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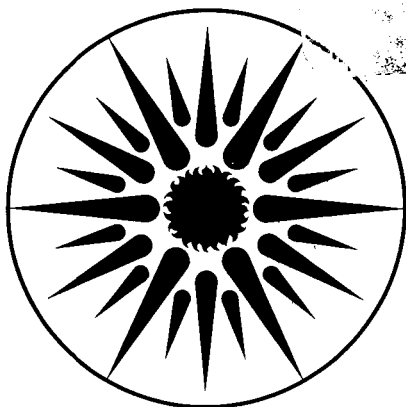
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An Intermediate to Sulfuric Acid in Acid Rain Formation

S.G. Chang, D. Littlejohn and K.Y. Hu[†]

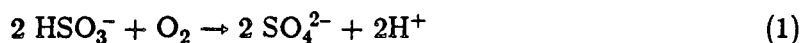
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ABSTRACT

The oxidation of bisulfite ion by dissolved oxygen to produce sulfate appears to involve the formation of a previously unknown intermediate which has a stoichiometry of 2HSO_3^- to 1 O_2 . The intermediate has a fairly strong Raman band at 1090 cm^{-1} , and a weak Raman band at 740 cm^{-1} , both probably due to S-O stretch. The intermediate is proposed to be $\text{S}_2\text{O}_7^{2-}$ and hydrolyzes into H^+ , SO_4^{2-} , and/or HSO_4^- with a half life of about 52 seconds.

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SO₂ produced from combustion of fossil fuels can be oxidized to sulfuric acid in the atmosphere and contribute to acid rain formation. Many oxidation pathways can occur in the atmosphere (1-12), one of which is the oxidation of SO₂ by O₂ in aqueous droplets such as in fog, clouds, and rain. This oxidation reaction has been studied for almost a century, yet the oxidation mechanism is unclear. Rate laws and rate constants obtained for this reaction by previous investigators have been inconsistent because the reaction is very sensitive to many kinds of impurities; some of these impurities act as catalysts, while others are inhibitors at very low concentrations. Most of these kinetic studies were carried out at atmospheric pressure by measuring the consumption rate of one of the reactants or the production rate of sulfate ion by conventional wet analytical methods. The concentrations of the other species were inferred from the stoichiometry of the reaction



Unlike the approaches used by previous investigators, we have studied this reaction, under high pressure conditions, using laser Raman spectroscopy (LRS) to monitor the dynamics of all known species involved during the course of the reaction. With this approach, we have found that a mass balance of sulfur and oxygen can not be achieved for the entire course of the reaction by just considering the known species. Subsequently, a previously unknown intermediate, present in substantial quantity and relatively long-lived, was discovered.

The high pressure rapid-mixing flow system used in our study is capable of being pressurized to 100 atm to permit a sufficiently high dissolved oxygen concentration for detection by LRS. Besides dissolved oxygen, use of LRS permits the observation of all important species in the reaction system: SO₂·H₂O, HSO₃⁻, SO₃²⁻, HSO₄⁻, SO₄²⁻, and S₂O₆²⁻. Sodium perchlorate is added to the reaction mixture as a reference so that

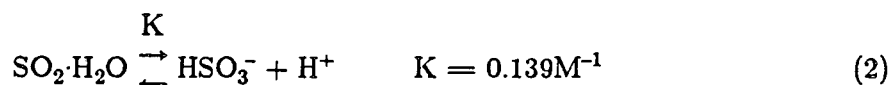
quantitative measurements can be made.

Atmospheric aqueous droplets are often very acidic. The pH of water droplets is 5.6 when in equilibrium with 0.03% CO₂ in air. The dissolution of SO₂ and NO_x will further lower this value. Measurements of fog droplets, and rain at many locations worldwide, have yielded pH values less than 4 (13,14). Under such conditions, HSO₃⁻ will be the dominant species from the dissolution of SO₂ in aqueous solutions. Therefore, we performed most of our experiments at conditions to study the oxidation of HSO₃⁻ by O₂.

Experiments were performed by driving solutions of oxygen and bisulfite from two cylindrical stainless steel containers to a mixer by O₂ and N₂ pressure respectively. The reaction was monitored by LRS through a quartz observation tube downstream from the mixer. The kinetics of the reaction were studied by two methods. First, a stable flow of the reactants was obtained and abruptly stopped while monitoring one compound with the Raman spectrometer. The behavior of the compound was observed for a period of time after the flow was stopped. The process was repeated until all the species had been observed. The reacted solution was then scanned with the Raman spectrometer to determine the concentrations of the compounds. Second, a continuous flow of the reaction mixture was scanned with the Raman spectrometer to observe the changes occurring during the reaction. By varying the flow rate and the volume between the mixer and the observation cell, the reaction could be observed from the beginning to the end of the reaction process. Therefore, we could determine the kinetic behavior of the reactants, the products, and intermediates involved.

A number of experiments have been done with dissolved oxygen concentrations ranging from 8x10⁻³ to 4x10⁻² M (after mixing) and bisulfite concentrations ranging from 6x10⁻² to 5x10⁻¹ M (after mixing). Most of these experiments involved conditions where

the bisulfite concentration was in excess of the oxygen concentrations. Initial O_2 to HSO_3^- ratios ranged from 0.02 to 0.4. The pH of the solution immediately after mixing was in the range of 3.5 to 4. The hydrogen ion concentration could be obtained from the concentrations of HSO_3^- and $SO_2 \cdot H_2O$ and the equilibrium between them (15):



A rapid initial drop in oxygen concentration was observed in almost all the experiments done. A concurrent drop in the bisulfite concentration was also seen. The stoichiometry of the rapidly reacting O_2 to HSO_3^- was about 1 to 2, the same as that for the oxidation reaction.

The curves of concentration vs. time for O_2 , HSO_3^- , $SO_2 \cdot H_2O$ and $(SO_4^{2-} + HSO_4^-)$ obtained from stop-flow experiments were used to develop mass balance for sulfur and oxygen for the experimental runs. The oxygen mass balance using $O_2 + 2x(SO_4^{2-} + HSO_4^-)$ shows a dip shortly after the flow is stopped with a gradual return to the original level. The sulfur mass balance using $HSO_3^- + SO_2 \cdot H_2O + (SO_4^{2-} + HSO_4^-)$ shows a similar dip after the flow is stopped. These are shown in Figure 1 for run 57. These curves are indicative of an intermediate formed from bisulfite and oxygen and decaying into sulfate and hydrogen ion.

While attempting to observe dithionate ion, $S_2O_6^{2-}$ at 1092 cm^{-1} , a curve was obtained that was similar to that which would be expected of the intermediate suggested by the mass balance plots for oxygen and sulfur. Checking nearby wave-number positions indicated that the signal maximum was at 1090 cm^{-1} rather than at 1092 cm^{-1} , the $S_2O_6^{2-}$ maximum. A second band of the intermediate with much lower intensity may occur at 740 cm^{-1} . Figure 2 shows Raman spectra of flowing (lower trace) and stopped

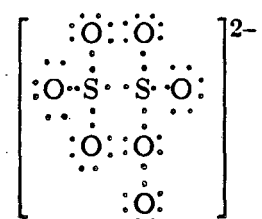
(upper trace) mixtures of oxygen and bisulfite solutions. The time delay between mixing and viewing in the flowing scan is about 15 seconds. The stopped solution had been mixed several minutes before it was scanned. The stopped spectrum shows the increase in SO_4^{2-} at 980 cm^{-1} and $\text{SO}_2\cdot\text{H}_2\text{O}$ at 1152 cm^{-1} resulting from the decay of the intermediate. That the intermediate decomposes into SO_4^{2-} and H^+ is shown in Figure 3, with the growth of the H^+ and total S(VI) (SO_4^{2-} and HSO_4^-) curves and the decay of the intermediate curve. The decay of the intermediate after its maximum agrees well with the formation rate of $(\text{SO}_4^{2-} + \text{HSO}_4^-)$, as would be expected.

Plotting $\ln[\text{relative intermediate concentration}]$ vs. time gives a straight line, indicating first order dependence on the intermediate concentration for the decay. No pH dependence on the decay was observed for the pH range of 2 to 4. The rate constant for the decomposition can be calculated from the slope of the plot. The values of the rate constant obtained from the intermediate decay and the growth of H^+ and S(VI) are listed in Table 1. The average values of the rate constant obtained from the reactant and the products agree well with one another. From these calculations, we determined the half life of the intermediate to be about 52 seconds. The decomposition rate of the intermediate is independent of the pH and trace metal ions such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Mn^{2+} .

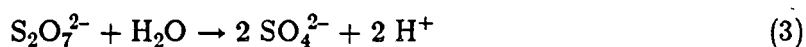
While we have not established unequivocally the identity of the observed intermediate, one such possibility can be deduced from our experimental results. The intermediate seems to be formed from one oxygen molecule and two bisulfite ions (Fig. 1). H^+ and SO_4^{2-} and/or HSO_4^- are produced only upon decomposition of the intermediate (Fig. 3). The intermediate has a fairly strong Raman band at 1090 cm^{-1} . Dithionate ion, $\text{S}_2\text{O}_6^{2-}$, is the only oxysulfur species with a Raman band near 1090 cm^{-1} (at 1092 cm^{-1} assigned to $\nu_{\text{S-O}}$). Dithionate ion is very stable and does not decay in the manner of the intermediate. We have studied the reaction mixture by ESR spectroscopy and found no

signal which can be ascribed to the intermediate, indicating that it is not a free radical.

The only structure we can formulate that is satisfied by the results mentioned above is



The intermediate could hydrolyze to form sulfate and hydrogen ions, as shown below:



The formation of the observed intermediate shows complicated dependence on reactant concentrations and trace amounts of metal ions such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Mn^{2+} . As the pH of the reaction mixture is raised above 4.5, the relative amount of intermediate formed decreases, suggesting the presence of another reaction channel. The fraction of S(VI) in the form of SO_3^{2-} increases rapidly as the pH increases. It may be that a second, faster oxidation reaction channel proceeds through the involvement of SO_3^{2-} , rather than HSO_3^- . The observed intermediate does not seem to be involved in this process. The factors that govern the formation of the intermediate are under investigation (16).

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16. This work was sponsored by the Assistant Secretary for Fossil Energy, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA. and Electric Power Research Institute, Palo Alto, CA.

Table 1
Initial Reactant Concentrations and Values Obtained
for the Rate Constant for the Decomposition of the Intermediate

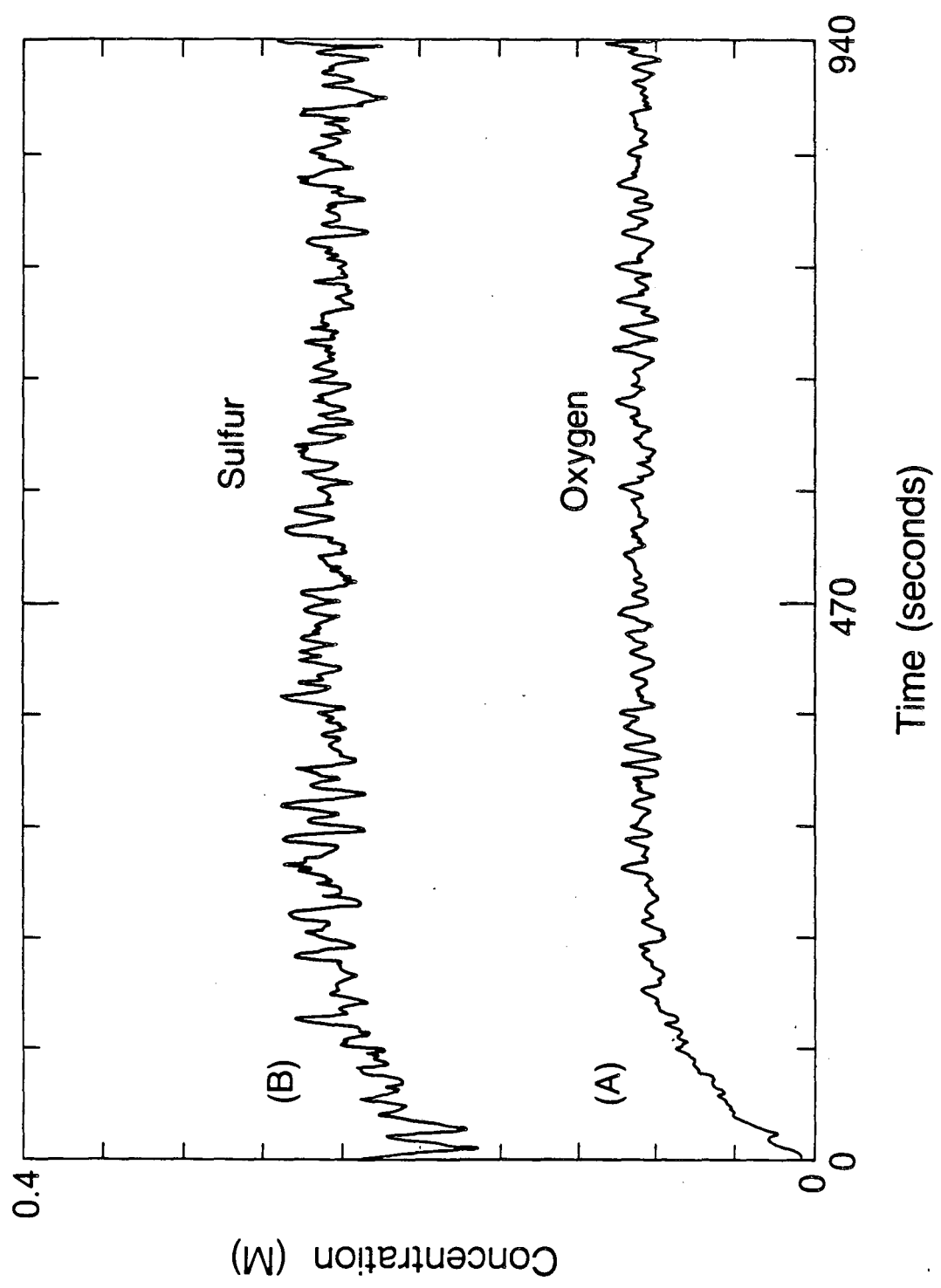
$[\text{HSO}_3^-]_{\text{init}}$ (M)	$[\text{O}_2]_{\text{init}}$ (M)	initial pH	from intermediate (sec^{-1})	from total sulfate (sec^{-1})	from total hydrogen ion (sec^{-1})
.34	.016	3.7	.0126	.0091	.0104
.34	.017	3.9	.0183	.0116	.0119
.34	.017	3.8	.0125	.0115	.0099
.34	.017	3.9	.0122	.0086	.0112
.19	.014	4.1	.0135	.0100	.0115
.27	.014	3.9	.0099	.0141	.0141
.475	.014	3.7	.0150	.0161	.0113
.23	.014	3.8	.0139	.0111	.0114
.68	.014	4.1	.0144	.0203	.0177
.25	.036	3.9	.0141	.0138	.0148
.30	.024	3.6	.0180	.0168	.0118
.22	.032	4.3	.0112	.0104	.0116
.22	.0385	3.8	.0178	.0132	.0127
.22	.038	3.7	.0133	.0153	.0126
.22	.016	4.0	.0139	.0130	.0183
.22	.012	4.1	.0141	.0124	.0130
average of each column (sec^{-1})			.0140 $\pm$.0022	.0130 $\pm$.0030	.0128 $\pm$.0023
Average of all points - $k = .0133 \pm .0026 \text{ sec}^{-1}$					
$t_{1/2} = 52 \pm 10 \text{ sec.}$					

Figure Captions

Fig.1 A: mass balance for oxygen-containing species
 B: mass balance for sulfur-containing species

Fig.2 A: Raman spectrum of flowing reaction mixture
 B: Raman spectrum of stopped (reacted) reaction mixture

Fig.3 Curves of concentration vs. time for intermediate (A), SO_4^{2-} and HSO_4^- (B), and total H^+ produced (C).



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Fig. 1

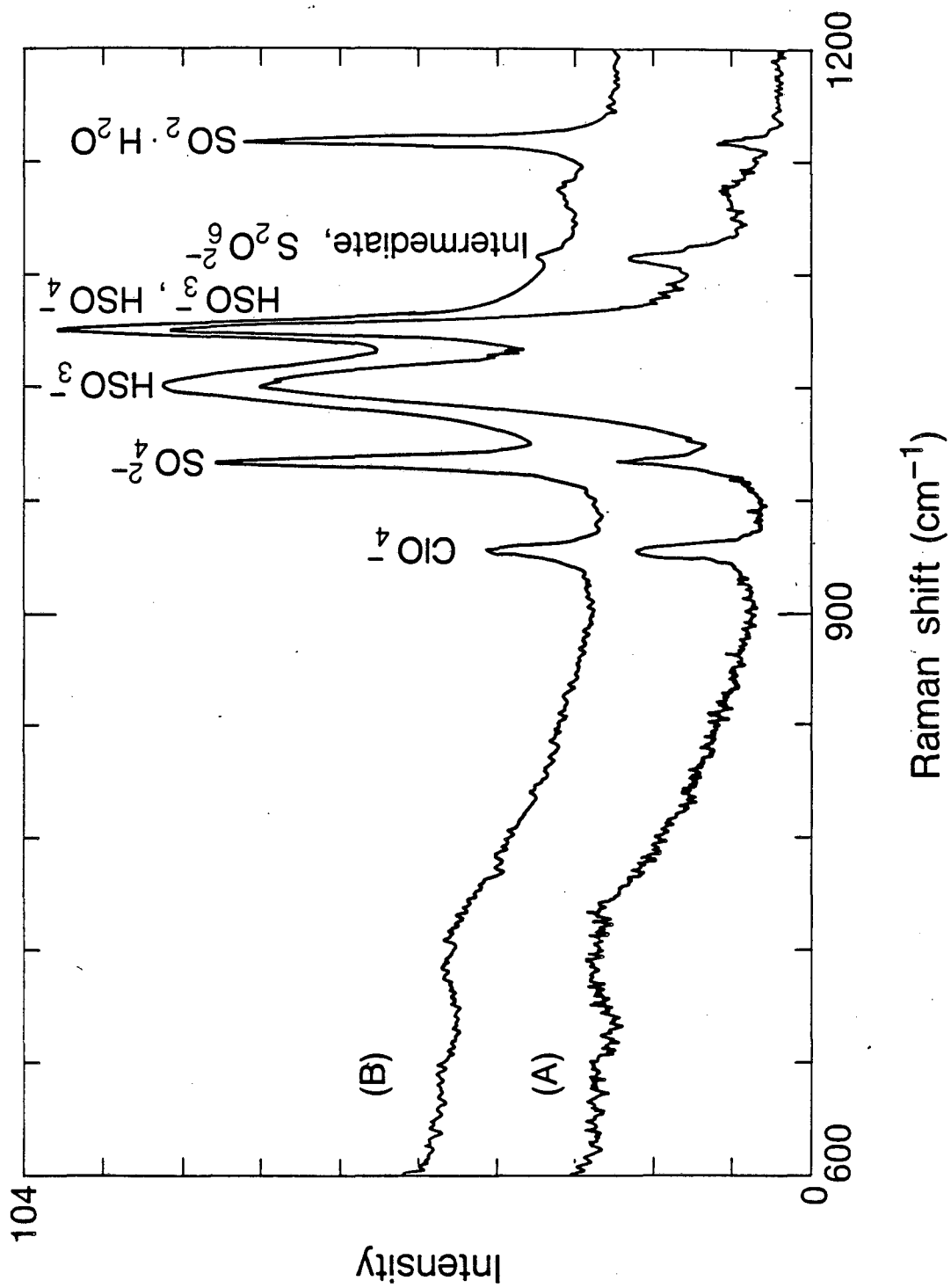
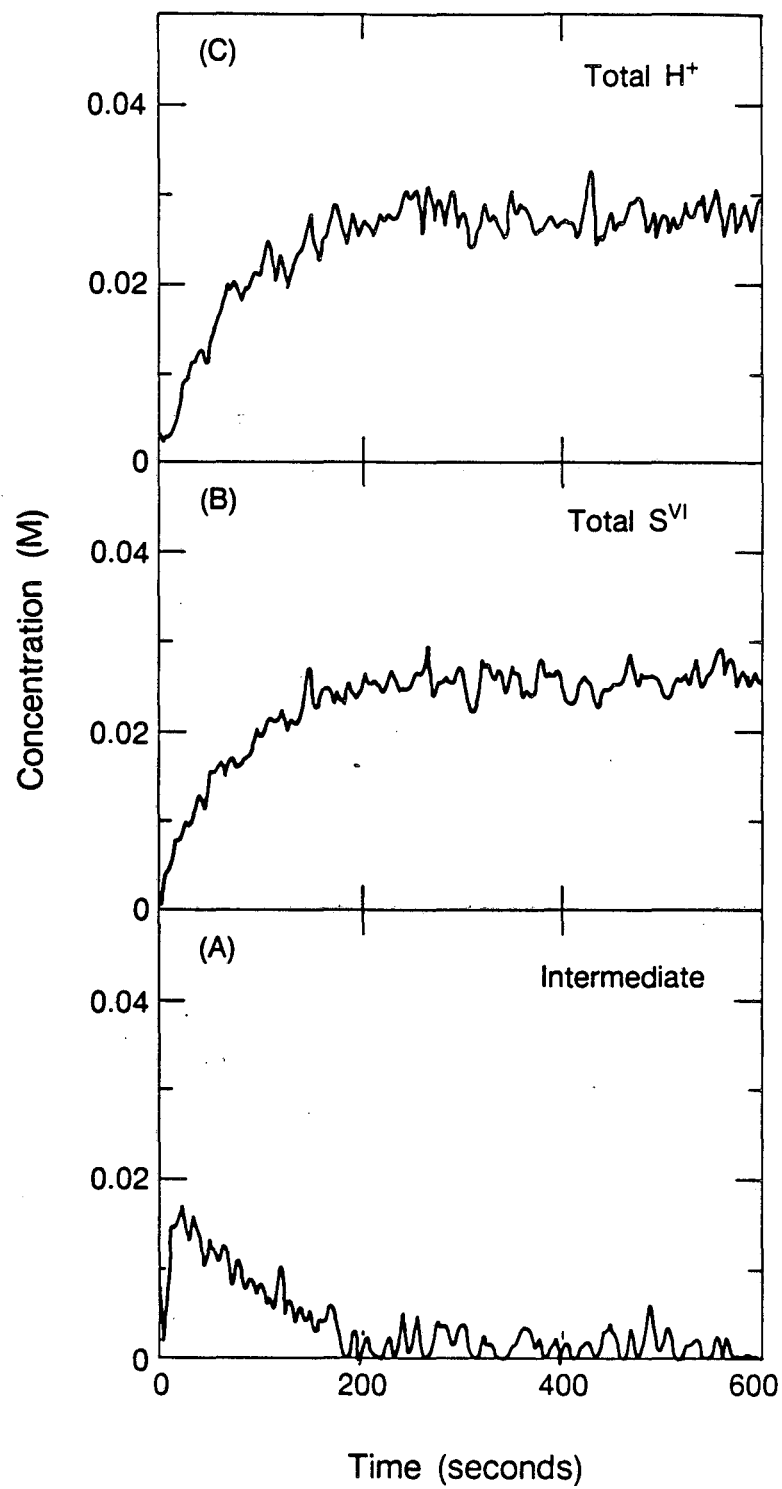


Fig. 2

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Fig. 3

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