A Dual-Phase Oscillatory Behavior in Belousov– Zhabotinsky System with Vanillin as the Substrate

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ABSTRACT: Dual-phase oscillations are observed in Belousov–Zhabotinsky system with 4-hydroxy-3-methoxybenzaldehyde (vanillin) as the substrate and manganous sulphate or ammonium Ce(IV) sulphate as the catalyst. The nonoscillatory period of time between the two phases decreases with increase in the concentration of the catalyst and the substrate. Under uncatalyzed and ferroin catalyzed conditions the system exhibits single-phase oscillations. The first-phase oscillations are due to vanillin whereas the second-phase oscillations are brought about by 4-hydroxy-3-methoxybenzoic acid (vanillic acid) formed during the course of the first-phase reactions. The reactions are explained with relevant steps of the FKN mechanism. © 1998 John Wiley & Sons, Inc. Int J. Chem. Kinet **30**: 201–206, 1998.

INTRODUCTION

Extensive investigation has been carried out in the Belousov–Zhabotinsky (B–Z) oscillatory system [1-3]. A variety of organic compounds have been employed as substrate in these systems. The serious limitation of substrate insolubility has been overcome by the use of aqueous-organic mixed media [4-6].

Sequential oscillations with mixed organic substrates have been reported [7]. Dual frequency oscillations with ethylacetoacetate as the substrate have been brought about by further addition of potassium bromate [8]. In this article, a novel dual-phase oscillatory system with 4-hydroxy-3-methoxybenzaldehyde (vanillin) as a single substrate and Mn(II) or Ce(IV) as catalyst is described. The single-phase oscillations are observed in the ferroin catalyzed and uncatalyzed systems. The characteristics are examined so as to unravel the sequential changes involved in the overall process.

EXPERIMENTAL

All the chemicals employed were of Analytical Grade purity. The reaction was carried out under batch conditions in a polythene beaker of 100 ml capacity. The addition of the last constituent (Potassium bromate) to the stirred and thermostated solution containing all other constituents starts the oscillations. Simultaneous recording of the potential profile with a platinum and bromide ion selective electrode (against a saturated calomel electrode) dipped in the solution was made on a X-t recorder. An aqueous-organic, mixed medium containing 20% (v/v) acetonitrile was employed because of the poor solubility of the substrate in water.

RESULTS AND DISCUSSION

The experimental results obtained in the uncatalyzed system as well as the catalyzed system involving Mn(II), Ce(IV), or ferroin provides valuable data regarding the course of the reaction. The composition of experimental solution and the oscillatory characteris-

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[Mn(II)] (M)	Phase	Number of Oscillations (n)	Time per Oscillation T_t (min)	Initial Amplitude (mV)	Potential Range V(vs SCE)	
					Base	Peak
0.001	Phase-I	9	0.11	150	0.62	0.83
	Phase-II	8	1.06	90	0.75	0.83
0.0025	Phase-I	7	0.14	150	0.63	0.83
	Phase-II	7	1.14	130	0.7	0.84
0.005	Phase-I	8	0.12	160	0.62	0.86
	Phase-II	6	0.86	160	0.62	0.80
0.01	Phase-I	8	0.16	160	0.65	0.90
	Phase-II	5	1.0	150	0.69	0.94
0.03	_	13	0.38	160	0.58	0.85

Table I Oscillatory Characteristics of the Platinum Profile: Vanillin—Mn(II) System. [Vanillin] = 0.03 M; $[H_2SO_4] = 0.6$ M; $[KBrO_3] = 0.09$ M; Acetonitrile = 20% (v/v); and Temperature = $30 \pm 0.1^{\circ}$ C

tics of the Mn(II) and Ce(IV) system are presented in Tables I and II respectively. The oscillatory potential profiles with the platinum indicator electrode and bromide ion selective electrode are presented in Figures 1 to 5. The potential profile in the Mn(II) system is characterized by high-frequency oscillations in the firstphase followed by low-frequency second-phase oscillations after a time lag of nearly 4 min at a concentration of 0.001 M of Mn(II) (Fig. 1(a)). The Br⁻ poten-

Table II Oscillatory Characteristics of the Platinum Profile: Vanillin—Ce(IV) System. [Vanillin] = 0.03 M; $[H_2SO_4] = 0.6$ M; $[KBrO_3] = 0.09$ M; Acetonitrile = 20% (v/v); and Temperature = 30 \pm 0.1°C

[Ce(IV)] (M)	Phase	Number of Oscillations (n)	Time per Oscillation T_t (min)	Initial Amplitude (mV)	Potential Range V(vs SCE)	
					Base	Peak
0.001	Phase-I	8	0.11	160	0.62	0.8
	Phase-II	8	1.62	60	0.78	0.84
0.0025	Phase-I	8	0.14	160	0.62	0.8
	Phase-II	6	2.0	90	0.81	0.9
0.005	Phase-I	9	0.13	160	0.62	0.8
	Phase-II	5	2.94	100	0.80	0.9
0.01	Phase-I	9	0.11	150	0.63	0.79
	Phase-II	2	5.20	100	0.90	1.0



Figure 1 Dual-phase oscillatory behavior of vanillin— Mn(II) system. (a), (c), and (e) potential profiles recorded with platinum electrode. (b), (d), and (f) corresponding Br[–] potential profiles. Concentration conditions: [Vanillin] = 0.03 M, [H₂SO₄] = 0.6 M; [KBrO₃] = 0.09 M; Acetonitrile = 20% (v/v); and Temperature = $30 \pm 0.1^{\circ}\text{C}$ [MnSO₄] = 0.001 M (a and b), 0.005 M (c and d), and 0.03 M (e and f).

tial profile has the same frequency as the platinum profile in both the phases (Fig. 1(b)). The amplitude of Br⁻ oscillations is small indicating a small change in the concentration of Br⁻ between the base and peak. An increase in the concentration of Mn(II) to 0.005 M leads to a decrease in the time lag between the two phases (Fig. 1(c)) and an increase in the amplitude of the platinum potential profile. An increase in the concentration of Mn(II) to 0.03 M results in the merging of the two phases (Fig. 1(e)). A similar trend is observed in the Br⁻ potential profile with respect to the frequency and amplitude of oscillations (Fig. 1(d) and (f)).

The decrease in time lag between the first-and second-phase of oscillations is a characteristic feature of the Ce(IV) system also (Fig. 2). However, even at the highest concentration of Ce(IV) employed, the second-phase oscillations, being at a higher potential range, do not completely merge with the first-phase oscillations (Fig. 2(e) and (f)). The time lag between the two phases decreased when the substrate concentration was increased from 0.01 to 0.04 M.

In the uncatalyzed bromate system the oscillations are in a single phase only (Fig. 3). Moreover, the platinum potential profile of the uncatalyzed system bears a close resemblance to the corresponding first-phase in the Mn(II) as well as Ce(IV) system in respect of number frequency, amplitude, and potential range. Such a resemblance is observed in the Br⁻ potential profile as well. With ferroin as the catalyst the system shows single-phase oscillation (Fig. 4).

The reactivity of vanillin is such that the bromination step is a highly favored one in the overall reaction and, hence, the first-phase of oscillation involves bromination of vanillin as the predominant reaction. Further, the longer time per oscillation in the second-phase rules out its participation in this phase of the profile. Therefore, the substrate in the secondphase is a derivative of vanillin which could probably be vanillic acid formed by the oxidation of vanillin by Ce(IV) or Mn(III)

The reactivity of vanillic acid is less compared to vanillin. Experiments were carried out by employing vanillic acid as the substrate in the uncatalyzed and catalyzed systems. Vanillic acid is characterized by illdefined oscillations in the uncatalyzed bromate system. The platinum potential profiles of Mn(II) and Ce(IV) system with vanillic acid as the substrate have a striking resemblance to the second-phase oscillation in the Mn(II) and Ce(IV) system, respectively (Fig. 5(a) and (b)). This lends further support to the above conclusions regarding the reactions taking place in the first-and second-phase.

The decrease in the time interval between the two phases as the metal ion and substrate concentration increases, is because of the faster build up of the oxidized product. The oxidation of vanillin by Ce(IV) or Mn(III), has been confirmed by following the variation in the potential of Mn(III) and Ce(IV) in presence of acidified vanillin under nonoscillatory conditions. There is a drastic decrease in the potential of a platinum electrode dipped in a solution of acidified Ce(IV) or Mn(III) on the addition of vanillin. However, such a decrease in potential is not observed when acidified ferrin is employed.

The oscillatory behavior of this system can be rationalized in terms of the following steps involved in the overall reaction [9].

$$Br^{-} + BrO_{3}^{-} + 2H^{+} \Longrightarrow HOBr + HBrO_{2}$$
 (1)

$$Br^{-} + HOBr + H^{+} \Longrightarrow Br_{2} + H_{2}O$$
 (2)



Figure 2 Dual-phase oscillatory behavior of vanillin—Ce(IV) system. (a), (c), and (e) potential profiles recorded with platinum electrode. (b), (d), and (f) corresponding Br⁻ potential profiles. Concentration conditions: [Vanillin] = 0.03 M, [H₂SO₄] = 0.6 M; [KBrO₃] = 0.09 M; Acetonitrile = 20% (v/v); and Temperature = $30 \pm 0.1^{\circ}$ C [Ce(IV)] = 0.0025 M (a and b), 0.005 M (c and d), and 0.01 M (e and f).



Figure 3 Oscillatory behavior of vanillin in uncatalyzed system; (a) platinum potential profile and (b) Br⁻ potential profile. Concentration conditions: [Vanillin] = 0.02 M [H₂SO₄] = 0.7 M; [KBrO₃] = 0.1 M; Acetonitrile = 20% (v/v); and Temperature = $30 \pm 0.1^{\circ}$ C.

$$HBrO_2 + BrO_3^- + H^+ \Longrightarrow 2BrO_2^{\bullet} + H_2O$$
 (3)

$$BrO_{2}^{\bullet} + M^{n+} + H^{+} \rightleftharpoons M^{(n+1)+} + HBrO_{2} \quad (4)$$

$$\mathbf{M}^{(n+1)+} + \mathbf{S} \longrightarrow \mathbf{H} \longrightarrow \mathbf{S}_{ox} + \mathbf{M}^{n+} + \mathbf{H}^{+}$$
(5)

$$S-H + Br_2 \longrightarrow S-Br + H^+ + Br^-$$
 (6)

where S—H is the substrate (vanillin) and S_{ox} is its oxidized product (vanillic acid).

Oscillations in the first-phase involve the bromine formation and consumption steps (Steps 1, 2, and 6) with the simultaneous accumulation of S_{ox} (Step 5). Subsequently, the oscillations stopped on account of



Figure 4 Oscillatory behavior of vanillin–ferroin system; (a) platinum potential profile and (b) Br[–] potential profile. Concentration conditions: [Vanillin] = 0.03 M [H₂SO₄] = 0.6 M; [KBrO₃] = 0.09 M; Acetonitrile = 20% (v/v); and Temperature = $30 \pm 0.1^{\circ}$ C.



Figure 5 Oscillatory behavior of vanillic acid system; (a) with 0.005 M Mn(II) as the catalyst and (b) with 0.005 M Ce(IV) as the catalyst. Concentration conditions: [Vanillic acid] = 0.02 M; [H₂SO₄] = 0.6 M; [KBrO₃] = 0.06 M; Acetonitrile = 20% (v/v); and Temperature = $30 \pm 0.1^{\circ}$ C.

the fact that the lower limit of vanillin concentration is reached. However, when a sufficient amount of vanillic acid has accumulated the second-phase oscillations are manifest. This was confirmed by the decrease in the time interval between the two phases when vanillic acid was added to the reaction mixture at the end of the first-phase oscillations. Further, the formation of vanillic acid in the reaction mixture was confirmed by TLC and IR spectrum. So the time interval between the two phases depends on the extent of formation of vanillic acid, which is decided by the concentration of metal ion and the substrate.

CONCLUSION

The oscillatory system employing vanillin as the substrate and Mn(III) or Ce(IV) as the catalyst has two distinct oscillatory domains differing in their characteristics. Such a behavior is a consequence of the participation of vanillin as the substrate in the first-phase and its oxidized product, vanillic acid in the second.

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