Photochemical phenomena in the redox reactions of sulfite ion

Summary of PhD thesis

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1. Introduction and objectives

Catalytic autoxidation of sulfur(IV) has attracted considerable interest because of its dominant role in acid rain formation and importance in industrial desulfurisation processes. The sulfite ion – oxygen system has been used for hydroxylation, epoxidation and oxidative cleavage of DNA. The autoxidation of sulfite ion is also important in metallurgical technologies and food chemistry. Multivalent metal ions are known to be very active catalysts of this reaction, and stoichiometric, kinetic and mechanistic aspects of several systems have been studied intensively since the 1930s. Bäckström postulated that the formation of transition metal sulfito complexes and their decomposition are mainly responsible for the catalytic effect. Since then, it has been shown that sulfito complexes may either trigger a radical-type chain reaction by generating the $\text{SO}_3^{-}$ radical or be part of a direct oxidation of sulfite ion to sulfate ion. All of the postulated mechanisms share the same feature that oxygen is involved only in secondary reaction steps in the overall process.

Opinions of different investigators have diverged on the importance of the ’uncatalytic’ pathway of sulfur(IV) autoxidation. In some studies, this reaction is claimed to be detected, whereas others argued that the seemingly uncatalytic pathway may be due to very low and uncontrolled levels of contaminants which have catalytic activity. Whatever the true nature of this ’uncatalytic’ pathway is, it is clearly vanishingly slow in acidic solutions but may be more important at higher pH.

Efforts to study possible photochemical aspects of sulfur(IV) chemistry have also been reported in the literature. These studies have mostly been carried out in the gas phase. Solution phase studies thus far focused on the sulfite and hydrogensulfite ions, $\text{SO}_3^{2-}$ and $\text{HSO}_3^{-}$, which cannot be responsible for photoreactions in acidic solutions. Although textbooks often mention photochemical processes as a possible way of the autoxidation of sulfur(IV) in the atmosphere, experimental evidence does not seem to support this because none of the aqueous or gas phase forms of sulfur(IV) have significant absorptions above 300 nm. However, possible photochemical reactions can still be interesting because they may offer important insight into the different pathways of the autoxidation of sulfur(IV), which is not easily obtained with other methods.
The aim of this work was to carry out a detailed study of the photochemical processes in acidic sulfur(IV) solutions using a recently introduced experimental technique. We also wanted to study how this process is influenced by the presence of iron(II) because the iron(III)/iron(II) redox pair is the single most important non-photochemical catalytic systems in the formation of acid rain in nature. During a study of redox reactions of dithionate ion in our research group, we obtained unique results and concluded that cerium(III) and iodide ions catalyze the autoxidation of sulfite ion. In further experiments, it was confirmed that light plays an important role in these processes. A detailed study on the autoxidation of sulfite ion in presence of cerium(III) and iodide ions was also an objective of this work.

2. Applied methods and equipments

In this study, all chemicals used were of analytical reagent grade and purchased from commercial sources. 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 (sulfuric or perchloric acid), therefore additional salt was not used to adjust the ionic strength. In the pH-dependent experiments, the ionic strength was set to 1.0 M with NaClO₄, which was prepared from Na₂CO₃ and perchloric acid as described elsewhere.

Under the circumstances used in our experiments, sulfite ion occurs mainly in a doubly protonated form as hydrated sulfur dioxide (H₂O·SO₂).

UV-vis spectra were recorded on a HP-8543 diode-array or a Perkin Elmer Lambda 2S scanning spectrophotometer. Constant temperature at 25.0 ± 0.1 °C was maintained with a built-in Hewlett-Packard 89090A Peltier thermostat and an external circulating thermal bath, respectively.

A YSI 5100 Dissolved Oxygen Meter and a YSI Model 5239 probe with YSI 5906 membrane cap were used for measuring the concentration of dissolved oxygen in aqueous solutions. These experiments were run in a stirred open batch reactor and provided only semi-quantitative results because O₂ transfer between the aqueous phase and air somewhat corrupted the measured kinetic effects. Furthermore, the decrease in the concentration of dissolved oxygen in certain experiments was faster than the response time of the electrodes, thus the
instrument was not suitable for following the process in time.

Two different lamps were used in some of the semi-quantitative photochemical experiments: an AvaLight DHS (Avantes, 250 W) and a high-power Quartz lamp (Medicor, Hungary, 500 W).

Quantitative kinetic measurements on the photochemical reaction were performed on the HP-8543 diode-array instrument in a standard quartz cuvette (optical path length: 1.000 cm). The built-in softwares of the instruments, Micromath Scientist 2.01, and MATLAB were used for the evaluation of the results.

Capillary electrophoresis measurements for product analysis were performed on a HP 3DCE 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. The spent reaction mixtures were analyzed for SO₄²⁻, S₂O₆²⁻ and S₂O₈²⁻ by capillary electrophoresis but only the formation of sulfate ion could be confirmed.

Some additional kinetic measurements on thermal reactions were performed with an Applied Photophysics DX-17 MV sequential stopped-flow apparatus using an optical path length of 1 cm.

3. Results

3.1 A novel experimental method was applied and improved to monitor photochemical reactions.

The method was first used by Lente and Espenson with a Shimadzu MultiSpec-1500 single-beam diode-array spectrometer. We used a HP-8543 diode-array spectrometer for the same type of experiments. The main difference between the double-beam spectrophotometer and the diode-array spectrophotometer is that 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 in the 190–1100 nm spectral region. The intensity of the polychromatic light is high enough to initiate a photochemical reaction, thus the equipment can provide the driving light and
Photochemical kinetic experiments can be performed with a HP-8543 diode array spectrophotometer in different ways. Essentially, the variants differ in the illumination time of the sample during the measurement of a single spectrum and in the duration of dark periods between recording two consecutive spectra, when the illuminating light is excluded by closing the shutter of the spectrophotometer. The intensity of the driving light cannot be changed directly as the diode-array spectrophotometer has a fixed and carefully stabilized light source. However, it is well known that the rate of a photochemical reaction is proportional to the absorbed photon count per unit volume ($N_V$), which can be changed readily by a filter or by varying the volume of the irradiated sample. The photochemical use of the diode array instruments also provides a way to determine quantum yields after careful calibration.

3.2 We concluded that the uncatalytic photochemical autoxidation of $H_2O\cdot SO_2$ is a non-chain reaction and proposed a mechanism.

We determined the quantum yield of oxygen loss relative to the number of photons absorbed by sulfur(IV). It was found to be 0.35 in all experiments. We concluded that the reaction is first-order with respect to light intensity and there is no detectable reaction progress in the dark periods. The reaction is zeroth-order with respect to the concentration of the oxygen and the rate is independent of the pH. The absence of radical recombination byproducts (dithionate and peroxodisulfate ions) was demonstrated in the product mixture.

In our proposed mechanism, excited hydrated sulfur dioxide, $^{*}H_2O\cdot SO_2$, first reacts with $O_2$ to form peroxomonosulfate ion, $HSO_5^-$, which rapidly oxidizes another $H_2O\cdot SO_2$ to give hydrogensulfate ion as a final product (Scheme 1).

3.3 We detected the formation of iron(III) in the presence of iron(II) in the autoxidation of sulfur(IV) and proposed a non-chain mechanism.

We observed that the rate of the autoxidation of sulfur(IV) is first-order with respect to light intensity also in the presence of iron(II). In the presence of iron(II), the formation of iron(III) was detected, which can be interpreted considering the simultaneous contributions of two additional pathways: i) some of the $HSO_5^-$ formed oxidizes iron(II) instead of sulfur(IV), ii) $^{*}H_2O\cdot SO_2$ transfers its excited energy to iron(II) and in further steps iron(III) forms (Scheme 1). We used model calculations to show that the proposed scheme gives
an excellent quantitative interpretation of experimental results. In these calculations, we used the steady-state assumptions for the intermediates.

\[
\begin{align*}
H_2O\cdot SO_2 & \overset{hv}{\rightarrow} *H_2O\cdot SO_2 & \overset{O_2}{\rightarrow} HSO_5^- & \overset{H_2O\cdot SO_2}{\rightarrow} HSO_4^- \\
& \downarrow Fe(II) & \downarrow Fe(II) & \downarrow \\
*Fe(II) & +H^+ & \rightarrow Fe(III) \\
& \quad \downarrow & \quad \uparrow H_2 & \quad \\
& & & \\
\end{align*}
\]

**Scheme 1** Mechanism of the photoinitiated autoxidation of aqueous, acidic sulfur(IV) in the absence and presence of the iron(II).

3.4 *We proved that light absorptions by both iodide and sulfite ions contribute to initiating a highly efficient radical chain reaction in the presence of iodide ion. We proposed detailed kinetics model for the interpretation of the results.*

In the sulfite – iodide – oxygen system, the overall rate of autoxidation depends on the reactant and catalyst concentrations, pH, and light intensity in a complex manner. The rate is independent of oxygen concentration. The quantum yields relative to the loss of oxygen spanned a range between 100 and 1000. This fact alone also implies an efficient chain reaction. This was also supported by the fact that the reaction was close to 0.5-order with respect to light intensity.

To interpret all the experimental findings, an elaborate scheme is proposed, in which the chain carriers are sulfite ion radical (SO$_3^-$), sulfate ion radical (SO$_4^{2-}$), peroxomonosulfate ion radical (SO$_5^{2-}$), iodine atom (I), and the iodine molecule radical (I$_2^-$). There are two termination steps, both of which are second-order with respect to chain carriers (*Scheme 2*).

In our model calculations the long chain approximation was used. This way of derivation is mathematically equivalent to simply setting steady-state approximations for all of the reactive intermediates in the system. Non-linear fitting have been used to show that the proposed scheme gives an excellent quantitative interpretation of experimental results.
It was shown that the photoinitiated and cerium(III) catalyzed autoxidation of sulfur(IV) is also an efficient chain reaction, and the photoactive species is cerium(III). To interpret all the experimental findings, a simple scheme was proposed.

We established that the reaction is zeroth-order with respect to the reactants, first-order with respect to cerium(III) and 0.5-order with respect to light intensity. Based on our experimental findings, we gave a rate equation to the loss of oxygen:

\[ v = k_1 [\text{Ce(III)}] N_v^{0.5} \]  

The value \( k_1 = 30 \pm 1 \ M^{-0.5} s^{-0.5} \) was determined by multivariate least-squares fitting of all relevant measured data.

We calculated quantum yields relative to the loss of oxygen, which were also very high in this system and varied under different experimental conditions.

We observed that the reaction continued in the dark period and we carried out a detailed analysis to explore the nature of the reaction in the dark periods. During the evaluation of the results, we developed and applied a new mathematical method to decide whether the chain termination step is first or second-order with respect to chain carriers.

To interpret all the experimental findings, a simple scheme is proposed, in which

**Scheme 2** Mechanism of the photoinitiated and iodide ion catalyzed autoxidation of aqueous, acidic sulfur(IV).
the additional chain carriers are sulfite ion radical (SO$_3^-$), sulfate ion radical (SO$_4^-$), and peroxomonosulfate ion radical (SO$_5^-$) (Scheme 3). The termination step is second-order with respect to the chain carriers. This follows from 0.5-order dependence on the light intensity and the mathematical analysis of experiments under interrupted illumination. The rate equations were deduced applying the long chain approximation (which was were in good agreement with the empirical observations).

The postulated model predicts that cerium(III) should have a co-catalytic or synergistic effect on the autoxidation of sulfite ion in the presence of other catalysts. This prediction was confirmed in the iron(III) – sulfite ion – oxygen system.

Scheme 3 Mechanism of the photoinitiated and cerium(III) catalyzed autoxidation of aqueous, acidic sulfur(IV).

4. The expected practical application of our results

This thesis summarizes detailed studies on the photoinduced autooxidation of aqueous, acidic sulfur (IV) solutions in the absence and presence of iron(II), iodide and cerium(III) ions. The photochemical experiments were performed by a newly introduced technique using a diode array spectrophotometer, in which the same light source is used to drive and detect the reaction. Due to the photoinitiated nature of the reactions, they can be started and ceased by turning illumination on and off, respectively. The demonstrated experimental method can also used to study other photoninitiated reactions.
The studied systems offer several unique advantages as compared to other studies of sulfite autoxidation in the presence of different catalysts. First of all, complex formation or direct redox reactions do not occur between the catalysts and sulfite ion, consequently there are no interferences from such processes. The autoxidation is zeroth-order with respect to dissolved oxygen, circumventing the problem of less accurate control over its concentration. Some reaction steps of our proposed mechanisms and the thermal reactions are the same. Thus, it is possible to obtain such information about the thermal reaction that is impossible or very difficult to obtain in other cases. The results presented here clarify important aspects of the autoxidation of sulfite ion and may be crucial in further mechanism research and exploring the detailed chemical background of the related analytical procedures. The synergistic effects demonstrated in the Ce(III) – sulfite ion – oxygen system offer the possibility of using Ce(III) as a co-catalyst in industrial oxidations of sulfur species. Beside that, the proposed mechanisms could be an important part of the chemical model of the atmosphere. The mathematical treatment used in this work are also applicable to a much wider range of photoinitiated chain reactions.
5. Publications

Publications connected to this thesis:

1. **Ildikó Kerezsi, Gábor Lente, István Fábián**
   
   **Highly Efficient Photoinitation in the Cerium(III)-Catalyzed Aqueous Autoxidation of Sulfur(IV). An Example of Comprehensive Evaluation of Photoinduced Chain Reactions**
   
   *Journal of the American Chemical Society, 2005, 127, 4785-4793.*

2. **Ildikó Kerezsi, Gábor Lente, István Fábián**
   
   **Kinetics of the Light-Driven Aqueous Autoxidation of Sulfur(IV) in the Absence and Presence of Iron(II)**
   

3. **Ildikó Kerezsi, Gábor Lente, István Fábián**
   
   **Kinetics and Mechanism of the Photoinitiated Autoxidation of Sulfur(IV) in the Presence of Iodide Ion**
   
   *Inorg. Chem., submitted*

Lectures and posters connected to this thesis:

1. **Kerezsi Ildikó, Lente Gábor, Fábián István (lecture)**

   **Szulfition fotoiniciált és cérium(III)-katalizált autooxidációja**
   
   (Photoinitiated and cerium(III)-catalyzed autoxidation of sulfite ion)


2. **Kerezsi Ildikó, Lente Gábor, Fábián István (lecture)**

   **Szulfition fotoiniciált és jodidion-katalizált autooxidációja**
   
   (Photoinitiated and iodide ion catalyzed autoxidation of sulfite ion)

3. Ildikó Kerezsi, Gábor Lente, István Fábián *(poster)*
   **Photoinitiated aqueous autoxidation of sulfur(IV): comparison of cerium(III) and iodide catalysis**
   *34th Inorganic Reaction Mechanisms Group Annual Meeting*, January 5-7, 2005, Liverpool, UK.

4. Gábor Lente, Ildikó Kerezsi, István Fábián *(poster)*
   **Photoinitiated aqueous autoxidation of sulfite ion: comparison of cerium(III) and iodide catalysis**

5. Kerezsi Ildikó, Lente Gábor, Fábián István *(lecture)*
   **Fotokémiai reakciók a vas(II)-sulfition oxigén rendszerben** (Photochemical reactions in the iron(II)-sulfite ion-oxygen system)

6. Kerezsi Ildikó, Lente Gábor, Fábián István *(lecture)*
   **A fény hatása a kén-dioxid katalitikus autooxidációjára** (Effect of light on the catalytic autooxidation of sulfur dioxide)
   *Annual Conference for Graduate Students*, May 5-8, 2005, Debrecen, Hungary.

7. Ildikó Kerezsi, Gábor Lente, István Fábián *(poster)*
   **Photoinitiated catalytical aqueous autoxidation of sulfur(IV)**

8. Ildikó Kerezsi, Gábor Lente, István Fábián *(lecture)*
   **Sulfur(IV) autoxidation enlightened**
   *35th Inorganic Reaction Mechanisms Group Annual Meeting*, January 4-7, 2006, Krakow, Poland.
Publication not connected to this thesis:

1. Ildikó Kerezsi, Gábor Lente, István Fábián
   Complex Formation Reaction of the Iron(III) Hydroxo Dimer with Periodate Ion

Lectures and posters not connected to this thesis:

1. Kerezsi Ildikó, Lente Gábor, Fábián István *(lecture)*
   A vas(III) hidroxodimer reakciója perjodátionnal (Reaction of the iron(III) hydroxo dimer with periodate ion)

2. Kerezsi Ildikó, Lente Gábor, Fábián István *(lecture)*
   A vas(III) hidroxodimer reakciója perjodátionnal (Reaction of the iron(III) hydroxo dimer with periodate ion)

3. Ildikó Kerezsi, Gábor Lente, István Fábián *(poster)*
   Reaction of the iron(III) hydroxo dimer with periodate ion