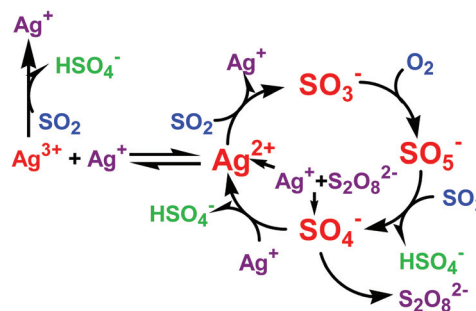


1

**Kinetics of the autoxidation of sulfur(IV)  
co-catalyzed by peroxodisulfate and silver(I) ions**

Éva Dóka, Gábor Lente\* and István Fábián

A radical chain reaction interprets the simultaneous catalytic effect of silver(I) and peroxodisulfate ions on the aqueous autoxidation of sulfur(IV).



Please check this proof carefully. **Our staff will not read it in detail after you have returned it.**

Translation errors between word-processor files and typesetting systems can occur so the whole proof needs to be read. Please pay particular attention to: tabulated material; equations; numerical data; figures and graphics; and references. If you have not already indicated the corresponding author(s) please mark their name(s) with an asterisk. Please e-mail a list of corrections or the PDF with electronic notes attached – do not change the text within the PDF file or send a revised manuscript. Corrections at this stage should be minor and not involve extensive changes. All corrections must be sent at the same time.

**Please bear in mind that minor layout improvements, e.g. in line breaking, table widths and graphic placement, are routinely applied to the final version.**

We will publish articles on the web as soon as possible after receiving your corrections; **no late corrections will be made.**

Please return your **final** corrections, where possible within **48 hours** of receipt, by e-mail to: dalton@rsc.org

## Queries for the attention of the authors

Journal: **Dalton Transactions**

Paper: **c4dt00900b**

Title: **Kinetics of the autoxidation of sulfur(IV) co-catalyzed by peroxodisulfate and silver(I) ions**

Editor's queries are marked like this [Q1, Q2, ...], and for your convenience line numbers are indicated like this [5, 10, 15, ... ].

Please ensure that all queries are answered when returning your proof corrections so that publication of your article is not delayed.

| Query Reference | Query   | Remarks |
|-----------------|---|---------|
| Q1              | For your information: You can cite this article before you receive notification of the page numbers by using the following format: (authors), Dalton Trans., (year), DOI: 10.1039/c4dt00900b. |         |
| Q2              | Please carefully check the spelling of all author names. This is important for the correct indexing and future citation of your article. No late corrections can be made.                     |         |

## PAPER

Kinetics of the autoxidation of sulfur(IV)  
co-catalyzed by peroxodisulfate and silver(I) ions†

Éva Dóka, Gábor Lente\* and István Fábián

Cite this: DOI: 10.1039/c4dt00900b

Received 26th March 2014,  
Accepted 6th May 2014

DOI: 10.1039/c4dt00900b

www.rsc.org/dalton

## Introduction

The redox reaction between aqueous sulfur(IV) and dissolved oxygen, which is extremely slow in the absence of catalysts, is still the single most important source of acid rain formation in the atmosphere.<sup>1–5</sup> The role of sulfur(IV) autoxidation in the hydroxylation, epoxidation and oxidative cleavage of DNA,<sup>6–10</sup> in certain metallurgical<sup>11,12</sup> and food technologies,<sup>13–16</sup> and microbiological processes<sup>17</sup> generates additional motivation to study its mechanistic details. It is now understood that the process does not proceed in the absence of a catalyst in acidic medium.

Since Backstrom's first studies in the early part of the previous century,<sup>18</sup> a large number of investigations have aimed to study the kinetics of various catalytic reaction systems involving sulfur(IV) autoxidation.<sup>19–43</sup> It is now widely accepted that the most efficient mechanisms involve radical chain mechanisms, in which the primary role of the catalyst is to initiate the chains, with some additional significance in chain propagation steps. The chain initiation can both be chemical<sup>21,35</sup> and photolytic,<sup>38,40</sup> the most important aspect is that it should involve a one-electron oxidation of sulfur(IV) to sulfite ion radical. The products formed in the decomposition of a metal (such as iron) sulfite complex or highly reactive species gener-

ated as a result of exposure to light can provide such a pathway.

In our previous studies, it was shown that light absorbed by sulfur(IV) also catalyzes the direct autoxidation, albeit a non-chain mechanism is operative in this case.<sup>36,39</sup> In addition, several autoxidation processes with chain mechanisms have been studied including the catalytic effect of iron(III),<sup>21,35</sup> and photocatalysis in the presence of cerium(III)<sup>38</sup> and iodide<sup>40</sup> ions. The chain carriers common to the different systems were sulfite ion radical ( $\text{SO}_3^{\cdot-}$ ), sulfate ion radical ( $\text{SO}_4^{\cdot-}$ ), and peroxomonosulfate ion radical ( $\text{SO}_5^{\cdot-}$ ). Sulfate ion radical seemed to be a central species for catalysis as it reacts with the catalysts in a chain propagation step, and its second-order recombination usually provides the only significant route of chain termination. These chain reactions are highly efficient with the average chain length exceeding 1000.<sup>38,40</sup>

A full understanding of the autoxidation mechanisms necessitates independent studies on all subsystems that might be operative. One such subsystem of the reaction between sulfur(IV) and oxygen could be the redox reaction between sulfur(IV) and peroxodisulfate ion ( $\text{S}_2\text{O}_8^{2-}$ ), whose stoichiometry is expected to produce sulfate ion only (synproportionation). Kinetic studies, however, showed that this process is undetectably slow in acidic medium in the absence of catalysts. Silver(I) ion is understood to be a very general redox catalyst in all reactions of  $\text{S}_2\text{O}_8^{2-}$ .<sup>44</sup> Therefore, we tried to catalyze the synproportionation in this way. Experiments revealed that the autoxidation of sulfur(IV) is initiated, and dissolved oxygen is consumed quite rapidly in this system. Thus, we realized that a non-photochemically initiated chain mechanism can be

University of Debrecen, Department of Inorganic and Analytical Chemistry,  
Debrecen 10, P.O.B. 21, H-4010, Hungary. E-mail: [lente@dfin.unideb.hu](mailto:lente@dfin.unideb.hu);  
Fax: +36 52 489-667; Tel: +36 52 512-900/22373

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c4dt00900b

studied in this case, which would add valuable new information to the previous studies. This paper presents the detailed results on this catalytic system and the mechanistic conclusions based on them.

## Experimental section

### Materials

All chemicals used in this study were of analytical reagent grade and were purchased from commercial sources. Sulfur(IV) stock solutions were prepared freshly from solid  $\text{Na}_2\text{S}_2\text{O}_5$  (Reanal) every day. Wherever necessary, piro-sulfite solutions were de-aerated by bubbling Ar (purity >99.95%) for at least 15 min in order to increase the reproducibility of measurements under anaerobic conditions.

Potassium peroxodisulfate stock solutions were prepared from  $\text{K}_2\text{S}_2\text{O}_8$  (Reanal), their concentrations were standardized iodometrically. These solutions were oxygenated during the  $\text{O}_2$ -dependent experiments by bubbling pure oxygen gas into it for 10–20 min. Silver(I) catalyst solutions were prepared by dissolving a weighed amount of  $\text{AgNO}_3$  (Reanal) to a known final volume. Doubly deionized and ultrafiltered water from a Millipore Q system was used in the entire work. Most of the experiments were carried out at high and constant acid concentration (0.10 or 0.33 M sulfuric acid), therefore additional salt was not used to adjust the ionic strength.

### Instrumentation

UV-vis spectra were recorded on a Perkin Elmer Lambda 2S or a Perkin Elmer Lambda 25 scanning spectrophotometer. Diode array spectrophotometers were not used to avoid known problems of photoinitiation by the analyzing light beam.<sup>38–40,45–48</sup> Kinetic experiments were carried out in standard quartz cuvettes (optical path length = 1.000 cm). Constant temperature ( $25.0 \pm 0.1^\circ\text{C}$ ) was maintained with an external thermostat and circulating thermal bath.

Samples were prepared by the following method: required aliquots of piro-sulfite, peroxodisulfate and sulfuric acid solutions were mixed with water and thermostated for 3–4 minutes. The process was started by adding silver(I) solution immediately prior to commencing the detection in the spectrophotometer.

Nanosecond flash photolysis measurements were carried out in an LKS.60 nanosecond transient absorption spectrometer manufactured by Applied Photophysics Ltd. The instrument is equipped with a Quantel Brilliant Nd:YAG laser (repetition frequency 10 Hz). The fourth harmonic generator operating at 266 nm and Q-switching were used in the present study (nominal energy: 40 mJ per pulse, pulse length: 6 ns, beam diameter: 6 mm). The analyzing light source was a 150 W ozone free xenon arc lamp (OSRAM 150 W/CR OFR) and its light beam entered a  $1 \times 1$  cm fluorescence quartz cuvette with cross-beam excitation. The analyzing light beam was positioned close to the front face of the cuvette, to maximize the detected concentration of transient species. A programmable

f/3.4 grating monochromator with a symmetrical Czerny–Turner optical configuration was combined with a R928 photo-multiplier for the transient signal detection at different wavelengths. Data points were collected by an Agilent Infiniium digital storage oscilloscope (model number DSO8064A) with a maximum sampling speed of  $4\text{ GSa s}^{-1}$  (0.25 ns between data points), bandwidth of 600 MHz, output impedance of  $50\ \Omega$ . Transient absorption kinetic curves were registered with the control software of the LFP instrument, Pro-Data LKS (version number 1.1.0.5) and visualized by Pro-Data Viewer (version number 4.2.5). Pro-Data Viewer has a built-in curve fitting application that was used in first order fitting. Other fitting procedures were carried out by the software Scientist (Micromath).<sup>49</sup>

## Results and discussion

### Preliminary observations

Sulfite ion and oxygen do not react in the absence of catalysts in acidic aqueous solutions, even at elevated temperatures.<sup>36</sup> Hydrated sulfur dioxide,  $\text{H}_2\text{O}\cdot\text{SO}_2$ , is the most important form of sulfur(IV) in most of the pH range of the present study. It should be noted that no evidence of the existence of a molecule corresponding to the commonly used formula of sulfurous acid ( $\text{H}_2\text{SO}_3$ ) has been obtained yet.<sup>50,51</sup> Hydrated sulfur dioxide is in equilibrium with hydrogensulfite ion with a  $\text{p}K_a = 1.74$  at  $25.0^\circ\text{C}$ :<sup>35</sup>

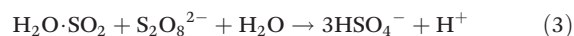
$$K_a = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{O}\cdot\text{SO}_2]} \quad (1)$$

$\text{H}_2\text{O}\cdot\text{SO}_2$  has a UV absorption band centered around  $276\text{ nm}$ <sup>49</sup> (see UV-vis spectrum in Fig. S1 in ESI†).

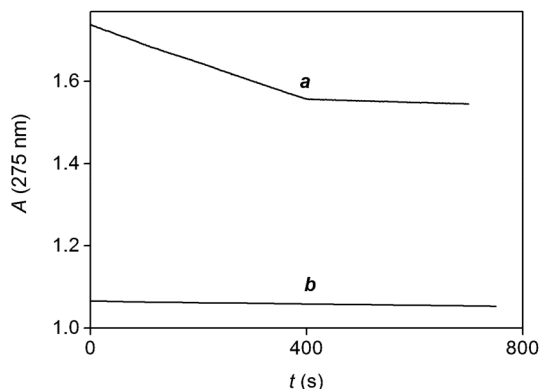
Preliminary experiments also showed that the reaction of sulfur(IV) and peroxodisulfate ion does not occur in the absence of a catalyst. In the presence of silver(I), the shape of recorded kinetic traces became quite unusual, a curve close to a straight line with a sharp break point was experimentally detected (Fig. 1). It is known from previous studies that the appearance of the break point most likely refers to the total depletion of dissolved oxygen from the system.<sup>21,38,40</sup> This was demonstrated in this work by showing that dissolved oxygen is the limiting reagent in the first phase under the conditions used in this study (Fig. S2 in ESI†). Therefore, the autoxidation process takes places before the break point.



During the subsequent period of the process, peroxodisulfate ion plays the role of the stoichiometric oxidizing agent according to the following equation:



The slope of the kinetic traces in this part is more than two orders of magnitude smaller than in the first phase. The difference between the initial absorbances of curves **a** and **b** in Fig. 1 is related to the higher acidity at curve **a**, which leads to



**Fig. 1** Typical kinetic traces measured during the autoxidation of sulfite ion in the absence and presence of catalyst. Optical path length = 1.000 cm;  $T = 25.0\text{ }^{\circ}\text{C}$ ; (a)  $[\text{S(IV)}] = 2.76\text{ mM}$ ;  $[\text{S}_2\text{O}_8^{2-}] = 33.3\text{ mM}$ ;  $[\text{H}_2\text{SO}_4] = 0.33\text{ M}$ ;  $[\text{Ag}^+] = 0.167\text{ mM}$ ; (b)  $[\text{S(IV)}] = 3.0\text{ mM}$ ;  $[\text{S}_2\text{O}_8^{2-}] = 37.0\text{ mM}$ ;  $[\text{H}_2\text{SO}_4] = 0.103\text{ M}$ ;  $[\text{Ag}^+] = 0$ .

higher concentration of the major absorbing species  $\text{H}_2\text{O}\cdot\text{SO}_2$ . In addition, the absorption of nitrate ion, which was the counterion used with the silver(I) catalysts, is significant at this wavelength, so higher absorbance readings are expected in its presence.

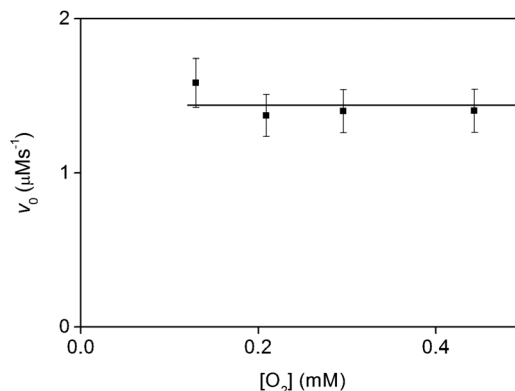
#### Detailed kinetic studies

Comprehensive kinetic studies were performed in order to find out how the reactant and catalyst concentrations and pH affect the reaction rate, which was calculated as the initial rate of sulfur(IV) loss from the initial rate of absorbance change measured at 275 nm using the molar absorption coefficient of  $\text{H}_2\text{O}\cdot\text{SO}_2$  and allowing for the effect of pH:

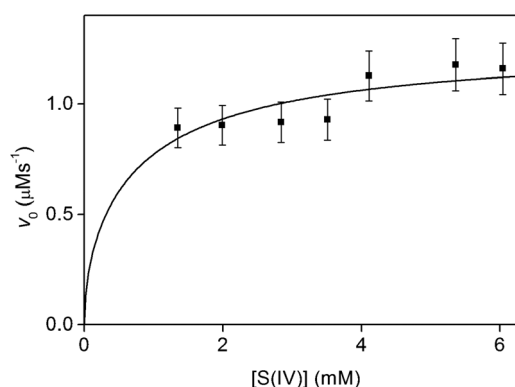
$$v_0 = \frac{dA_{275\text{ nm}}}{dt}(t=0) \frac{[\text{H}^+] + K_a}{\epsilon \ell [\text{H}^+]} \quad (4)$$

The value of  $\epsilon$  ( $364\text{ M}^{-1}\text{ cm}^{-1}$ ) and  $K_a$  ( $0.0181\text{ M}$ ) were known from previous studies,<sup>35</sup> the path length of the cell used was 1.000 cm. The initial rate of absorbance change was easily determined by linear fitting of a suitable initial portion as the curves were close to zeroth order.

Peroxodisulfate ion was usually present in excess over sulfur(IV), and silver(I) was added in catalytic amounts. First, the effect of dissolved oxygen is presented in Fig. 2. The amount of dissolved oxygen was varied by the length of the oxygenation of the  $\text{K}_2\text{S}_2\text{O}_8$  stock solution. The actual kinetic traces are shown in Fig. S2 in the ESI.† As already mentioned, these curves clearly prove that dissolved oxygen is the limiting reagent in the process. The exact initial oxygen concentrations could not be measured, as using an oxygen selective electrode before the measurement necessarily left some dead time between the end of this measurement and the start of the kinetic experiment, in which the dissolved oxygen concentration could change significantly. Instead, exact initial  $\text{O}_2$  concentrations were determined from the overall absorbance change in the first part of the kinetic traces preceding the break point. Data in Fig. 2 show that the reaction is zeroth



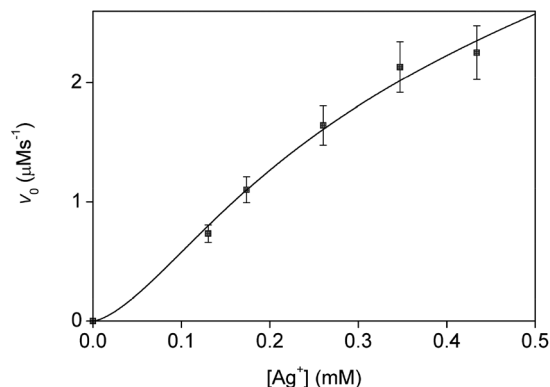
**Fig. 2** Reaction rates as a function of the dissolved oxygen concentration in the autoxidation of sulfur(IV). The solid line represents the best fit to the proposed mechanism shown in Scheme 1.  $[\text{S(IV)}] = 3.0\text{ mM}$ ;  $[\text{S}_2\text{O}_8^{2-}] = 3.00 \times 10^{-2}\text{ M}$ ;  $[\text{H}_2\text{SO}_4] = 0.103\text{ M}$ ;  $[\text{Ag}^+] = 0.260\text{ mM}$ ; path length 1.000 cm;  $T = 25.0\text{ }^{\circ}\text{C}$ .



**Fig. 3** Reaction rates as a function of the sulfur(IV) concentration in the autoxidation of sulfur(IV). The solid line represents the best fit to the proposed mechanism shown in Scheme 1.  $[\text{S}_2\text{O}_8^{2-}] = 0.0301\text{ M}$ ;  $[\text{H}_2\text{SO}_4] = 0.103\text{ M}$ ;  $[\text{Ag}^+] = 0.167\text{ mM}$ ; path length 1.000 cm;  $T = 25.0\text{ }^{\circ}\text{C}$ .

order with respect to dissolved oxygen, which is in very good agreement with the zeroth order (close to linear) shapes of the kinetic traces (Fig. 2) within experimental error. This may seem a rather interesting observation in an autoxidation process, where oxygen acts as a reactant, but it is common in similar systems.<sup>38,40</sup> The entire process is not zeroth-order, though, primarily because sulfur(IV) could not be used in high enough excess to be considered constant during a single kinetic run.

The rate of reaction (2) as a function of sulfur(IV) concentration is plotted in Fig. 3. A minor increase in the rate is observed as the concentration increases. Unfortunately, the concentration range for sulfur(IV) in this case was limited by two factors. First, sulfur(IV) had to be used in excess over oxygen. Second, sulfur(IV) was the monitored absorbing species, therefore the use of high concentrations would have resulted in immeasurably large absorbance values and meaningless absorbance changes. Fig. 3 in fact covers the entire range in which reasonably accurate experiments could be



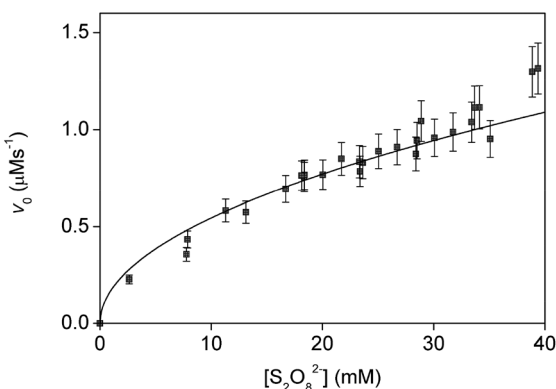
**Fig. 4** Reaction rates as a function of the silver(I) ion concentration in the autoxidation of sulfur(IV). The solid line represents the best fit to the proposed mechanism shown in Scheme 1.  $[S(IV)] = 3.0$  mM;  $[S_2O_8^{2-}] = 30.0$  mM;  $[H_2SO_4] = 0.103$  M; path length 1.000 cm;  $T = 25.0$  °C.

made. At first sight, the points in Fig. 3 might be seen as a straight line with a huge intercept. However, it must not be forgotten that a reactant cannot be consumed when it is absent, so the reaction rate is 0 by default if the concentration of sulfur(IV) is 0, and consequently, the origin is a certain point in any kinetic model used for fitting. The curve drawn in Fig. 3 represents the best of the proposed mechanism and will be discussed later.

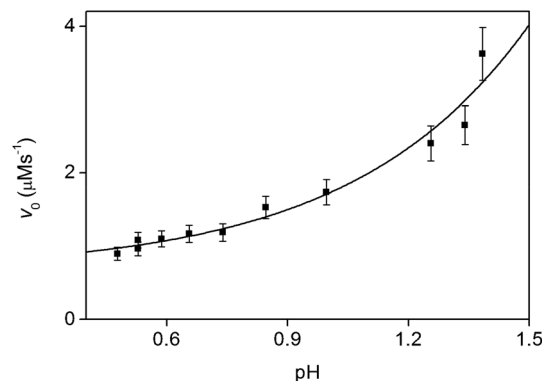
Fig. 4 displays the dependence of the reaction rate on the concentration of silver(I) ion.

The experimental points reflect a complex dependence on concentration, which will be interpreted by the model and discussed later.

The initial concentration of peroxodisulfate ion concentration also influenced the reaction rate in a complicated manner. Fig. 5 shows the data together with the best fit from the proposed mechanism. At this point, it should be noted that the concentration range of the studies for peroxodisulfate ion was less limited than for sulfur(IV).



**Fig. 5** Reaction rates as a function of the peroxodisulfate ion concentration in the autoxidation of sulfur(IV). The solid line represents the best fit to the proposed mechanism shown in Scheme 1.  $[S(IV)] = 3.0$  mM;  $[H_2SO_4] = 0.103$  M;  $[Ag^+] = 0.167$  mM; path length 1.000 cm;  $T = 25.0$  °C.



**Fig. 6** Reaction rates as a function of the pH in the autoxidation of sulfur(IV). The solid line represents the best fit to the proposed mechanism shown in Scheme 1.  $[S(IV)] = 3.0$  mM;  $[S_2O_8^{2-}] = 28.4$  mM;  $[Ag^+] = 0.167$  mM; path length 1.000 cm;  $T = 25.0$  °C.

Finally the effect of pH was also studied, and results are shown in Fig. 6. The main limiting factor in the pH range was that the spectrophotometrically followed signal was provided by  $H_2O-SO_2$ , so studies could not be extended into the range above its  $pK_a$  (1.74). At this point, it should be mentioned that sulfuric acid was used to set the acidity. The pH was always calculated from the composition of the solution considering that sulfuric acid is not a strong acid in its second deprotonation step ( $pK_{a2} = 1.06$  at 25 °C).<sup>52</sup> Fig. 6 shows that the rate of reaction increases by increasing the pH. This is different from what was observed in the case of cerium(III) initiated photocatalysis, where the reaction rate was independent of the pH.<sup>38</sup> There are more similarities with the case of iodide ion initiated photocatalysis, where decreasing acidity accelerated the reaction.<sup>40</sup> The findings displayed in Fig. 2–6 will be interpreted by postulating a mechanism in the next sections.

#### Direct study of the sulfate ion radical with silver(I)

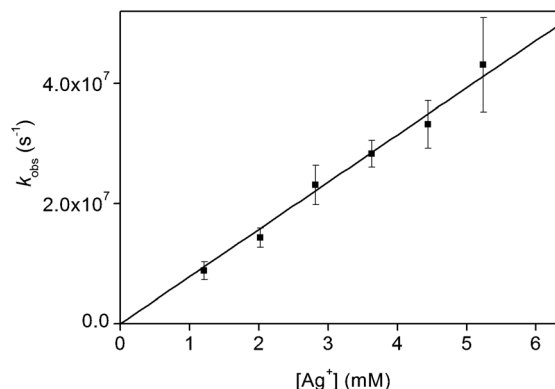
One of the key steps of the mechanisms proposed to interpret the previously described experimental findings is a reaction between the sulfate ion radical ( $SO_4^{\cdot-}$ ) and aqueous silver(I). Actually, the value for the rate constant was not needed directly in the model calculations, but we felt it necessary to confirm the fact that this reaction occurs as rapidly as expected. Therefore, laser flash photolysis was used to study the kinetics of this process.

Sulfate ion radicals were generated through the photolysis of peroxodisulfate ions initiated by a laser pulse at 266 nm:<sup>53–57</sup>



The absorbance of the sulfate ion radicals was followed directly at 450 nm. In the absence of any silver(I), the relatively slow (0.5 ms), second-order recombination of sulfate ion was detected as expected. When, silver(I) was added, however, the time scale of the kinetic traces was much shorter (0.1 μs, Fig. S3 in ESI†). These traces could be fitted very well to pseudo-first order curves, the pseudo-first order rate constants





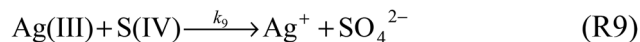
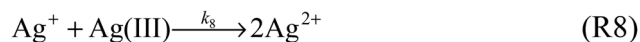
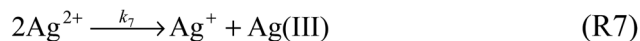
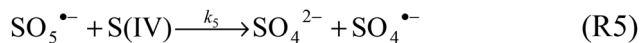
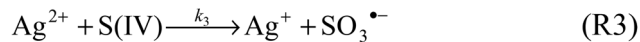
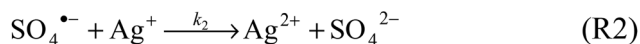
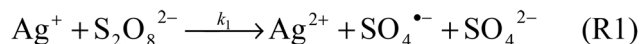
**Fig. 7** Pseudo-first order rate constants as a function of silver(I) concentration measured in the flash photolysis study of the reaction between the sulfite ion radical and silver(I) ion.  $[K_2S_2O_8] = 0.100\text{ M}$ ;  $[H_2SO_4] = 0.0270\text{ M}$ ;  $T = 25\text{ }^\circ\text{C}$ .

of which were directly proportional to the silver(I) concentration (Fig. 7). This proves that the reaction of silver(I) with sulfate ion radical is first order with respect to both of the reagents. The second-order rate constant was calculated from the slope of the straight line in Fig. 7:  $(7.1 \pm 1.4) \times 10^9\text{ M}^{-1}\text{ s}^{-1}$  at pH 1.4 set by sulfuric acid. The second order rate constant was also determined in an unbuffered solution at about pH 7 by measuring the silver(I)-dependence of the pseudo-first order rate constant. The value obtained was  $(6.9 \pm 0.4) \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ , which is not significantly different from the value measured in acidic medium and also within the range of values obtained with earlier pulse radiolysis experiments.<sup>58,59</sup> Based on these facts, the reaction itself seems to be a single elementary step.

### Proposed mechanism

Scheme 1 presents the kinetic scheme we propose to interpret experimental observation. The scheme comprises nine steps altogether, which may seem too many at first sight. However, each of these steps has significance in this model and independent evidence for their existence in earlier experimental studies.

The high rate of autoxidation and the zeroth order dependence on the oxygen concentration make it clear that a radical chain mechanism similar to the cases of photocatalysis by cerium(III)<sup>38</sup> and iodide ion<sup>40</sup> must be operative in this system. Reaction step (R1) is the well-known reaction of silver(I) ion with peroxodisulfate ion, which is understood to be responsible for the catalytic effect of silver(I) in almost all redox reactions of the otherwise rather inert  $S_2O_8^{2-}$ .<sup>44</sup> The products of this reaction are  $Ag^{2+}$  and  $SO_4^{\bullet-}$ . Sulfate ion radical is a known chain carrier in other autoxidation systems of sulfur(IV)<sup>21,35,38,40</sup> Step (R2) is assumed to occur during the direct reaction between  $Ag^+ + S_2O_8^{2-}$ ,<sup>44</sup> but was also confirmed independently in this work by laser flash photolysis and earlier by pulse radiolysis studies.<sup>58,59</sup> Step (R3) is a logical one to assume and also necessary to complete the cycling of radicals in this systems, it is the one-electron oxidation of sulfur(IV) by strong oxidant silver(II). Steps (R2) and (R3) took



**Scheme 1**

part as propagation reactions in the proposed chain mechanism. Steps (R4) and (R5) are further chain propagating steps that are well known from the literature of sulfur(IV) autoxidation<sup>1</sup> and also from pulse radiolysis studies.<sup>60–63</sup> Step (R6), the recombination of sulfate ion radical is again well established experimentally,<sup>64,65</sup> and is the typical chain termination step in the radical chain mechanism resulting in the autoxidation of sulfur(IV).<sup>38,40</sup> Considering only steps (R1)–(R6) already gives a viable possible mechanism for the silver(I) and peroxodisulfate ion catalyzed autoxidation of sulfur(IV). This mechanism was tested carefully. Unfortunately, it clearly failed to interpret the experimental data as it predicted very different curves for the sulfur(IV), silver(I), peroxodisulfate and pH dependences shown in the graphs. However, these steps must surely have some role in the overall process as their existence is known from sources independent of this work.<sup>44,58–65</sup> Therefore, further steps had to be considered in order to interpret the experimental observation. Steps (R7) and (R8) together represent the reversible disproportionation of silver(II) into silver(I) and silver(III). This process was assumed to play a role in an earlier system.<sup>44,66</sup> Finally, (R9) is a plausible step in which strong oxidant silver(III) oxidizes sulfur(IV) in a non-radical, two electron reaction.

An equation has been derived (see detailed derivation in ESI†) based on this scheme to describe the dependence of the reaction rate on the reactant concentrations. The derivation used steady-state approach for chain carriers and the assumption called the long chain approximation in chain mechanism,<sup>67</sup> which was clearly valid as the rate of consumption of sulfur(IV) was much faster than the independently known rate

of the initiating step of reaction (R1). The final formula shows reasonable complexity, but it is still an explicit equation:

$$v = [\text{S(IV)}] \sqrt{\frac{\frac{k_1 k_3^2 [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}]}{k_7}}{1 + \frac{k_6}{k_7} \left(\frac{k_3}{k_2}\right)^2 \frac{[\text{S(IV)}]^2}{[\text{Ag}^+]^2} - \frac{[\text{Ag}^+]}{(k_9/k_8)[\text{S(IV)}] + [\text{Ag}^+]}}}} \quad (6)$$

This formula gave an excellent interpretation of individual concentration dependencies measured. The best fits are always displayed in the individual graphs showing data at constant pH (Fig. 2–5). The zeroth order nature of the predicted rate with respect to oxygen is easily seen from eqn (6).

A fit to eqn (6) was also carried out in which all data measured at in 0.103 M  $\text{H}_2\text{SO}_4$  had been used simultaneously. However, a statistical analysis of the parameter values showed that the third term in the denominator under the square root was insignificant in comparison with the other two under all conditions. This fact, considering the concentration ranges of sulfur(IV) and silver(I) in the kinetic experiments, implies  $k_9/k_8 > 1$ . Therefore, the entire data set could be fitted with the following two-parameter formula:

$$v = [\text{S(IV)}] \sqrt{\frac{\frac{k_1 k_3^2 [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}]}{k_7}}{1 + \frac{k_6}{k_7} \left(\frac{k_3}{k_2}\right)^2 \frac{[\text{S(IV)}]^2}{[\text{Ag}^+]^2}}} \quad (7)$$

Fig. 8 visualizes the goodness of the best fit using eqn (7) by plotting predicted initial rates as a function of measured reaction rates. The reasonably good straight line seen in Fig. 8 shows that the proposed scheme accounts for all measured data within the experimental error limits. It is seen that despite the large number of reactions, eqn (7) actually only has two adjustable parameters, both of which are composite (products or ratios of rate constants). The values for these combinations were obtained as  $k_1 k_3^2/k_7 = 0.078 \pm 0.007 \text{ M}^{-2} \text{ s}^{-2}$ ,  $k_6 k_3^2/(k_7 k_2^2) = (8.1 \pm 1.3) \times 10^{-3}$  in 0.103 M  $\text{H}_2\text{SO}_4$ , which corresponds to  $[\text{H}^+] = 0.141 \text{ M}$  and  $\text{pH} = 0.85$ .

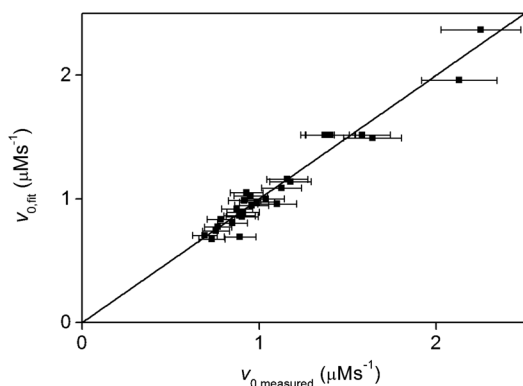


Fig. 8 Correlation between measured and calculated rates in the silver (I) and peroxodisulfate ion catalyzed autoxidation of sulfur(IV). All data measured at  $[\text{H}_2\text{SO}_4] = 0.103 \text{ M}$  shown on the axis, why the y axis shows the best fit based on eqn (7).

For the interpretation of the pH-dependence, it was assumed that the reactivities of the doubly protonated  $\text{H}_2\text{O}-\text{SO}_2$  and singly protonated  $\text{HSO}_3^-$  forms are different in reactions (R3), (R5) and (R9). Fully analogous assumptions successfully interpreted the pH-dependence of iodide ion catalyzed and photoinitiated autoxidation of sulfur(IV). Instead of  $k_3$ ,  $k_5$  and  $k_9$ , the following pH-dependent combinations were used:

$$k_3 = \frac{(k_{3B}[\text{H}^+] + k_{3A}K_a)}{[\text{H}^+] + K_a} \quad (8)$$

$$k_5 = \frac{(k_{5B}[\text{H}^+] + k_{5A}K_a)}{[\text{H}^+] + K_a} \quad (9)$$

$$k_9 = \frac{(k_{9B}[\text{H}^+] + k_{9A}K_a)}{[\text{H}^+] + K_a} \quad (10)$$

The subscript B refers to the reaction with  $\text{H}_2\text{O}-\text{SO}_2$ , whereas the subscript A means the reaction with  $\text{HSO}_3^-$  in eqn (8)–(10). As  $k_5$  and  $k_9$  do not appear in eqn (7), a formula that was already suitable to interpret all reaction rates at constant pH, it was concluded that only (R3) could be the source of the observed pH-dependence. Therefore, the pH-dependence given in eqn (8) was substituted into eqn (7). This gave a new formula which accounted for the changes of reaction rate in response to changes in the acidity of the solution. The parameters already determined at  $\text{pH} = 0.85$  were fixed in the ensuing calculations, which left only a single parameter to be fitted, which is  $k_{3A}/k_{3B}$ , the reactivity silver(II) toward  $\text{HSO}_3^-$  relative to  $\text{H}_2\text{O}-\text{SO}_2$ . The results gave  $k_{3A}/k_{3B} = 42 \pm 12$ , which is in agreement with the very general trend that less protonated species are oxidized easier than their more protonated counterparts.

## Conclusion

It was shown that silver(I) and peroxodisulfate ions act as co-catalysts in the autoxidation of sulfur(IV) in acidic solutions. The kinetics is described by a somewhat complicated rate equation. The reaction rates could be interpreted well with a radical chain reaction, in which the chain carriers are silver(II) ion, sulfite, sulfate and peroxomonosulfate radical ions. A comparison with previous mechanistic proposals reveals that sulfate ion radical plays the most versatile role in various catalytic sulfur(IV) autoxidation systems. Further studies on these species could provide into the mechanisms of such reactions.

## Acknowledgements

The authors thank the Hungarian Science Foundation for financial support under grant no. K77936 and NK 105156. The research was supported by the EU and co-financed by the European Social Fund under the project ENVIKUT (TÁMOP-4.2.2.A-11/1/KONV-2012-0043). The Hungarian Academy of Sciences



also supported these studies through funding Research Group on Homogeneous Catalysis and Reaction Mechanisms. Éva Dóka's participation in this research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP-4.2.4.A/2-11/1-2012-0001 'National Excellence Program'. Some experimental help was kindly provided by Dr Ildikó Kerezsi and Ms Ildikó Forró, whose assistance is gratefully acknowledged.

## References

- 1 C. Brandt and R. van Eldik, *Chem. Rev.*, 1995, **95**, 119–190 and references therein.
- 2 H. R. Pezza, C. F. F. Lopes, M. E. V. Suárez-Iha and N. Coichev, *Quim. Nova*, 1999, **22**, 529–540 and references therein.
- 3 V. Csordás and I. Fábián, *Adv. Inorg. Chem.*, 2003, **54**, 395–461 and references therein.
- 4 A. Tasneem Abbasi, P. Poornima, T. Kannadasan and S. A. Abbasi, *Int. J. Environ. Eng.*, 2013, **5**, 229–272.
- 5 C. J. Percival, O. Welz, A. J. Eskola, J. D. Savee, D. L. Osborn, D. O. Topping, D. Lowe, S. R. Utembe, A. Bacak, G. M. Figgans, M. C. Cooke, P. Xiao, A. T. Archibald, M. E. Jenkin, R. G. Derwent, I. Riipinen, D. W. K. Mok, E. P. F. Lee, J. M. Dyke, C. A. Taatjes and D. E. Shallcross, *Faraday Discuss.*, 2013, **165**, 45–73.
- 6 J. G. Muller, R. P. Hickerson, R. J. Perez and C. J. Burrows, *J. Am. Chem. Soc.*, 1997, **119**, 1501–1506.
- 7 R. G. M. Moreno, M. V. Alipazaga, M. H. G. Medeiros and N. Coichev, *Dalton Trans.*, 2005, 1101–1107.
- 8 M. V. Alipazaga, R. G. M. Moreno, E. Linares, M. H. G. Medeiros and N. Coichev, *Dalton Trans.*, 2008, 5636–5644.
- 9 M. V. Alipazaga, H. D. Moya and N. Coichev, *J. Coord. Chem.*, 2010, **63**, 2450–2460.
- 10 A. A. Ensafi, E. Heydari-Bafrooei and B. Rezaei, *Anal. Chem.*, 2013, **85**, 991–997.
- 11 E. H. Cho, *Metall. Trans. B*, 1986, **17**, 745–753.
- 12 L. Chen, X. Peng, J. Liu, J. Li and F. Wu, *Ind. Eng. Chem. Res.*, 2012, **51**, 13632–13638.
- 13 R. F. McFeeters, L. M. Barrangou, A. O. Barish and S. S. Morrison, *J. Agric. Food Chem.*, 2004, **52**, 4554–4557.
- 14 J. C. Danilewicz and P. J. Wallbridge, *Am. J. Enol. Vitic.*, 2010, **61**, 166–175.
- 15 J. C. Danilewicz, *Am. J. Enol. Vitic.*, 2011, **62**, 319–328.
- 16 U. Takahama and S. Hirota, *J. Agric. Food Chem.*, 2012, **60**, 1102–1112.
- 17 J. Simon and P. M. H. Kroneck, *Adv. Microb. Physiol.*, 2013, **62**, 45–117.
- 18 H. L. J. Bäckström, *Z. Phys. Chem., Abt. B*, 1934, **25**, 122–138.
- 19 J. M. Anast and D. W. Margerum, *Inorg. Chem.*, 1981, **20**, 2319–2326.
- 20 J. Berglund, S. Fronaeus and L. I. Elding, *Inorg. Chem.*, 1993, **32**, 4527–4538.
- 21 C. Brandt, I. Fábián and R. van Eldik, *Inorg. Chem.*, 1994, **33**, 687–701.
- 22 N. Coichev and R. van Eldik, *J. Chem. Educ.*, 1994, **71**, 767–767.
- 23 J. Berglund and L. I. Elding, *Atmos. Environ.*, 1995, **29**, 1379–1391.
- 24 R. E. Connick and Y. X. Zhang, *Inorg. Chem.*, 1996, **35**, 4613–4621.
- 25 A. N. Ermakov, G. A. Proskrebyshev and S. I. Stoliarov, *J. Phys. Chem.*, 1996, **100**, 3557–3560.
- 26 G. Lente and I. Fábián, *Inorg. Chem.*, 1998, **37**, 4204–4209.
- 27 S. Fronaeus, J. Berglund and L. I. Elding, *Inorg. Chem.*, 1998, **37**, 4939–4944.
- 28 I. Grgić, A. Dovžan, G. Berčič and V. Hudnik, *J. Atmos. Chem.*, 1998, **29**, 315–337.
- 29 H. D. Moya, E. A. Neves and N. Coichev, *J. Chem. Educ.*, 1999, **76**, 930–930.
- 30 V. Lepentsiotis, J. Domagala, I. Grgić, R. van Eldik, J. G. Muller and C. J. Burrows, *Inorg. Chem.*, 1999, **38**, 3500–3505.
- 31 I. Grgić, M. Poznić and M. Bizjak, *J. Atmos. Chem.*, 1999, **33**, 89–102.
- 32 H. R. Pezza and N. Coichev, *J. Coord. Chem.*, 1999, **47**, 107–119.
- 33 A. Wolf, F. Deutsch, P. Hoffmann and H. M. Ortner, *J. Atmos. Chem.*, 2000, **37**, 125–135.
- 34 E. A. Betterton and D. J. Anderson, *J. Atmos. Chem.*, 2001, **40**, 171–189.
- 35 G. Lente and I. Fábián, *J. Chem. Soc., Dalton Trans.*, 2002, 778–784.
- 36 G. Lente and I. Fábián, *Inorg. Chem.*, 2004, **43**, 4019–4025.
- 37 M. V. Alipazaga, D. Lowinsohn, M. Bertotti and N. Coichev, *Dalton Trans.*, 2004, 267–272.
- 38 I. Kerezsi, G. Lente and I. Fábián, *J. Am. Chem. Soc.*, 2005, **127**, 4785–4793.
- 39 I. Kerezsi, G. Lente and I. Fábián, *Dalton Trans.*, 2006, 955–960.
- 40 I. Kerezsi, G. Lente and I. Fábián, *Inorg. Chem.*, 2007, **46**, 4230–4238.
- 41 A. C. McQuilken and D. P. Goldberg, *Dalton Trans.*, 2012, **41**, 10883–10899.
- 42 T. Lan, L. Lei, B. Yang, X. Zhang and Z. Li, *Ind. Eng. Chem. Res.*, 2013, **52**, 4740–4746.
- 43 Y. G. Adewuyi and N. Y. Sakyi, *Ind. Eng. Chem. Res.*, 2013, **52**, 11702–11711.
- 44 D. A. House, *Chem. Rev.*, 1962, **62**, 185–203.
- 45 I. Fábián and G. Lente, *Pure Appl. Chem.*, 2010, **82**, 1957–1973.
- 46 M. Gombár, É. Józsa, M. Braun and K. Ösz, *Photochem. Photobiol. Sci.*, 2012, **11**, 1592–1595.
- 47 T. Lehoczi, É. Józsa and K. Ösz, *J. Photochem. Photobiol., A*, 2013, **251**, 63–68.
- 48 J. Kalmár, É. Dóka, G. Lente and I. Fábián, *Dalton Trans.*, 2014, **43**, 4862–4870.
- 49 *SCIENTIST, version 2.0*, Micromath Software, Salt Lake City, UT, USA, 1995.

- 1 50 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, U.K., 1984.
- 51 Y. Beyad, R. Burns, G. Puxty and M. Maeder, *Dalton Trans.*, 2014, **43**, 2147–2152.
- 5 52 G. Lente and I. Fábián, *Inorg. Chem.*, 2002, **41**, 1306–1314.
- 53 Y. Tang, R. P. Thorn, R. L. Mauldin and P. H. Wine, *J. Photochem. Photobiol., A*, 1988, **44**, 243–258.
- 54 W. J. McElroy, *J. Phys. Chem.*, 1990, **94**, 2435–2441.
- 10 55 W. J. McElroy and S. J. Waygood, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 2557–2564.
- 56 X. Y. Yu, Z. C. Bao and J. R. Barker, *J. Phys. Chem. A*, 2004, **108**, 295–308.
- 15 57 H. Herrmann, D. Hoffmann, T. Schaefer, P. Brauer and A. Tilgner, *ChemPhysChem*, 2010, **11**, 3796–3822.
- 58 A. Kumar and P. Neta, *J. Am. Chem. Soc.*, 1980, **102**, 7284–7289.
- 59 A. V. Gogolev, I. E. Makarov, A. M. Fedoseev and A. K. Pikaev, *Khim. Vys. Energ.*, 1986, **20**, 298–302.
- 60 E. Hayon, A. Treinin and J. Wilf, *J. Am. Chem. Soc.*, 1972, **94**, 47–57.
- 61 R. E. Huie and P. Neta, *J. Phys. Chem.*, 1984, **88**, 5665–5669.
- 5 62 R. E. Huie and P. Neta, *Chem.-Biol. Interact.*, 1985, **53**, 233–238.
- 63 R. E. Huie and P. Neta, *Atmos. Environ.*, 1987, **21**, 1743–1748.
- 64 L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 1967, **71**, 2511–2516.
- 10 65 M. S. Subhani and Z. Kauser, *Rev. Roum. Chim.*, 1978, **23**, 1129–1137.
- 66 M. Kimura, T. Kawajiri and M. J. Tanida, *J. Chem. Soc., Dalton Trans.*, 1980, 726–730.
- 15 67 J. H. Espenson, in *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill, New York, 2nd edn, 1995.
- 20
- 25
- 30
- 35
- 40
- 45
- 50
- 55