Propagating Waves and Pattern Formation in a Reaction-Diffusion System with Pyrogallol as Substrate

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The striking similarity between the nonlinear dynamical phenomena in chemical systems and those in biological systems, has enhanced the interest in the search of new reaction - diffusion systems. Here we report an oscillatory chemical system, which exhibits different types of chemical waves and patterns when kept unstirred. The reaction constituents are 1,2,3-trihydroxybenzene (pyrogallol), ferroin, sulphuric acid and potassium bromate. The system has a significant advantage of being gas-free.

Propagating waves leading to complex pattern formation in chemical[1,2] and biological[3] systems have gained a lot of interest in the past few years.

Propagating wave behavior has been observed in living organisms and biological tissues such as cardiac muscle tissue[4] aggregating slime mold cells[5], chicken retina[6], Xenopus laevis oocytes[7] and chemical systems[8] like the Belousov - Zhabotinsky (B-Z) reaction. Among these, the chemical system is very versatile because of its simplicity and reproducibility. An understanding of the reaction - diffusion mechanism of these chemical systems can often be qualitatively transferred to the biological systems which are otherwise very difficult to be analysed. For example, the familiar rotating spiral waves in B-Z systems are found to be the precursors of ventricular tachycardia[9]. Apart from this, the chemical medium developing propagating waves can also provide the basis for information processing and can be used as an image processor[10,11]. With such a wide applicability, any new report on the propagating waves is of current interest. For the first time, we report the formation of propagating waves and pattern formation in a system containing 1,2,3-trihydroxybenzene (pyrogallol, PG) - ferroin-sulphuric acid and bromate. Generally, systems with aromatic compounds exhibiting spatial dynamics are very rare[12].

The malonic acid - ferroin (or) $Ru(bpy)_3^{2+}$ - sulphuric acid - bromate system is perhaps the most commonly employed tool for experiments on chemical waves and pattern formation[13,14]. But an important drawback of this system is the production of CO_2 during the reaction resulting in the formation of bubbles that disturb the reaction - diffusion patterns thereby rendering it impossible to study for longer periods. It is noteworthy to mention that the PG - ferroin -sulphuric acid - bromate system is one of the bubble free system and also exhibits rich spatial dynamics as that of the malonic acid system.

The spatial behavior was studied with the reaction solution spread over a petri dish as a thin layer. Initially PG (0.048 M), ferroin (1.5 x 10^{-3} M), sulphuric acid (1.0 M) and potassium bromate (0.12 M) were well stirred until the first colour change from red to green occurred (induction time). Then the reaction mixture was poured in a thin layer in a petri dish of 8.6 cm diameter. The depth of the solution was varied from 0.85 to 2.6 mm. Similar behavior was observed in all the cases and the optimum reaction layer (1.6 mm) was chosen when the pattern could be clearly photographed. With lower reaction depths, the colour change was very feeble and hence could not be photographed clearly. All the experiments were carried out at a temperature of 30 ± 0.1° C. The petri dish was covered so as to eliminate the volatilisation of molecular bromine and the effect of atmospheric oxygen. The waves were initiated adventitiously at a dust particle or other heterogeneous center. The petri dish was illuminated with a white light of 25 W which helped to observe and capture the patterns formed. The images were captured as one frame per second with a charge-coupled device (CCD) video camera. The captured images were digitised and stored in a computer and then processed with a Halodesktop Image Scanner system.

After the induction time, when the solution (green in colour) was poured into the petri dish, the solution turned red as a consequence of bulk oscillation. Then the green coloured oxidising bands moved into the bright red coloured reduced medium of the solution. Depending on the initial concentration of the reaction mixture, the waves moved slowly as bands, Figure 1 or fastly as wave trains,

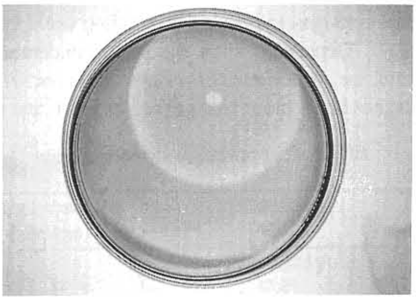

Figure 1. The propagating oxidation bands in the Pyrogallol-Ferroin-Sulphuric acid - Potassium bromate system. Concentration conditions: [PG] = 0.048M;$[H_2SO_4]$ = 0.75M; [Ferroin] = 1.5×10^{-3}M; $[KBrO_3]$= 0.12M; Temperature = 30 ± 0.1°C.

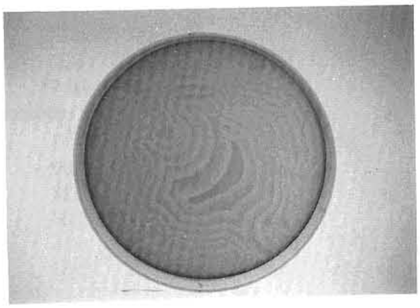

Figure 2. The fast moving wave trains at higher acid concentration, $[H_2SO_4]$ = 1.0M; Other concentrations are the same as given in Figure 1. Waves from two different pacemaker centers gets annihilated.

Figure 2. We also obtained the familiar target and spiral wave patterns in this system, Figure 3. The patterns persisted for one to several hours under these batch conditions. After that the intensity of colour due to ferroin and ferrin gradually faded as the reactants were consumed and subsequently the solution remained red

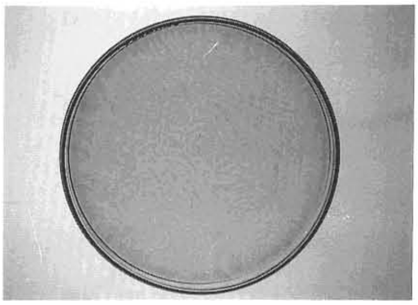

Figure 3. Photograph taken after 30 minutes following initial mixing. Initial reactant concentrations are same as in Figure 2. The pattern formed persisted for several minutes and then the solution slowly became red in colour.

corresponding to the reduced form of the catalyst. The propagating waves approaching each other from two different pacemaker centers get annihilated as in the usual reaction - diffusion systems.

The wave velocity was found to depend strongly on the initial concentration of the reagents. Velocity measurements were always made on bands moving into the bright red and where no other band had passed. These velocities are easier to interpret than those when bands may be interacting. Five series of experiments were conducted to determine the effect of reactant concentrations on the wave velocity. In each series, the concentration of one reactant was varied over a range and those of the other reactants were held constant. The concentration ranges and the corresponding wave velocities are given in Table 1. Depending upon the initial concentration of the reaction mixture, we encountered two types of waves: (i) The whole solution undergoes bulk colour change (red to green and vice versa).

Table 1. Effect of concentration on wave velocity

S.No.	Constituent [M]	Wave velocity (mm/min)
1.	[Sulphuric acid]	
1.1	0.75	4.50
1.2	1.0	7.07
1.3	1.25	9.75
1.4	1.50	Phase waves
1.5	1.75	Phase waves
2.	[Potassium bromate]	
2.1	0.10	4.71
2.2	0.12	7.07
2.3	0.14	8.37
2.4	0.16	10.47
2.5	0.18	Solution remained stable
3.	[Pyrogallol] x 10^2	
3.1	2.8	9.00
3.2	3.8	7.28
3.3	4.8	7.07
3.4	5.8	6.56
3.5	6.8	5.63
4.	[Ferroin] x 10^3	
4.1	0.5	7.07
4.2	1.5	7.07
4.3	2.0	6.75
4.4	2.5	7.90
4.5	3.5	7.28

Standard concentration condition: [PG] = 0.048M; [H_2SO_4] = 1.0 M; [ferroin] = 1.5 x 10^{-3} M; [$KBrO_3$] = 0.12M; Temperature = 30 ± 0.1° C. The concentration of one of the constituents was varied in each series of experiments.

These are phase waves. (ii) On the other hand, waves are generated periodically with a constant velocity around a heterogeneous center. These are trigger waves. In our experiments, except under two conditions (S.No.1.4 and 1.5 in Table 1), in all other cases, the medium developed trigger waves. Under these two conditions the medium developed phase waves for the first few minutes and subsequently formed trigger waves brought about by diffusion. In all cases the initial wave velocities were determined. But for these two concentrations, because of the time delay in the formation of trigger waves, the determined velocity was not comparable with that of the other velocities.

As in the case of usual malonic acid - ferroin - sulphuric acid - bromate system, the wave velocity depends strongly on the concentration of acid and bromate and is almost independent of the catalyst (ferroin) concentration. Moreover the wave velocity depends markedly on the concentration of the substrate (pyrogallol) also. To our knowledge, this is the first example in which the chemical waves strongly depend on the concentration of the organic substrate. This is because of the fact that apart from acting as a substrate, pyrogallol is involved in the generation of $HBrO_2$ also[15] which is not so with malonic acid or any other aliphatic substrate.

Thus, the preliminary experiments conducted on this system, clearly establish its versatility like that of other reaction-diffusion systems, with the additional advantage of being gas-free. The formation of three dimensional waves in the B-Z reaction can be disturbed even by the slightest perturbation like the evolution of gas bubbles. So a gas-free system would be ideal for the studies of three dimensional waves. Since it is bubble free, the system also exhibits excellent three dimensional wave forms when studied in vertical tubes with wide diameter. Our future work is focussed on these three dimensional waves which are quite significant and interesting[16]. Thus a detailed investigation of the wave behavior of the present system which is currently underway, would establish it to be a new reaction - diffusion system convenient for the study of spatial dynamics.

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