Dynamic Photochemical Response of Ruthenium (II)/(III) Redox Chemical Waves in Belousov-Zhabotinsky Reaction

Toshimasa Akagi and Takeko Matsumura-Inoue
Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630

(Received April 1, 1996)

The dynamic photochemical response of $Ru(bpy)_3^{2+}$-catalyzed Belousov-Zhabotinsky (B-Z) reaction was studied in a thin layer solution system with a mask. It was found that stable chemical waves are generated from a masked area and their features are dependent on the chemical components. A high $[MA]_0$ greatly contributes to the photosensitivity of the system.
(MA= $CH_2(COOH)_2$)

It is well known that chemical waves propagate in a target-like or spiral manner in the thin layer B-Z reaction.[1-3] Recently, the photomodulation of chemical oscillations in the B-Z reaction has attracted much attention.[4-7] $Ru(bpy)_3^{2+}$ has often been used as a catalyst of the B-Z reaction because of its excellent photocatalytic activity. The $Ru(bpy)_3^{2+}$-catalyzed thin layer B-Z system under illumination has been studied as a photochemical memory device,[8,9] a new kind of image processor.

The dynamic photochemical response of ruthenium(II)/(III) redox chemical waves were studied to obtain basic information about photochemical memory. When a part of the thin layer was masked with black film against illumination, the chemical waves propagate only from the edge of the masked area to the illuminated area, otherwise they are generated from the reaction surface at random.[10]

It was found that the mask acted as a pacemaker for stable wave generation. This effect of mask is referred to as the "mask effect". The mask effect greatly depends on initial concentrations of the reactants and the intensity of the illumination. As the reaction system is in excitable media under moderate illumination, chemical waves are triggered by mask. With higher illumination, chemical waves are completely inhibited.

Table 1. Ranges of initial concentration of B-Z reactants

$[Ru(bpy)_3^{2+}]_0$ / mM	$[BrO_3^-]_0$ / M	$[MA]_0$ / M
0.2-1.0	0.15	0.12
0.6	0.1-0.3	0.12
0.6	0.15	0.06-0.36

The other concentrations were fixed : $[H_2SO_4]_0$=0.8 M, $[NaBr]_0$=0.08 M.

We studied the mask effect as well as the features of the chemical waves under illumination by changing the initial concentrations of the B-Z reactants as listed in Table 1.

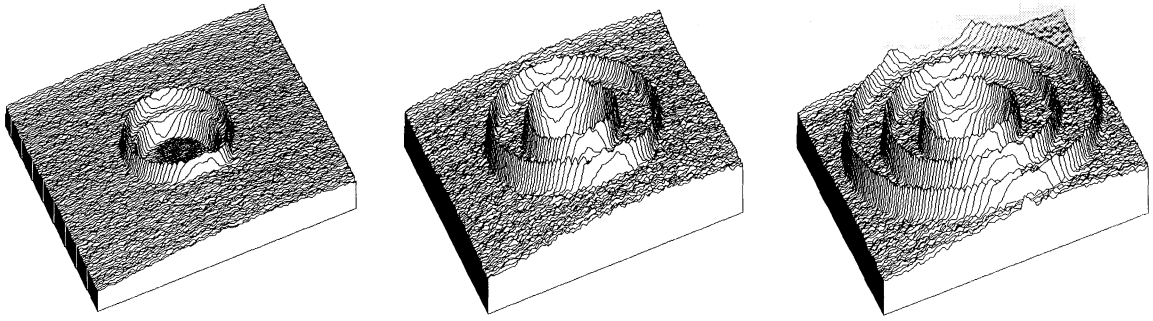
$Ru(bpy)_3(ClO_4)_2$ was synthesized using a microwave method.[11] MA, NaBr, H_2SO_4 were used without further purification. $NaBrO_3$ was recrystallized from water. All stock solutions were prepared with distilled water and were deoxygenated with N_2. The mask size was fixed at 5 mm (in diameter). All the experiments were carried out at 291 K.

The B-Z reaction mixtures were illuminated with visible light around 480 nm using a 200 W halogen-lamp. The light intensity was fixed at 0.20 $mW \cdot cm^{-2}$. Propagation of the chemical waves was monitored with a CCD camera (Victor, TKO-1070) connected to the binocular microscope (Nikon SMZ-U) and recorded as colored images (Visualfield : 20.0x16.2 mm) with a VTR (TOSHIBA, A-790HFD). The recorded images were processed with a personal computer(NEC, PC-9801) for a region of 17.5x15.8 mm.

Figure 1 shows typical three-dimensional images of the chemical waves of $Ru(bpy)_3^{3+}$ taken at suitable intervals during continuous illumination. Figure 1-A is the image of the chemical wave 30 s after the start of the reaction. In Figure 1-A, a central black field corresponded to a masked area and the background to $Ru(bpy)_3^{2+}$ and/or $Ru(bpy)_3^{2+*}$. The chemical waves appeared only from the periphery of the masked area and started to propagate toward the illuminated area. The first wave generated with an induction period of about 30-35 sec. and then the chemical waves successively generate with a constant period (Figure 1-B and C). The period of chemical wave generation becomes shorter as $[MA]_0$ increases.

The stable mask effect occurs under the concentration range, $[Ru(bpy)_3^{2+}]_0$: 0.6-0.7 mM, $[BrO_3^-]_0$: 0.15-0.16 M and $[MA]_0$: 0.06-0.30 M.

It was found that $[MA]_0$ significantly contributed to the photosensitivity of the system. The propagation rate and wavelength (distance between ***n**th* and **(n+1)***th* wave) of the chemical waves decrease with an increase in $[MA]_0$.



A **B** **C**

Figure 1. Typical three dimentional images of chemical wave under continuous illumination.
Initial concentrations : $[Ru(bpy)_3^{2+}]_0$=0.60mM, $[MA]_0$=0.18M, $[NaBrO_3]_0$=0.15M, $[H_2SO_4]_0$=0.8M, $[NaBr]_0$=0.08M

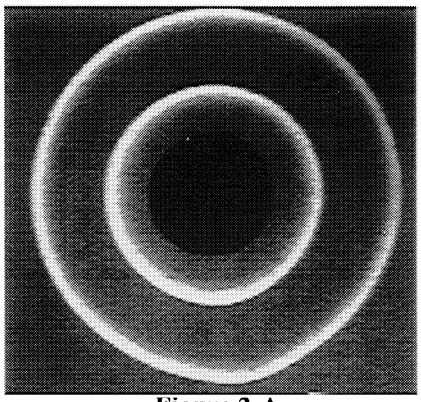


Figure 2-A

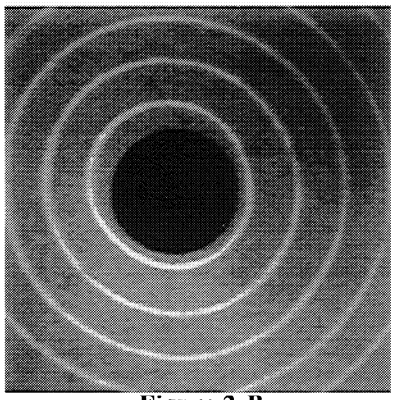
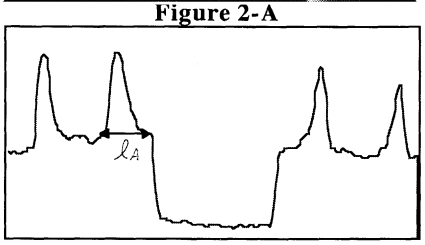
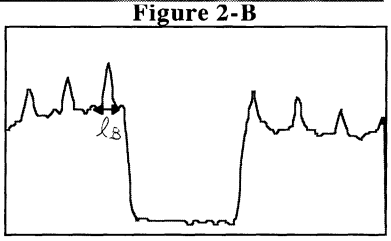


Figure 2-B



0 distance/mm 17.4

Figure 2-A'



0 distance/mm 17.4

Figure 2-B'

Initial concentrations : 2-A,A' : $[MA]_0$=0.06M
2-B,B' : $[MA]_0$=0.18M
The other concentrations were fixed : $[Ru(bpy)_3^{2+}]_0$=0.60mM,
$[NaBrO_3]_0$=0.15M, $[H_2SO_4]_0$=0.80M, $[NaBr]_0$=0.080M
Y-axis : Gray-level intensity (arbitrary scale). A width of chemical wave : $\ell_A > \ell_B$

Figure 2. The photo-image and cross-section of the chemical waves.

When light intensity increased, the maximum limit of $[MA]_0$ for the mask effect decreased.

With higher $[MA]_0$, the B-Z reaction takes place in the region where $Ru(bpy)_3^{2+}$ predominantly exists. Therefore chemical waves propagate in the domain where $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+*}$ predominate, which shortens the life of $Ru(bpy)_3^{3+}$ and sharpens the chemical waves of $Ru(bpy)_3^{3+}$. Figure 2-A and 2-B show the photo-image of the chemical waves and Figure 2-A' and 2-B', their cross-sections for two different $[MA]_0$s. By comparison of these figures, it is clearly seen that the higher $[MA]_0$, the shorter the wavelength, and sharper the image. These findings suggest that chemical conditions, especially $[MA]_0$, affect the dynamic response of the ruthenium redox chemical waves, which contribute to the image processing by the B-Z reaction.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

Reference and Notes

1 R.J.Fieldand R.M.Noyes, *J.Am.Chem.Soc.*,**96**,2001(1974).
2 M.Jinguji, M.Ishihara , and T.Nakazawa, *J.Phys.Chem.*, **94**, 1226 (1990).
3 S.C.Muller, O.Steinbock ,and J.Schutze, *Physica A*, **188**,47 (1992).
4 M.Jinguji, M.Ishihara , and T.Nakazawa, *J.Phys.Chem.*, **96**, 4279 (1992).
5 Y.Mori,Y.Nakamichi,T.Sekiguchi,N.Okazaki, T.Matsumura, and I.Hanazaki, *Chem. Phys. Lett.*, **421**, 211 (1993).
6 V.Gáspár, G.Bazsa ,and M.T.Beck, *Z.Phys.Chem.(Leipzig)*, **264**,43(1983).
7 T.Matsumura, Y.Nakamichi, T.Akagi, and Y.Yamaguchi, *Abstract of the International Workshop on Dynamism and Regulation in Non-linear Chemical Systems*,Tsukuba , Japan (1994), p151.
8 L.Kunert, *Nature* , **319**, 393 (1986).
9 L.Kunert, K.I.Agladze , and V.I.Krinsky, *Nature* , **337**, 244 (1989).
10 M.Jinguji, M. Ishihara, T. Nakazawa, and H. Nagashima, *Physica D*, **84**, 246 (1995).
11 T.Matsumura-Inoue , M.Tanabe , T.Minami , and T.Ohashi, *Chem. Lett.*,**1994**, 2443.