

Rate Constants for Reactions between Iodine- and Chlorine-Containing Species: A Detailed Mechanism of the Chlorine Dioxide/Chlorite-Iodide Reaction[†]

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Abstract: The chlorite-iodide reaction is unusual because it is substrate-inhibited and autocatalytic. Because analytically pure ClO_2^- ion is not easily prepared, it was generated *in situ* from the rapid reaction between ClO_2 and I^- . The resulting overall reaction is multiphasic, consisting of four separable parts. Sequentially, beginning with mixing, these parts are the (a) chlorine dioxide-iodide, (b) chlorine(III)-iodide, (c) chlorine(III)-iodine, and (d) hypoiodous and iodosic acid disproportionation reactions. The overall reaction has been studied experimentally and by computer simulation by breaking it down into a set of kinetically active subsystems and three rapidly established equilibria: protonations of chlorite and HOI and formation of I_3^- . The subsystems whose kinetics and stoichiometries were experimentally measured, remeasured, or which were previously experimentally measured include oxidation of iodine(-1,0,+1,+3) by chlorine(0,+1,+3), oxidation of I^- by HIO_2 , and disproportionation of HOI and HIO_2 . The final mechanism and rate constants of the overall reaction and of its subsystems were determined by sensitivity analysis and parameter fitting of differential equation systems. Rate constants determined for simpler reactions were fixed in the more complex systems. A 13-step model with the three above-mentioned rapid equilibria fits the overall reaction and all of its subsystems over the range $[\text{I}^-]_0 < 10^{-3}$ M, $[\text{ClO}_2^-]_0 < 10^{-3}$ M, $[\text{I}^-]_0/[\text{ClO}_2^-]_0 = 3-5$, $\text{pH} = 1-3.5$, and 25 °C. The derived model with all experimentally determined rate and equilibrium constants fits both the overall reaction and all of its subsystems within 1% relative accuracy.

Introduction

Rate constants of reactions between iodine- and chlorine-containing species are very important in the mechanisms of chlorite/chlorine dioxide and iodide/iodine/iodate-containing chemical oscillators. Among the "chlorite-driven" chemical oscillators¹ one of the most versatile is the chlorite-iodide reaction, which has become, next to the Belousov-Zhabotinsky (BZ) reaction, perhaps the most widely studied reaction in nonlinear chemical dynamics. The past 15 years has witnessed publication of more than 200 articles on this reaction. These studies have been concerned mainly with the system's nonlinear features, such as oscillations, bistability, stirring and premixing effects, and spatial phenomena.² However, only a few of these articles report detailed mechanistic investigations.

Previous attempts to model these complex dynamical systems utilized neither rate constant determinations by parameter fitting to experiments nor direct kinetics measurements of elementary reactions; essentially these studies were qualitative descriptions of oscillations in the chlorite-iodide reaction. Not surprisingly, rate constants vary considerably among the different models. For example, the rate constant for the reaction between HOCl and HOI was reported to be 0.3×10^3 ,³ 2×10^3 ,⁴ 5×10^5 ,⁵ and $2 \times$

$10^8 \text{ M}^{-1} \text{ s}^{-1}$,⁶ in different modeling efforts. Similarly large variation is seen in the rate constant found for the $\text{HOCl} + \text{HIO}_2$ reaction: 0.5×10^3 ,^{3,4} and $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.⁶ The treatment of iodine hydrolysis in the models differs substantially: the forward reaction is described as a pH-dependent^{3,7} or a pH-independent process.^{4,6} There are also smaller but significant variations for the rate constants of the $\text{HIO}_2 + \text{I}^- (+ \text{H}^+)$, $\text{HIO}_2 + \text{HOI}$, HIO_2 disproportionation, $\text{HClO}_2 + \text{HOI}$, and $\text{HClO}_2 + \text{HIO}_2$ reactions. Since most of the rate constants of previous models had not been measured directly, we decided to reinvestigate the chlorite-iodide reaction, which is at the heart of chlorite- and iodine-containing oscillators.

Among small molecule inorganic oxidation–reduction reactions, the chlorite-iodide reaction is quite unusual, because it is both substrate inhibited and autocatalytic. Iodide, which is a reactant, inhibits the reaction, and iodine, one of the products, accelerates the reaction. This feature was first recognized by Bray⁸ and later studied in more quantitative detail.^{9,10} Kern and Kim⁹ established a very accurate empirical rate law valid up to 90% of iodide conversion to iodine. They proposed that the reaction is controlled by HOI-generating iodine hydrolysis: HOI reacts rapidly with chlorous acid followed by even faster reactions of the intermediates with iodide. This picture is preserved in the subsequent detailed mechanisms of Epstein and Kustin⁶ and Citri and Epstein.³ The Citri-Epstein model (C&E), which is the most widely used model of the reaction, reproduces many qualitative features of the experiments, but significant differences remain, as shown by Ross and co-workers.^{11,12}

[†] Systematic Design of Chemical Oscillators. 94. Part 93: Epstein, I. R.; Kustin, K.; Lengyel, I. In *Taube Insights: From Electron Transfer Reactions to Modern Inorganic Chemistry*; Isied, S., Ed.; American Chemical Society: Washington, DC, 1996; In press.

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We believe that there are additional problems with these models. One shortcoming is that such models attempt to fit data in regions where incomplete mixing seriously affects oscillations,^{13–19} without explicitly taking into account any such interference with the chemical kinetics. The best model should contain a set of rate constants that make it possible to account for the effects of incomplete mixing using the appropriate physical mixing model. None of the models proposed to date includes triiodide ion explicitly. Inclusion of I_3^- in C&E, for example, would modify the entire dynamics. Another problem is that HOI, which is the most significant intermediate in the reaction, becomes protonated around pH 2 (the most frequently used experimental pH). One consequence of H_2OI^+ formation is that the mechanism of iodine hydrolysis changes in going from pH 3 to pH 1 (see a detailed analysis in ref 20). These models do not account for such changes and consequently cannot correctly describe the pH dependence below pH 3.

To obtain a more experimentally based mechanism of the title reaction we studied the kinetics not only of the chlorite-iodide reaction but also that of its subsystems, including the chlorite-iodine, hypochlorous acid-iodine, hypiodous acid, and iodous acid disproportionation reactions and fitted the appropriate rate constants of these reactions to the kinetics data. We therefore obtained a self-consistent set of rate constants for the overall reaction, which we now present.

Experimental Section

Materials. All chemicals were Fisher reagent grade unless noted otherwise. Sodium chlorite (80%, Aldrich) was purified as described earlier,²¹ and stock solutions were kept in the dark. The chlorite content of the purified chlorite was $98.8 \pm 0.5\%$ by iodometric titrations. Chlorine dioxide was prepared as described in the literature.²² Iodine stock solutions were prepared by dissolving crystalline iodine in double-distilled water. The iodide content was checked by measuring the spectrum of the solution at the experimental pHs. The iodide content was determined from this measurement, the spectra of iodine and triiodide, and the triiodide formation equilibrium constant. It was consistent with the equilibrium concentration of iodide originating from iodine hydrolysis.

The organic content of "distilled water" reacting with iodine could produce different iodide concentration levels in acidic media; consequently, special precautions were taken to avoid this interference. For studying the kinetics of the $HOCl + I_2$ and $HClO_2 + I_2$ reactions we used organic-free, high purity water for the stock solutions and determined the iodide content of iodine stocks in acidic media. In all cases $[I^-]$ was close to that concentration originating solely from iodine hydrolysis. These iodide concentrations were considered in the calculations as initial values, although they did not make a significant difference in the resulting kinetics curves.

Hypiodous acid was generated by the instantaneous hydrolysis of ICl^{23} dissolved in methyl alcohol. Small amounts (50–200 μL) of ICl solution were injected into 2.5 mL of sulfate buffer solutions. Iodine-

(III) was prepared from iodate and iodine in concentrated sulfuric acid.²⁴ In a spectrophotometric cell, a small volume (50–200 μL) of this solution was injected into a precooled NaOH solution, the concentration of which was calculated to allow the final solution to reach the desired pH of the sulfate buffer. The temperature of the solution after dilution was $25 \pm 1^\circ C$.

Hypochlorous acid was prepared from the reaction of chlorine water and HgO (Fluka).²⁵ Excess HgO was mixed with water and a CCl_4 solution of chlorine. After the solids were filtered off, CCl_4 was separated from the water phase containing HOCl, and the remainder of Cl_2O in the CCl_4 phase was extracted into water. The HOCl in the water phase was further purified by distillation. The distilled HOCl/ Cl_2O was dissolved in cool water. HOCl obtained this way was free from any lower or higher oxidation states of chlorine and from other ions and was stored at $5^\circ C$.

The ionic strength of the reaction mixtures was fixed at 0.3 M by adding calculated amounts of $NaClO_4$ to the buffer solutions. The $NaClO_4$ was obtained by titrating $HClO_4$ with NaOH.

Methods. Every reaction was studied by spectrophotometry with an HP diode array spectrophotometer. In the case of slower reactions a stirred spectrophotometric cell was used as a reactor, while in the case of the chlorite-iodine and hypochlorite-iodine reactions, the HP diode array spectrophotometer was combined with a HiTech stopped-flow. The dead-time of the stopped-flow apparatus was about 5 ms, and the maximum collection rate of the diode-array photometer was 10 Hz. Since the time scale of these reactions is in the 10 s range, time resolution errors are negligible. Every reaction was measured simultaneously at several different wavelengths or in a wavelength range. Comparisons were made between experiments that used a light filter which blocked light below 300 nm and those that used no filter. Within experimental error, no difference was detected. As a further check on whether light induced a reaction in this system, we varied the shutter opening time from 0.1 to 1 s at 1 Hz collection rate and found no detectable effect. At least three replicate runs were averaged for each concentration set. The spectra of the reaction mixtures were analyzed and the number of independent absorbing species was determined by Coleman-Varga-Mastin's method.²⁶ All measurements were performed at $25 \pm 0.2^\circ C$, except for the HIO_2 disproportionation where the temperature was $25 \pm 1^\circ C$.

In reactors stirred at moderate speeds (300–600 rpm), imperfect mixing can arise in the chlorite-iodide reaction, which causes irreproducible results. Fortunately, proper order of addition of reagents can prevent this occurrence. If the reactor contains a chlorine dioxide solution to which a lesser amount of iodide ion solution is added, which we refer to as CI-order, chlorite and iodine are so rapidly produced that the secondary reaction and mixing rates are competitive. Because the iodide concentration is so low, there is virtually no inhibition, and the reaction between chlorite and iodine follows immediately. Depending on the rate of iodide addition and the average mixing time, different amounts of iodine will be consumed *during mixing*. A similar situation occurs if chlorite replaces chlorine dioxide in the reactor when its concentration is above 10^{-3} M and the pH is 2 or less.

To avoid this source of error, the following reactor configuration was used. The reactor contains iodide ion, to which a lesser amount of chlorine dioxide solution is added (IC-order). In this case, iodide is always in excess, the chlorite-iodide reaction is slow (strong I^- inhibition) and the chlorite-iodine reaction does not occur to an appreciable extent during the mixing process. Reproducible kinetics curves were obtained with IC-order. At 300 rpm with CI-order, the time at which all the iodide is consumed (peak of Figure 1) can be as much as ten times shorter than that found with IC-order. At higher stirring rates, the CI-order experiments get closer to the IC-order experiments, and above 1200 rpm they are indistinguishable in the spectrophotometric cell we used. However, the higher stirring rate makes the spectrophotometric measurements extremely noisy, because of cavitation and vortex formation. With the IC-order the reaction is

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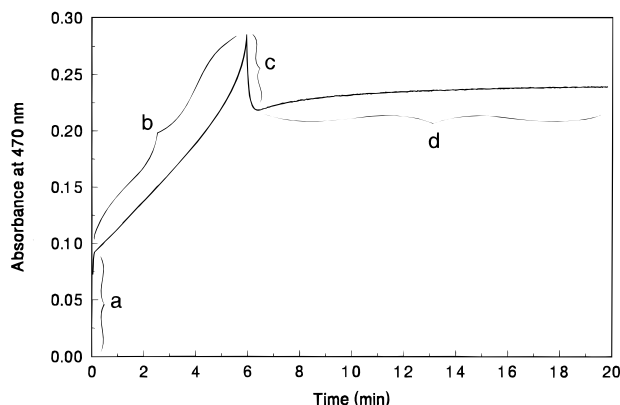
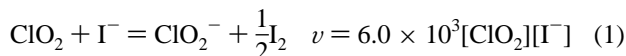


Figure 1. The multiphasic kinetics curve of the chlorine dioxide-iodide reaction. $[\text{ClO}_2]_0 = 2.47 \times 10^{-4} \text{ M}$, $[\text{I}^-]_0 = 8.0 \times 10^{-4} \text{ M}$, $\text{pH}_0 = 2.15$, $[\text{SO}_4^{2-}] + [\text{HSO}_4^-] = 0.05 \text{ M}$, ionic strength = 0.3 M.

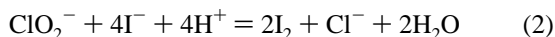
stirring rate independent if the stirring rate is higher than 300 rpm. We used the IC-order with stirring rates about 500 rpm.

Experimental Results

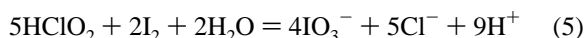
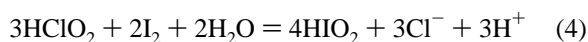
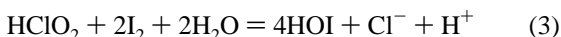
Overview. Since analytically pure chlorite is not easily prepared, in these studies we chose an *in situ* preparation of chlorite from the fast reaction between chlorine dioxide and iodide. By using chlorine dioxide as a source of chlorite, the purity of chlorite is not a question since chlorine dioxide can be purified very easily. Also, the initial presence of iodine, which is an autocatalyst, makes the reaction more reproducible and faster. Control experiments using pure chlorite, iodine, and iodide in comparable concentrations give the same kinetics curves as shown in Figure 1. The first part of the chlorine dioxide-iodide reaction is rapid in the 10^{-4} M concentration range.²² It is complete in a few seconds and produces chlorite and iodine according to the following stoichiometry and rate law:



It is useful to examine a characteristic kinetics curve for the whole course of the multistep chlorine dioxide-iodide reaction (Figure 1). The first fast increase of iodine, part (a), is due to reaction 1. Then, in part (b), the chlorite (chlorous acid) produced in reaction 1 reacts with the excess iodide to produce more iodine in an accelerating reaction. The stoichiometry of this part of the curve is well described by

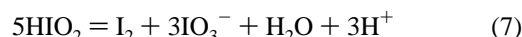
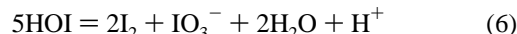


When iodide is consumed, the excess chlorite of reaction 2 reacts with iodine in a rapid reaction, which is part (c). The higher the chlorite excess of reaction 2, the more significant the portion of iodine that is consumed. The stoichiometry of this process varies with the ratio of chlorite and iodine; it also depends on their initial concentrations. During part (c), when iodine is in excess and the chlorine-containing species are Cl(III) and Cl^- , the iodine-containing products of this fast reaction, which is complete when all chlorite is consumed, are HOI, HIO_2 and IO_3^- . The combination of the next three overall stoichiometric processes can describe the actual product ratio:



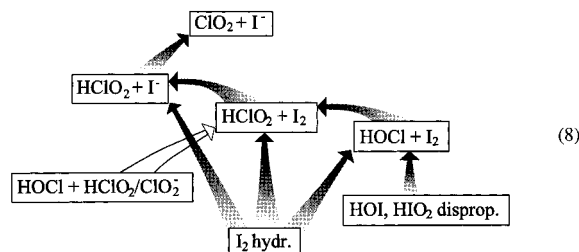
Iodate is always one of, but not the only, product of part (c) in any experiment, even at high iodine excess. At chlorite excess the stoichiometry is even more complicated, because reaction between Cl(III) and HOCl to produce ClO_2 becomes significant. The stoichiometry of this reaction also varies with the ratios of reactants and product chloride. However, for our experiments, chlorine dioxide formation never occurs in part (c). With ratios of $[\text{I}^-]_0/[\text{ClO}_2]_0$ between 3 and 5, the $[\text{ClO}_2^-]/[\text{I}_2]$ ratio in part (c) is always smaller than 0.33; consequently, iodine is in high excess. These conditions prevent chlorine dioxide formation, resulting in simpler reactions for part (c) and the ensuing part (d).

Part (d) is a slow disproportionation of HOI and HIO_2 to molecular iodine and iodate. The stoichiometries of the disproportionations are



The different parts of the overall reaction are well separated from each other (Figure 1). Parts (b), (c) and (d) are the chlorite-iodide reaction; the reaction between chlorite and iodine and the parallel hypochlorite-iodine reaction occur in parts (c) and (d); the disproportionation of iodine(+1,+3) takes place in part (d).

The relationships between the different reactions are diagrammed in eq 8. The direction of an arrow indicates that the reaction at the base of the arrow plays a determining role in the reaction at the tip of the arrow.



Although the reverse reactions of iodine hydrolysis are present in the disproportionation of HOI and HIO_2 , they do not have a determining role in the kinetics. However, in the cases of the chlorite-iodide, chlorite-iodine, and hypochlorite-iodine reactions, the iodine hydrolysis has different controlling roles discussed below. The unfilled arrow from the $\text{HOCl} + \text{HClO}_2/\text{ClO}_2^-$ reaction indicates that this reaction is important only at certain experimental conditions and can be completely separated from the others. Equation 8 will be a guide for investigating the component processes.

In this section we show experimental results beginning with the overall chlorine dioxide-iodide reaction, and then proceed systematically through its subsystems. In the following sections we present determinations of the rate constants of the component processes by fitting the parameters of the subsystems and a discussion of these rate constants and their relations to each other.

The Overall Chlorine Dioxide-Iodide Reaction. As we have seen (Figure 1), the chlorine dioxide-iodide reaction is complex, consisting of different, comparatively well separated subprocesses. By analyzing the spectrum of the reaction mixture (Figure 2) after the first fast consumption of chlorine dioxide, we can identify three absorbing species above 300 nm: iodine, triiodide, and HOI and/or HIO_2 . The species HOI and HIO_2 cannot be separated because of their overlapping spectra and their small absorbances between 300 and 320 nm. Triiodide ions are present until iodide is absent in the reaction mixture.

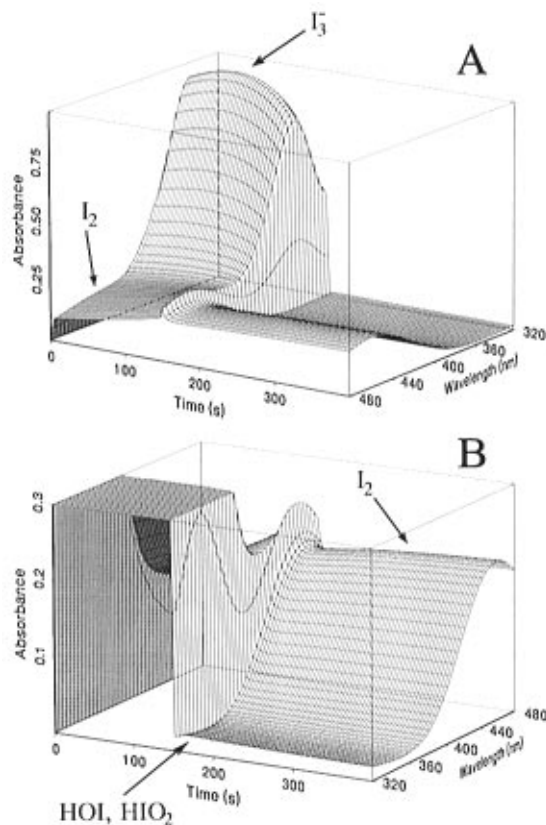


Figure 2. Spectra of the chlorine dioxide-iodide reaction in two different views showing characteristic absorbances of different species.

Iodide ions are consumed by the time the iodine concentration reaches its maximum, HOI and HIO₂ are formed during the fast iodine consumption, and their disproportionation produces more iodine. The optimum wavelengths for following the kinetics are 470 nm (isosbestic point of iodine and triiodide), 350 nm (triiodide maximum absorptivity), and 320 nm (HOI maximum absorptivity). The kinetics were studied at several fixed initial iodide concentrations (8, 4, 2, and 1 × 10⁻⁴ M), and the initial chlorine dioxide concentration was changed to reach ratios of [I⁻]₀/[ClO₂]₀ between 3.0 and 5.0. In this range of reactant ratios the reaction is easily measurable and very reproducible. The pH dependence of the reaction was investigated between pH 1 and 3. In Figure 3 we show some representative kinetics curves of the reaction with changing initial iodide concentration (A) and changing pH (B). The time at which the maximum in the iodine absorbance appears (*t*_{max}) depends critically on the ratio of reactants but changes only slightly with pH, although the change in hydrogen ion concentration is two orders of magnitude.

The Chlorous Acid-Iodine Reaction. This reaction is responsible for the kinetics of parts (c) and (d) of Figure 1. The reaction has already been studied,^{4,27} particularly at high chlorite excess. Rábai and Beck assigned a key role to ICl; however, the reaction occurs not only at high initial reactant concentrations, where ICl may be present, but also at low concentrations, and their model cannot account for the entire concentration range. More importantly, they assumed a slow rate of hydrolysis for ICl, but subsequent experimental studies revealed²³ that ICl hydrolysis is several orders of magnitude faster than assumed by Rábai and Beck. Consequently, the hydrolysis of ICl cannot have a rate-limiting role. In most experiments its equilibrium concentration is low (<5%) com-

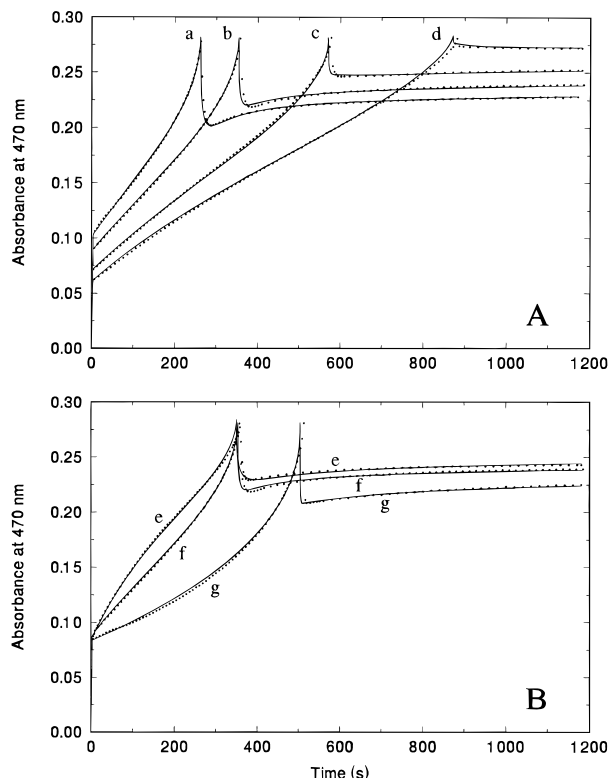


Figure 3. Kinetics curves of the chlorine dioxide-iodide reaction: (A) chlorine dioxide dependence and (B) pH dependence. Dots represent experimental points and solid lines are fitted. [I⁻]₀ = 8.0 × 10⁻⁴ M, [SO₄²⁻] + [HSO₄⁻] = 0.05, ionic strength = 0.3 M in every experiment. [ClO₂]₀ = 2.84 × 10⁻⁴ (a), 2.47 × 10⁻⁴ (b,e,f,g), 1.97 × 10⁻⁴ (c) and 1.70 × 10⁻⁴ (d) M. pH₀ = 2.15 (a–d,f), 1.62 (e), and 2.96 (g).

pared with HOI/H₂OI⁺. Its reactivity would have to be much higher than that of HOI to cause any significant kinetic effect. Because of these considerations, and to have more adequate kinetics curves for parameter fitting, we reinvestigated this reaction.

In Figure 4 we show how the spectrum of the reaction mixture changes in time for excess iodine (A) and chlorite (B). With iodine in excess, HOI and HIO₂ intermediates form in parallel with iodine consumption. With chlorite in excess, chlorine dioxide formation can be observed clearly from its characteristic spectrum.

Chlorine dioxide is important in the closed system oscillations of the chlorite-iodide-malonic acid reaction²² and in Turing pattern formation when chlorite is in high excess over iodide and at high initial reactant concentrations (> 10⁻³ M). However, ClO₂ formation need not occur under all conditions used in the chlorine dioxide-iodide reaction or in open system studies of the chlorite-iodide reaction, which are used in analyzing oscillations and stirring effects. Modeling studies showed that the kinetics of the chlorous acid-iodine reaction is independent of the chlorous acid/chlorite-hypochlorous acid reaction. After investigating the kinetics and mechanism of the latter reaction in detail, we found that the mechanism of chlorine dioxide formation in the HOCl + HClO₂/ClO₂⁻ reaction is much more complex than that of the chlorite-iodide reaction and is well separated from the latter. Since the mechanisms of the two reactions are distinct, rate constants derived from models of the two reactions are not correlated with each other. For clarity and a better understanding of the chlorite-iodide reaction, we will report the kinetics and mechanism of the HOCl + HClO₂/ClO₂⁻ reaction separately.

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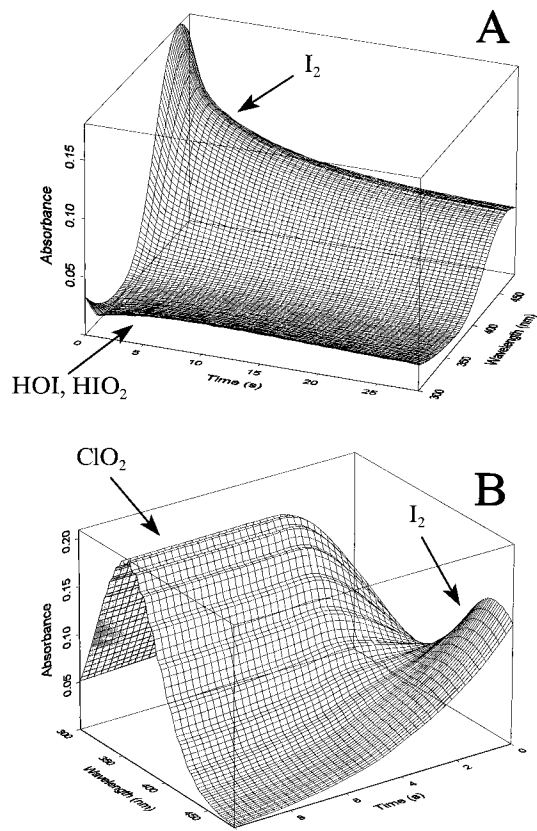


Figure 4. Spectra of the chlorous acid-iodine reaction at (A) iodine stoichiometric excess $[I_2]_0 = 2.3 \times 10^{-4}$ M and $[ClO_2^-]_0 = 3.04 \times 10^{-4}$ M; (B) chlorite excess, $[I_2]_0 = 1.9 \times 10^{-4}$ M and $[ClO_2^-]_0 = 1.2 \times 10^{-3}$ M. $[SO_4^{2-}] + [HSO_4^-] = 0.05$ M, ionic strength = 0.3 M and $pH_0 = 2.01$ in both cases.

Kinetics curves of the chlorous acid-iodine reaction are shown in Figures 5 and 6, in which the initial chlorite, iodine, and proton concentrations are varied. The initial rate is independent of the chlorite concentration (Figure 5A); however, it is iodine- and pH-dependent (Figure 6 (parts A and B)). Figures 5 and 6 indicate that the hydrolysis of iodine may be the rate limiting step in these chlorous acid-iodine experiments. The pH dependence of the reaction is interesting (Figure 6B): the kinetics becomes autocatalytic with decreasing pH.

The Hypochlorous Acid-Iodine Reaction. The HOCl- I_2 reaction was studied in excess HOCl.⁴ However, this condition hardly ever occurs in the chlorite(chlorine dioxide)-iodide reaction, because HOCl is produced by the reduction of chlorite by several species, each of which will react with HOCl, too. To obtain relevant data at stoichiometric excesses of iodine, we reinvestigated the reaction. Figure 7 shows how the spectrum of the hypochlorous acid-iodine reaction changes with excess iodine and hypochlorous acid. At low pH and excess hypochlorite the reaction is autocatalytic. At lower wavelengths the production and consumption of HOI and HIO₂ can be clearly seen. On a longer time scale, these species will disproportionate and produce iodine. Although the kinetics curves of this reaction are complex, it is simpler than the chlorous acid-iodine reaction, because all the reactions of HClO₂ with iodine-containing species are missing. Figure 8 shows the kinetics of this reaction with changing hypochlorite (curves a–d), iodine (curves d–g) and hydrogen ion concentrations (curves h–j). The initial rates are nearly independent of hypochlorite concentration but depend on the iodine concentration and pH as in the chlorite-iodine reaction. At hypochlorous acid excess and lower pH, the reaction is autocatalytic. The autocatalytic feature is much more pronounced than in the chlorite-iodine reaction.

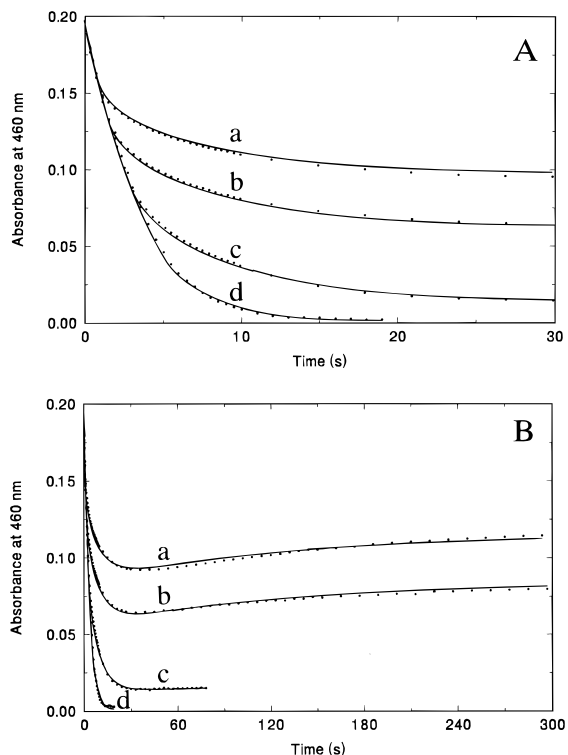


Figure 5. Kinetics curves of the chlorous acid-iodine reaction with changing initial chlorite concentrations, short (A) and long (B) time development. $[ClO_2^-]_0 = 2.13 \times 10^{-4}$ (a), 3.13×10^{-4} (b), 5.6×10^{-4} (c), and 8.7×10^{-4} (d) M; $[I_2]_0 = 2.61 \times 10^{-4}$ M, $pH = 2.0$, $[SO_4^{2-}] + [HSO_4^-] = 0.05$ M and ionic strength = 0.3 M. Dots represent experimental points and solid lines are fitted.

The Disproportionation of Hypoiodous Acid. Disproportionation of hypoiodous acid was studied by several groups^{28–30} at different conditions, and rate constants between 5 and 250 $M^{-1} s^{-1}$ were reported. Because of these differences, which cannot be explained by differences in experimental conditions, we carried out experiments to redetermine the kinetics of this reaction. Figure 9 shows the change in the spectrum of HOI with time. The three absorbing species are HOI, I_2 , and IO_3^- . An isosbestic point at 374 nm, where iodine and hypoiodous acid absorb, shows that there are no intermediates present at high concentrations during disproportionation.

The Disproportionation of Iodous Acid. The kinetics of this reaction were measured previously in highly acidic media and found to be slow and autocatalytic.^{24,28} Since our reaction system operates at lower acid concentrations, we reinvestigated the reaction close to our experimental conditions. Figure 10 shows the spectrum of the reaction mixture as it changes with time. The formation of iodine is autocatalytic, similar to Noszticzus *et al.*'s observations. Several kinetics curves were measured at different concentrations of HIO₂ and different pH values. Changes in pH between 1 and 2 do not modify the kinetics significantly. Because of the high sulfuric acid concentration used in the preparation of HIO₂, the experimental conditions for studying the disproportionation are very limited.

Determination of Rate Constants

To determine the rate constants of likely quasi-elementary and nonelementary processes we fitted the kinetics curves of

(28) Furrow, S. J. *Phys. Chem.* **1987**, *91*, 2129.

(29) Buxton, G. V.; Sellers, R. J. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 449.

(30) Thomas, T. R.; Pence, D. T.; Hasty, R. A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 183.

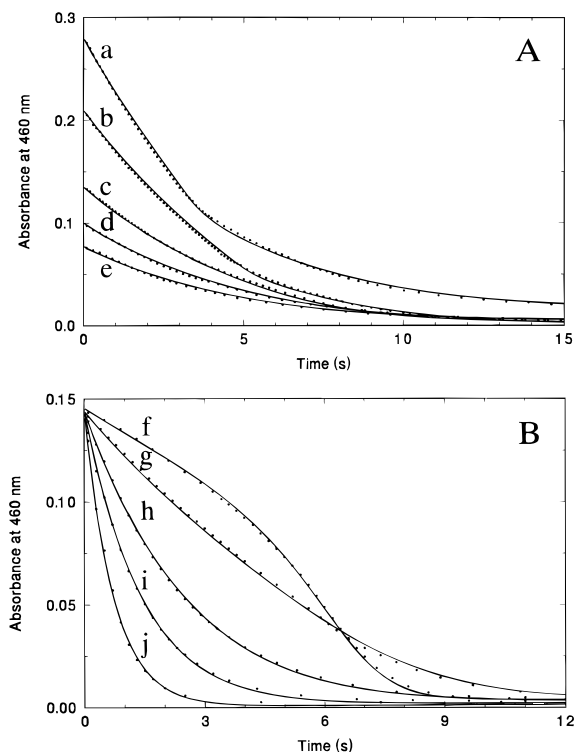


Figure 6. Kinetics curves of the chlorous acid-iodine reaction with changing initial iodine concentration (A) and pH (B). $[I_2]_0 = 3.81 \times 10^{-4}$ (a), 2.86×10^{-4} (b), 1.84×10^{-4} (c), 1.36×10^{-4} (d), 1.05×10^{-4} (e) and 1.96×10^{-4} (f–j) M; $[ClO_2^-]_0 = 9.0 \times 10^{-4}$ (a–e), 1.0×10^{-3} (f–j) M; $pH_0 = 1.89$ (a–e), 1.19 (f), 1.74 (g), 2.23 (h), 2.50 (i), 2.82 (j); $[SO_4^{2-}] + [HSO_4^-] = 0.05$ M and ionic strength = 0.3 M. Dots represent experimental points and solid lines are fitted.

the above experiments. Except for the hypiodous acid disproportionation, the parameters of the differential equation systems derived from possible simpler reactions were fitted. Sensitivity analysis³¹ was used to evaluate different reaction schemes to find the most plausible mechanisms.

Altogether, kinetics curves of the various reactions were measured at more than 60 different experimental conditions, and 3–5 replicate curves were averaged to improve the signal/noise ratio. We used 50–250 points from each experimental curve for fitting, depending on the complexity of the curves. For the chlorine dioxide-iodide reaction more than 200 points were used because of its multiphasic shape. Often, the fitting procedure suggested new experiments at different initial concentrations or with simpler subsystems to obtain additional data from which specific rate constants could be determined with greater sensitivity and with the least possible correlation with other parameters. For statistical analysis the goodness of fit statistics³² of different models were compared. With the exception of the iodous acid disproportionation, where $R^2 = 0.99$, $R^2 > 0.995$. In all other cases, Model Selection Criteria³³ > 6.5 . The elements of the main diagonal of the correlation matrix of fitted parameters were smaller than 0.6, and the residuals with absolute fitting were smaller than 3×10^{-3} and with orthogonal fitting were smaller than 10^{-2} . In the fitting procedure, we started from the simpler kinetic systems and proceeded to the more complicated ones, fixing the previously determined rate constants to make them uncorrelated with the

(31) Turányi, T. *Computers Chem.* **1990**, *14*, 253.

(32) Peintler, G. *Zita, Version 4.0: A Comprehensive Program Package for Fitting Parameters of Chemical Reaction Mechanisms*; Institute of Physical Chemistry, Attila József University: Szeged, Hungary, 1995.

(33) *MINSQ: Nonlinear Parameter Estimation and Model Development*; MicroMath Scientific Software: Salt Lake City, 1990.

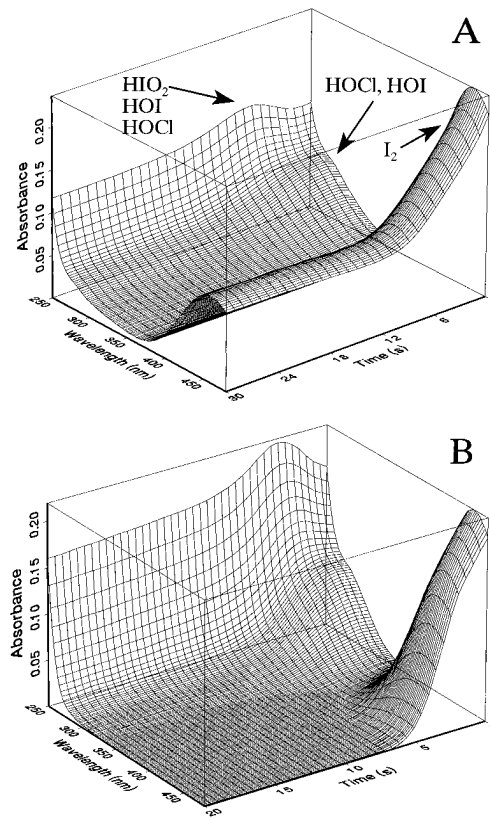


Figure 7. Spectra of the hypochlorous acid-iodine reaction at iodine (A) and HOCl (B) stoichiometric excess. $[I_2]_0 = 3.2 \times 10^{-4}$ M, $[HOCl]_0 = 8.03 \times 10^{-4}$ M in (A) and $[I_2]_0 = 2.95 \times 10^{-4}$ M, $[HOCl]_0 = 1.25 \times 10^{-3}$ M in (B). $pH_0 = 1.66$, $[SO_4^{2-}] + [HSO_4^-] = 0.05$ M and ionic strength = 0.3 M in both (A) and (B).

new unknown parameters. Consequently, rate constants at the higher level describe all of the lower level subsystems, the whole mechanism comprising a self-consistent set of rate constants.

The rate constants so determined depend on the values of certain equilibrium constants discussed below. For future modeling, we recommend using the rate constants with the related equilibrium constants to have a self-consistent set of parameters that describes all the experiments done at these experimental conditions.

Rapid Equilibria in the Chlorine Dioxide-Iodide Reaction.

The criterion used to define a rapid equilibrium was a relaxation time shorter than $50 \mu s$, which is about an order of magnitude shorter than the relaxation time of the next slowest equilibrium, the iodine hydrolysis. Foremost among the rapid equilibria is triiodide formation, since, as was observed by Kern and Kim,⁹ triiodide ions are not reactive. The reactivity of triiodide in other reactions is in accord with this observation.^{34–36} With formation of I_3^- , a significant portion of iodide and iodine is captured in this unreactive complex. Using the equilibrium constant $K_{I_3^-} = [I_3^-]/[I_2][I^-]$, with total iodide $T_{I^-} = [I^-] + [I_3^-]$ and total iodine $T_{I_2} = [I_2] + [I_3^-]$ concentrations as variables, the triiodide concentration can be expressed as

$$[I_3^-] = \frac{-1}{2(K_{I_3^-} + T_{I^-} + T_{I_2})} + \frac{1}{2} \sqrt{\left(\frac{1}{K_{I_3^-} + T_{I^-} + T_{I_2}}\right)^2 + 4T_{I^-}T_{I_2}} \quad (9)$$

(34) Bazsa, G.; Beck, M. T. *Acta Chim. Hung.* **1972**, *73*, 425.

(35) Adegite, A.; Egbob, H. *Inorg. Chim. Acta* **1977**, *21*, 1.

(36) Yiin, B. S.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 1559.

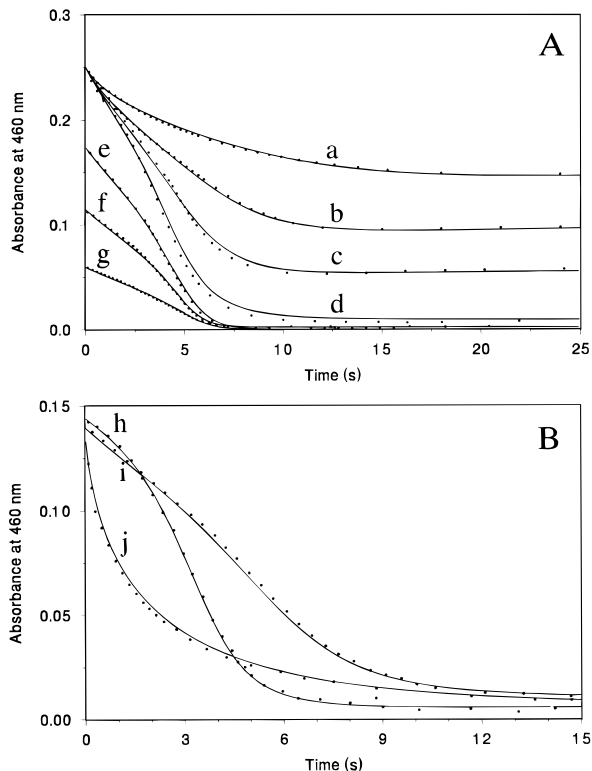


Figure 8. Kinetics curves of the hypochlorous acid-iodine reaction: hypochlorous acid (a–d), iodine (d–g) and pH dependence (h–j). $[I_2]_0 = 3.43 \times 10^{-4}$ (a–d), 2.42×10^{-4} (e), 1.61×10^{-4} (f), 8.41×10^{-5} (g), 1.94×10^{-4} (h), 1.92×10^{-4} (i), 1.85×10^{-4} (j) M; $[HOCl]_0 = 4.01 \times 10^{-4}$ (a), 8.04×10^{-4} (b), 1.15×10^{-3} (c), 1.56×10^{-3} (d–g), 7.38×10^{-4} (h–j) M; $pH_0 = 1.66$ (a–g), 1.05 (h), 1.39 (i), 2.82 (j). $[SO_4^{2-}] + [HSO_4^-] = 0.05$ M and ionic strength = 0.3 M in every case. Dots represent experimental points and solid lines are fitted.

The free, reactive iodide and iodine concentrations are

$$[I^-] = T_{I^-} - [I_3^-] \quad (10)$$

$$[I_2] = T_{I_2} - [I_3^-]$$

In the rate equations of the reactions of iodide and iodine we will refer to these free iodide and iodine concentrations.

The deprotonation constant of chlorous acid $K_{HClO_2} = [ClO_2^-][H^+]/[HClO_2]$ has been measured at several ionic strengths;³⁷ in our experiments the value is $2 \times 10^{-2} M^{-1}$. Keeping total chlorite $T_{ClO_2^-} = [ClO_2^-] + [HClO_2]$ as a variable, the concentrations of the different forms are

$$[HClO_2] = \frac{T_{ClO_2^-}[H^+]}{K_{HClO_2} + [H^+]} \quad (11)$$

$$[ClO_2^-] = \frac{T_{ClO_2^-}K_{HClO_2}}{K_{HClO_2} + [H^+]}$$

In the rate equations the two relations of eq 11 will be used to replace $[HClO_2]$ and $[ClO_2^-]$.

The deprotonation constant of H_2OI^+ $K_{H_2OI^+} = [HOI][H^+]/[H_2OI^+]$ was measured by Bell and Gelles,³⁸ who determined the pH dependence of iodine hydrolysis. Independent experiments³⁹ confirmed their results. Spectrophotometric experi-

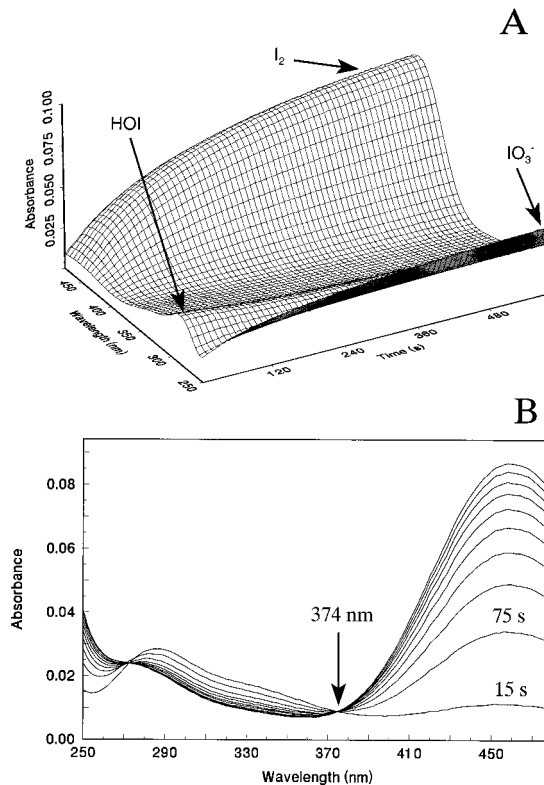


Figure 9. The course of spectra during the disproportionation of hypoiodous acid: (A) 3D representation and (B) showing the isosbestic point. $[HOI]_0 = 3.76 \times 10^{-4}$ M, $pH_0 = 1.8$, 0.1 M sulfate buffer.

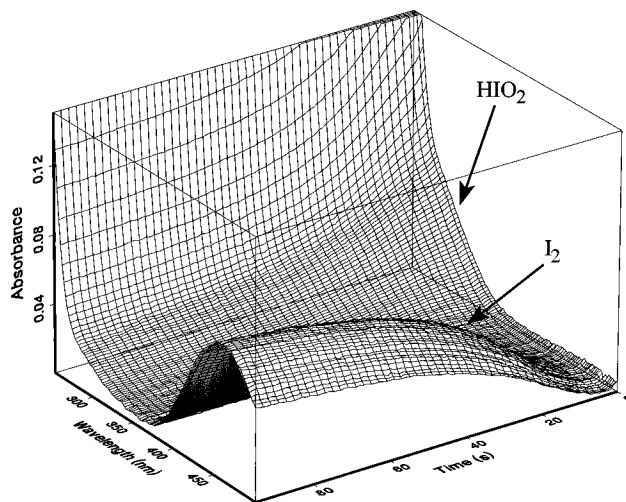


Figure 10. Spectra of the disproportionation of iodous acid. $[HIO_2]_0 = 5.1 \times 10^{-4}$ M, $pH_0 = 1.42$, 0.7 M sulfate buffer.

ments for studying the disproportionation of HOI show the existence of this equilibrium by a shift in the spectrum of HOI to lower wavelengths as pH decreases from 2 to 1. Keeping the total HOI concentration $T_{HOI} = [HOI] + [H_2OI^+]$ as a variable, the concentrations of the two iodine(+1) forms are

$$[H_2OI^+] = \frac{T_{HOI}[H^+]}{K_{H_2OI^+} + [H^+]} \quad (12)$$

$$[HOI] = \frac{T_{HOI}K_{H_2OI^+}}{K_{H_2OI^+} + [H^+]}$$

In the rate equations the two relations of eq 12 will be used to replace $[HOI]$ and $[H_2OI^+]$.

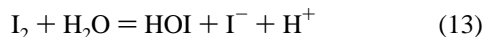
(37) Hong, C. C.; Rapson, W. H. *Can. J. Chem.* **1968**, *46*, 2053.

(38) Bell, R. P.; Gelles, E. *J. Chem. Soc.* **1951**, 2734.

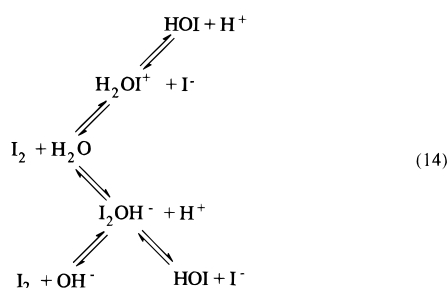
(39) Allen, T. L.; Keefer, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2957.

When the pH of the reaction mixtures is higher than 2.5, the buffer capacity of 0.05 M sulfate may not be high enough to keep an approximately constant pH. We therefore tested buffer capacity. The value of $[H^+]$ did not differ by more than 10% before and after the reaction, due to low reactant concentrations. Because of this result, we did not include the rapid protonation of sulfate ions explicitly in modeling, but treated the pH as constant.

Rate Constants for Iodine Hydrolysis. Iodine hydrolysis (and its reverse) is one of the most important processes in this reaction system. It participates in every subsystem of eq 8 in which iodine-containing species appear. The overall reaction is



The kinetics and mechanism of this reaction have already been studied,^{40,41} and rate constants have been suggested²⁰ to describe experiments in the pH range 3–7. The mechanism of the iodine hydrolysis is given by the following reaction scheme:



This complex equilibrium system can be simplified substantially for our experiments. (a) The $I_2 + OH^-$ reaction is not important at $pH < 6$. (b) All the protonation equilibria are fast. (c) I_2OH^- does not have any reactions other than those shown in eq 14. Thus iodine hydrolysis is considered to occur in two parallel pathways: formation of HOI and I^- through H_2OI^+ and HOI formation through I_2OH^- . With simplifications (a)–(c) the detailed mechanism is resolved into two parallel equilibria with the following rate equations:

$$v_{I_2,a} = k_{I_2,a}^f [I_2] [H^+]^{-1} - k_{I_2,a}^r [HOI] [I^-] \quad (15)$$

$$v_{I_2,b} = k_{I_2,b}^f [I_2] - k_{I_2,b}^r [H_2OI^+] [I^-]$$

The superscripts “f” and “r” refer to forward and reverse rate constants, respectively. With this scheme we simplify the entire iodine hydrolysis submechanism without losing significant kinetic detail, provided that I_2OH^- does not undergo any reactions that are substantially faster than its decay to iodine or to HOI and I^- . We found no evidence that any such fast reactions exist with either chlorine-containing species or HIO_2 .

To determine rate constants for the two k^f in eq 15, we ran experiments in which iodine hydrolysis is the rate limiting process: the $HClO_2 + I_2$ and $HOCl + I_2$ reactions. As shown in Figure 5, the initial rates of these reactions are independent of the chlorite concentration but depend on the iodine concentration (Figure 6A). The pH greatly affects the initial rate (Figure 6B), because it affects the iodine hydrolysis. The determination of the rate constants in eq 15 is extremely sensitive to these experiments; consequently, the values obtained are accurate and uncorrelated. The solid lines are fitted curves to the experiments. They show excellent agreement in the initial rates in Figures 5, 6, and 8, where the iodine and H^+

concentrations change. From a knowledge of the equilibrium constant of iodine hydrolysis, the two reverse rate constants (k^r) can also be calculated. The rate constants obtained are

$$k_{I_2,a}^f = 1.98 \times 10^{-3} \text{ M s}^{-1}$$

$$k_{I_2,a}^r = k_{I_2,a}^f / K_{I_2} \cong 3.67 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (16)$$

$$k_{I_2,b}^f = 5.52 \times 10^{-2} \text{ s}^{-1}$$

$$k_{I_2,b}^r = k_{I_2,b}^f K_{H_2OI^+} / K_{I_2} \cong 3.48 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

The rate constant of the proton-inhibited path is very close to that found by Furrow²⁸ (1.8×10^{-3}). The rate constant of the reverse reaction is the same as that found by Eigen and Kustin.⁴⁰ From these rate constants and the equilibrium constants of the reactions in the detailed mechanism of iodine hydrolysis,²⁰ the remaining rate constants of the detailed mechanism can also be determined, assuming diffusion limited rate constants for protonation processes. Our modeling procedure verified that the detailed and the simplified versions of iodine hydrolysis give the same kinetics curves for every subsystem, proving that our simplifying assumptions are justified. Therefore, we can use a single stoichiometry with a more complex rate equation for iodine hydrolysis.

Rate Constant for the Disproportionation of HOI. The disproportionation of hypoiodous acid was studied by several investigators; the large variation in rate constant cannot be explained by differences in experimental conditions.^{29,30} Direct measurements by Furrow determined values of $18\text{--}25 \text{ M}^{-1} \text{ s}^{-1}$ with different experimental methods. Fitting experimental curves similar to those shown in Figure 9 gives a simple second order dependence on the HOI concentration, using wavelengths where either iodine or HOI absorbs. Our results agree with Furrow's studies.

$$v = (22.0 \pm 1.5)[HOI]^2 \quad (17)$$

Rate eq 17 gives an accurate description of both the iodine formation and the HOI consumption. This simple second order dependence together with the presence of an isosbestic point suggests that the rate determining step in the production of iodine is the disproportionation process, and all other reactions of intermediates are faster. Therefore, in view of the above rate equation and the kinetics of iodine hydrolysis, there is another important relationship among the rate constants of intermediates, since HIO_2 does not accumulate in the system. Either the rate of HIO_2 disproportionation or the rate of the $HOI(H_2OI^+) + HIO_2$ reaction is significantly faster than the disproportionation of HOI. Moreover, the $HIO_2 + I^- + H^+$ reaction must be slower than the $HOI + I^-$ reaction; otherwise no second order dependence on HOI concentration could be observed.

Rate Constants for the Disproportionation of HIO_2 and the $HOI/H_2OI^+ + HIO_2$ Reactions. We are aware of two previous investigations aimed at finding rate constants for the disproportionation of HIO_2 .^{24,28} Perhaps because the preparation of HIO_2 is uncertain, the rate constants differ. Nosztcizius *et al.* followed the corrosion potential of iodide-selective electrodes in the system, and observed that the disproportionation process is autocatalytic. In our experiments, the production of iodine increases autocatalytically, and there is a parallel autocatalytic consumption of HIO_2 , providing evidence that the iodine production is not delayed, as would be observed for a sequence of consecutive reactions. This autocatalytic behavior suggests that the initiating disproportionation reaction is slower than the

(40) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.

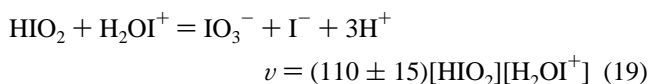
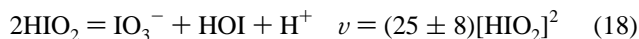
(41) Palmer, D. A.; van Eldik, R. *Inorg. Chem.* **1986**, *23*, 928.

Table 1. Mechanism of the Chlorine Dioxide-Iodide Reaction at $[I^-]_0/[ClO_2^-]_0 = 3-5$, pH = 1-3.5, and 25 °C^a

(M1)	$ClO_2 + I^- \rightarrow ClO_2^- + \frac{1}{2}I_2$	$v_1 = 6 \times 10^3 [ClO_2][I^-]$
(M2)	$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$	$v_{2a} = 1.98 \times 10^{-3} [I_2][H^+] - 3.67 \times 10^9 [HOI][I^-]$ $v_{2b} = 5.52 \times 10^{-2} [I_2] - 3.48 \times 10^9 [H_2OI^+][I^-]$
(M3)	$HClO_2 + I^- + H^+ \rightarrow HOI + HOCl$	$v_3 = 7.8 [HClO_2][I^-]$
(M4)	$HClO_2 + HOI \rightarrow HIO_2 + HOCl$	$v_4 = 6.9 \times 10^7 [HClO_2][HOI]$
(M5)	$HClO_2 + HIO_2 \rightarrow IO_3^- + HOCl + H^+$	$v_5 = 1.0 \times 10^6 [HClO_2][HIO_2]$
(M6)	$HOCl + I^- \rightarrow HOI + Cl^-$	$v_6 = 4.3 \times 10^8 [HOCl][I^-]$
(M7)	$HOCl + HIO_2 \rightarrow IO_3^- + Cl^- + 2H^+$	$v_7 = 1.5 \times 10^3 [HOCl][HIO_2]$
(M8)	$HIO_2 + I^- + H^+ \rightleftharpoons 2HOI$	$v_8 = 1.0 \times 10^9 [HIO_2][I^-][H^+] - 22 [HOI]^2$
(M9)	$2HIO_2 \rightarrow IO_3^- + HOI + H^+$	$v_9 = 25 [HIO_2]^2$
(M10)	$HIO_2 + H_2OI^+ \rightarrow IO_3^- + I^- + 3H^+$	$v_{10} = 110 [HIO_2][H_2OI^+]$
(M11) ^{b49}	$HOCl + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O$	$v_{11} = 2.2 \times 10^4 [HOCl][Cl^-][H^+] - 22 [Cl_2]$
(M12) ^b	$Cl_2 + I_2 + 2H_2O \rightarrow 2HOI + 2Cl^- + 2H^+$	$v_{12} = 1.5 \times 10^5 [Cl_2][I_2]$
(M13) ^b	$Cl_2 + HOI + H_2O \rightarrow HIO_2 + 2Cl^- + 2H^+$	$v_{13} = 1.0 \times 10^6 [Cl_2][HOI]$
Rapid Equilibria:		
(M14)	$HClO_2 \rightleftharpoons ClO_2^- + H^+$	$K_{HClO_2} = [ClO_2^-][H^+]/[HClO_2] = 2.0 \times 10^{-2}$
(M15)	$H_2OI^+ \rightleftharpoons HOI + H^+$	$K_{H_2OI^+} = [HOI][H^+]/[H_2OI^+] = 0.034$
(M16)	$I_2 + I^- \rightleftharpoons I_3^-$	$K_{I_3^-} = [I_3^-]/([I_2][I^-]) = 740$
Variables: T_I^- , ^c T_{I_2} , ^c T_{HOI} , ^c HIO_2 , ClO_2 , $T_{ClO_2^-}$, ^c $HOCl$, Cl_2 , ^b Cl^- , ^b		

^a All concentration units in M, times in s. ^b Reactions M11–M13 are important only at pH < 2.0 and high concentrations of HClO₂ (>10⁻³ M) or at high [Cl⁻]₀ or in the HOCl + I₂ reaction. Otherwise they can be neglected together with Cl₂ and Cl⁻ as variables. Fits shown in Figure 3 were produced without considering these reactions and variables. ^c The appropriate concentrations of I⁻, I₂, HOI, H₂OI⁺, and HClO₂ can be expressed using eqs 10–12.

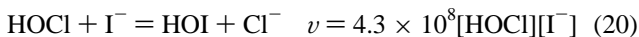
HOI/H₂OI⁺ + HIO₂ reaction. The set of reactions M8–M10 and the reverse of M2 in Table 1 provide an accurate description of the kinetics. Reactions M9 and M10 are rate limiting, and reactions M8 and the reverse of M2 are fast; consequently, the kinetics are sensitive only to M9 and M10. The rate constants for those steps are given in eqs 18 and 19.



Our disproportionation rate constant is higher (about 5 times) and that for the I(+1) + HIO₂ reaction is lower (about half) than Noszticzius *et al.* or Furrow's values, because they did not consider the protonation of HOI. The rate constant determination for the reaction between HOI and HIO₂ is not accurate, probably because of the high error of determining initial concentrations, and the very narrow limit of feasible experimental conditions. A rate constant below 20 M⁻¹ s⁻¹ for the HOI + HIO₂ reaction does not significantly affect the other experiments, and this step can be neglected.

Rate Constants for HOCl + Iodine-Containing Species.

In this group of reactions we analyze the reactions of HOCl with I⁻, I₂, HOI and HIO₂. The reaction of I⁻ with HOCl is fast, complex and involves many intermediates.⁴² The chlorine dioxide-iodide, chlorite-iodide and hypochlorous acid-iodine reactions are not sensitive to the rate constant of this process unless it is below 10⁸ M⁻¹ s⁻¹. Therefore, we used one overall stoichiometric equation with a simple rate law of the form



In the mechanism proposed by Nagy *et al.*⁴² one of the intermediates is ICl. Since the concentration of this species is quite low in our experiments, and since ICl is a form of iodine(+1), its reactivity would have to be much higher than that of HOI/H₂OI⁺ to observe any significant kinetic effect. However, the rates of the HOI/H₂OI⁺ + I⁻ reactions are already diffusion limited, therefore, the ICl + I⁻ reaction cannot be important.

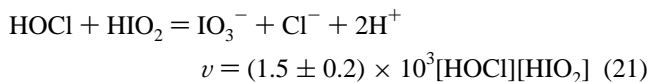
(42) Nagy, J. C.; Kumar, K.; Margerum, D. W. *Inorg. Chem.* **1988**, *27*, 2773.

Although ICl is more stable toward disproportionation than HOI, because of its low concentrations and small ratio to the total iodine(+1) concentration, it will not modify the iodine(+1) disproportionation rate significantly. This contention is supported by the fact that Cl⁻ does not have an effect on the chlorite-iodide and chlorite-iodine reactions at the low concentrations comparable to those produced in the reaction. For these reasons, we did not include ICl as an independent species.

From experiments performed with the HOCl + I₂ reaction, we can give a good estimate for the rate constant of this direct reaction. As can be seen (Figure 8, curves a–d), the initial rate of the reaction is almost independent of the concentration of HOCl. This observation indicates that the direct reaction must be slow compared with the reaction pathway regulated by iodine hydrolysis. Otherwise, with increasing HOCl concentration one would observe a significant increase in the initial rate. Furthermore, the HOCl + I₂ direct reaction should be a pH-independent process. In the real experimental system, however, we observe a decrease in the initial rate with decreasing pH (Figure 8B), which also shows that the direct reaction cannot have a significant contribution. From our experiments, the upper limit of this rate constant is 2 M⁻¹ s⁻¹, and with this or lower rate constants the HOCl + I₂ reaction can be neglected.

From a knowledge of the rate of the fast reaction between HOCl and I⁻ and the HOCl-independent initial rate of the HOCl + I₂ reaction, we obtain a reliable estimate for the upper limit of the rate constant for the HOCl + HOI reaction: approximately 20 M⁻¹ s⁻¹. With higher rate constants the description of the pH dependence and the stoichiometry of the experiments would not be correct. Lower rate constants, including zero, describe the experiments correctly; consequently, the reaction between HOCl and HOI can be neglected, like the HOCl + I₂ direct reaction.

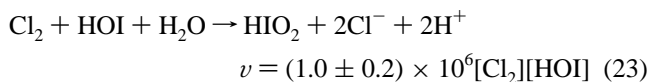
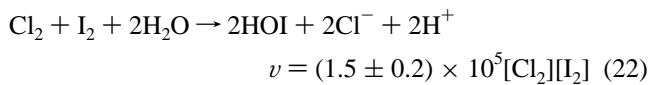
The reaction between HOCl and HIO₂ is an important component of the temporal development of the HOCl-I₂ reaction after the initial fast phase. It generates the correct stoichiometric amount of HOI and HIO₂ to produce the expected amount of I₂ during the disproportionation of the first two species. This reaction also has an important effect on the chlorite-iodine reaction and regulates the level of HOCl available for other reactions. The best fits for the experimental kinetics curves can be obtained with the following rate equation.



Rate Constants for Cl_2 + Iodine-Containing Species. Rate constants for chlorine reacting with iodine-containing compounds can be determined most sensitively from experiments done with the $\text{HOCl} + \text{I}_2$ reaction at HOCl excess (Figure 8, curves c–i). In this case chlorine, which is formed from the $\text{HOCl} + \text{Cl}^- + \text{H}^+$ reaction, could have a significant concentration and contribution to the overall rate.

From our experiments, nothing can be established about the rate of the direct reaction between chlorine and iodide. This is certainly a fast reaction; however, even with diffusion controlled rate constants it does not contribute significantly to the kinetics of the full system, because iodine and HOI , which are present at about 6 orders of magnitude higher concentration than iodide, react rapidly with chlorine.

Chlorine reacts rapidly with iodine and even faster with hypiodous acid. These reactions can explain the autocatalytic features of the $\text{HOCl} + \text{I}_2$ reaction at high HOCl excess and low pH. As we have shown in Figure 7, the intermediates of the $\text{HOCl} + \text{I}_2$ reaction are consumed autocatalytically and rapidly at high acid concentrations and hypochlorous acid excess. This process is fast because chlorine, the equilibrium concentration of which is high at higher acidities, reacts rapidly with the intermediate HOI . At lower acidities the chlorine level is low and its reactions are less important. The rate laws for these two reactions are



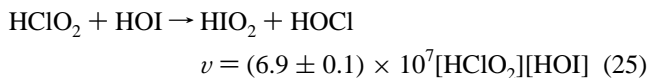
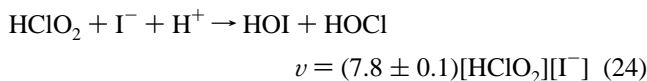
The reaction between chlorine and iodous acid does not contribute significantly in our experimental systems, since HOCl reacts comparatively rapidly with HIO_2 . Choosing a rate constant smaller than $10^6 \text{ M}^{-1} \text{ s}^{-1}$ does not affect the kinetics of the reactions under consideration. However, higher rate constants will destroy the correct stoichiometry. From our experiments the only certainty is that the rate constant should be smaller than $10^6 \text{ M}^{-1} \text{ s}^{-1}$ and that with such values this reaction can be neglected.

Reactions 22 and 23 have minor roles at the initial conditions used in the chlorine dioxide-iodide reactions; their contributions are less than 1% even after t_{max} on the kinetics curves. However, they have critical roles in the HClO_2 - I_2 and HOCl - I_2 reactions at high initial concentrations or an excess of oxidants.

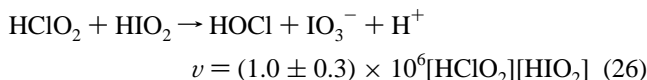
Rate Constants for HClO_2 + Iodine-Containing Species. The reactions of HClO_2 with iodine-containing species are probably the most important in determining the dynamics of the $\text{ClO}_2 + \text{I}^-$ and $\text{HClO}_2 + \text{I}^-$ reactions. Iodine does not react directly with HClO_2 . This statement can be verified by inspecting Figure 5, where the chlorite dependence of the chlorite-iodine reaction is shown. The initial rate is completely independent of the concentration of chlorite. If there were any significant direct reaction between HClO_2 and I_2 , the initial rate would depend on the chlorite concentration. The upper limit for this rate constant is about $0.01 \text{ M}^{-1} \text{ s}^{-1}$ from our experiments.

The direct reaction between HClO_2 and I^- is slow but has a determining role in the shape of the kinetics curves of Figure

3. Two reactions determine the rate of part (b) in Figure 1. One of them is the direct reaction between HClO_2 and I^- and the other is the $\text{HClO}_2 + \text{HOI}$ reaction. At low pH, where the $[\text{HClO}_2]/[\text{ClO}_2^-]$ ratio is high, and the HOI level from the iodine hydrolysis low, the contribution of the direct reaction between HClO_2 and I^- reaction will be high. At high pH, however, since most of the chlorite is in the form of ClO_2^- and this is not the reactive form, the direct reaction is slow. On the other hand, lower H^+ concentration shifts the iodine hydrolysis to increase the level of HOI , and the contribution of the $\text{HOI} + \text{HClO}_2$ reaction will be significantly higher. These two rate constants can be determined very sensitively from the experiments done with the chlorine dioxide-iodide reactions. The stoichiometries and rate laws are

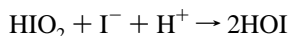


The reaction between HClO_2 and HIO_2 will determine the kinetics curves of the chlorite-iodine reaction after the first fast decrease in the iodine concentration (the part that is zeroth-order in chlorous acid concentration), before the complete consumption of chlorite. This step produces a slower decrease in the iodine concentration (Figure 5). Since the prominence of this reaction accounts for the most substantial difference between our model of the chlorite-iodide reaction and previous models, we tried to determine its kinetics by direct measurements. Since we have $\text{HIO}_2(\text{IO}^+)$ available, which was used in studying the kinetics of disproportionation of HIO_2 , we can use the same experimental procedure for investigating the $\text{HClO}_2 + \text{HIO}_2$ reaction. The sulfuric acid solution of IO^+ was added to alkaline ClO_2^- . After mixing, the change of the spectrum of the reaction mixture with time was studied. However, the reaction reached completion during mixing; no changes in the spectra were observed. In contrast to the HIO_2 disproportionation experiments, where iodine formed slowly, no iodine formed here, and no change in the absorption region of HIO_2 was observed after mixing. Knowing the initial concentrations and mixing time allows us to estimate the lower limit of the rate constant for this reaction: $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The fitted value to the experiments done with the chlorite-iodine reaction, together with the stoichiometry is



The rate constant of the reaction between HIO_2 and I^- . Interestingly, only the most complex subsystems of eq 8, the chlorite-iodine and chlorine dioxide-iodine reactions, are sensitive to the value of this rate constant. All the other reactions, even HIO_2 disproportionation, require only a rapid reaction with a rate constant higher than $10^6 \text{ M}^{-2} \text{ s}^{-1}$ (H^+ dependent). However, the more complex systems can tolerate only a narrow range for this rate constant, because of the fast reaction between HClO_2 and HIO_2 . If the $\text{HIO}_2 + \text{I}^-$ reaction were slow, most of the HIO_2 would react with HClO_2 rather than with I^- to produce iodate in part (b) of Figure 1. This reaction would destroy the correct stoichiometry and kinetics of the whole reaction. If the rate of the $\text{HIO}_2 + \text{I}^- + \text{H}^+$ reaction is faster than the $\text{HClO}_2 + \text{HIO}_2$ reaction, then HOI will be produced. Thus, in this model HIO_2 is a highly reactive species, reacting

rapidly with iodide to produce iodine. This step keeps HIO_2 in the reaction cycle and does not allow it to be removed as iodate, which is an inactive product. Consequently, any uncertainties in the rate constant of the $\text{HClO}_2 + \text{HIO}_2$ reaction increase the uncertainty of the rate constant of the $\text{HIO}_2 + \text{I}^- + \text{H}^+$ reaction. The stoichiometry and rate law consistent with our experiments are



$$v = (1.0 \pm 0.5) \times 10^9 [\text{HIO}_2][\text{I}^-][\text{H}^+] \quad (27)$$

which will ensure that HIO_2 remains in the reaction cycle. The pH dependence of this reaction comes from the pH dependence of the whole reaction. We tested the possibility of a pH independent process; however, the stoichiometry of the pH dependent kinetics curves in the chlorine dioxide-iodide reaction could not be reproduced.

Discussion

In Table 1 we list the important reactions in the chlorine dioxide/chlorite + iodide reaction system with their rate constants. These reactions were necessary and sufficient to describe the chlorine dioxide-iodide reaction in all of our experiments and, furthermore, to account for the kinetics of HOI and HIO_2 disproportionation (reactions M2 and M8–M10), the $\text{HOCl} + \text{I}_2$ reaction (reactions M2 and M6–M14), and the $\text{HClO}_2 + \text{I}_2$ reaction at excess iodine (reactions M2 and M4–M14) when $[\text{HClO}_2]_0/[\text{I}_2]_0 < 2.5$ and $[\text{HClO}_2]_0 < 2 \times 10^{-3}$ M in the pH range 1–3.5. We did not include several other reactions which certainly take place in the system but whose rates are too slow to make observable contributions to the overall kinetics. These are, e.g., the $\text{Cl}_2 + \text{I}^-$ and the $\text{IO}_3^- + \text{I}^-$ reactions.

With the exception of the chlorine dioxide-iodide reaction, all of the reactions considered are two-electron processes; the model does not include radical processes. Although the $\text{ClO}_2 + \text{I}^-$ reaction is rapid and first-order in both ClO_2 and I^- , it is not elementary. The rate limiting step is the direct reaction between ClO_2 and I^- , followed by a faster process; the process may occur through an inner-sphere mechanism.^{22,43} If fast radical processes occur, there is no evidence that the radical intermediates interact with any other species rapidly enough to have an effect on the overall kinetics. This reaction is well separated from the others, as illustrated by the observation that the kinetics of the chlorite-iodide reaction are the same as those of the chlorine dioxide-iodide reaction if we start from the same initial concentration that exists after completion of the fast chlorine dioxide-iodide reaction.

The two-electron reactions in this model which produce the kinetic feedback stand in contrast to the mechanisms of many other, non pH-regulated chemical oscillators. For example, in the case of the BZ reaction, the autocatalytic feedback process originates from the one-electron reaction of BrO_2 radical with the catalyst.⁴⁴ The Briggs-Rauscher reaction^{7,45,46} and the permanganate oscillators⁴⁷ have similar one-electron based feedback processes. The unique accelerating feature in part (b) of Figure 1 comes mainly from iodide inhibition. This conclusion is based on the observations that the direct reaction between HClO_2 and I^- is slow, but the $\text{HClO}_2 + \text{HOI}$ reaction

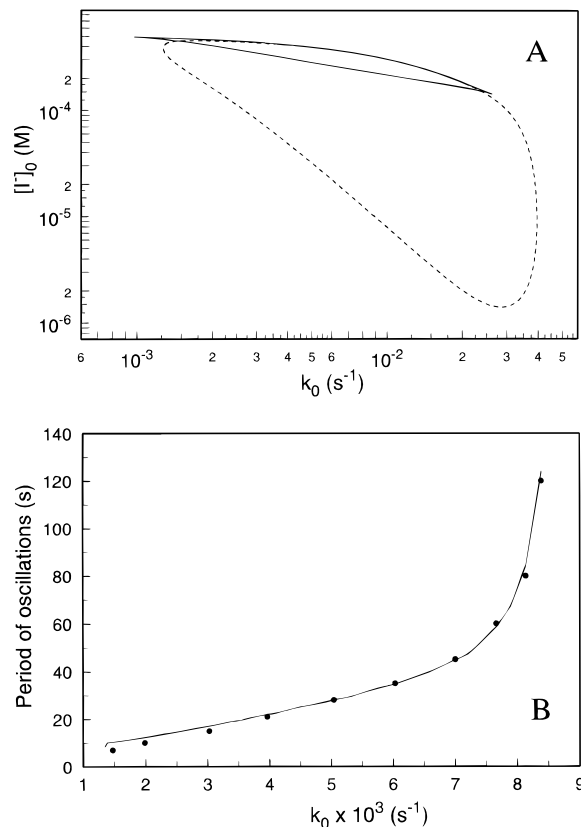


Figure 11. Modeling the open system behavior of the chlorine dioxide-iodide reaction using reactions M1–M10 and M14–M16 of Table 1. A) Bifurcation diagram (calculated using CONT⁵⁰) in the $[\text{I}^-]_0$ vs k_0 (reciprocal residence time) plane. The solid line encloses the area of bistability; the dashed line indicates Hopf bifurcations and encloses the range of oscillations. $[\text{ClO}_2]_0 = 1 \times 10^{-4}$ M and $[\text{H}^+] = 1 \times 10^{-2}$ M. The experimental bifurcation diagram is published in ref 48. (B) Dependence of the period of oscillations on k_0 . Filled circles are experimental points, and the solid line is calculated. $[\text{I}^-]_0 = 3 \times 10^{-4}$ M, $[\text{ClO}_2]_0 = 1 \times 10^{-4}$ M and $[\text{H}^+] = 1 \times 10^{-2}$ M.

is very fast. Because the HOI level is controlled by iodine hydrolysis, decreasing iodide concentration shifts reaction 13 to the right, to higher levels of HOI, which makes the reaction faster as the iodide concentration decreases.

Since there is no, or only a very slow, direct reaction between HClO_2 and I_2 , the same model holds true for the chlorite-iodine reaction. When iodide is present, HIO_2 cannot be oxidized to iodate by HClO_2 or H_2OI^+ , but reaction with iodide will produce HOI, and that will be converted to iodine. When iodide is consumed, nothing prevents HIO_2 from being oxidized to iodate, and iodine starts to decrease very rapidly, converting to HOI/ H_2OI^+ , HIO_2 , and IO_3^- .

Most of the reactions in the model have mass action kinetics, which might mean that they are elementary reactions. However, it is clear that most of these reactions are not elementary; they go through several intermediates. Some examples of rapid but not elementary reactions are the hypochlorous acid-iodide reaction,²³ the reaction between HIO_2 and I^- and chlorine hydrolysis.⁴⁰ In our reaction system, however, the details of these reactions are not important because of the different time scales. The reaction between HClO_2 , I^- , and H^+ is certainly not elementary, because its kinetics are $[\text{H}^+]$ independent. It is easy to construct a model consisting only of elementary reactions, which would include the protonation of IO^- or ClO^- ; however, this level of detail does not improve the kinetics fit and is not included in our model. Such a simplification guided our modeling efforts, for example, when we replaced the detailed

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mechanism of iodine hydrolysis with a simplified version that preserves all the important equilibrium and kinetics features of the detailed mechanism and used rapidly established equilibrium constants for the formation of I_3^- , H_2OI^+ and $HClO_2$. The number of concentration variables in the model decreased significantly, which benefits applications to more complex systems.

In the Introduction we mentioned some of the discrepancies between the C&E model and experiment. These are mainly (1) that it produces homogeneous oscillations where significant stirring effects occur and (2) that it does not produce oscillations in the chlorine dioxide-iodide reaction at 10^{-4} M initial concentration of ClO_2 .⁴⁸ This latter discrepancy is surprising, since a very simple model,⁴⁸ based on component processes, is capable of quantitative description of the open system behavior, and the Epstein–Kustin model, which lacks the disproportionation reactions of HOI and HIO_2 , also gives oscillations in the chlorine dioxide-iodide reaction. Our model (Table 1) does not produce homogeneous oscillations where stirring and mixing effects occur in the chlorite-iodide reaction. However, it produces homogeneous oscillations at the conditions observed in the chlorine dioxide-iodide reaction. In Figure 11 we show a two-parameter bifurcation diagram and the oscillation period *vs* flow rate curves. Both are in good agreement with experiment.

To find the reason for the discrepancy we compared rate constants of our present model and rate constants used by C&E. Besides small differences regarding iodine hydrolysis and the

$HOCl + I^-$ reaction, the main disparity lies in the difference between rate constants for the reactions of HIO_2 . In the C&E model, there is no reaction between $HClO_2$ and HIO_2 , the rate constant of $HIO_2 + I^- + H^+$ reaction is only $10^6 M^{-2} s^{-1}$, and the rate of disproportionation is two orders of magnitude faster ($3 \times 10^3 M^{-1} s^{-1}$) than the experimental value. These differences mean that in part (b) of Figure 1, the HIO_2 level is four orders of magnitude higher, the maximum concentration of HIO_2 at t_{max} is three times higher and HIO_2 is consumed faster after t_{max} than in our model. The existence of a reaction between $HClO_2$ and HIO_2 was shown experimentally. Since this is a fast reaction, the $HIO_2 + I^- + H^+$ reaction must be significantly faster than this; otherwise the stoichiometry of part (b) would not be correct in the model. The central role of HIO_2 in the C&E model is shown by the extreme sensitivity of oscillations in that model to the rate constant for the disproportionation of HIO_2 , which in the model is two orders of magnitude higher than the experimental value.

The model we have presented (Table 1) uses only experimentally determined rate and equilibrium constants. Further modeling of the interaction between chlorine- and iodine-containing species should be carried out, however, to investigate a wider range of conditions, including the effects of imperfect mixing.

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