Kinetics of Photoresponse of the Chlorine Dioxide-Iodine-Malonic Acid Reaction

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We studied the photoresponse of the chlorine dioxide−iodine−malonic acid (CDIMA) reaction. In a continuously fed stirred tank reactor, the photosensitivity increases with decreasing residence time and increasing concentration of chlorine dioxide. Under certain conditions, concentrations change in a sigmoidal fashion in response to a jump in the intensity of illumination. We propose a new mechanism for the effect of visible light on the CDIMA reaction. Simulations based on the proposed mechanism accurately describe the experimentally observed kinetics.

Introduction

The chlorite−iodide−malonic acid (CIMA) reaction[1] provided the first experimental demonstration of Turing structures.[2,3] Later it was shown[4,5] that the core reaction in this system is actually the chlorine dioxide−iodine−malonic acid (CDIMA) reaction. Today it is the latter reaction that is most often used to study Turing structures.[6,7] We recently demonstrated that visible light affects the CDIMA reaction[8] and can be employed to control Turing patterns.[9] In a stirred reactor, intense illumination of the CDIMA reaction results in suppression of oscillations within seconds, while transitional processes between steady states last much longer.[8] A mechanism for the photochemistry of the CDIMA reaction, suggested in ref 8, gives a qualitative description of the experimental results, but it predicts significantly faster transition processes between steady states than those observed in experiments.

Here we present new data on the photosensitivity of the CDIMA reaction in the steady-state mode and on the kinetics of transition between steady states. We propose an improved mechanism for the photochemistry of the reaction and perform numerical simulations, the results of which are in good agreement with our experimental data.

Experimental Section

Materials. Iodine (Aldrich, ACS reagent), water-soluble starch (Aldrich, ACS reagent), and malonic acid (Aldrich, 99+%) were used without further purification. Chlorine dioxide was prepared as described earlier.[10] The concentration of chlorine dioxide solutions was checked prior to each run by standard iodometric titration.

Procedures and Apparatus. We employed a continuously fed stirred tank reactor (CSTR) made from a thermostatted spectrophotometrical quartz cuvette. The temperature was kept constant at 25.0 ± 0.2 °C.

Four stock solutions were used in the experiments: (a) 0.04 M H_2SO_4; (b) 0.0022 M I_2 dissolved in 40% acetic acid; (c) malonic acid with starch; and (d) chlorine dioxide. Equal amounts of solutions (a) with (b), and (c) with (d) were premixed just before injecting them into the reactor via a Rainin Rabbit Plus peristaltic pump.

To examine the effects of malonic acid and iodomalonic acid, in some experiments we employed iodide as a feed reagent and eliminated malonic acid from the feed stream. In such cases, the concentration of the iodine stock solution was decreased to 0.00112 M to adjust [I_2] to its steady-state concentration. The solutions of iodine and of iodide (containing the desired amount of starch) were premixed just before they were injected into the reactor.

The reactor cell was illuminated from above by parallel, unfiltered light from a tungsten−halogen lamp. A mechanical shutter was employed to switch between the light and dark phases. The volume of solution in the reactor was 2 cm^3, which corresponds to a path length of 2 cm. The intensity of illumination in the wavelength range 380−620 nm at the surface of the solution in the reactor was 5.5 mW/cm^2, as measured by a Newport 1815 optical powermeter.

We employed starch as an indicator to study the relatively slow kinetics of the steady-state transitions because the relaxation time for the starch−triiodide (SI_3^-) complex formation is of the order of magnitude of a second.[11] Absorbances at 280, 350, 460, 620, 700, and 750 nm were continuously recorded with an HP 8452A diode array spectrophotometer.

Experimental Results

Figure 1 shows the responses of the CDIMA reaction to illumination for several concentrations of chlorine dioxide at wavelengths 350 and 750 nm. The starch−triiodide complex is the only light-absorbing species at 750 nm. There are at least five species that absorb light at 350 nm (I_3^-, SI_3^-, ClO_2, I_2, and IMA), with the main absorbance contribution coming from the SI_3^- complex. The absorbance at 750 nm during the dark phase is too high to extract reliable information, therefore the absorbance at 350 nm is also shown. At 350 nm, the main absorbance contribution still arises from the starch−triiodide complex and the recorded absorbance is well below 2.0, so the main qualitative trends of the kinetic curves can be determined from these experiments.

At $[ClO_2]_0 = 0.025$ mM, after the light is switched on, the concentration of the starch−triiodide complex decreases to a new steady-state level with a monotonically decreasing rate. When the light is switched off, the recovery process starts
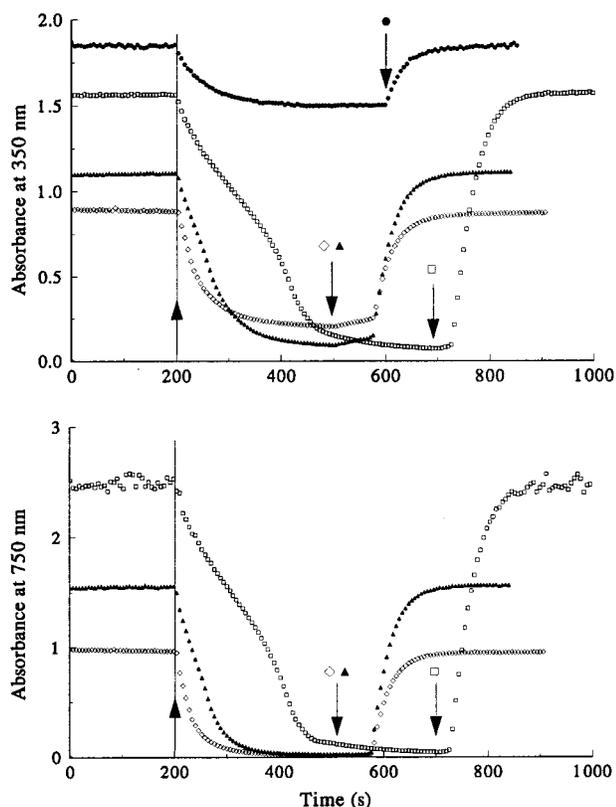
Figure 1. Response of the CDIMA reaction to illumination—dependence on input concentration of ClO_2. Residence time is 120 s. Upward arrows indicate time when the light is switched on, and downward arrows indicate when it is switched off. Input concentrations (mM): $[I_2]_0 = 0.55$; $[H_2SO_4]_0 = 10$; $[MA]_0 = 0.25$; $[S] = 0.1\%$ w/v, $[ClO_2]_0 = 0.025$ (●), 0.05 (□), 0.125 (▲), and 0.25 (◇).

immediately. At $[ClO_2]_0 \geq 0.05$ mM, illumination shifts the steady-state concentration of SI_3^- to much lower values. In these cases, when the light is switched off, the recovery process starts only after a delay period of 40−80 s. At $[ClO_2]_0 = 0.05$ mM, the decrease in $[SI_3^-]$ during illumination follows a sigmoidal curve.

Figure 2 shows the response of the system to light for several values of the residence time. We observe a sequence of curves similar to that shown in Figure 1. Hence, a decrease in residence time produces an effect on the kinetics of the CDIMA reaction photochemistry that parallels that of an increase in the chlorine dioxide concentration.

Figure 3 displays the response of the iodine−iodide−chlorine dioxide subsystem to illumination for several values of $[ClO_2]_0$. We find the same qualitative trends as in the CDIMA reaction: at the lowest chlorine dioxide concentration, the illumination produces only a relatively small drop in $[SI_3^-]$, whereas at higher chlorine dioxide concentrations, illumination shifts the starch−triiodide concentration to significantly lower values; at intermediate $[ClO_2]_0$, we observe a sigmoidal kinetic curve, similar to those shown in Figures 1 and 2. These experiments suggest that the iodine−iodide−chlorine dioxide subsystem is largely responsible for the effect of illumination in the CDIMA reaction. Though we cannot entirely exclude malonic acid and iodomalonic acid, we conclude that these species play only minor roles in the effect of illumination.

Model

The behavior of the CDIMA reaction in the presence of starch is described by the following reaction steps and associated rate equations:[5]
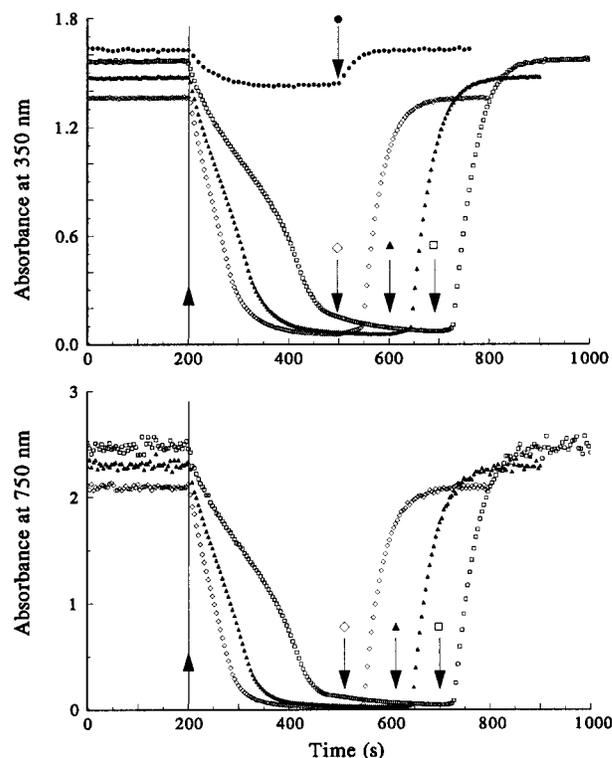
Figure 2. Response of the CDIMA reaction to illumination—dependence on residence time; $[ClO_2]_0 = 0.05$ mM. Upward arrows indicate time when the light is switched on, and downward arrows indicate when it is switched off. Input concentrations (mM): $[I_2]_0 = 0.55$; $[H_2SO_4]_0 = 10$; $[MA]_0 = 0.25$; and $[S] = 0.1\%$ w/v. Residence times (s) = 240 (●), 120 (□), 80 (▲), and 60 (◇).
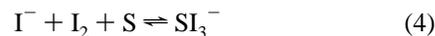
$$I_2 + MA \rightarrow IMA + I^- + H^+ \qquad (1)$$

$$v_1 = \frac{k_1[MA][I_2]}{k_{-1} + [I_2]}$$

$$ClO_2 + I^- \rightarrow \frac{1}{2}I_2 + ClO_2^- \qquad (2)$$

$$v_2 = k_2[ClO_2][I^-]$$

$$ClO_2^- + 4I^- + 4H^+ \rightarrow Cl^- + 2I_2 + 2H_2O \qquad (3)$$

$$v_3 = k_3[ClO_2^-][I^-][H^+] + k_3'\frac{[ClO_2^-][I_2][I^-]}{u + [I^-]^2}$$
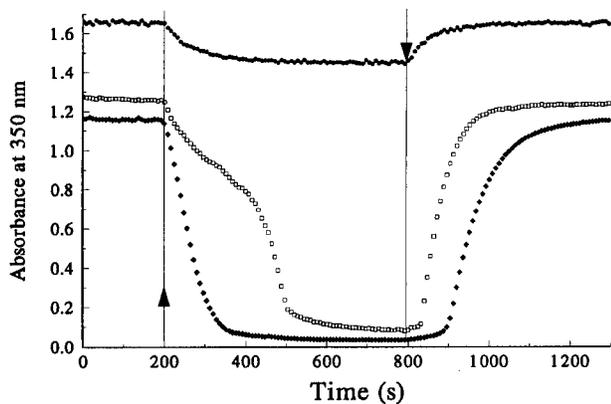
$$I^- + I_2 + S \rightleftharpoons SI_3^- \qquad (4)$$

$$v_4 = k_4[I_3^-][S] - k_{-4}[SI_3^-]$$

where $[S]$ is the concentration of binding sites on the starch.

The following mechanism has been suggested[8] to explain the effects of illumination on the CDIMA reaction:

$$I_2 + h\nu \rightarrow 2I \qquad (5a)$$

$$I + H_2O \rightarrow IH_2O \qquad (5b)$$

$$IH_2O + ClO_2 \rightarrow HOI + ClO_2^- + H^+ \qquad (5c)$$

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \qquad (5d)$$

with corresponding net reaction:

Figure 3. Response of iodine−chlorine dioxide−iodide reaction to illumination. Input concentrations (mM): $[I_2]_0 = 0.28$, $[H_2SO_4]_0 = 10$; $[S]_0 = 0.1\%$ w/v; $[I^-]_0 = 0.15$; $[ClO_2]_0 = 0.0375$ (●), 0.055 (□), and 0.075 (◆). Residence time is 120 s.
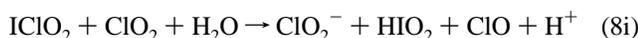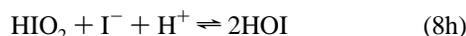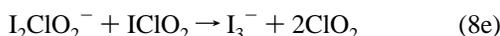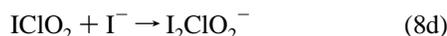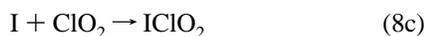
$$2I^- + 2ClO_2 \rightarrow I_2 + 2ClO_2^- \tag{6}$$

and with rate equation:

$$v_6' = \phi W \tag{7}$$

which results from the assumption that eq 5a is the rate-determining step. Here, ϕ is the quantum yield and W is the rate of absorption of the actinic photons divided by the reactor volume. W is proportional to the light intensity and to $[I_2]$.

Although a model based on the mechanism just presented gives results in qualitative agreement with earlier experimental data,[8] it fails to account for our experimental results, in particular the large drop in $[SI_3^-]$ after illumination at residence times of 120 s or less and the sigmoidal kinetics for intermediate values of the residence time and chlorine dioxide concentration. We suggest here a modified reaction scheme:

$$I_2 + h\nu \rightarrow 2I \tag{8a}$$

$$2I \rightarrow I_2 \tag{8b}$$

$$I + ClO_2 \rightarrow IClO_2 \tag{8c}$$

$$IClO_2 + I^- \rightarrow I_2ClO_2^- \tag{8d}$$

$$I_2ClO_2^- + IClO_2 \rightarrow I_3^- + 2ClO_2 \tag{8e}$$

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \tag{8f}$$

$$I_3^- \rightleftharpoons I_2 + I^- \tag{8g}$$

$$HIO_2 + I^- + H^+ \rightleftharpoons 2HOI \tag{8h}$$

$$IClO_2 + ClO_2 + H_2O \rightarrow ClO_2^- + HIO_2 + ClO + H^+ \tag{8i}$$

$$ClO_2 + ClO + H_2O \rightarrow 2ClO_2^- + 2H^+ \tag{8j}$$

which gives the same net reaction as eq 6.

Step 8a represents the photodissociation of molecular iodine, and step 8b represents the recombination of iodine atoms. The rate of photodissociation was estimated as described earlier.[8] The rate constant of recombination of iodine atoms in iodide solutions was determined by Grossweiner and Matheson.[15] At low iodide concentrations, as in our case, the estimated value is 1×10^{10} M^{-1} s^{-1}.

We assume that in the presence of relatively high concentrations of ClO_2, the production of $IClO_2$ described by reaction

TABLE 1: Parameters of Model

Constant	Values
k_1 (M^{-1} s^{-1})	0.0075
k_{-1} (M)	5×10^{-5}
k_2 (M^{-1} s^{-1})	6000
k_3 (M^{-2} s^{-1})	460
k_3' (s^{-1})	0.00265
u (M^2)	1×10^{-14}
k_4 (M^{-1} s^{-1})	1×10^6
k_{-4} (s^{-1})	1
k_6 (s^{-1})	0.0114
k_6'	1500

step 8c competes with the reaction step 8b. The species $IClO_2$ is analogous to the well-studied Cl_2O_2,[16−18] and we assume that the chemical properties of $IClO_2$ resemble those of Cl_2O_2. We employed the fitting software package Zita[13] to estimate some of the rate constants from our kinetics measurements. Our fitting procedure yields a lower limit of 5.7×10^5 M^{-1} s^{-1} for the rate constant k_{8c}.

We propose that iodide ion catalyzes the disproportionation of $IClO_2$ in reactions 8d and 8e. Together with reaction 8c, these steps constitute an additional route for the recombination of iodine atoms catalyzed by chlorine dioxide and iodide ion. If the reaction step 8d is the rate-limiting step, then using the quasi-steady-state approximation (QSSA), we can eliminate $[I_2ClO_2^-]$ from the differential equations obtained from the reaction scheme 8.

The rate coefficients for the well-known equilibria 8f−8h were adopted directly from a previous study.[12] Steps 8i and 8j describe the conversion of $IClO_2$ and ClO_2 into HIO_2 and ClO_2^-. Again, if we assume that reaction 8i is rate limiting, we can eliminate $[ClO]$ with the QSSA. If we further employ the QSSA to eliminate the concentrations of HIO_2, HOI, iodine atoms, and $IClO_2$, we obtain the following expression for v_6:

$$v_6 = \frac{2k_{8c}k_{8i}[ClO_2]^2(\sqrt{16\phi W k_{8b} + (k_{8c}[ClO_2])^2} - k_{8c}[ClO_2])}{4k_{8b}(2k_{8d}[I^-] + k_{8i}[ClO_2])} \tag{10}$$

At high intensity of illumination, this expression assumes a simple form:

$$v_6 = \frac{k_6[ClO_2]^2}{k_6'[I^-] + [ClO_2]} \tag{11}$$

where

$$k_6 = \frac{2k_{8c}}{k_{8b}}\sqrt{k_{8b}W\phi} \text{ and } k_6' = \frac{2k_{8d}}{k_{8i}} \tag{12}$$

Results of Simulations

In our simulations, we employ eqs 1−4 and eq 6 with the new rate equation, eq 11, to calculate the kinetics of $[SI_3^-]$ in the presence of light. The rate coefficients of the basic (dark) CDIMA reaction are taken from refs 5 and 12. The rate constants k_6 and k_6' were obtained by employing the fitting software package.[13] Table 1 summarizes the kinetic parameters used in our simulations.

Figure 4 shows the simulated response of $[SI_3^-]$ to illumination for several concentrations of chlorine dioxide. The numerical results are in good agreement with the experimental data (see Figures 1 and 2). When $[ClO_2]_0$ is low, the decrease in $[SI_3^-]$ after illumination is moderate, and the rise of $[SI_3^-]$ starts immediately after the light is switched off. At higher chlorine
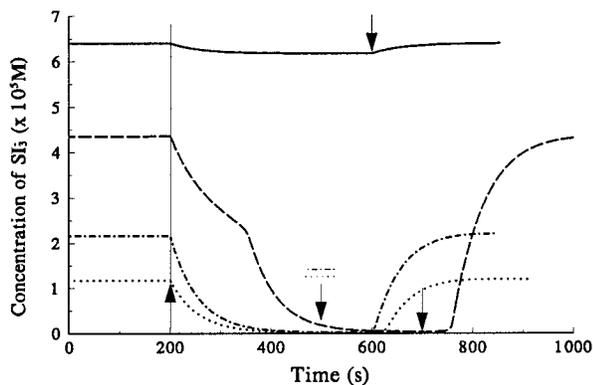
Figure 4. Simulated kinetics of response of the CDIMA reaction to illumination: $[ClO_2]_0$ (mM) = 0.025 (solid line), 0.05 (long-dashed line), 0.125 (dot-dashed line), and 0.25 (dotted line). All other conditions are as in Figure 1.
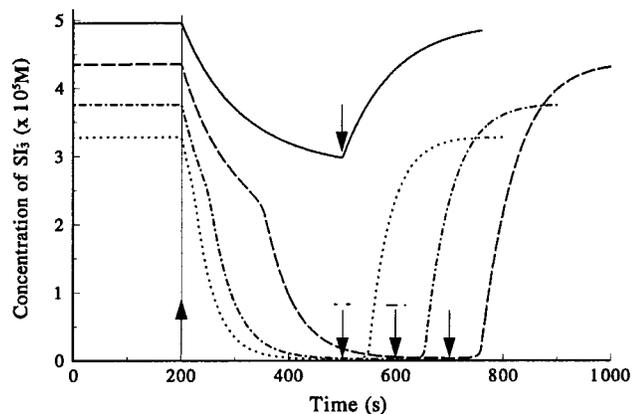
Figure 5. Simulated kinetics of response of the CDIMA reaction to illumination. Upward arrows indicate moments when light is switched on, and downward arrows indicate when it is switched off. Residence times (s) = 240 (solid line), 120 (long-dashed line), 80 (dot-dashed line), and 60 (dotted line). All other conditions are as in Figure 2.

dioxide concentration, $[SI_3^-]$ drops to much lower values and, after the light is switched off, the increase in the starch–triiodide concentration begins only after a clear delay period. At intermediate $[ClO_2]_0$, the kinetics of $[SI_3^-]$ follows a sigmoidal curve, as seen in the experiments. Comparison of Figure 4 with Figure 1 and of Figure 5 with Figure 2 shows that our model accurately simulates the experimental dynamics over a range of residence times and input concentrations of chlorine dioxide.

Discussion

Recently, Rábai and Hanazaki studied the photochemical decomposition of iodomalonic acid.[19] They showed that iodine,

iodide ion, malonic and tartronic acids are among the products of this process. In our case, the primary effect of illumination is the consumption of iodide ions. Therefore, a photochemical reaction that produces I$^-$ might affect our results. However, the reaction of iodine atoms with iodomalonic acid should be several orders of magnitude slower than their reaction with chlorine dioxide. Also, our light source is not strong enough to produce a noticeable direct photodissociation of iodomalonic acid. We thus conclude that the photochemistry of iodomalonic acid is not significant in our experiments.

We tried several other phenomenological rate equations for the photoinduced consumption of iodide atoms in the CDIMA reaction to simulate our data. Equation 11 is the simplest of the equations that yield plausible results. Our proposed reaction scheme is also the simplest among the chemically reasonable schemes that result in eq 11. We hope that this more accurate description of the photochemical kinetics of the CDIMA reaction will contribute to a better understanding of the dynamics of the photocontrol of Turing structures.[9]

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