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NEW SUBSTRATES IN BELOUSOV-ZHABOTINSKY REACTION EMPLOYING MIXED MEDIA

P.V. Lalitha and R. Ramaswamy*

Department of Chemistry, Indian Institute of Technology,
Madras 600 036, India

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Several substrates have been employed in different oscillatory systems. A serious limitation is the low solubility in water. This has been overcome by employing aqueous-organic mixed media in the iodate-system as well as the uncatalyzed and catalyzed [Ce(III) or Ferroin] systems. The present paper deals with the study of fifteen new substrates in the bromate–Mn(II) oscillatory system employing aqueous-organic mixed media.

Было использовано несколько субстратов в различных осциллирующих системах. Серьезным ограничением является их плохая растворимость в воде. Это удалось преодалеть, используя смешанные водно-органические среды, как в каталитических (Ce(III) или Ферроин), так и в некаталитических иодатных системах. В настоящей статье обсуждаются исследования пятнадцати новых субстратов в бромат-Mn(II) осциллирующих системах в сешанных водно-органических средах.

INTRODUCTION

The Belousov-Zhabotinsky reaction is one of the most extensively studied oscillatory system [1, 2]. Several substrates

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* Author for correspondence

Akadémiai Kiadó, Budapest

have been employed in the bromate system with the inclusion of the metal ion or in the absence of the metal ion [3]. The oscillatory behavior in the uncatalyzed system of a large number of polysubstituted aromatic compounds has been reported [4]. The oscillatory characteristics of several new substrates in the Ferroin-catalyzed bromate system were also reported [5]. A novel aspect in the bromate Mn(II)/Co(III) system is the removal of bromine by bubbling hydrogen [6] during the measurement. Extensive investigation of the bromate and iodate systems by the potentiometric follow up [7-9] has provided vital information about the course of the reaction. The effect of addition of small amounts of different organic solvents to the bromate-Mn(II) system [10] with malic acid as substrate has been studied.

The oscillatory characteristics of a system depend considerably on the nature of the substrate employed. The study of an interesting compound as substrate has often been rendered unfeasible because of its low solubility in aqueous medium. This difficulty has been overcome by employing mixed media containing an organic solvent of nearly twenty percent by volume. The behavior of several new substrates has been studied in mixed media in the iodate-hydrogen peroxide system as well as the bromate system with or without the inclusion of the metal ion (Ce(III) or Ferroin) [11-13]. The use of mixed media in the study of oscillatory systems brings within the scope of measurement a large number of new substrates in the bromate and iodate systems. These include polysubstituted aromatic compounds and compounds containing active methylene groups, respectively. The oscillatory behavior of fifteen new substrates in the bromate-Mn(II) system are discussed in the present communication.

EXPERIMENTAL

Triply distilled water was used to prepare all the solutions. All the chemicals used were of AnalaR reagent grade. The addition of the last constituent (thermostated potassium bromate) to the well stirred mixture of all the other constituents kept at 32 ± 0.1 °C triggered off the oscillations. In all the experiments, the total volume of the solution was kept constant at 25 ml. The potential oscillations were recorded on a Siemens Compensograph using a platinum indicator electrode coupled to a saturated calomel electrode through a potassium nitrate salt bridge.

RESULTS AND DISCUSSION

The concentration conditions employed for different substrates are presented in Table 1. The oscillatory characteristics corresponding to these substrates are given in Table 2. The concentrations of the constituents could not be maintained the same for the various substrates owing to their reactivity not being the same. However, a comparison of the reactivity of substrates reflected in the oscillatory characteristics would be meaningful if the concentration of constituents are also taken into account while making the comparison (Fig. 1).

A comparison of the oscillatory behavior of the substrates can be made for substrates which are structurally related among themselves. The substrates 1 to 4 (Table 1) differ in the functional group in position 1, the two hydroxy groups in position 2 and 4 being common to all the four substrates. The difference in the reactivity of the four substrates to electrophilic substitution is reflected in the oscillatory characteristics. The time per oscillation gradually increases from 0.5 min for 2,4-dihydroxybenzaldehyde to 1.70 min for 2,4-dihydroxybenzophenone. The amplitude decreases gradually from 250 mV to 60 mV. This is due to a gradual decrease in the reactivity of the substrate from the disubstituted benzaldehyde to the disubstituted benzophenone. The substituents in position 1 are electron-withdrawing in nature, which decreases gradually in the order -CHO, $-COCH_3$, $-COC_2H_5$ and $-COC_6H_5$. The hydroxy groups in 2 and 4 positions are common to all the four substrates and their presence increases the reactivity of the molecule for attack by the electrophile. The overall effect is a gradual decrease in the reactivity of the substrate from 1 to 4 and is reflected in the oscillatory characteristics as discussed above.

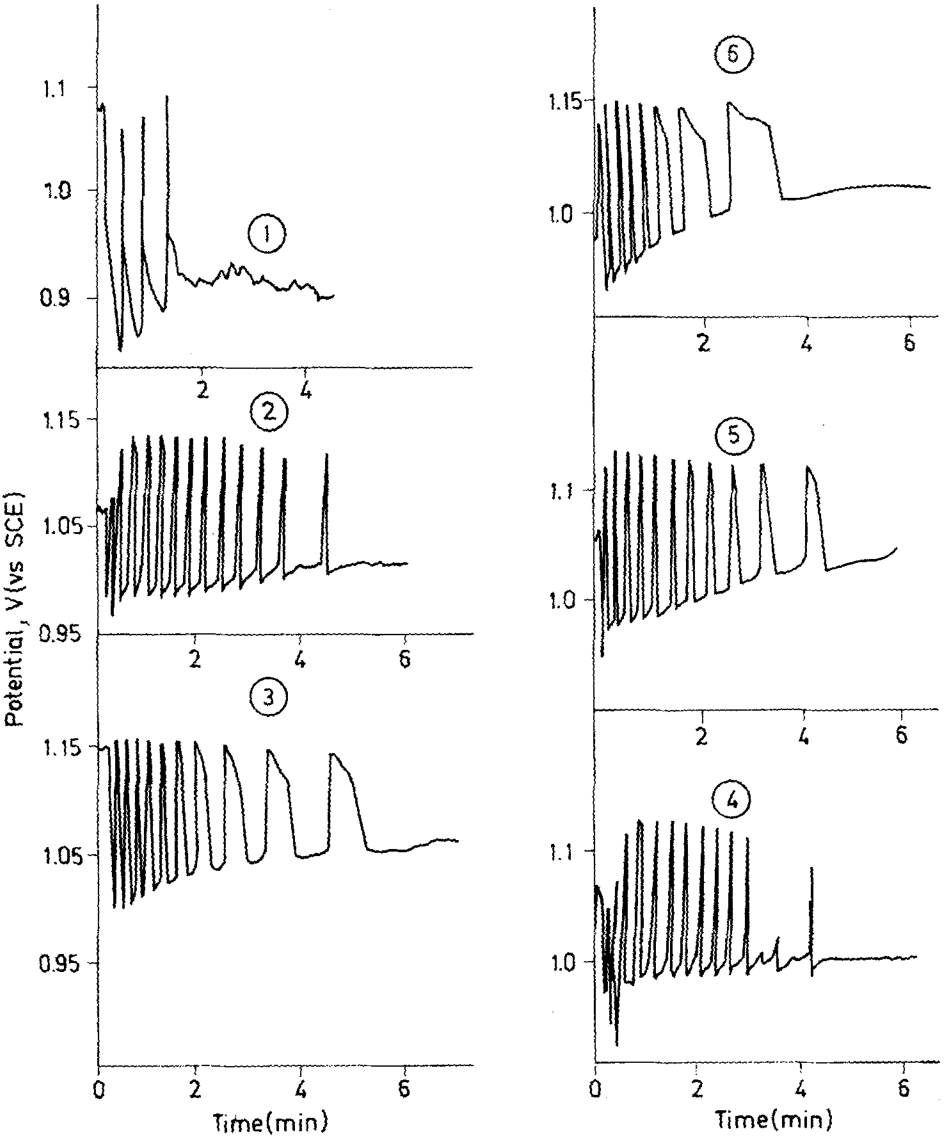

Fig. 1. Oscillatory profile of 2′,4′-dihydroxyacetophenone under different concentration conditions. Temp.: 32±0.1 °C. Effect of variation of [H_2SO_4]: [$MnSO_4$] = 0.005; [$KBrO_3$] = 0.1 M, [Substrate] = 0.02 M; [H_2SO_4]: (1) 1.2 M, (2) 1.5 M, (3) 2.0 M. Effect of variation of [$MnSO_4$] : [$KBrO_3$] = 0.1 M; [H_2SO_4] = 1.5 M. [Substrate] = 0.02 M; [$MnSO_4$]: (4) 0.003 M, (5) 0.01 M, (6) 0.02 M

Table 1

Concentration range for the different substrates. Temp.: 32±0.1°C

No.	Substrate	[Substrate] (M)	[H_2SO_4] (M)	[$MnSO_4$] (M)	[$KBrO_3$] (M)
1.	2,4-Dihydroxybenzaldehyde	0.01 - 0.02	0.8 - 1.2	0.005 - 0.04	0.08 - 0.14
2.	2',4'-Dihydroxyacetophenone	0.01 - 0.03	1.2 - 2.0	0.003 - 0.02	0.07 - 0.1
3.	2',4'-Dihydroxypropiophenone	0.01 - 0.02	1.2 - 1.8	0.005 - 0.02	0.05 - 0.09
4.	2,4-Dihydroxybenzophenone	0.01 - 0.02	1.2 - 1.5	0.003 - 0.005	0.05 - 0.09
5.	p-Vanillin	0.03	0.6	0.002 - 0.04	0.067
6.	o-Vanillin	0.017	0.6	0.002 - 0.04	0.067
7.	Veratric acid	0.02	0.3	0.01	0.05
8.	Veratronitrile	0.02	0.5	0.001 - 0.03	0.03 - 0.07
9.	Asaraldehyde	0.01 - 0.02	0.2 - 0.4	0.005 - 0.04	0.08 - 0.12
10.	Asaronic acid	0.008	0.4	0.02	0.12
11.	2-Hydroxy-4-methoxybenzoic acid	0.01 - 0.02	0.6 - 0.8	0.005 - 0.04	0.06 - 0.1
12.	Syringic acid	0.01	0.4	0.01 - 0.02	0.06 - 0.1
13.	Propyl gallate	0.046	1.45	0.002	0.06 - 0.1
14.	Adrenaline	0.02 - 0.03	0.4 - 0.8	0.01 - 0.04	0.06 - 0.1
15.	7-Acetoxy-4-methylcoumarin (in 40% AN)	0.02 - 0.03	0.7	0.005 - 0.02	0.03 - 0.05

Table 2

Oscillatory characteristics with different substrates at the optimum concentration conditions

No.	Substrate	T_{ind} (min)	T_{total} (min)	No. of oscillations	Time/osc. (min)	Amplitude (mV)	Potential range V (vs.SCE)
1.	2,4-Dihydroxybenzaldehyde	0.1	7.0	14	0.5	250	0.83-1.08
2.	2′,4′-Dihydroxyacetophenone	0.1	5.5	11	0.5	160	1.0 -1.16
3.	2′,4′-Dihydroxypropiophenone	0.4	7	8	0.8	140	0.98-1.12
4.	2,4-Dihydroxybenzophenone	0.1	20	12	1.7	60	0.89-0.95
5.	p-Vanillin	0.1	2	3	0.7	200	0.70-0.90
6.	o-Vanillin	0.3	5	5	0.9	530	0.40-0.93
7.	Veratric acid	0.5	82	23	3.5	340	0.61-0.95
8.	Veratronitrile	0.1	45	5	9.0	230	0.75-0.98
9.	Asaraldehyde	0.3	6	11	0.5	450	0.54-0.99
10.	Asaronic acid	0.2	21	15 (5 big + 10 small)	1.4	470 (140)	0.56-1.03 (0.91-1.05)
11.	2-Hydroxy-4-methoxybenzoic acid	0.1	10	9 (1 big + 8 small)	1.1	370 (40)	0.51-0.88 (0.87-0.91)
12.	Syringic acid	0.3	13	12	1.1	550	0.34-0.89
13.	Propyl gallate	1.4	11	5	1.9	400	0.45-0.85
14.	Adrenaline	1	55	16	3.4	510	0.45-0.96
15.	7-acetoxy-4-methylcoumarin (40% AN)	0.1	90	15	6.0	280	0.68-0.96

The reactivity of p-vanillin is found to be more than that of o-vanillin as evident from the smaller induction time (0.1 min) and smaller time per oscillation (0.7 min). The amplitude, however, is smaller (200 mV) for p-vanillin. Veratric acid is a better substrate compared to veratronitrile. There are 23 oscillations in 82 min with veratric acid as substrate, whereas with veratronitrile there are 5 oscillations in 45 min. The amplitude is also large (340 mV) for veratric acid. Both asaraldehyde and asaronic acid are good subtrates giving large amplitude oscillations. Asaraldehyde is more reactive towards bromination as indicated by the smaller time per oscillation (0.5 min). It can be judged from the potential range that asaronic acid gives double oscillations, initially oscillating in bromine as well as in the Mn(III)/Mn(II) couple (0.56 V to 1.03 V vs. SCE) and subsequently in Mn(III)/Mn(II) ratio alone (0.91 V to 1.05 V vs. SCE). Syringic acid is also found to be a good substrate in this system with oscillations of large amplitude (550 mV vs. SCE). The reactivity of the other substrates are reflected in their respective oscillatory parameters.

The reactivity is a resultant of the electronic effects caused by the presence of the different functional groups. The use of mixed solvents would enable the study of scores of new substrates since the limitation of getting them into the solution phase would no longer be an impediment.

The alteration of the oscillatory parameters on the addition of an organic solvent [10] has been attributed to complex formation between the organic solvent and the Mn(II) catalyst. It has been suggested that the organic solvent molecules compete with the substrate molecules to coordinate with the Mn(II). However, under the experimental conditions with 1-2 M H_2SO_4, complexing between Mn(II) and the solvent or the organic substrate would not be favored. Besides, the interaction involving the solvent and bromine must be taken into consideration as revealed by our experimental results.

The behavior of gallic acid in the Ferroin catalyzed bromate system in different mixed media has been studied [13]. The oscillatory characteristics in pure aqueous and aqueous-acetonitrile mixed media are as follows. The oscillatory profile in the mixed medium is characterized by a smaller induction time and time per oscillation compared to that in the pure aqueous medium. However, the amplitude is smaller. Further, in the mixed medium the base and peak potentials are higher. The presence of acetonitrile accelerates the reaction by reducing the time per oscillation to about half the value and at the same time reducing the number of oscillations and the total time.

Medium	T_{ind} (min)	T_{total} (min)	No. of oscill.	Time/osc. (min)	Potential range V(vs SCE)
Aqueous	0.6	45	37	1.2	0.86-1.06
Aqueous-acetonitrile (20% V)	0.1	6	10	0.59	0.93-1.07

Similarly in the uncatalyzed system also, with gallic acid as the substrate, the induction time (0.1 min) and time per oscillation (0.61 min) are smaller in aqueous acetonitrile medium than those (1.2 min and 0.79 min, respectively) in pure aqueous medium [12]. Spectrophotometric measurements with bromine solution indicate that the optical density of bromine is different in pure aqueous and mixed media. The values of optical densities for two concentrations of bromine are as given below:

$[Br_2]$ (M)	Pure aqueous	20% acetonitrile
2.5×10^{-3}	0.35	0.20
5×10^{-3}	0.75	0.56

The decrease in the optical density in the presence of acetonitrile is presumably due to the interaction between the organic solvent and bromine. The concentration of free bromine in the mixed medium is less compared to that in pure aqueous medium.

Since there is interaction between the added solvent and bromine as is evident from the spectrophotometric measurements, it can be concluded that the alterations are due to the following two factors. Interaction between oxidized and reduced forms of the metal ion and the organic solvent as well as that between the solvent and bromine, resulting in a change of the overall rates of the reactions involved in the system.

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