

# A kinetic study of the photooxidation of water by aqueous cerium(IV) in sulfuric acid using a diode array spectrophotometer

Judit Michnyóczy<sup>a</sup>, Virág Kiss<sup>a</sup>, Katalin Ósz<sup>b,\*</sup>

<sup>a</sup> University of Debrecen, Department of Physical Chemistry, Debrecen, Hungary

<sup>b</sup> University of Pécs, Department of General and Physical Chemistry, Pécs, Hungary

## ARTICLE INFO

### Keywords:

Water oxidation  
Oxygen formation  
Quantum yield determination  
Sulfate ion radical  
Photocatalysis

## ABSTRACT

The photooxidation of water by aqueous cerium(IV) has been investigated in dilute sulfuric acid quantitatively using a diode array spectrophotometer. An overview of experimental data on the speciation of cerium(IV) showed that several different absorbing species are present under almost all conditions, which makes straightforward interpretation of photochemical data very difficult. At submillimolar levels of cerium(IV) in 0.10 mol dm<sup>-3</sup> sulfuric acid, a consistent quantum yield of 0.12 for the loss of cerium(IV) could be determined, but even under these conditions, clear evidence of a parallel non-photochemical pathway was obtained. At higher concentrations of the metal ion, significant deviations from the expected direct proportionality between the illumination ratio and the initial rate were confirmed, which can only be interpreted by a complicated system of parallel, coupled photochemical and non-photochemical pathways. The inhibitory effect of aqueous cerium(III) in the process was also demonstrated. Based on indirect evidence, it seems likely that sulfate ion radicals play a significant role in the mechanism.

## 1. Introduction

The light sensitivity of various aqueous cerium(III) and cerium(IV) complexes has been known since the 1950s [1–13]. This property seems to be exceptional among lanthanide ions, where cerium also stands out because it has a characteristic oxidation state +4, which is reasonably stable in aqueous solution. The photooxidation of water by cerium(IV) [1–3,8], the photoreduction of water by cerium(III) [5,13], and the effects of a few additives such as thallium(I) ions [6] were characterized. Earlier, there was also interest in using cerium(IV) photochemistry in organic transformations of carboxylic acids [9–11], alcohols [10], and oxo compounds [12]. It must be noted that the photoactivities of the two oxidation states of cerium are often discussed together despite the fact that the origin of light absorption is certainly very different in the two systems, as cerium(III) show *f-f* transitions in contrast to cerium(IV), which does not have *f* electrons at all [14].

A very interesting work published in 1953 found that when an acidic aqueous cerium(III) solution is illuminated by UV light, water splitting occurs to form gaseous oxygen and hydrogen [4]. The essence of the interpretation was that excited cerium(III) ions are able to reduce water to liberate hydrogen, then cerium(IV) ions formed as a product oxidize

water to oxygen in a separate process. This sort of cerium-based photocatalytic cycle is still considered to be one of the possibilities in storing solar power in a chemical form [15].

In the 21 st century, there was a major surge of interest in cerium photocatalysis. This includes purely inorganic processes such as the autooxidation of sulfur(IV) [16], the reactions of peroxomonosulfate ion [17] and singlet oxygen [18] or the production of hydrogen [19]. The use of various cerium forms to enhance the degradation of organic pollutants has also been reported in several articles [20–24]. Most of these applications involves selective organic reactions such as aryl coupling reactions [25], functionalization of alkanes [26], dehydroxymethylation of alcohols [27], decarboxylative hydrazination [28], selective C—C bond scission of ketones [29], decarboxylative oxygenation and lactonization [30,31]. Very recently, these new trends have been termed a ‘renaissance of ligand-to-metal charge transfer by cerium photocatalysis’ [32], and a general strategy has also been proposed to improve the efficiency of cerium photocatalysis [33].

About 15 years ago, the use of diode array spectrophotometers was proposed as a photochemical device to yield highly quantitative information, which matches the standards of modern inorganic mechanism research [34]. The technique was later used successfully in a number of

\* Corresponding author.

E-mail address: [oszk@gamma.ttk.pte.hu](mailto:oszk@gamma.ttk.pte.hu) (K. Ósz).

<https://doi.org/10.1016/j.jphotochem.2020.113110>

Received 30 July 2020; Received in revised form 29 November 2020; Accepted 21 December 2020

Available online 26 December 2020

1010-6030/© 2020 The Author(s).

Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

particular systems [16,17,35–38]. The applicability of the method was extended by adding commercial LED light sources to the design [39], and ferrioxalate actinometry was developed and simplified in this setup for the reliable estimation of quantum yields [40]. As a side note, the development of this technique also highlighted the fact that the use of diode array spectrophotometers as a supposedly innocent detection method in kinetic studies can in fact be a major source of error: the risk is that a photochemical process is misidentified as a thermal reaction [35].

The objective of the present work was to investigate the photochemical reactions in the aqueous solutions of cerium(III) and cerium(IV) species with a new technique using diode array spectrophotometers in the hope that this will reveal some further, previously unexplored aspects of the reaction in a quantitative manner. A minor objective was also to study the long-time stability of cerium(IV) solutions and to characterize the possibility of photochemical contributions to reactions involving cerium(IV) ions.

## 2. Experimental section

Solutions of cerium(IV) were prepared by dissolving solid cerium(IV) sulfate tetrahydrate in sulfuric acid of known concentration (typically  $1.0 \text{ mol dm}^{-3}$ ). As cerium(IV) is a strong oxidant and may be reduced to cerium(III) during storage, the exact concentrations of cerium(IV) solutions were determined by iodometric titration. The stability of the stock solutions was monitored by the same method. Also, spectrophotometric detection of the concentration change was performed, showing a significant concentration decrease after 1 month. Cerium(III) solutions were prepared by dissolving a weighed amount of cerium(III) chloride hexahydrate in sulfuric acid. Here the purity of the solid was sufficient so that the concentration could be calculated from the mass measurements and final volumes. All solutions were prepared using highly purified water (Elix-3, Millipore, Darmstadt, Germany).

Mettler-Toledo T50 M titrator was applied for the potentiometric titrations and for pH measurements. One-point calibration was performed before each measurement with potassium hydrogen phthalate solution as reference ( $0.0500 \text{ mol dm}^{-3}$ ,  $\text{pH} = 4.005 \pm 0.003$  at  $25.0^\circ\text{C}$ ) [41]. After the one-point calibration, the Irving factor was determined before each measurement [42]. The exact concentrations of diluted acid solutions were determined by potentiometric titration (Mettler-Toledo T50 M titrator) and Gran functions (ABU9x\_v0.3 software).

Photochemical experiments were performed in a HP-8543 diode array spectrophotometer by a technique first published by Lente and Espenson [34]. For the quantitative experiments,  $1.000 \text{ cm}$  quartz cells were used with constant stirring at  $800 \text{ rpm}$ , which is understood to be essential in photochemical experiments and is a built-in option in this instrument. For some other measurements, cells with path lengths of  $1.000$  and  $0.100 \text{ mm}$  were also used. Stirring was not possible in these cases and these experiments served only qualitative purposes. A HP 89090A Peltier thermostat was used to keep constant temperature. The evaluation of raw data was performed by the control software of the instrument (HP 845x UV-vis system). Ferrioxalate actinometry was used to measure the intensity of the light source of the spectrophotometer as described in earlier publications [34,40]. As the photochemical use of the diode array spectrophotometer is central for the conclusions drawn in this study, more detailed explanations will be given in the Results and Discussion section. It should be noted that all photochemical experiments were carried out in the presence of a high excess of sulfuric acid so that any change in the pH within one kinetic curve was negligible. The measurements were initiated in solutions that were in equilibrium with air as an earlier work [16] showed that oxygen can only be a reactant in the cerium(III/IV)-sulfuric acid system if it also contains some sulfite ion. The only species that directly reacts with  $\text{O}_2$  in this case is the sulfite ion radical ( $\text{SO}_3^-$ ) [16], which cannot be formed under our conditions for thermodynamic reasons. The presence of oxygen is unavoidable in the present experiments anyway: even if the solutions are deoxygenated initially, the oxygen that is produced in the photoreaction cannot be

removed during the measurement.

Some UV-vis spectrophotometric measurements – for which excluding the possibility of photochemical reactions was important – were performed by a Shimadzu UV-1601 scanning instrument. Here the software UV Probe 2.21 was used for primary data treatment. The exact spectra of aqueous cerium(IV) and cerium(III) in sulfuric acid were of high importance for the evaluations carried out in these studies. Extreme care had to be taken in these measurements to avoid photochemical processes, this is why the scanning instrument was used. Also, possible contamination of cerium(IV) solutions with cerium(III) is a concern here, every precaution was taken to avoid this. Most fortunately, as Fig. 1 shows, molar absorptivity values of cerium(IV) are at least 4 times higher than those of cerium(III) at every wavelength, which reduces potential interference from cerium(III) contamination when pure cerium(IV) solutions are tested spectrophotometrically. The observations compared well with published data [43,44].

## 3. Results and discussion

### 3.1. Preliminary considerations

As a first test, a  $1.39 \text{ mmol dm}^{-3}$  solution of cerium(III) chloride was illuminated in a diode array spectrophotometer for one hour. No significant spectral changes were detected (Figure S1), from which it was safe to conclude that cerium(IV) is not formed in this experiment to any appreciable extent. This is in agreement with the observations of Lente et al. [17], who reported that detectable formation of cerium(IV) only occurs under illumination in this setup when a strong oxidant, such as peroxomonosulfate ion ( $\text{HSO}_5^-$ ) is added to the system. This reaction was photochemical (was not observed in the dark) and the fluorescence of cerium(III) was visible to the naked eye in a dark room [17]. These earlier reports were fully confirmed by our observations.

However, when the same experimental conditions were applied to a  $0.302 \text{ mmol dm}^{-3}$  cerium(IV) sulfate solution (in sulfuric acid), a significant decrease of absorbance was observed, which indicated that cerium(IV) was reduced to cerium(III) under illumination (Figure S2). This phenomenon was investigated in detail in a semi-quantitative way.

Before the detailed investigations, the long-term stability of cerium(IV) stock solutions was tested. Two solutions of cerium(IV), both containing  $0.30 \text{ mmol dm}^{-3}$   $\text{Ce(IV)}$ , the first in  $0.5 \text{ mol dm}^{-3}$  sulfuric acid, the second in  $0.05 \text{ mol dm}^{-3}$  sulfuric acid were monitored over a course of a month. The spectra were recorded each day. A selection of spectral data is shown in Figure S2, whereas the time course of absorbance change are depicted at  $320 \text{ nm}$  in Fig. 2. It should be noted that no special storing conditions were applied. Fig. 2 confirms the fact that at this small initial concentration of cerium(IV), there is an appreciable loss of cerium(IV), which amounts to an about 30 % decrease in its concentration. It is also very remarkable in Fig. 2 that the initial absorbances depend on the acidity despite the fact that the same concentration of cerium(IV) was used. However, concentration-absorbance calibration was carried out at both acidities, therefore the cerium(IV) concentration could be calculated as a function of time, which is shown in Fig. 2B. The data imply that the conversion of cerium(IV) into cerium(III) is not influenced very significantly by the acidity under these conditions. In the full data set (Figure S2), there is a minor maximum in the spectrum recorded after 29 days at  $241 \text{ nm}$ . This is in agreement with the molar absorptivity values of cerium(III) shown in Fig. 1. Fig. 2 implies that after this time, the decrease in cerium(IV) concentration is between 25 and 30 %, which gives about  $0.08 \text{ mmol dm}^{-3}$  as the expected concentration for the product cerium(III). Fig. 1 shows that the molar absorptivity of cerium(III) at the  $241 \text{ nm}$  peak is  $630 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ , so its expected absorbance contribution is 0.05, which does not contradict the minor feature seen in Figure S2.

These experiments indicate that the accumulation of cerium(III) and the loss of cerium(IV) may indeed be a source of problems in stock solutions. In addition, it is also revealed that the actual form of cerium(IV)

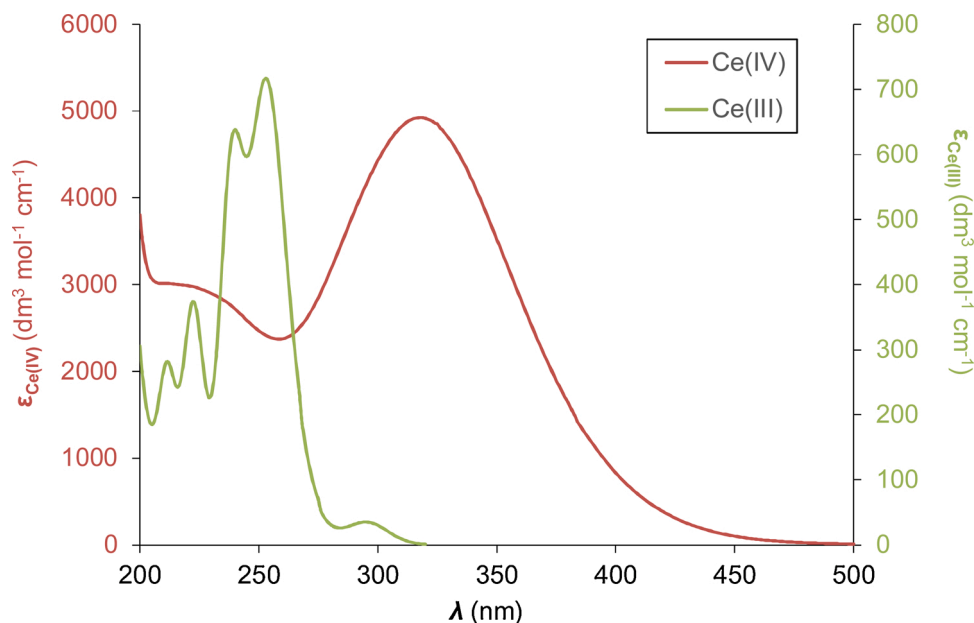


Fig. 1. UV-vis molar absorptivity values of aqueous Ce(III) and Ce(IV) solutions in  $c(\text{H}_2\text{SO}_4) = 0.5 \text{ mol dm}^{-3}$ .

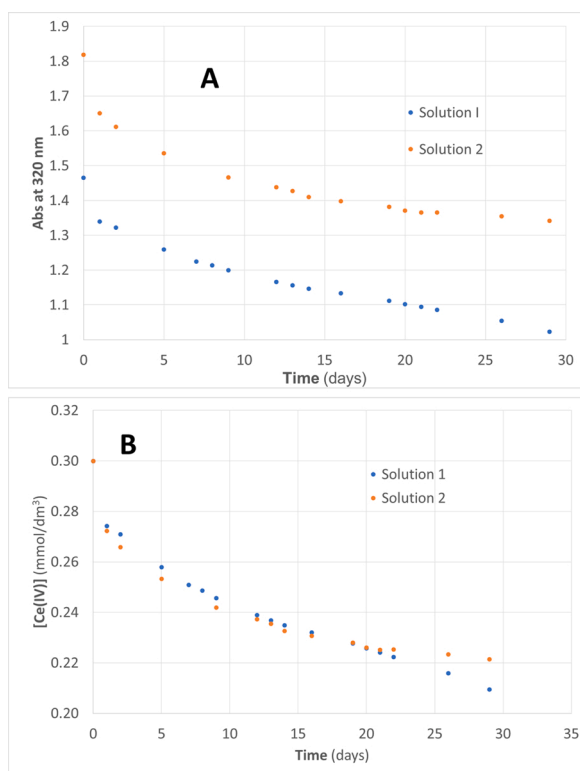


Fig. 2. Change of absorbance and concentration as a function of time in cerium(IV) sulfate solutions in the course of month. Solution 1:  $c(\text{Ce(IV)}) = 0.30 \text{ mmol dm}^{-3}$ ,  $c(\text{H}_2\text{SO}_4) = 0.5 \text{ mol dm}^{-3}$ ; Solution 2:  $c(\text{Ce(IV)}) = 0.30 \text{ mmol dm}^{-3}$ ,  $c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol dm}^{-3}$ ,  $c(\text{Na}_2\text{SO}_4) = 0.45 \text{ mol dm}^{-3}$ .

influences the absorbance values and, as a consequence, it must influence the photoactivity as well.

### 3.2. Speciation and redox stability in cerium(IV) solutions

Cerium(IV) is known to form stable complexes with sulfate ion [45–49]. Indeed, the most important specific stabilizing role of sulfuric

acid (as opposed to perchloric or nitric acids) is this complex formation. Two graphs showing species distribution diagrams for different total cerium(IV) concentrations are shown in Fig. 3; these were calculated based on the following published equilibrium constant data [45–49]:

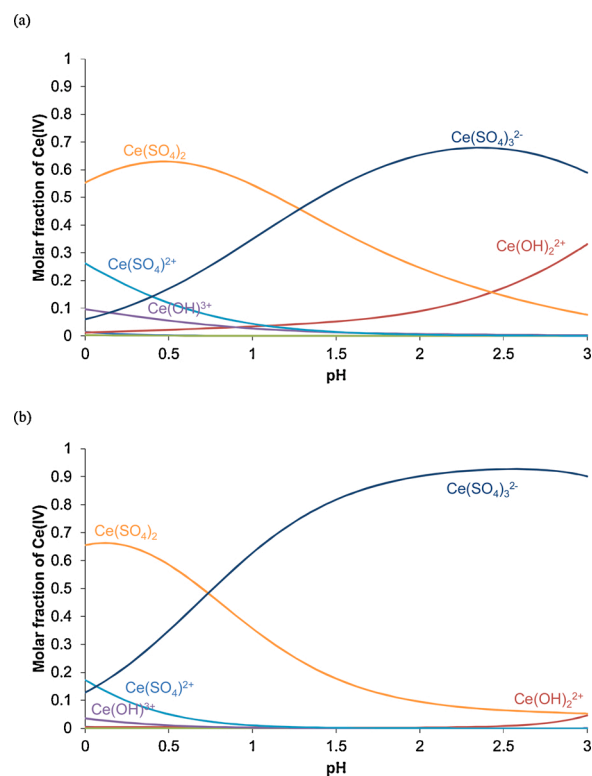
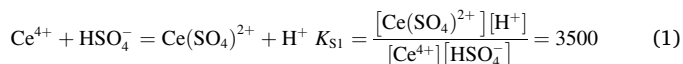
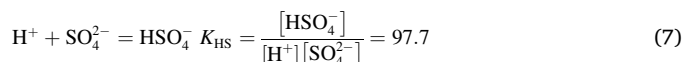
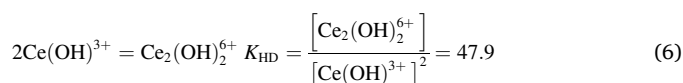
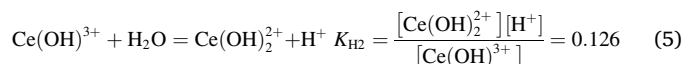
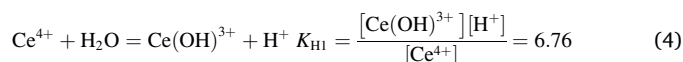
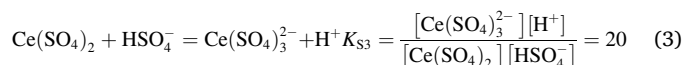
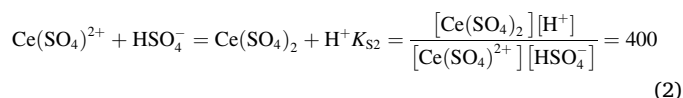


Fig. 3. Species distribution as a function of pH for the complexes formed in the Ce(IV) –  $\text{SO}_4^{2-}$  –  $\text{H}^+$  system at (a)  $c(\text{Ce(IV)}) = 3 \text{ mmol dm}^{-3}$ ,  $c(\text{SO}_4^{2-}) = 0.01 \text{ mol dm}^{-3}$  and (b)  $c(\text{Ce(IV)}) = 0.2 \text{ mmol dm}^{-3}$ ,  $c(\text{SO}_4^{2-}) = 0.01 \text{ mol dm}^{-3}$ .



Coordinated water molecules are excluded from the above formulas partly for clarity, partly because their exact numbers have never been confirmed beyond any doubt in experimental studies. Of course, it is very common and probably not misleading to assume that all such complexes are octahedral [49].

It can be seen in Fig. 3 that at least five different cerium(IV)-containing species appear in significant concentrations. Further calculations showed that the system of solution equilibria in cerium(IV) sulfate solutions excludes the possibility of studying the photoactivity of a single species. Even if one form dominates under a particular set of conditions, a thorough kinetic study should involve changing the concentration of the active species, which is impossible without changing the qualitative properties of the solution speciation. It is also notable that the different cerium(IV) species may show very different photoreactivity, so the contribution of minor components to an overall reaction rate may be quite substantial. Because of these fundamental problems, here it is not even attempted to attribute the photochemical process to a particular cerium species. Instead, the photoreactivity is described as an average property, which depends on the conditions such as cerium(IV) concentrations, sulfate ion concentration and pH.

The relevant literature data on the standard one-electron reduction potential of the Ce(IV)/Ce(III) couple have also been analyzed [49–51]. It was confirmed that this potential shows considerable variation between 1.42 V and 1.87 V depending on the medium (perchloric, nitric, sulfuric or hydrochloric acids), the cerium concentration and the pH. The smallest standard potentials are typically reported for sulfuric acid, but they are still in excess of 1.4 V. On one hand, this highlights the fact that the sulfato complexes of cerium(IV) are less reactive in redox processes than the other solution forms. On the other hand, these values still imply that the oxidation of water to gaseous oxygen by cerium(IV) is a thermodynamically favored, spontaneous reaction even in sulfuric acid. Apart from the issues with long-time storing of cerium(IV) solutions, this fact also confirms the need to address the question whether the light-dependent cerium(IV) reactions studied here are truly photochemical processes in a sense that the energy of light is necessary to drive the reaction, or photocatalyzed ones where light increases the rate which is not zero even in the dark.

Given the fact that cerium(IV) is involved in somewhat complicated solution equilibria and the primary method of monitoring in this work is spectrophotometry, we felt it necessary to confirm the linear relationship between measured absorbance and the concentration of cerium(IV) experimentally. A linear dependence was observed at 429 nm (Figure S3) under all conditions. Note that this is not a direct Beer's law, as there are multiple absorbing species present simultaneously and the apparent molar absorptivities determined in such an experiment depend

on the pH and overall sulfate ion concentration. Simply observing the shapes of the UV–vis spectra (Figures S4 and S5) proved that the number of significant absorbing species exceeded 1.

### 3.3. Detailed kinetic observations

As the observations showed that the concentration of cerium(IV) decreases substantially under illumination in ceric sulfate solution, the kinetics of this process was investigated in detail. The reaction was typically monitored for 60 min (sample curves are shown in Figure S6), and quantitative information was obtained as initial reaction rates. This technique is useful for exploring the kinetics of processes that do not adhere to simple kinetic equations [52], which is a very typical case for photoreactions [34,37,40]. The initial rates were directly determined as initial rates of absorbance change and then were converted into initial rates of concentration change using the separately measured value of the apparent molar absorptivity [53].

There are two series of possible experiments in photochemical studies that can be done without changing the composition of the sample to study the effect of light intensity without changing or modifying the light source [16]. The first is when the volume of the irradiated solution sample is changed. In this way, the number of absorbed photons per unit volume is changed without any other changes [16,34]. It is most common that the initial rate of a photoreaction is inversely proportional to the volume, which indicates a direct proportionality between reaction rate and light intensity [34]. It is rarer that the rate of the photoreaction is inversely proportional to the square root of the volume, which may be interpreted by a photoinitiated chain reaction [16]. In the present case, only two experiments were done: when the volume of the irradiated solution ( $c(\text{Ce(IV)}) = 1.43 \text{ mmol dm}^{-3}$ ,  $c(\text{H}_2\text{SO}_4) = 0.103 \text{ mol dm}^{-3}$ ) was  $3.40 \text{ cm}^3$ , the measured initial rate of cerium(IV) loss was  $(2.5 \pm 0.1) \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$ , whereas the initial rate was  $(4.3 \pm 0.2) \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$  for  $2.00 \text{ cm}^3$  of the same solution under the same geometry. This change is in full agreement with the expected inverse proportionality, which is characteristic of most photochemical reactions.

The other series of experiments is carried out by interrupting the illumination in a regular pattern. In a diode array spectrophotometer, it is easy to control the shutter of the instrument so that dark periods are introduced into the experiment between illuminated intervals [16]. In this case, it is natural to expect that the average rate of the reaction detected is directly proportional to the illumination ratio, which is the percentage of the time that the sample spends exposed to light. A deviation from this expectation indicates a more complicated reaction scheme and can be used for falsifying tests of the assumed mechanism [15]. In the present work, several such series of experiments were carried out. As shown in Fig. 4, at a low concentration of cerium(IV) ( $0.22 \text{ mmol dm}^{-3}$ ), a linear dependence between the reaction rate and the illumination ratio is observed. However, this is not the expected

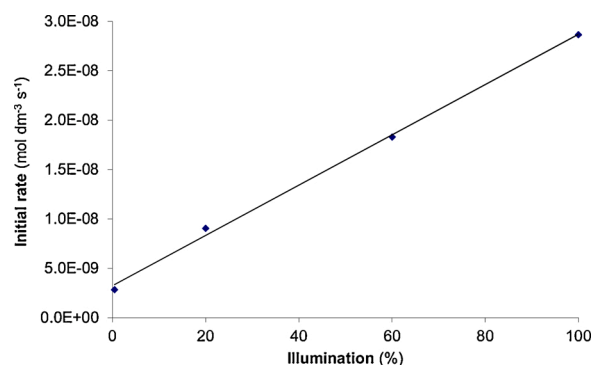


Fig. 4. Initial rate of the photoreaction as a function of the illumination ratio (%). Conditions:  $T = 25.0^\circ \text{C}$ ,  $V(\text{sample}) = 2.00 \text{ cm}^3$ ,  $c(\text{Ce(IV)}) = 0.22 \text{ mmol dm}^{-3}$ ,  $c(\text{H}_2\text{SO}_4) = 0.10 \text{ mol dm}^{-3}$ .



direct proportionality as the straight line has a very significant intercept. This is easily rationalized if one recalls the fact that the oxidation of water by cerium(IV) is thermodynamically favorable even without any extra energy from light. Therefore, the intercept here corresponds to the dark reaction, the rate at which the loss of cerium(IV) would occur without any illumination. In fact, this was experimentally confirmed at very low illumination ratios ( $< 1\%$ ). As a linear dependence was observed in Fig. 4, a quantum yield could be estimated based on these data. The difference between the rates at 0% and 100 % illumination under these conditions is  $2.6 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$  and the reactor volume is  $2.00 \text{ cm}^3 = 0.00200 \text{ dm}^3$ , which means that the amount of cerium(IV) decreases in the photochemical process at a rate of  $5.2 \times 10^{-11} \text{ mol s}^{-1}$ . Actinometric calibration (see Figure S7) [34,40] and the measured spectra were used to calculate that photons are absorbed in this solution at a rate of  $4.4 \times 10^{-10} \text{ mol s}^{-1}$ . Therefore, the value for the quantum yield is  $\Phi = 0.12 \pm 0.01$ .

Several analogous series of experiments were carried out in the presence of higher cerium(IV) concentrations. The graph obtained for  $c(\text{Ce(IV)}) = 1.4 \text{ mmol dm}^{-3}$  is shown in Fig. 5, whereas data measured at  $c(\text{Ce(IV)}) = 6.4 \text{ mmol dm}^{-3}$  are displayed in Fig. 6. Both graphs show obviously non-linear changes, and similarly to Fig. 4, the presence of a significant intercept is also detected. It is notable that the intercept only changes marginally between Fig. 4 and 5 in response to a more than 6-fold increase in the concentration of cerium(IV), which might indicate that the dark process is close to zeroth order with respect to it. However, a further concentration increase by about a factor of 5 causes a fivefold increase in the intercept. Observing the final values in the curves shown in Figs. 4, 5 and 6 is also instructive. At the lowest cerium(IV) concentration, the reaction rate measured under full illumination is slightly lower than at in the other graphs, where this final data point is practically the same. As the dependences shown in Figs. 5 and 6 are clearly non-linear, no meaningful quantum yield can be given under these conditions.

Two more semi-quantitative comparison experiments were also carried out. In the first, two experiments under the same conditions were started, the only difference was the temperature. As shown in Fig. 7, there were notable differences between the curves detected at  $25.0^\circ\text{C}$  and  $50.0^\circ\text{C}$ . The slight difference in the initial absorbances is caused by the fact that the equilibria (Eqs. (1)–(7)) are somewhat shifted by changing temperatures. There was slightly less than a factor of two difference in the initial rates and it is obviously visible that the absorbance change is faster at  $50.0^\circ\text{C}$  (323 K) than at  $25.0^\circ\text{C}$  (298 K). The minor change in the equilibrium distributions cannot be responsible for this relatively large increase in rate. For a purely photochemical process, no temperature dependence is expected [34]. For purely thermal reactions, a factor of 5–20 would be expected as a result of 25 K temperature difference. So, the observations seem to indicate a photochemical

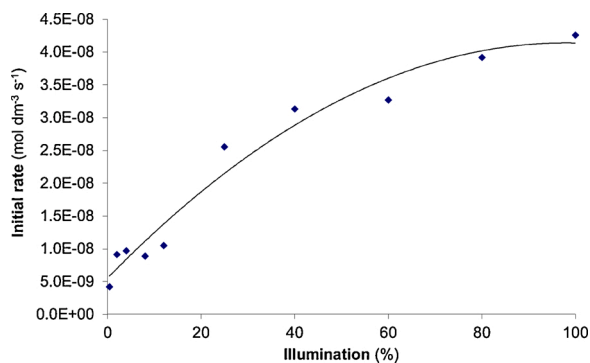


Fig. 5. Initial rate of the photoreaction as a function of the illumination ratio (%). Conditions:  $T = 25.0^\circ\text{C}$ ,  $V(\text{sample}) = 2.00 \text{ cm}^3$ ,  $c(\text{Ce(IV)}) = 1.4 \text{ mmol dm}^{-3}$ ,  $c(\text{H}_2\text{SO}_4) = 0.10 \text{ mol dm}^{-3}$ . The line shown in the graph is a spline that follows the trends of the experimental points.

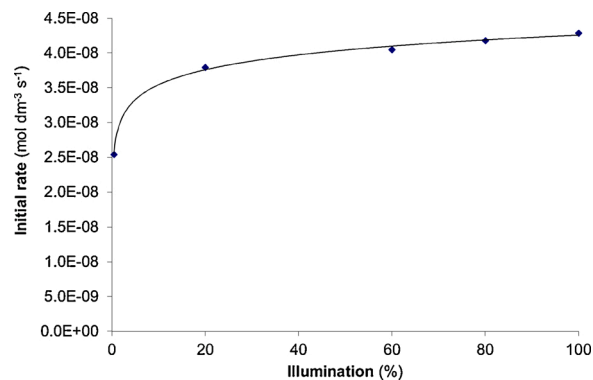


Fig. 6. Initial rate of the photoreaction as a function of the illumination ratio (%). Conditions:  $T = 25.0^\circ\text{C}$ ,  $V(\text{sample}) = 2.00 \text{ cm}^3$ ,  $c(\text{Ce(IV)}) = 6.4 \text{ mmol dm}^{-3}$ ,  $c(\text{H}_2\text{SO}_4) = 0.10 \text{ mol dm}^{-3}$ . The line shown in the graph is a spline that follows the trends of the experimental points.

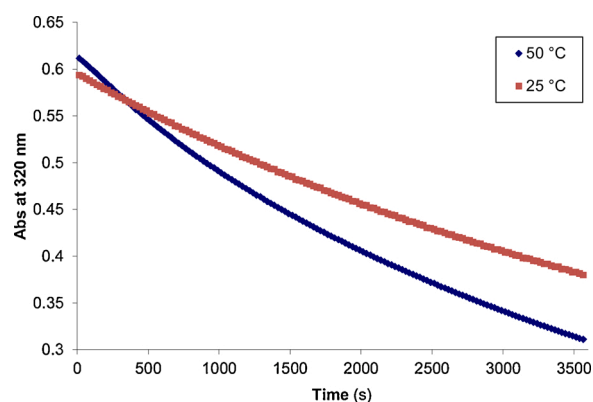


Fig. 7. Temperature dependence of the photoreaction. Conditions:  $V(\text{sample}) = 2.00 \text{ cm}^3$ ,  $c(\text{Ce(IV)}) = 0.22 \text{ mmol dm}^{-3}$ ,  $c(\text{H}_2\text{SO}_4) = 0.10 \text{ mol dm}^{-3}$ .

process with significant contributions from dark reactions. Taken all observations together, it is clear that the disappearance of cerium(IV) is not a clean photochemical process, but it is a photocatalyzed one. As pointed out earlier, the thermodynamic requirements are fulfilled (*i.e.* the process itself is downhill even without the energy from light).

A further semiquantitative test was carried out in which cerium(III) was added to the reaction solution before initiating the reaction (Figure S8). This was done at the initial cerium(IV) concentration of  $0.22 \text{ mmol dm}^{-3}$  and the concentration of added cerium(III) was  $0.24 \text{ mmol dm}^{-3}$ , close to equimolar. The complicated band structure of cerium(III), which is the consequence of the presence of *f* electrons, was clearly detectable in the far UV part of the spectrum in this experiment. The initial rate dropped from  $(2.9 \pm 0.2) \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$  to  $(1.1 \pm 0.1) \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$  in response to the addition of cerium(III). As Fig. 1 shows, the molar absorptivities of cerium(III) are significantly lower in aqueous solution than those of cerium(IV) at all wavelengths, which means that most of the light must be absorbed by cerium(IV) even in the presence of cerium(III). Therefore, the substantial (about 60 %) decrease in the initial rate cannot be caused exclusively by the inner filter effect of the added absorbing Ce(III) species [34]. It follows that the presence of cerium(III) must exert some sort of chemical inhibition effect. This is also in qualitative agreement with shapes of the kinetic traces shown in Figs. 7 and S6: these curves resemble pseudo-first order changes in a sense that the rate (*i.e.* the slope) changes significantly as the concentration drops. In fact, the theoretical expectation for a purely photochemical kinetic curve (the solution of the simplest photochemical rate equation) resembles a zeroth order kinetic curve much closer than a first-order one [52]. The somewhat unexpected deceleration in these

curves could also be the consequence of the appearance of cerium(III).

It is noted that the results thus far were based on monitoring the disappearance of cerium(IV), and some UV-vis spectral evidence confirmed cerium(III) to be the product. As there is no other reaction partner present, it must be assumed that water is oxidized in the process. As a qualitative confirmation of this fact, the photoreaction was also carried out at a high concentration of cerium(IV) in a cuvette of path length 0.100 mm in a very small volume. Clear evidence of the formation of gas bubbles, most probably containing oxygen, was observed (see the photograph in Figure S9).

### 3.4. Mechanistic implications

Although the reaction studied here is a seemingly simple one, the kinetic patterns revealed by the detailed experiments seem to be so complex that postulating a detailed mechanism is not possible. However, some qualitative points can still be made.

The simple linear dependence of the initial rate on the illumination ratio at low cerium(IV) concentrations (Fig. 4) might indicate that the tris-sulfato complex  $\text{Ce}(\text{SO}_4)_3^{2-}$  is a photoactive species, as this is the dominating form of aqueous cerium(IV) under these conditions. As cerium(IV) is a noble gas configuration ion, its strong absorption can only arise from ligand to metal charge transfer (LMCT). The core of the photoreaction could be an irreversible version of this process, which results in the formation of cerium(III) and sulfate ion radical ( $\text{SO}_4^{\cdot-}$ ).

Unfortunately, the formation of sulfate ion radicals cannot be detected directly because it is highly reactive, and its concentration remains very low during the entire process. There seems to be general agreement in the literature [8,13,16,54–57] that  $\text{SO}_4^{\cdot-}$  has a characteristic absorption band centered at about 450 nm, but published molar absorptivity values span almost an order of magnitude. Even if one uses the highest estimate of  $1600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  published by McElroy [55,56] and compares it to the known self-recombination rate constant of  $4.4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at room temperature [16], it is clear that sulfate ion radical must be produced at a very high rate to show any meaningful absorbance contribution. This high rate is impossible in a conventional chemical reaction, it is only plausible in a laser flash photolysis experiment by the direct homolysis of peroxodisulfate ion ( $\text{S}_2\text{O}_8^{2-}$ ) [54]. So, in a chemical system, the potential option of using a radical scavenger remains. However, the use of radical scavengers often leads to unreliable conclusions [52] because these chemicals are typically organic compounds that may be involved in a number of reactions independently of the one with the radical to be detected. In our special system, the presence of cerium(IV) would probably mean a major obstacle to such scavenging attempts as it is a strong and labile oxidant that is present in much larger concentrations than sulfate ion radical could ever achieve.

Nevertheless, chemical thinking seems to make it very likely that  $\text{SO}_4^{\cdot-}$  is involved in the photoreaction here. It is obvious that cerium(IV) is consumed in the reaction and cerium(III) is produced; therefore, one-electron oxidation of a suitable major species must happen simultaneously. There are only two logical choices: the first is sulfate ion, the second is the water molecule. From water, the oxidation product would be hydroxyl radical ( $\text{OH}^{\cdot}$ ), whereas from sulfate ion, it is sulfate ion radical ( $\text{SO}_4^{\cdot-}$ ). The known  $\text{OH}^{\cdot}/\text{H}^+/\text{H}_2\text{O}$  one-electron potential is +2.73 V [57], whereas the known one-electron potential  $\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}$  is +2.47 V [57]. So even on thermodynamic grounds only, it is more likely that sulfate ion radical rather than hydroxyl radical will be formed in the process as an intermediate. Also, these data show that the reaction of hydroxyl radical with sulfate ion is a spontaneous one and gives sulfate ion radical. In addition, it must also be considered that the primary photoreaction is caused by the tris-sulfato  $\text{Ce}(\text{SO}_4)_3^{2-}$  complex. This contains an  $f^0$  metal center, so its relatively strong absorption centered at 320 nm (see Fig. 1) can only be caused by ligand-to-metal-charge transfer (LMCT). As there is no water molecule in this complex, the charge transfer can only occur between sulfate ion and the metal center.

So as the result of the absorption, one of the sulfate ions in the coordination sphere is certainly left in an electron-deficient form. From this state, sulfate ion radical can be produced very easily by the dissociation of this electron deficient ligand. This is also in agreement with the fact that cerium(IV) complexes are known to be highly labile for ligand substitution or exchange [49].

Sulfate ion radical is known to be a chain carrier in a photoinitiated chain reaction involving the two oxidation states of cerium [16], and is also involved in the photooxidation of cerium(III) in the presence of peroxomonosulfate ion [17]. The appearance of sulfate ion radical may open several reaction paths simultaneously, which is responsible for the complicated kinetics observed. Sulfate ion radical is also known to react with aqueous cerium(III) rapidly [8,13,16,54]; this reaction could be the reason for the inhibition observed in the presence of cerium(III).

The non-linear initial rate-illumination ratio dependences in Figs. 5 and 6 may be explained by the fact that other solution forms of cerium (IV) are also photoactive, and are probably more reactive than the tris-sulfato complex. In this way, a complicated chain-like mechanism may be formed with several simultaneous sources of initiation and termination. Such a scenario would be in agreement with both the non-linear dependence of the rate on the illumination ratio and the observed temperature effect. Furthermore, the noted, unusual concentration dependence of the intercepts of Figs. 4–6 may be explained by assuming that the dimer  $\text{Ce}_2(\text{OH})_2^{6+}$  plays a very significant role in the non-photochemical oxidation of water by cerium(IV). Similar assumptions have been made earlier [3].

## 4. Conclusion

This work has established that the known photooxidation of water by cerium(IV) can be detected in a conventional diode array spectrophotometer and this technique is also suitable for studying the process in a quantitative way. Detailed studies have shown that kinetics of the photooxidation is much more complex than would be expected for a direct photoreaction, several simultaneous pathways must be operative, some of which are photochemical, whereas the others are thermally activated. A substantial chemical inhibitory effect of the product cerium (III) was described. The experimental method used in this study makes it very clear that the effect of light should always be considered as a contributing factor whenever the redox reactions of aqueous cerium(IV) with any reducing agents are studied, and may be of particular concern if the process is monitored by spectrophotometric methods.

### CRedit authorship contribution statement

**Judit Michnyóczy:** Investigation, Methodology, Formal analysis. **Virág Kiss:** Formal analysis, Methodology, Visualization. **Katalin Ósz:** Conceptualization, Methodology, Formal analysis, Resources, Supervision.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgements

This work was supported by the Higher Education Institutional Excellence Programme of the Ministry of Human Capacities in Hungary, within the framework of the 1<sup>st</sup> thematic programme of the University of Pécs. The work of Virág Kiss was supported by the EU and co-financed by the European Regional Development Fund under the project GINOP-2.3.2-15-2016-00008 and GINOP-2.3.3-15-2016-00004.

The authors wish to thank Gábor Lente and József Kalmár for helpful discussions.

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jphotochem.2020.113110>.

## References

- [1] J. Weiss, D. Porret, Photochemical reduction of ceric ions by water, *Nature* 139 (1937) 1019–1020, <https://www.nature.com/articles/1391019a0>.
- [2] M.G. Evans, N. Uri, Photo-oxidation of water by ceric ions, *Nature* 166 (1950) 602–603, <https://www.nature.com/articles/166602b0>.
- [3] L.J. Heidt, M.E. Smith, Quantum yields of the photochemical reduction of ceric ions by water and evidence for the dimerization of ceric ions, *J. Am. Chem. Soc.* 70 (1948) 2476–2481, <https://doi.org/10.1021/ja01187a050>.
- [4] L.J. Heidt, A.F. McMillan, Conversion of sunlight into chemical energy available in storage for man's use, *Science* 117 (1953) 75–76, <https://science.sciencemag.org/content/117/3030/75>.
- [5] L.J. Heidt, A.F. McMillan, Influence of perchloric acid and cerous perchlorate upon the photochemical oxidation of cerous to ceric perchlorate in dilute aqueous perchloric acid, *J. Am. Chem. Soc.* 76 (1954) 2135–2139, <https://doi.org/10.1021/ja01637a028>.
- [6] T.J. Sworski, Photoreduction of Ceric Ion in sulfuric acid solutions. Effect of thallous ion, *J. Am. Chem. Soc.* 79 (1957) 3655–3657, <https://doi.org/10.1021/ja01571a011>.
- [7] T.W. Martin, J.M. Burk, A. Henshall, Ligand sensitization. I. The photo- and oxidation-reduction activated decomposition of glacial acetic acid with ceric ammonium nitrate, *J. Am. Chem. Soc.* 88 (1966) 1097–1104, <https://doi.org/10.1021/ja00958a002>.
- [8] L. Dogliotti, E. Hayon, Transient species produced in the photochemical decomposition of ceric salts in aqueous solution. Reactivity of nitrogen oxide and hydrogen compd. with oxygen and sulfur (HSO<sub>4</sub>) free radicals, *J. Phys. Chem.* 71 (1967) 3802–3808, <https://doi.org/10.1021/j100871a014>.
- [9] R.A. Sheldon, J.K. Kochi, Photochemical and thermal reduction of cerium(IV) carboxylates. Formation and oxidation of alkyl radicals, *J. Am. Chem. Soc.* 90 (1968) 6688–6698, <https://doi.org/10.1021/ja01026a022>.
- [10] D. Greatorex, T.J. Kemp, Electron spin resonance studies of photo-oxidation by metal ions in rigid media at low temperatures. Part 1.—Ce(IV) photo-oxidation of alcohols, *Transact. Faraday Soc.* 67 (1971) 56–66, <https://doi.org/10.1039/TF9716700056>.
- [11] D. Greatorex, T.J. Kemp, Electron spin resonance studies of photo-oxidation by metal ions in rigid media at low temperatures. Part 2.—Ce(IV) photo-oxidation of carboxylic acids, *Transact. Faraday Soc.* 67 (1971) 1576–1586, <https://doi.org/10.1039/TF9716701576>.
- [12] D. Greatorex, T.J. Kemp, Electron spin resonance studies of photo-oxidation by metal ions in rigid media at low temperatures. Part 3.—Ce(IV) photo-oxidations of aldehydes, ketones, esters and amides, *J. Chem. Soc. Faraday Trans.* 68 (1972) 121–129, <https://doi.org/10.1039/F19726800121>.
- [13] R.W. Matthews, J. Sworski, Photooxidation and fluorescence of cerium(III) in aqueous sulfuric acid solutions, *J. Phys. Chem.* 79 (1975) 681–686, <https://doi.org/10.1021/j100574a003>.
- [14] T. Donohue, Lanthanide photochemistry initiated in f-f transitions, *J. Am. Chem. Soc.* 100 (1978) 7411–7413, <https://doi.org/10.1021/ja00491a048>.
- [15] H.B. Gray, Solar Fuel, *Eng. Sci.* 60 (1997) 28–33, <http://calteches.library.caltech.edu/3924/1/Fuel.pdf>.
- [16] I. Kerezi, G. Lente, I. Fábán, Highly Efficient Photoinitiation in the Cerium(III)-Catalyzed Aqueous Autoxidation of Sulfur(IV). An Example of Comprehensive Evaluation of Photoinduced Chain Reactions, *J. Am. Chem. Soc.* 127 (2005) 4785–4793, <https://doi.org/10.1021/ja0439120>.
- [17] G. Lente, J. Kalmár, Z. Baranyai, A. Kun, I. Kék, D. Bajusz, M. Takács, L. Veres, I. Fábán, One vs. Two Electron Oxidation with Peroxomonosulfate Ion: Reactions with Iron(II), Vanadium(IV), Halide ions, and Photoreaction with Cerium(III), *Inorg. Chem.* 48 (2009) 1763–1773, <https://doi.org/10.1021/ic801569k>.
- [18] T.O. Shekunova, L.A. Lapkina, A.B. Shcherbakov, I.N. Meshkov, V.K. Ivanov, A. Y. Tsivadze, Y.G. Gorbunova, Deactivation of singlet oxygen by cerium oxide nanoparticles, *J. Photochem. Photobiol. A: Chem.* 382 (2019) 111925, <https://doi.org/10.1016/j.jphotochem.2019.111925>.
- [19] M. Waqas, B. Yang, L. Cao, X. Zhao, W. Iqbal, K. Xiao, C. Zhu, J. Zhang, Tuning the N-bonded cerium(III) fraction/g-C<sub>3</sub>N<sub>4</sub> interface in hollow structures using an in situ reduction treatment for superior photochemical hydrogen evolution, *Catal. Sci. Technol.* 9 (2019) 5322–5332, <https://doi.org/10.1039/C9CY01305A>.
- [20] V.K. Klovchov, Yu.V. Malyukin, G.V. Grygorova, O.O. Sedyh, N.S. Kavok, V. V. Seminko, V.P. Semynozhenko, Oxidation-reduction processes in CeO<sub>2</sub>-x nanocrystals under UV irradiation, *J. Photochem. Photobiol. A: Chem.* 364 (2018) 282–287, <https://doi.org/10.1016/j.jphotochem.2018.06.025>.
- [21] R. Fiorenza, M. Bellardita, T. Barakat, S. Scirè, L. Palmisano, Visible light photocatalytic activity of macro-mesoporous TiO<sub>2</sub>-CeO<sub>2</sub> inverse opals, *J. Photochem. Photobiol. A: Chem.* 352 (2018) 25–34, <https://doi.org/10.1016/j.jphotochem.2017.10.052>.
- [22] A.R. Soleymani, M. Moradi, Performance and modeling of UV/persulfate/Ce(IV) process as a dual oxidant photochemical treatment system: kinetic study and operating cost estimation, *Chem. Eng. J.* 347 (2018) 243–251, <https://doi.org/10.1016/j.cej.2018.04.093>.
- [23] G.B. Vieira, H.J. José, M. Peterson, V.Z. Baldissarelli, P. Alvarez, R.F.P.M. Moreira, CeO<sub>2</sub>/TiO<sub>2</sub> nanostructures enhance adsorption and photocatalytic degradation of organic compounds in aqueous suspension, *J. Photochem. Photobiol. A: Chem.* 353 (2018) 325–336, <https://doi.org/10.1016/j.jphotochem.2017.11.045>.
- [24] M. Padervand, H. Heidarpour, A. Bargahi, A mechanistic study and in-vivo toxicity bioassay on acetamiprid photodegradation over the zeolite supported cerium-based photocatalyst, *J. Photochem. Photobiol. A: Chem.* 395 (2020) 112526, <https://doi.org/10.1016/j.jphotochem.2020.112526>.
- [25] H. Yin, P.J. Carroll, B.C. Manor, J.M. Anna, E.J. Schelter, Cerium Photosensitizers: Structure-Function relationships and applications in photocatalytic aryl coupling reactions, *J. Am. Chem. Soc.* 138 (2016) 5984–5993, <https://doi.org/10.1021/jacs.6b02248>.
- [26] A. Hu, J.J. Guo, H. Pan, Z. Zuo, Selective functionalization of methane, ethane, and higher alkanes by cerium photocatalysis, *Science* 361 (2018) 668–672, <https://science.sciencemag.org/content/361/6403/668/tab-article-info>.
- [27] K. Zhang, L. Chang, Q. An, X. Wang, Z. Zuo, Dehydroxymethylation of alcohols enabled by cerium photocatalysis, *J. Am. Chem. Soc.* 141 (2019) 10556–10564, <https://doi.org/10.1021/jacs.9b05932>.
- [28] V.R. Yatham, P. Bellotti, B. König, Decarboxylative hydrazination of unactivated carboxylic acids by cerium photocatalysis, *Chem. Commun.* 55 (2019) 3489–3492, <https://doi.org/10.1039/C9CC00492K>.
- [29] Y. Chen, J. Du, Z. Zuo, Selective C-C bond scission of ketones via visible-light-Mediated cerium catalysis, *Chem* 6 (2020) 266–279, <https://doi.org/10.1016/j.chempr.2019.11.009>.
- [30] S. Shirase, S. Tamaki, K. Shinohara, K. Hirohara, H. Tsurugi, T. Satoh, K. Mashima, Cerium(IV) carboxylate photocatalyst for catalytic radical formation from carboxylic acids: decarboxylative oxygenation of aliphatic carboxylic acids and lactonization of aromatic carboxylic acids, *J. Am. Chem. Soc.* 142 (2020) 5668–5675, <https://doi.org/10.1021/jacs.9b12918>.
- [31] K. Wadekar, S. Aswaleb, V.R. Yatham, Cerium photocatalyzed dehydrogenative lactonization of 2-arylbenzoic acids, *Org. Biomol. Chem.* 18 (2020) 983–987, <https://doi.org/10.1039/C9OB02676B>.
- [32] R. Zhao, L. Shi, A renaissance of ligand-to-metal charge transfer by cerium photocatalysis, *Org. Chem. Front.* 5 (2018) 3018–3021, <https://doi.org/10.1039/C8QO00893K>.
- [33] Y. Qiao, T. Cheisson, B.C. Manor, P.J. Carrola, E.J. Schelter, A strategy to improve the performance of cerium(III) photocatalysts, *Chem. Commun.* 55 (2019) 4067–4070, <https://doi.org/10.1039/C9CC00282K>.
- [34] G. Lente, J.H. Espenson, Photoreduction of 2,6-Dichloroquinone in aqueous solution. Use of a diode array spectrophotometer concurrently to drive and detect a photochemical reaction, *J. Photochem. Photobiol. A: Chem.* 163 (2004) 249–258, <https://doi.org/10.1016/j.jphotochem.2003.12.005>.
- [35] M. Galajda, G. Lente, I. Fábán, Photochemically induced autocatalysis in the chlorate ion-iodine system, *J. Am. Chem. Soc.* 129 (2007) 7738–7739, <https://doi.org/10.1021/ja072361l>.
- [36] I. Fábán, G. Lente, Light induced multistep redox reactions: the diode array spectrophotometer as a photoreactor, *Pure Appl. Chem.* 82 (2010) 1957–1973, <https://doi.org/10.1351/PAC-CON-09-11-16>.
- [37] É. Józsa, V. Kiss, K. Ósz, Photochemical processes of 1,4-benzoquinones in aqueous medium, *J. Photochem. Photobiol. A: Chem.* 360 (2018) 166–173, <https://doi.org/10.1016/j.jphotochem.2018.04.024>.
- [38] L. Valkai, A. Marton, A.K. Horváth, Some physical parameters influencing the comprehensive evaluation of kinetic data in photochemical reactions and its application in the periodate-chemistry, *J. Photochem. Photobiol. A: Chem.* 388 (2020) 112021, <https://doi.org/10.1016/j.jphotochem.2019.112021>.
- [39] M. Gombár, É. Józsa, M. Braun, K. Ósz, Construction of a photochemical reactor combining a CCD spectrophotometer and a LED radiation source, *Photochem. Photobiol. Sci.* 11 (2012) 1592–1595, <https://doi.org/10.1039/C2PP25166C>.
- [40] T. Lehóczki, É. Józsa, K. Ósz, Ferrioxalate actinometry with online spectrophotometric detection, *J. Photochem. Photobiol. A: Chem.* 251 (2013) 63–68, <https://doi.org/10.1016/j.jphotochem.2012.10.005>.
- [41] R.P. Buck, S. Rondinini, A.K. Covington, F.G.K. Baucke, C.M.A. Brett, M.F. Camoes, M.J.T. Milton, T. Mussini, R. Naumann, K.W. Pratt, P. Spitzer, G.S. Wilson, Measurement of pH. Definition, standards, and procedures (IUPAC Recommendations 2002), *Pure Appl. Chem.* 74 (2002) 2169–2200, <https://doi.org/10.1351/pac200274112169>.
- [42] H. Irving, G. Miles, L.D. Petit, A study of some problems in determining the stoichiometric proton dissociation constants of complexes by potentiometric titrations using a glass electrode, *Anal. Chim. Acta* 38 (1967) 475–488, [https://doi.org/10.1016/S0003-2670\(01\)80616-4](https://doi.org/10.1016/S0003-2670(01)80616-4).
- [43] H.G. Offner, D.A. Skoog, Hydrolysis constant of quadrivalent cerium from spectrometric measurements, *Anal. Chem.* 38 (1966) 1520–1521, <https://doi.org/10.1021/ac60243a015>.
- [44] L.J. Heidt, J. Berestecki, Optical studies of cerous solutions, *J. Am. Chem. Soc.* 77 (1955) 2049–2054, <https://doi.org/10.1021/ja01613a005>.
- [45] T.J. Hardwick, E. Robertson, Ionic species in ceric perchlorate solutions, *Can. J. Chem.* 29 (1951) 818–827, <https://doi.org/10.1139/v51-094>.
- [46] T.J. Hardwick, E. Robertson, Association of ceric ions with sulphate (A spectral study), *Can. J. Chem.* 29 (1951) 828–837, <https://doi.org/10.1139/v51-095>.
- [47] P.L. Brown, C. Ekberg, Hydrolysis of Metal Ions, first ed., Wiley-VCH, Weinheim, 2016, <https://www.wiley-vch.de/en/areas-interest/natural-sciences/hydrolysis-of-metal-ions-978-3-527-33010-2>.
- [48] R.M. Smith, A.E. Martell, Critical Stability Constants. Volume 4: Inorganic Complexes, Springer, New York, 1976, <https://www.springer.com/gp/book/9781475755084>.

- [49] D.T. Richens, *The Chemistry of Aqua Ions*, Wiley, Weinheim, 1997. <https://www.wiley.com/en-us/The+Chemistry+of+Aqua+Ions%3A+Synthesis%2C+Structure+and+Reactivity%3A+A+Tour+Through+the+Periodic+Table+of+the+Elements-p-9780471970583>.
- [50] E. Wadsworth, F.R. Duke, C.A. Goetz, Present status of cerium(IV)-Cerium(III) potentials, *Anal. Chem.* 29 (1957) 1824–1825, <https://doi.org/10.1021/ac60132a046>.
- [51] A.W. Maverick, Q. Yao, The cerium(IV)/cerium(III) electrode potential in hydrochloric acid solution, *Inorg. Chem.* 32 (1993) 5626–5628, <https://doi.org/10.1021/ic00076a034>.
- [52] G. Lente, *Deterministic Kinetics in Chemistry and Systems Biology. The Dynamics of Complex Reaction Networks*, Springer, Cham, 2015. <https://www.springer.com/gp/book/9783319154817>.
- [53] I. Kerezi, G. Lente, I. Fábán, Kinetics of the light-driven aqueous autoxidation of sulfur(IV) in the absence and presence of iron(II), *Dalton Transact.* (2006) 955–960, <https://doi.org/10.1039/B511363F>.
- [54] S. Fronaeus, On the mechanism of the thermal decomposition of peroxodisulfate ion in moderately acidic solutions, *Acta Chem. Scand.* 40 (1986) 572–578. [http://actachemscand.org/pdf/acta\\_vol\\_40a\\_p0572-0578.pdf](http://actachemscand.org/pdf/acta_vol_40a_p0572-0578.pdf).
- [55] W.J. McElroy, S.J. Waygood, Kinetics of the reactions of the  $\text{SO}_4^-$  radical with  $\text{SO}_4^-$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{H}_2\text{O}$  and  $\text{Fe}^{2+}$ , *J. Chem. Soc. Faraday Trans.* 86 (1990) 2557–2564, <https://doi.org/10.1039/FT9908602557>.
- [56] W.J. McElroy, A laser photolysis study of the reaction of sulfate(1-) with chloride and the subsequent decay of chlorine(1-) in aqueous solution, *J. Phys. Chem.* 94 (1990) 2435–2441, <https://doi.org/10.1021/j100369a044>.
- [57] C. von Sonntag, *Free-Radical-Induced DNA Damage and Its Repair*, Springer, Berlin, Heidelberg, 2006, p. 93, [https://doi.org/10.1007/3-540-30592-0\\_5](https://doi.org/10.1007/3-540-30592-0_5).