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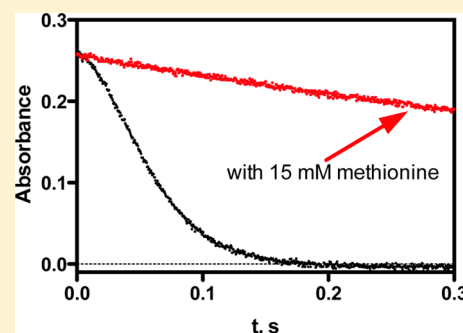
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Kinetics of the Initial Steps in the Aqueous Oxidation of Thiosulfate by Chlorine Dioxide

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S Supporting Information

ABSTRACT: The reaction of ClO_2^\bullet with $\text{S}_2\text{O}_3^{2-}$ in aqueous solution is a component of the “crazy clock” reaction of ClO_2^- with $\text{S}_2\text{O}_3^{2-}$, and under conditions of excess $\text{S}_2\text{O}_3^{2-}$ the absorbance at 360 nm due to ClO_2^\bullet decays with sigmoidal kinetics. A chain reaction mechanism is inferred on the basis that very small concentrations of SO_3^{2-} accelerate the reaction, and methionine inhibits the reaction. Pseudo-first-order kinetics is observed in the presence of relatively large methionine concentrations, leading to the simple rate law $-\text{d}[\text{ClO}_2]/\text{d}t = (k_a[\text{S}_2\text{O}_3^{2-}] + k_b[\text{S}_2\text{O}_3^{2-}]^2)[\text{ClO}_2]$, with $k_a = 452 \pm 16 \text{ M}^{-1} \text{ s}^{-1}$ and $k_b = (5.7 \pm 0.2) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ at 25 °C and pH 7.6. Under these conditions, the initial products are ClO_2^- and $\text{S}_4\text{O}_6^{2-}$. A classical electron-transfer mechanism is assigned to the reaction that occurs under conditions of methionine inhibition.



INTRODUCTION

There is interest in the reaction of chlorine dioxide with thiosulfate ($\text{S}_2\text{O}_3^{2-}$) because of its participation in the “crazy clock” reaction of chlorite with thiosulfate^{1–3} and its potential use as a means to remove excess ClO_2 during water treatment.⁴ A stopped-flow kinetic study of the reaction by Horváth and Nagypál has shown that under conditions of excess $\text{S}_2\text{O}_3^{2-}$ the loss of absorbance at 360 nm (where ClO_2 has its maximum absorbance) occurs with a sigmoidal time dependence, a clear indicator of kinetic complexity.⁵ The main reaction products are reported to be ClO_2^- and $\text{S}_4\text{O}_6^{2-}$ (tetrathionate), but significant amounts of Cl^- and SO_4^{2-} are also generated. The occurrence of such complex kinetics in this reaction is fascinating because a simple mechanism involving electron transfer from $\text{S}_2\text{O}_3^{2-}$ to ClO_2 , followed by conversion of the $\text{S}_2\text{O}_3^\bullet$ radicals to $\text{S}_4\text{O}_6^{2-}$, might be anticipated.

A detailed study of the kinetics of the $\text{ClO}_2/\text{S}_2\text{O}_3^{2-}$ reaction reported a 10-step mechanism that was fitted with excellent statistics to 131 kinetic traces simultaneously.⁵ In essence, the sigmoidal absorbance loss was modeled by a pseudo-first-order loss of ClO_2 and rise-fall kinetics of an absorbing intermediate identified as the $\text{S}_4\text{O}_6^{\bullet 3-}$ radical. It is quite unusual for a reactive species such as $\text{S}_4\text{O}_6^{\bullet 3-}$ to attain concentrations sufficient to contribute significantly to the absorbance on the stopped-flow time scale. Accordingly, we have been prompted to search for alternative explanations of the observed sigmoidal kinetics. Herein we report experiments that point toward autocatalysis as the basic mechanistic origin of the sigmoidal absorbance decay.

EXPERIMENTAL SECTION

Reagents and Solutions. L-Methionine was obtained from Acros and recrystallized from hot water. Solutions of ClO_2^\bullet

were prepared from the reaction of $\text{Na}_2\text{S}_2\text{O}_8$ with NaClO_2 as previously described.⁶ Concentrations of ClO_2^\bullet were determined spectrophotometrically at 360 nm ($\epsilon_{360} = 1200 \text{ M}^{-1} \text{ cm}^{-1}$).⁷ All solutions were prepared under N_2 or Ar and were permitted to contact only glass, Teflon, PEEK tubing, and platinum.

Instruments and Methods. Capillary electrophoresis experiments were performed as described by Lu.⁸ Specifically, a P/ACE MDQ capillary electrophoresis system (Beckman Coulter, Fullerton, CA) was used in the indirect mode with nitrate as the chromophore.^{9,10} The electrolyte consisted of 5 mM KH_2PO_4 , 5 mM $(\text{NH}_4)_2\text{SO}_4$, and 0.5 mM KNO_3 . The applied voltage was -30 kV , and the absorbance was measured at 214 nm.

Stopped-flow kinetic studies were performed at 25 °C and monitored at 360 nm as previously described.⁶ Values of k_{obs} were obtained by fitting the observed stopped-flow traces with an exponential decay function using the fitting routines supplied in the OLIS 4300 data analysis software. The fit of eq 1 was performed with Prism 5,¹¹ weighting the data as $1/(k_{\text{obs}}^2)$. Numerical simulations of the chain reaction were performed with the software package Specfit32.¹²

RESULTS

Initial experiments were performed to test whether the qualitative kinetic features reported by Horváth and Nagypál are reproducible.⁵ These experiments were performed at pH 7.33 in phosphate buffer with 0.5 mM $\text{S}_2\text{O}_3^{2-}$ and $[\text{ClO}_2]_0 = 0.22 \text{ mM}$. The initial absorbance at 360 nm was 0.25, its decay

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was sigmoidal with a first half-life of 50 ms, and the final absorbance was essentially zero. These results (shown in Figure 1A) are fully consistent with those reported previously, and

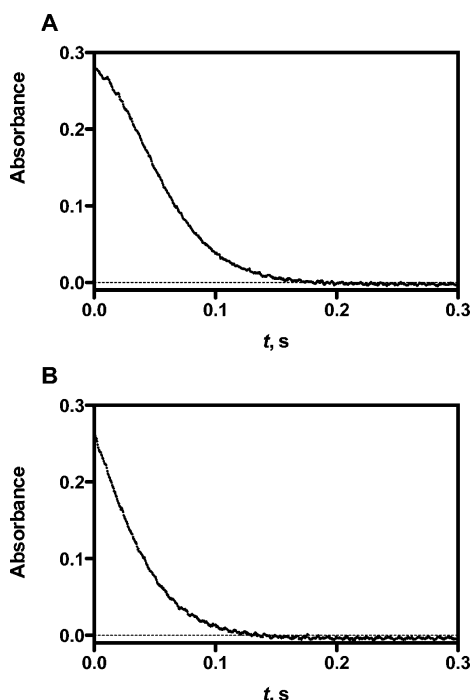


Figure 1. Stopped-flow traces of the reaction of 0.5 mM $\text{S}_2\text{O}_3^{2-}$ with 0.22 mM ClO_2 at pH 7.0 (phosphate buffer). (A) No added SO_3^{2-} . (B) 6 μM added SO_3^{2-} .

they are consistent with a process in which the initial absorbance is due to ClO_2 and then the ClO_2 is completely consumed. Experiments were also performed to test for metal-ion catalysis because this catalysis has been reported for the oxidation of $\text{S}_2\text{O}_3^{2-}$ by $[\text{Ni}^{\text{III}}(\text{tacn})_2]^{3+}$, $[\text{Fe}(\text{bpy})_3]^{3+}$, $[\text{Os}(\text{phen})_3]^{3+}$ and related species.^{13,14} The addition of 5 μM Cu^{2+} or 2 mM $\text{C}_2\text{O}_4^{2-}$ (a metal-ion chelator) to the reaction of 1 mM $\text{S}_2\text{O}_3^{2-}$ with 0.2 mM ClO_2 at pH 7 had no effect on the reaction rate, indicating that Cu^{2+} and other metal ions are not significant catalytic impurities.

Surprisingly, the reactions were highly sensitive to the addition of small amounts of sulfite (SO_3^{2-}). Thus, when the reaction of 0.22 mM ClO_2 with 0.5 mM $\text{S}_2\text{O}_3^{2-}$ at pH 7 was conducted with 6 μM SO_3^{2-} , the absorbance decay was exponential rather than sigmoidal and the first half life decreased by a factor of ~ 2 (Figure 1B). This behavior is reminiscent of that seen in the bromate/thiosulfate reaction, and it suggests an autocatalytic mechanism.¹⁵

On the hypothesis that the $\text{ClO}_2/\text{S}_2\text{O}_3^{2-}$ reaction is driven by an autocatalytic cycle with HOCl as a chain carrier, we performed a series of experiments with various additives that could serve as HOCl scavengers. Sulfamic acid has been reported to be an effective HOCl scavenger in the reaction of ClO_2 with styrene;¹⁶ when the reaction of 0.5 mM $\text{S}_2\text{O}_3^{2-}$ with 0.22 mM ClO_2 was performed at pH 7.3, the addition of 15 mM sulfamic acid extended the first half-life by 40% and changed the character of the decay to appear more exponential. This result supports the chain-reaction hypothesis, but sulfamic acid appears not to be sufficiently effective to completely block the chain reaction. Unfortunately, the rate of reaction of HOCl with sulfamic acid does not appear to have been reported.

Methionine was then tested as another HOCl scavenger; this sulfide has one of the largest known rate constants for reaction with HOCl ($k = 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$),^{17,18} and it is reported to react very slowly with ClO_2 .¹⁹ We find that only 15% of the ClO_2 is consumed in 10 min in a mixture of 0.24 mM ClO_2 and 15 mM methionine at pH 7.3, which implies that there is essentially no reaction on the time scale of the $\text{ClO}_2/\text{S}_2\text{O}_3^{2-}$ reaction. However, methionine has a profound effect on the kinetics of the $\text{ClO}_2/\text{S}_2\text{O}_3^{2-}$ reaction (Figure 2): for example, in

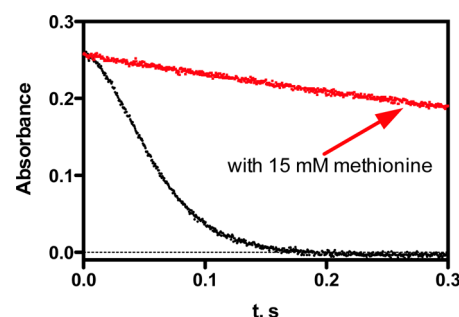


Figure 2. Effect of 15 mM methionine on the reaction of 0.22 mM ClO_2 with 0.5 mM $\text{S}_2\text{O}_3^{2-}$. pH 7.33.

the presence of 15 mM methionine, the reaction of 0.22 mM ClO_2 with 0.5 mM $\text{S}_2\text{O}_3^{2-}$ has a first half-life of ~ 0.9 s, whereas in the absence of methionine it is 0.06 s. Moreover, in the presence of methionine the decay is exponential instead of sigmoidal. This result provides strong evidence that the reaction of ClO_2 with $\text{S}_2\text{O}_3^{2-}$ is autocatalytic and that methionine inhibits the autocatalysis by consuming a chain-carrying intermediate. Analogous experiments with *S*-methylcysteine gave qualitatively similar results, although *S*-methylcysteine is not as effective as methionine in inhibiting the autocatalysis.

Further experiments reveal that methionine is not always entirely effective at scavenging the chain-carrying intermediate. Thus, when the methionine concentration is doubled from 15 to 30 mM, the reaction of 0.5 mM $\text{S}_2\text{O}_3^{2-}$ with 0.22 mM ClO_2 at pH 7.3 slows by $\sim 10\%$. Also, when the $\text{S}_2\text{O}_3^{2-}$ concentration is raised to 1 mM and higher in 50 mM methionine with 0.22 mM ClO_2 , the kinetic traces become nonexponential, showing evidence of catalysis. However, by conducting experiments at higher methionine and lower initial concentrations of ClO_2 , these effects can be largely avoided, and good exponential fits can be obtained. For a series of experiments at pH 7.62 and 0.1 M methionine with $[\text{ClO}_2]_0 = 0.029$ mM, the values of k_{obs} (the pseudo-first-order rate constant) increase monotonically but nonlinearly with increasing $[\text{S}_2\text{O}_3^{2-}]$, as shown in Figure 3 (data in Table S-1 in the Supporting Information). A two-term rate law as in eq 1 is suggested by these results.

$$k_{\text{obs}} = k_a[\text{S}_2\text{O}_3^{2-}] + k_b[\text{S}_2\text{O}_3^{2-}]^2 \quad (1)$$

The data in Figure 3 yield an excellent fit with eq 1, the fitted values being $k_a = 452 \pm 16 \text{ M}^{-1} \text{ s}^{-1}$ and $k_b = (5.7 \pm 0.2) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ (25.0 $^\circ\text{C}$, $\mu = 0.1 \text{ M}$). Note that an analogous rate law pertains to the oxidation of $\text{S}_2\text{O}_3^{2-}$ by $[\text{Os}(\text{phen})_3]^{3+}$ and related species.¹⁴

Under these conditions of low $[\text{ClO}_2]_0$ and high methionine concentrations, the values of k_{obs} are mildly pH-dependent. Thus, k_{obs} decreases from 0.32 to 0.22 s^{-1} as the pH is raised from 6.99 to 7.71 ($[\text{S}_2\text{O}_3^{2-}] = 0.3 \text{ mM}$, $[\text{ClO}_2]_0 = 0.029 \text{ mM}$,

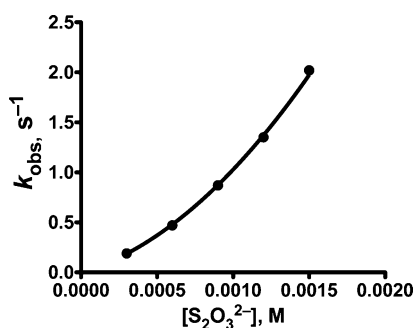
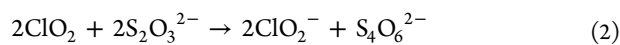


Figure 3. Dependence of k_{obs} on $[\text{S}_2\text{O}_3^{2-}]$ in 100 mM methionine at pH 7.62 (50 mM phosphate buffer). 25 °C, $[\text{ClO}_2]_0 = 0.029$ mM. The solid line is a fit to eq 1

[methionine] = 0.1 M). This effect is attributed to residual autocatalysis arising from incomplete scavenging by methionine, and it is expected to be pH-dependent, as shown below.

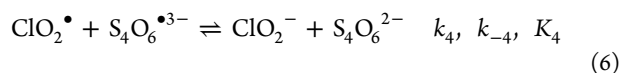
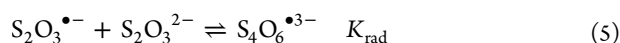
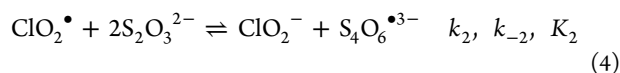
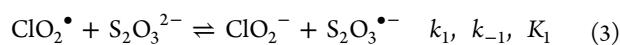
Tests for copper-ion catalysis in the presence of methionine were negative.

Capillary electrophoresis experiments were performed to examine the reaction products. Chlorite and tetrathionate were detected among the products of the reaction of 0.3 mM ClO_2 with 7.5 mM $\text{S}_2\text{O}_3^{2-}$ in 100 mM methionine at pH 7.2 (phosphate buffer). The concentration of tetrathionate was 0.146 mM immediately after the reaction, but it decreased after several minutes. In the same time interval, the concentration of ClO_2^- became undetectably low. These results are consistent with the major initial reaction being



DISCUSSION

When methionine is present in sufficient concentrations to suppress autocatalysis, the reaction of ClO_2 with $\text{S}_2\text{O}_3^{2-}$ follows the simple rate law 1, which is also observed for the reactions of other classical one-electron oxidants with $\text{S}_2\text{O}_3^{2-}$.¹⁴ Accordingly, an analogous mechanism is proposed:



This mechanism yields eq 2 as the overall chemical equation.

Under conditions where the reverse steps k_{-1} , k_{-2} , and k_{-4} can be neglected, the K_{rad} equilibrium is established rapidly, and the final step (eq 6) occurs rapidly, the derived rate law is

$$-d[\text{ClO}_2]/dt = 2k_1[\text{ClO}_2][\text{S}_2\text{O}_3^{2-}] + 2k_2[\text{ClO}_2][\text{S}_2\text{O}_3^{2-}]^2 \quad (7)$$

Thus, the fitted values of k_a and k_b for eq 1 lead to the following: $k_1 = 226 \pm 8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = (2.8 \pm 0.1) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$.

The value for k_{-1} can be calculated from the value of k_1 and detailed balancing by use of the known E° values: $E^\circ(\text{ClO}_2/\text{ClO}_2^-) = 0.934 \pm 0.003 \text{ V}$, $E^\circ(\text{S}_2\text{O}_3^{\bullet-}/\text{S}_2\text{O}_3^{2-}) = 1.35 \pm 0.03 \text{ V}$.^{20,21} Thus, we obtain $\log K_1 = -7.0 \pm 0.5$ and $\log k_{-1} = 9.35 \pm 0.5$, which places k_{-1} very close to the diffusion limit. It is

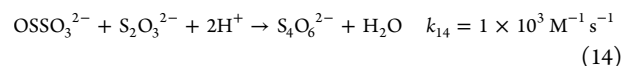
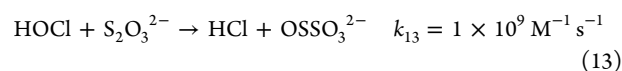
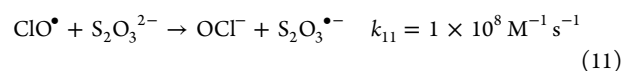
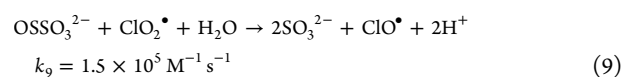
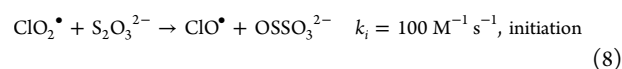
quite common for electron-transfer reactions of $\text{S}_2\text{O}_3^{2-}$ to show such behavior, although an exception can be found in the reaction with the sluggish $[\text{Ni}(\text{tacn})_2]^{3+/2+}$ couple.¹³

Detailed balancing can also be applied to the k_2 step, based on $E^\circ(\text{S}_4\text{O}_6^{\bullet 3-}/2\text{S}_2\text{O}_3^{2-}) = 1.07 \pm 0.03 \text{ V}$.²² The calculated results are $\log K_2 = -2.7 \pm 0.5$ and $\log k_{-2} = 8.1 \pm 0.5$. Thus, k_{-2} is significantly less than the diffusion limit and comparable to the values observed when the oxidant is $[\text{Os}(\text{phen})_3]^{3+}$ and related species.¹⁴ Although the overall third-order process in the k_2 step likely occurs with a sequence of weak association steps preceding electron transfer, as has been discussed for the Os^{III} reactions,¹⁴ the details of these steps are not revealed by our results.

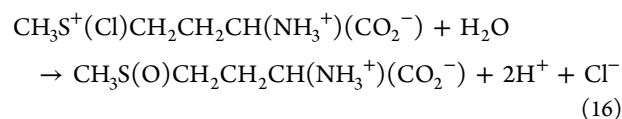
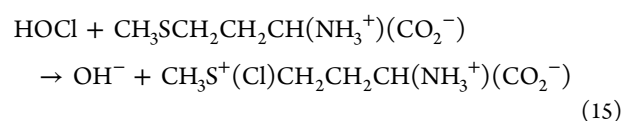
Association of the $\text{S}_2\text{O}_3^{\bullet-}$ radical with $\text{S}_2\text{O}_3^{2-}$ as in eq 5 is well established,^{22–25} occurs at an essentially diffusion-controlled rate, and has a favorable equilibrium constant (K_{rad}) of $7.7 \times 10^5 \text{ M}^{-1}$.

A value of -1.08 V has been estimated for $E^\circ(\text{S}_4\text{O}_6^{2-}/\text{S}_4\text{O}_6^{\bullet 3-})$,¹⁴ from which a value of 1×10^{34} can be calculated for equilibrium constant for reaction 6 (K_4). Because of this large driving force, it can be assumed that this electron-transfer reaction has a forward rate constant (k_4) that is essentially diffusion controlled. The combination of the rapid and favorable consumption of $\text{S}_2\text{O}_3^{\bullet-}$ through reaction 5 and the rapid and essentially irreversible reaction 6 makes reactions 3 and 4 effectively irreversible.

As is noted above, HOCl and SO_3^{2-} are implied as chain carriers in the reaction when methionine is absent. A hypothesis for the mechanism of the chain reaction is given by the following reactions:



The role of the methionine would be to terminate the chain by scavenging the HOCl



Oxygen-atom transfer is suggested as the initiation step in reaction 8. Although oxygen-atom transfer is unusual for ClO_2 , its occurrence has been documented in the reaction with

styrene,¹⁶ and it is suggested to occur also in the reaction with SO_3^{2-} .^{26,27} As is noted below, a value is suggested here for k_i that is less than the value of k_1 given above. As a result, the initiation step and its following reactions are insignificant when the reaction chain is inhibited.

The next step, oxidation of OSSO_3^{2-} by ClO_2 (eq 9), is entirely speculative; however, oxidation of OSSO_3^{2-} (or HOSSO_3^-) by various species has been suggested in several other reports.^{15,28–30} Oxidation of SO_3^{2-} by ClO_2 (eq 10) has a well-established rate constant k_{10} of $\sim 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$,^{27,31} it is thought to proceed via oxygen-atom transfer,^{26,27} although an electron-transfer mechanism has also been proposed.³¹ ClO is proposed to oxidize $\text{S}_2\text{O}_3^{2-}$ rapidly via electron transfer as in eq 11 on the basis that ClO is a strong one-electron oxidant with $E^\circ = 1.4 \text{ V}$.^{20,32} Reaction 12 is the well-known acid dissociation of HOCl with $\text{p}K_{\text{a,HOCl}} = 7.5$, which is treated here as a rapid equilibrium. Oxidation of $\text{S}_2\text{O}_3^{2-}$ by HOCl is depicted in eq 13 as a net oxygen-atom transfer reaction, but it quite likely proceeds through a sequence of Cl^+ transfer followed by hydrolysis, as is typical of HOCl reactions; on the basis of the Swain–Scott relationship developed for HOCl reactions by Gerritsen and Margerum,³³ we infer a rate constant for k_{13} that is nearly diffusion-controlled. A much lower value for k_{13} has been reported, but we suggest that the initial step was too fast to have been detected in that prior report.³⁴ The final step, reaction of $\text{S}_2\text{O}_3^{2-}$ with OSSO_3^{2-} to produce tetrathionate, is widely accepted to occur in the reaction of $\text{S}_2\text{O}_3^{2-}$ with H_2O_2 , although its rate constant is not yet established.^{35,36}

The above mechanism (eqs 3–6 and 8–14) with the indicated rate constants was used to simulate the reaction under conditions of $[\text{ClO}_2]_0 = 0.1 \text{ mM}$ and $[\text{S}_2\text{O}_3^{2-}] = 1 \text{ mM}$; the outcome was a sigmoidal decay of ClO_2 similar to that shown in Figure 1A. Concurrent with the loss of ClO_2 , the model predicts the formation of $\text{OS}_2\text{O}_3^{2-}$; then, this species converts to $\text{S}_4\text{O}_6^{2-}$ via reaction 14 with a half-life of $\sim 2 \text{ s}$. The simulation generates a final product mixture of $\text{S}_4\text{O}_6^{2-}$, SO_4^{2-} , ClO_2^- , and Cl^- consistent with the observations reported by Horváth and Nagypál.⁵ This model demonstrates that a plausible chain-reaction mechanism can explain the reaction kinetics; however, given the large number of unknowns in the model, it is quite likely that the true reaction mechanism differs significantly.

As is mentioned above, a previous mechanistic proposal for the $\text{S}_2\text{O}_3^{2-}/\text{ClO}_2$ reaction posited that the $\text{S}_4\text{O}_6^{3-}$ radical accumulates sufficiently to contribute significantly to the measured absorbance decay at 360 nm, causing the sigmoidal shape of the kinetic traces.⁵ Indeed, that model shows $\text{S}_4\text{O}_6^{3-}$ attaining a concentration of 0.25 mM under typical conditions (their figure 9). Such high concentrations do not occur in our model because of the large rate constant inferred for the strongly driven electron-transfer reaction of ClO_2^\bullet with $\text{S}_4\text{O}_6^{3-}$ (eq 6).

■ ASSOCIATED CONTENT

■ Supporting Information

Table S-1, a one-page listing of the values of k_{obs} as a function of $[\text{S}_2\text{O}_3^{2-}]$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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