Mechanism of Trees / Bushes Like Pattern in Chemical System

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Abstract: Trees / bushes like pattern have been investigated in succinic acid + ethylacetoacetate + BrO_3^- + $\text{Fe}(\text{phen})_3^{+2}$ + Ce^{+4} + H_2SO_4 system at 30 °C in a petridish after 6 hours. These patterns are dependent on initial concentration of reactants and temperature. The system first shows fast appearing / disappearing blue and red pattern then bifurcate into concentric waves and finally shows a tree / bushes type pattern which grows in length and breadth against time. Microphotographs of trees / bushes pattern, succinic acid and ceric ammonium sulphate shows that a new compound has been formed which is responsible for this pattern. It is further confirmed by X-ray powder spectrum of trees / bushes pattern material and succinic acid. IR spectra of pattern material show that presence of cyclic compound in which Ce^{+4} ion coordinated by hydroxyethylacetoacetate. A tentative mechanism of pattern formation is proposed.

Keywords: Trees, bushes like pattern, Mechanism, Coordination, Hydroxyethylacetoacetate

Introduction

Reactions that show oscillations in open system give rise to a range of interesting wave behaviour in unstirred systems. Clock reactions give rise to one-off reaction-diffusion fronts, with the reactants being completely consumed as the front passes¹⁻². In B-Z-type systems, the front corresponds to a wave of reactions involving the intermediates, with little consumption of major reactants. The system have a wave “break” following the front, returning the systems to its original, pre-front state and gives rise to a pulse. If there are further initiations, the system will also be able to support further waves, possibly giving rise to a series of pulses, a wave train. These wave trains can organize the reaction mixture in two or three dimensions into a variety of intricate evolving patterns³⁻⁵. Many of these studies of waves in the B-Z system have been carried out in thin films of solutions in petridish. The simplest situation arises when the reaction mixture is excitable, rather than spontaneously

oscillatory⁶. A point source initiation then naturally gives rise to an expanding circular wave pulse. Once these have expanded sufficiently, they propagate much as one-dimensional wave's. In the presence of a periodic or continuous stimulations, a series of concentric rings, giving rise to a target patterns of blue circles nested on red background, emerges. The inner rings rely on the resetting of the intermediate concentration and so are not possible in one-off clock type reactions. The spontaneous initiation of the waves in a target pattern appears to rely on the presence of heterogeneities, such as the presence of dust-particles or defects in the surface of the petridish. Careful filtering suppresses this spontaneous initiation in excitable systems. Each target reflects the frequency of the initiation at its center. If this is caused by random heterogeneities, different target cores may naturally have different frequencies. The speed of the waves varies from one target to another, with low frequencies leading to higher velocities. These two effects mean that the waves are more closely spaced for high frequency sources, *i.e.* these have a shorter wavelength. When waves from two targets collide, they annihilate each other. As the subsequent wave for the higher frequency patterns comes closer on the heels of the annihilated wave than that for the low frequency source, the next collision occurs closer to the later. Over the course of several collisions, waves from the higher frequency source eventually reach the vicinity of the low frequency core, which is then also annihilated. Higher frequency targets grow at the expense of low frequency ones; given sufficient time, the higher frequency source will entertain the whole dish. For a given target pattern also reveals that the outer most wave travels at a slightly higher speed than subsequent, inner waves, all of which have essentially the same speed.

Far from, equilibrium growth phenomena⁷⁻⁹ has been reported in electrochemical deposition. Irreversible aggregation of small particles to form large clusters is technologically and scientifically important¹⁰⁻¹². The formation of patterns and shapes of chemical and biological systems have considerable interest. The study of morphological stability of growing bodies, crystal growth, development of chemical waves and rhythmic crystallization in gel media offers one possibility for investigating non-equilibrium structures in physicochemical and biological systems¹³⁻¹⁴. Euclidean geometry have been used to model man-made objects¹⁵ and fractal geometry to model natural objects in computer.¹⁶⁻¹⁷ Bushes and tree like patterns in B-Z system seems to be interesting for elucidating the mechanism of natural patterns in biological systems.

Experimental

Succinic acid, ethylacetoacetate, H₂SO₄ (CDH), FeSO₄ · 7H₂O (S.D. Fine) 1-10-phenonphthrolin (CDH), ammonium ceric sulphate and KBrO₃ (E.Merck) of analytical grade were used as such without further purification. Experiment was performed in a completely flat petridish of 9.1 cm inner diameter. The experimental table was completely labeled by sprit level. The movement of the front and growth of the trees and bushes like pattern were measured by cathodometer. The photographs of patterns were taken by a zoom lens camera. The pattern material was completely soluble in methanol, and was purified by recrystallizing in methanol. The microphotographs of the crystallized pattern material were taken by Carlzeiss's ZENNAMED-2 electronic microscope with photographic attachment at the magnification of 400X. The IR spectrum was taken by an ABB Bomen FTLA 2000 FT-IR. X-ray spectrum was taken by Rigaku X-ray spectrophotometer.

Results and Discussion

Ethylacetoacetate = [0.1212 M], Succinic Acid = [0.1016 M], Ceric ammonium sulphate = [0.00486 M], Fe (Phen)₃⁺² = [0.0038 M], H₂SO₄ = [0.42 M] was taken in a petridish 9.1 cm (*i.d.*)

and thickness of the solution was kept 0.1 cm. The reaction was started by adding $\text{BrO}_3^- = [0.0553 \text{ M}]$ and making it homogeneous. Immediately after addition of BrO_3^- red color of solution turns into blue color and after a break of a minute it again turns into red color. Then color of the solution changes periodically from blue to red for 5 to 8 cycle within two to three minutes with decreasing frequency. A few stages of the color change are shown in Figure 1.

Figure 1. Fast appearing pattern up to 3 minutes.

Composition: Ethylacetoacetate $[0.1212 \text{ M}]$, Succinic Acid, $[0.1125 \text{ M}]$, Ce^{+4} $[0.00486 \text{ M}]$, $\text{Fe}(\text{phen})_3^{+2}$ $[0.0038 \text{ M}]$, H_2SO_4 $[0.42 \text{ M}]$, BrO_3^- $[0.0553 \text{ M}]$, Petridish (id) = 9.1 cm, thickness of solution = 0.1 cm. Temp = 30°C . (a) = after 30 seconds (b) after 90 seconds (c) after 150 seconds.

Immediately after this fast pattern the system bifurcate to a stable red color for about one minute. After this break, the system shows concentric circular waves nucleation at some point in the petridish and moves outward with definite velocity. The single nucleation containing about 14 to 17 concentric wave fronts as shown in Figure 2.

Figure 2. Number of concentric front nucleated against time. Concentration and conditions are same as in Figure 1.

The front velocity subsequently decreases with time *i.e.* velocity of second front is less than first, the velocity of third front is less than second front and so on. A typical photograph is shown in Figure 3. Several others nucleation's also occurs simultaneously and follows the same pattern. These nucleation processes continue to occur up to 10 to 15 minutes. When waves of two different nucleated fronts at different frequencies collides each other, the high frequency front inhilates low frequency front. Further, this high frequency fronts collides with other

nucleated wave fronts and inhilates. Finally waves merges into a few concentric big ring and becomes stationary for 5 to 8 minutes, subsequently outer ring disappears first and gradually all rings disappears. These phenomena occur up to about 25-30 minutes from the beginning of the reaction. After that color of the phenomena turns to red. The first fast appearing and disappearing waves are appears to be due to oxidation and bromination of ethylacetoacetate corresponding to high frequency oscillations and second pattern are due to low frequency oscillations¹⁸. Again after 60 minutes from the beginning red color of the system turns blue which are remain stable for two hours. Then system shows red (liquid) nucleation on blue background of the system. These nucleations are not homogeneous throughout the petridish, which moves slowly in irregular manner. The process continues up to three hours. The concentration of red color increases with time and finally solid nucleation starts on red background. It I thought that this process is very significant in tree like pattern formation. Since there are new products formed and concentration of these products fluctuates in fascinating order. These fluctuations of concentration of products determine the shape, size and morphology of patterns.

Figure 3. Photographs of concentric wave pattern and nucleation. Concentrations and conditions are same as in Figure 1. (a) after 4 min (b) after 6 minutes (c) after 12 min.

After this break, systems show small nucleation at few places in the petridish and grow slowly into the form of trees / bushes type pattern both in height and breadths. A typical growth velocity is shown in Figure 4.

Figure 4. Growth of trees / bushes pattern against time. Concentration and conditions are same as in Figure 1. I = vertical growth, II = horizontal growth.

The system takes 3 to 4 hours to produce fully grown trees / bushes like pattern. A typical photograph taken by a zoom lens camera is shown in Figure 5. The shape and nature of these trees / bushes like pattern changes on varying the initial concentration and condition of reactants. The color of the fully-grown pattern varies from yellow to red depending upon the initial composition of reactants and reaction temperature. On increasing the concentration of succinic acid pattern formed early but height and length decreases. This pattern remains stable up to 100 hours and then slowly decomposes. On keeping this pattern in a desiccator, it can be preserved for a long time. This means the pattern material is hygroscopic in nature. Atmospheric moisture destroys the structure.

Figure 5. Photographs of trees / bushes patterns.

Concentration and conditions are same as in Figure 1, except a = Succinic Acid [0.1016 M], b = Succinic Acid [0.1125 M], c = Succinic Acid [0.1380 M], and d = Succinic Acid [0.1380 M], after 100 h.

It was thought that pattern might be due to crystallisation of succinic acid or ceric ammonium sulphate. Therefore, the pattern material was purified by column chromatographic technique by taking methanol as solvent. Further, the pattern material was re-crystallized in methanol. The microphotographs of crystallized pattern material taken by Electronic microscope is shown in Figure 6(a) & 6(b), which shows several nodes and branching in the form of long thin wires bunched together as appears in the structure. The microphotographs of succinic acid and ceric ammonium sulphate are shown in Figure 6(c) & 6(d) respectively. The microphotograph of ceric ammonium sulphate shows small particles of yellow color material is uniformly distributed over the plate. Whereas microphotograph of succinic acid shows thick crystals of small size uniformly distributed over the plate. It is evident from the microphotographs of crystallized pattern material that the pattern material is entirely different product formed by periodic precipitation of two reaction products. It is further confirmed by X-ray diffraction pattern of crystallized pattern material and that of succinic acid. X-ray diffraction pattern of pattern material and succinic acid are shown in figure 7(a) and 7(b) respectively, which the pattern material is crystalline in nature entirely different than succinic acid.

Figure 6. Microphotograph of trees / bushes like pattern material along with microphotographs of succinic acid and ceric ammonium sulphate. (a) & (b) = pattern material, (c) = succinic acid, (d) = ceric ammonium sulphate.

Figure 7. X-ray powder spectrum of trees / bushes pattern material along with X-ray powder spectrum of succinic. (a) Pattern material (b) Succinic acid.

Mechanism of reactions

Shelter and Shefford¹⁸ have reported that oxidation and bromination of ethylacetoacetate by bromate produces dibromoethylacetoacetate, hydroxy ethylacetoacetate and formyl acetone.

It appears that the fast appearing / disappearing patterns and concentric ring pattern are due to oxidation / bromination of ethylacetoacetate. Further, four molecules of hydroxyl-ethylacetoacetate reacts with $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4$ in aqueous acidic medium and forms a Ce^{IV} (hydroxyethylacetoacetate) $_4$ which appears as clody material before the start of solid pattern nucleation. Simultaneously succinic acid decarboxylate and forms propionic acid. The oxidation of propionic acid in presence of cerium ion in acidic medium forms formyl acetic acid which undergo autooxidation to form malonic acid and finally dibromomalonic acid. Further, Ce^{IV} (hydroxyethylacetoacetate) $_4$ combines periodically with four $(-\text{CH}_2-)$ or $(-\text{CBr}_2-)$ or both unit of decarboxylated malonic acid/dibromomalonic acid to form trees / bushes like pattern (IV) or (V) or (VI). It is evident from the structure (IV), (V) and (VI) that it manifest the growth of pattern in all directions, as a reaction Scheme 1.

Scheme 1.

.....R₄

The structure IV, V and VI of the pattern material is supported by the FT-IR spectrum as shown in Figure 8. This shows the presence of several bands¹⁹⁻²³ below 1700 cm^{-1} . A careful study of the spectrum shows the presence of cyclic structure as ring breathing band at 1598 cm^{-1} , 1542 cm^{-1} and 1510 cm^{-1} are present, along with C-H deformation bands in di / tri substituted cyclic system at 885 cm^{-1} and 849 cm^{-1} . The spectra shows the presence of metal – oxygen band at 575 cm^{-1} and the presence of C-O stretching in metallic ester due to 1069 cm^{-1} and 1286 cm^{-1} vibrational band. Carbonyl (C=O) stretching band at 1700 cm^{-1} and bending vibration band at 1325 cm^{-1} , are also present. Further, -C-O-C- stretching vibrational band at 1005 cm^{-1} , C = C stretching vibrational band at 1616 cm^{-1} , C-Br stretching vibrational band at 614 cm^{-1} , $\text{OCH}_2 - \text{CH}_3$ stretching vibrational band at 717 cm^{-1} alongwith C-H deformation.

Figure 8. FT-IR spectrum of trees / bushes pattern material for conditions shown in Figure 1.

It appears that both the succinic acid and ethyl acetoacetate organic substances are important for trees / bushes pattern. This pattern does not occur with a single substrate as succinic acid or ethylacetoacetate. This pattern does not occur without ceric ammonium sulphate. Pattern is very sensitive to temperature, the time required for pattern formation decreases with increasing temperature. On increasing the thickness of the solution in petridish time required for tree / bush pattern increases. Pattern does not formed on closing the petridish, however pattern nucleates soon after removing the transparent cover of the petridish. If the pattern is half grown and we cover the petridish, no affect observes on growth. This shows that dehydration equilibrium is very important and is favours the pattern formation.

Effect of oxygen on trees / bushes pattern

It appears that oxygen play an important role in the last pattern formation, which is evident by the following experiments, on closing the petridish with transparent cover last pattern does not appear even for a long time. If we remove the cover of petridish pattern nucleates soon. To test the effect of oxygen on trees / bushes pattern, bromate from the reaction mixture was removed. It was found that in absence of bromate weak patterns appears, but growth of structures are very

weak and small shown in Figure 9(a) & 9(b) and depends on concentration, temperature and acidity. The microphotograph of pattern material in absence of bromate is shown in Figure 10. The formation of weak structure in absence of BrO_3 can be explained on the basis of Scheme I. Oxidation of ethylacetoacetate into hydroxyethylacetoacetate in absence of bromate is very slow and formation of dibromalonic acid is not possible. Therefore, a limited concentration of hydroxyethylacetoacetate is available for formation of $\text{Ce}^{\text{IV}}(\text{hydroxyethylacetoacetate})_4$. $[\text{Ce}^{\text{IV}}(\text{hydroxyethylacetoacetate})_4]$ combines with four $(-\text{CH}_2-)$ unit of decarboxylated malonic acid which is available in limited concentration to form only structure IV. Therefore, pattern structure formed is small, thin, unbranched and spread uniformly throughout the petridish.

Figure 9. Photographs of trees / bushes like pattern in absence of bromate and ferroin, (a) Succinic Acid, [0.128 M], Ce^{+4} , [0.022 M], Ethylacetoacetate, [0.120 M], H_2SO_4 [2.5 M], (b) Succinic Acid, [0.128 M], Ce^{+4} , [0.022 M], Ethylacetoacetate, [0.120 M], H_2SO_4 [1M], $id = 9.1$ cm, thickness of solution = 0.1 cm, Temperature = 30°C .

Figure 10. Microphotographs of trees and bushes like pattern without bromate and ferroin concentrations and conditions are same as in Figure 9.

Effect of solvent on trees / bushes pattern

The pattern material IV, V and VI are solvolized in polar solvents such as methanol and water. On dissolving the pattern materials into methanol, it solvolized as structure VII, VIII and IX. On evaporating the solvent molecules for 2 to 3 hours they re-agglomerate and form similar pattern. Similar behaviour was observed in water except time of agglomeration which is 7 to 8 hours.

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