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# Effect of Light on the Belousov−Zhabotinsky Reaction in Water-in-Oil Microemulsions of Aerosol OT in Octane

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The ferroin-catalyzed Belousov−Zhabotinsky (BZ) reaction was found to exhibit enhanced photosensitivity in the water-in-oil microemulsion of anionic surfactant aerosol OT (AOT). Some novel photoresponses were found in this system. In addition, it was found that illumination always resulted in the reduction of the catalyst in the micelle BZ system. On the basis of the results for the BZ subsystem without malonic acid, the reduction of photoexcited ferriin by AOT was found to be important, together with an additional photoreduction of catalyst with malonic acid in the case of the full BZ system in the AOT microemulsion.

## 1. Introduction

The effect of light on the dynamics of nonlinear chemical systems has been the subject of considerable attention of many scientists.[1−10] The use of light in controlling the system is advantageous over the other external parameters because of the feasibility of changing its intensity and wavelength. A change in the wavelength sometimes brings about a different nonlinear behavior. The light irradiation can sometimes create new nonlinear interactions and modify the system dynamics drastically from the dark behavior.[3,6,7] It is also feasible to study the system response to a pulsed perturbation by the use of light.

Recently we have studied in detail the behavior of the Belousov−Zhabotinsky (BZ) reaction in water nanodroplets of a reverse microemulsion of aerosol OT [AOT; bis(2-ethylhexyl)-sodium sulfosuccinate] in octane.[11−13] This system, hereafter referred to as the AOT-BZ system, shows some novel and interesting behaviors such as the dependence of its dynamics on the size and concentration of water nanodroplets,[11] the frequency-multiplying bifurcation,[12] and the occurrence of oscillations at extremely high pH values in the micellar aqueous pseudophase.[13] We have also shown that the BZ reaction catalyzed by the tris(1,10-phenanthroline)iron(II) ion (ferroin) assumes unexpectedly high photosensitivity in the reverse emulsion of Amicrome with water droplets.[14] This may be related to the elongation of the lifetime of photoexcited catalysts in the microheterogeneous media. Such an elongation of lifetime has also been reported for tris(α,α′-diimine)ruthenium(II).[15]

In this connection, it seems to be interesting to study the effect of light on the AOT-BZ reaction. Several photochemical pathways have been proposed to account for the effect of light on the BZ reaction in the homogeneous aqueous medium: for example, the catalyst in its reduced form is photoexcited to produce $HBrO_2$ or $Br^-$, which enhances or inhibits, respectively, the autocatalytic oxidation of the catalyst.[1,5,8,16−20] Schemes in which the catalyst in its oxidized form is photoexcited have also been proposed.[15,18,21] For the ultraviolet illumination, bromomalonic acid has been proposed to account for the photoinhibition of oscillations.[22] In this paper, we study the photoresponse of the ferroin-catalyzed AOT-BZ system and try to elucidate which process is responsible for the primary photochemical reaction in the reverse micelle system.

## 2. Experimental Section

**Materials.** The following analytical-grade chemicals were used without further purification: $NaBrO_3$, malonic acid [$CH_2(COOH)_2$; hereafter abbreviated to HMA] (Wako), $Fe_2SO_4 \cdot 7H_2O$, 1,10-phenanthroline, $H_2SO_4$ (Katayama), and bis(2-ethylhexyl)sodium sulfosuccinate (AOT) (Nakarai). *n*-Octane (Katayama) was purified by intensive stirring with concentrated sulfuric acid for 2 h. Ferroin was obtained by mixing the solutions of 1,10-phenanthroline and $Fe_2SO_4$ in a molar ratio of 3:1. Water was deionized and distilled twice. The preparation of AOT microemulsion loaded with the BZ solution has been described elsewhere.[12,13] The volume fraction of the aqueous pseudophase in AOT microemulsion is defined as $\phi_w = V_w/V_t$, where $V_w$ is the volume of the aqueous phase added to the volume $V_{oil}$ of the AOT solution in octane, and $V_t = V_w + V_{oil}$. The radius of the micellar water core, $R_w$, depends on the water/surfactant molar ratio $\omega = [H_2O]/[AOT]$ as $R_w = 0.175\omega$, where $R_w$ is expressed in units of nanometers. The AOT microemulsion loaded with the BZ subsystem solution ($NaBrO_3$, $H_2SO_4$, and ferroin; without HMA) was prepared as follows: the solution of $NaBrO_3$, $H_2SO_4$, and ferroin was prepared, which turned to a bluish color characteristic of ferriin [tris(1,10-phenanthroline)iron(III)]. A 0.2 mL sample of this solution was added to 20 mL of the 0.05 M AOT solution in octane. The resultant water-in-oil microemulsion is characterized by $\omega = 11$ and $\phi_w = 0.01$. During the formation of the microemulsion, a blue drop of the aqueous solution stained the microemulsion a reddish color. This is an evidence for the spontaneous reduction of ferriin during its penetration of reverse micelles. Then, ferroin, once produced in reverse micelles, was autocatalytically oxidized again by bromate to give a blue microemulsion.

**Methods.** The reaction was run in a thermostated ($t = 20 \pm 0.1$ °C) Teflon cylindrical reactor with a Teflon plug. It was equipped with four flat silica windows so that the illumination light beam and the monitoring beam cross each other at a right angle in the reactor. The optical path lengths of the reactor

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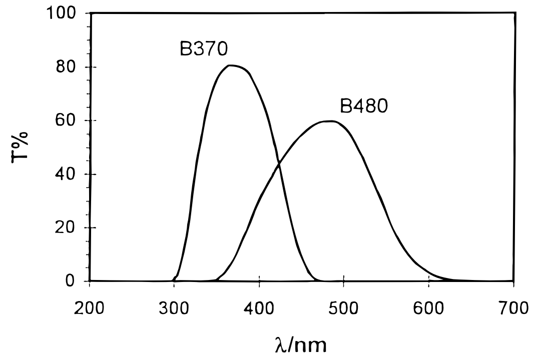

**Figure 1.** Transmission spectra of the broad-band filters B480 and B370 used for filtering white light during the illumination of the BZ reaction.

were 3 cm for the monitoring light beam and 2 cm for the illumination beam. Stirring at 500−700 rpm was performed throughout the experiments with a Teflon-coated magnetic stirrer bar, 12 mm long and 4 mm in diameter.

The reaction mixture in the reactor, whose volume was 20 mL, was illuminated by a 500 W Hg-lamp (USH-500D), after being passed through a water heat filter, a set of lenses, and a broad-band filter, B370 or B480, with the transparency maximum at 370 or 480 nm, respectively. The filter characteristics are shown in Figure 1. The light intensity was regulated by an additional diaphragm or by a set of neutral density (ND) filters. The power $P$ of the incident light was calculated by

$$P = S\int T(\lambda)\, I_0(\lambda)\, \mathrm{d}\lambda \qquad (1)$$

where $I_0(\lambda)$ is the light intensity of the lamp in units of W cm$^{-2}$ nm$^{-1}$, $T(\lambda)$ is the transmittance of filters, and $S$ is a cross section (cm$^2$) of the incident light beam. $P$ was found to be 6 W and 9.7 W for B480 and B370 filters, respectively, while $P = 28$ W for the illumination without a band pass filter.

The reaction was followed spectrophotometrically on a homemade setup[12] by recording the ferroin absorbance at 510 nm or the ferriin absorbance at 630 nm. An interference filter of corresponding wavelength was placed between the analysis light source and the reactor to minimize the undesired illumination effect. Although the optically transparent AOT microemulsion gave insignificant scattering of the photolysis light, another interference filter of the same optical characteristics is placed between the reactor and the photomultiplier to minimize the effect of scattered photolysis light.

## 3. Results and Discussion

As a standard set of initial concentrations of reagents in the aqueous pseudophase of microemulsions, we used the same one as employed in the earlier work;[12,13] namely, $[\mathrm{H_2SO_4}]_0 = 0.3$ M, $[\mathrm{HMA}]_0 = 0.25$ M, $[\mathrm{BrO_3^-}]_0 = 0.1$ M, and $[\text{ferroin}]_0 = 2.8$ or 2.24 mM. The reference BZ reaction (i.e., the BZ reaction running in the homogeneous aqueous solution) with the same initial concentrations was found not to be affected by the light irradiation (with B480 or B370 or without filter) either in a batch reactor or in a continuous-flow stirred tank reactor (CSTR).

At the standard initial concentrations of the reagents, the oscillatory AOT-BZ reaction may run in two different regimes in the dark, depending on $\omega$, $\phi_\mathrm{w}$, the reagent flow rate $F$, and the bubbling of the system with inert gas. At low $\phi_\mathrm{w}$ ($\phi_\mathrm{w} \leq 0.05$) or at a relatively high flow rate, the AOT-BZ system shows high-amplitude oscillations (close to the 100% conversion of ferroin to ferriin) and period $T = 10-12$ min. At extremely low $F$ ($0 \leq F < 0.02$ mL min$^{-1}$) and at higher $\phi_\mathrm{w}$ ($\phi_\mathrm{w} > 0.05$), without inert gas bubbling, the AOT-BZ system exhibits a spontaneous multiplication of oscillation frequency (by a factor of 2, 3, or 4) and a spontaneous sharp decrease in oscillation amplitude (frequency-multiplying bifurcation).[12] In the following, we shall examine the effect of illumination on the AOT-BZ reaction for both cases.

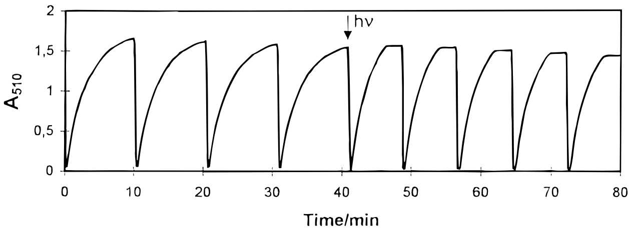

**Figure 2.** Kinetics of the BZ reaction in water nanodroplets of a water-in-oil microemulsion of AOT in octane followed by the ferroin absorbance at 510 nm. Conditions: $[\mathrm{H_2SO_4}]_0 = 0.3$ M, $[\mathrm{HMA}]_0 = 0.25$ M, $[\mathrm{NaBrO_3}]_0 = 0.1$ M, $[\text{ferroin}]_0 = 2.8$ mM, $\omega = 9.8$, $\phi_\mathrm{w} = 0.039$, and the rate of the reagents feeding $F = 0.066$ mL min$^{-1}$. The reaction starts in the dark. An arrow "$h\nu$" denotes the moment of switching on the light passed through the filter B480, $P = 6$ W.

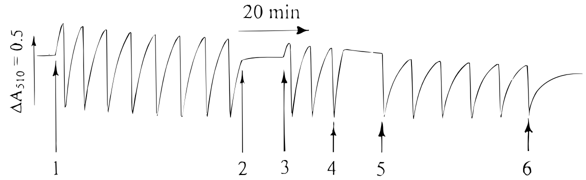

**Figure 3.** Effect of light on the AOT-BZ reaction. Conditions: $[\mathrm{HNO_3}]_0 = 0.8$ M, $[\mathrm{HMA}]_0 = 0.25$ M, $[\mathrm{NaBrO_3}]_0 = 0.1$ M, $[\text{ferroin}]_0 = 2.8$ mM, $\omega = 13.58$, $\phi_\mathrm{w} = 0.01$, and $F = 0$. $\mathrm{N_2}$ was continuously bubbled through the reactor. The arrows with numbers 1, 3, 4, and 5 denote the moments of switching on the light with the following characteristics: (1) B370 filter, $P = 4.8$ W; (3) B370 filter, $P = 4.8$ W; (4) B370, $P = 9.7$ W; and (5) B480, $P = 6$ W. Arrows with numbers 2 and 6 denote the moments of switching off the light.

Figure 2 shows the effect of blue light (with a B480 filter) on the AOT-BZ reaction in a CSTR with a relatively high flow rate ($F = 0.06$ mL min$^{-1}$). It is seen that the oscillation period $T$ decreases from 10.3 to 7.8 min, while the oscillation pattern shows unusual truncated peaks. Such a shape of oscillations should result from the fact that the oxidation of catalyst does not start immediately after its complete reduction. Oscillation amplitude, which is close to the 100% conversion of ferroin, does not change under the effect of light. Such a deep conversion of the catalyst in the course of oscillations leads to a beautiful succession of transparent-blue and deep-red colors of the microemulsion. Analogous oscillation patterns with truncated peaks were observed for various combinations of $\omega$ ($\omega = 18$ and 9.8) and $\phi_\mathrm{w}$ ($\phi_\mathrm{w} = 0.055$, 0.0214, and 0.009) in a CSTR. No illumination effect was detected if the illumination light intensity was decreased by a factor of 5 (B480 + ND20 filters). On the other hand, replacement of the filter B480 with B370 inhibited oscillations and brought the system to the completely reduced stationary state.

If we employ a higher initial concentration of acid, for instance, 0.6 M $\mathrm{H_2SO_4}$ or 0.8 M $\mathrm{HNO_3}$ instead of 0.3 M $\mathrm{H_2SO_4}$ of the standard set, the AOT-BZ system shows a few oscillations in the initial stage and turns to a stationary state characterized by an intermediate oxidation state of the catalyst in the dark (see Figure 3). Illumination of this system with light of relatively low intensity ($P = 4.8$ W, B370, or $P = 6$ W, B480) induces oscillations, while illumination at higher intensity ($P = 9.7$ W, B370) brings the system to the completely reduced stationary state, as in the previous case. Analogous behavior was observed for $\omega = 11$, 13.6, and 18, and for $\phi_\mathrm{w} = 0.01$.

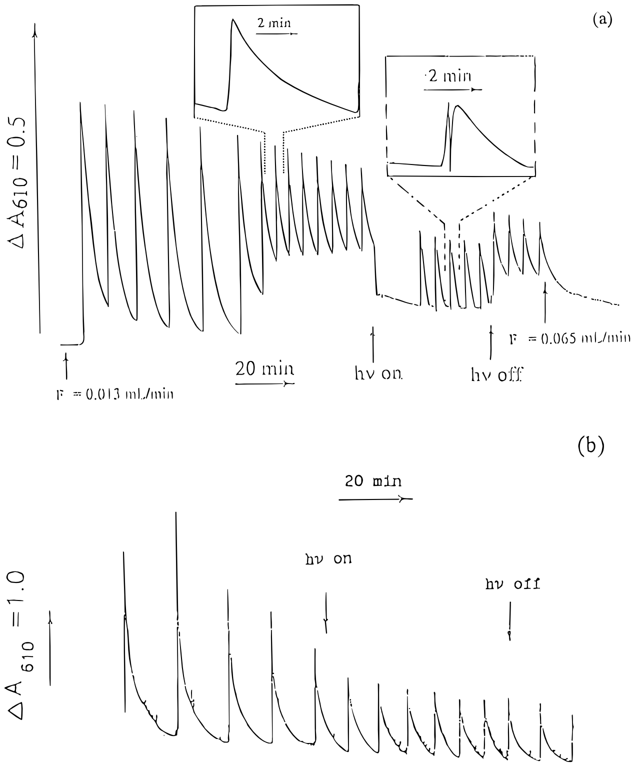

**Figure 4.** (a) Effect of light on the AOT-BZ reaction after the frequency-multiplying bifurcation. Conditions: $[H_2SO_4]_0 = 0.3$ M, $[HMA]_0 = 0.25$ M, $[NaBrO_3]_0 = 0.1$ M, $[ferroin]_0 = 2.24$ mM, $\omega = 18$, $\phi_w = 0.11$, and $F = 0.013$ mL $min^{-1}$. Arrows "*hν* on" and "*hν* off" denote the moments of switching on and switching off the white light with power $P = 28$ W. Enlarged views of a single peak are shown in the insets for each of the dark and illuminated oscillations. (b) Effect of illumination (B480, $P = 6$ W) on the homogeneous aqueous BZ system in a 20 mL batch solution. Conditions: $[H_2SO_4]_0 = 0.2$ M, $[HMA]_0 = 0.25$ M, $[NaBrO_3]_0 = 0.1$ M, $[ferroin]_0 = 2.24$ mM, and the stirring rate is 16 Hz.

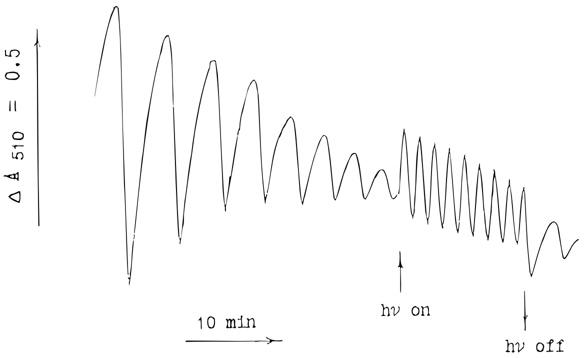

**Figure 5.** Effect of blue light (B480, $P = 6$ W) on the kinetics of the AOT-BZ reaction after the frequency-doubling bifurcation. Conditions: $[H_2SO_4]_0 = 0.3$ M, $[HMA]_0 = 0.25$ M, $[NaBrO_3]_0 = 0.1$ M, $[ferroin]_0 = 2.24$ mM, $\omega = 25$, $\phi_w = 0.05$, and $F = 0$.

These examples show that the illumination may lead to both initiation and cessation of oscillations and always brings the AOT-BZ system toward the reduced state.

Figures 4−6 show how the illumination affects the AOT-BZ reaction after the frequency-multiplying bifurcation in the dark. The first half of Figure 4a demonstrates the frequency-multiplying bifurcation in the dark (period *T* changes sharply from 12 to 4.8 min). Illumination of the system with white light ($P = 28$ W) after the bifurcation inhibits oscillations to bring the system to a reduced state. Under continued illumination, oscillations resume after a while (ca. 15 min) with the same period ($T \approx 5$ min) as before the illumination starts. The oscillation pattern, however, undergoes considerable change. First of all, the truncated peaks similar to the one shown in Figure 2 appear when the catalyst turns to a reduced state. Then, a sharp "recoil" peak emerges. The "recoil" peak is shown in one of the insets in Figure 4 in an expanded scale. As soon as the catalyst becomes completely oxidized, a sharp downward peak appears, showing that the system is reduced instantaneously and returns back to the oxidized state. All these take place within 20 s, after which a slow reduction of the catalyst occurs. When light is switched off, the oscillations regain their former dark pattern. A similar expanded waveform for the dark oscillations is given in the other inset of Figure 4a, which shows no indication of recoil peak. For the sake of comparison, Figure 4b shows a time evolution of the BZ system in the homogeneous aqueous solution. Illumination causes a change in the oscillation frequency, but there is no indication of truncated peaks or recoil peaks.

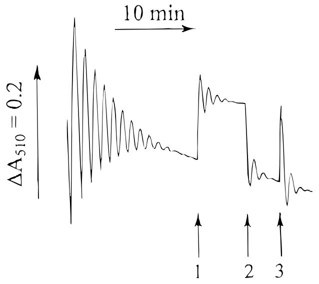

**Figure 6.** Effect of blue light (B480, $P = 6$ W) on the AOT-BZ reaction after the frequency-quadrupling bifurcation and after the cessation of oscillations. Conditions: $[H_2SO_4]_0 = 0.3$ M, $[HMA]_0 = 0.25$ M, $[NaBrO_3]_0 = 0.1$ M, $[ferroin]_0 = 2.24$ mM, $\omega = 18.9$, $\phi_w = 0.11$, and $F = 0$. Arrows 1, 2, and 3 denote the moments of switching on, switching off, and short-term (for 20 s) switching on the light, respectively.

Figure 5 shows another example of the effect of light on the AOT-BZ reaction after the frequency-multiplying bifurcation. The oscillation period drops in the dark from $T \approx 10$ min to $T \approx 5$ min and decreases smoothly to 3.1 min. Illumination of this system with blue light (B480) increases the oscillation amplitude markedly and makes the oscillation frequency twice as large (*T* changes from 3.1 to 1.5 min). This is an example of the photoinduced frequency-doubling.

Under some conditions, the AOT-BZ system exhibits frequency-quadrupling bifurcation in the dark. For example, at $\omega = 18.9$ or 9, $\phi_w = 0.11$, and $F = 0$, period *T* changes sharply from 12.4 to 3.1 min and then, after 2−3 h, oscillations stop. Illumination of this system during the oscillations with $T = 3.1$ min by blue light does not change *T*, although the average oxidation state of the system shifts somewhat toward the reduced state. After ca. 50 oscillations, the period *T* gradually decreases and oscillations stop. On the other hand, Figure 6 shows the response of the system to the illumination (B480) on the steady state reached after the frequency-quadrupling bifurcation in the dark. Switching on, switching off, and short-term (for 20 s) switching on the light give rise to damped oscillations with about the same period as before the cessation of oscillations in the dark.

These examples suggest the possibility of exploring several interesting and new phenomena such as truncated peaks, "recoil" peaks, and photoinduced frequency-doubling, induced by illuminating the AOT-BZ system, although more systematic studies are obviously required before we could establish the mechanism. Nevertheless, we can postulate the characteristic behavior of the AOT-BZ system from the given examples that the action of light always leads to the reduction of the catalyst.

**TABLE 1: $R_0/\phi_w$ for the $H_2SO_4$−$NaBrO_3$−Ferriin Subsystem in a Water-in-Oil Microemulsion of AOT in Octane Measured under Illumination**[a]

| no | filter | $R_0/\phi_w$ | remark[b] |
|---|---|---|---|
| 1 | B480 | 2.2 ± 0.4 | |
| 2 | B370 | 8.5 ± 1.2 | |
| 3 | | 15.2 | |
| 4 | B480 | 5.6 ± 1.1 | [HMA] = 0.2 M |
| 5 | B370 | 60.6 ± 20 | [HMA] = 0.2 M |
| 6 | B480 | 3 ±0.8 | $N_2$ bubbling |
| 7 | B370 | 8.5 ± 1.5 | $N_2$ bubbling |
| 8 | B480 | 2.9 | [phen] = 2 mM |
| 9 | B370 | 7.3 | [phen] = 2 mM |
| 10 | B480 | 2.1 ± 0.2 | $\phi_w = 0.005$ |
| 11 | B370 | 8.0 ± 0.25 | $\phi_w = 0.005$ |
| 12 | B370 | 14.8 | $\phi_w = 0.005$<br>$\omega = 5.5$ |
| 13 | B370 | 5.8 ± 0.4 | $[\text{ferroin}]_0 = 1.96$ mM |
| 14 | B370 | 4.3 ± 0.24 | $[\text{ferroin}]_0 = 1.4$ mM |
| 15 | B370 | opposite effect | $[Br_2]_{oil} = 0.6$ mM |
| 16 | B480 | opposite effect | $[Br_2]_{oil} = 0.6$ mM |
| 17 | | opposite effect | $[Br_2]_{oil} = 0.6$ mM |

[a] $R_0/\phi_w$ is given in units of absorbance/min, where $R_0$ is the initial rate of rise of the absorbance at 510 nm. [b] Experiments 1−3 were performed under the basic conditions $[H_2SO_4]_0 = 0.3$ M, $[NaBrO_3]_0 = 0.1$ M, $[\text{ferroin}]_0 = 2.8$ mM, $\omega = 11$, $\phi_w = 0.01$, batch stirred reactor, $N_2$ off. In 4−17, the difference from the basic condition is indicated.

To examine if it is really characteristic of the AOT-BZ system, we studied the action of light on the subsystem without HMA: namely, $NaBrO_3$−$H_2SO_4$−ferriin in the AOT microemulsion. Let us define the initial rate $R_0$ of the growth in the absorbance $A_{510}$ due to ferroin at 510 nm as

$$R_0 \equiv (\mathrm{d}A_{510}/\mathrm{d}t)_{t=0} \tag{2}$$

where $t = 0$ corresponds to the instant of switching on the light. We have examined the dependence of $R_0$ on various parameters, including the intensity and spectral composition of the light, and the size and concentration of reverse micelles. The results are summarized in Table 1. In Table 1, the quantity $R_0/\phi_w$ is shown, which is proportional to the initial rate $v_0$ of growth in [ferroin],

$$v_0 \equiv (\mathrm{d}[\text{ferroin}]/\mathrm{d}t)_{t=0} \tag{3}$$

since

$$R_0 = v_0 \phi_w L \epsilon_{510} \tag{4}$$

where $L$ is the optical pathlength and $\epsilon_{510}$ is the extinction coefficient of ferroin at 510 nm.

From the data presented in Table 1, the following conclusions may be derived. Ferriin is reduced by illumination even in the absence of HMA, although an addition of 0.2 M of HMA makes the rate of ferriin photoreduction several times larger (rows 4 and 5 are to be compared with rows 1 and 2). Replacement of B480 with B370 results in an increase in the rate of ferriin reduction by a factor of 4 (compare row 1 with row 2, and row 10 with row 11), while the intensity of the incident light grows only by a factor of 1.6.

$Br_2$, which may be liberated during the reaction in the aqueous or oil phase, could be the primary light absorber since it has an absorption band in the wavelength region concerned. To examine this possibility, the system with added $Br_2$ was illuminated (rows 15−17 in Table 1). An addition of 0.6 mM of $Br_2$ leads to a slow reduction of ferriin in the dark, while switching on the light leads (with any filter used) to very quick oxidation of ferroin, which is opposite of the ferriin photoreduction observed in the reference system. In addition, the bubbling of the standard mixture with pure nitrogen to eliminate $Br_2$ from the system has practically no effect on $R_0/\phi_w$ (rows 6 and 7 are to be compared with rows 1 and 2 in Table 1). Therefore $Br_2$ should not be the primary light absorber in the ferriin photoreduction. The ineffectiveness of the nitrogen bubbling also excludes the possibility of dissolved oxygen participating in the process by quenching the photoexcited molecules.

For the purpose of specifying the primary light absorber further, let us examine some possible reaction pathways responsible for the reduction of ferriin. First we assume that a primary light absorber, G, is photoexcited to G*, which then partly reduces ferriin and partly undergoes other reactions or is deactivated back to G:

$$\mathrm{G} + h\nu \xrightarrow{k} \mathrm{G}^* \tag{R1}$$

$$\text{ferriin} + \mathrm{G}^* \xrightarrow{k_r} \text{ferroin} \tag{R2}$$

$$\mathrm{G}^* \xrightarrow{k'} \tag{R3}$$

Assuming a steady state for G*, we get

$$[\mathrm{G}^*] = k[\mathrm{G}]/(k_r[\text{ferriin}] + k') \tag{5}$$

The rate of increase of [ferroin] is

$$v = k_r[\mathrm{G}^*][\text{ferriin}] \tag{6}$$

For $k' \gg k_r$[ferriin], we get from eqs 5 and 6

$$v \approx (k_r/k')k[\mathrm{G}][\text{ferriin}] \tag{7}$$

The rate constant $k$ of the photoexcitation can be calculated by[4,20]

$$k = (10^3 LS/VN_A)\int[T(\lambda)\, I_0(\lambda)/h\nu] \times [\{1 - 10^{-A(\lambda)}\}/A(\lambda)]\epsilon(\lambda)\, \mathrm{d}\lambda \tag{8}$$

in units of $s^{-1}$, where $N_A$ is Avogadro's number, $V$ is the volume of the reaction mixture, $L$ is the optical path length, $ST(\lambda)\, I_0(\lambda)/h\nu$ is the number of incident photons with wavelength $\lambda$ per unit time, $\epsilon(\lambda)$ is the extinction coefficient of G, and $A(\lambda)$ is the absorbance of the solution (including absorption due to species other than G).

If ferriin itself is photoexcited, scheme R1−R3 will be modified as

$$\text{ferriin} + h\nu \xrightarrow{k} \text{ferriin}^* \tag{R4}$$

$$\text{ferriin}^* + \mathrm{G} \xrightarrow{k_r} \text{ferroin} \tag{R5}$$

$$\text{ferriin}^* \xrightarrow{k'} \tag{R6}$$

If we assume $k' \gg k_r[\mathrm{G}]$, the rate of production of ferroin is

$$v \approx (k_r/k')k[\mathrm{G}][\text{ferriin}] \tag{9}$$

which is formally the same as eq 7.

In both cases, the ratio of the initial rates for the B480 and B370 filters is

$$\begin{aligned}\rho_t &\equiv v_0(\text{B370})/v_0(\text{B480})\\ &= k(\text{B370})/k(\text{B480})\end{aligned} \tag{10}$$

where $v_0$(B370) and $v_0$(B480), and $k$(B370) and $k$(B480) are the initial rates and the rate constants of photoexcitation when the B370 and B480 filters are used, respectively. The ratio $\rho_t$ can be calculated using eq 8. On the other hand, $\rho_t$ should correspond to

$$\rho_c \equiv [R_0(\mathrm{B370})/\phi_w]/[R_0(\mathrm{B480})/\phi_w] \tag{11}$$

which can be determined from the experimental data given in Table 1.

From the data in Table 1, it follows that $\rho_c = 4 \pm 0.5$ for the standard mixture (rows 1 and 2). If we assume that ferriin is the primary light absorber, we get from eq 8 $\rho_t = 5.3 \pm 1$, which is in reasonable agreement with the experimental value $\rho_c$. On the other hand, if we assume that $Br_2$ or ferroin is the primary light absorber, $\rho_t$ is calculated to be 1.3 and 0.65, respectively, with 25% accuracy. Thus, we may conclude that the photoexcitation of ferriin is the primary step in the photoreduction of ferriin in the AOT microemulsion without HMA, and we are to choose scheme R4−R6 rather than R1−R3.

The next question is what species corresponds to G in scheme R4−R6 to reduce the photoexcited ferriin to ferroin without any reducing reagent such as malonic acid or external supply of $Br^-$. The only possible candidate is the AOT molecules, which could reduce ferriin* as

$$\text{ferriin*} + \text{AOT}^- \xrightarrow{k_r} \text{ferroin} + \text{AOT}^\bullet \tag{R7}$$

or

$$\text{ferriin*} + \text{AOTH} \xrightarrow{k_r} \text{ferroin} + \text{AOT}^\bullet + \text{H}^+ \tag{R7$'$}$$

where $AOT^-$, $AOT^\bullet$, and AOTH stand for the AOT molecule in which the sulfonic group takes the form, $-SO_3^-$, $-SO_3^\bullet$, and $-SO_3H$, respectively. In this case, [G] in eq 9 should be replaced by [AOT].

The above assumptions, that the ferriin photoexcitation is the primary step and that ferriin* is reduced by AOT, may further be justified by the following observations: If a twice as large amount of the AOT solution in octane is used in preparing reverse micelles, both $\omega$ and $\phi_w$ are reduced by a factor of 2, and the AOT concentration in the aqueous pseudophase is doubled since $[\mathrm{AOT}] = [\mathrm{H_2O}]/\omega$. Then eq 9 predicts that the initial rate should increase by a factor of 2. Row 12 in Table 1 shows that $R_0/\phi_w$ becomes nearly twice as large compared with row 2. On the other hand, if a twice as large amount of octane solution with the same total amount of AOT is used, $\phi_w$ is reduced by a factor of 2 but $\omega$ remains unchanged. Therefore [AOT] is also unchanged. Equation 9 predicts no change of $v_0$ in this case, which is consistent with the experimental observation (rows 10 and 11 in Table 1). These observations support the assumption that AOT plays a role as the reductant. The value of $R_0/\phi_w$ decreases in proportion to $[\text{ferroin}]_0$ (rows 2, 13, and 14 in Table 1). This is also consistent with the expectation derived from eq 9.

It would also be of some interest to estimate the quantum yield

$$\begin{aligned}\varphi &\equiv k_r[\mathrm{AOT}]/(k_r[\mathrm{AOT}] + k') \\ &\approx k_r[\mathrm{AOT}]/k' \end{aligned} \tag{12}$$

of the photoreduction of ferriin. At t = 0, it can be written using eq 9 as

$$\varphi \approx v_0/k[\text{ferriin}]_0 \tag{13}$$

Using $v_0$ determined experimentally with eq 4 and $k$ calculated by eq 8, $\varphi$ is found to be on the order of $10^{-3}$.

Experimental data in Table 1, rows 4 and 5, give $\rho_c = 11 \pm 5$ for the full BZ system with HMA. If this is compared with $\rho_c = 4 \pm 0.5$ for the reference case without HMA (rows 1 and 2), there is a definite difference between them, suggesting that another primary photochemical process should be responsible for it in the case of the full AOT-BZ system in addition to the photoexcitation of ferriin followed by reaction R7 or R7′. Since $\rho_t = 0.65$ for ferroin and $\rho_t = 1.3$ for $Br_2$, neither of them can be the primary absorber.

Several schemes have been proposed so far for the illumination effect on the BZ reaction in the homogeneous aqueous solution, in which $HBrO_2$ or $Br^-$ is photoproduced through the photoexcitation of the reduced form of catalysts.[8,16,17,19,20] However, they are excluded in the present case since these schemes assume the photoexcitation of ferroin to be the primary step, which has been excluded in the above discussion.

Photodecomposition of bromomalonic acid [$CHBr(COOH)_2$; hereafter abbreviated BrMA], which is produced during dark oscillations, has been proposed for the ultraviolet illumination:[22]

$$\text{BrMA*} \rightarrow \text{Br}^\bullet + \text{MA}^\bullet \tag{R8}$$

$$\text{Br}^\bullet + \text{HMA} \rightarrow \text{Br}^- + \text{MA}^\bullet + \text{H}^+ \tag{R9}$$

$MA^\bullet$ or $Br^-$ produced in reaction R8 or R9 could reduce ferriin. However, this mechanism is hardly acceptable in the present case since BrMA has no light absorption for $\lambda > 300$ nm.[23]

Comparing rows 1 and 2 with 4 and 5, respectively, in Table 1, it is seen that the rate is enhanced by addition of HMA by a factor of 2.5 for the B480 filter, and the enhancement is even more pronounced (by a factor of ∼7) for shorter wavelengths (B370). The enhancement by adding HMA for the ultraviolet illumination may be understood on the basis of a slight overlap of the BrMA absorbance and the B370 transmittance around 300 nm. However, the enhancement by a factor of 2.5 for the B480 illumination can never be explained on this basis.

The only possibility to account for the enhancement observed by the addition of HMA is that the photoexcited ferriin undergoes a redox reaction with HMA or BrMA; for example,

$$\text{ferriin*} + \text{HMA} \xrightarrow{k^*} \text{ferroin} + \text{MA}^\bullet + \text{H}^+ \tag{R10}$$

where $MA^\bullet$ undergoes further reactions as those in the FKN model for the dark oscillations.[24] Similarly, photoenhancement of the reaction of ferriin with BrMA proposed in the FKN model would also be responsible.[24]

However, any scheme of the type of (R10) cannot account for the observed wavelength dependence as high as $\rho_c = 11 \pm 6$, since the corresponding calculated value is $\rho_t = 5.3 \pm 1$, the same as that calculated for scheme R7 or R7′. Unfortunately a large uncertainty in the determination of $\rho_c$ prevents us from going into further detail. However, if $\rho_c$ is larger than $\rho_t$ calculated on the basis of a reaction scheme such as (R10), it should lead us to the hypothesis that a direct reaction of ferriin photoexcited to its higher excited state (ferriin**) undergoes an additional reaction in which ferriin is reduced to ferroin. Ferriin has intense absorption bands due to the ligand $\pi-\pi^*$ transitions in the wavelength region below 300 nm, the tail of which gives considerable intensity in the 300−400 nm region corresponding to the transmission of B370. The absorbance in this region is much higher than that for the transition to the first excited state. If ferriin** undergoes a reaction such as (R10) before it is deactivated to the first excited state or to the ground state, or if it undergoes a reaction that is impossible for ferriin*, it would be possible to account for the present observation of a high $\rho_t$ value.

## 4. Conclusion

In this work, we have shown that the ferroin-catalyzed AOT-BZ reaction is photosensitive. The action of light leads to the reduction of ferriin in all cases. However, depending on the AOT-BZ reaction regime, various effects have been observed, such as the induction and inhibition of oscillations, change in the oscillation frequency, and variation in the shape of oscillations. In particular, we have found some new phenomena, such as the oscillations with truncated peaks and the emergence of "recoil" peaks. We are trying to reproduce the truncated peaks theoretically by incorporating the direct reaction of AOT with ferriin into the NFT mechanism. The appearance of recoil peaks is more difficult at present to explain mechanistically, but its similarity to those reported by Solli and Ruoff[25] may be pointed out. A role of the catalyst in a higher oxidation state [e.g., $Fe(phen)_3{}^{4+}$ or $Fe(phen)_3(H_2O)_2{}^{4+}$] has also been suggested for the self-reduction of ferriin after it is formed by oxidation of ferroin.[26] Nevertheless, since the corresponding BZ reaction in the homogeneous aqueous solution does not show similar light sensitivity, the emerging photoresponse in the AOT-BZ reaction should be associated with the new environment provided by the micelle formation. These findings should provide a key for more detailed study in the future on the mechanism of the photocontrolled AOT-BZ reaction.

Examination of the photoresponse in the BZ subsystem without HMA in the AOT reverse micelles has led us to conclude that the observed photoreduction of ferriin is due to the reaction of photoexcited ferriin with AOT. We suggest also that the photoreduction of ferriin observed in the full BZ system in the AOT reverse micelle may also be due to an additional reaction of ferriin photoexcited to its higher excited state. In the future, a careful measurement of the action spectrum[8] would be helpful in confirming this hypothesis.

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