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Effect of Adding Starch on the Photoinhibition of Oscillation in the Briggs-Rauscher Reaction

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Wavelength dependence of the relative cross section has been determined for the photoinhibition of oscillation in the starch-free and starch-added Briggs-Rauscher systems. In both cases, the primary light absorber was identified as iodine molecule, whereas starch-iodine complex was found to be inert as to the primary photochemical process.

Effects of light irradiation on chemical oscillators, including photoinduction and photoinhibition of oscillation have been attracting much attention in recent years.1-7) In order to understand the phenomena from reaction mechanistic point of view, specification of the light absorbing species should be of primary importance. For this purpose, photoresponse to the monochromatic light irradiation has been investigated for a number of chemical oscillators.1-4)

The Briggs-Rauscher (BR) system8) is one of the best-known photosensitive chemical oscillators. Dulos and De Kepper6) have found that continuous light irradiation makes the system bifurcate from an oscillatory state into a steady state (photoinhibition), and that periodic irradiation brings about a synchronization oscillation. A qualitative explanation has been given for these phenomena by the model calculation made by Kumpinsky *et al.*7) However, no experimental verification has been made as to the primary photochemical process responsible for these effects. The aim of the present study is to identify experimentally the primary light absorber responsible for the photoinhibition phenomenon in this system, by applying the concept of relative cross section recently developed by one of the authors.5) It is of particular interest to examine how the action spectrum (wavelength dependence of the relative cross section) is affected by the addition of starch indicator, which brings about drastic change in the absorption spectrum due to the formation of blue starch-iodine complex.

The light irradiation experiment was conducted under a CSTR (continuous flow stirred tank reactor) configuration. Reagent grade chemicals, KIO_3, $MnSO_4$, $CH_2(COOH)_2$, H_2SO_4, soluble starch (Katayama) and H_2O_2 (Mitsubishi Gas) were used without further purification. Prescribed concentrations of the four stock solutions, KIO_3, H_2O_2, $CH_2(COOH)_2$ + soluble starch and $MnSO_4 + H_2SO_4$ were independently introduced to a CSTR by a peristaltic pump (EYELA, MP-32). The initial concentrations employed throughout the series of experiment were $[MnSO_4]_0 = 50.0$ mM, $[KIO_3]_0 = 50.0$ mM, $[CH_2(COOH)_2]_0 = 5.00$ mM, $[H_2O_2]_0 = 200$ mM and $[H_2SO_4]_0 = 20.0$ mM (1 M = 1 mol dm^{-3}). The initial concentration of the soluble starch was varied from 0 to 25 mg/L. The reaction mixture was stirred vigorously by a magnetic stirrer and overflowed from the top of the reactor. The residence time

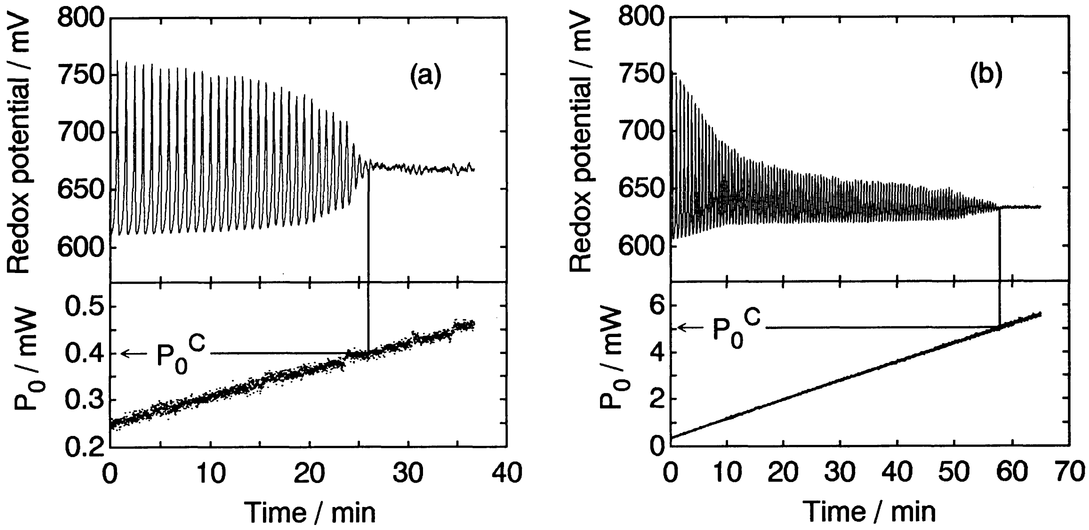

Fig. 1. Effect of 460 nm monochromatic light irradiation on the redox-potential oscillation in the BR-systems: (a) starch-free, (b) $[\text{starch}]_0$ = 25 mg/L. Incident light power (P_0) was continuously increased as shown in the lower panels. Definition of the critical light power is also illustrated. The volume, beam area and optical path length of the CSTR were 11 cm^3, 1.2 cm^2 and 2.0 cm, respectively.

was fixed at 2.6 min. The reaction temperature was maintained at 24.5±0.1°C by the heat exchange with pure water circulated between a water jacket of the reactor and a pure water pool immersed in the thermostated water bath (EYELA, NTT-1300). Oscillations were monitored by a combined Pt-electrode with reference Ag|AgCl (Horiba, 6861-10C).

Monochromatic light was supplied either by a light source of Okazaki Large Spectrograph[9] or by a pair of 500 W ultra-high-pressure mercury lamp (Ushio, USH-500D) and a monochromator (Ritsu, MC-20L). The spectral band widths were 12 nm and 11 nm, respectively. Light intensity was controlled by a continuously variable ND filter (Sigma Koki, Σ-782(U)) equipped with a stepping motor. A part of the incident beam was sampled by a quartz plate just in front of the reactor cell, and was continuously monitored by a photodiode (Hamamatsu, S1723-05). The present optical setup allows us an automatic light intensity scanning with a desired time profile, by applying PID control of the stepping motor with reference to the signal from the photodiode. Measurement of the absorption spectrum at the steady state close to the bifurcation point was either separately made by a spectrophotometer (Hitachi, U-3200) or simultaniously made by a photodiode monitoring the transmitting light power.

Effects of 460 nm (absorption peak of I_2) monochromatic light irradiation on the oscillations are compared in Fig. 1 for two systems: (a) $[\text{starch}]_0$ = 0 mg/L and (b) $[\text{starch}]_0$ = 25 mg/L. The bifurcation structures from an oscillatory state to a steady state can be directly envisualized by following the changes in redox potential oscillations while continuously increasing the incident light power (P_0). In the starch-free system, as P_0 is increased, the amplitude of oscillation decreased monotonically with a convex curvature until the steady state was reached. The light power needed to suppress the oscillation completely is defined to be the critical light power (P_0^C) as indicated in the figure. A novel feature discernible in the bifurcation structure of starch-added system (Fig. 1 (b)) is the appearance of small amplitude oscillation region which spreads over a relatively wide light power range. In this region, the amplitude of oscillation changes very little with light power, making the small amplitude oscillation itself look like almost photo-insensitive. The existence of this region makes the critical light power much higher than that of the starch-free system.

Dependence of the critical light power on the initial concentration of starch is shown in Fig. 2 for the 460 nm monochromatic light irradiation. As can be seen from the figure, the critical light power increases almost linearly with the starch concentration. It must be noted here that the absorbance of the reaction mixture in the visible region increases with the starch concentration due to the formation of blue starch-iodine complex (absorption peak centered at around 600 nm). The results shown in Fig. 2 cannot be explained if we consider starch-iodine complex as a primary light absorber responsible for the photoinhibition of oscillation.

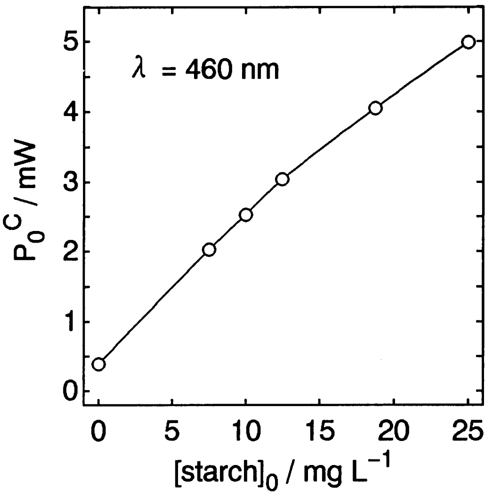

Fig. 2. Dependence of critical light power (P_0^C) on the initial concentration of starch. Dimension of the CSTR was the same as given in Fig. 1.

In order to identify the primary light absorber in the starch-free and the starch-added BR-systems, critical light power was measured as a function of wavelength (λ) and relative cross section was calculated for both cases. Relative cross section (σ_R), the value directly proportional to the molar extinction coefficient of the primary light absorber, is defined to be

$$\sigma_R = (h\nu D/P_0^C)[1 - \exp(-2.303D)]^{-1},$$

where D is the optical density of the reaction mixture at the bifurcation point and $h\nu$ is the photon energy.5)

Figure 3 shows the wavelength dependence of the relative cross section for (a) starch-free and (b) [starch]$_0$ = 25 mg/L systems. In the starch-free system, the relative cross section in the visible region and the absorption spectrum of aqueous iodine solution exhibit a quite similar tendency, both possessing the broad band at around 460 nm. This indicates strongly that the primary light absorber in the starch-free BR-system is identified as iodine, which was an *a priori* assumption employed in the model calculation made by Kumpinsky *et al.*7) The prominent increase in σ_R at the ultraviolet region is to be ascribed to the iodomalonate whose contribution to the absorption spectrum was quantitatively analyzed by Roux and Vidal.10) In the starch-added system, in spite of the strong and broad absorption around 600 nm due to the formation of starch-iodine complex, σ_R does not possess a sizable value in this region. Actually, we could not suppress the oscillation at λ = 600 nm even with the maximum available power. The outline of the action spectrum is essentially the same as that of the starch-free system, suggesting that the primary light absorber responsible for the photoinhibition in this case is

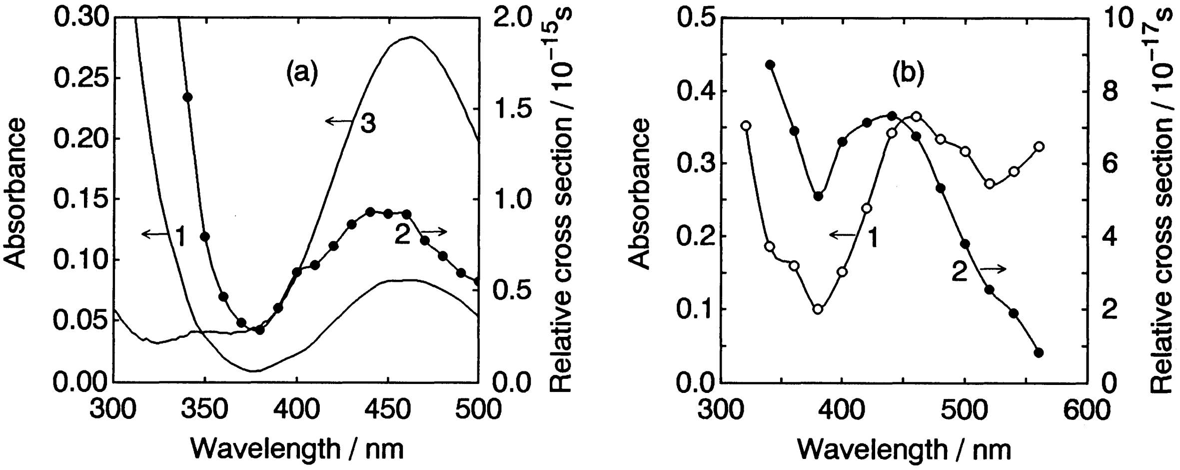

Fig. 3. Wavelength dependence in the BR-systems: (a) starch-free, (b) $[\text{starch}]_0 = 25$ mg/L. Curves labelled 1 and 2 correspond to the absorbance of reaction mixture at the bifurcation point and the relative cross section (σ_R), respectively. For comparison, absorption spectrum of 0.4 mM aqueous solution of I_2 (curve 3) is shown in panel (a). The volume, beam area and optical path length of the CSTR were: (a) 3.8 cm^3, 0.21 cm^2 and 1.0 cm, and (b) 11 cm^3, 1.2 cm^2 and 2.0 cm, respectively.

also a free iodine molecule. Note that the absolute value of σ_R is an order of magnitude smaller than that of the starch-free system. The difference in σ_R can be qualitatively explained as follows. If soluble starch is added to the system, it traps free iodine in its helical coil, thereby protecting iodine from photodissociation process, which is the triggering step in the photo-inhibition of oscillation. Thus, the apparent σ_R should be naturally decreased as the starch concentration is increased. It is interesting to examine if this simple model is capable of reproducing the small amplitude oscillation region introduced by the addition of starch. A quantitative treatment is currently under way.

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References

1) Y. Mori, P. K. Srivastava, and I. Hanazaki, *Chem. Lett.*, **1991**, 669.
2) P. K. Srivastava, Y. Mori, and I. Hanazaki, *Chem. Phys. Lett.*, **190**, 213 (1991).
3) P. K. Srivastava, Y. Mori, and I. Hanazaki, *Chem. Phys. Lett.*, **190**, 279 (1992).
4) Y. Mori and I. Hanazaki, *J. Phys. Chem.*, **96**, 9083 (1992).
5) I. Hanazaki, *J. Phys. Chem.*, **96**, 5652 (1992).
6) E. Dulos and P. De Kepper, *Biophys. Chem.*, **18**, 211 (1983).
7) E. Kumpinsky, I. R. Epstein, and P. De Kepper, *Int. J. Chem. Kinet.*, **17**, 345 (1985).
8) T. S. Briggs and W. C. Rauscher, *J. Chem. Educ.*, **50**, 496 (1973).
9) M. Watanabe, M. Furuya, Y. Miyoshi, Y. Inoue, I. Iwahashi, and K. Matsumoto, *Photochem. Photobiol.*, **36**, 491 (1982).
10) J. C. Roux and C. Vidal, *Nouv. J. Chim.*, **3**, 247 (1979).

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