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Wavelength Dependence of Light-Induced Chemical Oscillation. Hexacyanoferrate(II)-Hydrogen Peroxide-Sulfuric Acid System

Yoshihito MORI, Prem Kumar SRIVASTAVA, and Ichiro HANAZAKI*
Institute for Molecular Science, Myodaiji, Okazaki 444

We have measured the wavelength dependence of the light-induced chemical oscillation in the $Fe(CN)_6^{4-}$-H_2O_2-H_2SO_4 system in a continuous-flow stirred tank reactor. The primary process for the induction of oscillation is suggested to be the photo-excitation of $Fe(CN)_6^{3-}$.

Light-sensitive chemical oscillators have attracted much attention recently.[1-5] Exotic phenomena have been observed in chemical oscillators interacting with light, such as the synchronization with periodic light or the light induced chaotic behavior.[2] When an unstirred solution was irradiated through a negative film, the positive image was stored as the spatial distribution of the reactivity in the solution.[3,4] These phenomena are based on the photo-inhibition and photo-induction of chemical oscillation. Srivastava et al. found the photo-inhibition effect on some uncatalyzed chemical oscillators and measured the wavelength dependence to identify the primary absorber.[5] Rābai et al. reported the photo-induction of chemical oscillation by white light in the $Fe(CN)_6^{4-}$-H_2O_2-sulfuric acid system.[1] This simple system seems to be interesting because of its high sensitvity to light irradiation. In this letter, we report the measurement of wavelength-dependence for the photo-induced chemical oscillation in this system.

We used a continuous-flow stirred tank reactor (CSTR) made of acryl resin with two quartz windows for irradiation. A monochromatic light with resolution of 10 nm was supplied by a pair of a 500 W Xe lamp and a monochromator(Ritsu). The optical path length of the CSTR was 20 mm. The light intensity was controlled by varying the current across the lamp and was measured by a photodiode(HAMAMATSU, S1723-05) at the incident window of the reactor. Three independent flows of solutions containing $Fe(CN)_6^{4-}$, H_2O_2 and sulfuric acid, respectively, were introduced into the reactor by peristalic pumps and overflow was allowed from the top of the reactor. Potassium hexacyanoferrate(II), hydrogen peroxide(Mitsubishi

Gas) and sulfuric acid(Wako) were of reagent grade and used without further purification. Distilled and deionized water was used as solvent. Absorption measurements were carried out by a spectrophotometer(HITACHI UV-3400) in a flow cell with the optical path length of 5 mm. The pH of the solution was measured with a pH electrode (Horiba). All the measurement was carried out at 25 ± 0.5 °C.

The solution containing 3.3 mM $K_4Fe(CN)_6$, 50 mM H_2O_2, and 0.9 mM H_2SO_4 showed a constant pH of 5.00 ± 0.05 for three hours in the CSTR (residence time=368 s) in the dark(curve c in Fig.1). When the solution was irradiated at 280 nm with the intensity below the critical value, pH increased and then exhibited a steady value(curve b). Above the critical value, pH increased and started to oscillate with the period of 148 s and the amplitude of pH 1.5(curve a).

Similar bifurcation into oscillation was observed even in the dark when the residence time was increased. This means that the oscillation could occur if the system had more time to allow further reactions in the reactor. Therefore the effect of light irradiation to cause an oscillation may be to accelerate the rate of some steps involved in the oscillatory reaction. A mechanism has been proposed in which the reaction consists of 8 steps.[1)] Light absorption by $Fe(CN)_6^{4-}$ is assumed to accelerate the replacement of a ligand (CN^-) for H_2O. With this mechanism, the wavelength dependence of the efficiency of induction of oscillation must be correlated with the absorption coefficient of $Fe(CN)_6^{4-}$.

The experimental results shown in Fig.1 allow us to determine a threshold light intensity to induce oscillation. The relative

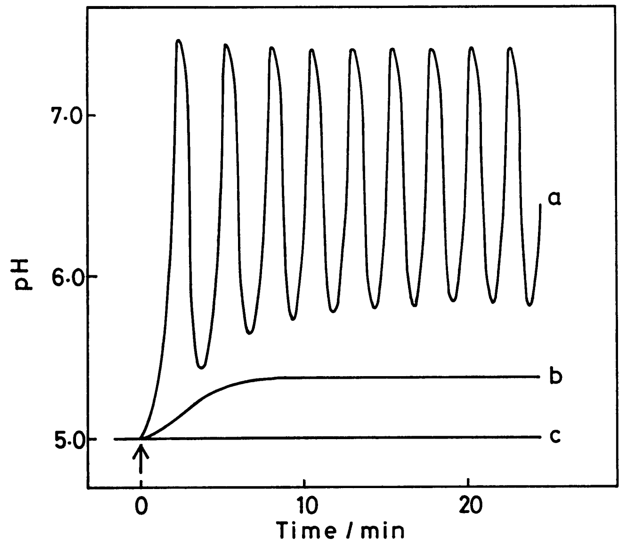

Fig.1. Time profile of pH in the solution irradiated at 280 nm in a CSTR. The arrow indicates the start of irradiation. Light power is 137 × 10^{-6} Watt (a), 66 × 10^{-6} Watt (b) and 0 Watt (c).

efficiency(RE) of the induction of oscillation is given for each wavelength by the following equation:

$$RE = (D/P_c)[1-\exp(-2.303D)]^{-1},$$

where P_c is the threshold light power (Watt) to induce oscillation. Details of the derivation was given elsewhere.[5)] Briefly, it was derived on the following assumptions: (1) oscillation is induced when the variation $\Delta[X]$ of the concentration of a certain species X exceeds a threshold value $\Delta[X]_c$, (2) $\Delta[X] = aI$, where I is the local light intensity given by Lambert-Beer's law, and (3) a rapid stirring averages $\Delta[X]$ over whole solution so that $\Delta[X] = a'(P/D)[1-\exp(-2.303D)]$, where P is the incident power. Hence, at the therehold, $a' = \Delta[X]_c(D/P_c)[1-\exp(-2.303D)]^{-1}$ and the relative efficiency may be defined as, $RE = a'/\Delta[X]_c$, since $\Delta[X]_c$ is independent of wavelength.

The calculated RE is plotted against wavelength in Fig.2 together with absorption spectra of the reacting solution at pH 5.0 (curve a), of the 2.11 mM aqueous solution of $K_3Fe(CN)_6$(curve b) and of the 1.19 mM aqueous solution of $K_4Fe(CN)_6$ (curve c). The concentrations of the latter two solutions were determined so that the sum of their absorbances reproduces that of the reacting solution containing 3.3 mM $K_4Fe(CN)_6$ as a starting material (curve a).

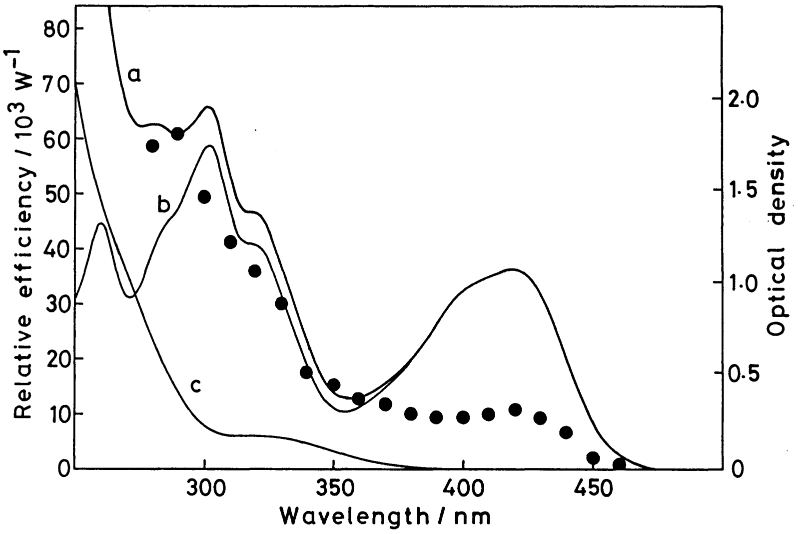

Fig.2. Wavelength dependence of relative efficiency RE (filled circles;left scale) and absorption spectra (right scale). a: Absorbance of the reacting solution at pH 5.0 under the same condition as in Fig.1. b: Absorbance of the 2.11 mM aqueous solution of $Fe(CN)_6^{3-}$. c: Absorbance of the 1.19 mM aqueous solution of $Fe(CN)_6^{4-}$.

The RE spectrum has a peak at 420 nm, which corresponds to the band at 420 nm in the absorption spectrum of $Fe(CN)_6^{3-}$. In the near UV region, it has a shoulder at 320 nm and a peak at 290 nm. The former coincides with the 310 nm shoulder in the absorption spectrum of $Fe(CN)_6^{3-}$, while the latter is slightly shifted to shorter wavelengths than the 300 nm peak of $Fe(CN)_6^{3-}$. Nevertheless, comparing the RE spectrum and the absorption spectra of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, it is clear that RE should be correlated to $Fe(CN)_6^{3-}$ rather than to $Fe(CN)_6^{4-}$. Therefore we conclude that the light absorption due to $Fe(CN)_6^{3-}$ is a primary step to the light induced oscillation.

This conclusion is in contradiction to the previous postulate that the light absorption by $Fe(CN)_6^{4-}$ accelerates the oscillation.1) Rābai et al. have reported that the white light irradiation of the $Fe(CN)_6^{4-}$ solution before mixing is also effective.1) We believe that this is either due to the presence of a trace of $Fe(CN)_6^{3-}$ in the solution, or due to the fact that the light absorption by $Fe(CN)_6^{4-}$ is also effective in shorter wavelengths. An application of the present wavelength-dependent efficiency measurement to the irradiation of the $Fe(CN)_6^{4-}$ solution would be helpful in resolving this contradiction and in clarifying the mechanism in further detail. This is under way in our laboratory.

References

1) G. Rābai, K. Kustin, and I. R. Epstein, J. Am. Chem. Soc., 111, 8271(1989).
2) E. Dulos and P. de Kepper, Biophys. Chem., 18, 211(1983).
3) L. Kuhnert, K. I. Agladze, and V. I. Krinsky, Nature, 337, 244(1989).
4) M. Jinguji, M. Ishihara, and T. Nakazawa, J. Phys. Chem., 94, 1226(1990).
5) P. K. Srivastava, Y. Mori, and I. Hanazaki, Chem. Phys. Lett., in press.

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