Oscillatory Photochemical Decomposition of Tetrathionate Ion
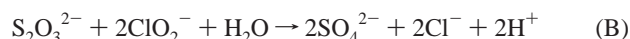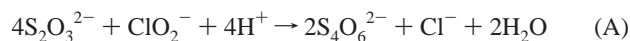
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The remarkable variety of phenomena, including chemical oscillation, pattern formation, chaos, and extreme sensitivity to stirring rate, that occur in chemical systems have led to kinetic studies of the nonlinear reactions that contribute to these behaviors. We have investigated the kinetics[1−3] of several subsystems of the thiosulfate-chlorite reaction, a system that exhibits an array of unusual dynamical phenomena.[4−6] With preliminary results now in hand, and having the algorithms needed to evaluate multiwavelength kinetic data,[7] we have begun a systematic kinetic examination of the full thiosulfate-chlorite system using spectrophotometric techniques. Previous studies[6] show that, depending on the concentration ratio of the reactants, tetrathionate and sulfate are formed in reactions A and/or B:

$$4S_2O_3^{2-} + ClO_2^- + 4H^+ \rightarrow 2S_4O_6^{2-} + Cl^- + 2H_2O \quad (A)$$

$$S_2O_3^{2-} + 2ClO_2^- + H_2O \rightarrow 2SO_4^{2-} + 2Cl^- + 2H^+ \quad (B)$$

At a 4:1 thiosulfate-chlorite concentration ratio, where reaction A predominates, in an unstirred cell the spectrum changes irregularly after tetrathionate formation is nearly complete. A more regular slow increase in absorbance is observed when the solution is stirred continuously during the measurement (Figure 1). These findings prompted us to carry out further experiments on aqueous solutions of tetrathionate ion to interpret Figure 1.

A surprising result of these preliminary investigations is illustrated in Figure 2. The absorbance, monitored for as long as 9 h on a HP 8452 diode array spectrophotometer, of a 0.001 M tetrathionate solution (buffered with acetate/acetic acid) shows − under continuous stirring − regular small periodic increases (0.002−0.003 absorbance unit) with a period of about 1 h. The slow decomposition of tetrathionate must result from illumination by the spectrophotometer's light source, because tetrathionate solutions are well known to be stable for long periods of time in slightly acidic media.[8] We have confirmed this statement experimentally.

Experimental examples of bistable photochemical systems[9] and models of oscillatory photochemical reactions[10] have been reported, but, to our knowledge, the reaction studied here is the first experimental demonstration of a photochemical oscillator in a stirred, batch system[11] supported by a chemically plausible model.

The increase of the absorbance in the wavelength range 250−330 nm might result from formation of either pentathionate or colloidal sulfur. Our preliminary experiments do not allow us to distinguish unambiguously between these possibilities, but colloidal sulfur seems more likely, because the molar absorbance difference between pentathionate and tetrathionate varies from 2000 to 10 M⁻¹
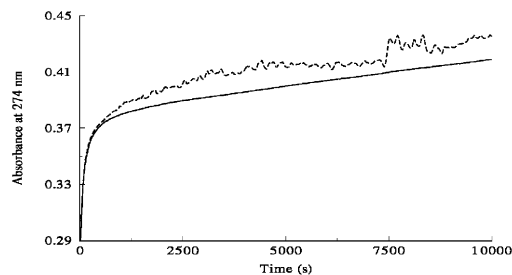
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Figure 1. Absorbance measured at 274 nm in thiosulfate-chlorite reaction in acetate/acetic acid buffer (pH 4.2); $[S_2O_3^{2-}]_0 = 0.0032$ M, $[ClO_2^-]_0 = 0.0008$ M. Reaction followed with (solid line) and without (dashed line) stirring.

cm⁻¹ in the wavelength range in question,[12,13] but our observed absorbance changes only between 0.06 and 0.03 absorbance units. We write P for the unidentified products, which are probably colloidal sulfur and trithionate ion (see below).

Our aim here is to provide at least a qualitative explanation for the observed oscillations. After examining many models to fit the experimental data, we propose the following scheme for the oscillatory photochemical decomposition of tetrathionate.
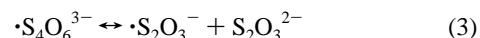
$$S_4O_6^{2-} \leftrightarrow 2 \cdot S_2O_3^- \quad (1)$$

$$v_1 = \Phi I_a = (6.9 \pm 0.1) \times 10^{-10} \, Ms^{-1}$$

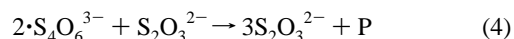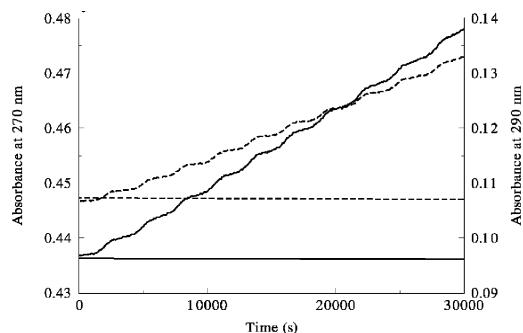$$v_{-1} = 3.5 \times 10^9 \, M^{-1}s^{-1} [\cdot S_2O_3^-]^2$$

$$S_4O_6^{2-} + \cdot S_2O_3^- \leftrightarrow \cdot S_4O_6^{3-} + S_2O_3 \quad (2)$$
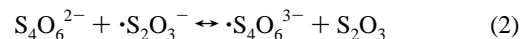
$$v_2 = (2.7 \pm 0.1) \times 10^2 \, M^{-1}s^{-1} [S_4O_6^{2-}][\cdot S_2O_3^-]$$

$$v_{-2} = (1.7 \pm 0.1) \times 10^3 \, M^{-1}s^{-1} [\cdot S_4O_6^{3-}][S_2O_3]$$

$$\cdot S_4O_6^{3-} \leftrightarrow \cdot S_2O_3^- + S_2O_3^{2-} \quad (3)$$

$$v_3 = (1.1 \pm 0.1) \times 10^{-1} \, s^{-1} [\cdot S_4O_6^{3-}]$$

$$v_{-3} = 1.8 \times 10^9 \, M^{-1}s^{-1} [\cdot S_2O_3^-][S_2O_3^{2-}]$$

$$2 \cdot S_4O_6^{3-} + S_2O_3^{2-} \rightarrow 3S_2O_3^{2-} + P \quad (4)$$

$$v_4 = 7.3 \times 10^4 \, M^{-1}s^{-1} [\cdot S_4O_6^{3-}][S_2O_3^{2-}]$$

where Φ represents quantum yield, and I_a, the rate of absorption of actinic photons divided by the volume of the solution, is proportional to the light intensity and to the concentration of tetrathionate.

Three (k_{-1}, k_{-3}, and k_4) of the seven rate constants in the scheme (1−4) are taken from the literature. The rate of recombination of thiosulfate radicals (k_{-1}) was measured by Dogliotti and Hayon[14] using flash photolysis; the reaction between thiosulfate ion and thiosulfate radical (k_{-3}) was studied by Schöneshöfer[15] by pulse radiolysis. The rate constant of the thiosulfate-catalyzed recombina-

Figure 2. Absorbance measured at 270 nm (solid line, left vertical axis) and 290 nm (dashed line, right vertical axis) of a 0.001 M $K_2S_4O_6$ solution containing acetate/acetic acid buffer at pH = 4.2. Periodically increasing curves were measured every 60 s, while horizontal lines represent absorbance of the same solution measured at 3600 s intervals.
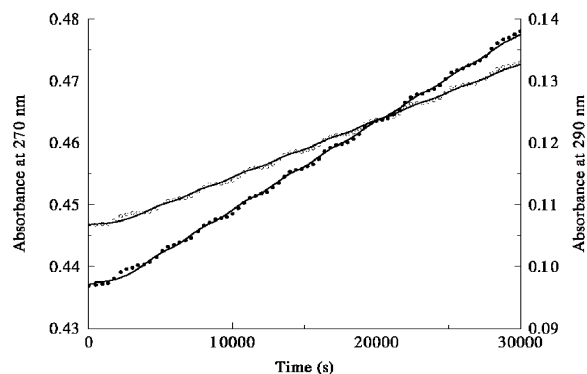

Figure 3. Absorbance measured at 270 nm (●, left vertical axis) and at 290 nm (○, right vertical axis) and simulated with the model (1–4) (solid lines). $[S_4O_6{}^{2-}]_0$ = 0.001 M, pH = 4.2.

tion (k_4) of tetrathionate radical is known from our previous work.[2] The remaining four parameters (v_1, k_2, k_{-2}, k_3) were obtained by optimizing the fit between experimental and simulated data using fitting package ZiTa.[16] Neither Φ nor I_a is known, so only their product v_1 could be fitted. In addition to the kinetic parameters, the molar absorbances of the "product" were fitted in the 252–292 nm wavelength range. They give a straight line (R^2 = 0.9983) as a function of $1/\lambda^4$, suggesting that the "absorbance" arises from light scattering by colloidal sulfur. The ability of the model to simulate the behavior of the system is illustrated in Figure 3 at two wavelengths.

The model (1–4) contains two reversible reactions (eqs 2 and 3), one photochemically forced pseudo-equilibrium (eq 1) and one irreversible autocatalytic step (eq 4). The origin of the oscillatory behavior can be understood from Figure 4.

The thiosulfate radical is continuously produced by illumination. Without the other steps, it would reach its photochemical stationary concentration within seconds. However, this state is not attained, because reaction 2 begins to consume $\cdot S_2O_3{}^-$, producing tetrathionate radical.[17] The tetrathionate radical generated in step 2 initiates the production of thiosulfate ion in step 3. As Figure 4A shows, the concentration of thiosulfate radical generated in process 1 is always smaller than its photochemical stationary concentration, and process 3 is always far from equilibrium (Figure 4B). When the concentration of thiosulfate ion reaches a sufficiently high level, its autocatalytic consumption via reaction 4 causes the concentration of tetrathionate radical to decrease. The concentration of thiosulfate ion, already above its equilibrium value, is then decreased by equilibrium 3, and the concentration of tetrathionate radical is regulated back by processes 1, 2, and 3. The oscillatory cycle is then ready to begin again.
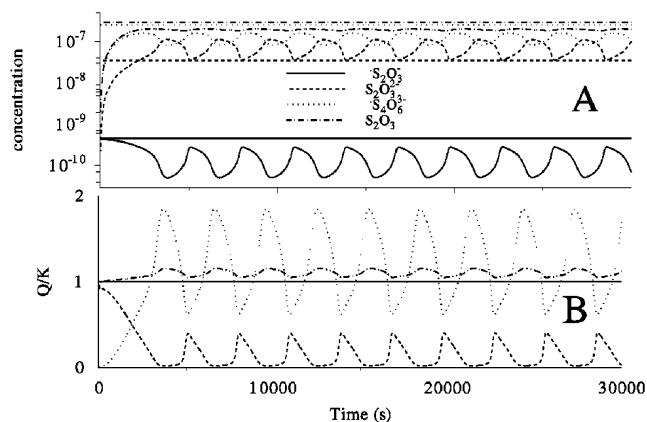

Figure 4. (A) Simulated concentrations at $[S_4O_6{}^{2-}]_0$ = 0.001 M. Straight lines represent equilibrium concentrations, taking v_4 = 0. (B) Ratio of reaction quotient (Q) to equilibrium constant (K) for eq 1 (dashed line), eq 2 (dotted line), and eq 3 (dot-dashed line).

The oscillatory behavior occurs only in a relatively narrow range of the fitted parameters: k_1 must lie between 4.8×10^{-10} and 8.4×10^{-10} M s^{-1}, k_2 between 260 and 460 M^{-1} s^{-1}, k_{-2} between 120 and 2000 M^{-1} s^{-1}, and k_3 between 0.085 and 0.15 s^{-1}, with the other parameters fixed at their experimentally determined values.

If P in step 4 were tetrathionate instead of trithionate ion and the light-scattering colloidal sulfur, the model would oscillate without damping. The impetus for the oscillation is the continuous illumination. The system is analogous in this respect to a flow reactor, where the input of reactants and the outflow of products are replaced by the continuous transformation of energy from light into heat. No experimental system with this behavior is yet known, but, as the model shows, continuous illumination of a reactive system may produce undamped oscillation.

The discovery of a reaction in which oscillation occurs only under illumination verifies suggestions based on abstract models[10] and provides the opportunity for a deeper understanding of the dynamics of photochemically driven systems.

References

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(17) The species denoted by S_2O_3 in reaction 2 might alternatively be $S_2O_4{}^{2-}$, dithionite ion. Our experiments provide no basis to distinguish between these possibilities.

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