Original Paper *Forma*, **15**, 213–218, 2000

Intensity Oscillation of Chemiluminescence in Ferroin-Catalyzed Belousov-Zhabotinsky Reaction

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(Received April, 2000; Accepted May 19, 2000)

Keywords: Belousov-Zhabotinsky Reaction, Chemiluminescence, Ferroin

Abstract. A weak chemiluminescence phenomenon was observed in ferroin-catalyzed Belousov-Zhabotinsky (BZ) reaction. The luminescence intensity oscillated with the self-oscillation of the visible color change and redox potential change in anti phase. A periodic signal of the luminescence was also detected even after the extinction of the self-oscillation. These results showed that the ferroin-catalyzed system has additional oscillatory reaction which concerned with photochemical processes similarly to $Ru(bpy)_3^{2+}$-catalyzed systems.

1. Introduction

Chemiluminescence is a frequently observed photochemical phenomenon in oxidation processes involving radicals or reactive oxygen species. The intensity of the luminescence is typically 10^{-16} to 10^{-15} W/cm^2. It is expected that the detailed mechanism of the reaction processes may be clarified by the detection of chemiluminescence from oscillatory chemical media (WATANABE and INABA, 1994) such as Belousov-Zhabotinsky (BZ) reactions.

The BZ reaction is one of well-known self-oscillation systems (FIELD and BURGER, 1985). Acompanying with its oscillation, spatiotemporally ordered patterns such as targets and spirals can be observed. These dissipative patterns have been much attracted in many scientific fields (NICOLIS and PRIGOGINE, 1977). Recently the novel behavior of the chemical waves, such as meandering patterns (PARISI *et al*., 1996), stochastic resonance (KÁDÁR *et al*., 1998), and bigwave (MIIKE *et al*., 1993) have been reported.

Spatio-temporal oscillations in the BZ reaction have been visualized by use of some catalysts of chelate compounds or metal ions, such as $Ru(bpy)_3^{2+}$, $Fe(phen)_3^{2+}$ (ferroin), Ce^{3+}, and Mn^{2+}. Among them the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction strongly responds to visible light (GÁSPAR *et al*., 1983; SRIVASTAVA *et al*., 1992) and therefore can be controlled

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by illumination of the light (FUJII *et al.*, 2000). Due to such a light sensitivity, the possibility of image processing and other functional devices have been studied (KUHNERT *et al.*, 1989; JINGUJI *et al.*, 1995). Simultaneously strong fluorescence is also observed in BZ reaction (BOLLETTA and BALZANI, 1982; KARAVAEV *et al.*, 1986). However only few works on photochemical properties in ferroin-catalyzed system have been reported so far (MIYAKAWA *et al.*, 1995).

GÁSPAR *et al.* (1983) have reported that the ferroin-catalyzed system also showed weak response to the visible light. It is suggested that the system may have photochemical processes similar to $Ru(bpy)_3^{2+}$-catalyzed system. Therefore we attempt to detect chemiluminescence in the ferroin-catalyzed BZ reaction using a photon-counting techniques for ultra-weak photon radiation.

2. Experimental Setup

The schematic block diagram of the detection system is shown in Fig. 1. The photo-multiplier (Hamamatsu R649) was used to detect weak photon, which had detectable wavelength of 300–850 nm, the minimal sensitivity 10^{-18} W/cm^2, and the quantum efficiency yield 0.3 to 2.0%. The equipment was shielded by a box chamber made of iron plates in the thickness of 2 mm in order to shut out external electro-magnetic noises. The photon counting method was employed using commercially available equipment (Hamamatsu Photonics C-2550). Temperature in the chamber was controlled at 25°C, and the photo-multiplier was cooled down to –30°C to reduce thermal noise (KAI *et al.*, 1995). The output signal from the multiplier was processed by a personal computer (EPSON PC-286VF).

The BZ solution was initially prepared with the following composition: 380 mM of sulfuric acid, 340 mM of sodium bromate, 95 mM of malonic acid, 48 mM of sodium bromide, and 3.5 mM of ferroin. A 10 ml of the solution was contained in a glass vessel,

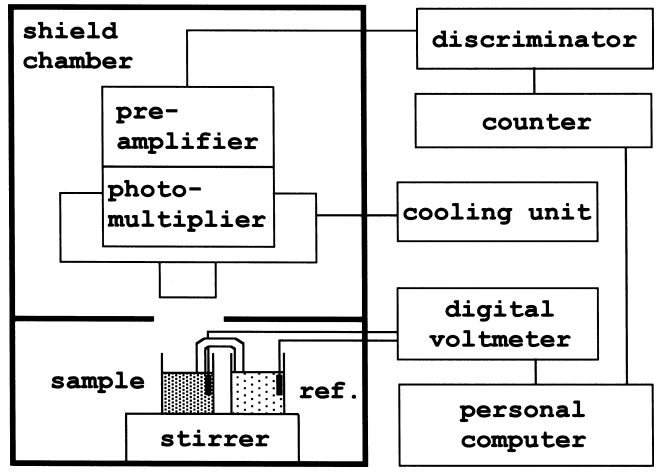

Fig.1. Block-diagram of experimental set-up. The chemiluminescence and the redox potential of the BZ reaction are measured simultaneously.

which was calmly stirred by a magnetic stirrer (constant speed at 240 r.p.m.). Under this condition a sustained self-oscillation (period of 30 s) was observed for about 30 minutes. The oscillation was monitored by redox potential between the sample and a reference solution (25 mM of cerium (III) diammonium nitrate tetrahydrate) using a salt bridge (3.0 M of potassium nitrate). The electrodes were made of platinum plates with 0.2 mm in thickness and 400 mm^2 in surface area.

3. Results and Discussion

First, we measured photon radiation from the BZ reaction and compared to the background noise. The background was determined by stirred pure water (the standard solution) under the same conditions. Figure 2 shows the temporally integrated photon numbers radiated from the sample and the standard. The photon intensity of the sample was about 3 times larger than that of the standard. This result clearly indicates the existence of chemiluminescence in ferroin-catalyzed BZ reaction with a rather good signal-to-noise ratio.

Secondly, we measured temporal change in the photon intensity together with the redox potential. Figure 3(a) shows redox potential change in the sample solution. The periodic oscillation of redox potential was extinguished at 360 s (D in the figure). The lifetime of the self-oscillation T_f was thus 360 s. The change in photon number was plotted in Fig. 3(b). Each point was averaged over 5 seconds. The intensity fluctuation had a periodicity of 30 s, which agreed with the period of the self-oscillation. The straight line in the figure shows the mean value of background noise (0.8 c.p.s.). Figure 3(c) shows the temporal change in the photon number after filtering its original signals to emphasize periodicity of the radiation. Before T_f, the photon intensity was gradually deceased with fluctuation, while after T_f it became almost constant in time. It is worthy noticing however that the oscillation of the photon intensity still remains after the redox oscillation is

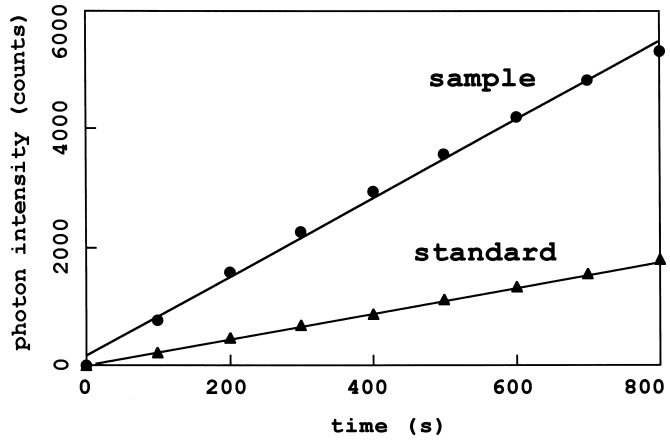

Fig. 2. Photon intensity radiated from BZ solution (sample) and water (standard). The luminescence intensity from the BZ solution is three times stronger than the standard.

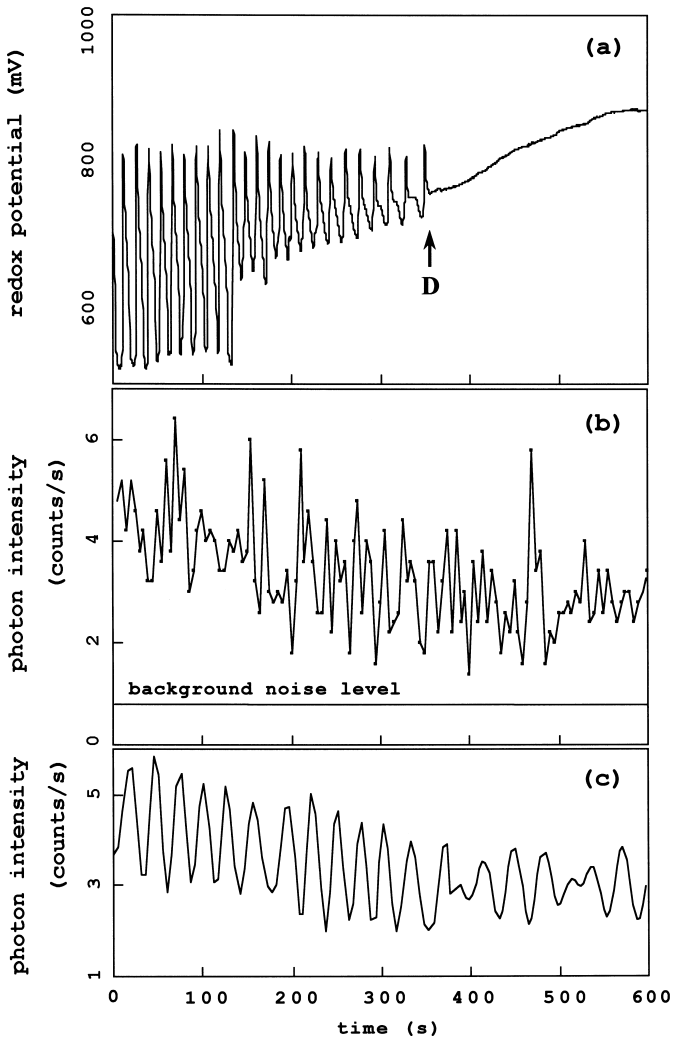

Fig. 3. Periodic signals of redox potential and photon intensity in time. (a) Periodic oscillation of redox potential in BZ solution. D shows the extinction time of redox potential. A lifetime of the reaction T_f (at D) is 360 s. (b) Fluctuation of photon intensity. At the beginning, the mean intensity decreases gradually, and after T_f it becomes almost constant. The solid line shows the intensity of background noise. (c) Photon oscillation after filtering.

extinguished. This fact suggests that a periodic production and excitation of radicals take place. Namely oscillatory reaction processes are still active which have very long time scale and are independent of the self-oscillation of the catalyst.

The temporal relationship between the luminescence and the self-oscillation is given in Fig. 4. The phase difference between two oscillations is about 180°. Radiation of the photon was periodically activated at sufficiently reduced states, that is, the strong photon

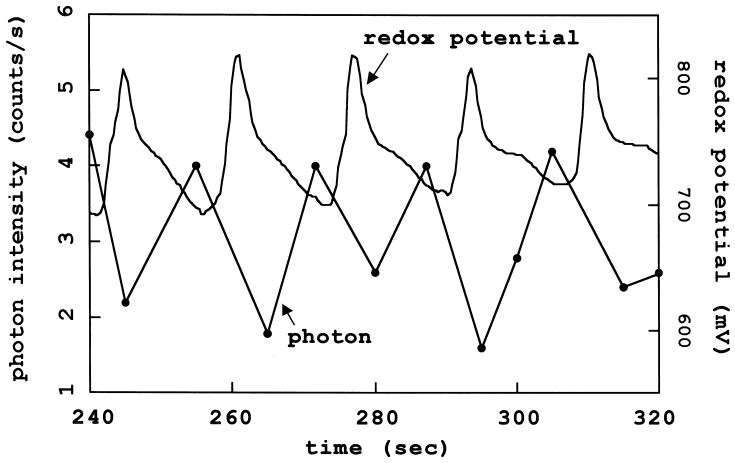

Fig. 4. Phase relation between the self-oscillation and the photon intensity oscillation. Both are in anti phase.

intensity was observed at the transient state from strong reduction to oxidation.

The chemiluminescence phenomenon reported in this article may result from organic radicals such as $BrO_2^{\bullet}$ and the malonyl radicals (FÖRSTERLING *et al*., 1990; NOSZTICZIUS *et al*., 1991; SIRIMUNGKALA *et al*., 1996), which are the intermediates of the BZ reaction. The spectrum of the luminescence should be measured in order to determine the chemical species resulting in the luminescence. It is left in future.

4. Summary

We reported the chemiluminescence phenomenon in ferroin-catalyzed BZ reaction. The following facts were clarified in this work:

(i) A weak chemiluminescence was observed in the ferroin-catalyzed system, of which intensity oscillated periodically with the same period as redox potential.

(ii) The intensity oscillation of the luminescence was in anti phase with the self-oscillation of the redox potential.

(iii) The periodic oscillation of the luminescence intensity did not disappear after the self-oscillation of the redox potential was extinguished. These results indicated the existence of different routes of oscillatory reactions.

The authors would like to thank Dr. Tomohiko YAMAGUCHI (Nat'l Inst. Materials Chem. Research, Japan) for helpful comments on the reaction processes in BZ reaction. This work was in part supported by the Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Science, Sports and Culture, Japan.

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