Control of the Chlorine Dioxide–Iodine–Malonic Acid Oscillating Reaction by Illumination

Alberto P. Muñuzuri,* Milos Dolnik, Anatol M. Zhabotinsky,* and Irving R. Epstein

Contribution from the Department of Chemistry and Volen Center for Complex Systems, Brandeis University, MS 015, Waltham, Massachusetts 02454-9110

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Abstract: We show that illumination of the chlorine dioxide–iodine–malonic acid reaction with visible light suppresses oscillations and shifts the steady state of the reaction to lower concentrations of iodide ions. In the system with starch, illumination results in a strong decrease of the steady-state concentration of the triiodide–starch complex. We suggest a simple mechanism, in which iodine atoms produced by photodissociation of molecular iodine initiate reduction of chlorine dioxide to chlorite and oxidation of iodide ions to iodine. This results in a decreased amplitude of oscillations and, at more intense illumination, the cessation of oscillations. Illumination also lowers the steady-state concentrations of iodide and the triiodide–starch complex. Results obtained from numerical simulations are in good agreement with the experimental data.

Introduction

The reaction between chlorine dioxide, iodine, and malonic acid (CDIMA reaction) is one of the most intensively studied oscillatory chemical systems. This reaction and its original chlorite-iodide-malonic acid (CIMA reaction) version have been widely used in the demonstration and study of the symmetry-breaking, reaction–diffusion Turing patterns.1–9 Together with the Belousov–Zhabotinsky (BZ) reaction,10,11 both the CIMA and CDIMA reactions represent the major prototypes for studying spatio-temporal patterns. In recent years the BZ reaction has often been studied under the influence of external forces.12 Reaction has often been studied under the influence of external forces.12–19 In many cases, the photosensitivity of the ruthenium-catalyzed BZ reaction13,20 has been used as a convenient tool for external forcing. Although the autonomous dynamics of Turing structures are well studied, there are very few data on the behavior of Turing patterns when external perturbations are introduced. The presence of iodine in the CDIMA reaction suggests that this reaction might be photosensitive and that this property might be effectively used in the study of Turing patterns under external influence.

In this paper, we demonstrate that the dynamics of the CDIMA reaction can be controlled by illumination with visible light. We suggest a simple mechanism, in which iodine atoms produced by photodissociation of molecular iodine initiate reduction of chlorine dioxide to chlorite and oxidation of iodide ions to iodine. The corresponding kinetic model simulates well our experimental data. This work demonstrates that it is possible to employ illumination for the control of Turing structures in experiment.

Experimental Section

Materials. I₂ (Aldrich, A. C. S. reagent) soluble starch (Aldrich, A. C. S. reagent), and malonic acid (Aldrich, 99+%) were used without purification. Chlorine dioxide was prepared as described in ref 21. The concentration of chlorine dioxide was determined spectrophotometrically (ε = 1260 cm⁻¹ M⁻¹ at λ = 358 nm) before each experiment was started.

Procedures and Apparatus. The CDIMA reaction was studied in a batch and in a continuously fed stirred tank reactor (CSTR). In both cases, the reactor was made from a thermostated standard spectrophotometrical cuvette. The temperature in the batch reactor was 20 ± 1 °C and in the CSTR 9 ± 1 °C. The lower temperature in the CSTR was chosen in order to study the reaction under conditions that lead to formation of Turing patterns in an unstirred system.

Two feed solutions were used in the CSTR experiments: one contained 0.02 M H₂SO₄ and 0.0012 M I₂ dissolved in 20% acetic acid; another contained variable concentrations of chlorine dioxide, malonic acid, and iodine.
acid, and, in some experiments, starch dissolved in distilled water. Equal amounts of the input solutions were fed into the CSTR without premixing by a Rainin Rabbit Plus peristaltic pump. The residence time was 70 s.

The reactor cell was illuminated from above by parallel, unfiltered light from a tungsten–halogen lamp. The volume of the reaction mixture in the reactor was 3 mL; this corresponds to a light absorbing layer of thickness \( 3 \) cm. The intensity of illumination at the surface of solution in the reactor in the wavelength range 380–620 nm, was 5.5 mW/cm\(^2\) for the batch system and 3.5 mW/cm\(^2\) for the CSTR. The light intensity was measured with a Newport 1815 optical power meter.

Continuous recording of the absorbance at 280, 350, and 750 nm was used to monitor the concentrations of triiodide ion and the triiodide–starch complex in the presence of other light-absorbing species such as iodine, chlorine dioxide, and iodomalonic acid.

Experimental Results

**Batch System.** The oscillatory CDIMA reaction was studied in the batch reactor with initial reagent concentrations of 0.15 mM ClO\(_2\), 0.5 mM I\(_2\), 1 mM malonic acid, and 5 mM H\(_2\)SO\(_4\). Figure 1 shows the temporal behavior of the absorbance at \( \lambda = 350 \) nm. At this wavelength, triiodide is the major absorbing species, but chlorine dioxide also has a significant absorption, and the downward slope of the curve results from consumption of ClO\(_2\). The oscillations start immediately after the reagents are mixed together. At time = 40 s (arrow up) the light is switched on; illumination at this phase leads to full suppression of oscillations. At = 80 s (arrow down) the light is turned off and oscillations recover. The light is switched on again at = 130 s, and illumination now results in a significant decrease in the amplitude of oscillations. After the light is switched off, the amplitude of oscillations recovers shortly before the oscillations cease because the concentrations of the initial reagents decrease below the critical level. Without illumination, the oscillatory phase lasts approximately 15% longer.

**Flow-Through System. A. CDIMA Reaction without Starch.** Figure 2 shows the effect of illumination of the CDIMA reaction in a CSTR at [MA]\(_0\) = 1 mM for wavelengths 280 and 350 nm. The reaction is oscillatory within the range of concentrations of ClO\(_2\) shown in Figure 2. The amplitude of oscillations decreases with increasing concentration of ClO\(_2\). The concentration [ClO\(_2\)]\(_0\) = 0.5 mM (Figure 2c) is very close to the onset of oscillations. Illumination leads to an instantaneous suppression of oscillations. The transition to a new steady state occurs with a relaxation time of about 100 s. After the illumination is switched off, the oscillations recover within a time interval of the same order of magnitude. The rising absorbance at 350 nm in Figure 2 is caused by the increase of [ClO\(_2\)] in the system.

**Model**

Our experiments in the batch the CSTR configurations suggest that illumination of the CDIMA reaction results in iodide ion consumption, which leads to a decrease in both triiodide and the SI\(_3^-\) complex. To account for the effect of illumination, we extend the Lengyel–Epstein (LE) model of the CDIMA reaction.\(^3\)–\(^7\)

The LE model consists of three overall processes:

\[
\text{MA} + \text{I}_2 \rightarrow \text{IMA} + \Gamma^- + \text{H}^+ \quad (1)
\]

\[
\text{ClO}_2 + \Gamma^- \rightarrow \text{ClO}_2^- + 0.5\text{I}_2 \quad (2)
\]

\[
\text{ClO}_2^- + 4\text{I}^- + 4\text{H}^+ \rightarrow 2\text{I}_2 + \text{Cl}^- + 2\text{H}_2\text{O} \quad (3)
\]

with the following rate equations:
where \([S]\) is the concentration of binding sites on the starch. The corresponding rate equation is:

\[ \]

\[ r_1 = \frac{k_{1a}[MA][I_2]}{k_{1b} + [I_2]} \]  
\[ r_2 = k_2[ClO_2][\Gamma] \]  
\[ r_3 = k_{3a}[ClO_2][\Gamma] - \frac{k_{3b}[ClO_2][I_2][\Gamma]}{u + [\Gamma]^2} \]

Formation of the triiodide–starch complex is considered a simple one-step reaction:

\[ \Gamma + I_2 + S \rightleftharpoons SI_3^- \]  

The corresponding rate equation is:

\[ r_4 = k_4[\Gamma][I_2][S] - k_{-4}[SI_3^-] \]

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

In the original LE model, the SI\(_3^-\) complex is considered unreactive, and the concentration of free triiodide ion is assumed negligible in the presence of starch. Here, we neglect photodissociation of the free triiodide ion and SI\(_3^-\) complex. To model the effect of illumination, we propose that iodine atoms produced by photodissociation of molecular iodine initiate reduction of chlorine dioxide to chlorite and oxidation of iodide ions to iodine according to the following scheme:

\[ I_2 + h\nu \rightarrow 2I \]  
\[ I + H_2O \rightarrow I\cdot H_2O \]  
\[ I\cdot H_2O + ClO_2 \rightarrow ClO_2^- + H^+ + HOI \]  
\[ HOI + H^+ + \Gamma \rightarrow I_2 + H_2O \]

The corresponding net reaction is:

\[ hv + 2ClO_2 + 2\Gamma \rightarrow 2ClO_2^- + I_2 \]  

There is another route

\[ I + \Gamma \rightarrow I_2^- \]  
\[ I_2^- + ClO_2 \rightarrow ClO_2^- + I_2 \]

which plays only a minor role, since the low iodide concentration leads to a low concentration of I\(_2^-\) in comparison with that of \(1\cdot H_2O\).

The reactions in eqs 8 and 9 are diffusion-controlled; by employing the quasi-steady-state approximation, the concentrations of iodine atoms and their hydrates can be eliminated. In this case, the rates of consumption of ClO\(_2\) and production of ClO\(_2^-\) and HOI are equal to \(2r_7\).

We estimate the rate of photodissociation of I\(_2\) as follows. Within the spectral range of our light source, the free iodine and starch–trioiide complex are the only species that absorb light significantly. We neglect the possible screening effect of the SI\(_3^-\) complex. We assume that stirring makes all concentrations of interest uniform throughout the reactor volume, which means that we can neglect the spatial distribution of light absorption due to the Lambert–Beer law. As a result, we obtain the following equation for the rate of iodine photodissociation:

\[ r_5 = \varphi W \]

where \(W (M \text{s}^{-1})\) is the rate of absorption of the actinic photons divided by the reactor volume and \(\varphi\) is the quantum yield.

The rate of reaction (eq 10) is according to ref 26:

\[ r_{10} = (k_{10a} + k_{10b}[I^-])[HOI][\Gamma] - (k_{-10a}[I^-] + k_{-10b}[I_2]) \]

At fixed [I\(_2^-\)], eq 15a becomes:

\[ r_{10} = k_{10b}[HOI][\Gamma] - k_{-10}[I_2] \]

The resulting kinetic equations for the CSTR configuration take the form:

\[ d[MA]/dr = -r_1 + k_0([MA]_o - [MA]) \]  
\[ d[I_2]/dr = -r_1 + 0.5r_2 + 2r_3 - r_4 - r_7 + r_{10} + k_0([I_2]_o - [I_2]) \]  
\[ d[ClO_2]/dr = -r_2 - 2r_7 + k_0([ClO_2]_o - [ClO_2]) \]  
\[ d[S]/dr = -r_3 + k_0([S]_o - [S]) \]  
\[ d[I_2^-]/dr = r_1 - r_2 - 4r_3 - r_4 - r_{10} - k_0[\Gamma] \]  
\[ d[HOI]/dr = 2r_7 - r_{10} - k_0[HOI] \]  
\[ d[SI_3^-]/dr = r_2 - r_3 + 2r_7 - k_0[ClO_2^-] \]  
\[ d[SI_3^-]/dr = r_4 - k_0[SI_3^-] \]

(22) Grossweiner, L. I.; Matheson, M. S. J. Phys. Chem. 1957, 61, 1089–1095.


We employed the rate constants from refs 7, 8, and 26 corrected for our experimental temperatures of 20 and 9 °C according to the activation energies from refs 7 and 27. To better fit the experimentally observed transitional processes in the system with starch, we have decreased the values of rate constants $k_3$ and $k_{-4}$ by 2 orders of magnitude while keeping their ratio the same as in ref 8. The rate constants used in our simulations are shown in Table 1.

Following ref 7, we assume that the starch binding site for I$_3^-$ consists of six glucose residues. As a result, the concentration of binding sites, [S]$_0$ = 0.005 M, corresponds to our starch concentration of 0.5% (w/v).

According to ref 28, the quantum yield for photodissociation of iodine $q$ is 0.46. For our experimental conditions, we calculate $W = 2.0 \times 10^{-6}$ M s$^{-1}$ for the batch system and $W = 1.4 \times 10^{-6}$ M s$^{-1}$ for the CSTR.

**Results of Simulation**

**Batch Reactor.** Figure 4 shows the results of simulations for the same conditions as shown in Figure 1. The time dependence of the solution absorbance at $\lambda = 350$ nm is calculated with molar absorbances for I$_3^-$, I$_2$, ClO$_2^-$, and iodomalonic acid equal to 26000, 20, 1250, and 10 M$^{-1}$ cm$^{-1}$, respectively. The triiodide concentration is calculated from [I$_2$] and [I$^-$] with dissociation constant $K = 1.3 \times 10^{-3}$ M.$^{29}$ Full suppression of oscillations during two successive illumination periods is obtained for rate $W = 6.0 \times 10^{-7}$ M s$^{-1}$. This value is roughly three times less than that estimated from the experimental data. With smaller $W$, the simulations show partial suppression during the first illumination period and full suppression during the second. Thus, the photosensitivity increases with time in the model, while it decreases in experiment.

**CSTR—Starch-Free System.** We found that calculations with $W = 4.35 \times 10^{-7}$ M s$^{-1}$ simulate the experimental records reasonably well in the starch-free system as well as in the presence of starch. This value is approximately three times less than the experimentally determined value. Figure 5 shows the calculated behavior of [SI$_3$], [ClO$_2^-$], and [ClO$_2^2$] for the experiments of Figure 2. The illumination results in instantaneous suppression of oscillations, and then the concentrations relax to a new steady state. After the illumination is switched off, the oscillations recover following a transition period. The transition times are close to those observed in the experiment. The concentrations of malonic acid and iodine change only slightly during illumination.

Figure 6 shows calculated absorption curves for 350 and 280 nm. For the latter wavelength, molar absorbances for I$_3^-$, I$_2$, ClO$_2^-$, and iodomalonic acid are 32000, 100, 90, and 300 M$^{-1}$ cm$^{-1}$, respectively. Comparison with Figure 2 shows a semi-quantitative correspondence.

**CDIMA Reaction in the Presence of Starch.** Figure 7 shows the response of [I$_3^-$] and [SI$_3^-$] to illumination. The iodide ion concentration quickly drops after the light is switched on. The relaxation time for the SI$_3^-$ concentration corresponds to the relaxation time of the absorbance in Figure 3. When the illumination is switched off, the back transition of the SI$_3^-$ concentration takes approximately the same time as in the experiments (see Figure 3) and also follows a sigmoidal curve. However, the shape of the lower part of the curve differs. In the simulations, the triiodide—starch complex decreases to very low concentrations during illumination. In the experiment, the

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absorbance does not decrease to zero, probably because there are other species beside $\text{SI}_3^{-}$ that absorb light at $\lambda = 750 \text{ nm}$.

**Conclusion**

In this work, we have shown that illumination of the CDIMA reaction with visible light suppresses oscillations in the starch-free system and strongly shifts the steady-state concentrations in the system with starch. This phenomenon is observed for a wide range of parameters and provides a convenient tool for controlling the Turing structures in spatially extended systems.

Our model demonstrates good agreement with the experiment. For a starch-free system the agreement is obtained by employing the rate constants from refs 7, 8, and 26 with the proper temperature corrections. However, to obtain better agreement with the temporal behavior of the triiodide–starch complex, we have adjusted the values of the rate constants for dissociation and association of the triiodide–starch complex. Previously, these rate constants had somewhat arbitrary values assigned to them, since the stationary Turing patterns depend only on the value of the equilibrium constant. The model presented in this paper is obviously simplified and further refinements to obtain better quantitative agreement with the experimental results can be expected.

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