Review

Photoresponse of self-organizing chemical systems

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Abstract: Research works on the self-organization phenomena in chemical systems are reviewed with particular emphasis on their response to the photo-irradiation, for which most of the works have been performed in the author's laboratory. In the present review, a brief survey is given for the recent developments of research on the self-organization phenomena observed in dark. Then, the determination of action spectra for the photo-irradiated self-organizing chemical systems is described with a few examples, together with a discussion on the advantages of employing the irradiated light intensity as a control parameter. Experimental results for the chemical systems under the stationary and pulse light irradiation are summarized and discussed for the redox oscillators including the Belousov-Zhabotinsky and the Briggs-Rauscher systems and their variations. Discussions are also given for various types of pH oscillators under photo-irradiation. Finally, experimental observations on chaos and multistability, the most characteristic features in the field of self-organizing chemical systems, are surveyed and discussed. Possibility of the photo-control of chaos and multistability is discussed with examples of the Briggs-Rauscher system and of the pH oscillator system, H_2O_2 - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ - HCO_3^- .

Key words: Autocatalysis; self-organization; photoresponse; chemical chaos.

Introduction. Recently, importance of the self-organization phenomena has been recognized more and more deeply. The self-organization can be defined as the phenomenon in which a system forms a temporal or spatial order spontaneously. For a chemical system to realize the self-organization, it is required that the system is open, namely, it can exchange materials and heat with outside, and that the chemical kinetics taking place in the system contains strong nonlinearity.

In the field of chemical reactions, the oscillatory chemical reactions caused by nonlinearity are known, as the Bray-Liebhafsky (BL) reaction,^{1,2)} the Belousov-Zhabotinsky (BZ) reaction,³⁾ and the Briggs-Rauscher (BR) reaction.⁴⁾ The redox potential of the system oscillates in these cases. In addition,⁵⁻⁸⁾ another class of

chemical oscillators is known in which pH of the solution oscillates (the pH oscillator). Chaotic oscillations and multistabilities are also observed in chemical systems. The spatial pattern formation is another topic which is realized as a result of the combination of temporal oscillations and spatial diffusion.

Although a number of reports have so far been presented, the photoresponse of such nonlinear chemical systems has not been studied systematically until recently, except for some pioneering reports published at relatively early stage in the history of research on the oscillatory chemical reactions.⁹⁻¹³⁾ In 1991, the author and his collaborators proposed how to determine the action spectrum for the illuminated nonlinear chemical systems, which was considered to be useful in specifying the initial stage of photochemical reactions.¹⁴⁻¹⁶⁾ This and the succeeding works¹⁷⁾ are considered to have contributed to find a new point of contact between the self-organization phenomena and the well-established field of molecular spectroscopy and molecular structure. In the present paper, studies on the photoresponse of the nonlinear chemical systems will be reviewed, with particular emphasis on the works performed in the

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Fig. 1. Experimental setup for photo-irradiation of a nonlinear chemical system. (A) A batch configuration. (B) A CSTR configuration. Solutions containing materials are flowed into a closed reaction cell by a peristaltic pump where solution is mixed by a magnetic stirrer and pushed out with a constant velocity characterized by k_0 . The distance between two optical windows (w) gives an optical path length.

author's laboratory.

Experimental set-up. Fig. 1(A) illustrates a batch experiment where material solutions are mixed and stirred in a reaction cell, while the system is monitored by measuring the redox potential or pH. For some oscillator systems, chemical oscillations or bifurcation among the stationary and oscillatory states can be observed with this configuration.

More quantitative experiments require the flow system as illustrated in Fig. 1 (B). Solutions of materials A, B, ... are provided with constant flow rates through a peristaltic pump and mixed in a reaction cell with a stirrer. The solution in the cell flows out at a constant flow rate k_0 (s^{-1}) $\equiv v/V$, where v (mL s^{-1}) is the rate of flow-out and V is the cell volume (mL). It is to be noted that $\tau \equiv 1/k_0$ is the average residence time of the solution in the cell. The initial concentrations of materials (say, $[A]_0$, $[B]_0$, ...) are defined as the concentrations of substances A, B, ..., respectively, which would be realized

after complete mixing if no chemical reaction took place in the cell. The reaction temperature is controlled by flowing water from a temperature controller around the reaction cell. This type of reactor is often called as a CSTR (Continuous-flow Stirred Tank Reactor).

In the case of photo-irradiation experiments, light from a mercury lamp or a halogen-tungsten lamp is monochromatized with a monochromator or a set of bandpass filters and introduced into the cell. The power (P_0) of the incident light is controlled with a neutral-density filter and monitored with a photomultiplier or a photodiode before it goes through the reaction cell.

A brief survey of nonlinear chemical reactions in dark. The Belousov-Zhabotinsky and related systems. In the BZ reaction, the following three steps are important to realize and control the autocatalysis:^{5),6)}

where $\text{Ru}(\text{bpy})_3^{2+}$, *tris*-(bipyridine) ruthenium(II), is the catalyst. $\text{Fe}(\text{phen})_3^{2+}$, *tris*-(*o*-phenanthroline) iron(II), or Ce^{3+} is also employed often as a catalyst. The most essential process to exhibit nonlinearity is the autocatalytic reaction which is obtained as $[1] + [2] \times 2$:

HBrO_2 increases autocatalytically in this process and the system originally in SSI turns into SSII at a stroke. Here SSI is the reduced stationary state in which all the catalyst exists as $\text{Ru}(\text{bpy})_3^{2+}$, while SSII is the oxidized stationary state where all the catalyst exists as $\text{Ru}(\text{bpy})_3^{3+}$.

On the other hand, equilibrium [3] is important to control the autocatalysis. [3] is strongly biased to the right, so that $[\text{HBrO}_2] = 0$ is kept as far as $[\text{Br}^-] > 0$. The autocatalytic process [4] never starts. [4] starts only when $[\text{Br}^-]$ becomes negligibly small. Another process required is that reduces the catalyst oxidized through [4] back to the initial oxidation state ($\text{SSII} \rightarrow \text{SSI}$). In the standard BZ reaction, malonic acid (MA) is used as a substrate to reduce the catalyst and to produce additional Br^- to inhibit the autocatalysis.⁵⁾ The oscillatory state (OSC), where the system redox potential oscillates spontaneously, can be realized when these three processes ([4], [3] and the reduction process) collaborate properly.

Sometimes we employ Br^- externally supplied to the cell instead of the substrate such as MA. In this case, the supplied Br^- works to bring the whole system back to the reduced state. This system is called as the Minimal Bromate Oscillator (MBO).⁵⁾

We have found that *o*-, *p*-, or *m*-acetylphenol is effective as a substrate in place of MA and succeeded in observing chemical oscillations with Ce^{3+} , $\text{Ru}(\text{bpy})_3^{2+}$ or $\text{Fe}(\text{phen})_3^{2+}$ as a catalyst in a batch reactor.¹⁸⁾

The Briggs-Rauscher system. The BR reaction in dark is controlled by [5] - [7], which are similar to [1] - [3] for the BZ reaction.⁵⁾

[5] + [6] $\times$ 2 gives the autocatalytic process;

where HIO_2 is multiplied nonlinearly. The reduced (SSI) and oxidized (SSII) stationary states correspond to the catalyst oxidation states of Mn^{2+} and Mn^{3+} (MnOH^{2+}), respectively. Control process [7] is similar to [3] for the BZ reaction.

The pH oscillators. In contrast to the BZ or BR system, where the solution redox potential oscillates, the solution pH oscillates in the pH oscillators. Various types of pH oscillators have been found and studied. For the H_2O_2 - $\text{Fe}(\text{CN})_6^{4-}$ - H^+ system, the essential part of the dark reactions can be written as^{19),20)}

[12] + [13] gives

which is the autocatalytic process for the hydroxyl radi-

Fig. 2. Bifurcation diagram for the $\text{Fe}(\text{CN})_6^{4-}$ - BrO_3^- - SO_3^{2-} system determined at 35 °C. $[\text{Fe}(\text{CN})_6^{4-}]_0 = 15 \text{ mM}$, $[\text{BrO}_3^-]_0 = 75 \text{ mM}$, $[\text{SO}_3^{2-}]_0 = 90 \text{ mM}$, $[\text{H}_2\text{SO}_4]_0 = 7.5 \text{ mM}$. Pairs of open circles represent the range of pH in the OSC state. The arrows indicate the direction of discontinuous transitions.

cal, $\text{OH}^\cdot$. On the other hand, [12] $\times$ 2 + [13] gives

giving rise to the autocatalytic process for $\text{HO}_2^\cdot$. Under normal experimental conditions, a sufficient amount of H_2O_2 is being supplied to the reactor so that $\text{OH}^\cdot$ produced by any reaction in the reactor is consumed at once by [12] to keep $[\text{OH}^\cdot] \approx 0$, preventing [16] to take place. Therefore [17] is effective in which $\text{HO}_2^\cdot$ is the carrier species.²¹⁾ This conclusion is also supported by the pulse-light experiments discussed below.

In [17], H^+ is consumed with increasing rate, bringing the system in SSL (the acidic steady state) to the neutral side autocatalytically. On the other hand, there is no efficient process to produce H^+ to bring the system back to the acidic state, except for the external supply of H^+ .¹⁹⁾ Hence the system stays in SSH (the neutral steady state) for lower k_0 values. A higher external supply of H^+ (*i.e.*, a higher k_0) is required to keep the system in SSL or in OSC (the oscillatory state).

Damped oscillations have been observed and analyzed for the H_2O_2 - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ system in a semi-batch reactor.²²⁾ The subsystem, H_2O_2 - SO_3^{2-} - H^+ , has also been examined in detail to determine the related rate constants and their temperature dependences.²³⁾

In the case of the BrO_3^- - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ - H^+ sys-

tem, we have proposed a new reaction scheme,²⁴⁾ [18] - [20], against the one previously known,²⁵⁾

As equilibrium [18] is strongly biased to the right, $[\text{H}^+] \approx 0$ as far as $[\text{SO}_3^{2-}] > 0$. [19] is a relatively slow reaction and H^+ produced in [19] is immediately consumed by SO_3^{2-} through [18]. Hence the system is neutral and [20] never proceeds. Once $[\text{SO}_3^{2-}]$ comes to 0, $[\text{H}^+]$ takes a finite value and [20] starts, producing H^+ autocatalytically. The system bifurcates into SSL at a stroke. H^+ thus produced is consumed through the process in which $\text{Fe}(\text{CN})_6^{4-}$ is oxidized. Fig. 2 illustrates a bifurcation diagram for this system as a function of k_0 .²⁶⁾ It is to be noted that a hysteresis region exists at the higher k_0 end of the oscillatory region. In addition, a rigorous theoretical treatment was found to be possible for the subsystem without $\text{Fe}(\text{CN})_6^{4-}$ and a detailed analysis has been given.²⁷⁾

An interesting result of temperature compensation has been observed for the H_2O_2 - $\text{S}_2\text{O}_3^{2-}$ - SO_3^{2-} - H^+ system,^{28),29)} where, in proper ranges of k_0 and of the initial concentrations, the oscillation period has been found to be 4.45 and 4.41 min. for 25.5 and 33.5 °C, respectively. The oscillation is composed of a set of sharp spikes from the neutral to the low pH region. If the temperature is raised, the time consumed by the low-pH spike decreases, while the time spent in the neutral region increases. The two opposite changes compensate with each other to keep the overall period constant. This type of temperature compensation might be important in relation to the biological problems, such as the biological clock.

Additional pH-oscillators studied include the BrO_3^- - SCN^- system,³⁰⁾ the IO_3^- - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ system,³¹⁾ the BrO_3^- - SO_3^{2-} - marble system,³²⁾ the H_2O_2 - HSO_3^- - HCO_3^- system,³³⁾ the BrO_3^- - SO_3^{2-} - Mn^{2+} (or - MnO_4^-) system³⁴⁾ and the BrO_3^- - SO_3^{2-} - HCO_3^- system.³⁵⁾

Photoresponse of nonlinear chemical reaction systems. Some of the nonlinear chemical reaction systems are sensitive to light. Study of the photo-irradiation on the nonlinear chemical systems is important for the following reasons: we can vary the light intensity (P_0) continuously, which means that we can add P_0 as a new controlling parameter to the previously known ones such as the initial concentrations of materials and k_0 . In other words, we can increase the number of freedom of

Fig. 3. Action Spectrum for the photo-inhibition of oscillations in the BZ system determined at 25.0 ± 0.3 °C. (a) Absorption spectrum of 0.125 mM $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in aqueous solution with 1.5 M H_2SO_4 . (b) Relative crosssection of photo-inhibition of oscillations in a CSTR with $k_0 = 6.2 \times 10^{-4} \text{ sec}^{-1}$; $[\text{BrO}_3^-]_0 = 0.025 \text{ M}$, $[\text{MA}]_0 = 0.0025 \text{ M}$, $[\text{Ru}(\text{bpy})_3]_0 = 0.25 \text{ mM}$, $[\text{H}_2\text{SO}_4]_0 = 1.5 \text{ M}$.

the experiment by employing the photo-irradiation technique. In addition, in the case of photo-irradiation, it is easy to apply a pulsed light with any pulse width you like. As will be discussed later, we can determine the characteristic pulse-response of the system, which is helpful in determining the reaction mechanism. We can also vary the wavelength of light, which gives a powerful tool to clarify the initial stage of the photochemical reaction to control the nonlinearity. Moreover, it would be possible in some systems to give completely different kind of perturbation to the system only by changing the light wavelength.

Determination of action spectrum for nonlinear systems.¹⁶⁾ It is possible to induce or inhibit chemical oscillations by applying light to nonlinear chemical reaction systems. When a system stays in a stationary state, one can determine a critical value for the incident light power, $P_0^c(\nu)$, for induction of chemical oscillations by applying monochromatic light with frequency ν with increasing intensity. Similarly, one can determine $P_0^c(\nu)$ for the inhibition of oscillations by applying light with increasing intensity to the system in OSC. If $P_0^c(\nu)$ is determined experimentally, the relative cross section, σ_R , for the photo-induction (or photo-inhibition) of chemical oscillations can be obtained as

Fig. 4. Action spectra for the BR system in a CSTR determined at $25.0 \pm 0.1^\circ \text{C}$. (a) $[I]_0 = 0.018 \text{ mM}$ and (b) $[I]_0 = 0.054 \text{ mM}$. σ_R^i , σ_R^{i+} , σ_R^{i-} and σ_R^{ii} are the relative crosssections corresponding to the bifurcation curves γ_{0+} , γ_{0-} , γ_i and γ_{ii} , respectively, shown in the state diagram (Fig. 9).

$$\sigma_R \equiv \{h\nu D / P_0^c(\nu)\} \{1 - \exp(-2.303D)\}^{-1} \quad [21]$$

as a function of the light wavelength $\lambda (\equiv 1/\nu)$. In [21], $h\nu$ and D are the photon energy and the optical density of the solution in the stationary state at the bifurcation point, respectively. If one plots σ_R against λ , one obtains an action spectrum for the photo-induction (or, photo-inhibition) of oscillations. A difficulty may arise in determining D for each bifurcation point under photo-irradiation. For a low P_0 , it is possible to determine D directly by measuring the absorption spectrum in a crossed beam configuration. However, for higher P_0 , this becomes difficult because of the scattered light from the irradiation light source. A way to avoid the difficulty is to design the experiment so that $D < 1$ by employing lower concentrations of substances and a smaller optical path length (see Fig. 1). In this case, [21] can be approximated to

$$\sigma_R \approx h\nu / 2.303 P_0^c(\nu) \quad [21']$$

which is independent of D .¹⁴⁾

Curve b in Fig. 3 illustrates the action spectrum for the photo-inhibition of chemical oscillations in the BZ system with $\text{Ru}(\text{bpy})_3^{2+}$ as a catalyst.¹⁶⁾ It is clear that the action spectrum is coincident qualitatively with the absorption spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ shown by curve a. This result suggests that the origin of the photo-inhi-

Fig. 5. Photo-bifurcation diagram for the $\text{H}_2\text{O}_2 - \text{Fe}(\text{CN})_6^{4-}$ system in a CSTR. P_0 is the power of irradiated light at 420 nm. $[\text{Fe}(\text{CN})_6^{4-}]_0 = 3.30 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 50.0 \text{ mM}$, $k_0 = 2.46 \times 10^{-4} \text{ s}^{-1}$. Temperature = $25.0 \pm 0.1^\circ \text{C}$.

tion of chemical oscillations in this system is the photo-oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Ru}(\text{bpy})_3^{3+}$.

Another example³⁶⁾ is shown in Fig. 4, which shows action spectra for the BR system corresponding to

Fig. 6. State diagram for the $\text{Ru}(\text{bpy})_3^{2+}$ -catalyzed BZ system in a CSTR. Visible light ($\lambda > 390 \text{ nm}$) was irradiated. OSC: oscillatory, SSI and SSI': reduced stationary. $[\text{MA}]_0 = 72 \text{ mM}$, $[\text{Ru}(\text{bpy})_3^{2+}]_0 = 0.20 \text{ mM}$, $[\text{H}_2\text{SO}_4]_0 = 0.80 \text{ M}$, $k_0 = 1.88 \times 10^{-3} \text{ s}^{-1}$. Temperature = $25.0 \pm 0.3^\circ \text{C}$.

various bifurcations given in Fig. 9 shown later. All the action spectrum coincides qualitatively with the absorption spectrum of I_2 near 450 nm , suggesting that any photo-induced bifurcation in the BR system is initiated by the photoexcitation of I_2 .

A similar experiment has been performed for the $\text{H}_2\text{O}_2 - \text{Fe}(\text{CN})_6^{4-}$ system, one of the pH oscillators.^{37,21,38} Fig. 5 shows a bifurcation diagram with P_0 as a control parameter.³⁸ In dark ($P_0 = 0$), the system stays in SSL. The solution pH increases with P_0 up to P_0^{C1} , where oscillations start. The oscillation amplitude decreases as P_0 increases further up to P_0^{C2} , where oscillations stop and the system stays in SSH for higher P_0 . If P_0 is decreased, the system in SSH starts oscillations at P_0^{C2} , while the oscillation stops at $P_0^{C3} < P_0^{C1}$. The bifurcation between SSH and OSC is the supercritical Hopf bifurcation, while the bifurcation between SSL and OSC is the subcritical Hopf bifurcation which shows up a hysteresis.³⁹ The action spectrum for this system in the visible region suggests that both of the photo-induction and photo-inhibition of oscillations are caused by the photoexcitation of $\text{Fe}(\text{CN})_6^{3-}$. On the other hand, for the photo-irradiation in the near ultraviolet region, both of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ are found to be responsible for the photo-induced bifurcations.

Action spectra show that light absorption by $\text{Fe}(\text{CN})_6^{3-}$ is responsible for the photo-induction of oscillations in the $\text{H}_2\text{O}_2 - \text{Fe}(\text{CN})_6^{4-} - \text{SO}_3^{2-}$ system,²⁰ while light absorption by $\text{Fe}(\text{CN})_6^{4-}$ or $\text{HFe}(\text{CN})_6^{3-}$ is

Fig. 7. State diagram for the BZ + Br^- system in a CSTR at 25.0°C . Visible light ($\lambda > 390 \text{ nm}$) was used for the irradiation. Open circle: OSC, closed square: SSI, open triangle: irregular oscillatory. $[\text{MA}]_0 = 7.5 \text{ mM}$, $[\text{Ru}(\text{bpy})_3^{2+}]_0 = 0.10 \text{ mM}$, $[\text{H}_2\text{SO}_4]_0 = 0.80 \text{ M}$, $[\text{BrO}_3^-]_0 = 50 \text{ mM}$, $k_0 = 3.3 \times 10^{-3} \text{ s}^{-1}$.

responsible for the photo-bifurcation in the $\text{BrO}_3^- - \text{Fe}(\text{CN})_6^{4-} - \text{SO}_3^{2-}$ system.²⁶⁾

Response of nonlinear systems to the stationary light. *Photoresponse of the Belousov-Zhabotinsky and related systems.* Fig. 6 shows a state diagram for the BZ system under photo-irradiation.⁴⁰⁾ At a higher value of $[\text{BrO}_3^-]_0$, the system is in OSC in dark. Increasing P_0 inhibits oscillations at some critical intensity, leading the system to SSI. For lower $[\text{BrO}_3^-]_0$, the system is in another reduced stationary state (SSI') in dark. Increase of P_0 here brings the system to OSC and then to SSI.

Fig. 6 would suggest that, as P_0 is increased from SSI', photo-excited catalyst, $\text{Ru}(\text{bpy})_3^{2+*}$, reacts as

to produce HBrO_2 , which, in turn, consumes Br^- by [3], accelerating autocatalytic process [4] to start.

Further increase of P_0 inhibits oscillations to bring the system into another reduced stationary state, SSI. The action spectrum shown in Fig. 3 corresponds to this bifurcation, and suggests that the photo-excitation of $\text{Ru}(\text{bpy})_3^{2+}$ is responsible for the bifurcation as

Fig. 8. State diagram for MBO in a CSTR determined at 25.0 °C. Open circle: OSC, open triangle: irregular oscillatory, closed square: SSI, and closed circle: SSII. Visible light ($\lambda > 390$ nm) was used for irradiation. $[\text{Ru}(\text{bpy})_3]_0 = 0.10$ mM, $[\text{H}_2\text{SO}_4]_0 = 0.80$ M, $[\text{BrO}_3^-]_0 = 25$ mM, $[\text{Br}^-]_0 = 0.25$ mM.

where HBrO_2 is consumed and Br^- is produced by photo-irradiation. Br^- consumes HBrO_2 in turn through [3] to make $[\text{HBrO}_2] = 0$ quickly. Then [4] is suppressed and the system turns back to the reduced state.^{40),41)}

Fig. 7 shows a state diagram spanned by P_0 and $[\text{Br}^-]_0$ for the BZ + Br^- system in which Br^- is externally supplied in addition to the ordinary materials for the BZ system.⁴²⁾ This system is often employed in the experiment of spatial pattern formation. Although overall tendency can be understood as the dominance of SSI with increasing $[\text{Br}^-]_0$, a characteristic feature, irregular oscillations, is observed in a relatively small region.

Photo-control of MBO has also been studied.^{43),44)} Fig. 8 shows the state diagram spanned by P_0 and k_0 . At $k_0 = (1.0 - 1.2) \times 10^3 \text{ s}^{-1}$, the system bifurcates from SSI to SSII through OSC as P_0 increases. In contrast to the BZ system, MBO is solely to be oxidized as P_0 increases.

The other BZ type systems for which the photo-irradiation effects have been examined include the photo-inhibition of oscillations in the BZ system without catalyst,⁴⁵⁾ the photoresponse of the BZ system without malonic acid⁴⁶⁾ and of the $\text{BrO}_3^- - \text{SO}_3^{2-} - \text{Ru}(\text{bpy})_3^{2+}$ system.⁴⁷⁾

The BZ reaction in the water-in-oil reverse microemulsions in octane with aerosol OT as a surfactant has been examined.⁴⁸⁾⁻⁵⁰⁾ In addition to the pH-dependence of oscillations and the bistability found in this system in dark, the effect of light irradiation has also been examined⁵⁰⁾ to show some new observations such as oscillations with truncated peaks and appearance of a sharp recoil peak at the top of the normal oscillation peak. Moreover, the photo-irradiation was found always

Fig. 9. State diagram for the BR system in a CSTR at 25.0 ± 0.1 °C irradiated with 460 nm light. $[\text{IO}_3^-]_0 = 17$ mM, $[\text{Mn}^{2+}]_0 = 2.3$ mM, $[\text{H}^+]_0 = 25$ mM, $[\text{H}_2\text{O}_2]_0 = 200$ mM, $[\text{MA}]_0 = 2.0$ mM, $k_0 = 4.69 \times 10^{-3} \text{ s}^{-1}$.

to reduce the system. Detailed analyses have explored that aerosol OT used as a surfactant works as a reductant in addition to MA, bringing the system to the reduced side. Several interesting results observed in this system should closely be related to the size of microemulsions containing the reacting solution and to their mutual interaction to form clusters. A more detailed study is required on their mechanistic aspects, since this type of nonlinear system should have a close relation to the living systems.

Photoresponse of the Briggs-Rauscher and related systems. The effect of photo-irradiation on the BR system is considered to be due to the photo-excitation of I_2 as mentioned above and processes [24] and [25] should be responsible in addition to dark reactions [5] - [7].³⁶⁾

Fig. 9 shows a state diagram spanned by P_0 and $[\text{I}^-]_0$. The diagram is interesting in two points; one is the existence of the tristable region (SSI + SSII + OS), and the other is the existence of the bistable region composed of two

Fig. 10. State diagram for the $\text{H}_2\text{O}_2 - \text{Fe}(\text{CN})_6^{4-}$ system in a CSTR at $25.0 \pm 0.1^\circ\text{C}$. Irradiation with visible light at 420 ± 6 nm. $[\text{Fe}(\text{CN})_6^{4-}]_0 = 3.3$ mM, $[\text{H}_2\text{O}_2]_0 = 50$ mM, $[\text{H}^+]_0 = 1.8$ mM.

oscillations (OS and OS') with different oscillation periods. These multistabilities are not observed in dark.

The effect of adding starch to the photochemical reaction in the BR system has also been examined.⁵¹⁾ Under the CSTR condition, in addition to the normal materials in the BR reaction, starch is flowed into the cell with concentrations of $[\text{starch}]_0 = 0 \sim 25$ mgL^{-1} . The critical power, P_0^C , for the photo-inhibition of oscillations was found to increase nearly proportionally to $[\text{starch}]_0$. This is presumably due to the trapping of I_2 by starch, preventing I_2 from photodissociation.

Photoresponse of the pH oscillators. As mentioned above,³⁸⁾ the initial process of photoresponse of the $\text{H}_2\text{O}_2 - \text{Fe}(\text{CN})_6^{4-} - \text{H}^+$ system is the photo-absorption by $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$. In Fig. 10, a state diagram spanned by P_0 and k_0 is shown for the irradiation at 420 nm. The bifurcation between SSL and OSC is the subcritical Hopf bifurcation with a hysteresis. The supercritical Hopf bifurcation is observed between OSC and SSH.

This system has no process for the autocatalytic production of H^+ . Instead, it is supplied only externally. The nonlinearity is introduced in [17] for the consumption of H^+ . Therefore, in dark, the system stays in SSL for a higher k_0 , since there is a sufficient supply of H^+ , while

Fig. 11. State diagram for the $\text{Fe}(\text{CN})_6^{4-} - \text{BrO}_3^- - \text{SO}_3^{2-}$ system in a CSTR at $35.0 \pm 0.5^\circ\text{C}$. Visible light ($\lambda > 400$ nm, $P_0^{\text{max}} = 1.3$ W) was used for irradiation. Closed circle: SSL, open circle: OSC, and closed rhombus: SSH. Open rhombus represents the bistable (hysteresis) region between SSH and OSC. $[\text{Fe}(\text{CN})_6^{4-}]_0 = 15$ mM, $[\text{BrO}_3^-]_0 = 75$ mM, $[\text{SO}_3^{2-}]_0 = 90$ mM, $[\text{H}^+]_0 = 15$ mM.

it turns to SSH through OSC for decreasing k_0 .

If one irradiates the system in SSL in dark and increase P_0 , the system bifurcates into SSH through OSC. Photo-irradiation in the visible region excites $\text{Fe}(\text{CN})_6^{3-}$, which should accelerate the following steps;

Additional $\text{Fe}(\text{CN})_5(\text{H}_2\text{O})^{3-}$ produced by light accelerates the autocatalytic process [17], consuming H^+ nonlinearly. Hence a higher k_0 (higher external supply of H^+) is required to keep the system in SSL under photo-irradiation. A similar discussion holds for the other bifurcation curves. This should account for the positive slopes of bifurcation curves in Fig. 10.

In the case of irradiation in the near UV region, $\text{Fe}(\text{CN})_6^{4-}$ is photo-excited in addition to $\text{Fe}(\text{CN})_6^{3-}$, both being effective to accelerate [17]. However, examination of the action spectrum³⁸⁾ shows that the excitation of $\text{Fe}(\text{CN})_6^{4-}$ is more effective. The lower efficiency for $\text{Fe}(\text{CN})_6^{3-}$ may be due to the additional step [26] incorporated to produce $\text{Fe}(\text{CN})_5(\text{H}_2\text{O})^{3-}$.

Fig. 11 illustrates a state diagram for the $\text{BrO}_3^- - \text{SO}_3^{2-} - \text{Fe}(\text{CN})_6^{4-} - \text{H}^+$ system.²⁶⁾ A characteristic feature with this diagram is the nature of bifurcations; the slopes of the bifurcation curves are negative, in contrast to Fig. 10

Fig. 12. Response of the BZ + Br⁻ system in a CSTR to a light pulse at 25.0 ± 0.3 °C. A 1 sec.-width pulse is applied at the point indicated by an arrow. Visible light pulse ($\lambda > 390$ nm) is used, the intensity of which is indicated in the figure. [Ru(bpy)₃]²⁺₀ = 0.10 mM, [BrO₃]₀ = 50 mM, [MA]₀ = 7.5 mM, [H₂SO₄]₀ = 0.80 M, [Br]₀ = 50 μM, $k_0 = 3.3 \times 10^{-3}$ s⁻¹. (A) Response of the system in SSI in dark. (B) Response of the system in SSI under the steady photo-irradiation with $P_0 = 0.91$ W.

Fig. 13. Response of the Fe(CN)₆⁴⁻ - H₂O₂ - SO₃²⁻ system in SSL to a light pulse in the visible region ($\lambda > 390$ nm). The arrows indicate the time of pulse application. CSTR with $k_0 = 2.50 \times 10^{-3}$ s⁻¹. Temperature = 30.0 ± 0.5 °C. Panel (A): Pulse duration = 1.0 sec., pulse intensity = 0.13 W (a), 0.26 W (b), 0.65 W (c), and 1.30 W (d). Panel (B): Pulse intensity = 1.30 W, pulse duration = 0.125 sec. (a), 0.25 sec. (b), 0.50 sec. (c), and 1.00 sec. (d).

for the H₂O₂ - Fe(CN)₆⁴⁻ - H⁺ system. As discussed above, the autocatalytic production of H⁺ in dark in the BrO₃⁻ - SO₃²⁻ - Fe(CN)₆⁴⁻ - H⁺ system is described by eqs. [18] - [20]. These processes imply that a higher k_0 supplies sufficient SO₃²⁻ to consume H⁺ produced in [19] to keep the system in SSH or OSC, while for lower k_0 , insufficient external supply of SO₃²⁻ allows the existence of free H⁺, initiating the autocatalytic production of H⁺ in [20], and the system turns into SSL.

It is to be noted that no species sensitive to the visible or near UV light is involved in [18] - [20]. Therefore, the nonlinear production of H⁺ under photo-irradiation should occur essentially in the same way as the dark reaction. On the other hand, the consumption of H⁺ occurs by²⁶⁾

Since Fe(CN)₅(H₂O)³⁻ produced in [28] has an absorption band in the 400 nm region similar to ferricyanide,²⁶⁾ the visible light ($\lambda > 400$ nm) excites it to enhance the consumption of H⁺ in [29]. Therefore, if the system in SSL in dark is irradiated, a lower k_0 (lower supply of SO₃²⁻) is required to keep the system in SSL. This should result in the negative slope for the SSL - OSC bifurcation seen in Fig. 11. Similarly, the bifurcations between OSC and SSH have negative slopes.

Additional pH-oscillators for which the photo-irradiation effect has been studied include the ClO₂⁻ - Cl⁻ - iodomalonic acid system^{52),53)} and the H₂O₂ - SO₃²⁻ - Fe(CN)₆⁴⁻ system in the presence of bromocresol purple.⁵⁴⁾

Response to the pulse light. Let us consider a pulse-light perturbation applied to a nonlinear system. If the system responds only to a perturbation above some threshold, the system is called to be excitable.⁵⁵⁾ An example is shown in Fig. 12 for the BZ system added with Br⁻ ([Br]₀ = 50 μM).⁵⁶⁾ Panel (A) shows the result of

a light pulse applied to the dark system, while (B) shows the effect of an additional pulse applied to the system under the stationary irradiation with $P_0 = 0.91$ W. The figure shows that the response to a light pulse has a threshold, and that, for the perturbation above the threshold, a single pulse response is observed with constant intensity. The threshold decreases with $[\text{BrO}_3^-]_0$ and increases with $[\text{Br}^-]_0$. These facts can be understood as due to the pulse light absorption by $\text{Ru}(\text{bpy})_3^{2+}$ to induce autocatalytic process [4], bringing the system temporarily to the oxidized state.

Response to the pulse irradiation has also been studied for MBO.^{44,57)} Pulse light applied to the system in SSI shows an excitability similar to the BZ system. On the other hand, no excitable response has been observed by applying a light pulse to the system in SSII in dark, or by applying a negative pulse to the system in SSII under stationary photo-irradiation.

Pulse response has also been examined in the H_2O_2 - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ system.²⁰⁾ An interesting observation with this system is that, in addition to the excitable pulse response, a broad pulse response without threshold is observed, the intensity of which is proportional to P_0 (Fig. 13).

Among the main reaction steps, [9] - [15], given above, those containing $\text{OH}^\cdot$ are [11] - [14]. The rate equation for $[\text{OH}^\cdot]$ is

$$d[\text{OH}^\cdot]/dt = \alpha + \beta[\text{OH}^\cdot] \quad [30]$$

where

$$\alpha \equiv k_{11}[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^3][\text{H}_2\text{O}_2] \quad [31]$$

$$\beta \equiv 2k_{12}[\text{H}_2\text{O}_2] - k_{14}[\text{Fe}(\text{CN})_6^{4-}] \quad [32]$$

The first term in β arises from the autocatalytic process [12] + [13], under the assumption that [12] is rate-determining. Since β has no term sensitive to the visible light, this mechanism cannot account for the observed excitability.

On the other hand, the reactions containing $[\text{HO}_2^\cdot]$ are [11], [12], [13] and [15]. The rate equation for $[\text{HO}_2^\cdot]$ is

$$d[\text{HO}_2^\cdot]/dt = \alpha' + \beta'[\text{HO}_2^\cdot] \quad [33]$$

where

$$\alpha' \equiv k_{11}[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^3][\text{H}_2\text{O}_2] \quad [34]$$

$$\beta' \equiv 2k_{13}[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^3][\text{H}^+] - k_{15}[\text{Fe}(\text{CN})_6^{4-}] \quad [35]$$

Fig. 14. Phase shift due to the single light pulse perturbation on the oscillatory MBO system in a CSTR at 25.0 ± 0.3 °C. Closed circles: experimental results, Open circles: shifts calculated⁴⁴⁾ for $\Delta[\text{HBrO}_2] = 2.0$ μM and $k_0 = 1.63 \times 10^{-3}$ s^{-1} . The visible light pulse ($\lambda > 390$ nm) was applied with intensity of 1.3 W and duration of 1 sec. The other conditions are: $[\text{Ru}(\text{bpy})_3^{2+}]_0 = 0.10$ mM, $[\text{BrO}_3^-]_0 = 25$ mM, $[\text{H}_2\text{SO}_4]_0 = 0.80$ M, $[\text{Br}^-]_0 = 0.25$ mM, $k_0 = 0.78 \times 10^{-3}$ s^{-1} .

In contrast to the $\text{OH}^\cdot$ case, [12] is assumed to be faster than [11] or [13]. α' arises from [11] + [12], where [11] is rate-determining. The first term in β' arises from autocatalytic process, $[12] \times 2 + [13]$, where [13] is rate-determining. In this case, photo-excitation of $\text{Fe}(\text{CN})_6^{4-}$ in the visible region increases $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^3]$ through [10] and the electron exchange reaction,

For $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^3] > [\text{Fe}(\text{CN})_5\text{H}_2\text{O}^3]_{\text{th}} \equiv (k_{15}[\text{Fe}(\text{CN})_6^{4-}]/k_{13}[\text{H}^+])$, β' becomes positive to start the autocatalytic reaction, giving an excitable response to the light pulse.

If the light pulse is not intense enough, β' remains negative so that autocatalysis does not start. However α' is proportional to $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^3]$ which increases in proportion to P_0 , giving rise to the thresholdless broad pulse response.²⁰⁾ This scheme is also consistent with the action spectrum which is coincident with the absorption spectrum of $\text{Fe}(\text{CN})_6^{3-}$.²⁰⁾

Oscillation phase shift due to the pulse light irradiation. A pulse light irradiation on the oscillating system causes a shift of oscillation phase. Magnitude of the shift depends on the position of pulse application in a single phase of oscillation. Repeated pulses cause the entrainment⁵⁾ of oscillation period into the external pulse period. Fig. 14 shows the phase shift observed for

Fig. 15. Photo-induced chaotic oscillations in the BR system in a CSTR at $20.00 \pm 0.05^\circ\text{C}$. Experimental conditions are; $[\text{KIO}_3]_0 = 20\text{ mM}$, $[\text{MnSO}_4]_0 = 2.5\text{ mM}$, $[\text{HClO}_4]_0 = 40\text{ mM}$, $[\text{MA}]_0 = 2.2\text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 160\text{ mM}$, $k_0 = 5.6 \times 10^{-5}\text{ s}^{-1}$. Monochromatic light at $460 \pm 5.4\text{ nm}$ from a Hg lamp is applied through a monochromator. $P_0(\mu\text{W}) = 139$ (a), 251 (b), 260 (c), 270 (d), 325 (e).

a single pulse application on the oscillating MBO.^{15),44)} Here ϕ is the phase of applied light pulse measured from the oscillation peak and $\Delta\phi$ is the resultant phase advance. The figure shows that the phase delays slightly for $\phi/2\pi = 0.3 - 0.4$, while it advances to $\Delta\phi = 0.4$ immediately at $\phi/2\pi \approx 0.4$, and comes back to $\Delta\phi = 0$ at $\phi/2\pi = 0.8$.

Phase-shift experiments for the BZ system⁵⁶⁾ gives essentially the same result as those for MBO. In the case of the BZ + Br^- system, only the delay of oscillation phase is observed; namely, $\Delta\phi$ is negative and its magnitude increases with increasing ϕ .^{14),58)} Presumably, a reaction such as [23] plays an important role in this case.

Multistability and chaos - possibility of their photocontrol. *Multistability and chaos in dark.* The hysteresis region shown in Fig. 2 for the $\text{BrO}_3^- - \text{SO}_3^{2-} - \text{Fe}(\text{CN})_6^{4-}$ system is an example of the bistability

Fig. 16. Next-amplitude return map for the BR system, corresponding to chaotic oscillations (c) in Fig. 15.

Fig. 17. Photo-induced chaos attractor for the BR system, corresponding to chaotic oscillations (c) in Fig. 15.

between the oscillatory and stationary states. This type of bistability has often been found in nonlinear chemical systems. A tristability among SSL, SSH and OSC has been found for the $\text{BrO}_3^- - \text{SO}_3^{2-} - \text{HCO}_3^-$ system in addition to several bistability regions.³⁵⁾ Double-frequency oscillations have been found in the BZ-type system with acetylphenols as substrates.¹⁸⁾

Fig. 18. Photo-induced period-doubling cascades to chaos measured for the H_2O_2 - HSO_3^- - HCO_3^- - $\text{Fe}(\text{CN})_6^{4-}$ system in a CSTR at $5.0 \pm 0.1^\circ\text{C}$. $[\text{H}_2\text{O}_2]_0 = 0.011$, $[\text{SO}_3^{2-}]_0 = 6.0 \times 10^{-3}$, $[\text{H}^+]_0 = 5.0 \times 10^{-4}$, $[\text{HCO}_3^-]_0 = 5.0 \times 10^{-4}$, and $[\text{Fe}(\text{CN})_6^{4-}]_0 = 1.0 \times 10^{-3}$ M. $k_0 = 2.07 \times 10^{-4} \text{ s}^{-1}$. Visible light ($> 390 \text{ nm}$) from a halogen-tungsten lamp was applied. Light power from the bottom: (Left) 0.0, 0.70, 1.15, 1.55 mW, (Right) 1.70, 2.05, 3.10, 5.15 mW.

The chaotic behavior is known for the BZ system in dark.^{59),60)} We have observed chaotic oscillations also in the pH oscillators under the dark condition.^{61),62),29)} Among them, the H_2O_2 - SO_3^{2-} - marble system⁵⁸⁾ shows the bursting oscillations and the period-doubling cascade of oscillations leading to chaos. In this system, the reactions, in which CaCO_3 from marble decomposes in the acidic media to release CO_2 , plays a role of the proton-consuming process in place of ferrocyanide. Chaotic oscillations have also been observed for the H_2O_2 - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ - HCO_3^- system.⁶²⁾ In this case, two H^+ -consuming processes (the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ and the CO_2 release from HCO_3^-) with different time constants would compete with each other, contributing to induce a chaotic behavior. Another example is the H_2O_2 - $\text{S}_2\text{O}_3^{2-}$ - SO_3^{2-} - H^+ system,²⁹⁾ where no catalyst such as ferrocyanide is incorporated. This system also shows a period-

doubling route to chaos.

Photocontrol of multistability and chaos. We have thus added several new findings of chaos and multistability to those previously known. Now, with an expectation of finding more rich information on chaos and multistabilities, we have conducted a series of research works by employing the photo-irradiation technique.

As discussed above for Fig. 9, the photo-irradiated BR system shows a tristability region among SSI, SSII and OS, and the bistability regions between OS and OS', between SSI and OS, and between SSI and SSII. These multistability regions were found for the first time in this system under the photo-irradiation. Photo-induced chaos has also been found in the BR system by applying light to the system in the OS - OS' bistable region. Fig. 15 shows oscillation patterns for various P_0 values.⁶³⁾

Chaotic oscillations are observed in (c) and (d). Fig. 16 shows a next-amplitude return map⁶³⁾ for (c) in Fig. 15. The pattern with a single-humped maximum appearing in this figure suggests that the observed chaos is deterministic.^{59),60)} Fig. 17 shows a three-dimensional chaos attractor for (c) in Fig. 15, where the representative point stays within a restricted region in the phase space but never comes through the same point.⁶³⁾

We have found the photo-induced chaos for the first time in the pH oscillator system, H_2O_2 - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ - HCO_3^- .⁶⁴⁾ This system shows chaotic behavior also in dark. However, as illustrated in Fig. 18, if the stationary light is applied to the system with k_0 at which regular oscillations are observed in dark, the system realizes chaotic oscillations through a period-doubling bifurcation cascade with increasing P_0 . Further increase of P_0 leads the system to regular oscillations with a longer period than the initial one through the inverse cascade. The corresponding return map shows that the chaos is deterministic.⁶⁴⁾

Summary and future prospects. We have succeeded in getting a number of interesting results, including multistabilities and chaotic behaviors, for the dynamical aspects of nonlinear chemical systems both in dark and under photo-irradiation. In this report, these results are reviewed with a particular emphasis on their photo-response. Discussions have been made as far as possible on the mechanism of these phenomena based on the consideration of rate processes. Although the photo-response to the stationary irradiation has been studied for most of the representative chemical oscillators, a further accumulation of experimental data would be necessary for the response to the pulse light and for the phase shift problem.

The spatio-temporal pattern formation is another interesting subject of nonlinear chemistry. In this case, the temporal variation of concentrations and the spatial inhomogeneity accompanied by diffusion are coupled together to form a spatial pattern varying with time. We have done only a few trials in this subfield.^{65),66)} A more sophisticated experimental technique is required to treat the phenomena quantitatively, especially for the system under irradiation, where the transparency varies with time and space according to the moving pattern.

Coupling experiments, in which two independent flow reactors are coupled through a pipe with appropriate size, have been performed for the BZ reaction to give some interesting results on the modes of interaction between two independent oscillators.^{67),68)} Control of

the interaction mode by photo-irradiation would be a future subject of research. Purely theoretical studies have also been tried^{69),70)} to simulate the molecular-dynamical behavior in the reaction-diffusion system.

The present author hopes sincerely that a more unified treatment is established in near future both experimentally and theoretically so that we could grasp the whole phenomenon more deeply and accurately as well as we could design a novel nonlinear system, which is interesting and useful, whenever it is required.

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