Photoinduced Reaction between Chlorine Dioxide and Iodine in Acidic Aqueous Solution

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Photoinduced reaction between ClO_2 and I_2 has been discovered under illumination with 460 nm lightband. The photochemical reaction has a variable stoichiometry in acidic aqueous solution because the induced disproportionation of ClO_2 to ClO_3^- and Cl^- competes with the oxidation of I_2 to IO_3^- by ClO_2 in the illuminated reaction mixture. The reaction rate depends on the light power of illumination and on the concentration of I_2, but it is independent of the concentration of ClO_2. It is also independent of the pH in the range of 0−2.0 and of the ionic strength in the range of 0.01−1.0 M. Reversible dissociation of I_2 has been identified as the primary photochemical process and rate-determining step in the mechanism. Reactive I atoms are considered to initiate fast reaction steps, leading to the formation of products through reactive intermediates such as $IClO_2$, ClO, IO, and HOCl. This mechanism is proposed for explaining the photoresponses of the CDIMA oscillatory reaction system to the illumination with visible light.

Introduction

Light illumination is a convenient tool for controlling photosensitive chemical oscillations and related nonlinear dynamical behavior in homogeneous solutions. In some cases, it is also applied for external forcing spatial structures in unstirred reaction−diffusion systems. The observed photoresponses are hoped to provide general information about the responses of complex systems to external stimuli and to help us understand the mechanism of composite chemical reactions responsible for the complex dynamics in such systems.[1]

The oscillatory chlorite ion−iodide ion−malonic acid reaction system (CIMA)[2] and some of its derivatives have long been known to be sensitive to the illumination by visible and UV light. Both the spatial structures[3] and exotic solution kinetics[4] exhibited by these reactions can be influenced by illumination. Recently, a related chlorine dioxide−iodine−malonic acid system (CDIMA) was also found to show sharp photoresponses both in a batch[5] and in a continuous-flow stirred tank reactor (CSTR) under illumination with light in the wavelength range of 380−620 nm.[6] Today, it is the CDIMA system that is often used to study Turing structures. Its light sensitivity may provide a convenient tool for controlling stationary Turing structures in spatially extended systems. An important task is deciphering which of the composite reactions or species can be held responsible for the observed photosensitivity. In other words, what is the primary photochemical process? For this question to be answered, photoresponses of composite reactions of the complex system should be studied separately, if possible.

Chlorine dioxide, iodomalonic acid, and iodine are among the major species of the CIMA and CDIMA systems, and they all appear to absorb light in the wavelength range of 380−620 nm applied in the recent photoperturbation experiments.[6] The photolysis of chlorine dioxide both in gas phase and in water has been studied extensively.[7] Intermediates of its photolysis (e.g., ClO) are expected to be involved in composite reactions in the oscillatory system. Photoinduced disproportionation of iodomalonic acid has also been investigated in details[8] and was assumed to be responsible for the peculiar photoresponses of the iodomalonic acid−chlorite ion reaction observed in a semibatch reactor.[4] However, according to Horváth et al.,[6] iodomalonic acid plays only a minor role, if any, in the photoresponses, but the iodine−iodide ion−chlorine dioxide subsystem is largely responsible for the response to the illumination in the CDIMA reaction. They suggest that the photodissociation of iodine induces some interaction between I_2 and ClO_2. However, we are not aware of any previous kinetic study of such a photoinduced reaction. On the contrary, it is known that this reaction is very slow, at least in the dark,[9] and it has not been considered as a component process in a model for the oscillatory CDIMA system.[10] Our present preliminary experiments, however, support Horváth's suggestion, as we found that the rate of ClO_2 consumption increased significantly under illumination. The most effective light band is around 460 nm, which corresponds to the maximum of the iodine absorption spectrum. Discovery of this photochemical reaction confirms the hypothesis that the composite reaction between I_2 and ClO_2 may be the main source and the primary reason for the photosensitivity of the oscillatory CDIMA system.

In this paper, we report on the investigation of the stoichiometry and the kinetics of the photoinduced reaction between I_2 and ClO_2. We suggest a simple mechanism, in which the primary photochemical process is the dissociation of molecular iodine that initiates the reduction and disproportionation of ClO_2 to Cl^- and ClO_3^-. Meanwhile, a part of iodine is oxidized to IO_3^-. On the basis of our results, we also suggest a modified mechanistic explanation for the photoresponses of the CDIMA system.

Experimental Section

Materials. Iodine and sulfuric acid were used as received. Chlorine dioxide gas was prepared from potassium chlorate and oxalic acid in sulfuric acid[11] and was purified by bubbling through saturated sodium carbonate solution to remove CO_2 as well as traces of HCl and Cl_2. The purified ClO_2 gas was dissolved in cold water. Stock solutions of ClO_2 were acidified to pH 2.0 with sulfuric acid and were stored in darkness in a refrigerator. The ClO_2 concentration was determined by spectrophotometry at 358 nm ($\epsilon = 1050\ cm^{-1}\ M^{-1}$).[9] Acidic aqueous

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TABLE 1: Consumed $[ClO_2]$/Consumed $[I_2]$ at Different Initial $[I_2]_0$'s[a]

$[I_2]_0 \times 10^4$ M	1.45	1.97	2.86	3.07	3.94	5.08	6.07	7.11
$\triangle[ClO_2]/\triangle[I_2]$	2.91	2.79	2.62	2.58	2.48	2.35	2.29	2.23

[a] $[ClO_2]_0 = 4.0 \times 10^{-4}$ M, pH = 2.0, and integrated light power = 14.6 mW dm^{-3}.

solution of saturated I_2 (at 25 °C) was prepared by dissolving I_2 crystals in water. Its pH was adjusted to 2.0 with sulfuric acid, and its concentration was measured at 460 nm ($\epsilon = 740$ cm^{-1} M^{-1}).[9]

Methods. For the stoichiometry, the consumed chlorine dioxide ($\Delta[ClO_2]$, usually equal to $[ClO_2]_0$) and the consumed iodine ($\Delta[I_2]$) concentrations were determined after 24 h of illumination time. For the kinetics, the reaction was started by mixing the acidic solution of I_2 with the acidic solution of ClO_2. The mixture was poured into a spectrophotometric cell. The cell was sealed with a stopper to avoid any loss of volatile ClO_2 and I_2 to the air. The light source was a 100 W tungsten lamp, the light of which was led through a 10 cm water layer to filter out the heat of the lamp. An interference optical filter was employed to obtain a light band in a wavelength interval of 454−466 nm. In this range, neither iodomalonic acid nor ClO_2 absorbs light. The only light-absorbing species is I_2. The optical cell ($1.0 \times 1.0 \times 3.0$ cm^3) filled with the reaction mixture was illuminated with the filtered light band. The illuminated surface of the cell was 3 cm^2, and the optical path length in the solution was 1.00 cm. The light intensity entering the cell was measured with a power meter. Integrated light power entering the reaction mixture was calculated and was divided by the cell volume (P, in milliwatts per cubic decimeter). The reaction was followed spectrophotometrically by measuring the absorbance at 358 nm as a function of the time of the illumination. The ClO_2 concentration was calculated from the measured absorbance. No I_3^- was formed in the reaction mixture under the experimental conditions. All experiments were conducted at 25 ± 1 °C.

Results and Discussions

Stoichiometry. Reaction 1 seems to be the most reasonable to assume for the stoichiometry

$$2ClO_2 + I_2 + 2H_2O \rightarrow 2Cl^- + 2IO_3^- + 4H^+ \qquad (1)$$

However, we found that eq 1 alone did not reflect exactly the measured mole consumption ratio ($\Delta[ClO_2]/\Delta[I_2]$); that depends on the relative concentrations of the reactants.

In our experiments, chlorine dioxide and iodine were allowed to react in acidic aqueous solution under illumination overnight. We applied initial concentrations where all the ClO_2 has been consumed but some I_2 remained unreacted. The remaining I_2 concentration was determined. Then the mole consumption ratio was calculated at different initial concentrations of iodine. The results are presented in Table 1. As seen, the measured values vary with the ratio of the initial concentrations of the reagents at pH 2.0. The limiting value (2) given by eq 1 is approached, but never reached with increasing excess of $[I_2]_0$. Very similar values and tendencies for the mole consumption ratio were obtained when these experiments were repeated in 0.05 and 0.50 M sulfuric acid solutions, indicating that the stoichiometry does not depend on the acidity of the reaction mixture. We have not carried out experiments above pH 2 because the hydrolysis of I_2 to I^- and HOI and the consequent formation of I_3^- would be significant at higher pH values. I_3^- absorbs strongly with a maximum at 353 nm ($\epsilon = 26\,400$ M^{-1} cm^{-1}),[12] and it would disturb the spectrophotometric determination of I_2 and ClO_2. Since the optimum pH for the oscillatory behavior in the CDIMA system is below pH 2, the results above pH 2 would not be of importance for the oscillatory system.

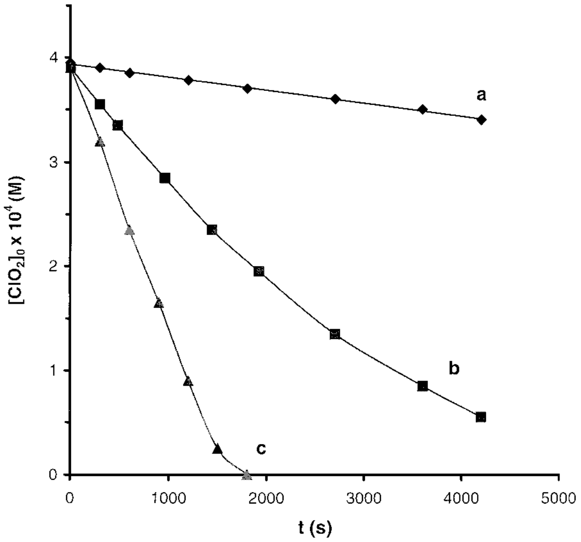

Figure 1. ClO_2 concentration as a function of time under illumination with 460 nm light. $P = 1.46$ mW dm^{-3}, $T = 25$ °C, and $[I_2]_0 = 0.0$ (a), 1.45×10^{-4} (b), and 5.08×10^{-4} M (c).

Our results suggest that not only reduction of ClO_2 takes place (reaction 1) in the presence of I_2, but some induced or spontaneous disproportionation of ClO_2 should also be considered which may be described by eq 2[13]

$$6ClO_2 + 3H_2O \rightarrow 5ClO_3^- + Cl^- + 6H^+ \qquad (2)$$

Disproportionation of ClO_2 is known to be very slow in acidic solution in the absence of I_2. But intermediates of the oxidation of I_2 are expected to induce the disproportionation process. The measured stoichiometry is assumed to result from the competition between reactions 1 and 2. Contribution of reaction 1 is always rather high, especially when the ratio $[I_2]_0/[ClO_2]_0$ is high, and somewhat smaller when the ratio is the opposite. The pure limiting stoichiometry indicated by eq 1 could not be reached in our experiments because of experimental limitations.

Kinetics. The observed kinetics turned out to be surprisingly simple. Figure 1 shows the measured typical concentration traces of ClO_2 as a function of time under illumination. A slow decrease in $[ClO_2]$ could be observed even in the absence of iodine (curve a) indicating that spontaneous disproportionation or some slow unknown escape of volatile ClO_2 takes place. In the presence of iodine, however, the decay of chlorine dioxide concentration was much faster. An important finding is that the rate does not depend on the ClO_2 concentration. This is concluded from curve c in Figure 1, where the concentration of I_2 is high enough to be considered constant during reaction. Curve c is a straight line that corresponds to a constant consumption rate with decreasing $[ClO_2]$. In other experiments, the initial rate was found to be independent of the initial concentration of ClO_2 as another indication of the zero order dependence. When $[I_2]_0$ was small, its concentration decreased significantly as the reaction proceeded. As a result, the reaction rate decreased in time (curve b in Figure 1). The initial rate ($d[ClO_2]/dt$) was determined from the slope of the initial part of the time−$[ClO_2]$ curves.

Shown in Figure 2 is the plot of the reaction rate as a function of the integrated light power (P) of illumination at $[I_2]_0 = 3.74$

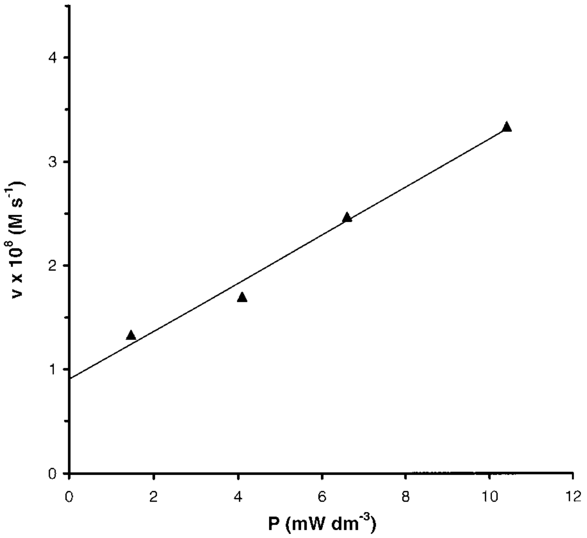

Figure 2. Reaction rate as a function of the light power. $[I_2]_0 = 3.74 \times 10^{-4}$ M, and $[ClO_2]_0 = 2.78 \times 10^{-4}$ M.

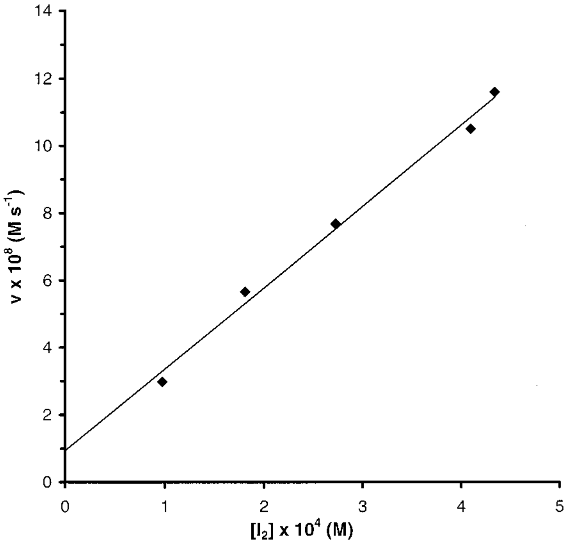

Figure 3. Reaction rate ($d[ClO_2]/dt$) as a function of I_2 concentration. $P = 8.5$ mW dm^{-3}, $T = 25$ °C, and $[ClO_2]_0 = 4.1 \times 10^{-4}$ M.

$\times 10^{-4}$ M and $[ClO_2]_0 = 2.78 \times 10^{-4}$ M. The linear dependence of the rate on the light power indicates that the rate-determining step in the mechanism is a photoinduced process. The intercept corresponds to the rate of the dark reaction.

Reaction rates at different iodine concentrations are shown in Figure 3. The straight line suggests that the reaction order is 1 with respect to I_2. The positive intercept in Figure 3 is an indication of the spontaneous disproportionation of ClO_2 which takes place even in the absence of iodine. (Again, we emphasize that some loss of volatile ClO_2 to the air cannot be excluded).

The reaction rate was found to be independent of the concentration of H_2SO_4 in the range of 0.005−1.0 M, indicating that the concentration of the proton does not affect the rate. Variation of the ionic strength in the range of 0.01−1.0 M was also found to be without any noticeable effect on the rate.

According to the results of the kinetic experiments, a rate law can be given for the photoinduced part of the reaction as

$$v = -d[ClO_2]/dt = k_{obs}[I_2] \tag{3}$$

where $k_{obs} = \phi k P$ and ϕ is the quantum yield (0.46),[14] k is a constant, and P is the integrated light power entering the cell. From the slope of Figure 2, $k_{obs} = 2.0 \times 10^{-4}$ s^{-1}. Here, we neglect both the slow dark reaction between ClO_2 and I_2 and the spontaneous disproportionation of ClO_2. Of course, rate law 3 is not valid at very low $[ClO_2]$.

Mechanism. A mechanism of the I_2−ClO_2 reaction should account for both the variable stoichiometry and the observed photoresponses. The results of illumination experiments can be explained by a single photosensitive process. In the first and rate-determining step, I_2 undergoes the well-known photoinduced dissociation (M1). The rate of the formation of reactive I atoms depends on the I_2 concentration and the light power. The rate of the recombination of I does not depend on the light power. As a result, the steady-state concentration of iodine atoms in the photostationary state is much higher than that in the dark equilibrium. I atoms react rapidly with ClO_2 to form supposedly the $IClO_2$ intermediate (M2). $IClO_2$ can either hydrolyze to IO_3^- and Cl^- in aqueous solution in several steps, the net of which is represented by reaction M3, or it can decompose according to M4. Reactions M1−M3 constitute the main channel and give the net reaction 1. ClO formed in M4 is a strong oxidizing agent, and it can oxidize both ClO_2 and I_2 according to M5 and M6, respectively

$$I_2 + h\nu \rightleftharpoons 2I \tag{M1}$$

$$I + ClO_2 \rightleftharpoons IClO_2 \tag{M2}$$

$$IClO_2 + H_2O \rightarrow IO_3^- + Cl^- + 2H^+ \tag{M3}$$

$$IClO_2 \rightarrow IO + ClO \tag{M4}$$

$$ClO_2 + ClO + H_2O \rightarrow ClO_3^- + HOCl \tag{M5}$$

$$I_2 + ClO \rightarrow ICl + IO \tag{M6}$$

M5 is responsible for the disproportionation of ClO_2, while M6 is a first step toward the oxidation of I_2. In M5 and M6, ClO_2 and I_2 compete with each other for ClO. This competition results in a variable net stoichiometry. Note that I is a strong oxidizing agent. As the data derived from Latimer[15] show, the reduction potential of I/I^- couple is higher than that of ClO_3^-/ClO_2 in acidic aqueous solution (1.23 and 1.175 V, respectively, at 25 °C). If the photostationary concentration of I is rather high, direct formation of some ClO_3^- is also possible according to reaction M7

$$ClO_2 + I + H_2O \rightarrow ClO_3^- + I^- + 2H^+ \tag{M7}$$

The I^- ion is oxidized back to I_2 immediately by excess ClO_2. Reaction M7 might be of stoichiometric significance under very strong illumination. The fate of intermediates IO, ICl is to be oxidized further to IO_3^-, while HOCl and ClO are reduced to Cl^- in further fast steps

$$I_2 + HOCl \rightarrow ICl + IOH \tag{M8}$$

$$ICl + H_2O \rightleftharpoons IOH + Cl^- + H^+ \tag{M9}$$

$$I_2 + H_2O \rightleftharpoons IOH + I^- + H^+ \tag{M10}$$

$$IO + ClO_2 \rightarrow IO_2 + ClO \tag{M11}$$

$$IO_2 + ClO_2 + H_2O \rightarrow IO_3^- + HClO_2 + H^+ \tag{M12}$$

$$IOH + HClO_2 \rightarrow HIO_2 + HOCl \tag{M13}$$

$$HIO_2 + ClO_2 \rightarrow IO_3^- + ClO + H^+ \tag{M14}$$

Modified Mechanism of the Photoresponses of the CDIMA Reaction System. Horváth et al. suggested that illumination of the CDIMA reaction resulted in an increased rate of iodide ion consumption, which led ultimately to a decrease in the steady-state concentration of triiodide ion and that of starch$-I_3^-$ complex when the reaction is run in a CSTR.[6] In addition to the direct electron transfer between ClO_2 and I^-, they assumed an indirect route for the oxidation of I^- which is induced by illumination. (Since the direct electron transfer between I^- and ClO_2 is rather fast even in the dark,[16] it is not likely that such a fast dark reaction can be directly accelerated by photoillumination.) They proposed a mechanism for the additional I^--consuming channel in which the primary photochemical step was the photodissociation of molecular I_2. We agree with this conclusion and emphasize the key role of the photosensitive ClO_2-I_2 reaction in the photoresponses of the CDIMA system. Our experiments indicated that the most effective light band is 460 nm, which is the absorption maximum of I_2. We believe that the increased rate or an extended degree of the iodide ion consumption is due to the fast reactions between I^- and some reactive intermediates (ClO, HOCl, ICl, etc.) and products (IO_3^-) formed in the photoinduced I_2-ClO_2 reaction.

Horváth et al. derived a rate law for the additional photoinduced route from their proposed mechanism. Their rate law shows a complex dependence of the rate of the light-induced route on the concentration of chlorine dioxide and iodide and on the rate of absorption of actinic photons (eq 11 in ref 6). This form is not consistent with our experimental rate law (eq 4) obtained for the photoinduced ClO_2-I_2 reaction because our experiments showed that the rate is independent of $[ClO_2]$. In the following, we show several inconsistencies which may be the source of the contradiction and propose alterations. Horváth's mechanism consists of steps H1$-$H9

$$I_2 + h\nu \rightleftharpoons 2I \tag{H1}$$

$$I + ClO_2 \rightarrow IClO_2 \tag{H2}$$

$$IClO_2 + I^- \rightarrow I_2ClO_2^- \tag{H3}$$

$$I_2ClO_2^- + IClO_2 \rightarrow I_3^- + 2ClO_2 \tag{H4}$$

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \tag{H5}$$

$$I_3^- \rightleftharpoons I_2 + I^- \tag{H6}$$

$$HIO_2 + I^- + H^+ \rightleftharpoons 2HOI \tag{H7}$$

$$IClO_2 + ClO_2 + H_2O \rightarrow ClO_2^- + HIO_2 + ClO + H^+ \tag{H8}$$

$$ClO_2 + ClO + H_2O \rightarrow 2ClO_2^- + 2H^+ \tag{H9}$$

First, reaction H4 seems unlikely in their mechanism since it requires the bimolecular reaction of reactive intermediates. Second, the net of reactions H1$-$H4 is the formation of I_3^- from I_2 and I^-. The light and ClO_2 both play only the role of a "catalyst" in this reaction sequence. Assumption of the catalytic effect of the light and ClO_2 on the formation rate of I_3^- is not reasonable chemically because the direct charge-transfer I_2-I^- reaction itself (H6) is a diffusion-controlled one,[17] which is not expected to be accelerated by a catalyst of any kind under the conditions applied in the experiments. We propose that H3 and H4 should be eliminated from the scheme. Third, reaction H9 is very unfavorable thermodynamically because ClO is a more powerful oxidant than ClO_2. It is not expected that ClO_2 can oxidize ClO to ClO_2^-. A more likely reaction between ClO_2 and ClO is M6.

Our suggestion for the additional photoinduced consumption of I^- is the reaction sequence M15$-$M18

$$ClO + I^- + H^+ \rightarrow I + HOCl \tag{M15}$$

$$HOCl + I^- \rightarrow IOH + Cl^- \tag{M16}$$

$$IO + I^- + H^+ \rightarrow I + IOH \tag{M17}$$

$$IO_3^- + I^- + 2H^+ \rightarrow IOH + HIO_2 \tag{M18}$$

Since M15$-$M18 are all fast reactions, the photoresponses of the CDIMA reaction is determined by the slow photodissociation of I_2.

Conclusion

It is known that the oxidation of I_2 by ClO_2 is a very slow process in an aqueous acidic solution in the dark. In this work, we have shown that the reaction accelerates significantly under illumination with white light. The most effective wavelength band is found to be around 460 nm, the absorption maximum of I_2. A logical conclusion is that photodissociation of I_2 molecules is the primary photochemical step, which is followed by fast steps between the reactive I atoms and ClO_2, leading through intermediates to the iodate, chlorate, and chloride ions as products.

Earlier, this reaction was not considered as an important composite reaction of the CIMA or CDIMA oscillatory system although both I_2 and ClO_2 are major components of those systems. We propose here that the I_2-ClO_2 reaction is the key to the photoresponse of the CDIMA system. The reactive intermediates of this reaction can react with the free iodide ions in fast reactions, providing an additional route for the iodide ion consumption. This mechanism explains the low steady-state concentration of I^- in a CSTR under illumination compared with the higher steady-state I^- ion concentration measured under the same conditions in the dark.

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