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An Oregonator-Class Model for Photoinduced Behavior in the $Ru(bpy)_3^{2+}$-Catalyzed Belousov−Zhabotinsky Reaction

Takashi Amemiya,* Takao Ohmori, and Tomohiko Yamaguchi*

Department of Chemical Systems, National Institute of Materials and Chemical Research (NIMC), 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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A modified Oregonator model exhibiting photoinduced behavior in the $Ru(bpy)_3^{2+}$-catalyzed Belousov−Zhabotinsky (BZ) reaction is presented. We incorporate the concentration of bromomalonic acid as a new variable into the Oregonator model and also take into account two separate photochemical processes: the production of bromide from bromomalonic acid and bromous acid from bromate. The resulting four-variable model can reproduce a variety of photoinduced behavior reported experimentally in both batch and flow systems. The model also exhibits photoinduced chaos in the photosensitive BZ system under certain flow-rate and illumination conditions.

I. Introduction

The $Ru(bpy)_3^{2+}$-catalyzed Belousov−Zhabotinsky (BZ) reaction has been studied extensively over years for its sensitivity to visible light.[1−9] In solution systems, constant illumination induced transitions from large amplitude periodic oscillations to steady-states,[1,10−13] small-amplitude periodic oscillations,[1,10,11] or irregular oscillations[14,15] under batch[1,10,12,13,15] and flow[11,14] conditions. On the other hand, opposite photoinduced behavior, i.e., photoinduced transitions from steady-state to oscillatory behavior, was also found under flow conditions, which is called photoinduction of oscillations.[6,14,16] The period of oscillation was also affected by constant illumination; it was either lengthened or shortened depending on the solute compositions.[13] Pulsed-light illumination gave rise to behavior such as quenching of oscillations,[17] phase-shifts in the oscillations,[6,16,18] and photoinduced excitability.[16] At present, light is known to work either as an inhibitor or as an accelerator depending on the solute compositions.[6,13,19,20]

Several mechanisms have been proposed to account for the effects of light on the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction. The primary photochemical process is absorption of visible light by $Ru(bpy)_3^{2+}$.[10,11,21] The excited state of the catalyst $Ru(bpy)_3^{2+}*$ is a strong reducing agent[22] and may react with inorganic and organic species in the BZ reaction. Kuhnert considered the inhibitory effect of light to explain his observation of image processing[2] and proposed a photochemical mechanism in which BrO_3^- is directly reduced by $Ru(bpy)_3^{2+}*$ to produce Br^- based on the reduction potentials of BrO_3^- and $Ru(bpy)_3^{2+}*$.[22,23] In addition, Reddy et al. proposed a different photochemical reaction path in which Br^- is produced indirectly from BrO_3^- on the basis of their experimental observations.[15] The above mechanisms were based on oxybromine chemistry, and no organic species have been considered.

Organic species such as bromomalonic acid (BrMA) derivatives were already noted to release Br^- by ultraviolet light illumination in the cerium-catalyzed BZ system.[24] The importance of such organic species as a source of the photochemical production of Br^- was also suggested in the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction under visible light illumination,[6,15,18] and Yamaguchi et al. have investigated the photochemical mechanism for an organic subset of the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction, namely in a solution containing BrMA, H_2SO_4, and $Ru(bpy)_3SO_4$ but no oxybromine species.[19] They have obtained an experimental rate equation for the photochemical production of Br^- as a function of the solute concentrations and the light intensities. The analysis of the empirical rate equation by considering the photocycles for the Br^- production has concluded that one molecule of Br^- is produced by the reaction between BrMA and $Ru(bpy)_3^{2+}*$, and one more molecule of Br^- is also produced by the reaction between BrMA and the oxidized catalyst $Ru(bpy)_3^{3+}$.[19] The latter process is known as process C in the Field, Körös, and Noyes (FKN)[23] mechanism of the BZ reaction. A subsequent study of the photochemical mechanism in another organic subset, i.e., malonic acid (MA), BrMA, H_2SO_4, and $Ru(bpy)_3^{2+}$, has also shown that the photochemical production rate of Br^- is first order in the concentration of $Ru(bpy)_3^{2+}*$ and BrMA, respectively.[12] These experimental results and the kinetic analyses give the following reaction mechanism

$$Ru(bpy)_3^{2+}* + BrMA + H^+ \rightarrow Br^- + Ru(bpy)_3^{3+} + \text{products} \quad (Y)$$

It is now confirmed that BrMA is a key source for the photochemical production of the inhibitor Br^- in the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction.[12,19]

On the other hand, the reaction mechanism for the photochemical production of the activator $HBrO_2$ has been studied extensively by Hanazaki et al.[6,14,16,21,25−27] They have investigated the effects of light on the $Ru(bpy)_3^{2+}$-catalyzed BZ system[14,16] and on the $Ru(bpy)_3^{2+}$-catalyzed minimal bromate oscillator,[25−27] i.e., $Ru(bpy)_3^{2+}/BrO_3^-/Br^-/H_2SO_4$ system, under flow conditions. On the basis of both their experimental observations and the thermodynamic data,[22,23] they have proposed the following net reaction for the photochemical production of $HBrO_2$:

$$Ru(bpy)_3^{2+}* + Ru(bpy)_3^{2+} + BrO_3^- + 3H^+ \rightarrow HBrO_2 + 2Ru(bpy)_3^{3+} + H_2O \quad (H1)$$

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* To whom correspondence should be addressed.

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This reaction is a sum of the following two reactions:

$$\mathrm{Ru(bpy)_3}^{2+}{*} + \mathrm{BrO_3}^- + 2\mathrm{H}^+ \rightarrow \mathrm{BrO_2}^{\bullet} + \mathrm{Ru(bpy)_3}^{3+} + \mathrm{H_2O} \quad \text{(H2)}$$

$$\mathrm{BrO_2}^{\bullet} + \mathrm{Ru(bpy)_3}^{2+} + \mathrm{H}^+ \rightarrow \mathrm{HBrO_2} + \mathrm{Ru(bpy)_3}^{3+} \quad \text{(R6)}$$

where H2 is the photochemical initiation reaction[6,16] and R6 is the reaction step in the FKN mechanism of the BZ reaction. The step R6 constitutes the autocatalytic cycle in the BZ reaction and produces the activator $HBrO_2$. The mechanistic details of the photoinduction can be found in the literature[6,14,16,27] in connection with the FKN mechanism.

A modeling study to explain the effects of light was carried out by Krug et al.[28] They have added a reaction step of photoinduced production of Br^- to the main scheme of the Oregonator model,[29] where the rate was given by zero-order kinetics and the source of bromide was not specified. Their model exhibits photoinduced transitions from oscillatory to steady-state behavior via small-amplitude or zero-amplitude oscillations, i.e., via supercritical or subcritical bifurcations.[28,30] It explains the inhibitory effects of light qualitatively and has been used for the studies of spatiotemporal behavior in the $Ru(bpy)_3^{2+}$-catalyzed BZ system.[4,8,31] However, the photoinduction of oscillations[6,14,16] cannot be exhibited by this model even if flow terms are taken into account.

Another model accounting for the light sensitivity in the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction has recently been proposed by Kádár et al.[12] This model includes two separate photochemical processes: the production of the inhibitor Br^- from BrMA and the production of the activator $HBrO_2$ from BrO_3^-. The concentration of BrMA was assumed to be constant and equal to an initial value during one batch experiment. Numerical results obtained from the model were in quantitative agreement with their experimentally observed transitions from oscillatory to steady-state behavior as a function of both the light intensities and the initial concentrations of BrMA.[12] Subsequent analysis of this model with flow terms showed that the photoinduction of oscillations is also exhibited under high-flow rate conditions via a Hopf bifurcation.[32] This model accounts for both the photoinhibition and the photoinduction of oscillations; however, it cannot cover a condition under which there exists no BrMA initially.

The purpose of the present study is to propose a simple model that can reproduce all of the photoinduced behavior observed experimentally so far. Our principal idea for constructing the present model is to use the chemical and analytical simplicities of the Oregonator model. Our model is an extension of a modified Oregonator model reported previously[12,32] and can also cover a condition where there exists no BrMA initially. This condition has commonly been used in solution systems under batch[1,7,10,15] and flow[6,11,14,16,17,33] systems, where BrMA is accumulated in the course of the BZ reaction.[23] In the present Oregonator-class model, the concentration of BrMA is newly treated as a fourth variable. This variable is involved in the dynamics only under illumination conditions. Therefore, the present four-variable model exhibits behavior exactly the same as that shown by the original three-variable Oregonator model without illumination.

Here, we will first show that the present model reproduces the previously reported photoinduced behavior[12] as a function of the light intensities and of the initial concentrations of BrMA. Second, we will simulate photoinduced behavior in other $Ru(bpy)_3^{2+}$-catalyzed BZ systems under constant illumination conditions and show that our model reproduces all of the experimentally observed behavior investigated in this study. The simulated results include photoinduced irregular oscillations in both batch[15] and flow[34] systems, photoinhibition and photoinduction of oscillations,[14] and a state diagram spanned by light flux and the in-flow concentration of Br^-.[16] We will also show that the present model can generate photoinduced chaos that is different from experimentally observed irregular oscillations.[14,34]

II. Model

Four-Variable Photosensitive Oregonator Model. The four-variable model in the present study is a modification of the Oregonator model[29] and is an extension of a model proposed previously.[12] The chemical reaction steps read

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

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

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

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

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

$$\mathrm{V} \rightarrow \text{products} \quad \text{(O6)}$$

$$\mathrm{E} + \mathrm{V} + \mathrm{H} \rightarrow \mathrm{Y} + \mathrm{Z} \quad \text{(L1)}$$

$$\mathrm{E} + \mathrm{A} + 2\mathrm{H} \rightarrow \mathrm{X} + 2\mathrm{Z} \quad \text{(L2)}$$

where $X = HBrO_2$, $Y = Br^-$, $Z = Ru(bpy)_3^{3+}$, V = BrMA, $A = BrO_3^-$, $H = H^+$, $E = Ru(bpy)_3^{2+}*$ (excited state of $Ru(bpy)_3^{2+}$), and h is the stoichiometric factor;[29] the four variables are X, Y, Z, and V; the concentrations of A and H are assumed to be constant; and the concentration of E is assumed to be steady-state as shown below. Steps O1−O6 represent a modification of the original Oregonator scheme, and steps L1 and L2 represent photochemical reactions. Note that H is specified in the photochemical steps to make clear the number of H involved in the reactions, though it is omitted in the other steps according to the original description.[29] Four extensions of the previous model[12] include the following: (i) The product P (HOBr) in the Oregonator scheme is replaced by V (BrMA). (ii) Decomposition of V is added to the Oregonator scheme as the step O6; this step consumes V and enables its concentration to oscillate in a realistic range with an appropriate value of the rate constant k_{O6}. (iii) Malonic acid is not involved in the step O5 and the rate constant k_{O5} is treated as an adjustable parameter that does not include the initial concentration of MA. The relation between the values of k_{O5} used in our simulations and the concentrations of MA used in the experiments will be discussed in a separate section. (iv) The concentration of H is apparently involved in the photochemical reaction step L1 as revealed by the experiment.[19] One can see that the present four-variable model can be reduced into the original three-variable Oregonator model under dark conditions because the fourth variable V affects the dynamics only under illumination conditions.

Photochemical Reaction Step. The overall photochemical reaction in the present model consists of the reaction steps L1 and L2 together with the primary photochemical reaction of $Ru(bpy)_3^{2+}$

$$\mathrm{G} \leftrightarrow \mathrm{E} \quad \text{(L0)}$$

where $G = Ru(bpy)_3^{2+}$. The forward reaction is the photoac-

TABLE 1: Differential Equations for the Four-Variable Photosensitive Oregonator Model

$$\left\{\begin{matrix}\dot{\mathrm{X}}\\ \dot{\mathrm{Y}}\\ \dot{\mathrm{Z}}\\ \dot{\mathrm{V}}\end{matrix}\right\} = \left\{\begin{matrix} k_{\mathrm{O1}}\mathrm{AY} - k_{\mathrm{O2}}\mathrm{XY} + k_{\mathrm{O3}}\mathrm{AX} - 2k_{\mathrm{O4}}\mathrm{X}^2 \\ -k_{\mathrm{O1}}\mathrm{AY} - k_{\mathrm{O2}}\mathrm{XY} + hk_{\mathrm{O5}}\mathrm{Z} \\ 2k_{\mathrm{O3}}\mathrm{AX} - k_{\mathrm{O5}}\mathrm{Z} \\ k_{\mathrm{O1}}\mathrm{AY} + 2k_{\mathrm{O2}}\mathrm{XY} + k_{\mathrm{O4}}\mathrm{X}^2 - k_{\mathrm{O6}}\mathrm{V} \end{matrix}\right\} + \left\{\begin{matrix} -\mathrm{X} \\ -(\mathrm{Y} - \mathrm{Y}_{\mathrm{in}}) \\ -\mathrm{Z} \\ -(\mathrm{V} - \mathrm{V}_{\mathrm{in}}) \end{matrix}\right\} k_{\mathrm{f}} + \left\{\begin{matrix} p_2(\mathrm{V}) \\ p_1(\mathrm{V}) \\ p_1(\mathrm{V}) + 2p_2(\mathrm{V}) \\ -p_1(\mathrm{V}) \end{matrix}\right\}\Phi$$

Y_{in}: Concentration of Y in an in-flow solution.
V_{in}: Concentration of V in an in-flow solution (zero in the present simulations).

Photosensitive Terms

$$p_1(\mathrm{V}) = \frac{\mathrm{HV}}{\dfrac{k_{-\mathrm{L0}}}{k_{\mathrm{L1}}} + \mathrm{HV} + \dfrac{k_{\mathrm{L2}}}{k_{\mathrm{L1}}}\mathrm{H}^2\mathrm{A}}$$

$$p_2(\mathrm{V}) = \frac{\dfrac{k_{\mathrm{L2}}}{k_{\mathrm{L1}}}\mathrm{H}^2\mathrm{A}}{\dfrac{k_{-\mathrm{L0}}}{k_{\mathrm{L1}}} + \mathrm{HV} + \dfrac{k_{\mathrm{L2}}}{k_{\mathrm{L1}}}\mathrm{H}^2\mathrm{A}}$$

Note: These terms give the same values as those obtained from the coefficients p_1 and p_2, respectively, reported in the literature,[32] if the concentration of V is constant and the concentration of H is 0.37 M.[12,32]

tivation of G with a rate proportional to the light flux Φ, and the reverse reaction is a first-order quenching process with a rate constant $k_{-\mathrm{L0}}$. The concentration of the excited state of the catalyst, E, is assumed to be constant by the steady-state approximation and can be derived from the steps L0−L2 as

$$\mathrm{E} = \frac{\Phi}{k_{-\mathrm{L0}} + k_{\mathrm{L1}}\mathrm{HV} + k_{\mathrm{L2}}\mathrm{H}^2\mathrm{A} + k_{\mathrm{f}}} \approx \frac{\Phi}{k_{\mathrm{L1}}\left(\dfrac{k_{-\mathrm{L0}}}{k_{\mathrm{L1}}} + \mathrm{HV} + \dfrac{k_{\mathrm{L2}}}{k_{\mathrm{L1}}}\mathrm{H}^2\mathrm{A}\right)} \tag{1}$$

where k_{f} is a flow rate. Here it is assumed that the rate constant $k_{-\mathrm{L0}}$ and the products $k_{\mathrm{L2}}\mathrm{H}^2\mathrm{A}$ and $k_{\mathrm{L1}}\mathrm{HV}$ are much larger than the value of flow rates.[35]

The rates for the steps L1 and L2 are given by

$$r_{\mathrm{L1}} = k_{\mathrm{L1}}\mathrm{HEV} \tag{2}$$

$$r_{\mathrm{L2}} = k_{\mathrm{L2}}\mathrm{H}^2\mathrm{EA} \tag{3}$$

Substitution of eq 1 into eqs 2 and 3 yields

$$r_{\mathrm{L1}} = \frac{\mathrm{HV}}{\dfrac{k_{-\mathrm{L0}}}{k_{\mathrm{L1}}} + \mathrm{HV} + \dfrac{k_{\mathrm{L2}}}{k_{\mathrm{L1}}}\mathrm{H}^2\mathrm{A}}\Phi \equiv p_1(\mathrm{V})\Phi \tag{4}$$

$$r_{\mathrm{L2}} = \frac{\dfrac{k_{\mathrm{L2}}}{k_{\mathrm{L1}}}\mathrm{H}^2\mathrm{A}}{\dfrac{k_{-\mathrm{L0}}}{k_{\mathrm{L1}}} + \mathrm{HV} + \dfrac{k_{\mathrm{L2}}}{k_{\mathrm{L1}}}\mathrm{H}^2\mathrm{A}}\Phi \equiv p_2(\mathrm{V})\Phi \tag{5}$$

Equations 4 and 5 indicate that the two rates are functions of Φ and V, since A, H, and the two ratios, $k_{-\mathrm{L0}}/k_{\mathrm{L1}}$ and $k_{\mathrm{L2}}/k_{\mathrm{L1}}$, are assumed to be constant. The values of the two ratios can be obtained from the reported values[12] that included the concentration of H as described in the discussion section.

TABLE 2: Parameters Used in the Model

	ref
rate constants	
$k_{\mathrm{O1}} = 2\ (\mathrm{M}^{-3}\ \mathrm{s}^{-1})\ \mathrm{H}^2$	36
$k_{\mathrm{O2}} = 3 \times 10^6\ (\mathrm{M}^{-2}\ \mathrm{s}^{-1})\ \mathrm{H}$	36
$k_{\mathrm{O3}} = 42\ (\mathrm{M}^{-2}\ \mathrm{s}^{-1})\ \mathrm{H}$	36
$k_{\mathrm{O4}} = 3 \times 10^3\ (\mathrm{M}^{-1}\ \mathrm{s}^{-1})$	36
$k_{\mathrm{O6}} = 2 \times 10^{-3}\ (\mathrm{s}^{-1})$	*a*
$k_{-\mathrm{L0}}/k_{\mathrm{L1}} = 0.0329\ (\mathrm{M}^2)$	*b*
$k_{\mathrm{L2}}/k_{\mathrm{L2}} = 5.54\ (\mathrm{M}^{-1})$	*b*
adjustable parameters	
$h = 0.501$	*c*
$k_{\mathrm{O5}}\ (\mathrm{s}^{-1})$	*d*
initial conditions	
$\mathrm{X}_0 = 0$ (M)	
$\mathrm{Y}_0 = 1 \times 10^{-6}$ (M)	
$\mathrm{Z}_0 = 0$ (M)	
$\mathrm{V}_0 = \mathrm{V}_0$ (M)	*e*

[a] Assigned arbitrarily in this work. This value enables V to oscillate in the concentration range of mM ~ 10 mM under the conditions investigated in this study. [b] Not included in the concentrations of H, and calculated from the literature.[12] [c] Fixed to this value except for the first simulation[12] in the text. [d] Optimized in each simulation. See the discussion section in the text. [e] Changed depending on the experimental conditions.

Differential Equations. The present model gives the differential equations as shown in Table 1, which are briefly expressed by

$$\dot{\boldsymbol{X}} = \boldsymbol{A} + \boldsymbol{F}k_f + \boldsymbol{P}\Phi \tag{6}$$

where $\dot{\boldsymbol{X}}$ is the production rate of X, Y, Z, and V; $\boldsymbol{A}$ is the kinetic term of the present model, $\boldsymbol{F}k_f$ is a flow term with a flow rate k_f, and $\boldsymbol{P}\Phi$ is the photosensitive term with light flux Φ.

The rate equations of the present model were numerically analyzed or integrated to simulate the photoinduced behavior of the $\mathrm{Ru(bpy)_3}^{2+}$-catalyzed BZ reaction in both batch and flow systems by using the values of the rate constants[36] and of parameters as shown in Table 2. In the simulations, the same solute compositions were used as those in the corresponding experiments except for the initial concentrations of MA and of the catalyst.[37] The value of the stoichiometric factor h was fixed to 0.501 throughout all of the simulations except for the first

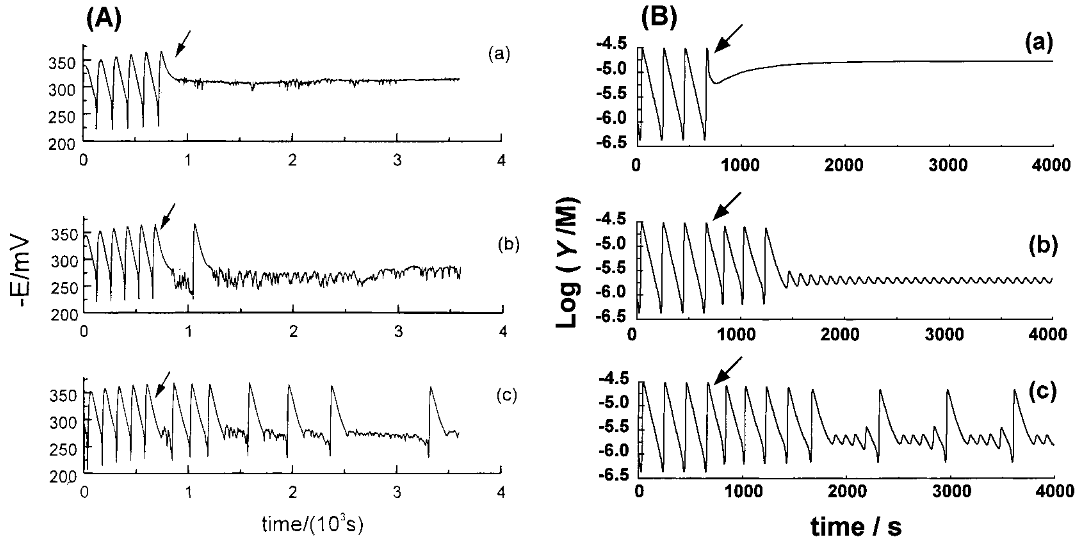

Figure 1. Photoinduced behavior in a batch system. (A) Experimental behavior in the potential of a bromide electrode reported by Reddy et al.[15] under the condition of $[BrO_3^-] = 0.06$ M, $[H_2SO_4] = 0.3$ M, [MA] = 0.10 M and $[Ru(bpy)_3^{2+}] = 1.32$ mM. Illumination intensities in mW/cm^2 were (a) 29.6, (b) 5.8, and (c) 2.3. (B) Simulated behavior in LogY obtained from the present model under the condition of A = 0.06 M, H = 0.3 M, $k_{O5} = 0.35$ s^{-1}, $h = 0.501$, and $k_f = 0$ s^{-1} with the values of the other constant parameters as listed in Table 2. The values of light flux (Φ) in M s^{-1} were (a) 1.0×10^{-5}, (b) 2.28×10^{-6}, and (c) 2.18×10^{-6}. Arrows indicate the time when the illuminations were started. ((A): Reprinted with permission from ref. 15, Copyright 1995 American Chemical Society.)

simulation[12] as shown below, and the rate constant k_{O5} was optimized in each simulation. The solute concentrations will hereafter be indicated by brackets such as [BrMA] used in the experiments and by the capital letter such as V in the simulations.

III. Results

Photoinduced Steady-State Behavior as a Function of Light Intensities and Initial Concentrations of BrMA in a Batch System. First we have confirmed that the present model can simulate the photoinduced transitions from oscillatory to steady-state behavior as a function of the light intensities and of the initial concentrations of BrMA in a batch system.[12] The concentrations of A = 0.2 M and H = 0.37 M were fixed in this simulation, and the initial concentrations of BrMA (V_0) were varied according to the experimental conditions.[12] The value of the stoichiometric factor h was 0.51 only in this simulation, and the value of k_{O5} was 1 s^{-1}. The batch condition was represented by $k_f = 0$ s^{-1}, and the values of the other parameters used are listed in Table 2. The illumination was started at a time of 600 s for 300 s in accordance with the experimental condition.

The dependence of the photoinduced behavior on the light intensities and on the initial concentrations of BrMA was found to be in agreement with the reported behavior (not shown).[12] The critical values of light flux for the abrupt transition from oscillatory to steady-state behavior were 2.9×10^{-6} M s^{-1} (the experimental value)[12] and 5.4×10^{-6} M s^{-1} (the simulated value) under the initial BrMA concentration of 0.05 M. On the other hand, the critical values of the initial concentration of BrMA for the abrupt transition were 0.025 M (the experiment), and 0.03 M (the simulation) under the constant light flux of 6.4×10^{-6} M s^{-1}. Note that the present model exhibits oscillatory behavior from the steady-state in the course of illumination under conditions of near the critical value of the light flux or near the critical value of the initial concentration of BrMA. This simulated behavior has not been reported in the experiments or in the previous model,[12] and it is due to the change in the concentration of V during the period of illumination.

Photoinduced Irregular Oscillations in a Batch System. We have next simulated the photoinduced behavior in a batch system observed by Reddy et al.[15] They observed photoinduced transitions from oscillations to steady-state of a high concentration of Br$^-$, small amplitude oscillations, and irregular oscillations with fine oscillatory structures, depending on the light intensities as shown in Figure 1(A). The simulated results by the present model are also shown in Figure 1(B), which are in good agreement with the experimental results. In particular, the photoinduced oscillations of a prolonged period with the low-amplitude fine structures were reproduced well at the lowest light intensity.

Photoinduction and Photoinhibition of Oscillations in a Flow System. In flow systems, both photoinhibition and photoinduction of oscillations have experimentally been observed.[14,16] Typical results of the photoinduced behavior observed by Mori et al.[14] are shown in Figure 2(A). The photoinhibition can be seen at a high light intensity under the conditions of both the low and the high in-flow concentrations of BrO_3^-. On the other hand, the photoinduction can be seen only under the low in-flow concentration of BrO_3^-. It is also noted that the redox potential showed low and high values of steady-state under dark and illuminated conditions, respectively. All of the photoinduced behavior has been reproduced by the present model as shown in Figure 2(B). Note that no photoinduction of oscillations occurs in the present model if the in-flow concentration of Br$^-$ is set to zero. This point will be discussed in the next section.

State Diagram and Photoinduced Irregular Oscillations in a Flow System. The photoinduction of oscillations has also been demonstrated experimentally in a state diagram spanned by light intensities and in-flow concentrations of Br$^-$ as shown in Figure 3(A).[16] Under the constant flow rate condition, photoinduction occurred in the in-flow concentration of Br$^-$ ranging from 0.03 mM to 0.07 mM, where the oscillatory region is interposed by the two boundary curves. We have simulated this state diagram by a linear stability analysis of the present model by the Routh–Hurwitz method,[38] and the result is shown in Figure 3(B). One can find good agreement between the two state diagrams. We also made a state diagram spanned by light

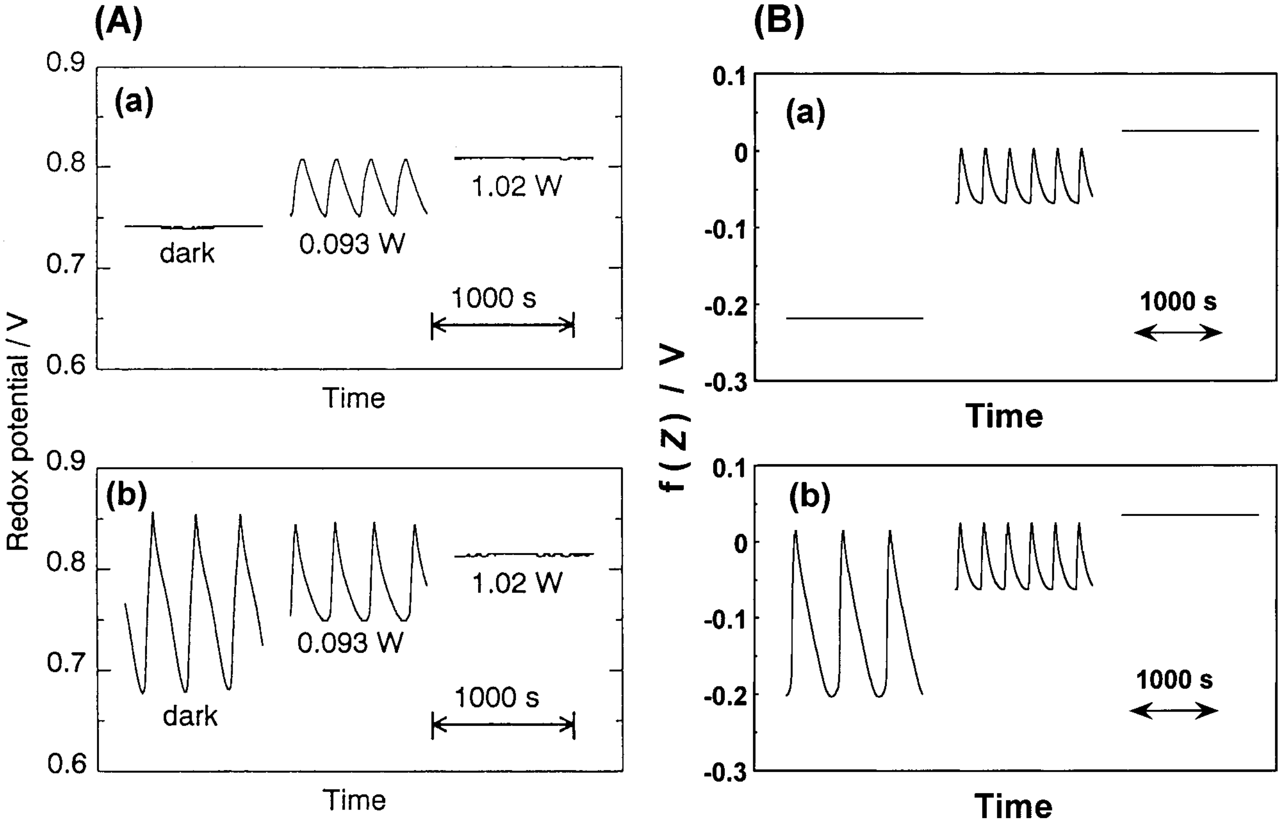

Figure 2. Photoinhibition and photoinduction of oscillations in a flow system. (A) Experimental behavior in the potential of a redox electrode reported by Mori et al.[14] under the following conditions: $[H_2SO_4] = 0.8$ M, $[MA] = 0.072$ M, $[Ru(bpy)_3^{2+}] = 0.2$ mM, and $k_f = 2.8 \times 10^{-3}$ s^{-1}; (a) $[BrO_3^-] = 0.013$ M, (b) $[BrO_3^-] = 0.015$ M. Illumination intensities are indicated in the figure. (B) Simulated behavior in Z in the form of $f(Z) = (RT/F)\mathrm{Log}(Z/(C_0 - Z))$, where R is the gas constant, F is the Faraday constant, $T = 298$ K is the absolute temperature, and C_0 is a total concentration of the catalyst, obtained from the present model under the following conditions: $H = 0.8$ M, $C_0 = 2.0$ mM, $k_{O5} = 0.02$ s^{-1}, $h = 0.501$ $k_f = 2.8 \times 10^{-3}$ s^{-1}, and $Y_{in} = 5 \times 10^{-6}$ M with the values of the other constant parameters as listed in Table 2; (a) A = 0.013 M, (b) A = 0.015 M. The values of light flux (Φ) in M s^{-1} were 0, 2.7×10^{-6}, and 3.0×10^{-5} from left to right. The in-flow concentration of Br^- is indispensable to reproduce the photoinduction phenomena as described in the text. Note that the value of C_0 used in the simulation was higher than that used in the experiment.[37] ((A): Reprinted from *Chem. Phys. Lett.*, 211, Mori, Y.; Nakamichi, Y.; Sekiguchi, T.; Okazaki, N.; Matsumura, T.; Hanazaki, I., p 421, 1993, with permission from Elsevier Science.)

flux and a flow rate under a constant in-flow concentration of Br^- as shown in Figure 4. The photoinduction of oscillations occurs in the flow rate ranging from 0.002 to 0.0045 s^{-1} under the conditions given in the figure caption.

Photoinduced irregular oscillations have been observed experimentally over the limited range of the in-flow concentration of Br^- as indicated in the caption of Figure 3(A), where the oscillatory region is interposed by the two boundary curves.[34] The reported irregular oscillatory behavior is shown in Figure 5(A) as a function of light intensities. The oscillations exhibited patterns of intermittency,[39] i.e., patterns of the type $L_{n1}S_{m1}L_{n2}S_{m2}...$, where L denotes oscillations with large amplitude and S denotes oscillations with substantially smaller amplitudes as compared with L, and $n1$, $m1$, $n2$, and $m2$... denote the number of the successive oscillations. A regular period-1 oscillation was also observed as shown in Figure 5(A), chart (c), between the two irregular oscillations (Figure 5(A), charts (b) and (d)). All of the photoinduced behavior has also been reproduced by the present model as shown in Figure 5(B): transition from steady state of a lower redox potential to irregular oscillations (chart (a) to chart (b)), regular period-1 oscillations (chart (c)), and again transition from the irregular oscillations to steady state of a higher redox potential (chart (d) to chart (e)). Note that the photoinduced irregular oscillations were intermittent in the present model as well.

Photoinduced Chaos in a Flow System. The present model is also found to generate photoinduced chaotic behavior, which is different from that of intermittent oscillations and has not been reported experimentally so far. The chaotic behavior is shown in the form of the temporal oscillations and of the attractor in Figure 6. The patterns are typical of chaos that has been induced by flow rates[40−43] or electrical current[44] in the cerium-catalyzed BZ system, and also induced by light in other chemical reaction systems.[45,46] The present photoinduced chaotic behavior has been exhibited with the values of the parameters nearly the same as those used in Figures 3−5. However, a value of k_{O5} larger than that used in Figures 3−5 was necessary to generate the chaotic behavior under the employed conditions. Furthermore, it can be generated only under the condition of the high in-flow concentrations of Br^- and of the high flow rates, where the photoinduction of oscillations occurs.

IV. Discussion

It is well known that the Oregonator model significantly simplifies the reaction steps involving organic species.[23,29] Detailed mechanistic studies for the BZ reaction have revealed that more reaction steps and different feed back loops are involved in steps O5 and O6.[47−51] In particular, Zeyer and Schneider[33] succeeded in reproducing most of the oscillatory behavior in the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction under dark conditions based on a model consisting of 19 reaction steps and 16 variables proposed by Gao and Försterling.[50] Such a detailed model with the photochemical steps L1 and L2 may reproduce

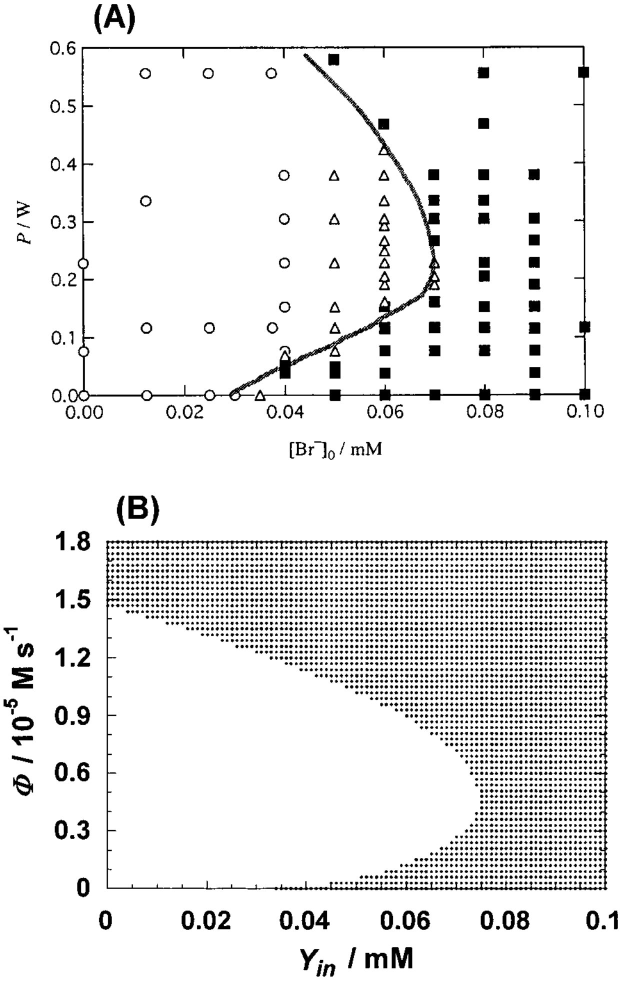

Figure 3. State diagram spanned by the in-flow concentration of Br^- and light intensities. (A) Experimental results reported by Kaminaga et al.[16] under the following conditions: $[BrO_3^-] = 0.05$ M, $[H_2SO_4] = 0.8$ M, [MA] = 7.5 mM, $[Ru(bpy)_3^{2+}] = 0.1$ mM, and $k_f = 3.3 \times 10^{-3}$ s^{-1}; (○)oscillations, (△) irregular oscillations, and (■) reduced steady-state. (B) Simulated results by a linear stability analysis of the present model under the following conditions: A = 0.05 M, H = 0.8 M, $k_{O5} = 0.59$ s^{-1}, $h = 0.501$, $k_f = 3.3 \times 10^{-3}$ s^{-1} with the values of the other constant parameters as listed in Table 2. Closed circles and white region indicate steady-states that are locally stable, and locally unstable, respectively. ((A): Reprinted from *Chem. Phys. Lett.*, 279, Kaminaga, A.; Mori, Y.; Hanazaki, I., p 339, 1997, with permission from Elsevier Science.)

the experimentally observed photoinduced behavior under conditions nearly the same as those used in the experiments. In contrast to these detailed studies, the major aim of the present investigation is to propose a simple model that can exhibit important features of the photoinduced behavior with a minimum number of adjustable parameters.

The present model has two modifications in the main scheme of the original Oregonator model; one is the replacement of P (HOBr) by V (BrMA), and the other is addition of step O6. The modified steps O1, O2, and O4 are the same as the first three steps in the four-variable model by Györgyi and Field,[41,52] while the remaining three steps O3, O5, and O6 in the present model are different from the remaining four steps in their model. The variable V plays an important role in constituting a second feed back loop in their model;[41,52] however, it does not affect the dynamics in our model without illumination.

The decomposition step O6 is adapted from Wang et al.[53] and Johnson et al.[54] and can remove V that appears to be able to grow unrealistically under dark conditions.[54] With an appropriate value (2×10^{-3} s^{-1}) of the rate constant k_{O6}, the concentration of V oscillate within the range of mM ~ 10 mM under both dark and illuminated conditions. Though bromide production is not involved in step O6, BrMA should release Br^- eventually in the course of the BZ reaction.[23,41,50,52,53] In the present model, all such steps producing Br^- from BrMA or any other organic species are lumped in step O5.

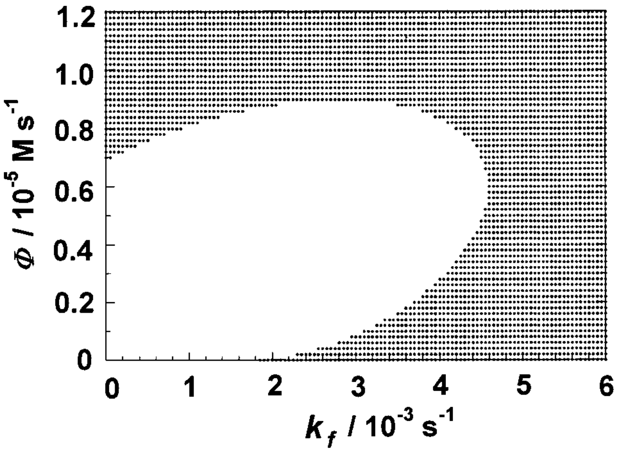

Figure 4. State diagram obtained by a linear stability analysis of the present model spanned by light flux and flow rates under the same conditions as those in Figure 3(B) except for the in-flow concentration of Br^- ($Y_{in} = 0.06$ mM).

In the original Oregonator model the rate constant k_{O5} is assumed to be proportional to the total concentration of MA and BrMA.[29] This total concentration may be nearly the same as the initial concentration of MA, therefore we first tried to simulate the experimentally observed photoinduced behavior with values of k_{O5} that were defined as the product of a constant value and the initial concentrations of MA used in the experiments. However, the simulated behavior gave no agreement with the corresponding experimental results when the value of k_{O5} was defined in this way. The values of k_{O5} finally used in the present simulations were neither proportional to nor monotonic functions of the initial concentrations of MA as shown in Figure 7.

Step O5 can be written by two separate steps according to the FKN mechanism of the BZ reaction,[23,55] i.e., the oxidized form of the catalyst can react with both MA and BrMA:

$$Z + M \rightarrow \text{products} \qquad (O5')$$

$$Z + V \rightarrow Y + \text{products} \qquad (O5'')$$

where M represents malonic acid. The rate of step O5 is equal to the sum of the total rate of steps O5′ and O5″, thus the following equation is obtained:[55]

$$k_{O5}\, Z = k_{O5'}\, MZ + k_{O5''}\, VZ \qquad (7)$$

namely

$$k_{O5} = k_{O5'}M + k_{O5''}V$$
$$\equiv k(M, V) \qquad (8)$$

We examined the relation between the values of k_{O5} used in our simulations and the values of the right-hand side of the equation, $k(M, V)$. This relation is also shown in Figure 7 by using appropriate values of $k_{O5'}$ (0.3 M^{-1} s^{-1}) and $k_{O5''}$ (30 M^{-1} s^{-1}) reported in the literature.[52,56] A linear relation was obtained between the two values for the investigated cases.[57]

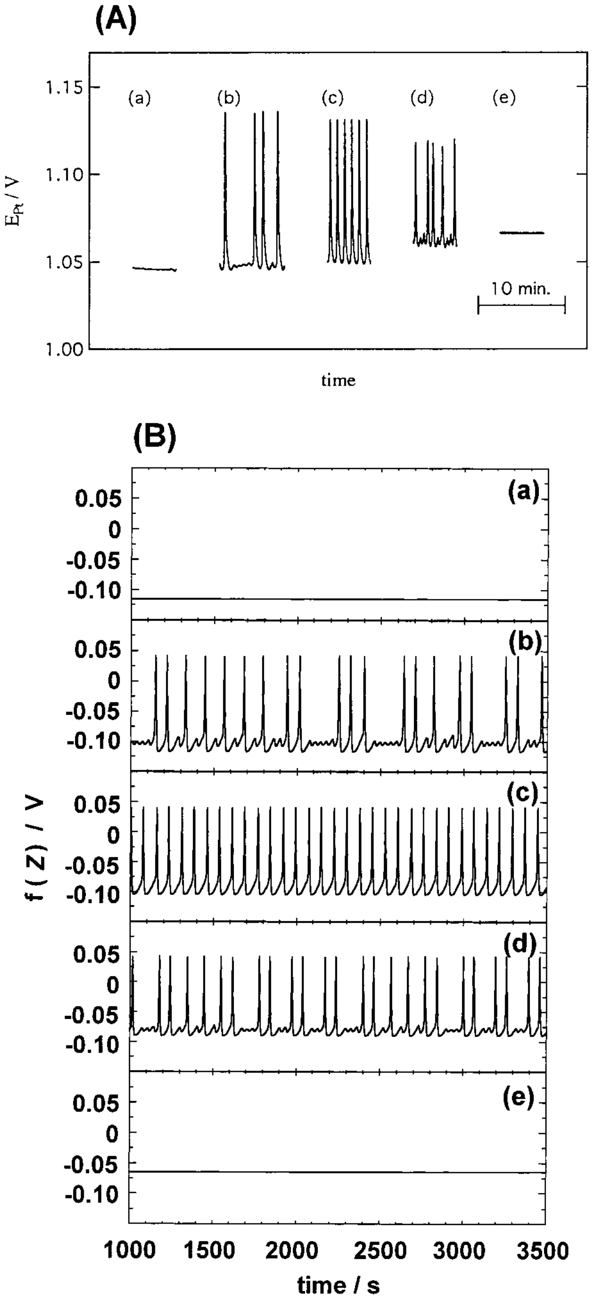

Figure 5. Photoinduced oscillatory behavior under the same conditions as those in Figure 3 except for the in-flow concentration of Br^- and the light intensities. (A) Experimental results observed by Kaminaga[34] with $[Br^-] = 0.06$ mM. Illumination intensities in W were (a) 0.11, (b) 0.15, (c) 0.20, (d) 0.33, and (e) 0.46. (B) Simulated behavior in Z in the form of $f(Z) = (RT/F)\mathrm{Log}(Z/(C_0 - Z))$, where R is the gas constant, F is the Faraday constant, $T = 298$ K is the absolute temperature, and C_0 is the total concentration of the catalyst, obtained from the present model with $Y_{in} = 0.06$ mM and $C_0 = 5.0$ mM.[37] Light flux was applied from a time of 500 s in each simulation, and the values in M s^{-1} were (a) 1.0×10^{-6}, (b) 1.74×10^{-6}, (c) 2.80×10^{-6}, (d) 4.99×10^{-6}, and (e) 1.0×10^{-5}.

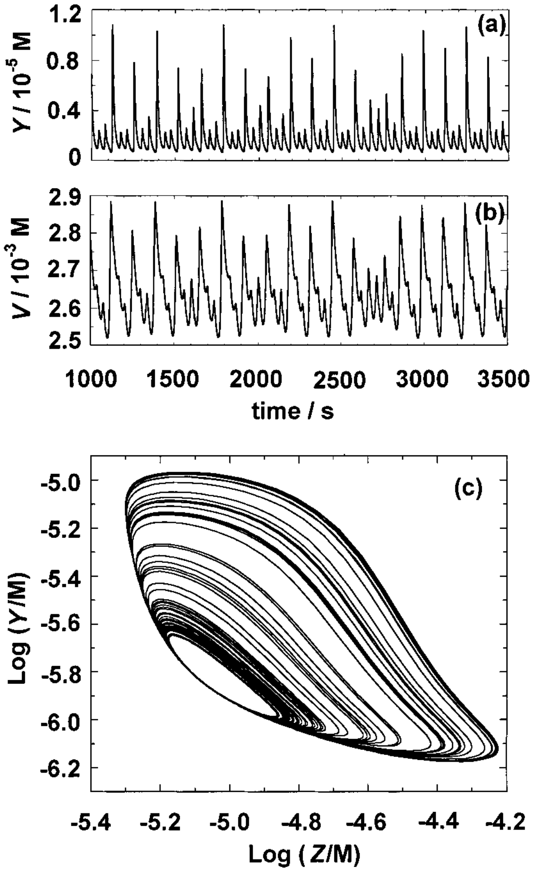

Figure 6. Photoinduced chaotic behavior in (a) Y, (b) V, and (c) LogY−LogZ attractor obtained from the present model under the following condition: A = 0.05 M, H = 0.8 M, $k_{O5} = 0.99$ s^{-1}, $h = 0.501$, $Y_{in} = 0.05$ mM, and $k_f = 2.7 \times 10^{-3}$ s^{-1}, with the values of the other constant parameters as listed in Table 2. Light flux was applied from a time of 500 s and the value was 2.64×10^{-6} M s^{-1}.

The photochemical reaction steps L1 and L2 respectively present the inhibitory and the inductory effects of light on the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction.[14,16,19] In the photochemical step L1, proton is involved as reported in the literature,[19] which has not been considered in the previous model.[12,32,58] In addition, the rate constant k_{L2} included the constant concentration of H in the previous model.[12,32,58] To let the rate constants k_{L1} and k_{L2} be general, we redefined them so that they do not include the solute concentration. We calculated the values of the two ratios, k_{-L0}/k_{L1} and k_{L2}/k_{L1}, by considering the reported value (0.37 M) of H.[12] The values of the parameters as listed in Table 2 are now useful for a system under different solute compositions.

To reproduce the photoinduction of oscillations as demonstrated in Figure 2, nonzero values of the in-flow concentration of Br^- (Y_{in}) are indispensable to the present model. Thus we have used the value of $Y_{in} = 5 \times 10^{-6}$ M to simulate the experimental results as shown in Figure 2(A), while no Br^- was added in the in-flow solutions experimentally. However, including the nonzero value of Y_{in} in the simulation may make sense if we admit a trace amount of Br^- included in the regent of BrO_3^-. The value (5×10^{-6} M) of the Y_{in} used in the simulation was 0.03 ∼ 0.04% of that (0.015 ∼ 0.013 M) of the BrO_3^- used in the experiments. This assumption may indicate that a trace amount of Br^- might be included in the solution of BrO_3^-.

Chaotic oscillations can be exhibited only under high flow rates and illumination conditions in the present model. Under dark conditions, the present model is mathematically identical with the original Oregonator model,[29] which is known to exhibit neither complex nor chaotic oscillations even under flow conditions.[59] Though our model exhibits neither complex nor burst-like oscillatory behavior as observed experimentally under dark conditions,[33] it reproduces photoinduced behavior in good agreement with experimental observations. The present investigation shows that the value of k_{O5} plays an important role to exhibit photoinduced chaotic behavior. In general, a low value of k_{O5}

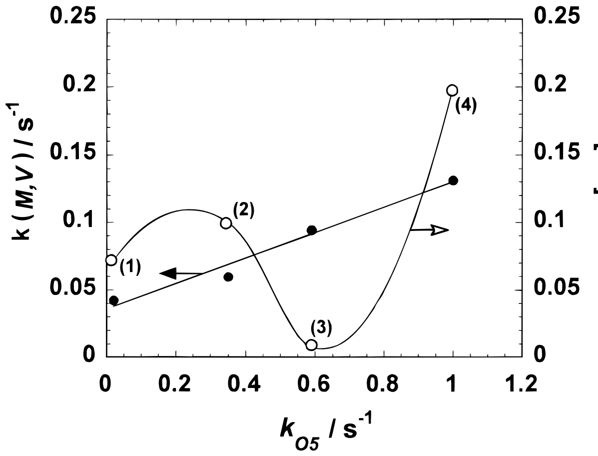

Figure 7. Plots of the concentrations of malonic acid [MA] used in the experiments (○) and the values of k(M, V) as defined by eq 8 (●) vs the values of k_{O5} used in our simulations. The numbers next to the open circles correspond to the investigated studies as follows: (1) Mori et al.,[14] (2) Reddy et al.,[15] (3) Kaminaga,[34] and (4) Kádár et al.[12] To calculate the value of k(M, V), the average value of V exhibiting stationary oscillatory behavior under the dark condition was used. The concentration of malonic acid, M, in eq 8, was calculated as the subtraction of the initial concentration of malonic acid used in the experiment from the average value of V as mentioned above. For the calculation of V in Mori et al.'s case (1), the solute concentration of A = 0.015 M was used as given in the caption of Figure 2(B), chart (b), under which oscillatory behavior was exhibited without illumination. For the calculation of V in Kaminaga's case (3), the in-flow concentration of Y_{in} = 0.03 mM was used instead of Y_{in} = 0.06 mM as given in the caption of Figure 5(B) in order to obtain oscillatory behavior without illumination. For the calculation of V in Kádár et al.'s case (4), four different values of the initial concentration of V_0 were used according to the experiments, and the average values of V were all the same under these initial conditions. The solid lines are to guide the reader's eye.

gives rise to intermittent patterns of the type $L_{n1}S_{m1}L_{n2}S_{m2}$. . ., and a high value of k_{O5} gives rise to small-amplitude regular oscillations. At present, we are not sure how to find an experimental condition in accordance with the change in the values of k_{O5}. However, one of the methods may be to control the concentration of BrMA, and such experiments are in progress in our laboratory.

Finally, we refer to behavior induced by pulsed-light stimulation. The photoinduced behavior includes quenching of chemical oscillations,[17] phase shifts in the oscillations,[6,18] and photoinduced excitable responses.[16] We have confirmed that all of the pulsed-light induced behavior can be reproduced by the present model.[60]

V. Conclusions

An Oregonator-class model for the $Ru(bpy)_3^{2+}$-catalyzed photosensitive BZ reaction has been constructed with a small modification of the original Oregonator model. We have adopted BrMA as a new variable in our model, and also taken into account the two different effects of light on the BZ system: photochemical production of both the inhibitor Br^- and the activator $HBrO_2$. The resulting four-variable model exhibits a variety of photoinduced behavior in both batch and flow systems observed experimentally.

In particular, the photoinduction of oscillations, i.e., photoinduced transitions from steady-state to oscillatory behavior, has been reproduced quantitatively by a stability analysis and numerical integration of the present model for the first time. The in-flow of Br^- was found to be indispensable for the photoinduction. This model has also generated photoinduced irregular oscillations observed experimentally in both batch and flow systems. The present model also predicts that chaotic oscillations can be exhibited only under certain high flow rates and illumination conditions.

The essence of the present work is demonstrated in Tables 1 and 2. Although there still remain a few uncertainties in the reaction mechanisms, the present model is useful to simulate and control the photoinduced behavior in the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction.

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