Nucleation Phenomenon in Oscillatory Reactions

R. P. RASTOGI, K. SINGH, P. RASTOGI & R. B. RAI

Chemistry Department, University of Gorakhpur, Gorakhpur 273001

Nature of nuclei formation in a oscillatory reaction system, viz citric acid/Mn^{2+}/$KBrO_3$/H_2SO_4 has been investigated; both temporal and space oscillations have been examined. Time of initiation of temporal oscillations is not associated with heterogeneous nucleation and hence remains the same for filtered reagents or when CO_2 is bubbled through the solution. It is significant that the chemical waves originate from the points where blue specks are first formed. Bands appear at heterogeneous centres or dust particles or at glass surfaces. The time of appearance of waves is enhanced when filtered solutions are used. It has been concluded that nucleation of a chemical wave and nucleation of a new phase have a formal similarity.

IN view of current interest in oscillatory chemical reactions[1-3] and chemical waves[4-7], attention has also been focussed on several phenomena associated with these. For instance, thermochemistry of oscillatory reactions has been studied[8]. Other phenomena like nucleation are also equally important in understanding the mechanism, for example, a certain time of initiation is usually needed for oscillations to start in a typical oscillatory system. The chemical waves have also been observed to be triggered after a time-lag and that too at different centres at random. The question therefore arises whether nucleation is essential for the appearance of oscillatory phenomenon? If so, what is the nature of nuclei formed?

In this paper, we report interesting experimental data which throw light on the nature of nuclei formation in an oscillatory reaction system. We have investigated both temporal and space oscillations from this angle.

Materials and Methods

Chemical waves — The waves were generated in the system citric acid/Mn^{2+}/$KBrO_3$/H_2SO_4. A mixture of solutions of desired concentrations of manganous sulphate and citric acid in sulphuric acid was taken while potassium bromate was taken separately in a cell[9]. The cell was kept in an air thermostat maintained at a constant temperature. When both the solutions attained a constant temperature, potassium bromate was mixed with the mixture of manganous sulphate and citric acid. Resulting mixture was stirred continuously. This mixture was allowed to undergo temporal oscillations for a fixed time. Two types of experiments were performed. In the first set of experiments, solutions were unfiltered and tubes were used without previous cleaning. In the second set of experiments, the solutions used were filtered through Sartorius membrane filter papers (pore size 120 μ) and the tubes were previously cleaned by steaming. The two sets of experiments were performed simultaneously in order

to have comparative data and the same time of reference. In each set of experiments the reaction mixture (5 ml) was poured into 30 cm long tube of diameter 0·5 cm. 0·5 ml of ferroin indicator (unfiltered) and the same amount of ferroin filtered through membrane filter paper were added in the two sets of experiments. Both the tubes were inverted 3-4 times simultaneously to mix the indicator thoroughly. After this the tubes were fitted in a stand and a stopwatch was switched on. The time taken for the appearance of the first wave front in both the tubes was noted. The experiments were repeated a number of times.

Attempts were made to generate waves using Zhabotinskii reagents using different organic substrates. Waves were formed with malonic acid, malic acid and citric acid, but no waves were formed with acetylacetone.

Time oscillations — The experiments for time oscillations were performed in the usual manner[9]. In one case solutions of desired concentrations of manganous sulphate and citric acid in sulphuric acid were taken in a cell. The reaction was started by adding potassium bromate to this mixture. From the potentiometric trace of the electronic recorder, time of initiation was noted. In other case the cell was steamed and all the reagents were filtered through Sartorius membrane filter paper before use. Time of initiation in this case was also noted from the potentiometric trace. Both the experiments were repeated several times. The experiment was repeated by bubbling CO_2 in the reaction mixture. The time of initiation for this case was also noted. The results are presented in Table 1.

Formation of Leisegang rings — Attempts were made to generate Leisegang rings by the procedure adopted by Chatterji[10]. Rings of PbI_2 were generated in silicic acid gel and agar-agar gel.

Surface tension measurements — The oscillating mixture containing citric acid/Mn^{2+}/$KBrO_3$/H_2SO_4 was taken and ferroin was added. The colour of the solution alternatively changed from red to blue. The surface tension of the oxidized and reduced

state of the reaction mixture was determined by a stalagmometer in the usual way. Observations show that there is no significant difference in the surface tensions of the two states.

Results and Discussion

Experiments on time of initiation of temporal oscillations described above show that it is not associated with heterogeneous nucleation and hence the time is unaltered when (i) filtered reagents are used (Table 2) and (ii) CO_2 is bubbled through the solution (Table 3). This is expected since the time of initiation is just the time required to reach the neighbourhood of steady state.

However, the situation is different in the case of waves. Our experiments on chemical waves show that: (i) waves originate from blue nuclei; (ii) the wave fronts can move in all directions; (iii) bands appear at heterogeneous centres or dust particles or at glass surfaces; (iv) the time of appearance of waves is enhanced when filtered solutions are used (Table 2); (v) waves are not formed in acetylacetone, these are formed in a very limited concentration range in the case of malic acid system; (vi) chemical waves are observed with ferroin only; (vii) frequency of appearance of red and blue bands in the lower part of the tube is larger than that in its upper part; (viii) the intensity of red and blue colours of the bands gradually diminishes with time; (ix) the reacting system becomes almost colourless after about 24 hr; and (x) the gas bubbles sticking to the wall of the tube are larger in number in the experiment wherein the frequency of the waves is large.

Observations (i) to (iii) are similar to those reported earlier[6,7]. It is significant that the chemical wave originate from the points where blue specks are first formed. In all the cases reported so far, chemical waves are always produced in a reduced medium and the nuclei of blue oxidized band is first formed. This is probably due to the fact that the chemical waves are triggered as soon as the Ce^{4+} or Mn^{3+} is produced in excess and the reaction (1) is favoured

$$BrO_3^- + 5Mn^{+2} + 6H^+ \rightarrow 5Mn^{+3} + \tfrac{1}{2}Br_2(aq) + 3H_2O \quad ...(1)$$
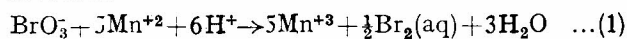
It has been pointed out by Noyes et al.[2] that the reduction product of BrO_3^- is HOBr and the above reaction is not kinetically favoured. However,

TABLE 1 — TIME OF APPEARANCE OF CHEMICAL WAVES*

{[Citric acid] = $0.128M$; [MnSO$_4$] = $0.0032M$; [KBrO$_3$] = $0.044M$; [H$_2$SO$_4$] = $1.5M$; time for temporal oscillation = 30 min; temp. = 37° ± 0.05°}

Run	Time of initiation (sec) in		Difference (sec)
	Steamed tube	Unsteamed tube	
1	440	288	152
2	323	148	175
3	460	200	260
4	470	258	220
5	274	224	50
		Av.	171

*Results of each run were taken simultaneously and with same time of reference.

TABLE 2 — TIME OF INITIATION OF OSCILLATORY REACTION OF UNFILTERED AND FILTERED USING SARTORIUS MEMBRANE FILTER PAPER

{[Citric acid] = $0.032M$; [MnSO$_4$] = $0.0032M$; [KBrO$_3$] = $0.044M$; [H$_2$SO$_4$] = $1.5M$; temp. 31·0° ± 0·05°}

Run	Time (sec) of initiation with filtered solution	Time of initiation with unfiltered solution
1	150	150
2	162	155
3	157	160
4	152	154
	Av. 155 ± 4	Av. 155 ± 3

TABLE 3 — EFFECT OF CO$_2$ BUBBLING ON TIME OF INITIATION OF OSCILLATIONS

{[Citric acid] = $0.032M$; [KBrO$_3$] = $0.044M$; [MnSO$_4$] = $0.0032M$; [H$_2$SO$_4$] = $1.5M$; temp. = 35° ± 0·05°}

Run	Time (sec) of initiation on bubbling CO$_2$	Time of initiation with no CO$_2$
1	100	102
2	104	102
3	100	104
4	98	100
	Av. 101 ± 2	Av. 102 ± 1

the above reaction can possibly occur at heterogeneous centres. Supersaturation of Br_2 perhaps occurs locally and the nucleation of Br_2 occurs at the heterogeneous centres like dust particles. Thus there is a time-lag in the appearance of waves and the waves are triggered by pace-makers like dust particles. Since, Br_2 is quickly consumed in the reaction with acetylacetone, the above type of supersaturation phenomenon cannot occur and no wave formation takes place with acetylacetone.

Oxidation reaction is more exothermic and hence the oxidized band would be lighter[7,8]. However, it is observed that blue band moves both ways with the same velocity and hence the wave formation is not related to the formation of convection currents due to thermal gradients. Further, since waves are formed even when previously well-mixed solutions are poured in the tube, the formation of waves cannot be ascribed to concentration gradient or density gradient as postulated by Kopell and Howard[11].

The above arguments show that nucleation of a chemical wave and nucleation of a new phase have a formal similarity.

Several workers have postulated that transition between one stable state to another involves supersaturation. Formal analogy with the theory of phase transition between stable states (between oxidized and reduced states in the present case) has been examined by several workers[12,13]. Nucleation in systems with multiple stationary states has also been examined[14]. On the basis of a stochastic theory, expression (2) has been deduced for the radius R_c of the critical nucleus

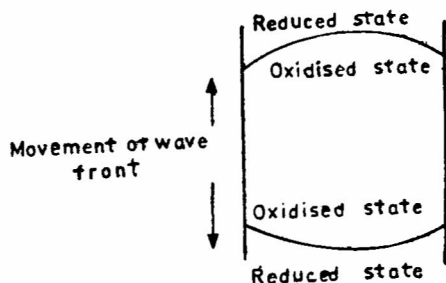$$R_c = \frac{D(\Psi_B - \Psi_A)^2(d-1)}{1\{G(\Psi_B] - G[\Psi_A]\}} \quad ...(2)$$

Fig. 1 — Nature of the interface between the oxidized and the reduced states

where D = diffusion coefficient; Ψ_B = column vector of concentration in state B; Ψ_A = column vector of concentration in state A, d = dimensionality; l = thickness of zone; $G[\Psi_B]$ = free energy in state B; $G[\Psi_A]$ = free energy in state A.

According to Eq. (2) $R_c \to \infty$ when $G[\Psi_B] \to G[\Psi_A]$. In other words, under such circumstances a wave front would be a horizontal plane. However, in actual experiment we get an undefined curvature and hence $G[\Psi_B]$ is expected to be different from $G[\Psi_A]$. There is no direct method of evaluating $G[\Psi_B] - G[\Psi_A]$. Consequently, it is difficult to estimate R_c for an actual case.

Thus, in the present case, transition from oxidized state to reduced state occurs. Since, the colours of the two states are different, these constitute different phases. The Gibbs free energy of the two states would be different, since pressure and concentrations would vary in the two states. The nature of the interface between the two states in actual experiment is found to be as shown in Fig. 1.

Since, the curve is concave towards reduced state, it shows that pressure of the oxidized state is greater than the pressure of the reduced state[15]. Further, the pressure difference would be given by Eq. (3)

$$\Delta P = \Upsilon \left[\frac{1}{R_1} + \frac{1}{R_2} \right] \qquad \ldots(3)$$

where R_1 and R_2 are the principal radii of curvature of the interface and Υ is the interfacial tension.

In order to examine whether Leisegang rings and chemical waves have any similarity, formation of Leisegang rings was investigated. The rings of PbI_2 were found to be made up of tiny crystals suspended in the medium. Apparently, when Pb (NO_3^-) is added from the top and the first nuclei of PbI_2 is formed, iodide ions diffuse from the surroundings, thus depleting the concentration of iodide ions. Consequently, a region is created where solubility product of PbI_2 cannot be reached. However, on further diffusion of $Pb(NO_3)_2$ downwards, fresh nucleation starts at fresh centres giving rise to periodic precipitation. The phenomenon is different from chemical waves since in the latter case actual propagation of wave occurs. Further work is in progress.

Acknowledgement

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