# Kinetics and Mechanism of Styrene Epoxidation by Chlorite: Role of Chlorine Dioxide

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Ⓢ Supporting Information

ABSTRACT: An investigation of the kinetics and mechanism for epoxidation of styrene and *para*-substituted styrenes by chlorite at 25 °C in the pH range of 5–6 is described. The proposed mechanism in water and water/acetonitrile includes seven oxidation states of chlorine (−I, 0, I, II, III, IV, and V) to account for the observed kinetics and product distributions. The model provides an unusually detailed quantitative mechanism for the complex reactions that occur in mixtures of chlorine species and organic substrates, particularly when the strong oxidant chlorite is employed. Kinetic control of the reaction is achieved by the addition of chlorine dioxide to the reaction mixture, thereby eliminating a substantial induction period observed when chlorite is used alone. The epoxidation agent is identified as chlorine dioxide, which is continually formed by the reaction of chlorite with hypochlorous acid that results from ClO produced by the epoxidation reaction. The overall stoichiometry is the result of two competing chain reactions in which the reactive intermediate ClO reacts with either chlorine dioxide or chlorite ion to produce hypochlorous acid and chlorate or chloride, respectively. At high chlorite ion concentrations, HOCl is rapidly eliminated by reaction with chlorite, minimizing side reactions between HOCl and Cl_2 with the starting material. Epoxide selectivity (>90% under optimal conditions) is accurately predicted by the kinetic model. The model rate constant for direct reaction of styrene with $ClO_2(aq)$ to produce epoxide is $(1.16 \pm 0.07) \times 10^{-2}$ M^{-1} s^{-1} for 60:40 water/acetonitrile with 0.20 M acetate buffer. Rate constants for *para* substituted styrenes (R = $-SO_3^-$, −OMe, −Me, −Cl, −H, and $-NO_2$) with ClO_2 were determined. The results support the radical addition/elimination mechanism originally proposed by Kolar and Lindgren to account for the formation of styrene oxide in the reaction of styrene with chlorine dioxide.
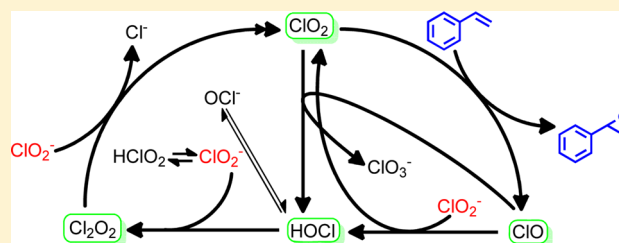
INTRODUCTION

Chlorine dioxide is a free radical known for its oxidative selectivity and stability in aqueous solution over a wide pH range. It is reversibly reduced to chlorite ion (eq 1, $E°$ = 0.954 V vs normal hydrogen electrode at 25 °C),[1−3] and much of the oxidative chemistry of chlorine dioxide has been attributed to

$$ClO_2(aq) + e^- \rightleftharpoons ClO_2^-(aq) \qquad (1)$$
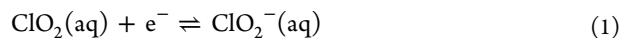
this one-electron transfer reaction.[4,5] The relatively low electrode potential leads to good oxidative selectivity when compared to indiscriminate radical oxidants such as OH. In contrast to Cl_2, ClO_2 does not hydrolyze in solution and is an active oxidant in the pH range of approximately 4−10.[6,7] Because of its selectivity and several other advantages of chlorine dioxide over chlorine, chlorine dioxide has become a widely used oxidant and disinfectant in industrial processes such as wood pulp bleaching, water treatment, and many others.[6,8−10] It also has excellent antimicrobial properties, which have led to its use as a decontaminant of medical devices, laboratory equipment, and persistent biological warfare agents in buildings.[6,8,10] Its usefulness as a cold sterilant has received increasing interest in recent years as a consequence of the emergence of new "superbugs" such as MRSA, norovirus, Legionella, and CRE.[11−16] The reactivity of pure chlorine

dioxide has been investigated for a variety of organic functional groups,[5,17−19] and separately the kinetics of chlorine dioxide formation in mixtures of other chlorine oxidation states have been studied by many researchers.[20−25]

Over the last 30 years, chlorine dioxide has largely replaced chlorine as the dominant agent for the bleaching of wood pulp because of its lower tendency to form chlorinated products in the oxidation of organic compounds,[8,9,26] significantly reducing the release of organochlorine pollutants into the environment. Several studies[27−29] concerning the reactions in "ClO_2 only" (elemental chlorine free (ECF)) pulp bleaching have shown that hypochlorous acid is produced as a byproduct of the reaction with lignin, and HOCl is now considered to be responsible for chlorination products in ECF pulp bleaching, although at a much-reduced level compared to traditional chlorine bleaching. Conjugated C−C double bonds are a common feature of organic chromophores in natural pigments in textiles and wood pulp,[30] so the present work contributes to an improved understanding of that complex oxidative chemistry.

As will be shown, the strong oxidant chlorite (ClO_2^-) is an important common reactant in mixtures that maximize the advantage of chlorine dioxide reactivity with certain functional groups (alkenes in the present case). Chlorite ion has a rich oxidative chemistry with organic compounds, most notably in the conversion of aldehydes to carboxylic acids.[31−35] Chlorite is also used in the textile bleaching industry, where it offers several advantages over chlorine bleach, but the chemistry of chlorite bleaching has not been investigated in appreciable detail to our knowledge.[36−38] Chlorite is not a direct oxidant for epoxidation of alkenes but can serve as a source of oxidizing equivalents.[39−41] One goal in the present work was to demonstrate how the selectivity and utility of chlorite can be enhanced as an oxidant in epoxidation applications via a thorough understanding of the reaction mechanism. We will show how the high oxidizing power of the chlorite ion can be successfully coupled to the selectivity of ClO_2 for the epoxidation of alkenes.

Introduction of chlorite into equilibrated chlorine solutions leads to formation of chlorine dioxide via oxidation of chlorite[22−25,42] and, to an extent dependent on acidity, the disproportionation of chlorous acid.[43−45] We have used the previous mechanisms for the former reaction proposed by Peintler and co-workers[23] and Margerum and co-workers[22] in our model. We show here that it is also necessary to incorporate other reactive oxidation states (specifically chlorine(II), chlorine(III), and chlorine(IV)) into a fully quantitative model for substrate oxidation that can account for product distributions under various initial conditions.

Three general pathways for chlorine dioxide oxidation reactions with electron-rich organic compounds have been proposed in the literature.[8,17,41,46] The initial reactions in chlorine dioxide oxidations have typically been described as either one-electron oxidations or hydrogen abstractions.[8,17,46−53] The former mechanism is commonly invoked for reactions with most organic compounds, leading to formation of radical organocations in reactions of the oxidant with neutral organic molecules. Hydrogen abstraction reactions are relatively uncommon since the OClO−H homolytic bond dissociation energy is rather low, estimated to be 71 kcal/mol.[54−56]

A less commonly invoked O atom transfer pathway of particular interest in the present study was proposed by Kolar and Lindgren in 1982 and consists of radical addition of ClO_2 to the substrate followed by elimination of the ClO radical.[41] In their investigation of the oxidation of excess styrene by chlorine dioxide, Kolar and Lindgren observed the formation of styrene oxide in addition to a number of chloro-substituted oxidation products and chlorinated styrenes. Under the conditions of their experiments, however, selectivity for styrene epoxidation was very low. Geng et al.[39] described an improved method for epoxidation of styrene by chlorite in a mixed solvent with heating and reported a yield of up to 77%. They showed that chlorine dioxide is likely to be the reactive species and cited the Kolar and Lindgren mechanism to explain the cis to trans isomerization observed in the epoxidation of *cis*-stilbene.

In 2010, Jangam and Richardson reported that high conversions (>99%) and selectivities as high as 89% could be achieved for oxidation of a variety of alkene substrates (including styrene) to epoxides at room temperature with excess chlorite ion in appropriate cosolvent/buffer mixtures.[40] They showed oxidation by chlorite ion alone proceeds only after a lengthy induction period, but this delay was eliminated

by introducing a small amount of chlorine dioxide in solution via either direct addition or reaction of an aldehyde with chlorite (which rapidly forms chlorine dioxide). The most likely mechanism was assumed to be that of Kolar and Lindgren, in which intermediate chlorine dioxide is the direct oxidant and chlorite is the ultimate source of oxidizing equivalents. Jangam and Richardson also proposed that hypochlorous acid formed in the reaction is responsible for the production of undesirable byproducts, but high concentrations of chlorite ion were used to react with hypochlorous acid and minimize these side reactions. It was noted that the proposed radical addition/elimination mechanism is analogous to that[57−59] for the epoxidation of alkenes by organoperoxyl radicals (ROO·), which are isoelectronic with ClO_2.

We investigated the detailed kinetics and mechanism of the selective epoxidation of styrene by excess chlorite in the pH range of 5−6. To build a complete mechanism for the epoxidation reaction it was first necessary to develop a quantitative model for the underlying chlorine reactions under our conditions. This chemistry is the source of complications in the interpretation of chlorine dioxide reactions with organic substrates, as chlorine species produced in the reactions can oxidize and/or chlorinate the substrate, producing numerous side products and reducing yields. A quantitative kinetic understanding of the chlorine chemistry allows us to account for reactions involving the formation of styrene oxide and various reaction byproducts. We propose a mechanism that can be used to predict selectivity for the epoxide and the distribution of side-products under a wide range of initial conditions. Notably, we find that it is necessary to account for seven oxidation states of chlorine (−I, 0, I, II, III, IV, and V), thereby vividly illustrating the well-known complexities of chlorine oxidation chemistry. We also provide evidence for the nature of the rate-determining step in the epoxidation reaction. The resulting mechanism and associated rate constants can serve as the basis for understanding and modeling complex reactions of chlorite/chlorine mixtures with other reactants, including biomolecules and pollutants.

■ EXPERIMENTAL SECTION

Reagents. Water was purified by using a Barnstead/Thermolyne E-Pure Model 04361 system to achieve a specific resistance of 18.2 MΩ cm. Aqueous chlorine dioxide solutions were prepared via the reaction of acetic anhydride and sodium chlorite in purified water.[60,61] The purity of aqueous ClO_2 solutions was assessed by ion chromatography, and the stock solutions were stored away from light and refrigerated between 0 and 4 °C. Chlorine dioxide concentrations were standardized by UV−visible spectrophotometry (Hewlett-Packard 8453) at 359 nm ($\varepsilon = 1250$ M^{-1} cm^{-1}) before each use in reaction solutions. Technical grade sodium chlorite (80%) was purchased from Fisher Scientific and recrystallized as described in the literature.[22,23] Its purity was verified by ion chromatography, and stock solutions were standardized spectrophotometrically at 260 nm ($\varepsilon = 154$ M^{-1} cm^{-1}).[60] Sodium hypochlorite (5% active chlorine, Fisher Scientific) was acidified, and hypochlorous acid was purified by fractional distillation under reduced pressure.[62,63] Stock solutions of HOCl were standardized spectrophotometrically at 292 nm ($\varepsilon = 362$ M^{-1} cm^{-1})[60] and buffered (acetic acid/sodium acetate) to obtain solutions of hypochlorous acid. All other chemicals/reagents (styrene, deuterated styrene, *p*-substituted styrene derivatives, acetic acid, sodium acetate, and naphthalene) were purchased from commercial suppliers, and their purity was assessed by NMR. No further purification was necessary, and fresh stock solutions were prepared prior to experiments. A Dionex Ion Chromatography (IC) System 1500 was

Table 1. Proposed Mechanism for the Oxidation of Styrene by Chlorite and Chlorine Dioxide

	Equilibrium	Equilibrium Constant [a]	References/Notes
(M1)	$Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- + H^+$	$K_{M1} = 6.1 \times 10^{-4}\ M^2$	23, 25, 42, b
(M2)	$HClO_2 \rightleftharpoons ClO_2^- + H^+$	$pK_a = 1.74$	25
(M3)	$HOCl \rightleftharpoons OCl^- + H^+$	$pK_a = 7.40$	25
(M4)	$CH_3COOH \rightleftharpoons CH_3COO^- + H+$	$pK_a = 4.75$	74

	Reaction	Rate Constant [c]	
(M5)	$ClO_2^- + HOCl + H^+ \longrightarrow Cl_2O_2 + H_2O$	$k_{M5} = (2.86 \pm 0.04) \times 10^6\ M^{-2}\ s^{-1}$ $k_{M5} = (9.41 \pm 0.09) \times 10^5\ M^{-2}\ s^{-1}$	22, 23, 25, d, e j
(M6)	$Cl_2O_2 + ClO_2^- \longrightarrow 2ClO_2 + Cl^-$	$k_{M6} = (8.1 \pm 0.3) \times 10^5\ M^{-1}s^{-1}$	23, 25, f
(M7)	$2HOCl + ClO_2^- \longrightarrow ClO_3^- + Cl_2 + H_2O$	$k_{M7} = (2.1 \pm 0.1) \times 10^3\ M^{-2}s^{-1}$	23, 25
(M8)	$ClO_2^- + Cl_2 \longrightarrow Cl_2O_2 + Cl^-$	$k_{M8} = 1.61 \times 10^6\ M^{-1}s^{-1}$	23, 25, b
(M9)	$Cl_2O_2 + H_2O \longrightarrow ClO_3^- + Cl^- + 2H^+$	$k_{M9} = 1.5 \times 10^1\ s^{-1}$	23, 25, g
(M10)	Ph⁀ + $ClO_2 \longrightarrow$ Ph epoxide + ClO	$k_{M10} = (1.17 \pm 0.02) \times 10^{-2}\ M^{-1}s^{-1}$	d
(M11)	Ph⁀ + $Cl_2 \longrightarrow$ Ph(Cl)(Cl)	$k_{M11} = 4.7 \times 10^7\ M^{-1}s^{-1}$	h, d
(M12)	Ph⁀ + $Cl_2 \longrightarrow$ Ph(Cl) + $Cl^- + H^+$	$k_{M12} = 1.3 \times 10^8\ M^{-1}s^{-1}$	h, d
(M13)	Ph⁀ + $HOCl + H^+ \longrightarrow$ Ph(OH)(Cl) + H^+	$k_{M13} = (1.5 \pm 0.4) \times 10^6\ M^{-2}s^{-1}$	d
(M14)	$ClO_2 + ClO + H_2O \longrightarrow ClO_3^- + HOCl + H^+$	$k_{M14} = (9.4 \pm 0.4) \times 10^9\ M^{-1}s^{-1}$ $k_{M14} = (3.9 \pm 0.2) \times 10^9\ M^{-1}s^{-1}$	21 d, e, i j
(M15)	$ClO_2^- + ClO \longrightarrow ClO_2 + OCl^-$	$k_{M15} = 9.4 \times 10^8\ M^{-1}s^{-1}$	75, i

[a]In aqueous solution. Values also used for mixed solvents (see text). [b]For 0.20 M acetate buffer, based on forward rate constant $k_{fM1} = 434\ M^{-1}\ s^{-1}$ (eq 4) and $k_{M8}/k_{fM1} = (3.7 \pm 0.2) \times 10^3\ M^{-1}$ (see text). [c]Unless otherwise noted, rate constants are estimated for 60:40 water/acetonitrile with 0.20 M acetate buffer at $T = 25\ °C$. Error limits are from literature cited or from this work as noted. Estimated standard error for reaction M5 obtained from fits to experimental data for the chlorite/hypochlorous acid reaction with no substrate. Estimated errors for reactions 10, 13, and 14 obtained from fits to substrate oxidation experimental data with $k_{M5} = 2.86 \times 10^6\ M^{-2}\ s^{-1}$. [d]This work. [e]Best fit simulation rate constant is given for 60:40 H_2O/CH_3CN and 0.20 M acetate buffer. Literature value for M14 in aqueous solution is $7 \times 10^9\ M^{-1}\ s^{-1}$. See text for other conditions. [f]$k_{M6}/k_{M9} = (5.4 \pm 0.2) \times 10^4\ M^{-1}$. [g]Set to this value in all fits. [h]Error limits on rate constant could not be estimated from fit because of low yield of product. The value given is an estimate used in fits. [i]M15 set to the literature value above in all fits. The estimated value of k_{M14}, therefore, is dependent on this rate constant as it determines the M14/M15 branching ratio (see text). [j]Value determined from experiments in D_2O with 0.20 M acetate buffer.

used to monitor the concentrations of anionic inorganic chlorine species (chlorite, chloride, and chlorate).

HOCl/ClO₂⁻ Reaction. The reactions of hypochlorous acid and sodium chlorite were carried out under excess chlorite conditions (4.74×10^{-3} M sodium chlorite and 1.50×10^{-4} M hypochlorous acid) in water or 60/40 water/acetonitrile. Solutions were prepared in a 1.0 cm path length quartz cuvette, with a Teflon stopper and a total reaction volume of 3.2 mL. Reaction temperatures were maintained at $25.0 \pm 0.1\ °C$ via a Fisher Scientific Isotemp Refrigerated Circulator (Model 901) and a thermostated cell holder in a Hewlett-Packard 8453 UV−visible spectrophotometer. Reactions were investigated in 0.50 M sodium acetate in water, 0.20 M sodium acetate in water, and 0.20 M sodium acetate in a water/acetonitrile mixture at three pH values (5.25, 5.55, and 5.95−stock solutions of sodium acetate were prepared and buffered by adding the appropriate amount of acetic acid). The reactions were initiated by the addition of sodium hypochlorite (in 0.50 or 0.20 M sodium acetate) to the reaction solution. Reaction kinetics were evaluated by monitoring the production of chlorine dioxide by UV−visible spectrophotometry at 359 nm. Control experiments confirmed that photochemical decomposition in the spectrophotometric beam was negligible under our conditions.

Styrene Oxidations. The reaction mixture for the oxidation of styrene was 0.005−0.075 M sodium chlorite, 0.0125 M substrate, and 0.200 M sodium acetate in a 60:40 water/acetonitrile solvent.

Naphthalene (5 mM) was added to the solution as an internal standard for quantitative GC analysis. Solutions were buffered (by adding the necessary amount of acetic acid), and the pH was verified by a Fisher Scientific Accumet Basic model AB15 digital pH meter equipped with a Thermo Orion 911600 electrode. Solution temperatures were maintained at $25.0 \pm 0.1\ °C$ throughout the reactions. The reactions were initiated with the addition of chlorine dioxide to the solution to achieve a final concentration of ~10 mM. Reactant and product concentrations were analyzed over a 6 h period at regular intervals. Diluted aliquots from the reaction mixture were analyzed to determine organic and inorganic reactant/product concentrations over the course of the reaction. Chlorite, chloride, and chlorate were monitored by ion chromatography. UV−visible spectrophotometry was used to monitor the chlorine dioxide concentration at 359 nm. The organic species (styrene, styrene oxide, and various chlorinated products) were characterized by gas chromatography−mass spectrometry (GC-MS) and by chromatographic comparison with pure standards by a Varian model CP-3800 gas chromatograph (GC) equipped with a flame ionization detector and a J & W Scientific DB-35MS Capillary Column, 0.5 μm, 30m × 0.53 mm. Diluted aliquots from the reaction mixture were analyzed to determine the inorganic reactant and product concentrations as described above. Organic species concentrations were calculated using a ratio of the styrene peak area to the naphthalene (internal standard) peak area:

$$[\text{styrene}]_t = 12.5 \text{ mM} \times \left(\frac{\text{styrene peak area}_t}{\text{naphthalene peak area}_t} \right.$$

$$\left. \div \frac{\text{styrene peak area}_0}{\text{naphthalene peak area}_0} \right)$$

$$[\text{product}_a]_t = (12.5 \text{ mM} - [\text{styrene}]_t)$$

$$\times \left(\frac{\text{product}_a \text{ peak area}_t}{\text{total product peak area}_t} \right)$$

4-Styrenesulfonate Oxidations. The oxidation of 4-styrenesulfonic acid was studied in D_2O solution, and the reaction mixture contained 0.010−0.075 M sodium chlorite, 0.0125 M acetonitrile (used as an internal standard), and 0.200 M sodium acetate buffered at pH 5.25 with the addition of acetic acid. Before the addition of substrate to the reaction mixture, approximately 0.010 M chlorine dioxide was generated in situ by the reaction of 0.005 M benzaldehyde and 0.015 M sodium chlorite.[19,64] The oxidation reaction was initiated by the addition of approximately 0.0125 M sodium 4-styrenesulfonate, and the reaction was monitored over a 5−7 h period at regular intervals. Inorganic products were monitored as described for styrene reactions. Organic reactant and product concentrations were analyzed by a 500 MHz Inova NMR spectrometer, and quantitative data were obtained using a ratio of the integrations of the reactant/products to the internal standard (acetonitrile, 0.0125 M).

Para-Substituted Styrenes. *p*-Chlorostyrene, *p*-methylstyrene, *p*-methoxystyrene, and *p*-nitrostyrene were investigated in 60:40 water/acetonitrile with $[ClO_2^-]_0 = 75$ mM, pH 5.25 sodium acetate buffer (200 mM in water), and $[ClO_2]_0 = 1.5$ mM (*p*-methoxystyrene), 20 mM (*p*-nitrostyrene), or 10 mM (*p*-chlorostyrene, *p*-methylstyrene); substrate concentrations were in the 5−12 mM range, as required to achieve solution homogeneity. The rate of consumption of substrate, the formation of organic products, and the rate of formation of ClO_2 were typically monitored by GC and UV−visible spectrophotometry, respectively (ClO_2 concentrations for nitrostyrene could not be determined due to the overlap of absorbance due to the substrate). Second-order rate constants for the rate equation $R = k [ClO_2]$-$[\text{styrene}]$ were estimated by determining the reaction rates at multiple time intervals that had essentially constant $[ClO_2]$ and averaging. As a check, the mechanism of Table 1 was also used to model the reaction curves numerically, and the rate constants for M10−M12 were optimized to achieve the best fit to the concentration versus time curves for all of the substrates (this method alone was used to obtain the *p*-nitrostyrene rate constant). For comparison, the reactions were also investigated under different conditions in a solvent that allows higher substrate concentrations and uses an alternative buffer, with $[ClO_2^-] = 170$ mM, pH 7 phosphate buffer (100 mM in water), a 20:55:25 acetonitrile/buffer/ethanol mixed solvent, 25 mM substrate, and small amounts (~2 mM) of ClO_2 to eliminate the induction period.

Numerical Methods. All kinetic models were analyzed using numerical methods to produce predicted concentration versus time curves for reactants, products, and intermediates. Gear integration was used,[65] and the numerical integration models were supplemented by fitting routines based on a combination of simplex[66] and Marquardt[67] optimizations to determine the best fit rate constants. Estimated parameter errors (for model rate constants) were determined using numerical matrix methods.[68] Further details are given in the Supporting Information.

■ RESULTS AND DISCUSSION

The HOCl/ClO_2^- Reaction. Reactions involving multiple chlorine oxidation states in solution result in significant complexity in building a kinetic model for chlorite oxidations of organic substrates. We began our modeling with a review of the much-investigated reaction of hypochlorous acid (HOCl)

and chlorite ion.[22−25] This step is central to the chain mechanism proposed by Kolar and Lindgren[41] and is of particular importance to our study of the selective oxidation of styrene under excess chlorite conditions described in detail below.

HOCl is formed at equilibrium by the well-known hydrolysis of Cl_2 (eq 2). The reaction of

$$Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- + H^+ \tag{2}$$

$$2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O \tag{3}$$
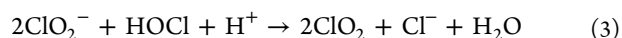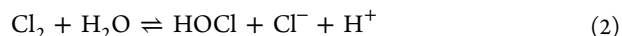
HOCl with ClO_2^- produces chlorine dioxide (eq 3), thereby reducing the concentration of HOCl in solution and increasing the availability of the epoxidizing agent ClO_2. It was our hypothesis that the resulting low steady-state concentration of HOCl, when compared to that of chlorine dioxide, reduces the probability of side reactions of HOCl with the substrate that would otherwise produce undesirable chlorinated byproducts.[41] In addition, the lessened formation of Cl_2 from HOCl and Cl^- by the reverse of eq 2 would presumably lead to reduced amounts of other chlorination products. The addition of chlorite to suppress HOCl side reactions in pulp bleaching has been proposed by Ni and co-workers.[69]

The kinetics and stoichiometry of the HOCl/ClO_2^- reaction and the related reaction of Cl_2 with ClO_2^- have been described extensively in the literature.[22,23,25,70−73] In 1990 Peintler et al. proposed a mechanism that modeled their experimental results for chlorine dioxide formation under a variety of initial conditions.[23] In 2008, the 1990 mechanism was expanded by Kormányos et al.[25] to include additional steps involved in catalysis by chloride ion. Margerum and co-workers have reported the large impact of buffer catalysis on the rate of chlorine dioxide formation (specifically for acetic acid/acetate)[22] and the rapid reaction of Cl_2 with chlorite.[42] In the pH range employed in the present work, the contribution of the acid-catalyzed disproportionation of chlorite to the production of ClO_2 is negligible.[43−45]

The mechanism we use for the HOCl/ClO_2^- reaction is summarized in Table 1 (steps M1−M9). The equilibrium constant for reaction M1 was set at $K_{M1} = 6.1 \times 10^{-4}$ M^2. The value of the forward rate constant for equilibrium M1 (k_{fM1}) was calculated based on the work of Nicoson and Margerum[42] that shows the rate of chlorine disproportionation at 25.0 °C is dependent on the acetate concentration, as summarized in eq 4.

$$k_{fM1} = 22 \pm 4 \text{ s}^{-1} + 2060 \pm 30[\text{Ac}^-] \text{ s}^{-1} \tag{4}$$

The rate constant for reaction M8 was determined from the ratio of $k_{M8}/k_{fM1} = (3.7 \pm 0.2) \times 10^3$ M^{-1} as determined by Nicoson and Margerum.[42] The rate constant for reaction M9 is set at 15 M^{-1} s^{-1}, and k_{M6} was calculated using the ratio of $k_{M6}/k_{M9} = (5.4 \pm 0.2) \times 10^4$ M^{-1}.[25] For reversible reactions the corresponding reverse reaction rate constants were set by the value of the equilibrium constants.

Numerical integration of steps M1−M9 reproduced the calculated concentration versus time curves in the work of Peintler et al. (1990) and Kormányos et al. (2008)[23,25] when ClO_2^- is in excess and no initial chloride is present. Although the Kormányos et al. mechanism incorporates the impact of Cl^- on the rate constant for the direct reaction of HOCl with $HClO_2/ClO_2^-$, we used the 1990 Peintler et al. mechanism because the generation of Cl^- in styrene epoxidation has a negligible effect on the overall reaction rates for the disappearance of reactants and generation of products (chloride

catalysis is significant in the overall rate only at much higher initial concentrations of chloride). Acetate/acetic acid (M4) is used only as a buffer in our mechanism and was included in the simulations. The reactions in the catalysis of M5 by acetic acid described in detail by Jia et al.[22] are not explicitly included in our reaction steps but are modeled by appropriate choices for the rate constants M1, M5, and M8, as discussed below. Therefore, the choice of pK_a for acetic acid[74] is not crucial to the mechanism used here.

As described below the conditions for the styrene epoxidation (i.e., addition of a cosolvent, decreased buffer concentration) required us to reset the value of the rate constant for reaction M5 in Table 1 for our reaction conditions. The mechanism of the sodium acetate/acetic acid effect on reaction M5 was investigated by Jia et al.[22] We used the mechanism of Jia et al. to assess the appropriateness of a single k_{M5} value to fit the observed yield of chlorine dioxide and its rate of production under the conditions used for the epoxidation of styrene. While an increase in pH will decrease [HAc] with [Ac$^-$] constant, thereby altering the value of k_{M5} according to the rate laws of Jia et al., the extent to which the value of the effective rate constant for M5 is altered within the pH range from 5.25 to 5.95 is <10%. Therefore, for simplicity, a single value of k_{M5} was used to fit our experimental data, as in the work of Peintler et al.[23] Note that models for the reaction outside of the pH range of this study would require inclusion of the effects of pH on acetate catalysis.

Although we did initial comparisons to the Peintler et al. study at [Ac$^-$] = 0.50 M (see Supporting Information), the epoxidation reactions required an acetate buffer concentration of 0.20 M. We find k_{M5} = (9.41 ± 0.09) × 10^5 M^{-2} s^{-1} for [Ac$^-$] = 0.20 M based on fits to our experimental data; Figure 1 shows the fits obtained by using this value. The error limits from fits for k_{M5} reflect the statistical analysis from the least-squares model but do not account for the expected variation with pH; therefore, it would be appropriate to consider the
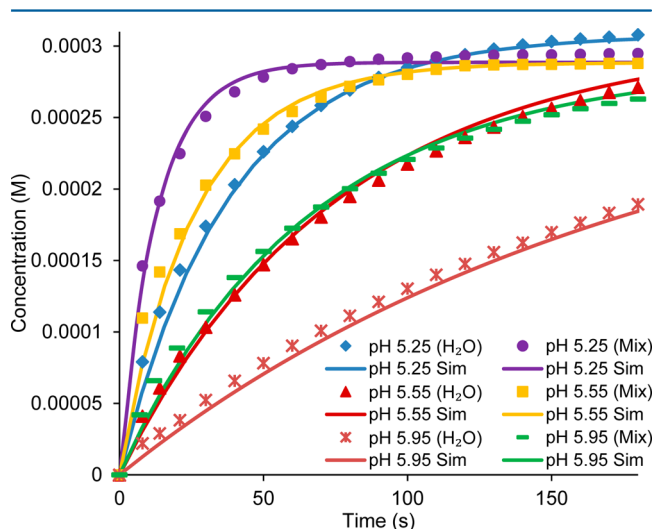
actual uncertainty in the rate constant to be around 10% in the pH range of 5−6.

Effect of Solvent Composition. Under the conditions described above for the HOCl/ClO$_2^-$ reactions (i.e., aqueous sodium acetate buffer) a heterogeneous mixture resulted upon addition of styrene and naphthalene (internal GC standard) to the reaction solution. A homogeneous solution can be obtained by using a cosolvent of 60:40 water/acetonitrile and a lower concentration of buffer (0.20 M acetate). Since the rate of chlorine dioxide production was observed to increase in acetonitrile/water compared to water, it was also necessary to accommodate this acceleration in the kinetic model.

To account for the cosolvent reaction conditions, only the rate constant for reaction M5 was adjusted with the understanding that the resulting k_{M5} value effectively incorporates any shift in the relevant acid−base equilibria (M1−M3) resulting from addition of acetonitrile. A value of k_{M5} = (2.86 ± 0.04) × 10^6 M^{-2} s^{-1} results from a fit of the mechanism to all experimental results in the mixed solvent reactions (Figure 1). Although limited in useful pH range, the mechanism successfully models the kinetics and stoichiometry of the HOCl/ClO$_2^-$ reaction in the mixed solvent used for epoxidations in this work.

Epoxidation of Styrene. The reaction of styrene with chlorite was investigated in buffered 60:40 water/acetonitrile with [Ac$^-$] = 0.20 M. The characteristic induction period for chlorite oxidation was avoided by adding ClO$_2$ to the reaction mixture.[40] With excess chlorite, styrene oxide is the major organic product, and small amounts of 1,2-dichloroethylbenzene, 2-chloro-1-phenyl ethanol, and 2-chlorovinylbenzene are also produced (an example GC is shown in Supporting Information). Although phenylacetaldehyde was observed by GC, it is well-known that rearrangement of styrene oxide to phenylacetaldehyde occurs in the injector port.[76,77] NMR was used to monitor the reaction over the course of 6 h under the same conditions (in D$_2$O/d$_3$-acetonitrile) to determine if the aldehyde was also produced as a result of styrene oxidation by chlorite. Phenylacetaldehyde was not observed in the NMR analysis, confirming that the aldehyde observed by GC is a result of styrene oxide rearrangement in the injector port. Aldehyde and epoxide peaks in GC were therefore combined to give the epoxide yield.

Results for a typical kinetic experiment at high [ClO$_2^-$] (74 mM) and pH 5.25 are shown in Figures 2 and 3. Chloride and chlorate were the major inorganic chlorine products, and the concentration of chlorine dioxide rose slowly from the initial concentration over the course of the reaction. See Supporting Information for kinetic data and fits at pH 5.88.

The mechanism of Table 1 was used to fit the styrene oxidation kinetics by using k_{fM1} = 434 s^{-1} (eq 4), k_{M5} = 2.86 × 10^6 M^{-2} s^{-1} (as obtained above), and k_{M8} = 1.61 × 10^6 M^{-1} s^{-1} (k_{M8} = 3.7 × 10^3 M^{-1} k_{fM1}). In addition to the previously established inorganic reactions, reactions were added producing styrene oxide, 1,2-dichloroethylbenzene, 2-chlorovinylbenzene, and 2-chloro-1-phenyl ethanol (M10−M13 in Table 1, respectively).

Fitting the pH dependence of reaction M13 required acid catalysis, which is common for chlorohydrin formation from HOCl and alkenes.[78,79] The reactions of HOCl and Cl$_2$ with hydrocarbons can involve a number of reactive intermediates[78,80] so the reactions M10−M13 must be considered tentative; however, as discussed below they are adequate to
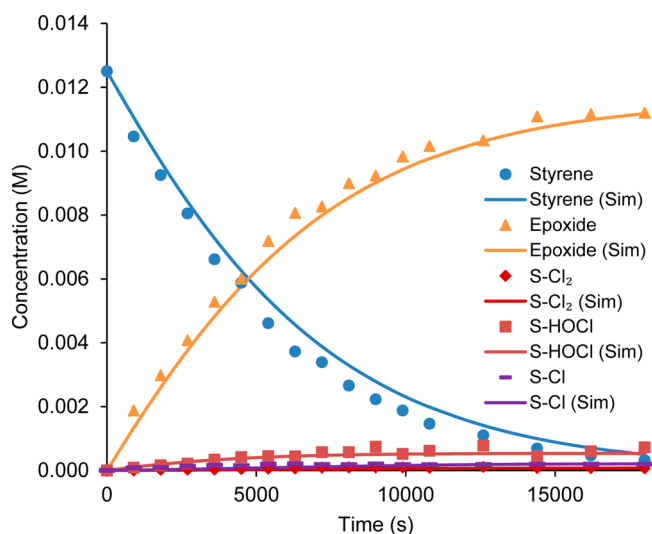

Figure 1. Experimental (symbols) and simulated (solid lines) [ClO$_2$] vs time in 100% water or 60:40 water/acetonitrile (mix). Conditions (100% H$_2$O): [ClO$_2^-$]$_0$ = 4.74 mM, [HOCl]$_0$ = 0.161 mM, [Ac$^-$] = 200 mM; simulations obtained using k_{M5} = 9.41 × 10^5 M^{-2} s^{-1}. T = 25 °C. Conditions (60:40 H$_2$O/CH$_3$CN): [ClO$_2^-$]$_0$ = 4.74 mM, [HOCl]$_0$ = 0.15 mM, [Ac$^-$] = 200 mM; simulated data obtained using k_{M5} = 2.86 × 10^6 M^{-2} s^{-1}. T = 25 °C. The pH values are those of the aqueous buffer used in the mixed solvent.

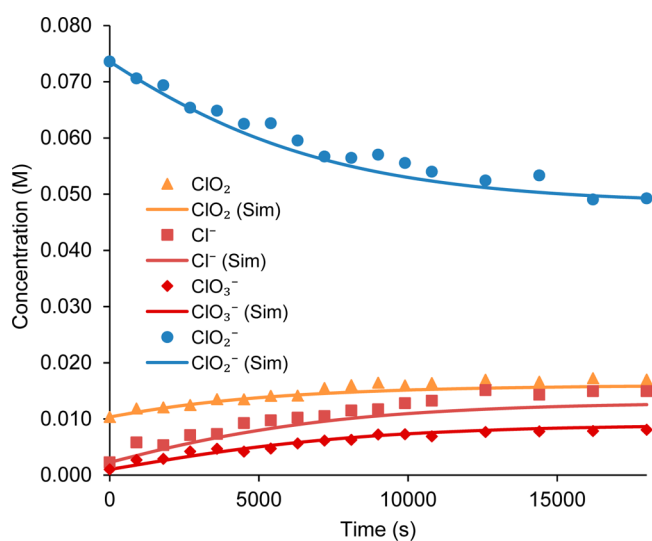**Figure 2.** Experimental (symbols) and simulated (solid lines) organic reactant/product concentrations: $[ClO_2]_0$ = 10.1 mM, $[ClO_2^-]$ = 73.6 mM, [styrene] = 12.5 mM, $[Ac^-]$ = 200 mM buffered at pH 5.25; 60:40 water/acetonitrile mixed solvent; simulated data obtained using k_{M5} = 2.86 × 10⁶ M^{-2} s^{-1}. T = 25 °C. The pH value is that of the aqueous buffer used in the mixed solvent. Abbreviations: S−Cl2 = 1,2-dichloroethylbenzene, S-HOCl = 2-chloro-1-phenyl ethanol, and S−Cl = 2-chlorovinylbenzene.

Figure 3. Experimental (symbols) and simulated (solid lines) inorganic reactant/product concentrations: $[ClO_2]_0$ = 10.1 mM, $[ClO_2^-]$ = 73.6 mM, [styrene] = 12.5 mM, $[Ac^-]$ = 200 mM buffered at pH 5.25; 60:40 water/acetonitrile mixed solvent; simulated data obtained using k_{M5} = 2.86 × 10⁶ M^{-2} s^{-1}. T = 25 °C. The pH value is that of the aqueous buffer used in the mixed solvent.

model the observed byproduct distributions in these chlorite oxidations.

Two additional known reactions were added to model the fast reactions of the chlorine oxide radical with chlorine dioxide and chlorite (M14 and M15). Changes to the ratio of the literature rate constants[21,75] for these reactions were allowed to best fit the experimental data. For purposes of the fits, the value of k_{M15} was set to a fixed value (Table 1) and k_{M14} was optimized.

All reactions M1−M15 were used to obtain simulated concentration versus time profiles via numerical integration,

and rate constants were obtained by optimization for reactions M10−M13 to give the best fit to the experimental data (Table 1). The observed stoichiometries of the reactions were as predicted by the mechanism, and observed oxidation electron equivalents for all inorganic and organic species were equal to reduction electron equivalents within experimental errors. All optimizations and statistical analyses for rate constant parameters were done by fitting all measured reactant and product concentrations in all data sets (for various pH values and initial concentrations of reactants) simultaneously. Uncertainties for the styrene reaction rate constants were deduced using statistical methods described in the Supporting Information are reported in Table 1; for reactions with low product yield (chlorinations), the estimated rate constants have large uncertainties, and the values reported in Table 1 are simply those found in the fitting routines and should be considered rough estimates. The ratio of k_{M14}/k_{M15} in the optimized fit was found to be 10.0 ± 0.4, which is close to the literature value for k_{M14}/k_{M15} of ∼7 from independent determinations of the rate constants in aqueous solutions.[21,75]

According to the mechanism proposed by Kolar and Lindgren[41] for the epoxidation of styrene, the reaction of 1 equiv of chlorine dioxide adds to the vinyl group, producing a radical intermediate (**1**).

1
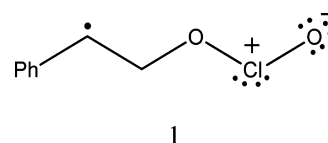
Free rotation around the C−C bond in **1** has been invoked in prior studies[39,40] to explain the observed isomerization in the epoxidation of *cis*-stilbene to a mixture of *cis*- and *trans*-stilbene oxide. The intermediate undergoes elimination of the chlorine oxide radical (ClO) to form the epoxide (M10) as shown in Figure 4.[41] Alternatives to this mechanism for this step are considered in a later section.
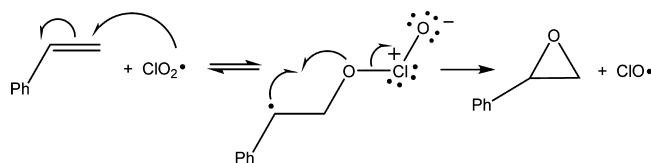

Figure 4. Epoxidation of styrene by radical addition/elimination mechanism. This mechanism for reaction M10 as an elementary step is supported by the low sensitivity of the reaction rate to para substituents on the styrene.

On the basis of the proposed mechanism, decreasing the initial amount of chlorite in the reaction should increase the extent of HOCl reaction with substrate via reaction M13, resulting in decreased selectivity for the epoxide. For example, with 5 mM initial chlorite the observed and simulated results (Figure 5) show the expected decrease in the amount of epoxide produced and an increase in 2-chloro-1-phenyl ethanol, and the selectivity for epoxide is only ∼60%.

The corresponding inorganic data and fits (Figure 6) for a low chlorite reaction show chlorate as the major product instead of chloride, which is the dominant product with excess chlorite. In addition, the initial chlorine dioxide is consumed during the low chlorite reaction, while, in contrast, chlorine
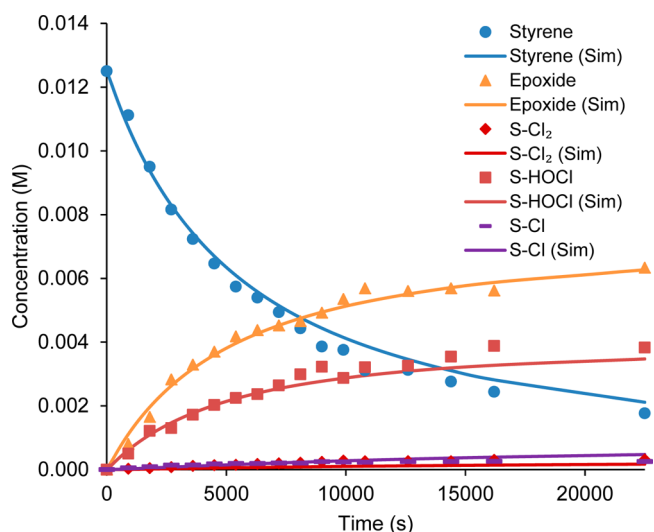
Figure 5. Experimental (symbols) and simulated (solid lines) organic reactant/product concentrations: $[ClO_2]_0$ = 9.73 mM, $[ClO_2^-]$ = 5.06 mM, [styrene] = 12.5 mM, $[Ac^-]$ = 200 mM buffered at pH 5.25; 60:40 water/acetonitrile mixed solvent; simulated data obtained using k_{M5} = 2.86 × 10^6 M^{-2} s^{-1}. T = 25 °C. The pH value is that of the aqueous buffer used in the mixed solvent. Abbreviations: S−Cl2 = 1,2-dichloroethylbenzene, S-HOCl = 2-chloro-1-phenyl ethanol, and S−Cl = 2-chlorovinylbenzene.
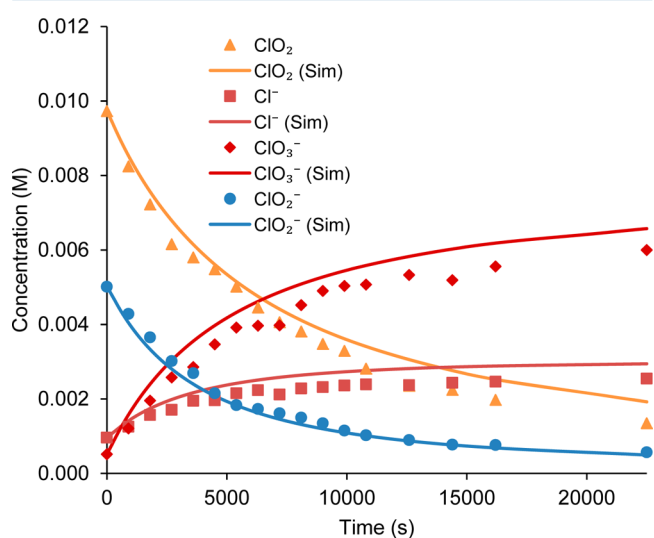

Figure 6. Experimental (symbols) and simulated (solid lines) inorganic reactant/product concentrations: $[ClO_2]_0$ = 9.73 mM, $[ClO_2^-]$ = 5.06 mM, [styrene] = 12.5 mM, $[Ac^-]$ = 200 mM buffered at pH 5.25, 60:40 water/acetonitrile mixed solvent; simulated data obtained using k_{M5} = 2.86 × 10^6 M^{-2} s^{-1}. T = 25 °C. The pH value is that of the aqueous buffer used in the mixed solvent.

dioxide is generated under excess chlorite conditions (Figure 3).

Epoxidation of 4-Styrenesulfonic Acid. The oxidation of 4-styrenesulfonic acid by ClO_2 under high and low ClO_2^- conditions was examined in aqueous solution to remove the influence of added nonaqueous solvent. An induction period was eliminated by using benzaldehyde to produce ClO_2 via its reaction with chlorous acid[19,64] in situ prior to the initiation of the reaction. The organic reactants and products were monitored by NMR; therefore, D_2O was used as the solvent. To assess the effect of D_2O on the background inorganic chlorine reactions, the $HOCl/ClO_2^-$ reaction was carried out as described above but in D_2O. A comparison of the rate of ClO_2 production in H_2O and D_2O demonstrated that D_2O had a negligible effect on the background chlorine kinetics. Additionally, calculations of pH and pK_a values in D_2O[81] (vs H_2O) revealed only small variations from H_2O to D_2O. Therefore, it was only necessary to change k_{MS} to 9.41 × 10^5 M^{-2} s^{-1}, reflecting the fit for the $HOCl/ClO_2^-$ reaction in water with 0.20 M Ac^- buffer as described above, and to optimize the substrate-containing steps (M16 and M17 in Table 2) and M14 to simulate the experimental data.

The epoxide (4-oxirane-phenylsulfonate) and chlorohydrin (4-(2-chloro-1-hydroxyethyl)phenylsulfonate) products were observed for the oxidation of 4-styrenesulfonate along with 4-(1,2-dihydroxyethyl)phenylsulfonate (the hydrolysis product of the epoxide). Other chlorination products were not observed, but the expected yields would not be measurable via NMR in light of the lower sensitivity compared to GC. Good fits of the available experimental data were obtained for both the excess and low chlorite conditions (see Figures 7 and 8 and the Supporting Information) using the rate constants in Table 2 in place of M10 and M13. The ratio of k_{M14}/k_{M15} under the aqueous reaction conditions was found to be 4.2 ± 0.2 (somewhat lower than the value of 10.4 in the 60:40 mixed solvent used in the styrene oxidations). For purposes of fitting M16, the observed amounts of epoxide and its hydrolysis product (diol) were combined. The epoxide (4-oxirane-phenylsulfonate) selectivities under low and excess chlorite conditions are ~60% and 90%, respectively.

Mechanism of Styrene Epoxidation. The overall proposed mechanism is illustrated in Figure 9. The main goal of our study was to model the much higher selectivity for the room-temperature styrene epoxidation observed when chlorite is in large excess, as observed in our previous work.[40] Under the optimal conditions with high chlorite concentrations described above, the reaction is >90% selective for epoxide. Jangam and Richardson[40] report a similar selectivity of 89% for styrene oxide under their conditions.

Table 2. 4-Styrenesulfonic Acid Reactions and Rate Constants in 100% Aqueous Solution

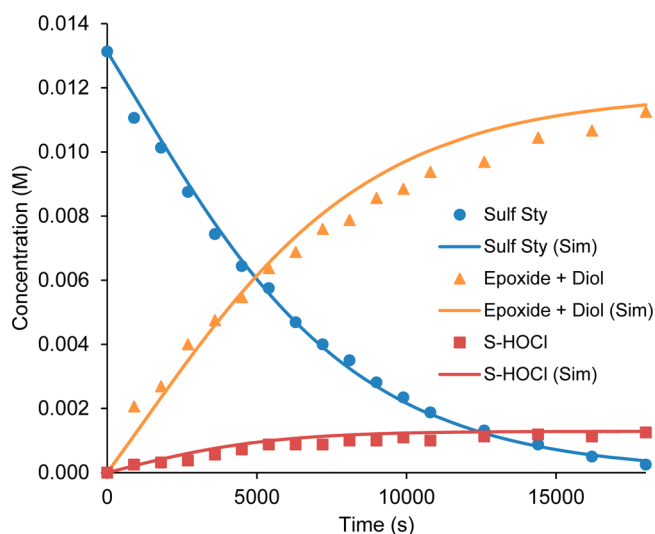|	Reaction	Rate Constant (k)
(M16)	^-O_3S⟨styrene⟩ + ClO_2 ⟶ ^-O_3S⟨epoxide⟩ + ClO / ^-O_3S⟨diol, OH OH⟩	(1.31 ± 0.02) x 10^{-2} M^{-1}s^{-1}
(M17)	^-O_3S⟨styrene⟩ + HOCl + H+ ⟶ ^-O_3S⟨chlorohydrin, OH Cl⟩ + H+	(1.32 ± 0.07) x 10^6 M^{-2}s^{-1}

Figure 7. Experimental (symbols) and simulated (solid lines) organic reactant/product concentrations: $[ClO_2]_0$ = 7.39 mM, $[ClO_2^-]$ = 72.1 mM, [4-styrenesulfonic acid] = 13.1 mM, $[Ac^-]$ = 200 mM buffered at pH 5.25 ; 100% D_2O; simulated data obtained using k_{M5} = 9.41 × 10^5 M^{-2} s^{-1}. T = 25 °C. Abbreviation: S-HOCl = 4-(2-chloro-1-hydroxyethyl) phenylsulfonate). Epoxide concentration is sum of epoxide and the diol hydrolysis product.
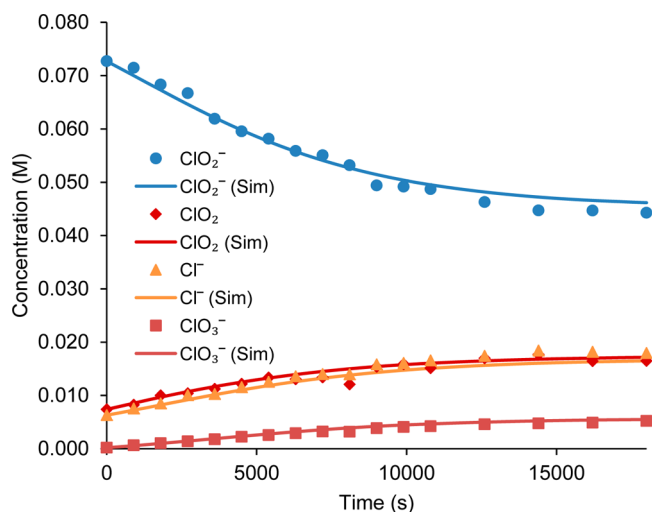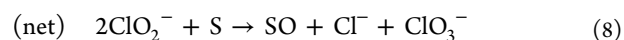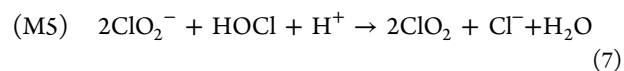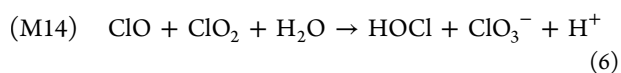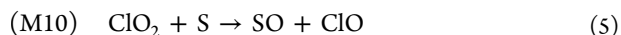

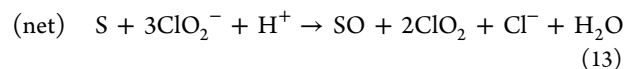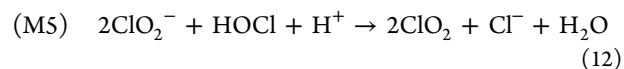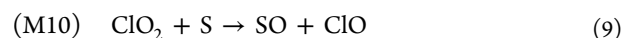**Figure 8.** Experimental (symbols) and simulated (solid lines) inorganic reactant/product concentrations: $[ClO_2]_0$ = 7.39 mM, $[ClO_2^-]$ = 72.1 mM, [4-styrenesulfonic acid] = 13.1 mM, $[Ac^-]$ = 200 mM buffered at pH 5.25; 100% D_2O; simulated data obtained using k_{M5} = 9.41 × 10^5 M^{-2} s^{-1}. T = 25 °C.

In our complete mechanism the epoxidation by chlorite occurs by *two* chain reactions. In the original Kolar and Lindgren proposal, ClO reacts only with ClO_2 (M14). For reactions that included chlorite ion (at relatively low concentrations) Kolar and Lindgren[41] proposed the following chain reaction (eqs 5−7), where S = styrene and SO = styrene oxide, with the net reaction forming equal amounts of chloride and chlorate (eq 8).

$$(M10) \quad ClO_2 + S \rightarrow SO + ClO \tag{5}$$

$$(M14) \quad ClO + ClO_2 + H_2O \rightarrow HOCl + ClO_3^- + H^+ \tag{6}$$

$$(M5) \quad 2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O \tag{7}$$

$$(net) \quad 2ClO_2^- + S \rightarrow SO + Cl^- + ClO_3^- \tag{8}$$

The second chain (eqs 9−12) arises as a consequence of the higher chlorite concentration used in our conditions, diverting a substantial fraction of ClO to reaction with chlorite (M15).

$$(M10) \quad ClO_2 + S \rightarrow SO + ClO \tag{9}$$

$$(M15) \quad ClO + ClO_2^- \rightarrow ClO_2 + OCl^- \tag{10}$$

$$(M3) \quad OCl^- + H^+ \rightarrow HOCl \tag{11}$$

$$(M5) \quad 2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O \tag{12}$$

$$(net) \quad S + 3ClO_2^- + H^+ \rightarrow SO + 2ClO_2 + Cl^- + H_2O \tag{13}$$

Reaction M15 was suggested by Kolar and Lindgren[41] as an alternative pathway in high chlorite conditions. The net reaction of the second chain (eq 13) produces chloride as the sole inorganic byproduct. The difference in predicted stoichiometries for the chlorine products in eqs 8 and 13 allows a quantitative assessment of the relative contributions of the two chains in our study. The net reaction of eq 8 does not consume ClO_2, and eq 13 produces the increase in ClO_2 noted for high initial chlorite reactions.

The branching fraction based on the relative rates of steps M14 and M15 is affected by the concentrations of ClO_2 and ClO_2^-. The ratio of $R_{M15}/(R_{M15} + R_{M14})$ when half of the substrate has been consumed ($[styrene]$ = $[styrene]_0/2$) is shown as a function of initial values for $[ClO_2]_0$ and $[ClO_2^-]_0$ in Figure 10. As $[ClO_2]_0$ values increase the branching fraction generally decreases due to increased availability of ClO_2 for reaction M14 (eq 6). At very low values of $[ClO_2^-]_0$ (i.e., such as 5 mM chlorite in Figure 10) with higher $[ClO_2]_0$ values, reaction M14 dominates since chlorine dioxide is more readily available to react with the ClO intermediate. However, with both low $[ClO_2]_0$ (<5 mM) and low $[ClO_2^-]_0$ (5 mM) the reaction does not go to completion, and reaction M15 eventually dominates. The small amount of ClO_2 initially present will react rapidly with the starting material, leaving ClO_2^- in excess of ClO_2 and, therefore, making the ClO_2^- more readily available to react with the ClO intermediate (eq 10) when half of the styrene has been consumed.

The overall stoichiometry depends on the relative contributions of eq 8 and eq 13 to the reaction. The rates of these two reactions under our highest chlorite conditions are roughly equal, thereby accounting for the higher concentrations of Cl^- compared to ClO_3^- in the final reaction mixtures for high chlorite reactions (Figure 3, for example).

The high selectivity for epoxidation in a large excess of chlorite is attributed to the reaction of ClO_2^- with HOCl, ultimately forming chlorine dioxide and markedly lowering the concentration of HOCl during the reaction. This diversion to the ClO_2 pool reduces the rate of side reaction M13 and thereby reduces formation of the resulting byproducts to <10% of the overall conversion. The branching fraction $R_{M5}/(R_{M5}+R_{M13})$ via eq 14
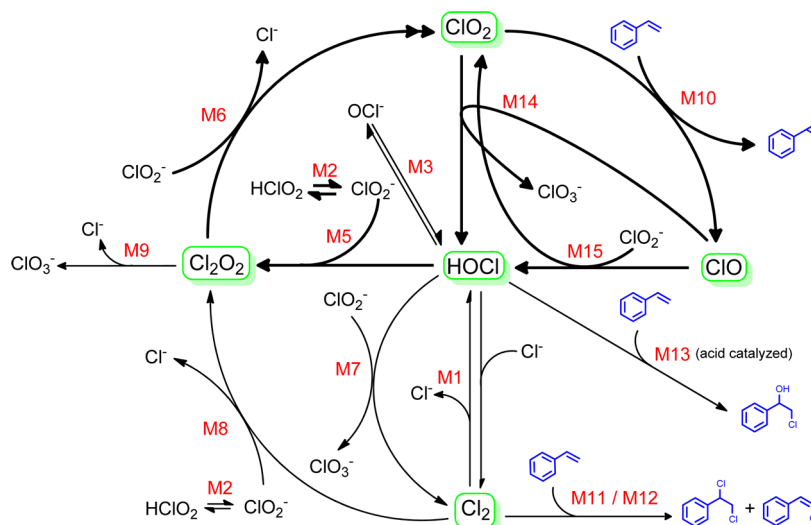
Figure 9. Mechanism for the epoxidation of styrene by chlorite. Bold arrows represent the highest flux reactions when chlorite is in large excess and the pH is 5−6. The double-headed arrow indicates 2 equiv of ClO_2 are produced in reaction M6. The reaction details for M1−M15 are in Table 1.
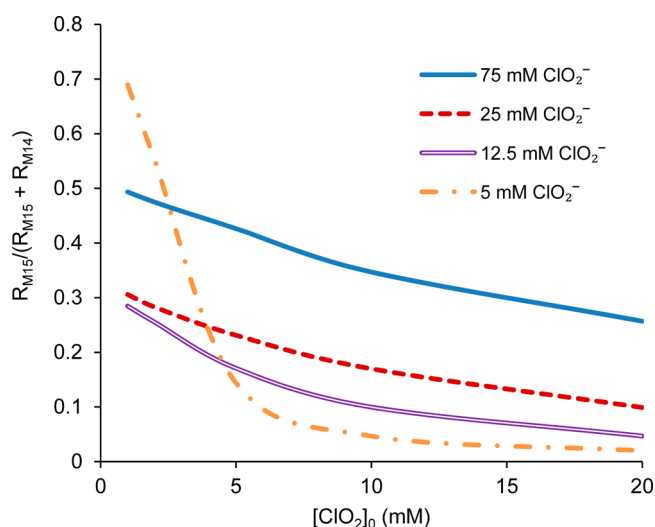

Figure 10. Simulated branching fraction $R_{M15}/(R_{M15} + R_{M14})$ vs initial $[ClO_2]$ for varying initial $[ClO_2^-]$ calculated at $t = 1/2[styrene]_0$. Conditions: $[styrene] = 12.5$ mM, $[Ac^-] = 0.20$ M.

$$\begin{aligned} BF &= k_{M5}[H^+][ClO_2^-]/(k_{M5}[H^+][ClO_2^-] \\ &\quad + k_{M13}[styrene][H^+]) \\ &= k_{M5}[ClO_2^-]/(k_{M5}[ClO_2^-] + k_{M13}[styrene]) \end{aligned} \quad (14)$$

was calculated throughout the reaction using the reaction conditions stated in Figures 2 and 3 and is ∼0.95, thereby accounting for the high yield of epoxide (steps M1 and M7 can be ignored as they have a negligible impact on [HOCl]). Additional details are in the Supporting Information. Addition of chlorite to suppress organochlorine products in ECF pulp bleaching has been advocated by Ni and co-workers,[69] and their rationale is supported by our results.

Under high chlorite conditions, the instantaneous rates of the reactions M1−M15 in the epoxidation model were calculated and compared at all time points (see Supporting Information). Comparing the rates, it is possible to identify the reactions with the highest flux during the oxidation, and bold arrows were used to note those steps in Figure 9. Essentially, under the

optimal conditions examined in the pH range of 5−6, the reactions involving Cl_2 (M1, M8, M11, M12) are only minor contributors. With high $[ClO_2^-]$ (∼0.1 M) the calculated steady-state concentration of ClO_2 (∼10^{-2} M) is greater than [HOCl] (∼10^{-6} M) and $[Cl_2]$ (∼10^{-14} M), showing that the rate of formation of epoxide can be favored over the formation of chlorinated side products *despite the much lower rate constant for reaction of ClO_2 with substrate* (∼0.01 M^{-1} s^{-1}) *in comparison to HOCl* (∼15 M^{-1} s^{-1} at pH 5) *and Cl_2* (∼10^8 M^{-1} s^{-1}). In the reaction mechanism, the strong oxidant chlorite appears in several reactions, and via the net reactions of eqs 8 and 13 it is the ultimate oxidant when $[ClO_2] \ll [substrate]$.

The observations at low chlorite (for example, Figures 4 and 5) are readily explained by the shift in balance of the two chain reactions, with eq 8 now dominating, and the decreased trapping of intermediate HOCl by chlorite. The excess chlorate produced in Figure 5 is a result of the relatively high $[ClO_2^-]_0$ at the outset of the reaction coupled to the significant reaction of HOCl with substrate instead of chlorite. Chlorine dioxide initially present will react with styrene to produce the epoxide and ClO radical (M10). With low chlorite in the reaction mixture reaction M14 (ClO_2 + ClO) is favored over M15 (ClO_2^- + ClO). Reaction M14 generates ClO_3^- and HOCl, which accounts in part for the consumption of chlorine dioxide shown in Figure 5. Furthermore, because [HOCl] is not rapidly decreased by the chlorite-dependent reaction M5 in low chlorite reactions, the reaction of styrene with HOCl (M13) becomes significant, resulting in the higher observed yield of 2-chloro-1-phenyl ethanol.

The uniformly good fit to the kinetics and product distributions in both low and high chlorite reactions at various pH values, in both water and mixed solvent, strongly supports the proposed mechanism in Table 1. Further discussion of predicted conversions and selectivities based on the simulations of the mechanism in Table 1 is presented in the Supporting Information.

Notably, beyond the epoxide there is no other product apparent from the reaction of ClO_2 with the substrate. All of the undesirable side products arise from reactions of other chlorine species formed with the substrate, particularly HOCl.

This model serves to illustrate why oxidations using ClO_2 alone often display relatively poor selectivity, and it is also a likely reason that industrial bleaching with ClO_2 is often accompanied by chlorination side reactions.[27−29,69,82]

Epoxide Yield As a Function of Chlorite and Initial Chlorine Dioxide Concentrations. A useful quantitative mechanism allows calculation of product yield as a function of the initial reaction conditions. The mechanism of Table 1 was tested by comparison of experimental and predicted of organic product distributions as a function of initial chlorite and chlorine dioxide concentrations. As shown in Figure 11
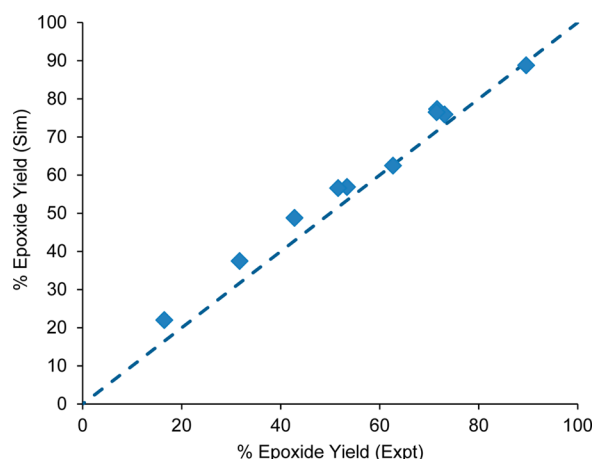

Figure 11. Comparison of styrene oxide yields from experiments and predictions via the mechanism in Table 1 at various initial concentrations ClO_2 and ClO_2^-. $[ClO_2] = 1−15$ mM and $[ClO_2^-]$ $= 5−25$ mM. See Supporting Information for details. The dashed line represents theoretical perfect agreement between predicted and experimental selectivities.

(conditions and results tabulated in Supporting Information), good agreement between observed and predicted yield for styrene oxide is found for a wide range of initial conditions (R^2 $= 0.992$).

Styrene Chlorination Reactions. The formations of chlorinated products of styrene, namely, 1,2-dichloroethylbenzene, 2-chloro-1-phenyl ethanol, and 2-chlorovinylbenzene, are described by reactions M11−M13. 2-Chlorovinylbenzene could in principle be formed as a result of dehydration of 2-chloro-1-phenyl ethanol; however, from the experimental results the amount of 2-chlorovinylbenzene is clearly not dependent on the amount of HOCl available. Therefore, M12 is tentatively written as a chlorination by Cl_2. The formation of 1,2-dichloroethylbenzene (M11) is the result of chlorination of styrene by molecular chlorine. Simulations show that Cl_2 is not at equilibrium with HOCl due to the slow equilibration of reaction M1, and its concentration is ~10^{-14} M under all conditions we studied.

The formation of 2-chloro-1-phenyl ethanol (M13) is written as the product of an acid-dependent chlorination of styrene by HOCl since the chlorohydrin concentration increases proportionately with the product $[HOCl][H^+]$. As illustrated recently by Sivey et al., the active chlorinating agent in reactions of this nature may be a less-abundant yet more-reactive chlorine species (e.g., Cl_2O or H_2OCl^+).[78,80] Although we have been successful in modeling the chlorination side reactions under a number of initial conditions, further studies on the HOCl reactions themselves are necessary to determine definitively the

active chlorinating agent(s) and to probe the mechanistic details of chlorohydrin and other byproduct formation.

Radical Addition/Elimination Versus Electron-Transfer Epoxidation Mechanisms. Our proposed mechanism for M10 involves the epoxidation of styrene via radical addition of chlorine dioxide to the double bond, forming **1**, followed by the elimination of the ClO radical to form epoxide (Figure 6). Rav-Acha and co-workers,[83] however, have suggested that epoxidation occurs via an outer-sphere electron-transfer reaction initially forming the styrene radical cation (**2**) and chlorite.

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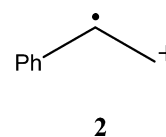
In their view, subsequent addition of water and a *second* equivalent of chlorine dioxide to the radical cation yields the epoxide and chlorous acid.[83] Both Kolar et al. and Rav-Acha et al. observed a decrease in the rate of epoxidation as the polarity of the solvent decreases. Rav-Acha et al. attribute this solvent effect to an increasing solvent barrier for the electron-transfer reaction, while Kolar and Lindgren consider the solvent effect to be attributable to a charge separation in the styrene-ClO_2 adduct (**1**).[41,83]

While neither scenario can be ruled out based on observations related to the polarity of the transition state in the rate-determining step, the predicted stoichiometry for the Rav-Acha et al. mechanism (consumption of 2 equiv of chlorine dioxide and the production of 2 equiv of chlorite/chlorous acid) is not observed experimentally. In addition, the mechanism proposed by Rav-Acha includes steps involving the reaction of starting material with HOCl; however, no step in their mechanism provides for the production of chlorine(I). In contrast, the Kolar and Lindgren addition/elimination mechanism posits the production of the chlorine oxide radical, which goes on to react with ClO_2 or ClO_2^-, forming HOCl (M14 and M15).[41,83]

Our molecular mechanism for epoxidation of olefins by chlorine dioxide is analogous to the well-studied epoxidation reaction by isoelectronic alkylperoxy radicals (ROO·), which proceeds via addition of ROO· to the alkene followed by elimination of RO· radical.[57−59] The heat of reaction for the epoxidation of olefins with the peroxy radical is approximately −20 kcal/mol.[84,85] Using literature values for heats of formation of ClO_2 and ClO,[54] we estimated $\Delta H° \cong −23$ kcal/mol for reaction M10. It is reasonable that both exothermic epoxidation reactions would proceed by a similar radical addition/elimination mechanism. However, based on the results for styrene alone we cannot eliminate an alternative mechanism for M10 in which an initial endoergic outer-sphere electron-transfer reaction is followed by exoergic chlorite addition and decomposition of the adduct (Figure 12). In this case, the rate-determining step would be an electron-transfer reaction as opposed to adduct formation.

Effect of Substituents on the Rate of Epoxidation. We further probed the nature of the rate-determining step for M10 by investigating the reaction of ClO_2 with *para*-substituted styrenes with X = MeO−, Me−, H−, Cl−, and −NO_2 at the *para* position. In the first two cases (X = MeO− and Me−), reactions in our standard 60:40 water/acetonitrile solvent were accompanied by some phase separation. We therefore reduced initial concentrations of substrate in 60:40 water/acetonitrile so
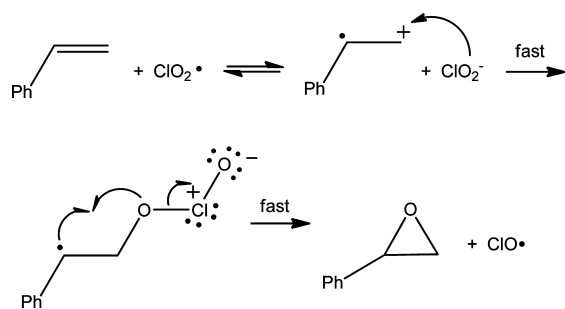
Figure 12. Alternative elementary mechanism for epoxidation of styrene via outer-sphere electron transfer followed by addition of chlorite.

that we could make direct comparisons to the styrene results from our detailed studies. Table 3 gives the best-fit rate constants for M10 for the substituted styrenes using the full mechanism of Table 1.

Table 3. Rate Constants for Reaction M10 for *p*-Substituted Styrenes

R	k_{M10} (M^{-1} s^{-1}) $T = 25°C$	
	60:40 H$_2$O/CH$_3$CN [a]	20:55:25 CH$_3$CN/H$_2$O/EtOH [b]
R = H	$(1.17 \pm 0.02) \times 10^{-2}$	0.05 ± 0.02
R = OMe	$(4.8 \pm 0.5) \times 10^{-1}$	>0.35
R = Me	$(6.1 \pm 0.8) \times 10^{-2}$	0.15 ± 0.03
R = Cl	$(9.3 \pm 0.9) \times 10^{-3}$	0.04 ± 0.02
R = NO$_2$	$(1.5 \pm 0.2) \times 10^{-3}$	--

[a] Rate constants and errors based on an optimized fit for k_{M10} using the mechanism in Table 1. [b] Rate constants and estimated errors using $R = k[ClO_2][sub]$

We found that a 20:55:25 acetonitrile/water/ethanol mixture prevented phase separation even with higher substrate concentrations, so this solvent was also used to investigate substituent effects using a more polar solvent. Ethanol complicates the kinetic interpretation since we noted in control reactions that the alcohol reacts with chlorine dioxide slowly over the course of styrene oxidations. It was generally observed that the concentration of ClO$_2$ increased during the reactions (as a result of the reaction of HOCl with chlorite), as expected from the mechanism, but the stoichiometries were not reliable due to the slow reaction of solvent with ClO$_2$. We were able to determine the direct rates of reaction of chlorine dioxide with substituted styrenes by following the loss of styrene and formation of the epoxides along with the concentration of ClO$_2$ throughout the initial part of the reaction. In the more polar solvent, methoxystyrene was completely consumed in <300 s, and it was only possible to determine the minimum rate constant. For *p*-nitrostyrene, the ClO$_2$ UV–visible peak was obscured by the strong absorbance in the same region by the substrate. The other three observed reaction profiles were fit to the simple rate law $R = k[ClO_2][sub]$. As a further check, we did a numerical fit to the reaction data using a simple kinetic model in which the observed small $[ClO_2]$ increase during the run was simulated, and a best-fit value for k was determined. Both methods gave the same rate constants within ranges quoted in Table 3.

The energetics of a hypothetical outer-sphere electron-transfer reaction (Figure 12) can be estimated from the electrode potentials for the styrene derivatives[86,87] and the ClO$_2$/ClO$_2^-$ couple.[1−3] Although the potentials in water and mixed acetonitrile/water, respectively, are not known, it is apparent that the hypothetical one-electron transfer reaction in Figure 11 is highly endoergic. Given self-exchange rate constants for the two couples, these outer-sphere reaction rate constants for the substituted styrenes with ClO$_2$ could be estimated via the Marcus cross relation.[88,89] However, the styrene/styrene radical cation self-exchange rate constants are not known, and the equilibrium constants in the solvent mixtures are only estimated, so it is not possible to definitively exclude the electron-transfer mechanism of Figure 12 on the basis of a Marcus cross reaction analysis of the individual predicted rate constants. While an outer-sphere reaction mechanism could in principle be eliminated for these highly endoergic reactions in view of the relatively high observed forward rate constants, the uncertainty in the reaction free energies requires that additional evidence be considered.

We can predict the *relative* rates of cross reactions with some confidence by making the simplifying assumption that the substituents do not substantially alter the self-exchange rates for the styrenes and their radical cations. (Given the narrow size range of the reactants, this assumption appears reasonable; see, for example, the Marcus analysis of organic hydrazine radical cation/neutral electron-transfer reactions by Nelsen and Pladziewicz[90] and radical anion/neutral self-exchange rates for similarly substituted benzonitrile by Kowert et al.[91]) The change in free energy for the electron-transfer reaction going from −Cl to −OMe substituents (∼0.6 V)[86] would predict a large increase in the outer-sphere electron-transfer rate constant via the cross relation ($k_{OMe}/k_{Cl} \approx 10^5$), but the observed ratio is only ∼50 (also see Table S2 in Supporting Information). From −Cl to −Me, the potential difference is ∼0.4 V, and the cross relation prediction is $k_{Me}/k_{Cl} \approx 1500$, but a factor of only ∼6 is observed. The kinetic impact of varying para substituents is more in line with the energetic effects of the same substituents on the relative stabilities of benzyl radicals.[92] In the absence of experimental data for the para-substituted styrene(0/+) self-exchange reaction rates, caution is warranted for this analysis; however, the substituent effects on the epoxidation reaction rate constants are more consistent with an addition/elimination mechanism (Figure 6) than they are with a rate-determining outer-sphere electron-transfer reaction followed by addition of chlorite (Figure 12).

■ CONCLUSION

This investigation shows how efficient chlorite oxidations of alkenes can be achieved through control of pH and initial chlorite and chlorine dioxide concentrations. The stoichiometry and inorganic products are determined by the competition of two chain reactions for the consumption of chlorite and substrate, and both chains involve the epoxidation of the vinyl group by ClO$_2$. As proposed by Jangam and Richardson[40] and confirmed by this work, the addition of chlorine dioxide to the initial reaction mixture initiates the chain reactions and predictably contributes to the overall stoichiometry. If ClO$_2$ is used as the *only* initial chlorine reagent in reactions with alkenes, then the subsequent reactions produce HOCl in abundance and result in copius amounts of chlorinated side products.

It is well-known that chlorinated organics are observed in ClO_2-only (ECF) bleaching plants, and Ni and co-workers[28,29] suggested that addition of chlorite to the process reduces the concentration of HOCl and therefore reduces the undesirable chlorinated byproducts. Their explanation for the effect as well as the pioneering work of Kolar and co-workers[27] are validated by the present studies using vinylbenzene substrates in place of the complex mixture of substrates in lignin. The successful quantitative modeling by the detailed mechanism of Figure 11 puts the earlier proposals on firm mechanistic grounds, at least for reactions involving oxidation of double bonds. The model quantitatively explains the formation of chlorinated hydrocarbons in chlorine dioxide oxidations, produced, for example, in a variety applications including water treatment and pulp bleaching, by accounting for the formation of HOCl rather than attributing that formation to reactions of substrate with chlorine impurities.[83,93−96]

This work also supports a less commonly invoked pathway for chlorine dioxide oxidations in which radical addition/elimination occurs in lieu of an initial one-electron outer-sphere electron-transfer reaction. The probability of the former pathway, which is closely analogous to certain reactions of peroxyl radicals, is significantly enhanced when the intermediate radical adduct has special stability, as in the case of styrene and its derivatives studied here.

We are presently investigating the use of mechanisms based on the overall scheme in Figure 9 to provide quantitative models for chlorite and/or chlorine dioxide oxidations of a variety of other substrates, such as sulfides, phenols, and related biological molecules. Other substrates will of course require the introduction of additional steps for ClO_2 reactions and reactions of other chlorine intermediates with substrate to account for product distributions and kinetics. It is encouraging that the highly interdependent chemistry of multiple chlorine oxidation states in complex mixtures can be modeled quantitatively by a series of known reactions.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Included here: introductory material, error analysis, HOCl/ClO_2^- reaction, oxidation of styrene and 4-styrenesulfonic acid, reaction selectivity and epoxidation mechanism, rate constant correlation matrices. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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dx.doi.org/10.1021/ic500512e | *Inorg. Chem.* 2014, 53, 6715−6727