

DOI:10.1002/ejic.201500654



Mechanism Involving Hydrogen Sulfite Ions, Chlorite Ions, and Hypochlorous Acid as Key Intermediates of the Autocatalytic Chlorine Dioxide–Thiourea Dioxide Reaction

Ying Hu,^[a] Attila K. Horváth,^{*[b]} Sasa Duan,^[a] György Csekő,^[b] Sergei V. Makarov,^[c] and Qingyu Gao^{*[a]}

Keywords: Autocatalysis / Kinetics / Reaction mechanisms / Reactive intermediates / Oxides

The kinetics of the chlorine dioxide–thiourea dioxide reaction was investigated by monitoring absorbance–time profiles at $\lambda = 360$ nm. Under acidic conditions, the primary carbon-containing product is cyanamide, not urea as considered previously for many oxidation reactions of thiourea dioxide. Increase of the rate of the reaction by an increase of pH can be readily explained by the slow pH-dependent formation of a more reactive form of thiourea dioxide (TDO) that is produced steadily and unavoidably as the stock TDO solution ages. We have also found that the absorbance–time profiles of the chlorine dioxide–TDO reaction are sigmoidal with

Introduction

The reaction of chlorite ions with thiourea (TU) has attracted the extensive attention of scientists as a new chlorite oscillator in continuous-flow stirred-tank reactors (CSTRs) since 1985.^[1] Subsequently, several studies indicated that this reaction displays more common nonlinear phenomena such as chaos^[2] and chemical waves.^[3] Although many aspects of this fascinating reaction are qualitatively wellknown, no detailed kinetic investigation of this system has been reported owing to the complexity of the overall reaction, which involves multiple-valence sulfur- and chlorinecontaining intermediates in its subsystems.

ClO₂ as a long-lived chlorine-containing intermediate^[3] and thiourea dioxide (TDO) as a long-lived sulfur-containing intermediate^[4] have already been confirmed in the oxidation of thiourea. Therefore, it is undisputed that the ClO₂– TDO reaction is a subsystem of the chlorite–thiourea par-

- [b] Department of Inorganic Chemistry, University of Pécs, Ifjúság u. 6, 7624 Pécs, Hungary E-mail: horvatha@gamma.ttk.pte.hu www.pte.hu
- [c] State University of Chemistry and Technology, Sheremetevsky str. 7, 153000 Ivanovo, Russia

excess TDO. The addition of methionine as a hypochlorous acid scavenging agent inhibits the reaction significantly, whereas the addition of chlorite ions and trace amounts of hydrogen sulfite ions accelerates the decay of chlorine dioxide. On the basis of these experiments, a sixteen-step kinetic model involving hypochlorous acid, chlorite ions, and hydrogen sulfite ions as key intermediates that provide an autocatalytic cycle is proposed to account for the overall kinetic behavior observed, including the slow rearrangement of TDO.

ent reaction. To pave the way towards detailed mechanistic insights into the chlorite-TU reaction, knowledge of the kinetics and mechanism of the title reaction is eagerly anticipated. Owing to the formation of SO₂H⁻/SO₂²⁻ ions from the rapid decomposition of TDO in alkaline solutions,^[5,6] TDO has been extensively applied in chemistry and chemical technology as a special and effective reducing agent,^[7-10] especially for the potential chemical reduction of graphene oxide in recent years.^[11,12] Its reducing ability increases with aging in alkaline solution. The stability of sulfoxylate ions increases with increasing pH under anaerobic conditions.^[13] Some oxidation reactions of TDO have been controlled in acidic solutions.^[14-16] The oxidations of TDO with chlorite ions, iodine, and bromine have been performed by Simoyi et al.^[15-18] Regrettably, the tautomerization of TDO, which seems to occur relatively slowly from (NH₂)₂CSO₂ to NH₂NHCSO₂H^[19,20] at low pH values, has so far not been taken into account in these reactions, though the two tautomers may have quite different reactivity towards chlorine dioxide and other chlorine-containing intermediates.

Chlorine dioxide has long been known as an antimicrobial agent, and recent interest has focused on its application in gaseous form because it seems to be more effective than it is in aqueous solutions.^[21–24] As a radical with an odd number of valence electrons, ClO₂ could react readily with various sulfur-containing compounds and even display nonlinear autocatalytic behavior, as in its reactions with

 [[]a] School of Chemical Engineering, China University of Mining and Technology, Xuzhou 2221111, Jiangsu Province, P. R. China E-mail: gaoqy@cumt.edu.cn

www.cumt.edu.cn



thiourea,^[25] thiocyanate ions,^[26] and thiosulfate ions.^[27,28] During the autocatalytic process, HOCl and the corresponding reactive sulfur intermediates, thiourea monoxide, HOSCN, and sulfite ions, serve important governing roles, as these reactive sulfur intermediates consume chlorine dioxide rapidly.

In our previous study,^[19] we observed for the first time that autocatalysis also occurs in the reaction between ClO₂ and TDO, though at that time we focused our interest on an explanation for the aging effect of TDO in acidic medium on the basis of the remarkable reactivity difference between the tautomeric forms of TDO without a direct insight into the mechanistic details of the given reaction. We also found that the addition of hydrogen carbonate ions decreases the length of the induction period of autocatalysis; therefore, the otherwise inert hydrogen carbonate ions may also have an important effect on the autocatalytic cycle.^[19] On the basis of a general interest on the application of TDO, we report here a detailed, systematic study on the kinetics of the ClO₂-TDO reaction to obtain better insights into the mechanism of the fascinating chloritethiourea reaction.

Results

Identification of Products and Intermediates

Chlorine dioxide is a versatile oxidizing agent because its reactions are often accompanied by the formation of a chlorate side-product.^[29–31] To check this possibility, we performed capillary electrophoresis (CE) measurements to detect possible chloride- and sulfur-containing oxyanions.

As shown in Figure 1a, in addition to chloride ions, chlorate ions also form in a significant amount during the course of reaction. Other chlorine-containing products cannot be detected under our experimental conditions. It is also clarified by Figure 1a that a significant amount of sulfate ions are found by the end of the reaction. As thiourea trioxide (TTO) is also a conceivable product, HPLC measurements were performed for the possible identification of this compound. As indicated in Figure 1b, we did indeed find detectable amounts of TTO. The results of the quantitative determination of the sulfur-containing products are shown in Table 1.



Figure 1. Typical (a) electropherogram and (b) chromatogram during the course of the TDO–ClO₂ reaction. The electropherogram and the chromatogram were taken at t = 30 and 13 min, respectively. Initial conditions: pH 2.49, [TDO]₀ = 1.03 mM, [ClO₂]₀ = 3.12 mM, the detection wavelength was 214 nm.

The sulfur balance is perfect within the experimental error; therefore, sulfite ions should only appear as a shortlived intermediate under these conditions. These results also imply that the majority of the initial amount of sulfur forms sulfate ions; therefore, in addition to TTO, other nitrogenand carbon-containing species must form. As many oxidation reactions of TDO with different oxidizing agents were supposed to form urea under acidic conditions^[3,16,17] and as carbonate and ammonium ions were considered in our recent article,^[19] we performed ¹³C NMR spectroscopy measurements to identify the major carbon- and nitrogencontaining products. The ¹³C NMR spectrum of the end products after the chlorine dioxide completely disappeared from the solution is shown in Figure 2.

Surprisingly, the ¹³C NMR spectrum clearly shows that the carbon-containing end product is not urea or hydrogen carbonate but is cyanamide. As we did not find the peak of cyanamide in the ¹³C NMR spectrum in our previous report,^[19] this apparent contradiction deserves a conceivable explanation. The main difference during the measurement of the NMR spectrum was the acquisition time. In our previous report, the acquisition time was more than 18 h, whereas it was only ca. 45 min in the present report. From these results, we concluded that cyanamide is indeed

Table 1. HPLC determination of TDO, TTO, and sulfate ions with different initial conditions. All concentrations are given in mM. The pH was adjusted to 2.35 with phosphoric acid/dihydrogenphosphate buffer. The final concentrations were determined after the completion of the reaction but not earlier than 1 h.

Entry	[ClO ₂] ₀	[TDO] ₀	[TDO]∞	[TTO]∞	[SO ₄ ^{2−}]∞	[TDO] _∞ sim	[TTO] _∞ sim	[SO4 ^{2–}] _∞ sim
1	3.00	2.03	0.00	0.14	1.79	0.00	0.02	2.01
2	1.10	3.39	2.01	0.23	1.26	2.31	0.10	0.98
3	2.01	2.03	0.15	0.17	1.63	0.23	0.09	1.71
4	3.12	1.03	0.00	0.10	0.97	0.00	0.00	1.03



Figure 2. (A) ¹³C NMR spectroscopy study of the product of the ClO_2 -TDO reaction. The chemical shift of TDO is 177.6 ppm. $[ClO_2]_0 = 0.06 \text{ M}$, $[TDO]_0 = 0.25 \text{ M}$, the pH was ca. 2.0. The ¹³C NMR spectroscopic data collection was started ca. 90 min later when the ClO_2 was completely reacted. The number of scans was 1024. (B) ¹³C NMR spectrum of 3.0 M cyanamide. The chemical shift is 118.0 ppm. (C) ¹³C NMR spectrum of a 0.15 M urea solution. The chemical shift is 162.6 ppm.

the primary product of the reaction under our experimental conditions, but cyanamide appears to be transformed into ammonium ions and carbon dioxide on a longer timescale in the presence of excess TDO. As thiourea dioxide may also serve as an oxidant,^[32] this possibility may explain the difference between our previous and recent reports, but this phenomenon certainly requires further detailed investigations. Furthermore, the CE and HPLC experiments presented above also confirm that both chlorite ions and hypochlorous acid can only be short-lived intermediates of the reaction.

Effect of Methionine, Chlorite Ions, Sulfite Ions, and pH

To demonstrate indirectly that hypochlorous acid is a key intermediate of the title reaction, the reaction was studied at a certain composition in the absence and presence of methionine. As Figure 3 demonstrates, methionine decreases significantly the rate of consumption of chlorine dioxide. This straightforwardly suggests that hypochlorous acid is indeed a key intermediate because methionine is a very efficient HOCl scavenger.^[28,33,34]

Moreover, the addition of a small amount of chlorite ions into the reaction solution has a huge impact on the absorbance measured at the first time point. The chlorine dioxide concentration drops immediately within the mixing period of the reactants (see Figure 4). As no reaction at all occurs between chlorite ions and chlorine dioxide, the



Figure 3. The effect of methionine on the ClO_2 -TDO reaction. The initial conditions were as follows: $[ClO_2]_0 = 0.416 \text{ mM}$, $[TDO]_0 = 10 \text{ mM}$, $[methionine]_0 = 30 \text{ mM}$, I = 0.1 M, T = 18 °C, pH 2.35.

TDO-chlorite reaction should be very fast and should produce an intermediate that removes chlorine dioxide efficiently. Indeed, the reaction between TDO and chlorite ions is rapid and can be measured conveniently with a stopped-flow instrument.^[18] These experiments indirectly imply that chlorite ions must play a significant role in the kinetics of the title reaction. A conceivable explanation of this experimental fact is that the TDO-chlorite reaction produces hydrogen sulfite ions as an essential intermediate, which then remove chlorine dioxide in a rapid reaction.^[35]



Figure 4. The effect of chlorite ions on the ClO₂–TDO reaction. The initial conditions were as follows: $[ClO_2]_0 = 0.49 \text{ mM}$, $[TDO]_0 = 2.0 \text{ mM}$, $[ClO_2^{-}]_0 = 0.2$ (black), 0.4 (blue), and 0.7 mM (green), I = 0.1 M, T = 25 °C, pH 2.35.

If our argument about the influence of chlorite ions on the TDO-chlorine dioxide reaction is correct, the addition of hydrogen sulfite ions should also have a notable effect on the kinetic runs. As is shown in Figure 5, trace amounts of added hydrogen sulfite ions accelerate the initial part of the reaction; therefore, the fast hydrogen sulfite-chlorine dioxide reaction produces either chlorite ions or hypochlorous acid, which have a huge impact on the kinetics.

The pH also has a profound effect on the shape of the kinetic curves. As Figure 6 depicts, the rate of decay of chlorine dioxide increases significantly with increasing pH.

It is also interesting that the absorbance–time profiles of the TDO–ClO₂ reaction are sigmoidal. In our previous paper,^[19] we provided experimental evidence that the addition of hydrogen carbonate ions significantly shortens the induc-



Figure 5. The effect of trace amounts of S^{IV} on the ClO₂–TDO reaction. The initial conditions were as follows: $[ClO_2]_0 = 0.416 \text{ mM}, [TDO]_0 = 10.0 \text{ mM}, [SO_3^{2-}]_0 = 0 \text{ (black)}, 10 \text{ (green)}, \text{ and } 30 \text{ }\mu\text{M} \text{ (red)}, I = 0.1 \text{ M}, T = 18 \text{ }^\circ\text{C}, \text{ pH } 2.35.$



Figure 6. Experimental (symbols) and fitted (solid lines) absorbance–time series in the ClO_2 –TDO reaction. The initial conditions were as follows: $[ClO_2]_0 = 0.50 \text{ mM}$, $[TDO]_0 = 10.0 \text{ mM}$, I = 0.1 M, T = 25 °C, pH = 1.87 (black), 2.05 (blue), 2.36 (green), 2.66 (cyan), and 3.07 (red).

tion period through the enhancement of the tautomeric rearrangement of TDO, but the experiments performed here rather support that the interactions of the key intermediates of the reaction eventually result in the autocatalytic behavior of the system.

Proposed Kinetic Model

On the basis of the experimental results presented, the following essential species must be considered for the construction of the kinetic model: the reactants (TDO and ClO₂), the products (TTO, sulfate ions, chloride ions, chlorate ions, and cyanamide), and indirectly identified or feasible intermediates (such as HOCl, chlorite ions, hydrogen sulfite ions). Furthermore, in our previous paper,^[19] we showed that TDO tends to rearrange slowly into aminoiminomethanesulfinic acid (AIMSA) under acidic conditions, and these forms have different reactivity towards chlorine dioxide. Therefore, AIMSA has to be considered as a reactant as well. In addition, Cl_2O_2 was also considered as a feasible intermediate in the well-known hypochlorous acid–chlorite reaction.^[36] Then, we considered all of the conceivable reactions among these species along with their H⁺- and OH⁻-catalyzed pathways as an initial model and systematically removed all of the steps from the model that had no influence on the quality of the fit. This method has been successfully applied to several different chemical systems. As a result of a long but straightforward elimination process, we finally arrived at the following compact kinetic model that is able to describe all of the measured characteristics of the kinetic curves.

$H_3PO_4 \rightleftharpoons H_2PO_4^-$	(E1)
TDO→AIMSA	(R1)
$TDO + ClO_2 \rightarrow TTO + ClO$	(R2)
AIMSA + $ClO_2 \rightarrow TTO$ + ClO	(R3)
$ClO_2 + ClO \rightarrow Cl_2O_3$	(R4)
$Cl_2O_3 + H_2O \rightarrow HOCl + ClO_3^- + H^+$	(R5)
$AIMSA + Cl_2O_3 \rightarrow TTO + Cl_2O_2$	(R6)
$Cl_2O_2 + H_2O \rightarrow ClO_3^- + Cl^- + 2H^+$	(R7)
$TTO + Cl_2O_2 + H_2O \rightarrow 2HOCl + SO_4^{2-} + NH_2CN + 2H^+$	(R8)
$TDO + HOCl \rightarrow NH_2CN + HSO_3^- + Cl^- + 2H^+$	(R9)
$TTO + HOCl \rightarrow NH_2CN + SO_4^{2-} + Cl^- + 3H^+$	(R10)
$\mathrm{HSO}_{3}^{-} + \mathrm{ClO}_{2} \rightarrow \mathrm{SO}_{3}^{-} + \mathrm{ClO}_{2}^{-} + \mathrm{H}^{+}$	(R11)
$SO_3^- + ClO_2 + H_2O \rightarrow SO_4^{2-} + ClO_2^- + 2H^+$	(R12)
$\mathrm{HSO}_{3}^{-} + \mathrm{ClO}_{2} \rightarrow \mathrm{SO}_{4}^{2-} + \mathrm{ClO} + \mathrm{H}^{+}$	(R13)
$TDO + ClO_2^{-} \rightarrow NH_2CN + HSO_3^{-} + HOCl$	(R14)
$HSO_3^- + ClO_2^- \rightarrow SO_4^{2-} + HOCl$	(R15)
$HSO_3^- + HOC1 \rightarrow SO_4^{2-} + Cl^- + 2H^+$	(R16)

The rate coefficients determined by nonlinear simultaneous parameter estimation are illustrated in Table 2. The average deviation was found to be 4.0% by a relative fitting procedure. Altogether only nine fitted and eight fixed parameters were used. The quality of the fits for representative examples are demonstrated in Figures 6, 7, and 8, which also support that the proposed kinetic model works properly under our experimental conditions.

Table 2. Fitted and fixed rate coefficients of the proposed model. If no error is indicated, the given rate coefficient was fixed during the calculation.

R1)	k_1 [TDO]	$7.4 imes 10^{-6} ext{ s}^{-1}$
	k_1' [TDO][H ⁺] ⁻¹	$(1.56 \pm 0.05) imes 10^{-7} \mathrm{ms^{-1}}$
R2)	k_2 [TDO][ClO ₂]	$(2.74 \pm 0.12) \times 10^{-2} \text{ m}^{-1} \text{ s}^{-1}$
R3)	k_3 [AIMSA][ClO ₂]	$(2.85 \pm 0.10) \times 10^3 \mathrm{m}^{-1} \mathrm{s}^{-1}$
R4)	$k_4[ClO_2][ClO]$	$10^9 \text{ m}^{-1} \text{ s}^{-1}$
R5)	$k_5[Cl_2O_3]$	$\geq 1 \mathrm{s}^{-1}$
R6)	k_6 [AIMSA][Cl ₂ O ₃][H ⁺]	$(8.85 \pm 0.60) \times 10^8 \text{ m}^{-2} \text{s}^{-1}$
R7)	$k_7[\text{Cl}_2\text{O}_2]$	$\geq 1 \mathrm{s}^{-1}$
R8)	k_8 [TTO][Cl ₂ O ₂][H ⁺] ⁻¹	$(66.0 \pm 3.5) \mathrm{s}^{-1}$
R9)	k ₉ [TDO][HOCl]	$\geq 10^8 \text{ m}^{-1} \text{s}^{-1}$
R10)	k_{10} [TTO][HOC1]	$(2.01 \pm 0.32) \times 10^9 \text{ m}^{-1} \text{s}^{-1}$
R11)	$k_{11}[\text{HSO}_3^-][\text{ClO}_2]$	$(17.0 \pm 0.2) \text{ M}^{-1} \text{ s}^{-1}$
R12)	$k_{12}[SO_3^{-}][ClO_2]$	$10^9 \text{ M}^{-1} \text{ s}^{-1}$
R13)	$k_{13}[\text{HSO}_3^-][\text{ClO}_2][\text{H}^+]^{-1}$	$(6.77 \pm 0.98) \times 10^{-2} \text{ s}^{-1}$
R14)	k_{14} [TDO][ClO ₂ ⁻]	$(1.20 \pm 0.10) \times 10^5 \text{ m}^{-1} \text{s}^{-1}$
R15)	$k_{15}[\text{HSO}_3^-][\text{ClO}_2^-][\text{H}^+]$	$8.2 \times 10^9 \mathrm{M}^{-2} \mathrm{s}^{-1}$
R16)	$k_{16}[\text{HSO}_3^-][\text{HOCl}]$	$7.6 imes 10^8 \text{ m}^{-1} \text{s}^{-1}$



Figure 7. Experimental (symbols) and fitted (solid lines) absorbance-time series for the ClO_2 -TDO reaction. The initial conditions were as follows: $[ClO_2]_0 = 0.51 \text{ mM}$, pH 1.87, I = 0.1 M, T = 25 °C, [TDO] = 10.0 (black), 8.0 (blue), 7.0 (green), 5.0 (cyan), 3.0 (red), 1.4 (magenta), 1.0 (brown), 0.7 (grey), 0.5 (purple), and 0.25 mM (yellow).



Figure 8. Experimental (symbols) and fitted (solid lines) absorbance–time series for the ClO_2 –TDO reaction. The initial conditions were as follows: [TDO]₀ = 0.5 mM, pH 2.36, *I* = 0.1 M, *T* = 25 °C, [ClO₂] = 1.4 (black), 1.0 (blue), 0.7 (green), 0.3 (cyan), and 0.18 mM (red).

Discussion

As indicated, step E1 is only necessary to take the slight pH change into account during the course of the reaction. The ratio of rate coefficients for the rapid forward and reverse reaction was fixed during the whole calculation process to give the pK_a of phosphoric acid to be 2.10 under the given experimental conditions.^[37]

The initiation of the reaction in our kinetic model starts with the relatively slow rearrangement of TDO into AIMSA in aqueous solution.^[19] For completeness, it should be noted that the calculation indicated that two different forms of TDO are required to explain our kinetic data, a less and a more reactive form with a slow transformation process. Therefore, in addition to tautomerization, other feasible explanation may exist to describe our kinetic data. One reasonable possibility is that TDO changes from a less reactive form (oligomeric) to a more reactive form upon dissolution of the solid in aqueous solution.^[38] Unfortunately, there is no way to distinguish between these possibilities in our kinetic measurements; consequently, TDO and

AIMSA in the kinetic model may also mean two different forms of thiourea dioxide, not specifically the dioxide and the aminoimino form. Our calculations also indicated that the transformation of two different forms of TDO is accelerated by an increase of pH, which is reflected by the k_1' value indicated in Table 2. This result was indirectly confirmed by a further calculation that indicated that the elimination of k_1' from the kinetic model would lead to an unacceptably high average deviation of 7.6%. Many other reasonable possibilities were checked to eliminate k_1' from the proposed model with no success, including the hydroxide dependence of the subsequent step of the reaction. Thus, we concluded that the transformation between the two forms of TDO in aqueous solution also depends on pH.

Step R2 is the initiation of the reaction by a formal oxygen transfer from chlorine dioxide to TDO to form TTO and a ClO radical. The rate coefficient of this reaction was found to be $k_2 = (2.74 \pm 0.12) \times 10^{-2} \text{ m}^{-1} \text{ s}^{-1}$. Although this value seems to be quite low, the elimination of this step from the model would result in a significant increase in the average deviation to 5.6%. From this, we concluded that this reaction is necessary for the adequate description of our kinetic data.

Step R3 is the other alternative way to initiate the reaction by a direct attack of chlorine dioxide to AIMSA. As there is no information about the rearrangement of TTO to aminoiminomethanesulfonic acid (AIMSOA, NH₂NHCSO₃H) in aqueous solution, we assume that this reaction results in the formation of the same product as Step R2. We calculated k_3 to be $(2.85 \pm 0.10) \times 10^3 \text{ m}^{-1} \text{ s}^{-1}$, that is, five orders of magnitude higher than k_2 . Therefore, there is a significant reactivity difference between these forms towards chlorine dioxide in aqueous solution. This seems to be analogous to the case of acetone, which is more sluggish to react with iodine than its enol form.^[39]

Step R4 is just a rapid radical–radical reaction to produce Cl₂O₃, and its rate coefficient has to be close to the diffusion control limit. Therefore, we fixed it to $k_4 = 10^9 \text{ m}^{-1} \text{ s}^{-1}$ during the course of the whole calculation process.

Step R5 is one of the possible routes for the rapid removal of Cl_2O_3 by hydrolysis. This reaction produces chlorate ions and the key intermediate hypochlorous acid. Its individual rate coefficient cannot be determined from our experiments; only the k_6/k_5 ratio could be calculated. Any value of k_5 higher than 1 s^{-1} would lead to the same final result; therefore, we set k_5 at the lower limit.

Step R6 is the other pathway for the reaction of Cl₂O₃ with AIMSA through a formal oxygen transfer process to produce Cl₂O₂ and TTO. As k_6/k_5 was found to be $(8.85 \pm 0.60) \times 10^8 \text{ M}^{-2}$, k_5 was set to 1 s^{-1} to provide the actual value of k_6 . One might also expect that Cl₂O₃ could react with TDO. We tried to include this reaction with no success. Thus, we concluded that TDO does not react directly with Cl₂O₃.

Step R7 is the well-known hydrolysis of Cl_2O_2 to produce chloride and chlorate ions. As these are short-lived interme-



diates, the individual rate coefficient k_7 cannot be calculated from our experiments, and only k_8/k_7 could be determined. We set k_7 as 1 s⁻¹ during the calculation process and actually calculated k_8/k_7 owing to total correlation of these parameters.

Step R8 is the oxidation of TTO by Cl₂O₂ to produce the key intermediate HOCl through a nonelementary reaction. This was found to be an important step to maintain the concentration of HOCl at an appropriate level to produce the sigmoidal kinetic curves. This reaction was already suggested by Jones et al.^[18] with a rate coefficient of $8 \times 10^4 \text{ m}^{-1} \text{ s}^{-1}$, but we found no opportunity to obtain the individual rate coefficient of this reaction from our measurements as a result of the total correlation mentioned above. We have also found that the rate of this reaction is inversely proportional to [H⁺], which indicates that the removal of chlorine dioxide is actually faster at higher pH values. As the kinetic model reported by Jones et al.^[18] suffers from other serious problems, which have been enlightened by Stanbury and Figlar,^[40] we are inclined not to compare these rate coefficients directly.

Step R9 is one of the reactions responsible for the removal of hypochlorous acid to produce hydrogen sulfite ions as another important intermediate. Evidently this step is also a nonelementary reaction, and there is no firm experimental basis to divide it unambiguously into elementary ones. Hypochlorous acid does not act as a formal oxygen transfer agent; instead, it breaks up the central C-S bond to produce HSO₃⁻ ions and cyanamide. The former intermediate then participates in a chain reaction that results in the efficient removal of chlorine dioxide. This pathway will be discussed later. From our measurements, the individual rate coefficient of this reaction cannot be determined, and only k_{10}/k_9 could be calculated from our experiments. As we expect that the TDO-HOCl reaction should be relatively fast, we set k_9 to $10^8 \text{ m}^{-1} \text{ s}^{-1}$ to efficiently maintain the catalytic cycle with the controlling and terminating reaction of Step R16 (see below).

Step R10 produces directly the major sulfur-containing end product, sulfate ions, through the TTO–HOCl reaction. With k_9 fixed to $10^8 \text{ M}^{-1} \text{ s}^{-1}$, we found a somewhat unexpectedly high value for k_{10} of $(2.0 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Without the direct investigation of this reaction, we cannot provide a reasonable explanation for this value. However, it should be mentioned that the total correlation between the parameter sets opens up the possibility that the otherwise fixed parameters of those reactions in which the key intermediates are involved (k_{15} , k_{16}) may change slightly. Therefore, a different k_{10}/k_9 value is possible, but it is difficult to track the problem without direct experimental information.

Step R11 is an electron-transfer process suggested by Merényi et al. as an initiation of the sulfite–chlorine dioxide reaction in the presence of a huge chlorite concentration at alkaline pH.^[41] They found this rate coefficient to be $2.6 \times 10^6 \text{ m}^{-1} \text{ s}^{-1}$. However, the rate of the S^{IV}–chlorine dioxide reaction decreases with decreasing pH.^[42] As the pH was ca. 2.0 in our study and as sulfite (not hydrogen sulfite) is the kinetically active species towards chlorine dioxide,^[43]

our value of $k_{11} = (17.0 \pm 0.2) \text{ m}^{-1} \text{ s}^{-1}$ presented here is in a very good agreement with the one obtained from independent research groups (see below) if one considers that the pK_a of hydrogen sulfite is ca. $7.0^{[35,41,42]}$ This reflects a value of $1.7 \times 10^6 \text{ m}^{-1} \text{ s}^{-1}$ for the rate coefficient of the sulfite–chlorine dioxide reaction.

Step R12 is also a rapid radical-radical reaction to produce chlorite ions, the third key intermediate of the title reaction. The rate coefficient of this step was fixed to $10^9 \text{ m}^{-1} \text{ s}^{-1}$ during the whole calculation process.

Step R13 is a formal oxygen transfer from chlorine dioxide to a sulfite ion. This means that the sulfite–chlorine dioxide reaction occurs through parallel oxygen- and electron-transfer reactions. Again, if we consider that the pK_a of hydrogen sulfite is 7.0, then we can obtain an apparent rate coefficient of $6.77 \times 10^5 \text{ m}^{-1} \text{ s}^{-1}$ for the sulfite–chlorine dioxide reaction; therefore, the overall rate coefficient of the parallel pathways is $2.4 \times 10^6 \text{ m}^{-1} \text{ s}^{-1}$, which is in sound agreement with those found previously.^[41–43] The most important conclusion is that we have provided indirect experimental evidence that the sulfite–chlorine dioxide reaction proceeds through parallel pathways.

Step R14 is the reaction between TDO and a chlorite ion to form a hydrogen sulfite ion and hypochlorous acid, both of which are required to maintain the catalytic cycle. The rate coefficient of this reaction cannot be determined from our experiments because k_{14} and k_{15} were found to be in total correlation with each other. As we fixed k_{15} to $8.2 \times 10^9 \text{ m}^{-2} \text{ s}^{-1}$, a value of $(1.2 \pm 0.1) \times 10^5 \text{ m}^{-1} \text{ s}^{-1}$ could be calculated for the rate coefficient. The result for this reaction is in agreement with an independent result,^[18] although the rate coefficients differ by a factor of 50. This difference may stem from the fact that the k_{15} value used in our fitting procedure may not be determined precisely. Indeed, independently reported values of this rate coefficient span the range $2.2 \times 10^8 - 8.2 \times 10^9 \text{ m}^{-2} \text{s}^{-1}$ (see below).^[43-45] Although this may explain the difference quite well, at least one serious problem mentioned above questions the validity of the kinetic model reported by Jones et al.^[18] Therefore, we conclude that this may also account for the difference.

Steps R15 was first studied at approximately neutral pH and with a huge excess of chlorite ions by Huff-Hartz et al.,^[44] who found k_{15} to be $5.0 \times 10^8 \text{ m}^{-2} \text{ s}^{-1}$. Frerichs et al. obtained a k_{15} value of $2.2 \times 10^8 \text{ m}^{-2} \text{ s}^{-1}$ by simulating the dynamic behavior of the chlorite–sulfite reaction in a continuous stirred-tank reactor. Under the closest experimental conditions, a k_{15} value of $8.2 \times 10^9 \text{ m}^{-2} \text{ s}^{-1}$ was obtained for this reaction.^[43] Therefore, we used this value for k_{15} .

Step R16 was independently studied by Fogelman et al.,^[46] and its rate coefficient was determined to be $7.6 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$. We directly adopted this value in our kinetic model.

The direct reaction of TTO with chlorine dioxide and the rearrangement of TTO are not included in the proposed kinetic model. Our separate kinetic experiments on this reaction showed that a very slow reaction could be observed within the timescale of the title reaction under the experimental conditions studied (Figure 9), and the rate of decay



of chlorine dioxide does not depend on the age of the solution.



Figure 9. Effect of aging on the thiourea trioxide–chlorine dioxide reaction. The initial conditions were as follows: $[TTO]_0 = 10.0$ mM; $[ClO_2]_0 = 0.41$ mM; T = 25 °C; pH 2.36. The age of the TTO solution was 135 (black), 1355 (blue), 4135 (green), 9099 (cyan), and 13650 s (red).

From Figure 9, we can predict that the rate coefficient of the first-order decomposition of TTO is ca. 10^{-6} s⁻¹ under the experimental conditions studied; this value is in very good agreement with the value of 2.5×10^{-6} s⁻¹ found by Makarov and co-workers.^[47]

The inclusion of Equation (1) in the kinetic model with a fixed rate coefficient of $2.5 \times 10^{-6} \,\mathrm{s^{-1}}$ does not change the average deviation, from which we concluded that this process may only have a very minor contribution to the kinetics of the title reaction. Qualitatively, the initial drop in the absorbance can be explained by the formation of hydrogen sulfite ions from the slow aging of TTO solution to efficiently remove ClO₂ through the rapid hydrogen sulfite–chlorine dioxide reaction already included in the proposed kinetic model. It should be emphasized again that the decomposition of TTO in acidic solution is very slow and, therefore, cannot compete with the title reaction.

TTO +
$$H_2O \rightarrow N$$
-containing products + $HSO_3^- + H^+$ (1)

As the kinetic model was proposed on the basis of the absorbance-time profiles of chlorine dioxide, it seems crucial to test whether the proposed kinetic model is able to account for the final concentration distribution of sulfate ions and TTO, as measured at the end of the reaction by HPLC. A comparison of the simulated data of Table 1 with the measured data shows that the proposed kinetic model predicts soundly the trends in the concentration distribution of the sulfur-containing end products, though one may notice that the amount of TTO in each sample is underestimated by approximately 0.1 mm. However, as the error in the sulfur balance of the measured samples is ca. 0.11 mm, this agreement also validates our results.

The proposed kinetic model can be validated further by simulating qualitatively the effect of the addition of hydrogen sulfite ions, chlorite ions, and methionine, as

shown in Figure 10. The proposed model soundly explains the effect of the addition of hydrogen sulfite ions on the absorbance-time profiles (Figure 10A). The semiquantitative explanation of the effect of methionine requires the extension of the kinetic model with the rapid direct reaction between hypochlorous acid and methionine to produce a kinetically inactive product. In a fair agreement with the experimental results, we found that the consumption of chlorine dioxide is delayed significantly as a result of the efficient removal of hypochlorous acid (Figure 10B). We also found that the effect of chlorite ions can be semiquantitatively described if the TDO-ClO₂⁻ reaction is extended with a process that generates an intermediate or a product (hydrogen sulfite alone is not enough to account for this effect) that is able to remove chlorine dioxide efficiently (Figure 10C). Evidently, Step R14 in the proposed model is not an elementary reaction, and a detailed independent investigation is required to elucidate the mechanism of the chlorite-TDO reaction itself. Nevertheless, these simulations further support that the main core of the mechanism presented here accounts for all of the experimentally observed phenomena. For completeness, it should be mentioned that the disappearance of ClO2 indicated in Figure 10 (A and B) is much faster than that in the corresponding experiments shown in Figures 3 and 5. However, as indicated in the figure captions, these kinetic curves were acquired at 18 °C, which is much lower than the temperature at which the parameters of the kinetic models were determined. Consequently, the simulated results necessarily show much faster decay of ClO_2 . This is consistent with our



Figure 10. Simulation of the effect of initially added (A) hydrogen sulfite ions, (B) methionine, and (C) chlorite ions on the TDO– ClO_2 reaction. The initial concentrations are given in Figures 5, 3, and 4, respectively. For the simulation of the kinetic curves of (B) and (C), the proposed model was supplemented by the rapid methionine–hypochlorous acid reaction and a rapid reaction between an intermediate/product of the TDO– ClO_2^- reaction with chlorine dioxide (see text).



recent report, in which we showed that the half-life of ClO_2 increased five to nine times as the temperature decreased from 25 to 11 °C.^[19] From this, we concluded that the different temperature applied accounts for the half-life difference observed in the measured and calculated curves.

Another important issue that should also be discussed is the possible production of sulfoxylate ions with aging of TDO, as it is not included in the proposed model. Our previous study^[19] evidenced that the addition of formaldehyde (a well-known sulfoxylate scavenging agent) does not influence the reaction; consequently, the decomposition of TDO to produce sulfoxylate ions can be ruled out.

Finally, an explanation of the origin of the sigmoidal shape of the kinetic curves should be discussed. The reaction starts with the slow direct reactions of TDO and AIMSA to produce HOCl. The hypochlorous acid then produces hydrogen sulfite ions from TDO, followed by the hydrogen sulfite-chlorine dioxide reaction to produce both chlorite ions and Cl₂O₃ through Steps R11 and R13. The well-known rapid reaction of chlorite ions with sulfite ions and TDO under the pH range studied leads again to the formation of hypochlorous acid. Concurrently, the TDO- ClO_2^- reaction partially rebuilds the hydrogen sulfite ion concentration to keep the catalytic cycle alive. The autocatalytic nature of the system is manifested when Step R8 takes the governing role to increase [HOCl]. However, the concentration of hypochlorous acid is further regulated by its reactions with TDO, TTO, and hydrogen sulfite ions; therefore, under certain experimental conditions, sigmoidal kinetic curves cannot be observed. The overall effect is also enhanced by the slow rearrangement of TDO and the remarkable reactivity difference of the two forms of TDO in aqueous acidic solution. This result also implies that the kinetic model of the chlorite-TDO reaction^[18] should be revised thoroughly, not only because of the questionable significance of the vanishingly slow chlorine dioxide-chloride reaction realized correctly by Stanbury and Figlar.^[41] On one hand, the slow rearrangement of TDO was not taken into consideration by Jones et al.,^[18] and, most importantly, on the other hand, the autocatalytic loop involving hypochlorous acid, hydrogen sulfite ions, chlorite ions, and chlorine dioxide seems to also play a key role in that reaction. It should also be noted that the present kinetic model is a single feasibility to describe our kinetic data. Alternative models may also exist, but we do not see any known experiments that would contradict our proposed model at this point. Further refinement is expected after the elucidation of the kinetics of the subsystems of the title reaction, but the central part of the model seems to be firmly established.

Conclusions

As a subsystem of the chlorite-thiourea reaction, the chlorine dioxide-thiourea dioxide reaction can be used to distinguish the reactivity of two different forms of thiourea dioxide and also displays sigmoidal kinetic curves for the disappearance of chlorine dioxide. The kinetic model proposed here indicates that hypochlorous acid and hydrogen sulfite ions are key intermediates for the autocatalytic decrease of chlorine dioxide. The hydrogen sulfite oxidation by oxychlorine compounds is responsible for pH autocatalysis^[45] in unbuffered solution and may further enhance the nonlinear nature of the title reaction. The elucidation of the mechanism of the chlorine dioxide-thiourea dioxide reaction may also contribute to a better understanding of the mechanistic background of the oscillatory and chaotic chlorite-thiourea system,^[48,49] for which an autocatalytic loop involving the key intermediates hypochlorous acid, hydrogen sulfite ions, and chlorite ions might also play a critical role. More importantly, our results suggest that the elucidation of the reactions of TDO in aqueous acidic solution should be taken with special circumspection owing to the possible reactivity difference of the two forms of TDO presented. Therefore, the use of differently aged TDO solutions may lead to a misinterpretation of the results.

Experimental Section

Material and Buffers: The TDO (≥98%) was purchased from Sigma-Aldrich and used in all experiments without further purification. The other reagents were of analytical grade, including phosphoric acid, potassium dihydrogen phosphate, sulfuric acid, potassium nitrate, tetrabutylammonium hydroxide (TBAOH), and hexadimethrine bromide (HDB). Methanol (chromatographic grade) was applied in HPLC as a component of the mobile phase. The solution of the oxidizing agent chlorine dioxide was prepared according to the previous literature method^[19] and was protected from light at low temperature. The ClO₂ concentration was standardized spectrophotometrically at $\lambda = 360 \text{ nm}$ ($\varepsilon \approx 1200 \text{ m}^{-1} \text{ cm}^{-1}$). All working solutions were prepared in Milli-Q water. The pH value of the reaction system was controlled with phosphoric acid/ dihydrogenphosphate with the pK_a of phosphoric acid taken to be 2.1. The ionic strength was always maintained at 0.1 м with a 0.1 м potassium dihydrogen phosphate buffer component.

Methods: Fresh TDO solutions were prepared by dissolving solid samples in a certain volume of buffer solution for each kinetic measurement. The reaction was initiated by mixing appropriate volumes of TDO and ClO₂ solutions in a quartz cuvette with 1 cm optical path at (25 ± 0.1) °C, and all kinetic experimental data were recorded with an S600 diode array spectrophotometer ($\lambda = 200$ -400 nm) equipped with a Peltier thermostat and magnetic-stirring attachments. For all kinetic experiments, it was necessary to ensure that the age of the TDO solution was always kept the same. All of the kinetic experiments were initiated by a TDO solution aged for 180 s. The reaction was investigated at five pH values by changing the initial concentrations of ClO₂ and TDO. Several series of reactions were followed by CE and HPLC to clarify the important intermediates and the end products of the reactions. The HPLC separations were performed with a Dionex chromatographic system consisting of a Model P680 pump, a Phenomenex Ginimi C18 separation column (250×4.6 mm, 5 µm), and a UVD 170 UV detector. The eluent was a mixture of 1 mmol/dm3 tetrabutylammonium hydroxide (TBAOH) aqueous solution (pH 6.7) and methanol (95 vol-%) at a flow rate of 0.4 cm³min⁻¹. Capillary electrophoresis analysis with indirect ultraviolet detection was performed with a Beckman Coulter P/ACE MDQ CE system. The CE running buffer





was composed of a mixture of 2.0×10^{-5} mM HDB and 20 mM KNO₃ at pH 7.0 (adjusted with sodium hydroxide). A fused silica capillary of 57.5 cm (75 µm i.d., 375 µm o.d.) was used. The conditions for the kinetic runs were as follows: separation voltage 15 kV, capillary temperature 25 °C, cathodic pressure injection for 5 s with 0.5 psi. The carbon-containing products of the ClO₂–TDO reaction were identified by ¹³C NMR spectroscopy (Bruker AVANCE III HD 600 MHz) with D₂O as a frequency lock. A certain amount of solid P₂O₅ was added to the solution to control the pH, and the reaction was initiated by the addition of ClO₂ solution to the TDO solution. The collection of the ¹³C NMR spectroscopic data was started when the color of ClO₂ disappeared. In addition, the ¹³C NMR spectra of urea and cyanamide were acquired for comparison.

Data Treatment: The absorbance at $\lambda = 360$ nm, at which only chlorine dioxide absorbs light, was used for evaluation. Absorbance values higher than 1.2 were excluded from the data evaluation, because the absorbance-concentration curves start to deviate from linearity above this value. The concentration ranges of the reactants ClO₂ and TDO were varied between 0.18–1.4 and 0.25–10.0 mM, respectively, and the pH was kept between 1.87 and 3.07. For the HPLC and CE tests, calibration curves for all detectable species were determined to transform the measured peak areas into concentrations after qualitative information was collected. The correlation coefficients were always above 0.999, which indicates that the relationship between the peak area and the concentration is perfectly linear. To obtain the kinetic parameters for the proposed model, the ZiTa/Chemmech program package[50] was used. Our criterion for an acceptable fit for the relative fitting procedure to obtain reliable kinetic parameters for the model was to achieve 4%, as the precision of the concentration determination of the volatile chlorine dioxide is ca. 3-5% during the course of the reaction.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (NSFC) (grant number 51221462), by the Natural Science Foundation of Jiangsu Province (grant number BK20131111), the Fundamental Research Funds for the Central Universities (grant number 2015QNA19), the Priority Academic Program Development of Jiangsu Higher Education Institutions (grant number JS-2014-37) and by the Hungarian Research Fund OTKA (grant number K116591). The authors are grateful for the financial support of Chinese–Hungarian Cooperative (grant number K-TÉT-CN-1-2012-0030). Financial support by the Social Renewable Operational Program (SROP-4.2.2.D-15/1/Konv-2015-0015, Synthesis of supramolecular systems, examination of their physico-chemical properties and their utilization for separation and sensor chemistry project) is also gratefully acknowledged.

- [1] M. Alamgir, I. R. Epstein, Int. J. Chem. Kinet. 1985, 17, 429– 439.
- [2] C. J. Doona, R. Blittersdorf, F. W. Schneider, J. Phys. Chem. 1993, 97, 7258–7263.
- [3] C. R. Chinake, R. H. Simoyi, J. Phys. Chem. 1994, 98, 4012– 4019.
- [4] I. R. Epstein, K. Kustin, R. H. Simoyi, J. Phys. Chem. 1992, 96, 5852–5856.
- [5] Z. Kis, S. V. Makarov, R. Silaghi-Dumitrescu, J. Sulfur Chem. 2010, 31, 27–39.
- [6] S. A. Svarovsky, R. H. Simoyi, S. V. Makarov, J. Phys. Chem. B 2001, 105, 12634–12643.
- [7] S. V. Makarov, A. K. Horváth, R. Silaghi-Dumitrescu, Q. Gao, *Chem. Eur. J.* 2014, 20, 14164–14176.

- [8] S. V. Makarov, Russ. Chem. Rev. 2001, 70, 885-895.
- [9] H. Wang, Q. Li, C. Gao, J. Cleaner Prod. 2014, 84, 701-706.
- [10] A. A. Cuadri, P. Partal, F. J. Navarro, M. Garcia-Morales, C. Gallegos, *Fuel* 2011, *90*, 2294–2300.
- [11] C. K. Chua, A. Ambrosi, M. Pumera, J. Mater. Chem. 2012, 22, 11054–11061.
- [12] Y. Wang, L. Sun, B. Fugetsu, Bull. Chem. Soc. Jpn. 2012, 85, 1339–1344.
- [13] S. V. Makarov, R. Silaghi-Dumitrescu, J. Sulfur Chem. 2013, 34, 444-449.
- [14] Q. Gao, B. Liu, L. Li, J. Wang, J. Phys. Chem. A 2007, 111, 872–877.
- [15] S. V. Makarov, C. Mundoma, J. H. Penn, S. A. Svarovsky, R. H. Simoyi, J. Phys. Chem. A 1998, 102, 6786–6792.
- [16] E. Mambo, R. H. Simoyi, J. Phys. Chem. 1993, 97, 13662– 13667.
- [17] C. R. Chinake, R. H. Simoyi, S. B. Jonnalagadda, J. Phys. Chem. 1994, 98, 545–550.
- [18] J. B. Jones, C. R. Chinake, R. H. Simoyi, J. Phys. Chem. 1995, 99, 1523–1529.
- [19] G. Csekő, Y. Hu, Y. Song, T. R. Kégl, Q. Gao, S. V. Makarov, A. K. Horváth, *Eur. J. Inorg. Chem.* **2014**, 1875–1879.
- [20] S. V. Makarov, E. V. Kudrik, Russ. Chem. Bull. Int. Ed. 2001, 50, 203–205.
- [21] V. C. H. Wu, A. Rioux, Food Microbiol. 2010, 27, 179-184.
- [22] Y. Han, T. L. Selby, K. K. Schultze, P. E. Nelson, R. H. Linton, J. Food Prot. 2004, 67, 2450–2455.
- [23] I. Popa, E. J. Hanson, E. C. D. Todd, A. C. Schilder, E. T. Ryser, J. Food Prot. 2007, 70, 2084–2088.
- [24] Y. Lee, G. Burgess, M. Rubino, R. Auras, J. Food Prot. 2015, 144, 20–28.
- [25] G. Rábai, R. T. Wang, K. Kustin, Int. J. Chem. Kinet. 1993, 25, 53–62.
- [26] J. N. Figlar, D. M. Stanbury, J. Phys. Chem. A 1999, 103, 5732– 5741.
- [27] A. K. Horváth, I. Nagypál, J. Phys. Chem. A 1998, 102, 7267– 7272.
- [28] C. Pan, D. M. Stanbury, J. Phys. Chem. A 2014, 118, 6827– 6831.
- [29] A. K. Horváth, I. Nagypál, I. R. Epstein, J. Phys. Chem. A 2003, 107, 10063–10068.
- [30] G. Csekő, A. K. Horváth, J. Phys. Chem. A 2012, 116, 2911– 2919.
- [31] L. Xu, G. Csekő, A. Petz, A. K. Horváth, J. Phys. Chem. A 2014, 118, 1293–1299.
- [32] W. Gao, W. Qi, J. Lai, L. Qi, S. Majeed, G. Xu, Chem. Commun. 2015, 51, 1620–1623.
- [33] X. L. Armesto, L. M. Canle, M. I. Fernandez, M. V. Garcia, J. A. Santabella, *Tetrahedron* 2000, 56, 1103–1109.
- [34] D. I. Pattison, M. J. Davies, Chem. Res. Toxicol. 2001, 14, 1453–1464.
- [35] A. K. Horváth, I. Nagypál, J. Phys. Chem. A 2006, 110, 4753– 4758.
- [36] G. Peintler, I. Nagypál, I. R. Epstein, J. Phys. Chem. 1990, 94, 2954–2958.
- [37] IUPAC Stability Constant Database, Royal Society of Chemistry, London, 1990–1997.
- [38] J. Shao, X. Liu, P. Chen, Q. Wu, X. Zheng, K. Pei, J. Phys. Chem. A 2014, 118, 3168–3174.
- [39] M. J. Pilling, P. W. Seakins, *Reaction Kinetics*, Oxford University Press, Oxford, UK, 1995.
- [40] D. M. Stanbury, J. N. Figlar, Coord. Chem. Rev. 1999, 187, 223– 232.
- [41] G. Merényi, J. Lind, X. Shen, J. Phys. Chem. 1988, 92, 134– 137.
- [42] K. Suzuki, G. Gordon, Inorg. Chem. 1978, 17, 3115-3118.
- [43] A. K. Horváth, I. Nagypál, I. R. Epstein, *Inorg. Chem.* 2006, 45, 9877–9883.
- [44] K. E. Huff-Hartz, J. S. Nicoson, L. Wang, D. W. Margerum, *Inorg. Chem.* 2003, 42, 78–87.



- [45] G. A. Frerichs, T. M. Mlnarik, R. J. Grun, R. C. Thomson, J. Phys. Chem. A 2001, 105, 829–837.
- [46] K. D. Fogelman, D. M. Walker, D. W. Margerum, *Inorg. Chem.* 1989, 28, 986–993.
- [47] S. V. Makarov, C. Mundoma, J. H. Penn, J. L. Petersen, S. A. Svarovsky, R. H. Simoyi, *Inorg. Chim. Acta* 1999, 286, 149– 154.
- [48] R. Rushing, R. C. Thomson, Q. Gao, J. Phys. Chem. A 2000, 104, 11561–11565.
- [49] Q. Gao, J. Wang, Chem. Phys. Lett. 2004, 391, 349-353.
- [50] ZiTal Chemmech: A Comprehensive Program Package for Fitting Parameters of Chemical Reaction Mechanism, versions 2.1–5.0, G. Peintler, 1989–2001

Received: June 25, 2015 Published Online: October 5, 2015