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Kinetics and Mechanism of the Photoinitiated Autoxidation of Sulfur(IV) in the Presence of Iodide Ion

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The kinetics and mechanism of the photoinitiated and iodide ion-catalyzed aqueous autoxidation of sulfur(IV) has been studied in a diode-array spectrophotometer using the same light beam for excitation and detection. Light absorption of both the iodide ion and sulfur(IV) contribute to the initiation of a highly efficient radical chain reaction, the overall rate of which depends on the reactant and catalyst concentrations, the pH, and the light intensity in a complex manner. To interpret all the experimental findings, an elaborate scheme is proposed, in which the chain carriers are $SO_3^{-\bullet}$, $SO_4^{-\bullet}$, $SO_5^{-\bullet}$, $I^\bullet$, and $I_2^{-\bullet}$. There are three termination steps, each of them is second-order with respect to the chain carriers. Model calculations and nonlinear fitting have been used to show that the proposed scheme gives an excellent quantitative interpretation of the experimental results.

Introduction

Autoxidation of sulfur(IV)[1] has attracted considerable attention because it is the dominant source of acid rain formation.[2−4] Detailed mechanistic information on this reaction can also be used to design more efficient industrial desulfurization processes. In addition, the sulfur(IV)−oxygen system has some importance in hydroxylation, in epoxidation, in the oxidative cleavage of DNA,[5] in metallurgical technologies,[6] and in food chemistry.[7] Metal ions often catalyze the autoxidation of sulfur(IV) leading to the formation of predominantly S(VI)

$$2H_2O{\cdot}SO_2 + O_2 = 2HSO_4^- + 2H^+$$

$$v = -\frac{1}{2}\frac{d[H_2O{\cdot}SO_2]}{dt} = -\frac{d[O_2]}{dt} \qquad (1)$$

Stoichiometric, kinetic, and mechanistic aspects of several metal ion-catalyzed systems have been studied intensively since Bäckström's initial studies in the 1930s.[8] Postulated mechanisms usually involve the formation of metal sulfito complexes and the $SO_3^{-\bullet}$ radical.[2−19]

Efforts to study the possible role of light on the autoxidation of sulfur(IV) have also been made both in gas phase[20−21] and solution phase.[19,22−23] Photochemical processes

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(1) Thoroughout this work, we use the term sulfur(IV) in a general sense to refer collectively to SO_3^{2-} and its singly and doubly protonated forms. Distinction between these forms in the text is only made when it is particularly important for clarity of the presentation. Because no evidence for the existence of sulfurous acid, H_2SO_3, is known, we adopt the notation $H_2O{\cdot}SO_2$ for hydrated sulfur dioxide emphasizing that it is the doubly protonated conjugate acid form of SO_3^{2-}.

(2) Brandt, C.; van Eldik, R. *Chem. Rev.* **1995**, *95*, 119 and references therein.

(3) Pezza, H. R.; Lopes, C. F. F.; Suárez-Iha, M. E. V.; Coichev, N. *Quim. Nova* **1999**, *22*, 529 and references therein.

(4) Csordás, V.; Fábián, I. *Adv. Inorg. Chem.* **2003**, *54*, 395 and references therein.

(5) Muller, J. G.; Hickerson, R. P.; Perez, R. J.; Burrows, C. J. *J. Am. Chem. Soc.* **1997**, *119*, 1501.

(6) Cho, E. H. *Metall. Trans. B* **1986**, *17*, 745.

(7) McFeeters, R. F.; Barrangou, L. M.; Barish, A. O.; Morrison, S. S. *J. Agric. Food Chem.* **2004**, *52*, 4554.

(8) Bäckström, H. L. J. *Z. Phys. Chem., Abt. B* **1934**, *25*, 122.

(9) Anast, J. M.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 2319.

(10) Berglund, J.; Fronaeus, S.; Elding, L. I. *Inorg. Chem.* **1993**, *32*, 4527.

(11) Brandt, C.; Fábián, I.; van Eldik, R. *Inorg. Chem.* **1994**, *33*, 687.

(12) Connick, R. E.; Zhang, Y. X. *Inorg. Chem.* **1996**, *35*, 4613.

(13) Fronaeus, S.; Berglund, J.; Elding, L. I. *Inorg. Chem.* **1998**, *37*, 4939.

(14) Grgić, I.; Poznić, M.; Bizjak, M. *J. Atmos. Chem.* **1999**, *33*, 89.

(15) Wolf, A.; Deutsch, F.; Hoffmann, P.; Ortner, H. M. *J. Atmos. Chem.* **2000**, *37*, 125.

(16) Ermakov, A. N.; Purmal, A. P. *Kinet. Catal.* **2001**, *42*, 479.

(17) Lente, G.; Fábián, I. *J. Chem. Soc., Dalton Trans.* **2002**, 778.

(18) Kerezsi, I.; Lente, G.; Fábián, I. *J. Am. Chem. Soc.* **2005**, *127*, 4785.

(19) Kerezsi, I.; Lente, G.; Fábián, I. *Dalton Trans.* **2006**, 955.

(20) Knappenberger, K. L., Jr.; Castleman, A. W., Jr. *J. Phys. Chem. A* **2004**, *108*, 9.

(21) Cosofret, B. R.; Dylewski, S. M.; Houston, P. L. *J. Phys. Chem. A* **2000**, *104*, 10240.

(22) Hayon, E.; Treinin, A.; Wilf, J. *J. Am. Chem. Soc.* **1972**, *94*, 47.

(23) Fischer, M.; Warneck, W. *J. Phys. Chem.* **1996**, *100*, 15111.

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are often implied as a possible pathway of sulfur(IV) autoxidation in the atmosphere despite the aqueous or gas phase forms of sulfur(IV) not having significant absorptions above 300 nm.[17,19,22−23] Photochemical studies can still provide highly relevant information for atmospheric processes because they may offer important insight into the operative pathways of the thermal autoxidation of sulfur(IV), which is not easily accessible with other methods. An example of this concept is reported in our recent mechanistic studies on the photoinitiated and cerium(III)-catalyzed sulfur(IV) autoxidation.[18]

In that work, useful conclusions could be drawn regarding the dominant steps of thermal autoxidation despite cerium(III) itself having no importance in atmospheric chemistry. The specific features of that system offered distinct advantages.[18] There were no detectable complex formation processes, and the redox reactions could be studied without spectral or kinetic interference from such processes. Consequently, it was possible to monitor the concentration of sulfur(IV) directly by spectrophotometry, which yielded high-quality kinetic data. Because of the photoinitiated nature of the reaction, it could be started and stopped by turning illumination on and off. Finally, the kinetic observations were independent of the concentration of dissolved oxygen, which is otherwise difficult to control at the same precision level as other reactant concentrations are controlled.

In our earlier work on various redox reactions of dithionate ion,[24] we confirmed that the iodide ion is an efficient catalyst of reaction 1. In this paper, we report our detailed studies on the photoinitiated and iodide ion-catalyzed autoxidation of sulfur(IV). The strategy used in this work is similar to the one developed for the study of the cerium(III) catalysis[18] and offers the same advantages. However, the kinetics of the overall reaction in the presence of iodide ion is much more complex, and the results provide more insight into the chain reaction in the core of sulfur(IV) autoxidation.

Experimental Section

Materials. All chemicals used in this study were of analytical reagent grade and were purchased from commercial sources. Fresh sodium sulfite stock solutions were prepared from $Na_2S_2O_5$ (Reanal) every day. Doubly deionized and ultrafiltered water from a Millipore Q system was used to prepare the stock solutions and samples. Most of the experiments were carried out at high and constant acid concentration (0.575 M sulfuric or 1.00 M perchloric acid in different sets of experiments); therefore, additional salt was not used to adjust the ionic strength. In the pH-dependent experiments, perchloric acid was used, and the ionic strength was set to 1.00 M with $NaClO_4$, which was prepared from $NaHCO_3$ and perchloric acid as described elsewhere.[25]

Instrumentation. UV−vis spectra were recorded on a HP-8543 diode-array or a Perkin-Elmer Lambda 2S scanning spectrophotometer. A YSI 5100 dissolved oxygen meter and a YSI model 5239 probe with a YSI 5906 membrane cap were used for the measurement of the concentration of dissolved oxygen in aqueous solutions. Two different lamps were used in the experiments with the oxygen electrode: an AvaLight DHS (Avantes) and a high-power quartz lamp (Medicor, Hungary). Quantitative kinetic measurements on the photochemical reaction were performed in the HP-8543 diode-array instrument using the method and general operating procedures described in earlier publications.[18,26] A built-in Hewlett-Packard 89090A Peltier thermostat was used to maintain constant temperature (25.0 ± 0.1 °C). The solutions were kept homogeneous during the photochemical experiments using the built-in magnetic stirrer of the standard cell compartment of the HP-8543 instrument. A 3 mm stirring rod was used inside standard quartz cuvettes (optical path length = 1.000 cm). The geometry of the setup was carefully tested, and it was ensured that the stirring rod never disrupted the light beam. The light source was calibrated by both ferrioxalate actinometry[27] and reproduction of observations on the known photoreaction of 2,6-dichloro-1,4-benzoquinone.[26] Solution filters were inserted into the light beam in a 0.100 cm standard quartz cuvette.

Capillary electrophoresis measurements for product analysis were performed with a HP ^{3D}CE instrument using a fused-silica capillary of 48 cm × 50 μm i.d. (CS-Chromatographie, Langerwehe, Germany) and indirect detection. The electrolyte contained 5 mM chromate ion and 0.2 mM cetyl trimethyl ammonium bromide; the pH of the solution was 8.0. The method was optimized in an earlier work.[28]

Results and Discussion

Preliminary Observations. Sulfur(IV) and oxygen do not react in the absence of catalysts in aqueous solutions, even at elevated temperatures.[17−19,24] Our earlier high-temperature study on the effect of dissolved oxygen on the aqueous redox reactions of dithionate ion confirmed that the iodide ion catalyzes reaction 1.[24] The kinetic observations indicated that the mechanism of the iodide catalysis is more complex than that of the cerium(III) catalysis.[24] It is now understood that this higher complexity arises partially from the fact that light absorption of sulfur(IV), in contrast with the cerium(III) system, is also an important factor in the presence of iodide ion.

Hydrated sulfur dioxide, $H_2O{\cdot}SO_2$, is the most important form of sulfur(IV) in most of the pH range of the present study (pK_a = 1.74 at 25.0 °C in 1.0 M $NaClO_4$).[17] It has a UV absorption band centered around 276 nm.[17,19] The photochemical activity of $H_2O{\cdot}SO_2$ was studied recently in our laboratory.[19] It was shown that photochemical autoxidation of sulfur(IV) without catalysts is a rather slow and relatively simple process with a quantum yield of 0.35. A nonchain mechanism was proposed which involves the peroxomonosulfate ion as a reactive intermediate. It was also concluded that significant formation of radicals is very unlikely in this process.[19]

Under illumination, reaction 1 becomes much faster in the presence of iodide ion. In preliminary studies, the same experiments were carried out in conventional double-beam and HP-8453 diode-array spectrophotometers. Measurable progress of sulfur(IV) decay was observed only with the latter instrument. The main difference in the experiments is that

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(24) Lente, G.; Fábián, I. *Inorg. Chem.* **2004**, *43*, 4019.
(25) Gordon, G.; Tewari, P. *J. Phys. Chem.* **1966**, *70*, 200.
(26) Lente, G.; Espenson, J. H. *J. Photochem. Photobiol., A* **2004**, *163*, 249.
(27) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.
(28) Jandik, P.; Jones, R. *J. Chromatogr.* **1991**, *546*, 431.

the double-beam unit scans the spectrum with a low-intensity monochromatic light beam, whereas the diode-array spectrophotometer irradiates the sample with a relatively high-energy undispersed light beam in the 190−1100 nm spectral region. The observations confirm that illumination of the samples with sufficient light intensity is essential in the iodide ion-catalyzed autoxidation of sulfur(IV) and that the reaction can be driven even by the light source of a commercial spectrophotometer.

The photochemical nature of the process was further demonstrated by experiments where the variation in the concentration of dissolved oxygen was followed in an acidic solution containing sulfur(IV) and iodide ion (see Figure S2 in the Supporting Information). A slow decrease in the oxygen concentration was observed under normal laboratory light conditions, probably because of the slow thermal reaction between the iodide ion and dissolved oxygen, followed by the fast reduction of I_2 by S(IV). The decrease was orders of magnitude faster when the sample was illuminated by a quartz lamp. The loss of oxygen was so rapid in this case that reliable kinetic measurements were not possible because of the relatively slow response time (several seconds) of the oxygen electrode.

To confirm the stoichiometry of the process, product analysis was performed by capillary electrophoresis (CE).[28] This method can be used readily to separate and determine sulfate, dithionate, peroxodisulfate, and sulfur(IV) ions.[19] In all experiments, detectable amounts of dithionate or peroxodisulfate ions were not observed; therefore, the sulfate ion is the only product. This fact gives experimental support to the simple stoichiometry given in eq 1. Consequently, the rate of oxygen depletion, v, can be calculated by dividing the rate of sulfur(IV) loss by two.

Under the conditions of the kinetic studies, both $H_2O{\cdot}SO_2$ and I^- contribute significantly to the overall absorbance in the UV range, although the relative absorption values are different at different wavelengths. Consequently, both of these species can in principle be photoactive. Matrix rank analysis[29] of the spectra showed that the number of absorbing species is 2 for the overall process, so further absorbing species do not appear in the system. The UV spectra of $H_2O{\cdot}SO_2$ and I^- are markedly different, and an attempt was made to identify the photoactive species using chloroform as an optical filter. Chloroform is an efficient cutoff filter below 250 nm where I^- has a strong absorbance band. In Figure 1, curve b shows an experiment without the filter, whereas curve a was recorded by insertion of a 0.1 cm cuvette with $CHCl_3$ into the light path. The number of photons absorbed by sulfur(IV) decreased by less than a factor of 2 from experiment a to b, whereas the number of photons absorbed by iodide ion decreased by more than an order of magnitude. Nevertheless, the rate of sulfur(IV) loss only decreased slightly. From this observation, it can be concluded that sulfur(IV) must be an active absorbing species in this system. It should be added that this experiment does not allow us to draw any conclusion regarding the role of the iodide ion, and its contribution to the photoinitiation process cannot be excluded.

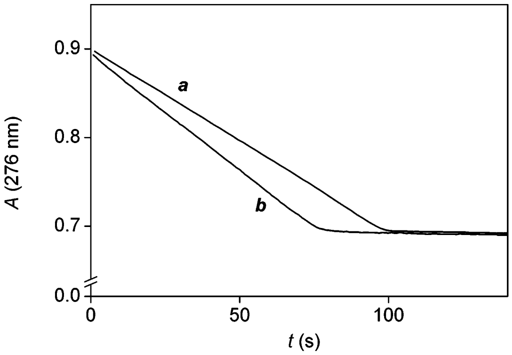

Figure 1. Kinetic traces measured in a diode-array instrument during the photoinitiated and iodide-catalyzed autoxidation of sulfur(IV): (a) curve with chloroform filter and (b) curve without the filter. $[I^-] = 0.050$ mM. $[S(IV)] = 2.0$ mM. $[O_2] = 0.20$ mM. $[H_2SO_4] = 0.575$ M. $V = 3.00$ cm^3. $T = 25.0$ °C.

Detailed Kinetic Studies. Detailed photochemical kinetic experiments were performed with a diode-array spectrophotometer. Each experiment was performed with sulfur(IV) in excess over oxygen, and representative kinetic curves at 276 nm are shown in Figure 1. At this wavelength, S(IV) is selectively monitored, and the sharp break points in the kinetic traces indicate the time when all dissolved oxygen has been used. Although the kinetic traces seem to be close to zero-order, a small but definite rate deceleration was observed as time proceeded within a single kinetic experiment. Consequently, the relatively simple evaluation method used for the strictly zero-order kinetic traces in the cerium(III) system[18] could not be applied here. Therefore, we used the initial rate method to explore the kinetics of the iodide ion system. Initial rates could be determined reasonably well because the first sections of the kinetic traces did not deviate significantly from linearity. The evaluation of spectral data proved that no higher oxidation-state iodine species (I_3^-, I_2, or IO_3^-) were detectable during the entire process. Therefore, negligible amounts of iodide ion are transformed during the process, and the reaction is truly catalytic in I^-. Detailed kinetic studies were carried out to explore how the reactant and catalyst concentrations, the pH, and the light intensity influence the reaction rate.

First, the effect of light intensity is discussed. A diode array spectrophotometer has a fixed and carefully calibrated light source, and it is not possible to change the intensity of the light directly. However, it is possible to change the light intensity per unit volume indirectly by changing the reaction volume, using a series of optical filters, or blocking the light beam partially.[18,19,26] In this study, a number of different optical filters were created using KNO_3 solutions of different concentrations. The efficiency of each filter solution was determined by the same spectrophotometer in the absence of any sample solution (see Supporting Information). The photon count per unit volume (N_V) was calculated with consideration of the absorption properties of the filter and the reaction mixture. The logarithm of the measured rates is plotted against the logarithm of N_V in Figure 2 to determine

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(29) Peintler, G.; Nagypál, I.; Jancsó, A.; Epstein, I. R.; Kustin, K. *J. Phys. Chem. A* **1997**, *101*, 8013.

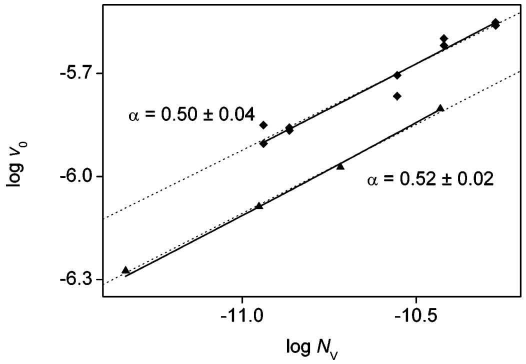

Figure 2. Reaction rates as a function of the photon count during the photoinitiated and iodide-catalyzed autoxidation of sulfur(IV): (solid line) dependence predicted by the proposed model shown in Scheme 1 and (dotted line) best-fitting straight line. $[I^-]$ = 0.050 (triangles) and 0.20 mM (diamonds). [S(IV)] = 2.00 mM. $[H_2SO_4]$ = 0.575 M. T = 25.0 °C.

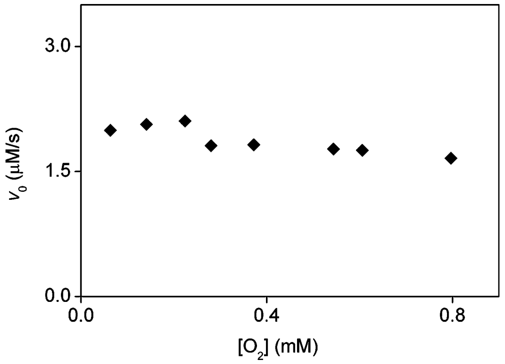

Figure 3. Initial rate as a function of oxygen concentration during the photoinitiated and iodide-catalyzed autoxidation of sulfur(IV). $[I^-]$ = 0.20 mM. [S(IV)] = 2.0 mM. $[H_2SO_4]$ = 0.575 M. V = 3.00 cm^3. T = 25.0 °C.

the order of reaction with respect to light intensity. The experimental points could reasonably be fitted to a straight line (dotted lines) in both series of measurements shown in Figure 2. The slopes of these lines are 0.5; thus, the reaction rate is half-order in the light intensity. This is characteristic of chain reactions where the termination step is second-order with respect to chain carriers, as demonstrated in the cerium(III) system.[18] However, it will be shown that the half-order dependence on N_V should be considered only as an approximation because some of the observations indicate a more complex kinetic behavior. The kinetic model developed for the reaction is consistent with this finding. Nevertheless, the data fitted on the basis of the model (shown as solid lines in Figure 2) are very close to the linear fit under most of the conditions applied.

The initial concentration of oxygen was changed by bubbling oxygen (for higher concentrations) or argon (for lower concentrations) gas into the reagent solutions. The results in Figure 3 show that the initial rates do not depend on the concentration of dissolved oxygen. This finding is similar to those in the cerium(III)[18] and catalyst-free systems.[19] The initial concentration of oxygen could be calculated to high precision in each completed experiment from the overall loss of sulfur(IV) concentration and the stoichiometry of eq 1, which was thoroughly confirmed.

The initial rate exhibits a saturation character as a function of sulfur(IV) concentration (Figure 4). This is an inherent feature of the system and can be understood by taking into account that the main photoactive species is $H_2O{\cdot}SO_2$. The amount of absorbed light by S(IV) increases nonlinearly with increasing concentration. However, the change in absorption alone is not sufficient for quantitative interpretation of the results shown in Figure 4. It follows that additional effects through thermal reactions must also play some role. The final model discussed in subsequent parts of the paper predicts this dependence reasonably well as demonstrated by the fitted curve (solid line) in Figure 4.

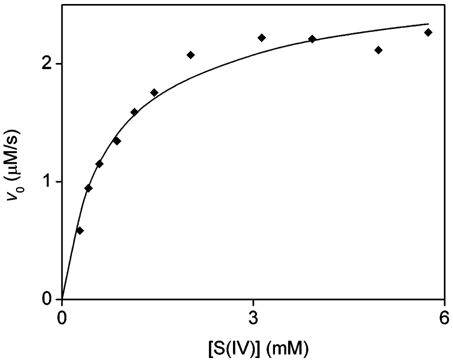

Figure 4. Initial rate as a function of sulfur(IV) concentration during the photoinitiated and iodide-catalyzed autoxidation of sulfur(IV). The solid line represents the best fit to the proposed mechanism shown in Scheme 1. $[I^-]$ = 0.025 mM. $[H_2SO_4]$ = 0.575. V = 3.00 cm^3. T = 25.0 °C.

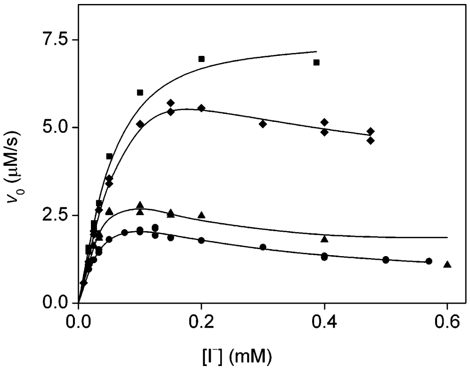

Figure 5. Initial rate as a function of iodide ion concentration during the photoinitiated and iodide-catalyzed autoxidation of sulfur(IV). The solid lines represent the best fit to the proposed mechanism shown in Scheme 1. [S(IV)] = 3.00 (squares), 2.00 (diamonds), 1.00 (triangles), and 0.70 mM (circles). $[H_2SO_4]$ = 0.575 M. V = 3.00 cm^3. T = 25.0 °C.

The dependence on iodide ion concentration is even more complex, as demonstrated in Figure 5 at four different sulfur(IV) concentrations. Three of the curves show a clear maximum and reach a somewhat lower final value at relatively high iodide ion concentrations. One possible explanation of curves like these is that the iodide ion also contributes to the light absorption. At lower iodide ion concentration, the reaction rate increases because this species is involved in thermal reaction steps. Eventually, light absorption by I^- would lower the reaction rate if $H_2O{\cdot}SO_2$ were the only photoactive species because the number of photons absorbed by $H_2O{\cdot}SO_2$ is getting lower when the iodide ion concentration increases. However, this explanation was ruled out experimentally because the same feature was observed in the concentration dependency when the chloroform filter was used and the absorption of iodide ion was

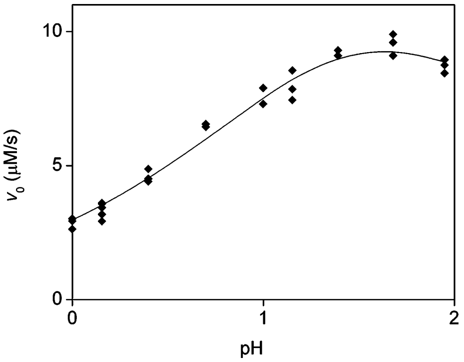

Figure 6. Initial rate as a function of pH during the photoinitiated and iodide-catalyzed autoxidation of sulfur(IV). The solid line represents the best fit to the proposed mechanism shown in Scheme 1. [S(IV)] = 2.00 mM. $[I^-] = 0.20$ mM. $\mu = 1.0$ M $(Na,H)ClO_4$. $V = 3.00$ cm^3. $T = 25.0$ °C.

negligible (Figure S07). It should be added that the final model predicts that the iodide ion has a direct role in photoinitiation of the overall reaction, and the noted effect cannot just simply be assigned to light absorption phenomena.

The effect of pH change is shown in Figure 6 and was somewhat surprising at first sight. An increase in pH from 0 to 2 considerably reduces the concentration of $H_2O{\cdot}SO_2$ with simultaneous formation of the very weakly absorbing HSO_3^- ion. Therefore, a decrease would be expected in the reaction rate with increasing pH because the number of absorbed photons decreases considerably. Instead, a definite increase was observed which roughly followed the deprotonation pattern of $H_2O{\cdot}SO_2$. This can be qualitatively explained by the chain somehow becoming more efficient with increasing pH and this overcompensates for the effect of decreasing photon counts. Figure 6 features a rather vague maximum in the reaction rate at pH ~1.8, and measurements at higher pH would have been essential to make this claim unambiguous. This was not possible because the reaction was followed through the absorption of $H_2O{\cdot}SO_2$, and the spectral effects became too small for quantitative analysis at higher pH. Again, the solid curve in Figure 6 shows the fitted curve based on the final model.

All the experiments discussed thus far involved continuous illumination of the reaction mixture. As pointed out in our previous studies,[18,19] experiments with interrupted illumination could provide important additional kinetic information. In such measurements, the illuminating light is excluded by periodically closing the shutter of the photometer, that is, dark intervals are introduced between two consecutive spectra being recorded. Several series of kinetic runs were recorded in this manner. These experiments clearly confirmed that the progress of the reaction is not strictly proportional to the total time of illumination at constant light intensity. This phenomenon is not unexpected on the basis of our experience in the cerium(III) system[18] and clearly indicates that a chain mechanism is operative, in which the role of light is only to initiate but not to maintain the chain. In the dark periods, termination through thermal reactions diminishes the concentration of chain carriers relatively slowly; thus measurable progress in the overall reaction also occurs in the dark period. Unlike in the cerium(III) system,[18] simple quantitative treatment of the data is not possible when the illumination is not continuous because the kinetic traces are not zero-order and the rate is dependent on the sulfur(IV) concentration. It should be added that these experiments positively prove that a chain process contributes significantly to the progress of the reaction, but it does not exclude a possible contribution from a parallel nonchain mechanism.

Quantum yields for the loss of oxygen have been determined in several experiments and, similar to the cerium(III) system,[18] depend on the reactant and catalyst concentrations, the light intensity, and the lengths of the intermittent dark periods. The quantum yields were between 100 and 1000, again confirming an efficient chain reaction.

Identification of the Chain Initiation Steps. The observations undoubtedly confirmed that a chain reaction is operative in this system, and a series of experiments were performed to identify the chain initiation step. The iodide ion, similar to other halides, is known to be involved in photochemical reactions by illumination with UV light in aqueous solutions.[30,31] In the absence of other reagents, illumination of an iodide ion solution yields iodine. It was shown in our independent experiments that this reaction can in fact be driven by the lamps of the diode-array spectrophotometer. The mechanism of the process was studied both in the absence and presence of oxygen in earlier studies.[30,31] The formation of iodine atom, $I^{\cdot}$, as an intermediate is very likely, and it would without doubt be a chain carrier in the autoxidation process because it quickly reacts with sulfur(IV).[32]

It should be noted that absorption of the iodide ion alone does not account for our experimental findings. The experiments presented in Figure 1 clearly prove that $H_2O{\cdot}SO_2$ is also an active absorbing species in the system, and potentially, both the iodide ion and $H_2O{\cdot}SO_2$ can be involved in the photoinitiation of the chain reaction. Our independent study on the photochemically initiated autoxidation of sulfur(IV) showed that light absorption by $H_2O{\cdot}SO_2$ alone does not initiate a chain reaction in the absence of catalysts.[19] It was also confirmed that HSO_5^- forms as an intermediate in that reaction.

To identify the role of iodide ion in the photoinitiation phase, a series of experiments was devised using an oxygen-sensing electrode. The oxygen concentration of an acidic sulfur(IV) solution was followed in the dark after the addition of I_2 (a), HSO_5^- (b), and HSO_5^- and I^-, simultaneously (c). A sudden decrease of oxygen concentration is expected if the added species is a chain carrier in the autoxidation of sulfur(IV) or if it initiates a chain reaction without light. In the cerium(III)−sulfur(IV) system, such a test could be used to confirm that cerium(IV) is a chain carrier.[18] A similar sudden decrease in dissolved oxygen concentration was not observed in any of experiments a, b, and c. This proves that I_2 and HSO_5^- are not chain carriers, and the intermediates of the known and fast reaction between I_2 and sulfur(IV)[33]

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(30) Jortner, J.; Ottolenghi, M.; Stein, G. *J. Phys. Chem.* **1964**, *68*, 247.
(31) Jortner, J.; Ottolenghi, M.; Stein, G. *J. Phys. Chem.* **1962**, *66*, 2042.
(32) Alfassi, Z. B.; Huie, R. E.; Marguet, S.; Natarjan, E.; Neta, P. *Int. J. Chem. Kinet.* **1995**, *27*, 181.
(33) Yiin, B. S.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 1559.

Scheme 1

$$\mathrm{I^- + h\nu + H_2O{\cdot}SO_2 + O_2 \rightarrow I^{\bullet} + SO_4^{-\bullet} + H_2O} \qquad v_1 = \alpha_1 N_{\mathrm{I}} \tag{R1}$$

$$\mathrm{H_2O{\cdot}SO_2} + h\nu \rightarrow \mathrm{{}^*H_2O{\cdot}SO_2} \qquad v_2 = \alpha_2 N_{\mathrm{S}} \tag{R2}$$

$$\mathrm{{}^*H_2O{\cdot}SO_2 + I^- + O_2 \rightarrow I^{\bullet} + SO_4^{-\bullet} + H_2O} \qquad v_3 = \text{fast} \tag{R3}$$

$$\mathrm{SO_4^{-\bullet} + I^- \rightarrow I^{\bullet} + SO_4^{2-}} \qquad v_4 = k_4[\mathrm{SO_4^-}][\mathrm{I^-}] \tag{R4}$$

$$\mathrm{I^{\bullet} + H_2O{\cdot}SO_2 \rightarrow SO_3^{-\bullet} + I^- + 2H^+} \qquad v_{5a} = k_{5a}[\mathrm{I^{\bullet}}][\mathrm{H_2O{\cdot}SO_2}] \tag{R5a}$$

$$\mathrm{I^{\bullet} + HSO_3^- \rightarrow SO_3^{-\bullet} + I^- + H^+} \qquad v_{5b} = k_{5b}[\mathrm{I^{\bullet}}][\mathrm{HSO_3^-}] \tag{R5b}$$

$$\mathrm{SO_3^{-\bullet} + O_2 \rightarrow SO_5^{-\bullet}} \qquad v_6 = k_6[\mathrm{SO_3^{-\bullet}}][\mathrm{O_2}] \tag{R6}$$

$$\mathrm{SO_5^{-\bullet} + H_2O{\cdot}SO_2 \rightarrow SO_4^{-\bullet} + HSO_4^- + H^+} \qquad v_7 = k_7[\mathrm{SO_5^{-\bullet}}][\mathrm{H_2O{\cdot}SO_2}] \tag{R7}$$

$$\mathrm{I + I^- \rightleftharpoons I_2^{-\bullet}} \qquad v_8 = \text{fast} \quad K_8 = \frac{[\mathrm{I_2^{-\bullet}}]}{[\mathrm{I^{\bullet}}][\mathrm{I^-}]} \tag{R8}$$

$$\mathrm{I_2^{-\bullet} + H_2O{\cdot}SO_2 \rightarrow SO_3^{-\bullet} + 2I^- + 2H^+} \qquad v_{9a} = k_{9a}[\mathrm{I_2^{-\bullet}}][\mathrm{H_2O{\cdot}SO_2}] \tag{R9a}$$

$$\mathrm{I_2^{-\bullet} + HSO_3^- \rightarrow SO_3^{-\bullet} + 2I^- + H^+} \qquad v_{9b} = k_{9b}[\mathrm{I_2^{-\bullet}}][\mathrm{HSO_3^-}] \tag{R9b}$$

$$\mathrm{SO_4^{-\bullet} + SO_4^{-\bullet} \rightarrow S_2O_8^{2-}} \qquad v_{10} = k_{10}[\mathrm{SO_4^{-\bullet}}]^2 \tag{R10}$$

$$\mathrm{SO_4^{-\bullet} + I_2^{-\bullet} \rightarrow SO_4^{2-} + I_2} \qquad v_{11} = k_{11}[\mathrm{SO_4^{-\bullet}}][\mathrm{I_2^{-\bullet}}] \tag{R11}$$

$$\mathrm{I_2^{-\bullet} + I_2^{-\bullet} \rightarrow I_3^- + I^-} \qquad v_{12} = k_{12}[\mathrm{I_2^{-\bullet}}]^2 \tag{R12}$$

$$\mathrm{I_2 + H_2O{\cdot}SO_2 + H_2O \rightarrow HSO_4^- + 2I^- + 3H^+} \qquad v_{13} = \text{fast} \tag{R13}$$

$$\mathrm{H_2O{\cdot}SO_2 \rightleftharpoons HSO_3^- + H^+} \qquad v_{14} = \text{fast} \quad K_{\mathrm{a}} = \frac{[\mathrm{HSO_3^-}][\mathrm{H^+}]}{[\mathrm{H_2O{\cdot}SO_2}]} \tag{R14}$$

$$\mathrm{I_2^- + I^- \rightleftharpoons I_3^-} \qquad v_{15} = \text{fast} \quad K_{\mathrm{tri}} = \frac{[\mathrm{I_3^-}]}{[\mathrm{I_2}][\mathrm{I^-}]} \tag{R15}$$

are not chain carriers, either. The observations also exclude the possibility of a chain initiation via the dark reactions between HSO_5^- and sulfur(IV) or between HSO_5^- and I^-. It is also known that HSO_5^- can only form in a small steady-state concentration, even in the absence of iodide ion,[19] and it does not have sufficiently large absorption to influence the process photochemically. In fact, it can be concluded that HSO_5^- is very unlikely to play a role in the initiation under any conditions.

The simplest interpretation of all relevant observations is that $H_2O{\cdot}SO_2$ is able to photosensitize iodide ion. This assumption is exploited in the postulated kinetic model and will be discussed in the next section in more detail.

Mechanistic Considerations. The detailed mechanism proposed for the overall photoinitiated reaction is given in Scheme 1. Reactions R1−R3 are the initiation steps in the chain mechanism. They are written as non-elementary steps: the eventual formation of $SO_4^{-\cdot}$ most probably proceeds through hydrated electrons and superoxide radical ions. Reactions R4−R9 are chain propagation steps; R10−R12 are termination steps. R13 is a non-elementary post-termination step known independently;[33] R14 is the known acid dissociation equilibrium of $H_2O{\cdot}SO_2$,[22,34] and R15 is the known equilibrium of triiodide ion formation.[35] Other known acid base equilibria of sulfur(IV) involving the formation of SO_3^{2-} and $S_2O_5^{2-}$ are only significant at higher pH or sulfur(IV) concentration[34] and were not included in our model. At first sight, the large number of reaction steps may suggest that the mechanism is supererogatory. However, many of the individual steps were established in thorough independent studies on the subsystems.

As discussed above, both the iodide ion and $H_2O{\cdot}SO_2$ must be photoactive absorbing species. Therefore, the corresponding photochemical reactions must be part of the model. Reactions R1 and quantum efficiency α_1 are known from independent studies on the photochemistry of aqueous iodide ion solutions.[30,31] In addition to reaction R2, two more steps were identified in photochemical autoxidation of $H_2O{\cdot}SO_2$ in the absence of catalysts[19]

$$\mathrm{{}^*H_2O{\cdot}SO_2 + O_2 = HSO_5^- + H^+} \tag{2}$$

$$\mathrm{HSO_5^- + H_2O{\cdot}SO_2 = 2HSO_4^- + H^+} \tag{3}$$

However, later evaluation showed that these steps do not have a noticeable influence in the presence of iodide ions, and they were excluded from the final model.

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(34) Lente, G.; Fábián, I. *Inorg. Chem.* **1998**, *37*, 4204.

(35) Turner, D. H.; Flynn, G. W.; Sutin, N.; Beitz, J. V. *J. Am. Chem. Soc.* **1972**, *94*, 1554.

On the basis of the previous arguments, the reaction is a chain process, in which light only initiates the chains. It follows that the kinetic model needs to include a series of thermal chain propagation steps. Reactions R6, R7, and R10 have been proposed many times in detailed kinetic models for catalytic autoxidation reactions of sulfur(IV).[2−4,11,18,36,37] Independent data from a study of the reactions of the iodine atom show that reactions R5b occurs.[32] Independent kinetic and equilibrium data for reaction R8 are readily available from the literature.[38−41] It is also known that iodine atoms do not react readily with O_2;[32] therefore this process does not have to be considered in the model. Data on reaction R9b have also been published.[42−43] The peculiar maximum-shape seen in the iodide ion concentration dependence (Figure 5) can only be explained if $I_2^{-\bullet}$ is assumed to have a role in a termination step as well; the most likely option is a reaction between $I_2^{-\bullet}$ and sulfate ion radical (a strong oxidant) producing sulfate ions and I_2 (R11). The recombination of $I_2^{-\bullet}$ was also studied in earlier work and is included in the model as reaction R12.[38−41] I_3^- and I_2, which form in termination steps R11 and R12, respectively, are rapidly consumed in a non-elementary post-termination step (R13), which is known from independent experiments,[33] and it was also shown that its intermediates are not chain carriers in the autoxidation.

After all these considerations, only reactions R3 and R4 remain to be discussed. Reaction R3 is an energy transfer step from excited $H_2O{\bullet}SO_2$ to the iodide ion. A similar reaction between excited $H_2O{\bullet}SO_2$ and iron(II) has already been proposed in an earlier study.[19] As pointed out in the previous section, reaction R3 is most probably the simplest way to interpret how $H_2O{\bullet}SO_2$ participates in the initiation. In step R4, the thermodynamically rather strong oxidant and kinetically reactive sulfate ion radical oxidizes iodide ion (a good reducing agent) to form sulfate ion and iodine atom. In addition, this step is also necessary to maintain the chain reaction because without it there would be no way to reproduce iodine atom in a propagation step and consequently there would be no chain at all.

The pH dependence of the initial rate in this system (Figure 6) is unique in that significant pH effects were not observed in the cerium(III)-catalyzed autoxidation of sulfur(IV)[18] or in the direct photochemistry of $H_2O{\bullet}SO_2$ or I^- in the same pH region.[19,30,31] Therefore, the noted pH dependence can only arise through propagation steps between iodine- and sulfur-containing chain carriers. We suggest that the observations can be interpreted by consideration of the protolytic equilibrium between $H_2O{\bullet}SO_2$ and HSO_3^- (R14), that is, the reactivities of these two species are expected to be different toward $I_2^{-\bullet}$ (R9). Analogous steps with $I^\bullet$ are also considered in the model (R5). Acid−base reactions with the iodine-containing species cannot be envisioned under the conditions applied, and as a source of pH dependence, such reactions can be ruled out from the kinetic model.

Calculations confirmed that the lack of oxygen dependence (Figure 3) would not be possible if the independently described reactions in eqs 2 and 3 played a significant role in the overall process. In this case, there would be a competition between steps R3 and the one in eq 2, which would also mean competition between a chain and nonchain mechanism. This would imply sensitive oxygen dependence in the kinetics, that is, marked decrease in the rate of the overall reaction as the concentration of oxygen increases. The lack of significance for reactions in eqs 2 and 3 means that practically the total amount of absorbed light is involved in chain initiation and only an undetectably small portion leads to the formation of HSO_5^-. This was taken into account in further derivations.

Based on the model presented in Scheme 1, the classical mathematical treatment of chain reactions can be used.[44] The most important element of this treatment is that the rates of formation and consumption of chain carriers are equal. Steps R10, R11, and R12 consume chain carriers, and the formation of chain carriers is possible only through photoinitiation. Therefore the equation

$$2a_1N_I + 2a_2N_S = 2k_{10}[SO_4^{-\bullet}]^2 + 2k_{11}[SO_4^{-\bullet}][I_2^{-\bullet}] + 2k_{12}[I_2^{-\bullet}]^2 \quad (4)$$

applies, where N_I is the photon count per unit volume for iodide ion and N_S is the photon count per unit volume for sulfur(IV). They can be calculated from the known spectra of iodide ion and sulfur(IV) and the known emission properties of the lamps[26]

$$N_I = \frac{C}{V}\sum_{\text{all}\lambda} \frac{\epsilon_I^{\lambda}[I^-]}{\epsilon_I^{\lambda}[I^-] + \epsilon_S^{\lambda}[H_2O{\bullet}SO_2]} \times E_{\text{lamp}}^{\lambda}\lambda(1 - 10^{\epsilon_I^{\lambda}[I^-]+\epsilon_S^{\lambda}[H_2O{\bullet}SO_2]}) \quad (5)$$

$$N_S = \frac{C}{V}\sum_{\text{all}\lambda} \frac{\epsilon_S^{\lambda}[H_2O{\bullet}SO_2]}{\epsilon_I^{\lambda}[I^-] + \epsilon_S^{\lambda}[H_2O{\bullet}SO_2]} \times E_{\text{lamp}}^{\lambda}\lambda(1 - 10^{\epsilon_I^{\lambda}[I^-]+\epsilon_S^{\lambda}[H_2O{\bullet}SO_2]}) \quad (6)$$

In these formulas, ϵ_I^{λ} is the molar absorbance of the iodide ion at wavelength λ, ϵ_S^{λ} is the molar absorbance of $H_2O{\bullet}SO_2$ at wavelength λ, $E_{\text{lamp}}^{\lambda}$ is the relative energy of the lamp at wavelength λ, C is the constant determined from actinometric measurements needed to obtain absolute photon and V is the volume of the sample.[26]

To derive a formula for the overall rate of the reaction, it should be considered that the oxygen consumption in the

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(36) Das, T. N.; Huie, R. E.; Neta, P. *J. Phys. Chem. A* **1999**, *103*, 3581.
(37) Das, T. N. *J. Phys. Chem. A* **2001**, *105*, 9142.
(38) Grossweiner, L. I.; Matheson, M. S. *J. Phys. Chem.* **1957**, *61*, 1089.
(39) Baxendale, J. H.; Bevan, P. L. T.; Stott, D. A. *Trans. Faraday Soc.* **1968**, *64*, 2389.
(40) de Violet, P. F.; Bonneau, R.; Logan, S. R. *J. Phys. Chem.* **1974**, *78*, 1698.
(41) Norg, G.; Pedersen, B.; Florian-Løvborg, F.; Pagsberg, P. *Inorg. Chem.* **1982**, *21*, 2327.
(42) Neta, P.; Huie, R. E. *J. Phys. Chem.* **1985**, *89*, 1783.
(43) Shoute, L. C. T.; Alfassi, Z. B.; Neta, P.; Huie, R. E. *J. Phys. Chem.* **1991**, *95*, 3238.
(44) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995; pp 181−189.

initiation sequence (R1 and R3) is most likely negligibly small compared to the rate of chain-carrying step R6. Consequently, the long-chain approach can be used here.[44] All propagation steps without parallel paths have the same rate, which is equal to the overall reaction rate. In Scheme 1, reactions R8−R9 and reaction R5 are parallel paths, the sum of the rates of these parallel paths is equal to the reaction rate. Oxygen loss occurs predominantly in the propagation phase, and its rate is therefore also equal to the rate of step R4

$$v = k_4[\mathrm{SO_4}^{-\bullet}][\mathrm{I}^-] \tag{7}$$

A combination of eqs 4 and 7 yields an explicit equation (see derivation in Supporting Information) which describes how the rate of the reaction depends on the reactant concentrations

$$v = \sqrt{\frac{(a_1N_\mathrm{I} + a_2N_\mathrm{S})k_4{}^2[\mathrm{I}^-]^2(p_1[\mathrm{S(IV)}] + p_2[\mathrm{I}^-][\mathrm{S(IV)}])^2}{k_{10}(p_1[\mathrm{S(IV)}] + p_2[\mathrm{I}^-][\mathrm{S(IV)}])^2 + k_{11}k_4[\mathrm{I}^-]^2(p_1[\mathrm{S(IV)}] + p_2[\mathrm{I}^-][\mathrm{S(IV)}]) + k_{12}k_4{}^2[\mathrm{I}^-]^4}} \tag{8}$$

In this formula, p_1 and p_2 are functions of pH, but they are independent of the reactant or catalyst concentrations

$$p_1 = \frac{k_{5\mathrm{a}}[\mathrm{H}^+] + k_{5\mathrm{b}}K_\mathrm{a}}{K_8([\mathrm{H}^+] + K_\mathrm{a})} \tag{9}$$

$$p_2 = \frac{k_{9\mathrm{a}}[\mathrm{H}^+] + k_{9\mathrm{b}}K_\mathrm{a}}{[\mathrm{H}^+] + K_\mathrm{a}} \tag{10}$$

There are eight parameters in eq 8. Four of these parameters are reliably known from independent studies. Quantum efficiencies α_1 and α_2 are known from independent photochemical studies of the iodide ion[30,31] and sulfur(IV).[19]

$$\alpha_1 = 0.29 \text{ and } \alpha_2 = 0.35 \tag{11}$$

Rate constants k_{10} (recombination of $\mathrm{SO_4}^{-\bullet}$)[45] and k_{12} (recombination of $\mathrm{I_2}^{-\bullet}$)[38] are also available from the literature, although they were measured at somewhat different ionic strengths

$$k_{10} = 4.4 \times 10^8\ \mathrm{M^{-1}\ s^{-1}} \tag{12}$$

$$k_{12} = 7.7 \times 10^9\ \mathrm{M^{-1}\ s^{-1}} \tag{13}$$

These parameters were fixed in the final fitting with the known values. An attempt was made to determine the remaining four parameters from a comprehensive fitting procedure that included all data measured in constant 0.575 M H_2SO_4 (95 individual kinetic experiments). This was not successful because of the strong correlation between parameters. The problem was resolved by calculating an estimate of p_2 ($2.4 \times 10^4\ \mathrm{s^{-1}}$) from a literature value of $k_{9\mathrm{b}}$ ($1.4 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$)[43] and assuming that $k_{9\mathrm{b}}K_\mathrm{a} \gg k_{9\mathrm{a}}[\mathrm{H}^+]$ in 0.575 M H_2SO_4 (i.e., $\mathrm{I_2}^{-\bullet}$ is much more reactive toward $\mathrm{HSO_3}^-$ than $H_2O{\cdot}SO_2$). After the value of p_2 was fixed at this estimate, the three free parameters left in eq 8 could be resolved

$$k_4 = (1.8 \pm 0.1) \times 10^8\ \mathrm{M^{-1}\ s^{-1}} \tag{14}$$

$$k_{11} = (1.5 \pm 0.3) \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}} \tag{15}$$

$$p_1 = (1.4 \pm 0.2) \times 10^4\ \mathrm{M\ s^{-1}} \tag{16}$$

These fitted values do not seem unreasonable: k_{11} is essentially diffusion controlled, which is not unexpected for a reaction between two radicals; k_4 is also quite high as expected. The consistency of the value obtained for p_1 will be discussed after the interpretation of the effect of pH.

It is not easy to make a simple figure which shows the overall goodness of fit because it would require a multidimensional graph. The best fits to experimental data are represented by solid lines in Figures 2, 4, and 5. A graph in which the fitted initial rates are plotted as a function of measured initial rates for all 95 experiments (Figure S10) also confirms that the model provides excellent quantitative interpretation of the kinetic results.

It was also determined that the average chain length[44] exceeds 500 in all experiments; therefore, the use of the long-chain approach in the derivations is justified. The high average chain length also explains why the peroxodisulfate ion, a product of one of the chain termination steps, is not detectable in the product mixture. It simply does not accumulate in high enough concentrations.

Efforts were made to explore whether all of the reactions in Scheme 1 are really necessary for the interpretation of the experimental data. As already discussed, initiation steps were carefully identified in qualitative experiments. Among the chain propagation steps, excluding one or two of steps R5, R8, and R9 would still leave a meaningful model. However, the resulting smaller models do not describe the maximum-shaped curves for iodide ion dependence shown in Figure 4 and predict monotonous change of the rate instead. None of the other propagation steps (R4, R6, and R7) can be left out without breaking the chain. Among the three independent chain termination steps (R10−R12), one would actually be enough to give a chemically sensible model. When reaction R10 or R11 was disregarded, the sum of residuals for the overall fit increased by at least 3 orders of magnitude indicating that the smaller models without these steps do not interpret the findings quantitatively. Finally, setting $k_{12} = 0$ in model calculations (i.e., omitting reaction R12) resulted in an increase in the sum of squares by a factor of 3. This is not very significant and indicates that the chain termination goes primarily through reactions R10 and R11. However, because step 12 is well documented in the literature, its inclusion does not increase the number of free parameters (its rate constant is known and fixed) and it does improve the fit somewhat; therefore, we decided to leave it in the final model.

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(45) Huie, R. E.; Clifton, C. L. *Chem. Phys. Lett.* **1993**, *205*, 163.

The pH-dependent data were evaluated using the full, pH-dependent formula, which is obtained by the substitution of eqs 9 and 10 into eq 8. In the final evaluation of the pH dependence, k_4 and k_{11} were fixed at the values determined previously (eqs 14−15). The value of K_8 was also fixed at a literature value[38] of 1.2×10^4 M^{-1}. In a manner similar to the evaluation of constant pH data, the literature value of k_{9b} (1.4×10^6 M^{-1} s^{-1})[43] was fixed, and it was assumed that $k_{9b}K_a \gg k_{9a}[H^+]$. These considerations left only two free parameters, k_{5a} and k_{5b}. These could be resolved by least-squares fitting of 26 initial rate experiments in $HClO_4$

$$k_{5a} = (1.2 \pm 0.2) \times 10^8\ M^{-1}\ s^{-1} \qquad (17)$$

$$k_{5b} = (6.3 \pm 1.0) \times 10^8\ M^{-1}\ s^{-1} \qquad (18)$$

The rate constants of the reaction between $I^{\bullet}$ and HSO_3^-/SO_3^{2-} at pH 7 in 1:1 methanol/water was reported to be (1.0 ± 0.3) $\times 10^9$ M^{-1} s^{-1},[32] which seems to be in reasonable agreement with our fitted value given in eq 18, especially if the different medium is taken into account. From the resolved values of k_{5a} and k_{5b}, $p_1 = 1.1 \times 10^4$ M s^{-1} can be calculated for $[H^+] = 0.6$ M (in perchloric acid), which is in good agreement with the fitted value of p_1 in 0.575 M H_2SO_4.

On the basis of these results, the following interpretation can be given for the pH-dependency. At high acidities, the formation of chain carrier $I_2^{-\bullet}$ is a dead end with respect to the chain propagation because $I_2^{-\bullet}$ reacts only relatively slowly with $H_2O{\cdot}SO_2$ and is involved mainly in the termination step. However, the propagation reaction between $I_2^{-\bullet}$ and HSO_3^- is much faster and a considerably smaller fraction of $I_2^{-\bullet}$ takes part in the termination step as the pH is increased. Thus, the overall process becomes faster despite the decreasing number of photons absorbed by the system.

The species $I_2^{-\bullet}$ has a central role in shaping the somewhat unusual, maximum-shaped iodide ion concentration dependence (Figure 5). An increase in the concentration of iodide ion first accelerates the process for the following reasons: (i) more photons are absorbed and (ii) the relative rate of propagation step R4 is increased compared to that of the termination steps (R10 and R11). However, at intermediate iodide ion concentrations, iodine atoms are diverted from reaction R5 to form $I_2^{-\bullet}$ in reaction R8. As $I_2^{-\bullet}$ accelerates the termination, the overall process slows down. This effect is less pronounced at higher sulfur(IV) concentrations because of the enhanced kinetic role of step R5.

It should also be noted that, theoretically, eq 8 does not predict a strict half-order dependence with respect to the overall photon count N_V. In fact, two different photon counts have to be taken into account because there are two different photoactive absorbing species. However, the experimental reaction order with respect to N_V is very close to 0.5, and fitted results on the basis of eq 8 also confirm this observation (dotted and solid lines in Figure 2). This somewhat unusual finding may be connected to the coincidence that the quantum efficiencies of the two initiating processes are quite close to each other (eq 11).

Conclusion

This study has shown that photochemically initiated sulfur(IV) autoxidation in acidic aqueous solutions is strongly catalyzed by the iodide ion. Detailed kinetic data together with independent information obtained in relevant subsystems could be used to build a model that gives a satisfactory quantitative interpretation of the experimental results under all conditions. It is also shown that the photochemical method using a diode-array spectrophotometer for simultaneous excitation and detection can be used to gain insight into somewhat complicated inorganic reaction mechanisms, and it is also possible to handle cases where two photoactive absorbing species are present simultaneously. These results may also contribute to better understanding of catalytic thermal autoxidation reactions of sulfur(IV).

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Supporting Information Available: Ten figures demonstrating various kinetic effects in the title reaction (sometimes referred to in the text) and a detailed derivation of eq 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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