and dioxins formed in the laboratory apparatus from [$^{13}C_6$]pentachlorophenol, from a mixture of selected PVC pyrolysis products, and from a mixture of PVC combustion products (Table 3). The chromatograms show the similarity in the isomer distributions of dioxins formed from labeled pentachlorophenol and from PVC combustion products with that of dioxins extracted from fly ash collected from the municipal incinerator.

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9. About 20 g of the fly ash was placed in a borosilicate glass reservoir of 35-ml capacity which had a coarse glass frit at one end. A bed of glass beads 35 mm deep was placed in a section of borosilicate glass tube that also had a coarse glass frit at the end. A 100-μl methanol solution that contained either a single pure compound or a mixture of compounds at a concentration of about 1 g/liter was deposited onto the glass beads just upstream of the fly ash. Attached to the other end of the reservoir was a long-armed impinger of 200-ml capacity. The reservoir and glass beads were heated to the reaction temperature; high-purity nitrogen was then passed through the connected tube and reservoir. Organic compounds formed in the experiment that either desorbed from the fly ash or passed through unreacted were collected in the impinger held at −10°C. At the end of the experiment the organic compounds on the fly ash were extracted by placing the reservoir with the fly ash in a soxhlet extractor and refluxing with 300 ml of benzene for 18 hours. The inside surfaces of the impinger were rinsed with dichloromethane. The extracts were concentrated by evaporation to a final volume of 100 μl. Fly ash and impinger extracts were analyzed separately.
10. Pentachlorophenol melts at 180°C and vaporizes at 340°C [H. P. Langer, T. P. Brady, L. A. Dalton, T. W. Shannon, P. R. Briggs, in *Chlorodioxins—Origin and Fate*, vol. 120 of *Advances in Chemistry Series* (American Chemical Society, Washington, DC, 1973), p. 26]. At 150°C the vapor pressure would be very low. The low yield of dioxins could be due to the small amount of pentachlorophenol that was transferred to the fly ash; thus 100 μg of pentachlorophenol was deposited directly to the fly ash in the reservoir and the experiment at 150°C was repeated. Almost 250 ng of octachlorodioxin was produced, which was a 125-fold increase over the amount in the previous experiment at 150°C. Also, the amount is comparable to the amount of octachlorodioxin formed at 300°C in the absence of fly ash. The fly ash seems to promote the condensation of two phenol molecules into a dioxin molecule in addition to catalyzing chlorination and dechlorination reactions.
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12. We thank the Natural Sciences and Engineering Research Council, Canada, and the Ontario Ministry of the Environment for financial support. We also thank M. O'Mara of the Vinyl Institute for characterizing the particulate samples.

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Disulfate Ion as an Intermediate to Sulfuric Acid in Acid Rain Formation

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The oxidation of the bisulfite ion by dissolved oxygen to produce sulfate ion involves the formation of a previously undetected intermediate. This intermediate has a fairly strong Raman band at 1090 wave numbers and a weak Raman band at 740 wave numbers, both of which are probably due to sulfur-oxygen stretches. The intermediate is proposed to be the disulfate ion $S_2O_7^{2-}$, which hydrolyzes into H^+ and either SO_4^{2-} or HSO_4^{2-} with a half-life of about 52 seconds at 25°C.

SULFUR DIOXIDE (SO_2), WHICH IS 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*), one of which is the oxidation of SO_2 by O_2 in aqueous droplets such as in fog, clouds, and rain. This oxidation reaction has been studied for almost a century and 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 performed 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

$$2HSO_3^- + O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad (1)$$

Unlike the approaches used by previous investigators, we have studied this reaction under high-pressure conditions with 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 cannot be achieved for the entire course of the reaction by just considering the known species. Subsequently, a previously undetected intermediate that is present in substantial quantity and relatively long-lived was discovered.

The high-pressure rapid-mixing flow system used in our study can be pressurized to 100 atm so that a sufficiently high dissolved oxygen concentration can be detected by LRS. In addition to dissolved oxygen, all of the other important species in the reaction system can be observed with LRS: SO_2 (aq), HSO_3^-, SO_3^{2-}, HSO_4^-, SO_4^{2-}, $S_2O_5^{2-}$, and $S_2O_6^{2-}$. Sodium perchlorate was added to the reaction mixture as a reference so that quantitative measurements could be made.

Atmospheric water droplets are often very acidic. The *p*H of water droplets is 5.6 when in equilibrium with 0.03% CO_2 in air. The dissolution of SO_2 and NO_x can further lower this value. Measurements of fog droplets and rain at many locations worldwide have yielded *p*H values less than 4 (*2*). Under acidic conditions HSO_3^- will be the dominant species from the dissolution of SO_2 in aqueous solutions. Thus we performed most of the experiments in our study

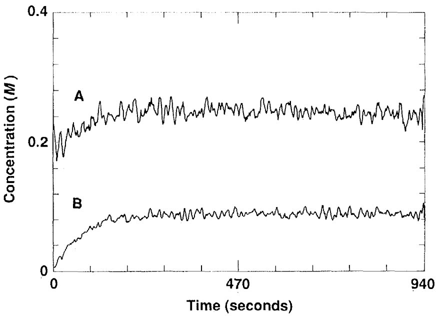

Fig. 1. Mass balance as a function of time (run 57) for (**A**) sulfur-containing and (**B**) oxygen-containing species. In both cases the initial *p*H was 4. The initial sulfur concentration was 0.25*M* in (A), whereas the initial oxygen concentration was 0.08*M* in (B).

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of the oxidation of HSO_3^- by O_2 under conditions similar to these.

Experiments were performed by driving solutions of O_2 and HSO_3^- from two cylindrical stainless steel containers to a mixer with O_2 and N_2 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 kinetic 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 that occurred during the reaction. By varying the flow rate and the volume between the mixer and the observation cell, the reaction could be observed from beginning to end. Thus we could determine the kinetics of the reactants, the products, and the intermediates involved.

A number of experiments were done with dissolved oxygen concentrations that ranged from 8×10^{-3} to $4 \times 10^{-2}M$ (after mixing) and bisulfite concentrations that ranged from 6×10^{-2} to $5 \times 10^{-1}M$ (after mixing). The concentration of $S_2O_5^{2-}$ was always less than 5% of the HSO_3^- concentration. All of these experiments involved conditions such that the bisulfite concentration was in excess of the oxygen concentrations. Initial ratios of O_2 to HSO_3^- concentrations ranged from 0.02 to 0.4. All work was done at 25°C with an ionic strength of 0.5*M*. The *p*H of the solution immediately after mixing was in the range from 3.5 to 4. The solution was not buffered and the *p*H dropped as the reaction proceeded. The hydrogen ion concentration could be approximated from the concentrations of HSO_3^- and SO_2 (aq) and the equilibrium between them

$$SO_2\ (aq) \overset{K}{\rightleftarrows} HSO_3^- + H^+$$

$$K = 0.0139M^{-1} \qquad (2)$$

where *K* is the equilibrium constant by using the parameters established by Huss and Eckert (*3*).

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 O_2 to HSO_3^- in the rapidly reacting solution was about 1 to 2, which is the same as that for the oxidation reaction.

The curves of concentration versus time for O_2, HSO_3^-, SO_2 (aq), and (SO_4^{2-} + HSO_4^-) obtained from stop-flow experiments were used to develop a mass balance for sulfur and oxygen for the experimental runs. The oxygen mass balance, which used $[O_2] + 2 \times ([SO_4^{2-}] + [HSO_4^-])$, showed a dip shortly after the flow was stopped and then a gradual return to the original level. The sulfur mass balance which used $[HSO_3^-] + [SO_2\ (aq)] + ([SO_4^{2-}] + [HSO_4^-])$ showed a similar dip after the flow was stopped (Fig. 1). These curves indicate that an intermediate was formed from bisulfite and oxygen that decayed into sulfate and hydrogen ion.

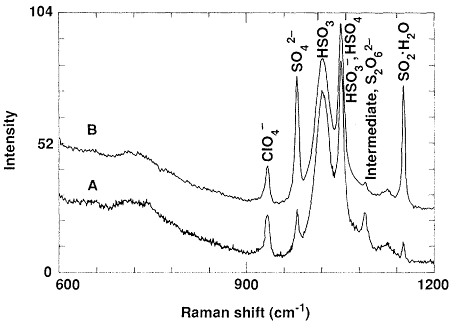

Fig. 2. Raman spectra of (**A**) the flowing reaction mixture and (**B**) the stopped (reacted) reaction mixture. The initial conditions were: $[HSO_3^-]$ = 0.59*M*; $[ClO_4^-]$ = 0.03*M*; and *p*H = 4.

Table 1. Initial reactant concentrations and values obtained for the rate constant *k* for the decomposition of the observed intermediate based on various species. The average value of *k* from all points was 0.0133 ± 0.0026 sec^{-1}. The half-life of the reaction was 52 ± 10 seconds at 25°C.

Initial concentrations (*M*)		Initial *p*H	*k* (sec^{-1})*		
$[HSO_3^-]$	$[O_2]$		Intermediate	Total sulfate	Total hydrogen ion
0.34	0.016	3.7	0.0126	0.0091	0.0104
0.34	0.017	3.9	0.0183	0.0116	0.0119
0.34	0.017	3.8	0.0125	0.0115	0.0099
0.34	0.017	3.9	0.0122	0.0086	0.0112
0.19	0.014	4.1	0.0135	0.0100	0.0115
0.27	0.014	3.9	0.0099	0.0141	0.0141
0.475	0.014	3.7	0.0150	0.0161	0.0113
0.23	0.014	3.8	0.0139	0.0111	0.0114
0.68	0.014	4.1	0.0144	0.0203	0.0177
0.25	0.036	3.9	0.0141	0.0138	0.0148
0.30	0.024	3.6	0.0180	0.0168	0.0118
0.22	0.032	4.3	0.0112	0.0104	0.0116
0.22	0.0385	3.8	0.0178	0.0132	0.0127
0.22	0.038	3.7	0.0133	0.0153	0.0126
0.22	0.016	4.0	0.0139	0.0130	0.0183
0.22	0.012	4.1	0.0141	0.0124	0.0130

*Average values for all points are: intermediate, 0.0140 ± 0.0022 sec^{-1}; total sulfate, 0.0130 ± 0.0030; and total hydrogen ion, 0.0128 ± 0.0023.

When we attempted to observe dithionate ion, $S_2O_6^{2-}$, at 1092 cm^{-1}, a time-dependent curve was obtained that was similar to that which would be expected for the intermediate that was suggested by the mass balance plots for oxygen and sulfur. A check of 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 also be present at 740 cm^{-1}. Figure 2 shows Raman spectra of flowing and stopped 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 SO_2 (aq) at 1152 cm^{-1} that resulted from the decay of the intermediate. The intermediate decomposes into SO_4^{2-} and H^+ (Fig. 3), as determined from 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 concentration agrees well with the formation rate of (SO_4^{2-} + HSO_4^-).

A plot of the logarithm of the relative concentration of the intermediate versus time yields a straight line, which indicates a first-order dependence on the intermediate concentration for the decay. No *p*H dependence on the decay was observed for the *p*H range from 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

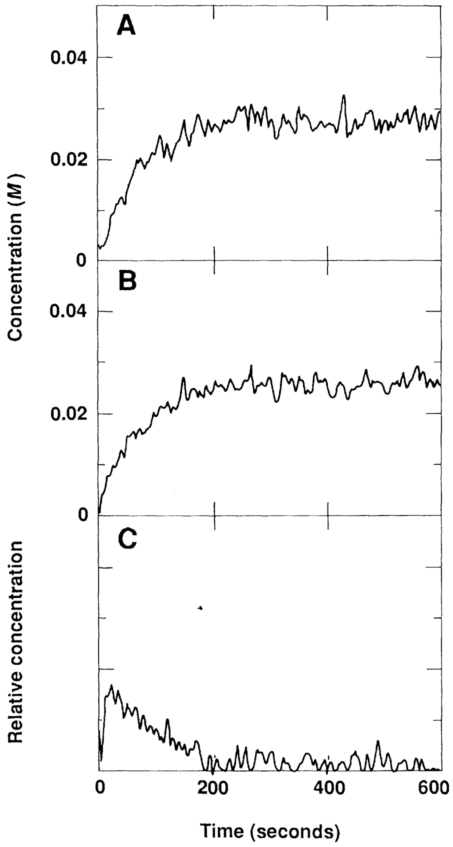

Fig. 3. Concentration as a function of time for (**A**) total H^+, (**B**) SO_4^{2-} + HSO_4^-, and (**C**) the intermediate. The initial conditions were: $[HSO_3^-] = 0.27M$; $[O_2] = 0.13M$; and $pH = 4$.

half-life of the intermediate to be about 52 seconds at 25°C and at an ionic strength μ of $0.5M$. The decomposition rate of the intermediate appeared to be independent of the *p*H and of trace metal ions such as Fe^{2+}/Fe^{3+} and Mn^{2+} over the range studied.

From our experimental results it appears that the intermediate is formed from one oxygen molecule and two bisulfite molecules (Fig. 1) and that SO_4^{2-} or HSO_4^- or both are produced only upon decomposition of the intermediate (Fig. 3). The reaction mixture was studied by electron spin resonance (ESR) spectroscopy; no signal was observed that could be attributed to the intermediate, which indicated that it is not a free radical. The Raman spectrum of the intermediate is similar to that of dithionate ion, which is very stable and does not decay in the manner of the intermediate. From this information we propose a formula of $S_2O_7^{2-}$ for the intermediate. It could hydrolyze to form sulfate and hydrogen ions, as shown below:

$$S_2O_7^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2H^+$$

The decomposition process of the intermediate, as well as the decomposition rate constant and the Raman spectrum, are very similar to those for the disulfate ion, $S_2O_7^{2-}$. The Raman spectrum of disulfate ion in solution obtained by Millen (*4*) has peaks at 325 and 1092 cm^{-1}, and possibly at 735 cm^{-1}. Two studies of the hydrolysis rate of disulfate ion (*5, 6*) agree well with one another and yield values of the hydrolysis rate constant very close to the value we obtained at 25°C. Sodium ions have been reported (*5*) to catalyze the hydrolysis somewhat. However, the effect is fairly small and does not create disagreement between our hydrolysis rate constant and the values reported for the hydrolysis of disulfate ion. With the close similarity between our results for the reaction intermediate and published data for the disulfate ion, we conclude that the intermediate is disulfate ion. The formation appears to occur by a different process than those generally used to produce disulfate, in which either gaseous SO_3 is added to sulfate solutions or a bisulfate salt is heated.

Previously Connick and co-workers (*7*) found evidence for an intermediate in the oxygen-bisulfite reaction at lower reactant concentrations (about $10^{-4}M$ in O_2 and $10^{-2}M$ in HSO_3^-). Their first-order rate constant for decomposition at 25°C of 0.0128 sec^{-1} agrees well with that reported here.

In contrast to the case for the decomposition of the intermediate, its formation appears to show a complicated dependence on reactant concentrations and trace amounts of metal ions such as Fe^{2+}/Fe^{3+} and Mn^{2+}. When the initial *p*H of the reaction mixture was increased, the relative amount of intermediate formed decreased, which suggested the presence of another reaction channel. Since the solution was unbuffered and the *p*H probe was downstream of the mixer, the initial *p*H at which this occurred is somewhat uncertain. It appears to occur at near *p*H 5. The fraction of S(IV) in the form of SO_3^{2-} increased rapidly as the *p*H increased. 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.

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Cell-Autonomous Determination of Cell-Type Choice in *Dictyostelium* Development by Cell-Cycle Phase

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The developmental fate of individual cells has been examined in a system that allows *Dictyostelium discoideum* cells to differentiate in the absence of aggregation. The results show that the propensity of single amoebae to differentiate into either prespore or prestalk cells occurs by a cell-autonomous mechanism dependent on the cell's position in the cell cycle at the initiation of development. Cells that divide between ~1 1/2 hours before and ~40 minutes after the differentiation-inducing starvation become prestalk, whereas cells dividing at other times become prespore cells. These results suggest mechanisms by which an initial proportioning of the two cell types within the aggregate is achieved.

UNDERSTANDING THE MECHANISMS controlling cell-type and tissue differentiation is a central issue in developmental biology. To study the molecular basis of differentiation, we have chosen to use the eukaryote *Dictyostelium discoideum*. This organism has a relatively simple pattern of tissue differentiation and is

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