumed and thus the ratio of rate constants for reaction 3 to that of reaction 4 is 0.60:0.40. This ratio must

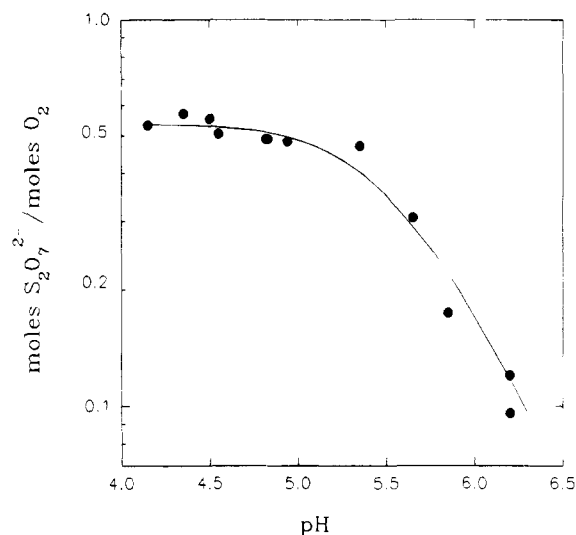


Figure 4. Yield of $S_2O_7^{2-}$ per O_2 consumed in the HSO_3^- - O_2 reaction as a function of pH. Filled circles are experimental results. The solid line is the yield of $S_2O_7^{2-}$ per HSO_5^- consumed in the HSO_3^- - HSO_5^- reaction, taken from ref 17. This curve has been corrected from ionic strength 0.005 M to 0.05 M and shifted vertically from the its original position by a proportionality constant to fit the experimental data from the HSO_3^- - O_2 reaction. The experimental points above pH 5.0 were taken at ionic strength 0.050 M. For points below pH 5.0 the ionic strength increased from 0.055 to 0.0675 M with decreasing pH. Correction for this change in ionic strength produces less than a one percent change in the solid curve.

hold at least fairly well over the pH region 4–6, because the pH dependence of the data points tracks closely the solid curve in Figure 4.

From photolysis of sulfite solutions in the presence of alcohol, Deister and Warneck²² have deduced a ratio of rate constants for the analogues of reactions 3 and 4 where SO_3^{2-} reacts with SO_5^{*-} . Since both reactions 3 and 4 have an inverse first power hydrogen ion dependence (see later) it is presumed the bisulfite ion first dissociates, followed by reaction of SO_3^{2-} with SO_5^{*-} . Therefore Deister and Warneck's ratio should agree with ours of 0.60:0.40. Instead they found 0.28:0.72 with an uncertainty in the ratio of $\sim 30\%$. They pointed out that their result depends on assumptions about the fate of HSO_5^- that may not be correct.

C. Initiation. At this point chain carriers SO_3^{*-} , SO_5^{*-} , and SO_4^{*-} seem fairly well identified and with them the chain reactions of eqs 2–5. The termination probably does not involve SO_3^{*-} because if it did, chain step (2) would have to enter the rate law in the numerator, thus introducing the oxygen concentration into the rate law. Therefore it is likely that the chain-terminating step is reaction 8.

As mentioned earlier the literature is bereft of any plausible suggestions for the chain initiation reaction for the uncatalyzed reaction. While impurities have been suggested, it is quite difficult to think of impurities that might reasonably be present that could react with O_2 , HSO_3^- or SO_4^{2-} to form SO_3^{*-} , SO_5^{*-} , and/or SO_4^{*-} . A powerful oxidizing reagent would be necessary to form the latter two directly from HSO_3^- and a fairly strong one to form SO_3^{*-} . The reduction potentials of pertinent sulfur compounds at pH 4.50 and 25 °C are approximately

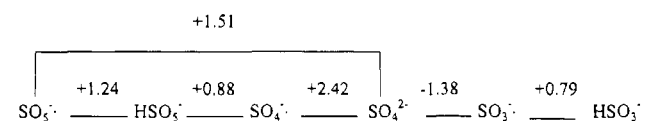


Table 1. Aqueous ΔG^o_f of Species Appearing in the Mechanism of the Oxidation of HSO₃⁻ by O₂

species	ΔG ^o _f (kJ/mol)	ref
HSO ₃ ⁻	-527.7	a
H ₂ O	-237.13	a
SO ₄ ²⁻	-744.5	a
S ₂ O ₈ ²⁻	-114.9	a
SO ₃ ^{*-}	-426	b
SO ₅ ^{*-}	-493	b
SO ₄ ^{*-}	-511	c
S ₂ O ₇ ²⁻	-1193	d
HSO ₅ ⁻	-638	e

^a Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2. ^b Huie and Neta (Huie, R. E.; and Neta, P. *J. Phys. Chem.* **1984**, *88*, 5665) proposed a potential of 1.1 V for the SO₅^{*-}/HSO₅⁻ couple which leads to a ΔG^o_f for SO₅^{*-} of -493 kJ/mol. The assumption that the free energy change is zero for HO₂^{*} + HSO₅⁻ = H₂O₂ + SO₅^{*-} yields -500 kJ/mol for SO₅^{*-}. ^c Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69. ^d From heat of formation data in reference a and an estimated value of the entropy. ^e Price, J. S.; Tasker, I. R.; Appelman, E. H.; O'Hare, P. A. G. *J. Chem. Thermodyn.* **1986**, *18*, 923.

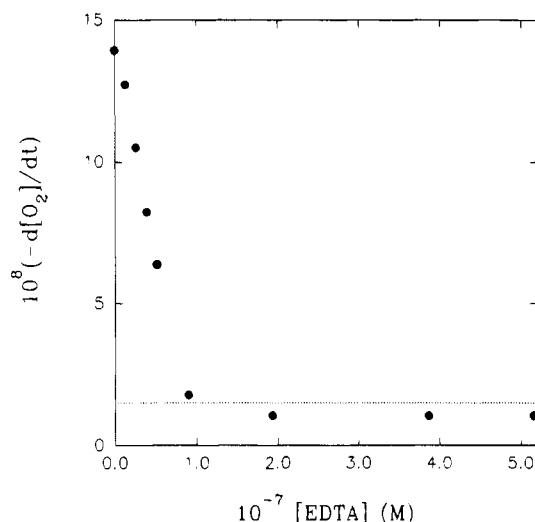
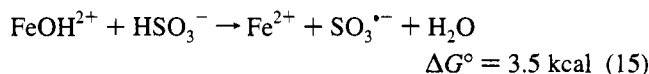


Figure 5. The effect of EDTA on the HSO₃⁻-O₂ reaction with FeSO₄ added as a catalyst. Filled circles are the steady state rate of the reaction at different total EDTA concentrations. The dotted line represents the steady state rate of the reaction in the absence of Fe²⁺ and EDTA. Conditions: [HSO₃⁻]₀ = 2.2 × 10⁻³ M, [Fe²⁺]₀ = 1.03 × 10⁻⁷ M, T = 25 °C, pH = 4.50 and μ = 0.050 M.

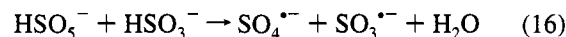
The potentials were obtained from the standard free energies of formation shown in Table 1. All values were from literature references cited except for the free energy of formation of SO₅^{*-} which was estimated as described in footnotes to the table. The one obvious initiation reaction which might occur from an impurity is



Addition of EDTA, however, under conditions where it should complex Fe(III) strongly, has little effect on the rate. The results of an experiment in which EDTA was added in increments to a reaction solution where Fe(II) had deliberately been added are shown in Figure 5. When Fe(II) salts are added to oxygen-containing bisulfite solutions at pH 4.5, the rate increases over a period of some minutes to reach a steady state. If Fe(III) salts are added, the rate is much greater but decreases over some minutes to reach the same steady state rate as with Fe(II) salts of the same concentration. The measurements in Figure 5 all relate to steady state rates. The rapid fall-off in rate with

increasing EDTA concentration to yield a nearly constant rate, after one EDTA has been added per Fe(II), shows that iron impurities cannot be responsible for the initiation. Further, if trace impurities of iron were initiating the reaction, greater irreproducibility of rate would be expected than is observed. Cation ion exchange resin also had little effect on the rate under conditions where +2 and +3 iron ions should have been removed, although the iron might be in the form of sulfite complexes and consequently not taken up by the resin.

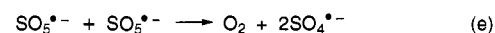
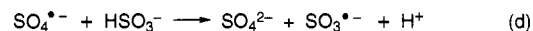
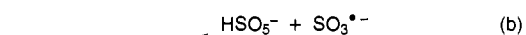
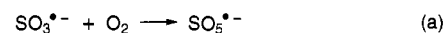
It occurred to us that HSO₅⁻, peroxymonosulfate ion, might be a sufficiently powerful oxidizing agent to form free radicals according to



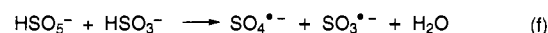
The free energy change is -2 kcal and therefore it is easily a candidate since the products would be at very low concentrations. It was this suggestion that led to the study of the rate of the reaction of HSO₅⁻ with HSO₃⁻. The finding that S₂O₇²⁻ is one of the products of that reaction provided strong evidence that HSO₅⁻ is an intermediate in the HSO₃⁻-O₂ reaction. The proposed initiation is then reaction 16, but only as a side reaction of the reaction of HSO₅⁻ with HSO₃⁻ to form S₂O₇²⁻ or SO₄²⁻.¹⁷ The identification of reaction 16 as the initiation is given strong support by the action of inhibitors, as will be discussed later.

The suggested mechanism for the uncatalyzed reaction, without regard to acidity dependence, is as follows:

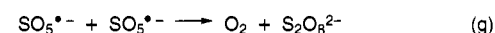
propagation



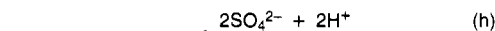
initiation



termination



follow reactions



The ratio of rates of reaction g to reaction e is taken to be 1:7.²¹ The split between reactions h and i is 90% reaction i from pH 4-5, falling off inversely with pH at higher pH.¹⁷

For the steady state rate with a long chain and neglecting (e) relative to (b) and (c) the above mechanism gives

$$-\frac{d[\text{O}_2]}{dt} = \text{rate propagation} = \text{rate propagation} \left\{ \frac{\text{rate initiation}}{\text{rate termination}} \right\}^n = (k_b + k_c)[\text{SO}_5^{*-}][\text{HSO}_3^-] \left\{ \frac{2k_f[\text{HSO}_3^-][\text{HSO}_5^-]}{2k_g[\text{SO}_5^{*-}]^2} \right\}^n \quad (17)$$

Assuming a steady state for the very small concentration of

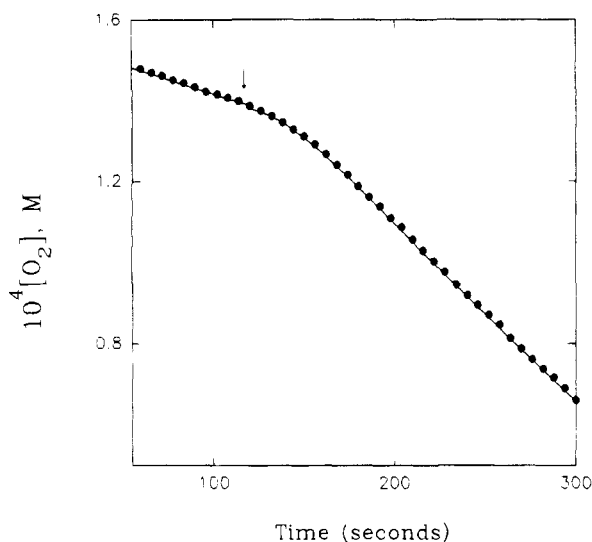


Figure 6. Typical result from a relaxation experiment on the $\text{HSO}_3^- - \text{O}_2$ reaction. The perturbation from the initial steady state was made by injecting a small volume of concentrated HSO_3^- solution into the reactor at the time indicated by the arrow. Circles are experimental data and the solid line after the perturbation is from the nonlinear regression with the expression in eq 25. The slope of the line before the perturbation is R_0 . Conditions: $[\text{HSO}_3^-]$ before and after the perturbation are 6.01×10^{-3} and 1.09×10^{-2} M, respectively. $T = 25^\circ\text{C}$, $\text{pH} = 4.50$, and $\mu = 0.050$ M.

HSO_5^- through reactions b and h + i

$$-\frac{d[\text{O}_2]}{dt} = (k_b + k_c)[\text{SO}_5^{*-}][\text{HSO}_3^-] \times \left\{ \frac{k_f[\text{HSO}_3^-]}{k_g[\text{SO}_5^{*-}]^2} \left(\frac{k_b[\text{SO}_5^{*-}][\text{HSO}_3^-]}{(k_h + k_i)[\text{HSO}_3^-]} \right)^n \right\} \quad (18)$$

Choosing $n = 1$ to cancel out the chain carrier concentration yields

$$-\frac{d[\text{O}_2]}{dt} = \frac{k_b(k_b + k_c)k_f}{k_g(k_h + k_i)}[\text{HSO}_3^-]^2 \quad (19)$$

Thus the mechanism is consistent with the experimentally observed square power dependence of the rate on the bisulfite ion concentration (Figure 2).

D. Relaxation Experiments. While the suggested mechanism agrees with the steady state experiments, other mechanisms exist that will also do so. To test the mechanism further one can seek information on the separate rate laws of the initiation, propagation and termination reactions. By suddenly perturbing the reaction away from the steady state and then following the rate as the reaction relaxes back to a new steady state, one can obtain such information. Fortunately the relaxation occurs at a measurable rate. The perturbations were carried out by adding small volumes of acid, base, or bisulfite solutions. The volume added was sufficiently small that the dilution effect was negligible.

Perturbation by Change in $[\text{HSO}_3^-]$. An example of what we will refer to as a relaxation experiment is shown in Figure 6. A reaction at the steady state was suddenly perturbed by adding a small volume of a bisulfite solution to raise the bisulfite concentration. Before and subsequent to this addition the pH was held constant at 4.5. From Figure 6 it is seen that the relaxation to the new steady state occurs rather rapidly. The required careful fitting of the data was made difficult by the slowness of response of the oxygen probe and the finite rate of

mixing. While an accurate correction can be made,²³ the complexity of the rate equations made such an approach impractical. Instead the zero time (perturbation) was shifted 9 s forward in time in agreement with the measured lag in the oxygen probe when at the steady state. In the fitting of the data the first few points were discarded and experiments with relaxation times (reciprocal of parameter C , see below) of less than 12 s were excluded. The data of these relaxation experiments were analyzed as follows:

The rate of change of chain carriers is

$$\frac{d[\text{cc}]}{dt} = (\text{rate initiation}) - (\text{rate termination}) \quad (20)$$

where cc stands for chain carriers. Then

$$\begin{aligned} \frac{d[\text{cc}]}{dt} &= 2k_f[\text{HSO}_3^-][\text{HSO}_5^-] - 2k_g[\text{SO}_5^{*-}]^2 \\ &= \frac{2k_f k_b[\text{SO}_5^{*-}][\text{HSO}_3^-]}{k_h + k_i} - 2k_g[\text{SO}_5^{*-}]^2 \end{aligned} \quad (21)$$

assuming $[\text{HSO}_5^-]$ remains at its steady state value. It is believed that $[\text{SO}_5^{*-}] \gg [\text{SO}_3^{*-}] + [\text{SO}_4^{*-}]$ because the latter two chain carriers react more rapidly in reactions a and d than does SO_5^{*-} in reactions b and c. Then

$$d[\text{cc}]/dt \approx d[\text{SO}_5^{*-}]/dt \quad (22)$$

Integration yields

$$[\text{SO}_5^{*-}] = \left\{ \frac{k_g(k_h + k_i)(1 - e^{-Ct})}{k_b k_f [\text{HSO}_3^-]} + \frac{e^{-Ct}}{[\text{SO}_5^{*-}]_i} \right\}^{-1} \quad (23)$$

where the subscript i indicates the concentration immediately after the perturbation, which is taken as zero time, and $[\text{HSO}_3^-]$ is assumed constant in a given experiment.

From reactions b and c

$$-d[\text{O}_2]/dt = (k_b + k_c)[\text{SO}_5^{*-}][\text{HSO}_3^-] \quad (24)$$

Substituting for $[\text{SO}_5^{*-}]$ from (23) and integrating once again, one obtains

$$[\text{O}_2]_i - [\text{O}_2] = A/C \ln\{1 + B/A(e^{Ct} - 1)\} \quad (25)$$

The parameters A , B , and C have the following values:

$$A = \frac{k_b(k_b + k_c)k_f}{k_g(k_h + k_i)}[\text{HSO}_3^-]^2 \quad (26)$$

$$B = (k_b + k_c)[\text{HSO}_3^-][\text{SO}_5^{*-}]_i \quad (27)$$

$$C = \frac{2k_b k_f}{k_h + k_i}[\text{HSO}_3^-] \quad (28)$$

The initial SO_5^{*-} concentration in B can be replaced by

$$[\text{SO}_5^{*-}]_i = \frac{1}{(k_b + k_c)[\text{HSO}_3^-]} \{-d[\text{O}_2]/dt\}_i \quad (29)$$

to give

$$B = \{-d[\text{O}_2]/dt\}_i = R_i \quad (30)$$

The set of A , B , and C parameters can now be used to check the rate laws for the initiation, propagation, and termination reactions in the suggested mechanism. In fitting the data in a given experiment to the A , B , and C parameters, no assumption

Table 2. The HSO_3^- Dependence of Reactions b plus c from Relaxation Experiments with HSO_3^- Perturbation

$10^3[\text{HSO}_3^-]_0$ (M)	$10^3[\text{HSO}_3^-]_i$ (M)	$10^7 R_0$ (M/s)	$10^7 R_i$ (M/s)	y
3.36	9.92	0.83	2.37	0.96
4.51	13.55	0.78	1.98	0.85
5.80	17.44	0.85	2.29	0.90
6.45	12.90	1.51	2.74	0.86
6.45	16.32	1.75	3.33	0.70
5.76	11.52	1.32	2.71	1.04
3.74	9.71	0.56	1.39	0.96
2.23	6.69	0.486	1.36	0.94

$y_{av} = 0.90 \pm 0.04$

about the bisulfite dependence was necessary. The test of the proposed mechanism is then whether the experimental bisulfite dependences of A , B , and C do in fact agree with the predictions of the mechanism in eqs 26–28.

The A parameter is of course the rate law of the steady state which already has been shown experimentally (Figure 2) to have the square power dependence on the bisulfite concentration predicted by the mechanism in eq 26.

The bisulfite dependence of the B parameter requires special consideration as according to the mechanism B is the sum of the rates of reactions b and c but contains the unmeasurable quantity $[\text{SO}_5^{\bullet-}]_i$. For long chains the overall rate of the reaction can be written as the rate of any of the propagation steps. At constant pH, let the rate of the propagation step involving the major (most populous) chain carrier be

$$-d[\text{O}_2]/dt = k[\text{X}][\text{HSO}_3^-]^y = R \quad (31)$$

where X is the major chain carrier. The concentration of X immediately after the perturbation must equal the concentration just before the perturbation (assuming a negligible volume change), since it is known that relaxation to the steady state occurs at a finite rate. Using the subscript symbols o and i to indicate immediately before and after the perturbation, one can write

$$R_i/R_o = \{[\text{HSO}_3^-]_i/[\text{HSO}_3^-]_o\}^y \quad (32)$$

Thus from a given experiment one can determine y , the bisulfite power dependence of the propagation step. The results are shown in Table 2.

As will be discussed later there is evidence that $\text{SO}_5^{\bullet-}$ is the major chain carrier. Therefore we identify eq 31 with reactions b and c of the proposed mechanism. The first power bisulfite dependence of reactions b and c is consistent with the data of Table 2, within the experimental accuracy. That reactions b and c have the same bisulfite dependence is known from the experimental invariance of the yield of $\text{S}_2\text{O}_7^{2-}$ to bisulfite ion concentration. The accuracy is not great, in large part because of the rapidity of the relaxation relative to the response of the oxygen probe.

The bisulfite dependence of the C parameter is shown in Figure 7. The least-squares fit yields a power of 1.17. From the mechanism it is predicted to be unity (eq 28). There probably is agreement within the experimental accuracy of the data.

The right hand sides of the equations for A , B , and C can be thought of as products and ratios of rates of the reactions indicated by the rate constants. If the conclusion of the first power bisulfite dependence is accepted for B and C , it follows from C that the initiation reaction f must also be first order in bisulfite, since reactions h and i are known to have a first-power dependence.¹⁷ Similarly it may be concluded from A that reaction g, termination, must be independent of bisulfite ion

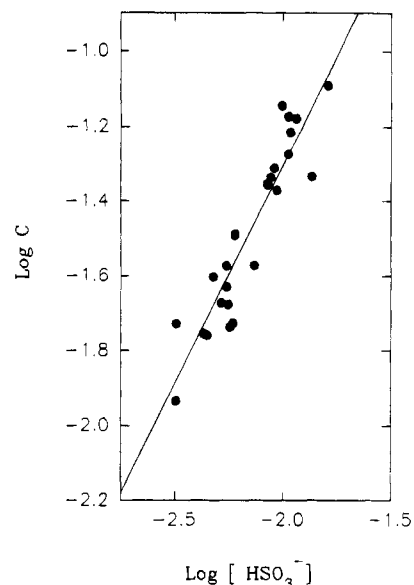


Figure 7. Dependence of parameter C in eq 25 on the concentration of HSO_3^- . Filled circles are from the nonlinear least-squares fittings to the relaxation experiments with eq 25. Solid line is the least-squares fit to the filled circles.

concentration. Both conclusions are consistent with the proposed mechanism.

Perturbation by Change in pH. In these experiments the bisulfite concentration was held essentially constant as the system was perturbed from the steady state by a sudden addition of HCl or NH_3 solution. Relaxation to the new steady state was followed while maintaining the pH constant at the new value.

All of the equations previously derived in obtaining A , B , and C can be used, with the understanding that each rate constant may be a function of hydrogen ion concentration. The acidity dependence of reactions h and i can be represented at 25 °C and ionic strength 0.050 M by¹⁷

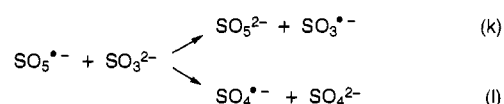
$$k_h + k_i =$$

$$9.9 \times 10^6 a_{\text{H}^+} + 1.73 \times 10^{-4} a_{\text{H}^+}^{-1} + 70.7 \text{ M}^{-1} \text{ s}^{-1} \quad (33)$$

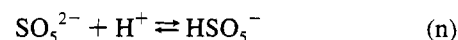
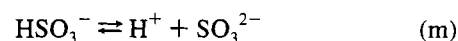
where the rate constants have been corrected to 0.050 M ionic strength using Kielland's²⁴ single ion activity coefficients. As before the B parameter equals the rate of the reaction just after the perturbation and

$$R_i/R_o = \{[\text{H}^+]_i/[\text{H}^+]_o\}^z \quad (34)$$

where z is the hydrogen ion power dependence of $k_b + k_c$. The data in Table 3 give an average value for z of -0.96 , but with considerable variation. It may be concluded that the rate of reactions b and c are inversely proportional to approximately the first power of the hydrogen ion concentration and should be written primarily as



along with the rapid equilibria



Both A and C contain the rate constants k_h and k_i which are acid dependent. To simplify the analysis, A and C were

(24) Kielland, J. *J. Am. Chem. Soc.* **1937**, *59*, 1675.

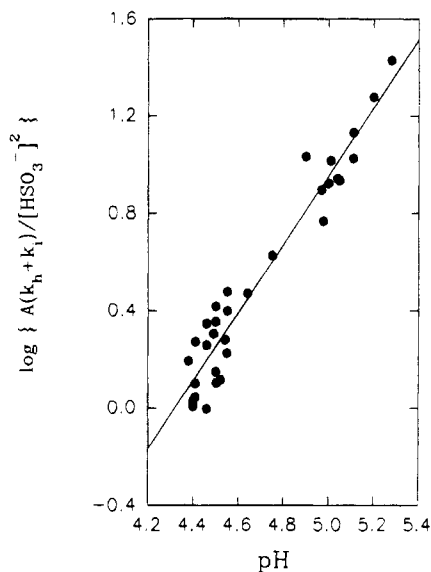


Figure 8. Dependence of $A(k_h + k_i)/[\text{HSO}_3^-]^2$ on pH. Filled circles are from the nonlinear least-squares fittings to the experimental data from the relaxation experiments with eq 25. Solid line is a least-squares fit to the filled circles.

Table 3. Hydrogen Ion Concentration Dependence of $(k_b + k_c)$ from Relaxation Experiments with Perturbation by Addition of HCl or NH_3 Solution

$10^6 a_{\text{H}^+_0}$	$10^5 a_{\text{H}^+_i}$	$10^6 R_0$ (M/s)	$10^6 R_i$ (M/s)	z
6.31	1.78	2.84	1.23	-0.81
6.31	1.48	5.46	2.64	-0.85
6.31	1.86	4.84	1.91	-0.86
7.08	2.51	11.1	2.49	-1.18
6.31	1.44	3.81	1.56	-1.08
5.01	2.29	4.52	1.95	-0.55
32.4	0.63	0.0655	0.348	-1.02
36.3	1.26	0.057	0.221	-1.28
7.08	3.16	6.37	1.58	-0.93
31.6	1.00	0.485	1.79	-1.13
28.2	0.98	0.277	0.787	-0.99
25.1	0.78	0.299	1.07	-1.09
32.3	1.05	0.578	1.75	-0.99
6.61	3.23	6.89	1.57	-0.93
5.62	3.47	2.13	0.483	-0.82
34.7	0.52	0.0716	0.369	-0.86
5.62	3.47	4.07	0.562	-1.09
5.01	3.16	1.98	0.460	-0.79

$$z_{\text{av}} = -0.96 \pm 0.04$$

multiplied by the right hand side of eq 33 and plotted in Figures 8 and 9. The least squares slopes, corresponding to hydrogen ion concentration dependence, are -1.59 and -0.75 for $(k_h + k_i)A$ and $(k_h + k_i)C$, respectively, but again with appreciable uncertainty. With the hydrogen ion exponent for $(k_h + k_i)A$ approximately twice that of $(k_h + k_i)C$, it is tempting to ascribe all of the hydrogen ion dependence to k_b and k_c because A contains $k_b(k_b + k_c)$ while C contains k_b .

If one accepts -1.00 for the k_b and k_c hydrogen ion dependence and solves for the acid-dependence power of k_f and k_g , the results are $+0.21$ for k_f and -0.12 for k_g .

One possible interpretation of the results, probably consistent with the accuracy of the experiments, is that k_f and k_g are acid independent and that the whole acidity dependence arises through k_b and k_c . Then in the region of pH studied, k_b and k_c would be primarily inversely proportional to the first power of the hydrogen ion concentration, as in reactions $k-n$. At the lower pH, reaction of $\text{SO}_5^{\cdot-}$ with HSO_3^- , rather than SO_3^{2-} , could start to become significant and account in part for the rapid flattening of the rate in Figure 3 around pH 4.0.

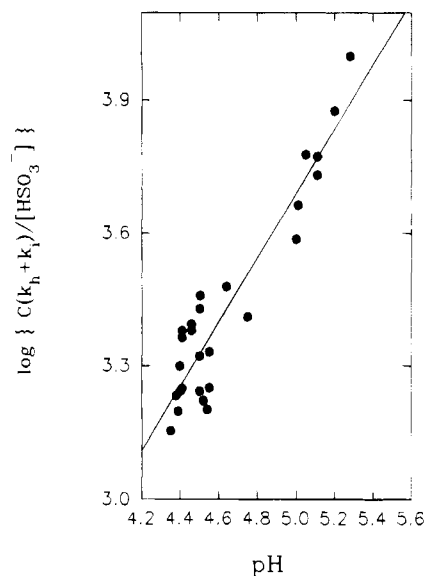


Figure 9. Dependence of $C(k_h + k_i)/[\text{HSO}_3^-]$ on pH. Filled circles are from the nonlinear least squares fittings to the experimental data from the relaxation experiments with eq 25. Solid line is the least-squares fit to the filled circles.

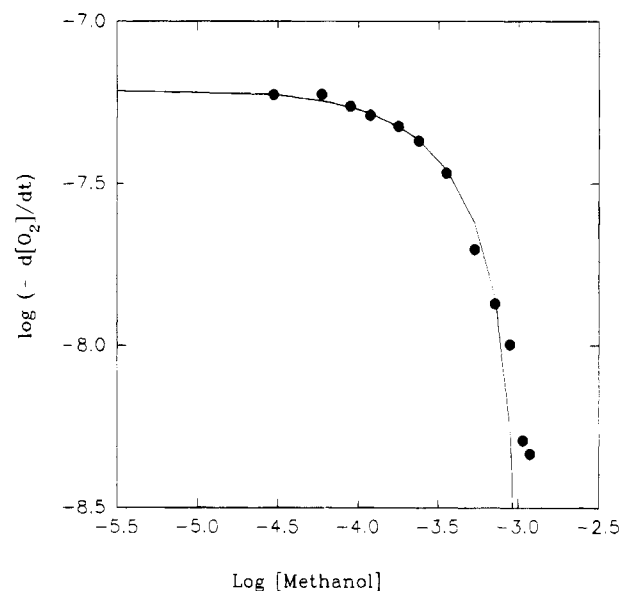
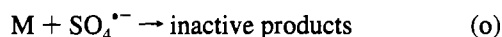


Figure 10. Effect of methanol on the reaction of HSO_3^- and O_2 . Initial conditions: $[\text{HSO}_3^-] = 3.65 \times 10^{-3}$ M, $[\text{O}_2] = 2.5 \times 10^{-4}$ M, $\mu = 0.050$ M, $T = 25$ °C. The filled circles are experimental data and solid line is the theoretical curve from eq 39.

E. Alcohol Inhibition and the Initiation Reaction. The nature of the inhibition by alcohol adds confirmatory evidence to the choice of initiation reaction *f*. The effect of alcohol at $\text{pH} \sim 4.5$ is quite unlike that reported by Bäckström⁶ at $\text{pH} \sim 8$. Results of steady state rates at constant bisulfite ion concentration and pH are shown in Figure 10. The fall-off in rate with increasing methanol concentration is quite spectacular, with a maximum experimental slope corresponding to a greater than inverse 4th power dependence on alcohol. Similar results are obtained with ethanol and 2-propanol as well as arsenious acid. No explanation for such an abrupt decrease in rate was apparent until reaction *f* was proposed for the initiation.

Hayon et al.,¹³ using pulse radiolysis, showed that alcohols react rapidly with $\text{SO}_4^{\cdot-}$ but not with $\text{SO}_5^{\cdot-}$ or $\text{SO}_3^{\cdot-}$. Representing methanol by *M*, the termination reaction by alcohol can be written as



At the steady state initiation equals termination:

$$2k_f[\text{HSO}_5^-][\text{HSO}_3^-] = 2k_g[\text{SO}_5^{\bullet-}]^2 + k_o[\text{M}][\text{SO}_4^{\bullet-}] \quad (35)$$

For long chains the steady state value for $[\text{SO}_4^{\bullet-}]$ from eqs c and d at fixed pH is

$$[\text{SO}_4^{\bullet-}] = k_c[\text{SO}_5^{\bullet-}]/k_d \quad (36)$$

Replacing both $[\text{SO}_4^{\bullet-}]$ and $[\text{HSO}_5^-]$ by their steady state values results in

$$\frac{2k_b k_f}{k_h + k_i} [\text{SO}_5^{\bullet-}][\text{HSO}_3^-] = 2k_g[\text{SO}_5^{\bullet-}]^2 + \frac{k_c k_o}{k_d} [\text{M}][\text{SO}_5^{\bullet-}] \quad (37)$$

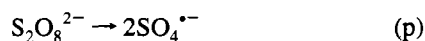
$$[\text{SO}_5^{\bullet-}] = \frac{k_b k_f [\text{HSO}_3^-]}{(k_h + k_i) k_g} - \frac{k_c k_o [\text{M}]}{2k_d k_g} \quad (38)$$

Thus at sufficiently high $[\text{M}]$ the concentration of $\text{SO}_5^{\bullet-}$ will go to zero, and therefore the rate will go to zero (eq 24). The solid curve in Figure 10 is calculated using the form

$$-d[\text{O}_2]/dt = R_o - b[\text{M}] \quad (39)$$

where R_o is the rate with no alcohol and parameter b is a constant chosen to best fit the data. The fit is quite satisfactory except at high alcohol where some additional effect is entering to keep the reaction rate from actually going to zero. Examination of the equations shows that it is the role of the intermediate HSO_5^- in the initiation step which leads to the remarkable fall-off in rate with alcohol concentration.

F. Chain Initiation by Peroxydisulfate Ion $\text{S}_2\text{O}_8^{2-}$. Peroxydisulfate ion has been widely used as a chain initiator in various reactions such as polymerization processes.²⁵ It is also an excellent chain carrier generator in the $\text{HSO}_3^- - \text{O}_2$ reaction. The addition of $\sim 10^{-4}$ M $\text{S}_2\text{O}_8^{2-}$ increases the rate of the reaction several fold for a typical run in our study. The direct reaction between $\text{S}_2\text{O}_8^{2-}$ and HSO_3^- has been studied previously.^{26,27} The reaction was found to be slow and obeys a simple second-order rate law. The mechanism of this reaction does not seem to involve a radical chain process. The enhancement of the $\text{HSO}_3^- - \text{O}_2$ reaction rate by $\text{S}_2\text{O}_8^{2-}$ is therefore believed to be due to $\text{SO}_4^{\bullet-}$ radicals produced from $\text{S}_2\text{O}_8^{2-}$ decomposition:



With this additional chain initiation reaction added to the mechanism the following rate law is obtained:

$$-\frac{d[\text{O}_2]}{dt} = \frac{k_b k_f (k_b + k_c)}{2k_g (k_h + k_i)} [\text{HSO}_3^-]^2 + \left\{ \frac{k_b (k_b + k_c) k_f}{2k_g (k_h + k_i)} [\text{HSO}_3^-]^2 + \frac{k_p (k_b + k_c)}{k_g} [\text{HSO}_3^-]^2 [\text{S}_2\text{O}_8^{2-}] \right\}^{1/2} \quad (40)$$

If R is written for the rate and since $k_b (k_b + k_c) k_f [\text{HSO}_3^-]^2 / k_g (k_h + k_i) = R_o$ (the rate of the reaction without $\text{S}_2\text{O}_8^{2-}$), eq 40 can be rewritten as

$$R/R_o = 1/2 + \{ 1/4 + ((k_h + k_i)(k_b + k_c) k_p / k_b k_f) [\text{S}_2\text{O}_8^{2-}] / R_o \}^{1/2} \quad (41)$$

The plot R/R_o vs $[\text{S}_2\text{O}_8^{2-}] / R_o$ should yield a universal curve for experimental data with different $[\text{S}_2\text{O}_8^{2-}]$ and $[\text{HSO}_3^-]$, for a given temperature, pH, and ionic strength. Indeed this prediction agrees well with the experimental data as shown in Figure 11. The HSO_3^- concentration ranged from 3.22×10^{-3} to 9.66×10^{-3} M in the separate experiments while the $\text{S}_2\text{O}_8^{2-}$ concentration varied from 6.8×10^{-7} to 3.0×10^{-4} M. The value of $(k_b + k_c)(k_h + k_i) k_p / k_b k_f$ that results from the best fit to the experimental data is 2.26×10^{-3} .

G. Rate Constants and Chain Length. The experimental data along with data from the literature make possible the calculation of chain length and the rate constants of the proposed mechanism. The relaxation experiments gave three parameters A, B, and C. The unknowns contained in the parameters are four, i.e. k_b or k_c , k_f , k_g , and $[\text{SO}_5^{\bullet-}]_i$. One or more of these unknowns or an additional relationship between them must be obtained in order to evaluate all of the rate constants and the chain length. Several sources of such information are available.

From the inhibition by alcohol and data from the literature, one can obtain the initiation rate constant, k_f . Substituting into eq 24 the expression for $[\text{SO}_5^{\bullet-}]$ from eq 38, one finds

$$\frac{b}{R_o} = \frac{k_c k_o (k_h + k_i)}{2k_b k_d k_f [\text{HSO}_3^-]} \quad (42)$$

From the literature,²⁸ k_d is 1.11×10^9 (corrected to ionic strength 0.050 M) while k_o is^{28,29} $8.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The ratio k_c/k_b is known from the present work while $k_h + k_i$ was determined previously.¹⁷ The ratio b/R_o for the experiment of Figure 10 is 1.08×10^3 . The value of k_f found is $0.28 \text{ M}^{-1} \text{ s}^{-1}$. If one alcohol molecule terminates two chain carriers instead of one as assumed, k_f would be doubled.

This value of k_f can be used to calculate the chain length, c.l.

$$\begin{aligned} \text{c.l.} &= \frac{\text{rate propagation}}{\text{rate initiation}} = \frac{(k_b + k_c) [\text{SO}_5^{\bullet-}] [\text{HSO}_3^-]}{2k_f k_b [\text{SO}_5^{\bullet-}] [\text{HSO}_3^-] / (k_h + k_i)} \\ &= \frac{(k_b + k_c)(k_h + k_i)}{2k_b k_f} \quad (43) \end{aligned}$$

Substitution gives $\text{c.l.} = 1.16 \times 10^3$, independent of the bisulfite concentration. The calculated value is only a minimum value if some of the free radicals formed by reaction o return to the

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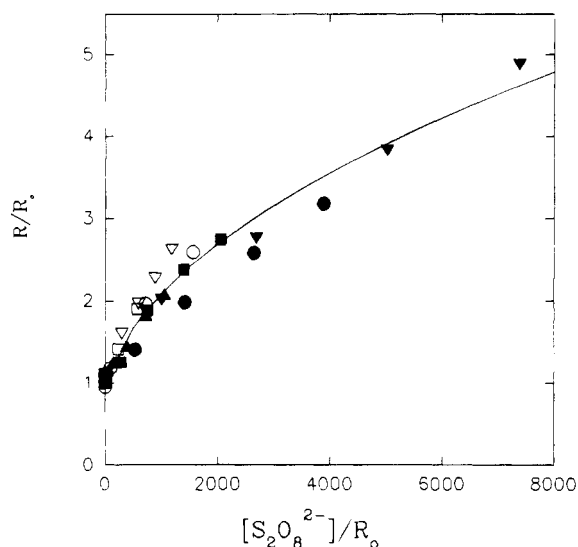


Figure 11. Relative rate of reaction of HSO_3^- with O_2 in the presence of $\text{S}_2\text{O}_8^{2-}$ as chain initiator. Conditions: pH 4.50, $\mu = 0.050$ M, 25 °C. $[\text{HSO}_3^-]_0$: (○) 3.22×10^{-3} M, (●) 4.29×10^{-3} M, (▲) 5.11×10^{-3} M, (■) 5.37×10^{-3} M, (▼) 7.51×10^{-3} M, (□) 9.66×10^{-3} M.

chain, and the chain length would be halved if an alcohol terminates two chain carriers.

An analysis of the chain length of the experiment of Figure 10 with alcohol present shows that the chain length is independent of the alcohol concentration. The assumption of long chains is satisfied at all alcohol concentrations.

From the peroxydisulfate experiment the constant $(k_b + k_c) \cdot k_p(k_h + k_i)/(k_b k_f) = 2.26 \times 10^{-3}$ can also be used to calculate k_f . The value of k_p at 25 °C is reported³⁰ to be $2.4 \times 10^{-8} \text{ s}^{-1}$. Substitution gives $k_f = 6.9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$.

As discussed earlier there are values in the literature for $k_g + k_e$ and their ratio. Using Huie et al.'s¹⁹ value of 1×10^8 for $k_g + k_e$ and Yermakov et al.'s²¹ branching ratio of 1:7 for $k_g:k_e$, one calculates $k_g = 1.25 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. To compare with k_f from the alcohol and $\text{S}_2\text{O}_8^{2-}$ experiments, k_f can be calculated from A, C, and k_g :

$$k_f = \frac{C^2(k_b + k_c)(k_h + k_i)}{4Ak_b k_g} = 0.07 \text{ M}^{-1} \text{ s}^{-1} \quad (44)$$

From experiments on the inhibition of the $\text{HSO}_3^- - \text{O}_2$ reaction by thiosulfate ion, a rough value of 1.3×10^3 was obtained for the chain length by measuring the decreased effect on the rate as thiosulfate was destroyed and assuming one thiosulfate was consumed in each chain termination. From the chain length the value of k_f is calculated to be $0.25 \text{ M}^{-1} \text{ s}^{-1}$.

A value of $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for $k_b + k_c$ at pH 4.9 and ionic strength approximately 0.6 M was reported by Huie and Neta.¹⁸ For a related value the uncertainty was estimated to be ~50%. Correcting to ionic strength 0.050 M will reduce the value perhaps as much as 4-fold and correcting to pH 4.50 will reduce it another 2.5-fold, thus yielding a very approximate value of ca. 3×10^4 at $\mu = 0.050$ M and pH 4.50. From the value of C, k_f is calculated to be $0.05 \text{ M}^{-1} \text{ s}^{-1}$.

The five values calculated for k_f are 0.28 (alcohol), 0.25 ($\text{S}_2\text{O}_8^{2-}$), 0.07 ($k_g + k_e$), 0.05 ($k_b + k_c$), and 0.0069 ($\text{S}_2\text{O}_8^{2-}$) $\text{M}^{-1} \text{ s}^{-1}$. Each value depends on mechanistic assumptions and/or is subject to considerable experimental uncertainty. The result from the peroxydisulfate initiation differs considerably from the other values and presumably there is something wrong

with the interpretation or the value of k_o . The remaining values span a factor of nearly 6. Obviously further work is necessary to obtain a reliable value.

For the purpose of showing the magnitude of the other rate constants, i.e. $k_b + k_c$ and k_g , we arbitrarily use the thiosulfate value for k_f and calculate the others from A and C:

$$k_f = 0.25 \text{ M}^{-1} \text{ s}^{-1} \text{ (assumed)}$$

$$k_b + k_c = 5.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \text{ (pH 4.5)}$$

$$(k_k + k_i) = 1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_g = 3.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

$$\text{c.l.} = 1.3 \times 10^3 \text{ (pH 4.5)}$$

Since A and C should be fairly accurate, the relative values should be more reliable than the absolute values. The values refer to 25 °C, ionic strength of 0.050 M, and pH ~4.5. The chain length is predicted to be independent of the bisulfite concentration in the region where the assumed mechanism holds, but will depend on acidity because of the acidity dependence of $k_h + k_i$.

The steady state concentrations of chain carriers and HSO_5^- are of interest. As an example, we take the experiment in Figure 6 for the steady state conditions at 200 s:

$$[\text{SO}_5^{\bullet-}] = 7.4 \times 10^{-9} \text{ M}$$

$$[\text{SO}_4^{\bullet-}] = 1.5 \times 10^{-14} \text{ M}$$

$$[\text{SO}_3^{\bullet-}] = 3.7 \times 10^{-12} \text{ M}$$

$$[\text{HSO}_5^-] = 6.6 \times 10^{-8} \text{ M}$$

A value¹⁹ for k_a of 1.1×10^9 was used in calculating the $\text{SO}_3^{\bullet-}$ concentration.

It is concluded that the assumption of long chains in the pH 4.5 region when deriving rate laws was justified. In addition it is easy to show that the chain termination is proceeding almost entirely by reaction g, rather than reactions 6, 7, and 10 and that reaction e is unimportant in deriving the rate laws.

H. Effect of Ionic Strength. Figure 12 shows the very strong effect of ionic strength on the $\text{HSO}_3^- - \text{O}_2$ reaction at pH 4.5 and 25 °C. Ionic strength was increased by the addition of KNO_3 . The straight line is the theoretical limiting slope according to the proposed mechanism assuming reactions k and l in place of b and c. Note that the rate constants that involve hydrogen ion are defined in terms of activity of hydrogen ion, taken to be $10^{-\text{pH}}$, so no correction for the activity coefficient of hydrogen ion is necessary.

Conclusion

The most important result of the present work is the identification of reaction f as the chain initiation step in the noncatalyzed reaction. Evidence for this conclusion comes from a study of the steady state rate law as well as from relaxation experiments which yielded rate laws for the three components of the chain reaction, i.e. initiation, propagation, and termination. In addition the striking inhibitory effect of methanol was explainable by reaction f. Finally, no other plausible initiation reaction occurred to us.

While initiation by reaction f was determined for the noncatalyzed reaction of bisulfite ion with oxygen in the pH

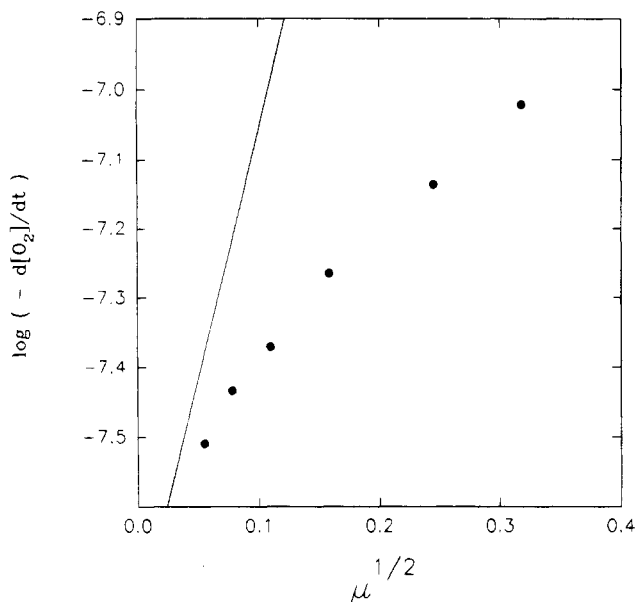


Figure 12. Effect of ionic strength on the HSO_3^- - O_2 reaction at pH 4.50 and 25 °C. $[\text{HSO}_3^-] = 3.12 \times 10^{-3}$ M. The added electrolyte was KNO_3 . The solid line indicates the theoretical limiting slope, but its position is arbitrary.

range 4–5.5, it should be of importance in catalyzed reactions if the catalysis is of a propagation step. Unpublished research indicates this to be the case with manganous ion.

Since reaction f involves HSO_5^- , which is an intermediate in the overall reaction, the question arises as to how the reaction gets started if there is no HSO_5^- present initially. One possibility is the reaction $\text{HSO}_3^- + \text{O}_2 \rightarrow \text{HSO}_5^-$, which has a favorable free energy change of -110 kJ/mol. The reaction is slow because of the triplet to singlet electronic conversion that must take place starting with triplet oxygen. (The chain reaction avoids this difficulty by occurring in a series of one electron steps.) Though slow, the direct reaction may be fast enough to form a very small amount of HSO_5^- , which would then permit the chain reaction to build up autocatalytically to the steady state.

There are other possibilities, however. Any reaction that produced free radicals, which could in turn be converted to one of the chain carriers, would suffice to get the reaction started. Light, cosmic rays, or any radioactive impurities might fill this role.

Experimentally it is observed that a finite time is required for the rate to build up to the steady state, as seen in Figure 1. It is difficult, however, to start with no chain carriers in the bisulfite solution because of the presence of small amounts of oxygen. If the reaction in a closed container and with a

deficiency of oxygen is allowed to go to “completion”, the chain carriers will disappear mostly by reactions 6 and 7 as $\text{SO}_5^{\bullet-}$ is converted to $\text{SO}_3^{\bullet-}$ through the propagation steps a and b plus c at low oxygen concentration. These termination reactions are second order in chain carriers, and therefore the rate of disappearance falls off strongly with time. If oxygen is now added rapidly to the solution, the buildup to the steady state occurs by a first-order, autocatalytic process and therefore much more rapidly. Rough estimates give the order of a few minutes for build up for a solution allowed to stand half an hour after “completion” of the reaction. Experiments of this type did show induction periods of several minutes, but the results were not very reproducible, suggesting that at low concentrations of chain carriers impurities may be playing a significant role.

That HSO_5^- is an intermediate in the reaction under our conditions was strongly supported by the finding that $\text{S}_2\text{O}_7^{2-}$ (pyrosulfate ion) is formed in significant yield,¹⁶ just as it is when HSO_5^- reacts with bisulfite ion.¹⁷ Even more telling was the fact that the pH dependence of the yields was the same. From the comparison of the two yields it was deduced that only 60% of the O_2 - HSO_3^- reaction goes through HSO_5^- by reaction b, while the remaining 40% occurs through reaction c. We believe this is the first reliable measurement of the relative rates of these two reactions.

When peroxydisulfate ion was added to the solution as an initiator forming $\text{SO}_4^{\bullet-}$ free radicals, the resulting rate law agreed with that expected; i.e., the limiting rate law was proportional to the square root of $\text{S}_2\text{O}_8^{2-}$ concentration and the first power of the bisulfite ion concentration.

Although the relaxation experiments yielded the form of the rate laws for the initiation, propagation, and termination reactions, only two relationships were obtained between the three rate constants. Therefore, one additional piece of experimental information on the rate constants was required in order to calculate individual values of the rate constants, as well as the chain length. Five additional sources of information yielded five values of k_t , covering a range of a factor of 6, if the result calculated from the peroxydisulfate experiment is omitted. It is concluded that absolute values of the three rate constants $k_b + k_c$, k_f , and k_g are not known reliably. The chain length appeared to be about 10^3 at pH 4.5, independent of the HSO_3^- concentration.

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