Reaction Mechanism for Light Sensitivity of the $Ru(bpy)_3^{2+}$-Catalyzed Belousov−Zhabotinsky Reaction

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The effects of light on the $Ru(bpy)_3^{2+}$-catalyzed Belousov−Zhabotinsky (BZ) reaction are investigated. Experiments were carried out on an organic subset of the reaction comprised of bromomalonic acid, sulfuric acid, and $Ru(bpy)_3^{2+}$ as well as on an inorganic subset comprised of bromate, sulfuric acid, and $Ru(bpy)_3^{2+}$. Experiments were also carried out on the full $Ru(bpy)_3^{2+}$-catalyzed BZ system. The experiments, together with modeling studies utilizing an Oregonator scheme modified to account for the light sensitivity, show that irradiation gives rise to two separate processes: the photochemical production of bromide from bromomalonic acid and the photochemical production of bromous acid from bromate.

I. Introduction

The effect of light on the Belousov−Zhabotinsky[1,2] (BZ) reaction was noted almost 30 years ago by Vavilin et al.[3] When the cerium-catalyzed BZ system was irradiated with ultraviolet light, the oscillations were either modified or completely suppressed depending on the light intensity and chemical composition. Ultraviolet light was also found to initiate chemical waves in a thin layer of ferroin-catalyzed BZ solution.[4] The tris(2,2′-bipyridine)ruthenium(II) complex, $Ru(bpy)_3^{2+}$, was first used in the BZ reaction as a luminescent indicator for oscillatory behavior when irradiated with UV light.[5] Gáspár et al.[6] investigated the influence of visible light on BZ reactions with various catalysts and found the ferroin- and ruthenium-catalyzed systems to be significantly affected but the cerium-catalyzed system to be unaffected. The ruthenium-catalyzed system has become increasingly important over the years, particularly in studies of spatiotemporal behavior, since the medium excitability can be conveniently varied by adjusting the illumination intensity. Light at 452 nm produces an excited state of the ruthenium catalyst,[7] which gives rise to a sequence of photochemical reactions that affect the basic chemistry of the BZ reaction.[8] Kuhnert et al.[9,10] used an illuminated ruthenium-catalyzed system as a photochemical memory device, where the image of a mask was retained as a phase shift through successive oscillations. Illuminated ruthenium-catalyzed systems have subsequently been used for developing geometrical patterns,[11] generating diffusion-phase waves,[12] and initiating[13] and controlling[14] spiral waves.

Several mechanisms have been proposed to account for the light sensitivity of the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction. The primary photochemical process is absorption of visible light by the $Ru(bpy)_3^{2+}$ complex.[15,16] The excited state of the complex, $Ru(bpy)_3^{2+}*$, is an extremely strong reducing agent, with a Ru(III)/Ru(II) reduction potential of −0.86 V compared to a reduction potential of 1.26 V for the ground state.[7] Kuhnert[9] and, later, Jinguji et al.[15] therefore proposed that $Ru(bpy)_3^{2+}*$ serves to reduce the reactant BrO_3^- to Br^-, which is the primary autocatalysis inhibitor in the BZ reaction. An indirect path for the photochemical reduction of bromate to bromide in the presence of oxygen has also been proposed by Reddy et al.[17] In a series of papers, Hanazaki and co-workers[16,18−21] have examined the photochemical mechanism for the inorganic subset of the ruthenium-catalyzed BZ reaction, namely the illuminated $Ru(bpy)_3^{2+}$-bromate reaction in sulfuric acid. They proposed a scheme involving the photochemical production of the autocatalyst $HBrO_2$ and the inhibitor Br^- to account for the experimentally observed inhibition as well as inducement of oscillatory behavior by light.[20,21]

Much less is known about the photochemical reactions of the organic subset of the ruthenium-catalyzed BZ reaction. The importance of the organic subset in the light sensitivity has been recently suggested,[17,21,22] and the role of bromomalonic acid (BrMA) as a bromide source has been pointed out by Yamaguchi and co-workers.[23]

We consider the light sensitivity of both the inorganic and organic subsets of the ruthenium-catalyzed BZ reaction in this paper and develop a reaction mechanism that accounts for the photosensitivity of the overall reaction. We find, contrary to previous studies, that bromide is photochemically generated from bromomalonic acid, while bromous acid is photochemically produced from bromate. In BZ systems that initially contain bromomalonic acid, which is common in the systems used for spatiotemporal studies,[9,10,13−15] the predominant effect of illumination is production of the inhibitor Br^-. The sensitivity of such systems to illumination can be adjusted by varying the initial concentration of bromomalonic acid in the reaction mixture.

II. Experimental Section

Commercially available analytical grade reagents (malonic acid, sulfuric acid, and sodium bromate) were used with laboratory preparations of the $Ru(bpy)_3^{2+}$ catalyst and bromomalonic acid. The $Ru(bpy)_3^{2+}$ was synthesized from $RuCl_3$ and 2,2′-bipyridine, with the sulfate salt precipitated and purified to remove Cl^- ion.[24] The bromomalonic acid was prepared in the form of the potassium salt and purified in an organic medium according to Forsterling et al.[25] The ^{13}C NMR spectrum of the purified bromomalonic acid was in good agreement with the literature spectrum.[25] Doubly distilled, oxygen-free water was used to prepare stock solutions, which were stored under an argon gas atmosphere. All measurements were carried out on solutions maintained under a constant flow of argon gas.

The experimental setup is shown in Figure 1. Reactions were carried out in a 60 mL, thermostated container with two parallel quartz windows for illumination. The reaction mixture was

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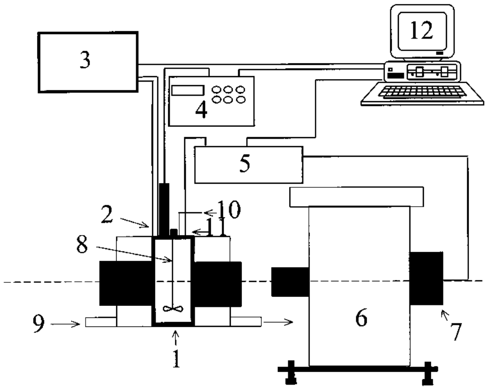

Figure 1. Schematic representation of the experimental setup: (1) reactor, (2) Br^--selective electrode, (3) diode-array spectrophotometer, (4) ion analyzer, (5) data acquisition unit, (6) tungsten−halogen lamp, (7) photomultiplier tube (PMT), (8) stirrer, (9) thermostating liquid, (10) argon gas input, (11) thermocouple, (12) computer.

stirred with a propeller stirrer (Spectrocell Inc., SYS-D1) and monitored with a combination bromide-selective electrode/double-junction reference electrode (Cole-Parmer, H-27502-05). The temperature of the solution was maintained at 25.0 ± 0.1 °C. The light source was a 1.0 kW tungsten-halogen lamp (ORIEL, 66187) equipped with a cold-mirror heat sink and a 350−500 nm blue filter. The light intensity was monitored with a photomultiplier tube. Electrode voltages were collected with a data-acquisition unit (Omega Tech., OM-900) and processed on a personal computer. A flow-through cell with a 0.1 mm optical path length was used with a diode-array spectrophotometer (HP 8152) for light absorbance measurements. A peristaltic pump was used to circulate the reaction mixture between the reactor and the spectrophotometer cell. The reaction mixture was monitored at 460 nm in order to measure the concentration of $Ru(bpy)_3^{2+}$.

III. Results

A. Organic Subset: Bromomalonic Acid, $Ru(bpy)_3^{2+}$, and Sulfuric Acid. Reactions carried out with different light intensities and a constant initial bromomalonic acid concentration exhibited a higher rate of bromide production with higher light intensity, as shown in Figure 2a. Reactions were also carried out with a constant light intensity and different initial bromomalonic acid concentrations. As shown in Figure 2b, the rate of bromide production depends strongly on the initial bromomalonic acid concentration. No significant dependence of bromide production was found on the initial concentrations of malonic acid[26] or $Ru(bpy)_3^{2+}$, as shown in Figure 3a,b. Spectrophotometric monitoring showed that the concentration of $Ru(bpy)_3^{2+}$ remained nearly constant during the course of an experiment.

B. Inorganic Subset: $NaBrO_3$, $Ru(bpy)_3^{2+}$, and Sulfuric Acid. Experiments were carried out under both light and dark conditions. When the reaction mixture was exposed to the highest light intensity employed, the concentration of $Ru(bpy)_3^{2+}$ decreased in a process that is apparently autocatalytic. When the experiment was carried out in the dark, no significant change in the $Ru(bpy)_3^{2+}$ concentration was observed over a comparable time scale. Curves a and b in Figure 4 show the absorbance at 460 nm, corresponding to the concentration of $Ru(bpy)_3^{2+}$, under light and dark conditions, respectively. The concentration of bromide remained below the detectable limit of the bromide-selective electrode during both the light and dark reactions.

C. The Full $Ru(bpy)_3^{2+}$-Catalyzed BZ Reaction. The effect of light on the full reaction was studied by irradiating

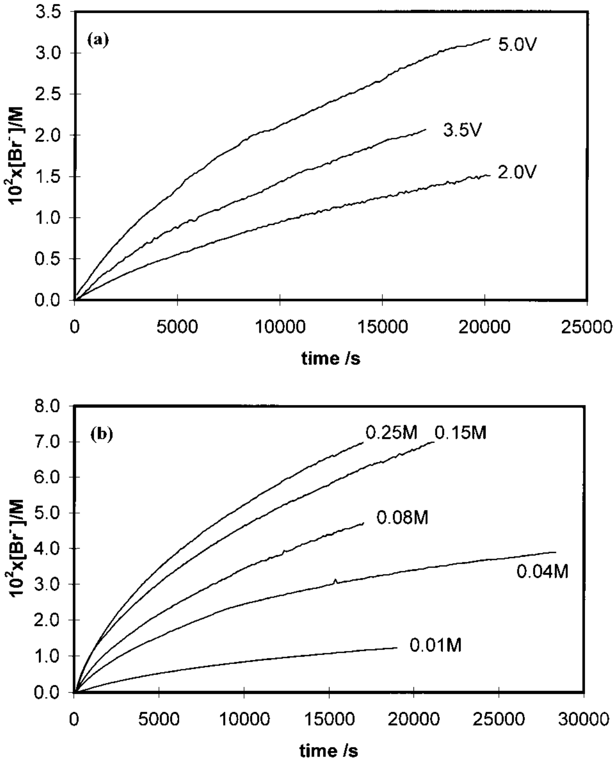

Figure 2. (a) Bromide accumulation in the organic subsystem as a function of time at different light intensities (expressed as photomultiplier tube (PMT) voltage, V) and (b) initial bromomalonic acid concentration. (a) [BrMA] = 0.04 M, [H_2SO_4] = 0.25 M, [MA] = 0.25 M, [$Ru(bpy)_3^{2+}$] = 0.90 mM. (b) [H_2SO_4] = 0.25 M, [MA] = 0.25 M, [$Ru(bpy)_3^{2+}$] = 0.90 mM. Light intensity PMT voltage: 5.0 V.

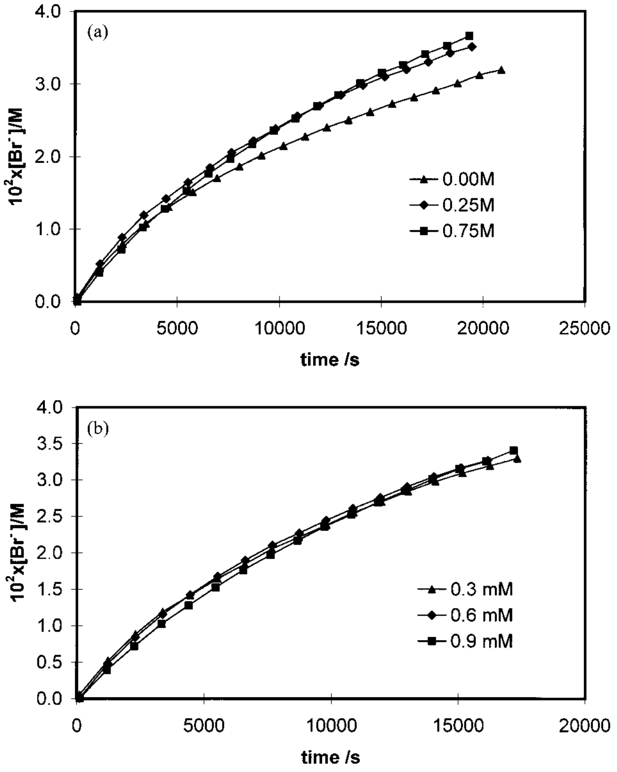

Figure 3. Dependence of bromide production in the organic subsystem on (a) the initial malonic acid concentration and (b) the initial $Ru(bpy)_3^{2+}$ concentration. (a) [MA] = 0.75 M (■), 0.25 M (◆), 0.0 M (▲); [$Ru(bpy)_3^{2+}$] = 0.90 mM. (b) [$Ru(bpy)_3^{2+}$] = 0.90 mM (■), 0.6 mM (◆), 0.3 mM (▲); [MA] = 0.25 M. Other concentrations: [BrMA] = 0.04 M, [H_2SO_4] = 0.25 M. Light intensity PMT voltage: 5.0 V.

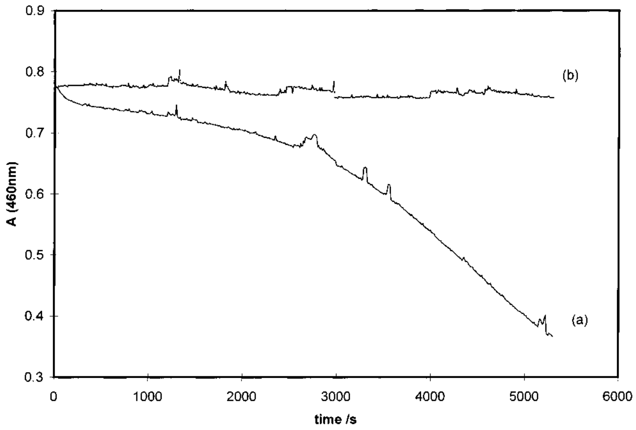

Figure 4. Absorption at 460 nm as a function of time in the inorganic subsystem. (a) Reaction mixture under light conditions, with light intensity PMT voltage of 5.0 V; (b) reaction mixture under dark conditions. Composition: $[BrO_3^-] = 0.20$ M, $[H_2SO_4] = 0.35$ M, $[Ru(bpy)_3^{2+}] = 0.60$ mM.

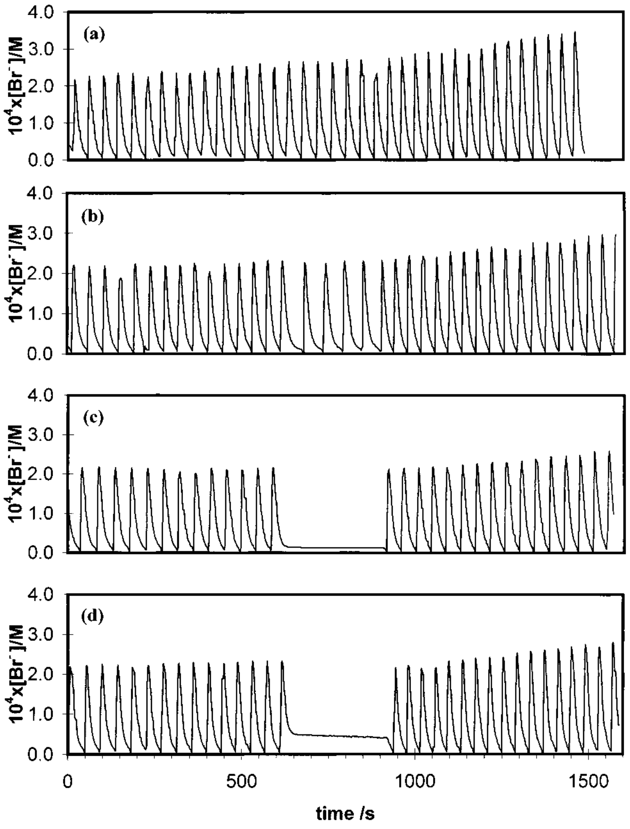

Figure 5. Effect of illumination of the full BZ system at various light intensities. The light was switched on at 600 s and off at 900 s. Light intensity PMT voltages: (a) 1.00 V, (b) 2.25 V, (c) 2.30 V, (d) 5.00 V. Initial conditions: [BrMA] = 0.05 M, $[H_2SO_4] = 0.37$ M, [MA] = 0.20 M, $[Ru(bpy)_3^{2+}] = 0.90$ mM, $[BrO_3^-] = 0.20$ M.

the solution for 300 s with different light intensities beginning at 600 s after the initiation of the reaction. Figure 5 shows how increasing light intensity affects the oscillatory behavior of the reaction. No effect was observed at low light intensities, time series a, while increasing the intensity resulted in a longer oscillatory period during the illumination, time series b. Oscillatory behavior was inhibited above a critical intensity, as shown in time series c. At high illumination, a significantly increased steady state bromide concentration was exhibited during the irradiation period, as shown in time series d. Time series c and d show how the oscillations resumed, virtually unchanged, when the illumination was terminated.

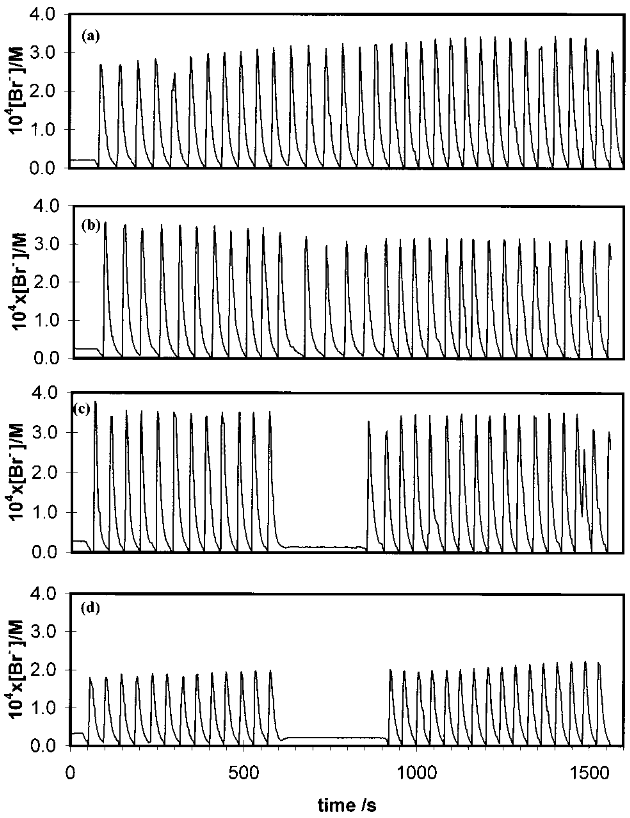

Figure 6. Effect of illumination of the full BZ system at various initial bromomalonic acid concentrations. Light was switched on at 600 s and off at 900 s. Initial bromomalonic acid concentrations: (a) 0.010 M, (b) 0.020 M, (c) 0.025 M, (d) 0.050 M. Other concentrations: $[H_2SO_4] = 0.37$ M, [MA] = 0.20 M, $[Ru(bpy)_3^{2+}] = 0.90$ mM, $[BrO_3^-] = 0.20$ M; light intensity PMT voltage: 5.0 V.

The effects of initial bromomalonic acid concentration were also studied. The light intensity was held constant, and, as in the previous experiments, the period of illumination was for 300 s beginning at 600 s after the reaction was initiated. As shown in Figure 6, the qualitative behavior is similar to that observed when the light intensity was varied with constant bromomalonic acid concentration. At bromomalonic acid concentrations below a critical value of about 0.025 M, the oscillatory period increases with increasing concentration during the period of irradiation, as shown in Figure 6a,b. At BrMA concentrations above the critical value, oscillations were suppressed during the irradiation and the stationary state Br^- concentration increased with increasing concentrations of BrMA, as shown in Figure 6c,d.

The effects of light intensity and the initial concentration of bromomalonic acid are summarized in Figure 7a,b. Oscillations are completely suppressed above a critical light intensity and critical BrMA concentration, with a sharp transition exhibited between the oscillatory and steady state behavior.

IV. Discussion

We propose a simple photochemical cycle to model the photoinduced bromide production in acidic solutions containing bromomalonic acid and $Ru(bpy)_3^{2+}$, i.e., the organic subset:

$$\mathrm{Ru(II)} \rightleftharpoons \mathrm{Ru(II)^*} \quad (1)$$

$$\mathrm{Ru(II)^*} + \mathrm{BrMA} \rightarrow \mathrm{Ru(III)} + \mathrm{Br^-} + \mathrm{org.\ prod.} \quad (2)$$

$$\mathrm{Ru(III)} + \mathrm{BrMA} \rightarrow \mathrm{Ru(II)} + \mathrm{Br^-} + \mathrm{org.\ prod.} \quad (3)$$

Here, Ru(II), Ru(II)*, Ru(III), and BrMA are $Ru(bpy)_3^{2+}$,

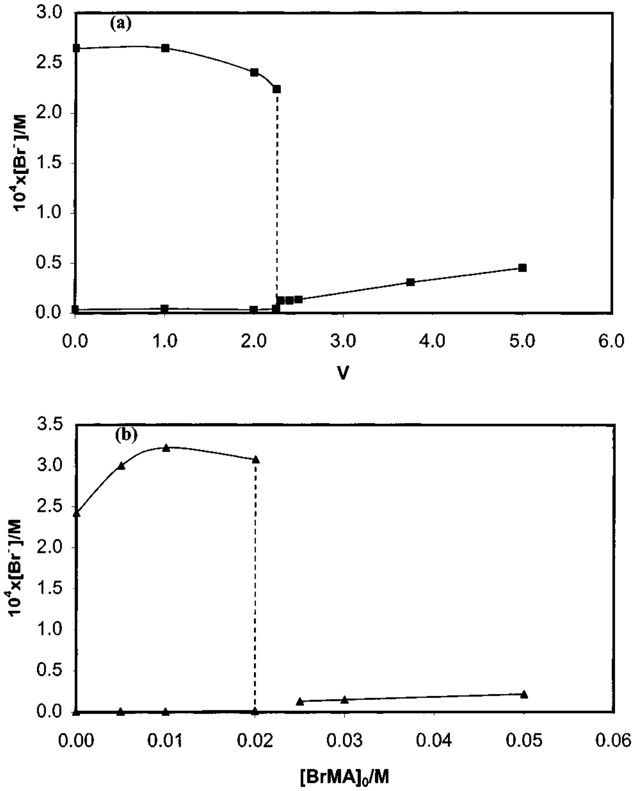

Figure 7. Effects of illumination intensity and initial bromomalonic acid concentration in the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction. Amplitude of oscillations and steady-state bromide concentration (a) as a function of light intensity; (b) as a function of initial BrMA concentration.

$Ru(bpy)_3^{2+}$*, $Ru(bpy)_3^{3+}$, and bromomalonic acid, respectively. The first process is the photoactivation of $Ru(bpy)_3^{2+}$, with the forward reaction rate proportional to the light flux, $k_1 = \Phi$, and the reverse reaction a first-order quenching process with a rate constant of k_{-1}. The excited ruthenium catalyst, a powerful reducing agent, reacts in the second process with bromomalonic acid to produce bromide. We neglect the reaction of $Ru(bpy)_3^{2+}$* with malonic acid on the basis of our observation that bromide production is virtually independent of the initial malonic acid concentration in the time scale of interest (cf. Figure 3a). The third process, the Ru(III) oxidation of BrMA, is the primary means for the reduction of the metal catalyst and the generation of bromide in the FKN mechanism[8] of the BZ reaction. It also serves to regenerate the catalyst Ru(II) in the photochemical cycle.

On the basis of our spectrophotometric measurements of a constant $Ru(bpy)_3^{2+}$ concentration, we assume quasi steady-state concentrations for $Ru(bpy)_3^{2+}$* and $Ru(bpy)_3^{3+}$. The rate of bromide production is then given by

$$r_{Br} = \frac{d[Br^-]}{dt} = \frac{2k_1k_2}{k_{-1} + k_2[BrMA]}[BrMA] \tag{4}$$

or, after rearrangement:

$$\frac{1}{r_{Br}} = \frac{k_{-1}}{2k_1k_2}\frac{1}{[BrMA]} + \frac{1}{2k_1} \tag{5}$$

A plot of the initial rate of bromide production as a function of initial bromomalonic acid concentration is shown in Figure 8a. Plotting $1/r_{Br}$ as a function of 1/[BrMA] according to eq 5 allows the rate parameters to be determined for the first and second reactions of scheme 1−3. The least-squares fit, shown in Figure 8b, yields the following values from the slope and intercept of the line:

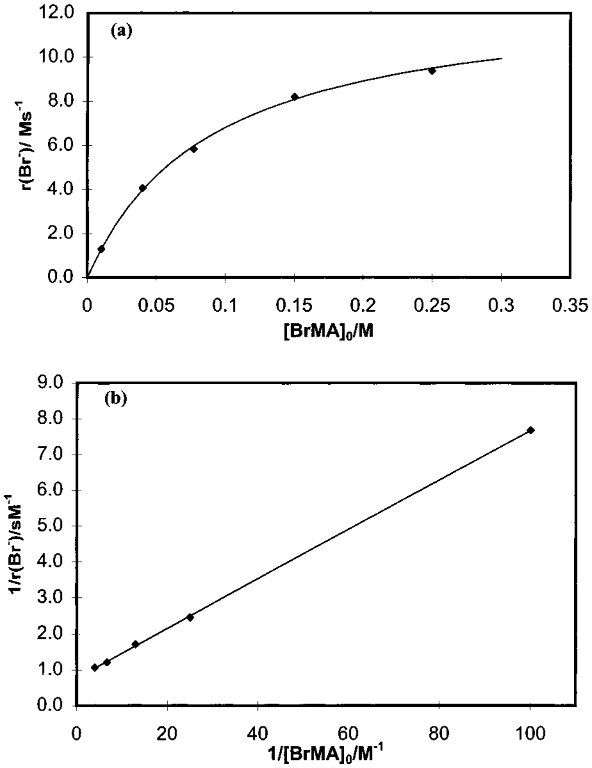

Figure 8. Dependence of bromide production in the organic subsystem on the initial bromomalonic acid concentration. (a) Plot of initial rate as a function of initial bromomalonic acid concentration. Points show experimental values; curve shows values predicted by eq 4. (b) Plot of reciprocal initial rate as a function of reciprocal initial bromomalonic acid concentration. Points show experimental values; line calculated from eq 5. Parameters are given in eq 6.

$$\begin{aligned} k_1 &= (6.4 \pm 0.4) \times 10^{-6}\ \mathrm{M\ s^{-1}} \\ k_{-1}/k_2 &= (8.9 \pm 0.1) \times 10^{-2}\ \mathrm{M} \end{aligned} \tag{6}$$

Using these values, together with $k_3 = 55.0\ s^{-1}\ M^{-1}$ from Gao and Forsterling,[24] numerical integrations of the rate equations for scheme 1−3 yield time series in good agreement with the experimental measurements of bromide concentration for different light intensities and different initial bromomalonic acid concentrations.

Photochemical generation of bromide in the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction by processes involving oxybromine species has been proposed by several authors.[9,15,17] Hanazaki at al.[16,18−21] proposed a dual effect of light on the BZ reaction: low-intensity illumination inducing oscillations, due to the generation of $HBrO_2$ from BrO_3^-, and high-intensity illumination suppressing oscillations, due to the generation of Br^- from BrO_3^-. For our experimental conditions, which correspond to low-intensity illumination, the excited ruthenium(II) reduces bromate in the initiation reaction[21]

$$Ru(II)^* + BrO_3^- + 2H^+ \rightarrow BrO_2^{\bullet} + H_2O + Ru(III) \tag{7}$$

followed by the autocatalytic cycle:

$$\begin{aligned} BrO_2^{\bullet} + Ru(II) + H^+ &\rightarrow HBrO_2 + Ru(III) \\ BrO_3^- + HBrO_2 + H^+ &\rightarrow 2BrO_2^{\bullet} + H_2O \end{aligned} \tag{8}$$

After the photoinitiation process, the autocatalysis occurs by the same mechanism as the autocatalytic production of $HBrO_2$ in the BZ reaction. Because reaction 7 is rate determining, the overall initiation process can be represented as:

$$\mathrm{Ru(II)^* + Ru(II) + BrO_3^- + 3H^+ \rightarrow 2Ru(III) + HBrO_2 + H_2O} \quad (9)$$

We found no evidence of Br^- production from the interaction of $Ru(bpy)_3^{2+*}$ with BrO_3^- for our experimental conditions of relatively low-intensity illumination. Studies of systems exposed to much higher light intensities have demonstrated that Br^- production[9,15] or $HBrO_2$ consumption[21] may also occur.

We now consider a modified Oregonator[27] model for the light-sensitive BZ reaction that includes the photoinduced generation of Br^- and $HBrO_2$ from the reaction of $Ru(bpy)_3^{2+*}$ with BrMA and BrO_3^-, respectively:

$$\mathrm{A + Y \rightarrow X + P} \quad \text{(O1)}$$

$$\mathrm{X + Y \rightarrow 2P} \quad \text{(O2)}$$

$$\mathrm{A + X \rightarrow 2X + 2Z} \quad \text{(O3)}$$

$$\mathrm{2X \rightarrow A + P} \quad \text{(O4)}$$

$$\mathrm{M + Z \rightarrow} h\mathrm{Y} \quad \text{(O5)}$$

$$\mathrm{E + V \rightarrow Y + Z} \quad \text{(P1)}$$

$$\mathrm{E + A \rightarrow X + 2Z} \quad \text{(P2)}$$

where X = $HBrO_2$, Y = Br^-, A = BrO_3^-, P = HOBr, M = MA, V = BrMA, Z = Ru(III), and E = $Ru(bpy)_3^{2+*}$. Processes O1−O5 represent the Oregonator, process P1 represents Br^- production according to scheme 1−3, and process P2 represents $HBrO_2$ production according to eq 9. The rates for processes P1 and P2 are given by

$$r_{\mathrm{P1}} = k_{\mathrm{P1}}[\mathrm{E}][\mathrm{V}] \quad (10)$$

$$r_{\mathrm{P2}} = k_{\mathrm{P2}}[\mathrm{E}][\mathrm{A}] \quad (11)$$

where [E], the photostationary-state concentration of $Ru(bpy)_3^{2+*}$, is given in terms of A and V according to

$$[\mathrm{E}] = \frac{k_1}{k_{-1} + k_{\mathrm{P1}}[\mathrm{V}] + k_{\mathrm{P2}}[\mathrm{A}]} \quad (12)$$

The rate constants for eqs 10 and 11 were obtained from eqs 2 and 7, where $k_{\mathrm{P1}} = k_2$ and $k_{\mathrm{P2}} = k_7[\mathrm{H}^+]^2$ includes the constant concentration of H^+. Substituting eq 12 into eqs 10 and 11 yields

$$r_{\mathrm{P1}} = \frac{k_1 k_2[\mathrm{V}]}{k_{-1} + k_2[\mathrm{V}] + k_{\mathrm{P2}}[\mathrm{A}]} = \frac{k_1[\mathrm{V}]}{\dfrac{k_{-1}}{k_2} + [\mathrm{V}] + \dfrac{k_{\mathrm{P2}}[\mathrm{A}]}{k_2}} \quad (13)$$

$$r_{\mathrm{P2}} = \frac{k_1 k_{\mathrm{P2}}[\mathrm{A}]}{k_{-1} + k_2[\mathrm{V}] + k_{\mathrm{P2}}[\mathrm{A}]} = \frac{k_1 \dfrac{k_{\mathrm{P2}}[\mathrm{A}]}{k_2}}{\dfrac{k_{-1}}{k_2} + [\mathrm{V}] + \dfrac{k_{\mathrm{P2}}[\mathrm{A}]}{k_2}} \quad (14)$$

The second form of eqs 13 and 14 indicates the experimentally measured quantities, k_1 and k_{-1}/k_2, and the group k_{P2}/k_2, which was used as an adjustable parameter.

TABLE 1: Differential Equations for Modified Oregonator Model

$$d[\mathrm{A}]/dt = -k_{\mathrm{O1}}[\mathrm{A}][\mathrm{Y}] - k_{\mathrm{O3}}[\mathrm{A}][\mathrm{X}] + k_{\mathrm{O4}}[\mathrm{X}]^2 - k_{\mathrm{P2}}[\mathrm{E}][\mathrm{A}]$$

$$d[\mathrm{X}]/dt = k_{\mathrm{O1}}[\mathrm{A}][\mathrm{Y}] - k_{\mathrm{O2}}[\mathrm{X}][\mathrm{Y}] + k_{\mathrm{O3}}[\mathrm{A}][\mathrm{X}] - 2k_{\mathrm{O4}}[\mathrm{X}]^2 + k_{\mathrm{P2}}[\mathrm{E}][\mathrm{A}]$$

$$d[\mathrm{Y}]/dt = -k_{\mathrm{O1}}[\mathrm{A}][\mathrm{Y}] - k_{\mathrm{O2}}[\mathrm{X}][\mathrm{Y}] + hk_{\mathrm{O5}}[\mathrm{M}][\mathrm{Z}] + k_{\mathrm{P1}}[\mathrm{E}][\mathrm{V}]$$

$$d[\mathrm{Z}]/dt = 2k_{\mathrm{O3}}[\mathrm{A}][\mathrm{X}] - k_{\mathrm{O5}}[\mathrm{M}][\mathrm{Z}] + k_{\mathrm{P1}}[\mathrm{E}][\mathrm{V}] + 2k_{\mathrm{P2}}[\mathrm{E}][\mathrm{A}]$$

$$d[\mathrm{M}]/dt = -k_{\mathrm{O5}}[\mathrm{M}][\mathrm{Z}]$$

$$d[\mathrm{V}]/dt = -k_{\mathrm{P1}}[\mathrm{E}][\mathrm{V}]$$

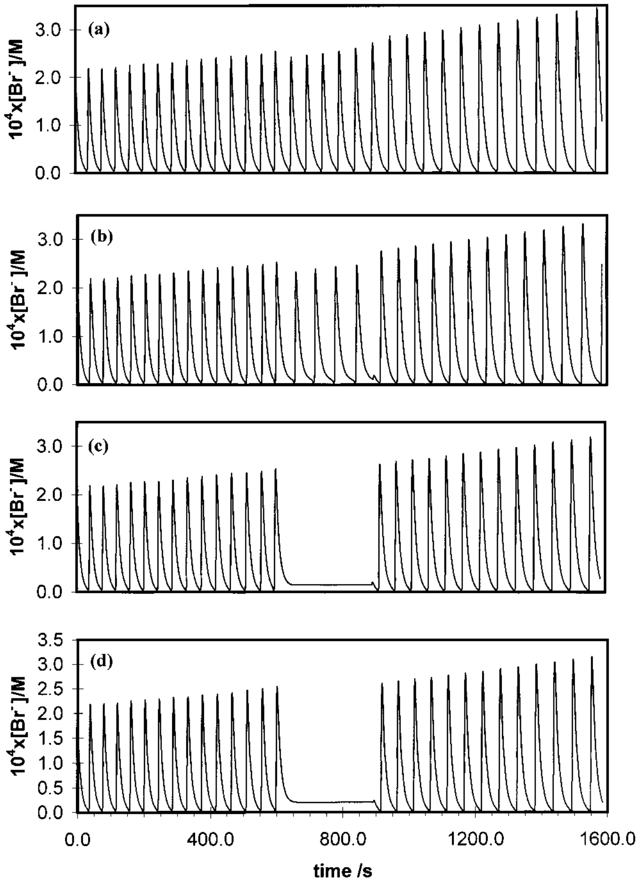

Figure 9. Effect of illumination intensity in the modified Oregonator model. Intensities correspond to PMT voltages: (a) 1.0 V, (b) 2.25 V, (c) 2.4 V, (d) 5.0 V. Initial bromomalonic acid concentration: 0.05 M; other parameters listed in Table 2.

The rate equations of the modified Oregonator, given in Table 1, were numerically integrated to simulate the dependence of the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction on light intensity and BrMA concentration. The behavior for different light intensities and initial bromomalonic acid concentrations is shown in Figures 9 and 10, respectively. In each calculation, a 300 s period of illumination was imposed beginning at 600 s after the initiation of the reaction. The rate parameters used in the calculation, listed in Table 2, were either taken from the literature[28,29] or derived from our experimental measurements, with the exception of the adjustable parameter k_{P2}/k_2.

Figure 11a,b show plots of the oscillatory and photoinduced steady-state behavior as a function of light intensity and initial bromomalonic acid concentration. The agreement between the simulated behavior in Figures 9−11 and the experimental measurements in Figures 5−7 is very good, particularly the abrupt transition from oscillatory to steady-state behavior exhibited at the critical values of illumination intensity and initial bromomalonic acid concentration.[30] The predominant process in the photosensitivity of the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction is the light-induced production of Br^- from the reduction of BrMA in the photochemical cycle of scheme 1−3. All of the qualitative features of the dependence on illumination intensity and initial bromomalonic acid concentration can be generated with a modified Oregonator that includes only process P1. The

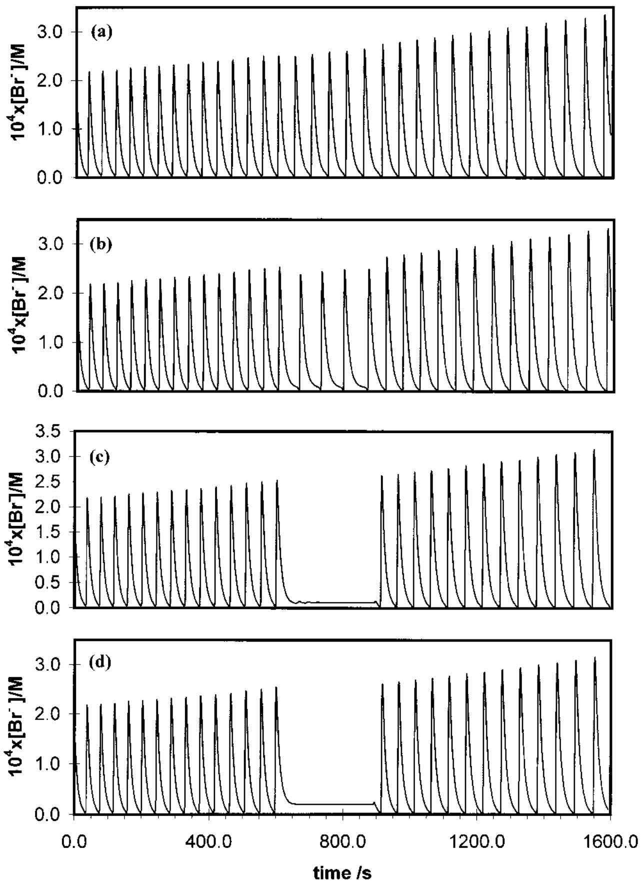

Figure 10. Effect of bromomalonic acid concentration in the modified Oregonator model. Initial bromomalonic acid concentrations: (a) 0.01 M, (b) 0.02 M, (c) 0.03 M, and (d) 0.05 M. Light intensity corresponds to PMT voltage of 5.0 V; other parameters listed in Table 2.

TABLE 2: Parameters Used in Modeling Calculations

parameters	ref
$k_{O1} = 2\ M^{-3}\ s^{-1}\ [H^+]^2$	27, 28
$k_{O2} = 1 \times 10^6\ M^{-2}\ s^{-1}\ [H^+]$	27, 28
$k_{O3} = 40\ M^{-2}\ s^{-1}\ [H^+]$	27, 28
$k_{O4} = 2 \times 10^3\ M^{-1}\ s^{-1}$	27, 28
$k_{O5} = 6\ M^{-1}\ s^{-1}$	*a, b*
$k_1 = 6.4 \times 10^{-6}\ M\ s^{-1}$	this work: exptl value
$k_{-1}/k_2 = 0.089$ M	this work: exptl value
$k_{P2}/k_2 = 2.05$	this work: *a,c*
$h = 1$	*a*
$[H^+] = 0.37$ M	

initial conditions
$[BrO_3^-]_0 = 0.2$ M
$[MA]_0 = 0.2$ M
$[Ru(bpy)_3^{2+}]_0 = 6 \times 10^{-4}$ M
$[Ru(bpy)_3^{3+}]_0 = 0.0$ M
$[BrMA]_0 = 0.005{-}0.050$ M
$[Br^-]_0 = 0.0$ M
$[HOBr]_0 = 0.0$ M

[a] Adjustable parameter. [b] Does not include [MA]. [c] k_{P2} includes $[H^+]^2$.

quantitative agreement between simulation and experiment is substantially improved, however, by also including the photoinduced production of $HBrO_2$ from BrO_3^- according to process P2.

Earlier studies of the light-sensitive BZ reaction have proposed a photoinduced production of Br^- arising from the reduction of BrO_3^-, where the rate is given by zero-order kinetics.[31] Our study shows that the photochemical production of bromide arises from the reduction of bromomalonic acid according to eqs 1−3. This mechanism also gives rise to zero-order kinetics if the bromomalonic acid concentration is sufficiently high, according to eq 13. If the initial bromomalonic acid concentration is low, however, eq 13 yields a rate dependence that is first-order in bromomalonic acid concentration.

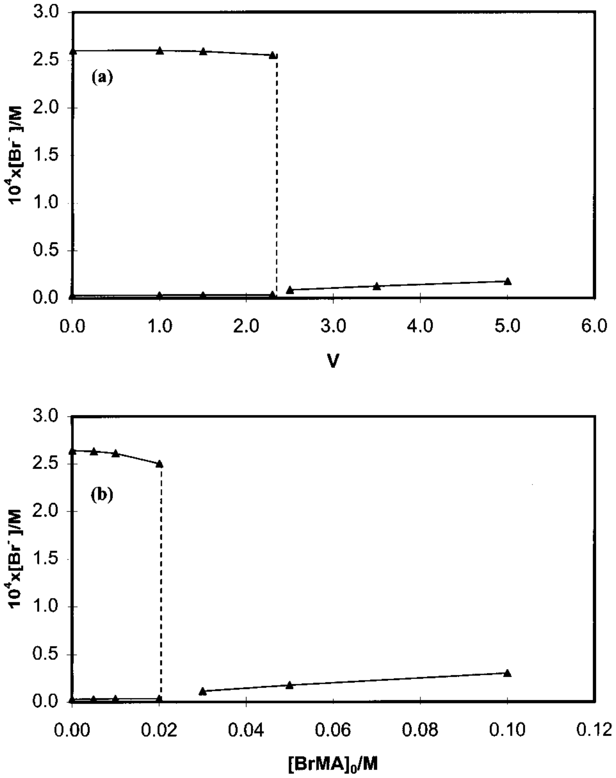

Figure 11. Effects of illumination intensity and initial bromomalonic acid concentration in the modified Oregonator model. Amplitude of oscillations and steady-state bromide concentration (a) as a function of light intensity; (b) as a function of initial BrMA concentration.

V. Conclusion

The behavior of the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction is dramatically affected by exposure to visible light. The excitability is reduced in proportion to the illumination intensity, which leads to the inhibition of oscillatory behavior in reaction mixtures with appropriate reactant concentrations. This effect provides a useful tool for studies of spatiotemporal behavior, since wave activity can be conveniently suppressed either locally or globally. Our study shows that light affects the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction via two separate photochemical pathways. The predominant effect is the production of Br^- from the reduction of bromomalonic acid by the photoexcited catalyst, $Ru(bpy)_3^{2+*}$. A secondary, but nonetheless important, effect is the generation of $HBrO_2$ from the reduction of BrO_3^- by the excited catalyst. These pathways were determined by studying the effects of light on the organic component system, comprised of bromomalonic acid and $Ru(bpy)_3^{2+}$, and the inorganic component system, comprised of BrO_3^- and $Ru(bpy)_3^{2+}$, both in sulfuric acid solutions. Numerical results obtained from an Oregonator model modified to include the photochemical production of Br^- and $HBrO_2$ are in semiquantitative agreement with the experimentally observed behavior.

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