

Kinetics and Mechanism of the Oxidation of  $\text{HSO}_3^-$  by  $\text{HSO}_5^-$ Robert E. Connick,\* Shaoyung Lee,<sup>1a</sup> and Raymond Adamic<sup>1b</sup>

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The oxidation of bisulfite ion by peroxymonosulfate ion,  $\text{HSO}_5^-$ , to form sulfate ion has been studied in the pH region 3.8–7.9. The reaction  $\text{HSO}_5^- + \text{HSO}_3^- \rightarrow 2\text{SO}_4^{2-} + 2\text{H}^+$  was found to obey the rate law  $-\text{d}[\text{HSO}_5^-]/\text{d}t = \{k_a a_{\text{H}^+} + k_b a_{\text{H}^+}^{-1} + k_c\}[\text{HSO}_5^-][\text{HSO}_3^-]$ , where  $a_{\text{H}^+}$  is the activity of hydrogen ion. At 25 °C and ionic strength 0.0050 M the rate constants  $k_a$ ,  $k_b$ , and  $k_c$  have the values  $1.27 \times 10^7$ ,  $6.4 \times 10^{-5}$ , and  $55 \text{ M}^{-1} \text{ s}^{-1}$ , with the activity of hydrogen ion taken to be dimensionless. For the reaction path corresponding to the  $k_a$  term, 90% of the reaction yields the intermediate pyrosulfate ion,  $\text{S}_2\text{O}_7^{2-}$ , which then hydrolyzes with about a 1-min lifetime to sulfate and hydrogen ions. Similarly the  $k_c$  path forms mostly  $\text{S}_2\text{O}_7^{2-}$  as an intermediate. The  $k_b$  path appears to all go directly to sulfate ion. Possible mechanisms for the various reaction paths are discussed.

## Introduction

The oxidation of bisulfite ion is of importance in flue gas desulfurization processes and in the conversion of gaseous  $\text{SO}_2$  into acid rain in water droplets in the atmosphere. Therefore the oxidation of bisulfite ion by oxygen,<sup>2–6</sup> nitrogen dioxide,<sup>7–9</sup> and hydrogen peroxide<sup>10–14</sup> has been studied extensively.

In the oxidation of bisulfite ion by oxygen, it was proposed by Bäckström<sup>2</sup> in one of the earliest studies that peroxymonosulfate ion,  $\text{HSO}_5^-$ , is formed and rapidly reacts with bisulfite ion to yield two sulfate ions. While this suggestion has attracted only limited support, Devuyt, Ettel, and Mosoiu<sup>15</sup> have given experimental evidence for the presence of  $\text{SO}_5^{2-}$  in the reaction carried out in alkaline solution.

One of the peculiarities of the  $\text{O}_2$ – $\text{HSO}_3^-$  reaction is that at moderate pH disulfate ion,  $\text{S}_2\text{O}_7^{2-}$ , is first formed, at least in part, followed by its rapid hydration to two, considerably more stable, sulfate ions. The existence of this intermediate was first detected by Braga and Connick in this laboratory; its identity was established by Chang, Littlejohn, and Hu<sup>16</sup> using a high-pressure stopped-flow apparatus. In the present work it will be shown that the reaction of peroxymonosulfate ion with bisulfite ion also leads to the formation of  $\text{S}_2\text{O}_7^{2-}$ , thereby adding convincing evidence for the presence of  $\text{HSO}_5^-$  as an intermediate in the  $\text{O}_2$ – $\text{HSO}_3^-$  reaction.

In the study of the  $\text{O}_2$ – $\text{HSO}_3^-$  reaction, it is important to know the behavior of any intermediate such as  $\text{HSO}_5^-$ . The present study was undertaken to determine the rate law for the reaction of  $\text{HSO}_5^-$  with bisulfite ion, the yield of  $\text{S}_2\text{O}_7^{2-}$  as an initial product, and the mechanisms of the various reaction paths.

The kinetics of the  $\text{HSO}_5^-$ – $\text{HSO}_3^-$  reaction has been studied at 5 °C in the pH range 0.6–3.0 by Betterton and Hoffman.<sup>17</sup> We were interested in a higher pH range.

## Experimental Section

**Materials.** Sodium bicarbonate, sodium hydroxide, hydrochloric acid, ammonium formate, and succinic acid (Fisher, certified ACS grade); sodium phosphate and sulfuric acid (Mallinckrodt Chemical, analytical reagent grade); and malonic acid (Matheson Coleman & Bell Division) were used directly without further purification. Sulfur dioxide and ammonia were obtained from Matheson Gas Products.

A commercially prepared salt containing peroxymonosulfate ion is available from Du Pont Co. under the trade name of oxone ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ), a white granular powder. Purification of oxone to yield  $\text{KHSO}_5 \cdot \text{H}_2\text{O}$  was achieved by the modification of Appelman's method.<sup>18,19</sup> A 30-g sample of solid was dissolved in 30 mL of water, and insoluble material was filtered off. Potassium bicarbonate was added to the filtrate until the pH of the solution approached ~3.5. The precipitate was again filtered off. Methanol was added to the filtrate; a white precipitate formed and was filtered off. The filtrate was evaporated until white crystals formed. The crystals were collected and air dried. The crude product contained ~95%  $\text{KHSO}_5 \cdot \text{H}_2\text{O}$  as shown by oxidation of iodide ion. Recrystallization of this crude product in a small amount of water gave a pure product of  $\text{KHSO}_5 \cdot \text{H}_2\text{O}$  (99.8% by I<sup>-</sup> oxidation).

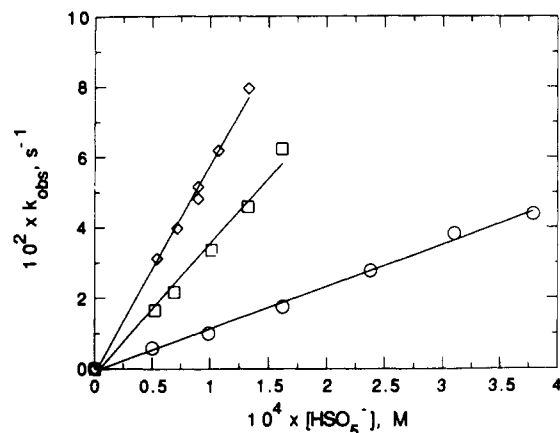
Bisulfite stock solutions were prepared by bubbling sulfur dioxide gas into water in the presence of an appropriate base ( $\text{NaHCO}_3$ ,  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ ) until the pH of the solution approached 4.5.

**Kinetics.** The kinetics of the reaction of peroxymonosulfate ion with bisulfite ion was followed by use of a Cary 118 spectrophotometer. All rate measurements were performed under pseudo-first-order conditions with a 5-fold or greater excess of peroxymonosulfate ion. Temperature was maintained to  $\pm 0.2$  °C. Absorption changes, which were mainly due to the disappearance of  $\text{HSO}_3^-$ , were monitored at  $\lambda = 195 \text{ nm}$  as a function of time.

**Yield of the  $\text{S}_2\text{O}_7^{2-}$  Intermediate.** The yield of intermediate was determined by measuring the amount of base needed to keep the pH constant after the peroxymonosulfate ion was essentially all consumed and then extrapolating this value back to zero time. The following is a typical example for those measurements: 2.00 mL of 1.00 M  $\text{HSO}_3^-$  with appropriate buffer solution was injected into 635 mL of  $2.00 \times 10^{-4}$  M  $\text{HSO}_5^-$  solution which had been purged with nitrogen for at least 1 h. Additional base was added right after the oxidation step was finished (~2–7 s) to bring the pH of the solution to ~9.5 or to pH ~4.5 in the case of the first two experiments of Table II. Then the amount of base added to keep the pH of the solution constant as the  $\text{S}_2\text{O}_7^{2-}$  decomposed

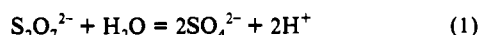
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**Figure 1.** Dependence of  $k_{\text{obs}}$  on the concentration of peroxymonosulfate ion at pH values: 4.45,  $\diamond$ ; 5.50,  $\circ$ ; 6.65,  $\square$ .

was recorded:



The total amount of acid from the decomposition of the intermediate,  $\text{S}_2\text{O}_7^{2-}$ , was calculated by extrapolation back to the time of mixing using the first-order decomposition rate constant<sup>16,20-22</sup> at 25 °C and low ionic strength ( $1.28 \times 10^{-2} \text{ s}^{-1}$ ). Small corrections were made for the fact that not all of the  $\text{S}_2\text{O}_7^{2-}$  was formed instantly and the mixing was not instantaneous. The reaction vessel was all Pyrex glass enclosed in a glass water jacket and equipped with ground-glass joints through the top for the insertion of a buret, an oxygen meter probe, a glass electrode, and pipets. The vessel was filled with liquid to eliminate the gas phase while a small capillary opening to the outside maintained constant pressure. A magnetic stirrer provided mixing. All reactions were followed at 25 °C unless otherwise noted. An Orion Research Model 601 A Ionalyzer was used to measure the pH of the solution and a Yellow Springs Model YSI 57 oxygen meter gave oxygen concentrations.

## Results

For oxidation of S(IV) by peroxymonosulfate ion under pseudo-first-order conditions with  $\text{HSO}_5^-$  in excess, plots of  $\ln(A_1 - A_\infty)$  vs time gave good linear behavior to establish the first-order dependence on [S(IV)], the total sulfur (IV) concentration. From slopes of these plots pseudo-first-order rate constants,  $k_{\text{obs}}$ , were obtained. The plots of  $k_{\text{obs}}$  values against peroxymonosulfate concentration are linear, Figure 1, which indicates a first-order dependence on peroxymonosulfate ion concentration. Table I summarizes the experimental conditions and second-order rate constants defined as

$$-d[\text{HSO}_5^-]/dt = k_2[\text{HSO}_5^-][\text{S(IV)}] \quad (2)$$

Yields of  $\text{S}_2\text{O}_7^{2-}$  are listed in Table II and plotted in Figure 2 as a function of pH. In separate experiments the yield was found to be insensitive to the concentrations of the reactants.

The  $\text{S}_2\text{O}_7^{2-}$  intermediate of the oxidation of bisulfite ion by peroxymonosulfate ion was also detected indirectly by spectrophotometry. Solutions of  $\text{HSO}_5^-$  and  $\text{HSO}_3^-$  were rapidly mixed in a spectrophotometer cell at pH 4.0, and the absorbance was followed as a function of time at 200 nm. The reaction of  $\text{HSO}_5^-$  and  $\text{HSO}_3^-$  to form  $\text{S}_2\text{O}_7^{2-}$  should have been more than 99% complete in 2 s. The absorbance increased with time as the  $\text{S}_2\text{O}_7^{2-}$  hydrolyzed to sulfate ion according to eq 1. The data gave a first-order rate constant of  $1.28 \times 10^{-2} \text{ s}^{-1}$ . Two sulfate ions apparently absorb more strongly than one  $\text{S}_2\text{O}_7^{2-}$  at 200 nm. This was confirmed by making the absorbance measurements on an authentic sample of  $\text{K}_2\text{S}_2\text{O}_7$ .

**Table I.** Kinetic Data<sup>a</sup> for the Oxidation of S(IV) by Peroxymonosulfate Ion

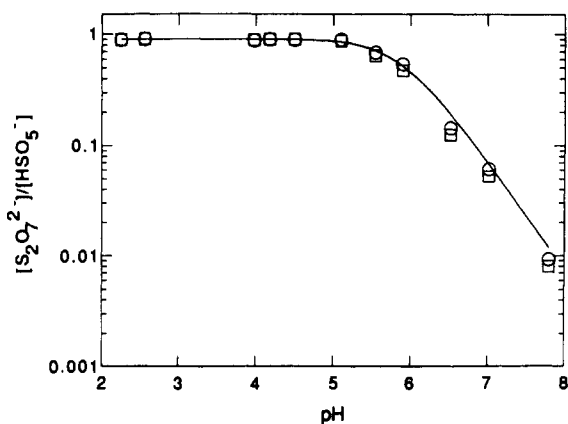
pH	$10^3[\text{buffer}]_{\text{T}}, \text{M}^b$	$10^3\mu, \text{M}$	$\log(k_2)_{\text{expt}}$	$\log(k_2)_{\text{corr}}^c$
3.77	1.82	2.28	3.38	3.37
3.95	1.81	2.10	3.20	3.19
4.15	1.89	2.06	2.97	2.96
4.45	1.97	2.07	2.73	2.72
4.65	2.02	2.07	2.53	2.52
4.90	3.90	3.92	2.29	2.31
5.15	7.91	7.94	2.17	2.18
5.50	7.38	7.95	2.05	2.04
5.60	3.00	3.24	2.00	2.04
5.83	4.52	5.16	2.10	2.10
6.48	3.00	4.20	2.30	2.31
7.05	3.00	6.00	2.75	2.73
7.87	6.13	17.0	3.11	2.94

<sup>a</sup> 25 °C,  $[\text{HSO}_5^-] = 2.5 \times 10^{-5} - 4 \times 10^{-4} \text{ M}$ ;  $[\text{HSO}_3^-] = (4-12) \times 10^{-6} \text{ M}$ . <sup>b</sup> Buffer was formate for experiments with pH less than 5.0 and phosphate for experiments with larger pH. This column gives the total concentration of buffer. The formate buffer reacted slowly with  $\text{HSO}_5^-$  but negligibly during the short time of the reaction. <sup>c</sup> Correction was made to an ionic strength of 0.005 M.

**Table II.** Yield of  $\text{S}_2\text{O}_7^{2-}$  in the Oxidation of  $\text{HSO}_3^-$  by  $\text{HSO}_5^-$ <sup>a</sup>

pH	$\mu, 10^{-3} \text{ M}$	$Y_{\text{expt}}$	$Y_{\text{corr}}^c$	$Y_{\text{corr}}^d$
2.25	8.33	0.894	0.895	0.895
2.56	10.5	0.905	0.904	0.904
3.98	10.5	0.886	0.884	0.884
4.18	4.00	0.900	0.900	0.900
4.50 <sup>b</sup>	4.36	0.894	0.894	0.895
5.10 <sup>b</sup>	11.2	0.856	0.866	0.888
5.55 <sup>b</sup>	13.6	0.600	0.636	0.684
5.90 <sup>b</sup>	19.3	0.399	0.469	0.539
6.52	5.68	0.124	0.124	0.143
7.02	7.44	0.049	0.053	0.061
7.80	8.88	0.007	0.008	0.009

<sup>a</sup> [S(IV)]  $\sim 4 \times 10^{-3} \text{ M}$ ,  $[\text{HSO}_5^-] = (1.33-3.30) \times 10^{-4} \text{ M}$ . <sup>b</sup> At pH 5.90, malonate buffer of total concentration  $6.4 \times 10^{-3} \text{ M}$ . At pH 5.55 and 5.10, succinate buffer of total concentration  $4.8 \times 10^{-3} \text{ M}$ . At pH 4.50, acetate buffer of total concentration  $3.1 \times 10^{-3} \text{ M}$ . The buffers reacted slowly with  $\text{HSO}_5^-$  but negligibly during the short time of the reaction. <sup>c</sup> Yields of  $\text{S}_2\text{O}_7^{2-}$  were corrected to  $\mu = 0.005 \text{ M}$ , assuming that the reaction occurred at the final ionic strength of mixed solution, shown in column 2. <sup>d</sup> Yields of  $\text{S}_2\text{O}_7^{2-}$  were corrected to  $\mu = 0.005 \text{ M}$ , assuming that on average the reaction occurred at twice the final ionic strength shown in column 2.



**Figure 2.** Dependence of yield of  $\text{S}_2\text{O}_7^{2-}$  on pH:  $\square$ , assuming reaction occurred at final ionic strength of solution;  $\circ$ , assuming reaction occurred on average at twice final ionic strength of solutions. The solid line is a least-squares fit to eq 5 using twice final ionic strength.

## Discussion

**Rate Law.** From the experimental results the rate of reaction has a first-order dependence on both the  $\text{HSO}_5^-$  and the sulfur(IV) concentrations in the region investigated. The pH dependence is more complex. At low pH the value of  $k_2$  is directly proportional to the concentration of hydrogen ion; around pH 6.5

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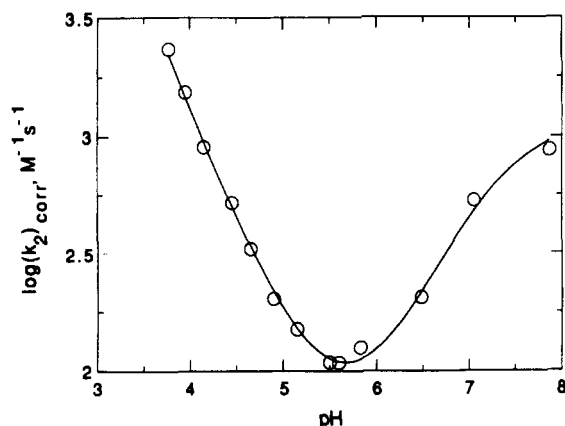


Figure 3. Dependence of  $k_{2\text{corr}}$  on pH.

it appears to be inversely proportional to  $[\text{H}^+]$  while at higher pH it seems to be leveling off to no dependence on  $[\text{H}^+]$ . (See Figure 3.) The change from  $[\text{H}^+]^{-1}$  dependence to no dependence on hydrogen ion concentration starting around pH 7 merely arises from the ionization of bisulfite ion to form  $\text{SO}_3^{2-}$  as the principal S(IV) species above  $\text{pH} \sim 7$ .

Because the experiments were done at different ionic strengths, the values of  $k_2$  were all corrected to an ionic strength of 0.005 M using Kielland's<sup>23</sup> values for single ion activity coefficients. The corrections were made using the rate law and rate constants finally deduced for the reaction. It is these corrected values,  $k_{2\text{corr}}$ , shown in the last column of Table II, that are plotted in Figure 3.

In the pH region where the change occurs from first power hydrogen ion dependence to inverse first power hydrogen ion dependence, it was found that the data could not be fitted satisfactorily with these two terms and that it was necessary to introduce a zero-order hydrogen ion dependent term as well. This last term at most only accounted for 40% of the rate of reaction and therefore was somewhat suspect. It turned out, however, that its presence was strongly confirmed in the  $\text{S}_2\text{O}_7^{2-}$  yield experiments discussed below.

In all of the experiments the hydrogen ion concentration was not measured directly; only the pH was determined. In fitting the data to a rate law and in correcting data from one ionic strength to another, it was convenient, therefore, to assume that the pH equals the negative logarithm of the activity of hydrogen ion,  $a_{\text{H}^+}$ , and to use this quantity in rate laws and equilibrium quotients. An example of the latter is the equilibrium quotient for the ionization of bisulfite ion, where activity is used for hydrogen ion but concentrations for the other species:

$$Q_2' = a_{\text{H}^+}[\text{SO}_3^{2-}]/[\text{HSO}_3^-] \quad (3)$$

The rate data of Table I, corrected to an ionic strength of 0.005 M, were fitted to the following expression:

$$-d[\text{HSO}_5^-]/dt = -d[\text{S(IV)}]/dt = \{k_a a_{\text{H}^+} + k_b a_{\text{H}^+}^{-1} + k_c\}[\text{HSO}_5^-][\text{S(IV)}](1 + Q_2' a_{\text{H}^+}^{-1})^{-1} \quad (4)$$

The terms  $[\text{S(IV)}]/(1 + Q_2' a_{\text{H}^+}^{-1})$  equals  $[\text{HSO}_3^-]$ . The value of  $\log Q_2'$  at ionic strength 0.005 M and 25 °C was determined independently to be  $-7.17$ . The least-squares fit gave  $k_a = (1.27 \pm 0.05) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_b = (6.4 \pm 0.3) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_c = 55 \pm 5 \text{ M}^{-1} \text{ s}^{-1}$  (with  $a_{\text{H}^+}$  taken as dimensionless). The fit is shown as the solid curve in Figure 3.

**Yield Of  $\text{S}_2\text{O}_7^{2-}$ .** The yield of  $\text{S}_2\text{O}_7^{2-}$  varies with pH (Figure 2) from about 90% at low pH to almost none at pH 7.8. The yield should be related to the rate law. Apparently the  $k_a$  rate law term is giving about 90%  $\text{S}_2\text{O}_7^{2-}$  and the  $k_b$  term is contributing

essentially 0%, while it is difficult to tell by eye the yield for the  $k_c$  term. The data were fitted to the following expression where  $Y$  is the fraction of the reaction that goes through  $\text{S}_2\text{O}_7^{2-}$ :

$$Y = \{f_a k_a a_{\text{H}^+} + f_c k_c\} / \{k_a a_{\text{H}^+} + k_b a_{\text{H}^+}^{-1} + k_c\} = \{f_a a_{\text{H}^+} + f_c k_c/k_a\} / \{a_{\text{H}^+} + k_b/(k_a a_{\text{H}^+}) + k_c/k_a\} \quad (5)$$

In addition to the rate constants  $k_a$ ,  $k_b$ , and  $k_c$ , eq 5 contains the two parameters  $f_a$  and  $f_c$ , which represent the yield of  $\text{S}_2\text{O}_7^{2-}$  in the reaction paths corresponding to the  $k_a$  and  $k_c$  terms in the rate law. It is assumed that  $f_a$  and  $f_c$  are constants, independent of pH and ionic strength. Attempts to fit the data with the four independent parameters  $f_a$ ,  $f_c$ ,  $k_b/k_a$ , and  $k_c/k_a$  resulted in very large uncertainties in their values. Therefore the values of  $k_b/k_a$  and  $k_c/k_a$  were taken from the kinetic results and the data fitted for  $f_c$  assuming  $f_a$  equal to 0.90. The fit is shown as the solid curve in Figure 3. The data used were  $Y_{\text{corr}}$  shown in the last column of Table II, where the  $Y$  values have all been corrected to ionic strength 0.005 M using Kielland's<sup>23</sup> single ion activity coefficients. There is uncertainty as to what to use for the ionic strength of the reaction because it changed during the course of the reaction. Almost all of the ionic strength came from the small volume of concentrated bisulfite solution with buffer that was added to the large volume of dilute peroxymonosulfate solution. Concentrations were such that the lifetime for the reaction was of the order of 0.4–3 s, i.e. about the same or more rapid than the mixing. In order to correct approximately for the changing ionic strength, an average value corresponding to half-mixing, i.e. twice the final ionic strength (column 2 of Table II), was used as the ionic strength of the reaction in calculating  $Y_{\text{corr}}$ . The rate constants previously found were corrected for ionic strength using Kielland's<sup>23</sup> values of activity coefficients, and  $f_a$  and  $f_c$  were both taken to be 0.90 in making the corrections.

As may be seen from Table II the corrections are small except in the region where  $Y$  is decreasing rapidly with increasing pH. The changing ionic strength also causes the pH of the reacting solution to change. This correction, however, is considerably less than the effect on the rate constants and was not made.

In the next to last column of Table II are given values of  $Y$  corrected to an ionic strength of 0.005 M assuming that the reaction took place at the final ionic strength of the reaction solution (column 2). Comparison of the last two columns shows that the assumption about ionic strength makes a small but significant difference. The choice of twice the final ionic strength as the average for the reaction should be much closer to the experimental situation.

The values of  $Y_{\text{corr}}$  of the last two columns of Table II are plotted in Figure 2 as a function of pH, with squares for column 4 and circles for column 5. The solid curve is the least-squares fit to the data of the last column of Table II. The value of  $f_c$  found was 0.88, but it could easily be as high as 1.0 or as low as 0.7.

The question arises whether the 90% yield of  $\text{S}_2\text{O}_7^{2-}$  at low pH should actually be 100% and differs from the latter value only because of some artifact of the measurements, such as experimental error, impurities, etc. The experiments were reproducible to  $\pm 2\%$ . On mixing there was an immediate drop in pH as the reaction between  $\text{HSO}_5^-$  and  $\text{HSO}_3^-$  occurred; the drop in pH corresponded within experimental error to ca. 10% of the reaction going directly to sulfate and hydrogen ions (eq 6). The overall



acid stoichiometry, after the  $\text{S}_2\text{O}_7^{2-}$  had hydrolyzed, agreed with the known initial concentrations of reactants. Different preparations of  $\text{HSO}_5^-$ , including a different method of preparation, gave the same results. Therefore it is concluded that the ca. 10% direct reaction at low pH is real.

As discussed earlier, the small contribution of the acid-independent term to the rate of reaction raised questions as to its reality. The evidence for its presence is greatly strengthened by the experiments on the yield of  $S_2O_7^{2-}$ . Attempts to fit the yield data of Table II with only the  $k_a$  and  $k_b$  rate constants and  $f_a = 0.90$  gave very poor results. The reason for this is readily seen in Figure 2. If the  $k_c$  term is absent, the falloff in  $Y$  with increasing pH should approach a negative slope of 2. If the  $k_c$  term is present, the falloff should approach a negative slope of one, as indicated by the calculated curve.

One interesting result of the first experiments on measuring the yield of  $S_2O_7^{2-}$  was a set of data giving results similar to those in Figure 2 but shifted about one pH unit to higher pH. The experiments were performed by adding a small volume of a rather concentrated peroxymonosulfate solution to a large volume of a bisulfite solution with bisulfite in at least 5-fold excess stoichiometrically and with concentrations such that the reaction was complete in a fraction of a second. The pHs of the two solutions were the same before mixing and 0.05–0.3 pH units lower immediately after mixing because of the part of the reaction that goes directly to sulfate and hydrogen ions (eq 6). The excess S(IV) acted as a buffer to prevent a larger pH change. It seemed reasonable to assume that the reaction occurred in the pH range between the initial pH and the "final" pH measured after mixing. On finding that the data bore no relationship to the pH dependence of the rate of reaction, it was realized that the pH at which most of the reaction was occurring was considerably lower than the initial and final pH. Because the mixing was slower than the reaction, the reaction occurred primarily in the region where the solution of  $HSO_5^-$  was added. In this localized region most of the bisulfite was consumed, consequently reducing greatly its buffering capacity. To correct the problem the mixing order was reversed, i.e. a small volume of concentrated bisulfite solution was added to a large volume of peroxymonosulfate solution, and, where necessary, buffer solutions were added to the bisulfite solution. (See Table II.)

**Mechanisms.** With three terms in the rate law and two of these giving partial yields of  $S_2O_7^{2-}$ , there are five independent reaction paths to be accounted for.

There is no evidence from the experiments that the reaction goes by a chain mechanism, and therefore it will be assumed to be nonchain, a conclusion also reached by Betterton and Hoffmann.<sup>17</sup>

Betterton and Hoffmann<sup>17</sup> found the rate law in the pH range 0.62–2.95 to be of the form:

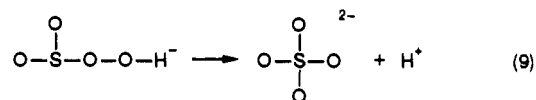
$$-d[HSO_5^-]/dt = k_1[HSO_5^-][HSO_3^-][H^+]/(1 + k_2[H^+]) \quad (7)$$

They proposed two possible mechanisms for the reaction, one of which had  $S_2O_7^{2-}$  as an intermediate. They were unable to determine experimentally whether  $S_2O_7^{2-}$  was formed and therefore could not decide which rate law was invalid. As seen from eq 7 their rate law at the high end of their pH range becomes the same as that found here for the  $k_a$  term.

**Acid-Dependent Term.** From pH 3.7 to 5.3 the principal term in the rate law is  $k_a[HSO_5^-][HSO_3^-][H^+]$ . About 90% of the reaction goes through the intermediate  $S_2O_7^{2-}$ , disulfate ion, while the remaining ~10% proceeds directly to sulfate ion by a separate path. In the analogous chemical reaction between hydrogen peroxide and bisulfite ion, Halperin and Taube<sup>24</sup> showed by <sup>18</sup>O tracer experiments that both oxygens of the peroxide were incorporated into the sulfate ions formed. To explain this result they proposed that a peroxydisulfite species is first formed:

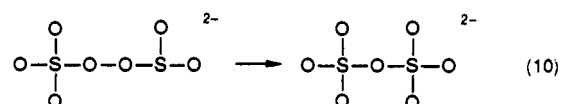


This peroxydisulfite ion could then rearrange to form a sulfate ion containing the two peroxide oxygens.



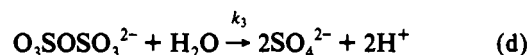
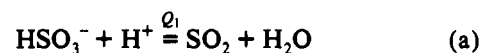
In subsequent work, Hoffman and Edwards<sup>13</sup> determined the rate law for the  $H_2O_2$ - $HSO_3^-$  reaction from pH 4 to 8 and showed that a mechanism could be written consistent with the above suggestion of Halperin and Taube. The rate law they found was identical to that found here for the acid-dependent term of the  $HSO_5^-$ - $HSO_3^-$  reaction if hydrogen peroxide is replaced by peroxymonosulfate ion.

In addition to the likely similarity of the reaction of bisulfite ion with the two peroxides, the rearrangement of peroxydisulfite ion to sulfate ion, eq 9, nicely accounts for the formation of disulfate ion through the analogous rearrangements of the corresponding peroxydisulfite species formed in the  $HSO_5^-$ - $HSO_3^-$  reaction:

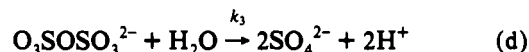
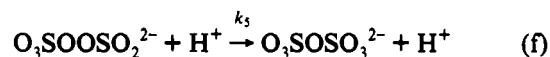
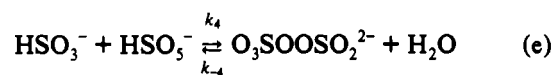


Considering for the moment only the acid-catalyzed reaction path in which disulfate ion is formed as an intermediate, the mechanism must have an activated complex of formula  $HSO_3^- \cdot HSO_5^- \cdot H^+ \pm H_2O$  as well as account for the formation of the disulfate ion intermediate. Two plausible possibilities for the rate-determining step would be (1) the formation of the peroxydisulfite species or (2) its rearrangement to disulfate ion, and mechanisms for each can be written.

mechanism 1:



mechanism 2:



Mechanism 2 is the second mechanism proposed by Betterton and Hoffmann<sup>17</sup> except for eq d which they have mistakenly shown as acid catalyzed.<sup>20–22</sup> The rate-determining steps are b and f for mechanisms 1 and 2, respectively. Steps a and b could be condensed into a single step, as far as the rate law is concerned:



Although steps e and f when combined would also fit the rate law, in the analogous  $H_2O_2$ - $HSO_3^-$  reaction this possibility is excluded at low pH by a change in the rate law discussed below. The rate

laws for the two mechanisms are

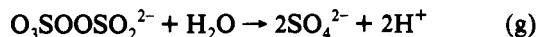
$$-d[\text{HSO}_5^-]/dt = k_1 Q_1 [\text{HSO}_5^-] [\text{HSO}_3^-] [\text{H}^+]$$

$$-d[\text{HSO}_5^-]/dt = (k_4 k_5 / k_{-4}) [\text{HSO}_5^-] [\text{HSO}_3^-] [\text{H}^+]$$

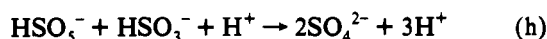
While the experimental data for the  $\text{HSO}_5^-$ - $\text{HSO}_3^-$  reaction do not permit a choice between mechanisms 1 and 2, in the case of the  $\text{H}_2\text{O}_2$ - $\text{HSO}_3^-$  reaction Hoffman and Edwards<sup>13</sup> chose the analogue to mechanism 2 because their data indicated generalized acid catalysis of the reaction, a result subsequently confirmed by McArdle and Hoffman.<sup>14</sup> In the present work the possible presence of generalized acid catalysis was not investigated because of the difficulty of finding acid-base systems that would not obscure the absorbance of bisulfite ion at the short wavelengths employed. Betterton and Hoffmann<sup>17</sup> also did not investigate generalized acid catalysis.

At low pH, Betterton and Hoffmann found the rate law to change to first power in  $[\text{HSO}_3^-]$  and  $[\text{HSO}_5^-]$  but zero order in  $[\text{H}^+]$ . (See eq 7.) In the case of the  $\text{H}_2\text{O}_2$ - $\text{HSO}_3^-$  reaction, at acidities in the neighborhood of 1 M, the rate law written in terms of bisulfite ion also changes to first order in  $\text{H}_2\text{O}_2$  and  $\text{HSO}_3^-$  and zero order in  $\text{H}^+$  concentration.<sup>12,14</sup> This change in rate law is to be expected from mechanism 2 when the e step becomes rate determining as the acidity is increased. In the case of mechanism 1 the corresponding change in rate law would occur if step c became rate determining as the acidity is increased. The effect, however, lay outside of the pH range studied here.

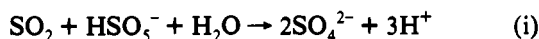
Next consider the acid-dependent term of the rate law when  $\text{S}_2\text{O}_7^{2-}$  is not formed as an intermediate. This term could be fitted into the scheme of mechanism 1 by replacing step c by



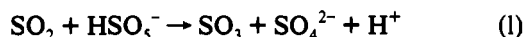
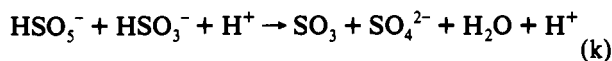
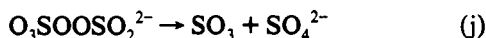
or replacing step ab by



or replacing step b by



Actually there is sufficient driving force to permit formation of  $\text{SO}_3$  in steps g-i:



In the scheme of mechanism 2 the acid-dependent term that does not yield  $\text{S}_2\text{O}_7^{2-}$  as an intermediate can be accounted for by replacing step f by

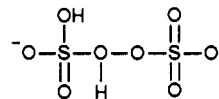


or



There is no obvious best choice between the various alternatives for the acid-dependent term which does not yield  $\text{S}_2\text{O}_7^{2-}$ .

The first mechanism given by Betterton and Hoffmann<sup>17</sup> could only be correct for the ca. 10% part of the  $\text{HSO}_5^-$ - $\text{HSO}_3^-$  reaction that does not go through the intermediate  $\text{S}_2\text{O}_7^{2-}$ , since the mechanism does not involve this species. The mechanism seems implausible, however, for two reasons. First, it is postulated that the species



exists as an intermediate. The formula would require a pair of electrons to be accommodated in a *nonbonding* d orbital on a sulfur or in an antibonding molecular orbital and therefore is suspect. Second, the peroxide group in this species is required to be a weak acid, contrary to the known behavior of such peroxides, e.g. peroxydisulfate ion.

**Acid-Independent Term.** Around pH 5.5 the term corresponding to  $k_c[\text{HSO}_5^-][\text{HSO}_3^-]$  is appreciable, although never more than 40% of the reaction rate. Again  $\text{S}_2\text{O}_7^{2-}$  is formed as an intermediate with a probably constant yield of about 90%. Since  $\text{S}_2\text{O}_7^{2-}$  is formed, it is reasonable to try to fit the mechanism into the scheme of mechanism 1 and mechanism 2 of the acid-dependent term.

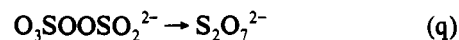
First consider the reaction path in which  $\text{S}_2\text{O}_7^{2-}$  is formed. The term could be accommodated in the mechanism 1 scheme by replacing step ab by



or replacing step b by



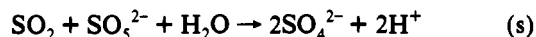
In the scheme of mechanism 2, the terms could be fitted in by replacing step f by



For the acid-independent term where the path does not involve  $\text{S}_2\text{O}_7^{2-}$  the mechanism could be adapted to the scheme of mechanism 1 by replacing step ab by



or by altering step b to



or by changing step b to

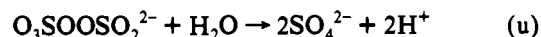


followed by step g or by replacing step ab by



followed by step g.

The scheme of mechanism 2 would have to be altered by replacing step f by



As before,  $\text{SO}_3$  might be formed instead of  $\text{SO}_4^{2-} + 2\text{H}^+$  in steps r, s, and u.

Again, for the acid-independent paths the choice of mechanistic schemes is not obvious. As pointed out earlier, the yields of  $\text{S}_2\text{O}_7^{2-}$  by the acid-dependent and acid-independent paths are at least comparable and may be the same. If the latter is the case, this result would be readily explained if in both the acid-dependent and the acid-independent reactions the  $\text{S}_2\text{O}_7^{2-}$ - $\text{SO}_4^{2-}$  split occurs when  $\text{O}_3\text{SOOSO}_2^{2-}$  reacts 90% by step c and 10% by step g or j. The mechanisms that would result are

acid-dependent rate:

90%: steps a, b or ab, c, and d

10%: steps a, b or ab, and g or j

acid-independent rate:

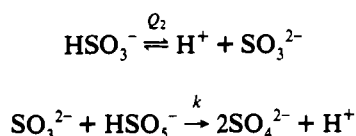
90%: steps a, p or t, c, and d

10%: steps a, p or t, and g or j

A similar explanation is not possible with the scheme of mechanism 2. The similarity in the  $S_2O_7^{2-}$ – $SO_4^{2-}$  split therefore provides some evidence in favor of the scheme of mechanism 1 and the choice of particular steps. Because the accuracy of the  $S_2O_7^{2-}$  yield data for the acid-independent term is not great, the result is suggestive but not conclusive.

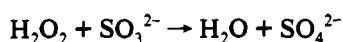
The close correspondence between the acid-dependent term of the rate law for the  $HSO_3^-$ – $HSO_5^-$  reaction with that of the  $HSO_3^-$ – $H_2O_2$  reaction, both in form and value of the rate constant (see below), is suggestive that the two mechanisms are similar. Since the  $HSO_3^-$ – $H_2O_2$  reaction is subject to general acid catalysis,<sup>13,14</sup> perhaps the  $HSO_3^-$ – $HSO_5^-$  reaction is also. If so, general acid catalysis could be accounted for in mechanism 2 by step f, with hydrogen ion replaced by another acid. In mechanism 1, general acid catalysis could be introduced through the alternative step ab, a termolecular reaction. While termolecular reactions are usually considered improbable, it does not seem possible to rule it out with the present information. Should the ab step be correct, the  $HSO_3^-$ – $H_2O_2$  mechanism could be reinterpreted in terms of the analogue of mechanism 1 with the step ab analogue of a termolecular reaction between  $H_2O_2$ ,  $HSO_3^-$ , and an acid. In these termolecular reactions the acid consumed would likely be involved in removing an  $OH^-$  group from the  $HSO_3^-$  to form  $H_2O$  while the acid formed was liberated from the peroxide group.

**Inverse Hydrogen Ion Dependent Term.** This term in the rate law is most simply accounted for by the mechanism



in which the oxygen–oxygen bond of  $HSO_5^-$  is broken with transfer of one oxygen to the sulfite ion. Tracer oxygen experiments would be interesting to do, since for the inverse hydrogen ion dependent term it would be predicted that one of the peroxide oxygens would end up on each sulfate ion while for the acid-dependent and acid-independent reaction paths it is expected that half the time both peroxide oxygens would end up on one sulfate and half the time one peroxide oxygen on each sulfate when the reaction proceeds by way of  $S_2O_7^{2-}$ .

The reaction of hydrogen peroxide with bisulfite (or sulfite) ion has a corresponding term in its rate law, i.e.  $k[H_2O_2][SO_3^{2-}]$ .<sup>10</sup> It is not known how many of the peroxide oxygens end up on the sulfate ion when this path is important. As pointed out by Halperin and Taube,<sup>24</sup> the tracer experiments of Winter and Briscoe<sup>25</sup> show that one water molecule is formed in the reaction



but give no information on the source of the oxygen, i.e. whether it came from the hydrogen peroxide or the sulfite ion.

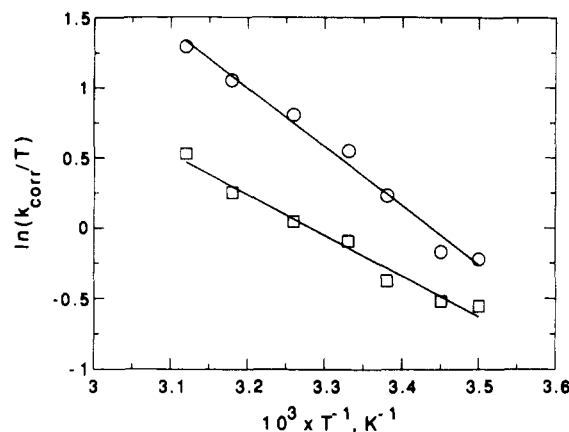


Figure 4. Dependence of  $\ln(k_{\text{corr}}/T)$  on  $T^{-1}$ : O, at pH 4.68; □, at pH 6.46.

**Temperature Dependence of the Rate.** Activation parameters were determined for the reaction at pHs 4.68 and 6.46. The same stock solutions and volumes were used in each set of experiments at each pH. For the set at pH 4.68 the solutions contained formate buffer at a total concentration of  $3.00 \times 10^{-3}$  M. The measured pH changed with temperature because of the temperature dependence of the formate buffer. The observed  $k_2$  values were corrected to pH 4.68 assuming that the 17% contribution of the  $k_c$  term at 25 °C remained the same over the whole temperature range and therefore the  $k_2$  values were proportional to the activity of hydrogen ion. In Figure 4 these  $k_{\text{corr}}$  values, divided by the absolute temperature, are plotted versus  $1/T$ . The resulting values of  $\Delta H^\ddagger = 35 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = 8 \text{ J mol}^{-1} \text{ K}^{-1}$  must be considered as only approximate values for the  $k_a$  term.

At pH 6.46 the temperature dependence of the rate was measured in solutions containing phosphate buffer of a total concentration  $3.09 \times 10^{-3}$  M. At this pH appreciable concentrations of sulfite ion are present in addition to bisulfite ion. The  $k_2$  values at each temperature were first corrected to correspond to the actual amount of  $HSO_3^-$  present using the experimentally determined  $Q_2$  value for the ionization of bisulfite ion at 25 °C and ionic strength 0.0045 M, along with  $\Delta H = 4.0 \text{ kcal}$  for the ionization.<sup>26</sup> These values were then corrected to pH 6.46 on the assumption that the contribution of 23% to the rate by the acid-independent term remained the same over the temperature range and that therefore the  $k_2$  values were inversely proportional to the activity of hydrogen ion. These values are also plotted as  $k_{\text{corr}}/T$  in Figure 4. Because of the above assumption, the resulting values of  $\Delta H^\ddagger = 24 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -120 \text{ J mol}^{-1} \text{ K}^{-1}$  are only approximately related to the  $k_3$  rate constant.

**Comparison with the  $HSO_3^-$ – $H_2O_2$  Reaction.** As noted by Betterton and Hoffman<sup>17</sup> and as pointed out in the discussion of mechanisms, there is a marked similarity in the rate law terms as well as the rate constants of the reaction of bisulfite ion with peroxymonosulfate ion and with hydrogen peroxide. The comparison is shown in Table III. For the first two rate law terms (rows 1 and 2) the similarity in rate constants is quite striking. Replacing a proton by  $SO_3$  on  $H_2O_2$  has very little effect on the rate and would indicate that neither this proton nor the  $SO_3$  is importantly involved up through the rate-determining step.

The acid-independent term (3rd row) is not reported in the hydrogen peroxide case; Mader's<sup>10</sup> report of an empirical rate law in the pH region 7–8 of the form

$$\text{rate} = [H_2O_2][SO_3^{2-}](10^{-1.8\text{pH}}k_1 + k_0)$$

may be an indication of a contribution from a  $[HSO_3^-][H_2O_2]$

(25) Winter, E. R. S.; Briscoe, H. V. A. *J. Am. Chem. Soc.* **1951**, *73*, 496.

(26) Smith, R. N.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1976.

**Table III.** Comparison of Rate Constants for the  $\text{HSO}_5^-$ - $\text{HSO}_3^-$  Reaction with Those of the  $\text{H}_2\text{O}_2$ - $\text{HSO}_3^-$  Reaction

rate law <sup>a</sup>	$\text{HSO}_5^-$ - $\text{HSO}_3^-$ reactn		$\text{HSO}_3^-$ - $\text{H}_2\text{O}_2$ reactn	
	$k^b$	conditions	$k^b$	conditions
$k[\text{HSO}_3^-][\text{per}]$ (low pH)	$1.21 \times 10^6$ <sup>c</sup>	5 °C, $\mu = 0.2$ M	$2.6 \times 10^6$ <sup>d,e</sup>	15 °C, $\mu = 1.0$ M
$k[\text{HSO}_3^-][\text{per}]a_{\text{H}^+}$	$7.14 \times 10^6$ <sup>c</sup>	5 °C, $\mu = 0.2$ M	$4.2 \times 10^7$ <sup>d,e</sup>	15 °C, $\mu = 1.0$ M
	$1.27 \times 10^7$ <sup>f</sup>	25 °C, $\mu = 0.005$ M		
$k[\text{HSO}_3^-][\text{per}]$ (high pH)	55 <sup>f</sup>	25 °C, $\mu = 0.005$ M	not obsd	
$k[\text{HSO}_3^-][\text{per}]a_{\text{H}^+}^{-1}$	$6.4 \times 10^{-5}$ <sup>f</sup>	25 °C, $\mu = 0.005$ M	$5.6 \times 10^{-8}$ <sup>g</sup>	25 °C, $\mu = 1.0$ M

<sup>a</sup> [per] represents the concentrations of the peroxides  $\text{HSO}_5^-$  and  $\text{H}_2\text{O}_2$  for the  $\text{HSO}_5^-$ - $\text{HSO}_3^-$  and  $\text{HSO}_3^-$ - $\text{H}_2\text{O}_2$  reactions, respectively. <sup>b</sup> Units are in seconds and M. <sup>c</sup> Reference 17. <sup>d</sup> Reference 14. <sup>e</sup> The concentration of hydrogen ion, rather than its activity, was used in the rate law. <sup>f</sup> This work. <sup>g</sup> Reference 10.

term, since otherwise the pH-dependent term above should have been  $10^{-2\text{pH}}$ . In any event the rate constant for the third rate law of Table III would appear to be considerably smaller for the  $\text{H}_2\text{O}_2$  reaction than for the  $\text{HSO}_5^-$  reaction. The inverse hydrogen ion term (last row) shows significantly different rate constants for the two reactions.

As shown in Table III, one unusual feature of the  $\text{HSO}_5^-$ - $\text{HSO}_3^-$  reaction is that the same rate law but with different rate constants dominates in two different pH regions. (See the first

and third rate laws of the table.) Of course the reaction is occurring in these two different pH regions by two separate reaction paths.

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