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Effect of Ions on the Hydrolysis of Disulfate Ion

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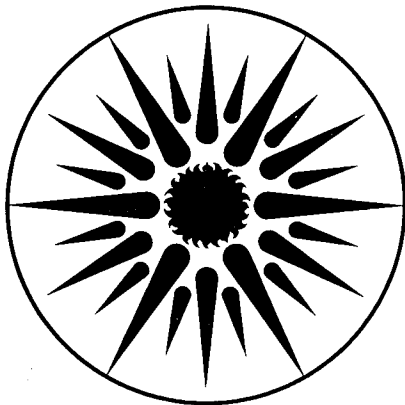
### Effect of Ions on the Hydrolysis of Disulfate Ion

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November 1989

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## Effect of Ions on the Hydrolysis of Disulfate Ion

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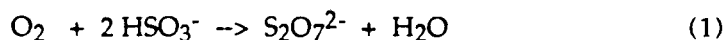
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## Abstract

The influence of anions and cations commonly found in flue gas scrubber systems on the hydrolysis rate of disulfate ion ( $S_2O_7^{2-}$ ) has been studied. The cations studied include  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Mn^{2+}$ . The anions studied include  $SO_3^{2-}$ ,  $SO_4^{2-}$ ,  $S_2O_3^{2-}$ ,  $S_2O_6^{2-}$ ,  $HSO_3^-$ ,  $Cl^-$ ,  $H_2PO_4^-$ , and  $HPO_4^{2-}$ . Of these ions,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $SO_3^{2-}$ , and  $S_2O_6^{2-}$  were found to demonstrate a catalytic effect on  $S_2O_7^{2-}$  hydrolysis. Adipic acid was also tested and was found to have no effect on  $S_2O_7^{2-}$  hydrolysis at the conditions studied. Activation energies were determined for the  $S_2O_7^{2-}$  hydrolysis rate catalyzed by  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $SO_3^{2-}$ , as well as for the uncatalyzed rate.

The oxidation of bisulfite ion ( $\text{HSO}_3^-$ ) is a process that is important in the chemistry of atmospheric aerosols and flue gas desulfurization systems. It was recently discovered that disulfate ion is formed as an intermediate in the oxidation of bisulfite ion by oxygen in aqueous solutions (Chang et al, 1987; Littlejohn et al, 1988).



The disulfate ion then hydrolyzes to form bisulfate ion and/or sulfate ion.



There have been several studies of the disulfate ion hydrolysis reaction reported in the literature. The temperature dependence of the reaction has been studied and the activation energy ( $E_a = 11.3 \text{ kcal/mol}$ ) has been established by several groups (Hofmeister and Van Wazer, 1962; Thilo and von Lampe, 1963; Ryss and Drabkina, 1973; Plathotnick and Drabkina, 1976,1977). The rate of hydrolysis of disulfate ion is influenced by other ions present in solution (Thilo and von Lampe, 1963,1964,1967). In flue gas desulfurization systems, it is desirable to be able to predict and control the rate of oxidation of bisulfite ion to sulfate ion. To be able to accurately predict the disulfate hydrolysis rate, the cumulative effects of the ions present in solution must be determined. Thilo and von Lampe (1963, 1964) have studied the effect of cations on the hydrolysis reaction at  $0^\circ\text{C}$ . They found that cations accelerate the hydrolysis and that the degree of acceleration is increased by increasing ionic charge and decreasing ionic radius of the cation. The catalysis of the hydrolysis reaction by metal ions is related to their stability constants for complex formation with EDTA, suggesting that metal ions form a complex with the disulfate ion to hasten the hydrolysis. In contrast to studies of cation effects, there has been little work done on effects of anions on the disulfate hydrolysis rate, particularly those anions found in

solutions used in flue gas desulfurization processes. Also, most work has been done at 0°C, where the longer hydrolysis half-life makes it easier to study the reaction. Information is needed on the reaction at higher temperatures and on the effect of ions found in flue gas scrubbing solutions.

## Experimental Section

Sodium disulfate salt was prepared by heating sodium bisulfate to a temperature of about 180°C for 3 to 5 days (Hofmeister and Van Wazer, 1962). The progress of the conversion was monitored by taking Raman spectra of samples of the heated solid. There are other methods for preparing disulfate salts (Thilo and von Lampe, 1963). The other compounds used in this study were reagent grade chemicals. Doubly-deionized water was used for preparing solutions.

Initial studies of the disulfate hydrolysis reaction were done using Raman spectroscopy. Disulfate ion and its hydrolysis products, sulfate ion and bisulfate ion, have fairly strong Raman lines at 1090, 981, and 1050  $\text{cm}^{-1}$ , respectively (Millen, 1950; Littlejohn et al., 1988). The hydrolysis reaction was studied by rapidly dissolving the disulfate salt in water or aqueous solution of the desired composition and inserting a sample in the Raman spectrometer. The signal intensity was monitored at 1090, 981, or 1050  $\text{cm}^{-1}$ . The decay or build-up of the signal was used to determine the hydrolysis rate constant. Raman spectroscopy is not a very sensitive technique, and was not usable for disulfate ion concentrations below about 0.1 M. However, it does allow unambiguous determination of the reaction products.

For studies involving lower concentrations of disulfate ion, a pH meter is used to monitor the change in the acidity of the solution during the hydrolysis of disulfate ion. The signal from the pH meter is sent to a chart recorder. The combined response of the pH electrode, meter and recorder is faster than the rate of hydrolysis of the disulfate ion under

the conditions of our studies. The recorded signal is used to determine the  $H^+$  production as a function of time, which was used, in turn, to calculate the hydrolysis rate constant. The initial pH of the solution is adjusted to alkaline conditions (pH 11-12) before the addition of the disulfate salt. The final pH was usually 3 or higher, so catalysis by  $H^+$  was generally not a problem. Measurements by Thilo and von Lampe indicate that  $H^+$  catalysis of disulfate hydrolysis occurs only below pH 3. This may be due to the formation of the species  $HS_2O_7^-$ , which could hydrolyze more quickly than  $S_2O_7^{2-}$ .

Most experiments were done with 0.010 M sodium disulfate solutions at a temperature of 20°C. For temperature dependent studies, runs were done from 0 to 30°C. The concentrations of the added salts tested for catalytic effects generally ranged from 0.01 to 1.0 M. The activation energies for the hydrolysis reaction in the presence of different ions was determined from Arrhenius plots in which  $\ln(k_{hyd})$  was plotted against  $1/T$  for the values of  $k_{hyd}$  at 0, 10, 20 and 30°C.

## Results and Discussion

### A) Cations

A series of hydrolysis runs at 20°C were done to determine if the observations of the cation effect at 0°C made by Thilo and von Lampe (1963,1964) were valid at higher temperatures. 0.010 M solutions of the salts under study were mixed with  $Na_2S_2O_7$  to create an initial disulfate ion concentration of 0.010 M. The salts and the averaged rate constants at 20°C are listed in Table 1 and with the values obtained by Thilo and von Lampe (1964) at 0°C. Chloride and nitrate salts were used because these anions have been found to have essentially no catalytic effect on disulfate ion hydrolysis.



Table 1

Effect of Cations on the Hydrolysis Rate Constant of  $S_2O_7^{2-}$ 

Salt		This study $k \times 10^3 \text{ sec}^{-1}$ at 20°C	Thilo and von Lampe $k \times 10^3 \text{ sec}^{-1}$ at 0°C
Chlorides:	$Na^+$	$8.0 \pm 1.6$	2.2
	$Ca^{2+}$	$19.0 \pm 1.0$	3.55
Nitrates:	$K^+$	$7.5 \pm 0.7$	2.2
	$Mg^{2+}$	$18.0 \pm 1.5$	3.5
	$Ca^{2+}$	$19.0 \pm 1.2$	3.55

$$[Na_2S_2O_7]_0 = 0.010 \text{ M}$$

It appears that the catalytic influence of the +2 ions is larger at higher temperatures. This is discussed in more detail later. The effect of metal ion concentration on the hydrolysis rate constant at 0°C for  $Mg^{2+}$  and  $Mn^{2+}$  is shown in Figure 1.

#### B) Anions

In their studies of the disulfate hydrolysis reaction, Thilo and von Lampe (1967) did only a cursory study of anion effects. They observed that  $Na^+$  and  $Li^+$  salts of  $Cl^-$ ,  $NO_3^-$ ,  $ClO_4^-$ , and  $SO_4^-$  had very similar small effects on disulfate ion hydrolysis, except at high concentrations. We did a systematic study of the effect on the rate of disulfate ion hydrolysis by anions commonly present in flue gas scrubbing solutions. Sodium salts were used in this part of the study because sodium ions were found to have no effect on the  $S_2O_7^{2-}$  hydrolysis. Sodium salts of sulfite ( $SO_3^{2-}$ ), sulfate ( $SO_4^{2-}$ ), thiosulfate ( $S_2O_3^{2-}$ ), dithionate ( $S_2O_6^{2-}$ ), monohydrogen phosphate ( $HPO_4^{2-}$ ), bisulfite ( $HSO_3^-$ ), chloride ( $Cl^-$ ), and

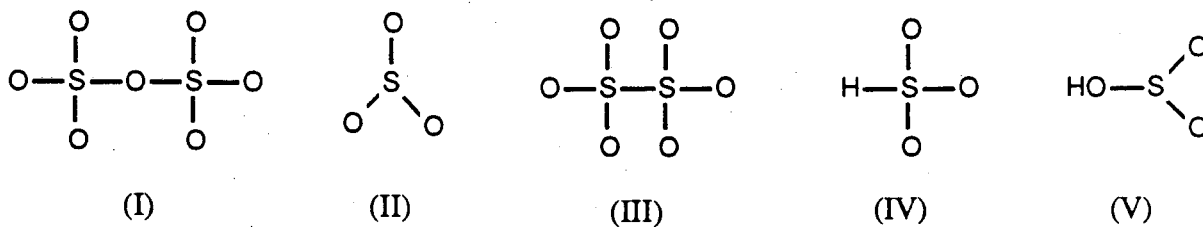
dihydrogen phosphate ( $\text{H}_2\text{PO}_4^-$ ) were used to study their effects on the disulfate ion hydrolysis rate at  $20^\circ\text{C}$  at concentrations of 0.010 M.  $\text{Na}_2\text{S}_2\text{O}_7$  was added to the solutions to obtain an initial  $\text{S}_2\text{O}_7^{2-}$  concentration of 0.010 M. The results are compiled in Table 2.

Table 2

Effect of Cations of the Hydrolysis Rate Constant of  $\text{S}_2\text{O}_7^{2-}$  at  $20^\circ\text{C}$

Anion	Rate Constant, $k$ ( $\text{sec}^{-1} \times 10^3$ )
$\text{SO}_3^{2-}$	$32.0 \pm 2.0$
$\text{SO}_4^{2-}$	$8.2 \pm 1.1$
$\text{S}_2\text{O}_3^{2-}$	$9.7 \pm 0.2$
$\text{S}_2\text{O}_6^{2-}$	$28.4 \pm 3.8$
$\text{HSO}_3^-$	$9.0 \pm 0.3$
$\text{Cl}^-$	$8.0 \pm 1.6$
$\text{H}_2\text{PO}_4^-$	$9.2 \pm 3.0$
$\text{HPO}_4^{2-}$	$9.4 \pm 1.8$

The effect of  $\text{SO}_3^{2-}$  concentration on the  $\text{S}_2\text{O}_7^{2-}$  hydrolysis rate constant at  $0^\circ\text{C}$  is shown in Figure 1. Sulfite and dithionate are the only anions of those tested that exhibits significant catalytic activity at these concentrations. It is interesting to note that  $\text{SO}_3^{2-}$  has a much larger effect on the disulfate ion hydrolysis than  $\text{HSO}_3^-$ . At conditions where  $\text{HSO}_3^-$  predominates ( $< \text{pH } 7$ ), the hydrolysis rate observed is close to the uncatalyzed rate. Since  $\text{SO}_3^{2-}$  (II) and  $\text{S}_2\text{O}_6^{2-}$  (III) have a similar structure to  $\text{S}_2\text{O}_7^{2-}$  (I), they may interact with



$\text{S}_2\text{O}_7^{2-}$  to speed the attack by  $\text{H}_2\text{O}$  on it.  $\text{HSO}_3^-$  exists as two isomers, as indicated by

structures IV and V, and is primarily in the form of IV at room temperature (Horner and Connick, 1986). The bonding of the  $H^+$  to  $SO_3^{2-}$  could sufficiently alter the  $SO_3^{2-}$  structure so that it can no longer effectively interact with  $S_2O_7^{2-}$ .

### C) Combined Effects

Since the  $SO_3^{2-}$  anion, as well as the  $Ca^{2+}$  and  $Mg^{2+}$  cations, strongly catalyzes the hydrolysis of disulfate ion, it seemed logical to investigate the possibility of a synergistic effect between  $SO_3^{2-}$  and  $Ca^{2+}$  or  $Mg^{2+}$ .  $CaSO_3$  has limited solubility, so it was decided to do experiments with  $Mg^{2+}$  and  $SO_3^{2-}$ . The measurements were made at  $20^\circ C$  with  $Na_2S_2O_7$  added to yield an initial concentration of 0.010 M. In one series of experiments, the  $Na_2SO_3$  concentration was kept constant at 0.010 M, while the  $Mg(NO_3)_2$  concentration was varied from 0 to 0.005 M. In the second series of experiments, the concentration of  $Mg(NO_3)_2$  was kept constant at 0.010 M, while the  $Na_2SO_3$  concentration was varied from 0 to 0.005 M. The rate constants obtained from these measurements are shown in Figures 2 and 3, respectively. The results clearly show that  $Mg^{2+}$  interferes with the  $SO_3^{2-}$  catalytic effect. These results suggest that two different processes are occurring. The process by which some metal ions catalyze the hydrolysis reaction appears to be capable of interfering with the  $SO_3^{2-}$  catalytic process. The formation of a complex between the metal ion and disulfate ion could sufficiently modify the  $S_2O_7^{2-}$  structure such that  $SO_3^{2-}$  can no longer effectively interact with it. Thus, it appears that catalysis by metal ions will control the  $S_2O_7^{2-}$  hydrolysis rate.

Some experiments were done on the temperature dependence of the disulfate hydrolysis in the presence of metal ions and sulfite ion for comparison with the temperature dependence of the uncatalyzed hydrolysis. Measurements were made at 0, 10, 20, and  $30^\circ C$  with  $Na_2S_2O_7$  added to yield an initial concentration of 0.010 M. 0.010 M solutions of  $Mg(NO_3)_2$ ,  $Ca(NO_3)_2$  and  $Na_2SO_3$  were used in the study. The activation energies are tabulated in Table 3.

Table 3

## Activation Energies for Disulfate Ion Hydrolysis

Solution	Activation Energy (kcal/mol)
Water	11.6 ± 0.6
Mg(NO <sub>3</sub> ) <sub>2</sub>	11.9 ± 1.3
Ca(NO <sub>3</sub> ) <sub>2</sub>	8.4 ± 0.7
Na <sub>2</sub> SO <sub>3</sub>	9.0 ± 1.0

$$[\text{Na}_2\text{S}_2\text{O}_7] = 0.010 \text{ M}$$

The values obtained for water and Mg<sup>2+</sup> are close to those obtained by Thilo and von Lampe (1967). It is somewhat unexpected that Ca<sup>2+</sup> differs from Mg<sup>2+</sup> to such a degree when the ions are both of the alkaline earth group and have a similar effect on the hydrolysis reaction. Since the SO<sub>3</sub><sup>2-</sup> catalysis process is hindered by metal ions, it is not surprising that it has a smaller activation energy than Mg<sup>2+</sup>. It appears that the SO<sub>3</sub><sup>2-</sup>-S<sub>2</sub>O<sub>7</sub><sup>2-</sup> interaction weakens with increasing temperature, to the point that the catalyzed hydrolysis rate would equal the uncatalyzed hydrolysis rate. From the activation energies listed, this would occur at about 150°C.

## D) Other Compounds

To ensure that the adjustment of solutions to high pH conditions (pH about 12) with addition of NaOH would not alter the hydrolysis rate information obtained, some experiments were performed with NaOH solutions at pH 12.3 at a temperature of 20°C. Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> was added to generate an initial S<sub>2</sub>O<sub>7</sub><sup>2-</sup> concentration of 0.010 M. The results indicated that OH<sup>-</sup> has no catalytic effect under these conditions.

Adipic acid is used as a buffering agent in some scrubbing systems. While mixtures of disulfate solutions and several organic compounds have been studied, the effect of carboxylic acids on disulfate hydrolysis has not been reported. Experiments were done at 20°C with initial  $S_2O_7^{2-}$  concentrations of 0.010 M and adipic acid concentrations ranging from 0.01 to 0.09 M. The adipic acid produced no significant effect on the disulfate hydrolysis rate at these concentrations. The inhibitory effects of the organic compounds studied by Thilo and von Lampe (1967) were observed at higher concentrations than those used for the adipic acid measurements. Adipic acid may also display an inhibiting effect at high concentrations.

In conclusion, the rate of disulfate hydrolysis in aqueous solution is influenced by a number of ions in solution. Metal ions appear to accelerate the hydrolysis by complexing with the disulfate ion. The degrees of acceleration by metal ions can be qualitatively predicted by comparing the EDTA complex stability constants of the metal ions. Some anions, such as  $SO_3^{2-}$  and  $S_2O_6^{2-}$ , can also accelerate the hydrolysis rate of disulfate ion. This process appears to involve the interaction of disulfate ion with anions of similar structure. Metal ions interfere with the anion acceleration of the hydrolysis rate. Adipic acid has no effect on the disulfate ion hydrolysis at low concentrations (0.1 M).

### Acknowledgement

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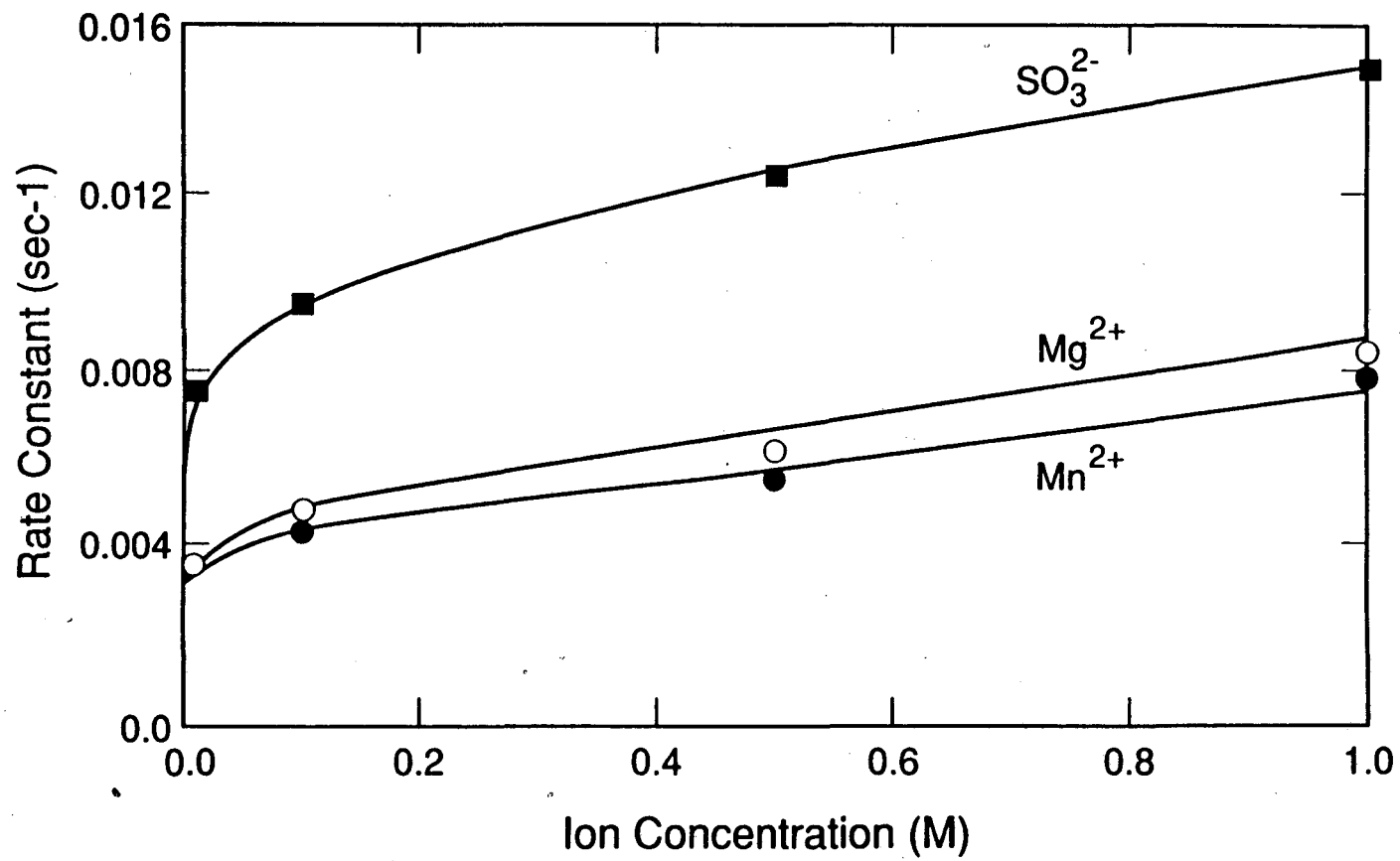
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## Figure Captions

Figure 1. Effect of concentration on the disulfate ion hydrolysis rate constant at 0°C for  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{SO}_3^{2-}$ .

Figure 2. Effect of  $\text{Mg}^{2+}$  concentration on the disulfate ion hydrolysis rate constant at 0°C in the presence of 0.010 M  $\text{SO}_3^{2-}$ .

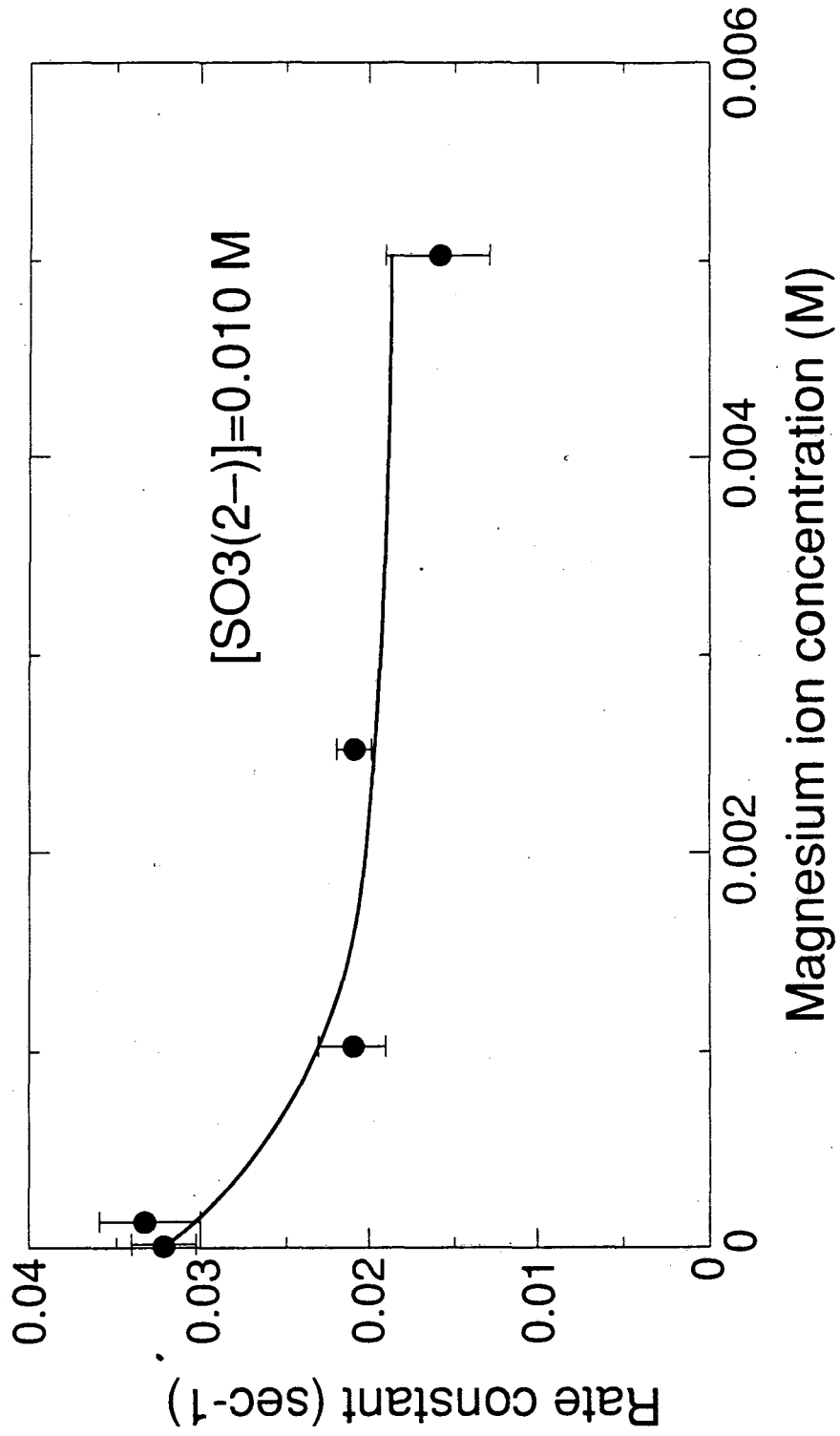
Figure 3. Effect of  $\text{SO}_3^{2-}$  concentration on the disulfate ion hydrolysis rate constant at 0°C in the presence of 0.010 M  $\text{Mg}^{2+}$ .



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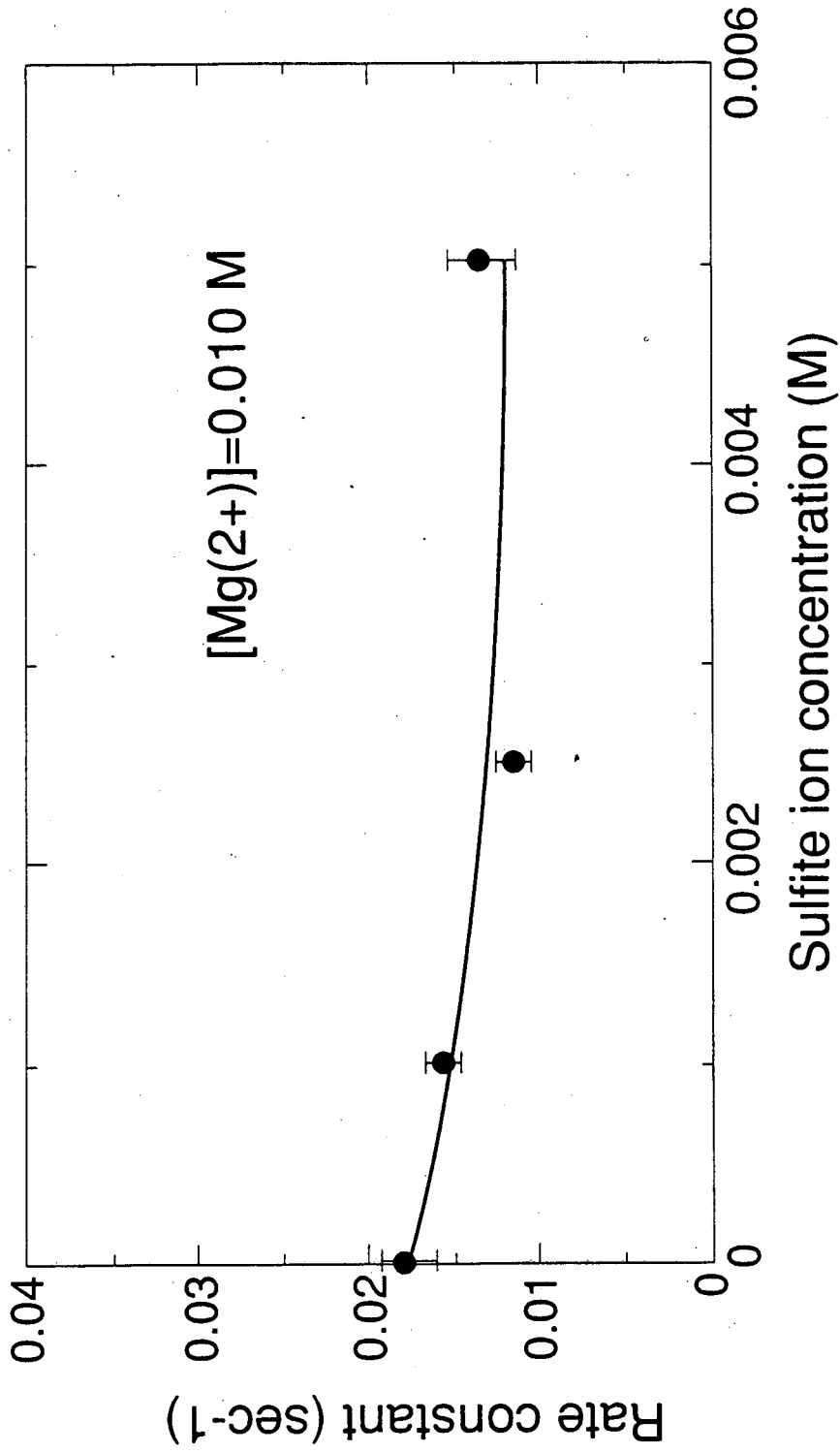
Fig. 1





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Fig. 2



XBL 899-6294

Fig. 3

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