Novel experimental findings in the B–Z system employing mixed substrates

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Abstract: Certain novel features of the Belousov–Zhabotinsky (B–Z) system employing different mixed substrates and Mn(II) as the catalyst are presented. Malic acid is the common substrate together with one of malonic, citric, cyanoacetic, maleic, acetic, oxalic, or tartaric acid as the second substrate. The correlation of the oscillatory behaviour with values of exchange current density establishes the oscillatory control by the redox couple, namely, Mn(III)/Mn(II) and (or) Br_2/Br^-. Each substrate when used alone gives rise to an oscillatory behaviour with characteristic features that can be compared with the system containing mixed substrate. The combination of substrates provides different modes of oscillatory behaviour such as entrainment, independent, partial inhibition, or complete inhibition. These observations are rationalized in terms of relevant steps involved in the mechanism of the reaction.

Key words: mixed substrate, exchange current density, entrainment, independent, inhibition.

Résumé : On présente certaines caractéristiques nouvelles du système de Belousov–Zhabotinsky (B–Z) dans lesquelles on utilise des substrats mixtes et du Mn(II) comme catalyseur. L'acide malique est un substrat courant avec l'un ou l'autre des acides malonique, citrique, cyanoacétique, maléique, acétique, oxalique ou tartrique comme deuxième substrat. La corrélation du comportement oscillatoire avec les valeurs de la densité du courant d'échange permet d'établir que le contrôle oscillatoire dérive du couple redox, Mn(III)/Mn(II) et (ou) Br_2/Br^-. Lorsqu'on utilise les substrats seuls, ils donnent lieu à un comportement oscillatoire dont les caractéristiques particulières peuvent se comparer à celles d'un système contenant un substrat mixte. Les combinaisons de substrats conduisent à des modes différents de comportement tels qu'entraînement, indépendant, inhibition partielle ou inhibition complète. On peut rationaliser ces observations en fonction d'étapes appropriées impliquées dans le mécanisme de la réaction.

Mots clés : substrat mixte, densité du courant d'échange, entraînement, indépendant, inhibition.

[Traduit par la rédaction]

Introduction

Oscillatory reactions in the Belousov–Zhabotinsky (B–Z) and Briggs–Rauscher (B–R) systems have been investigated by employing a variety of organic substrates in aqueous as well as aqueous–organic mixed media (1–3). Oscillatory reactions with mixed organic substrates (4–6) have also received considerable attention. The present paper deals with certain novel experimental findings in the B–Z system employing mixed substrates with malic acid as the common substrate.

Experimental

The constituents of the experimental solution, with the exception of potassium bromate, were kept well stirred and thermostated in a polythene beaker. The addition of the last constituent ($KBrO_3$) triggered off the oscillations. The EMF oscillatory profile between a platinum indicator electrode and a saturated calomel (SCE) reference electrode was continously recorded. Different substrates were employed for the study, either individually or in combination with malic acid as the

common substrate. The structures of the substrates employed have been tabulated for convenient reference.

Structures of different substrates employed.

S.No.	Substrate	Structure
1.	Malic acid	$HOOC-CH_2-CH(OH)-COOH$
2.	Citric acid	CH_2-COOH $\|$ $C(OH)-COOH$ $\|$ CH_2-COOH
3.	Malonic acid	$HOOC-CH_2-COOH$
4.	Cyanoacetic acid	$NC-CH_2-COOH$
5.	Maleic acid	$HOOC-CH=CH-COOH$
6.	Acetic acid	CH_3-COOH
7.	Tartaric acid	$CH(OH)-COOH$ $\|$ $CH(OH)-COOH$
8.	Oxalic acid	$COOH$ $\|$ $COOH$

Results and discussion

(i) Malic acid and citric acid

The oscillatory profile of the malic acid – citric acid mixed substrate system under the concentration conditions indicated

Table 1. Oscillatory characteristics with malic acid and citric acid as substrates.[a]

Substrate	[S] M	Number of oscillations	Potential (V vs. SCE)		Amplitude (V)	Time per oscillation (min)	Duration (min)
			Base value	Peak value			
Malic acid	0.05	40	0.775	1.050	0.275	1.00	40
Citric acid	0.05	30	0.600	0.825	0.225	0.50	15
	0.05 +	32	0.475	0.925	0.450	0.56	18
Malic acid + citric acid	0.05						
	0.025 +	1–30	0.590	0.820	0.230	0.50	15
	0.025	31–54				1.66	40

[a][KBrO$_3$] = 0.05 M; [H$_2$SO$_4$] = 2.0 M; [MnSO$_4$] = 0.005 M; temperature = 30 ± 0.1°C.

in Table 1 is presented in Fig. 1b. Each substrate when used alone in the B–Z reaction gives rise to characteristic features that permit identification of its oscillatory behaviour in the system with mixed substrates. The oscillatory reactions with the individual substrate under the concentration conditions indicated in Table 1 are presented in Figs. 1a and 2. The potential developed at the platinum indicator electrode is determined by the relative values of the exchange current density and (or) the relative concentrations of the redox couples involved. The values of the exchange current density for Pt/Mn(III), Mn(II), and that of Pt/Br$_2$, Br$^-$ are comparable (10^{-5} A/cm^2). Therefore the potential range of oscillation can be decided by the relative concentration of Mn(III)/Mn(II) and Br$_2$/Br$^-$. The potential range of oscillation with malic acid as the substrate is 0.775–1.05 V (vs. SCE). The peak potential is as high as 1.05 V, indicative of the predominant potential control by the Mn(III)/Mn(II) redox couple. The standard potentials (vs. SHE) of the Mn(III)/Mn(II) and Br$_2$/Br$^-$ redox systems are 1.488 and 1.066 V, respectively. However, the prevailing concentrations of the different species are much smaller. Thus the malic acid oscillatory profile is predominantly controlled by the Mn(III)/Mn(II) redox couple due to the nominal reactivity of the substrate towards bromination.

On the other hand, the potential range of oscillation in the citric acid system is 0.60–0.825 V (vs. SCE), which is indicative of mixed control of potential by both redox couples, namely, Mn(III)/Mn(II) and Br$_2$/Br$^-$. This is presumably due to the high reactivity of the substrate towards bromination, leading to considerable production and consumption of bromine.

This can be well understood in terms of the relevant steps involved in the FKN mechanism.

[1]   HOBr + Br$^-$ + H$^+$ ⇌ Br$_2$ + H$_2$O

[2]   BrO$_2^{\cdot}$ + M^{n+} + H$^+$ ⇌ HBrO$_2$ + M$^{(n+1)+}$
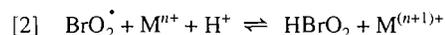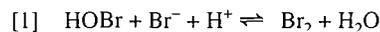
These steps lead to the formation of bromine and the oxidized form of metal ion. In addition, the reaction involving the substrate would lead to the consumption of bromine as well as the oxidized form of the metal ion according to the following steps:

[3]   S + Br$_2$ ⇌ Br·S + Br$^-$ + H$^+$

[4]   S + M$^{(n+1)+}$ ⇌ M^{n+} + product
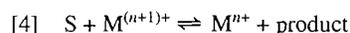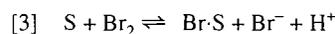
Steps [3] and [1] are more favoured in the citric acid system because of its high reactivity towards bromination. Enhancement in the production and consumption of bromine in the citric acid system is also reflected in the smaller time per oscillation (0.5 min) compared to that of malic acid (1.0 min) as indicated in Table 1. Thus the high reactivity of the substrate contributes considerably to the high frequency and mixed control of potential by both redox couples, namely, Mn(III)/Mn(II) and Br$_2$/Br$^-$.

The oscillatory profile observed in this mixed substrate system is almost identical to the oscillatory parameters with citric acid except for the increase in the amplitude of oscillations. The wave form, potential range, and the oscillatory period also clearly indicate that the oscillations are of the citric acid type and the role of malic acid is just to increase the amplitude of oscillations to the extent of 225 mV. Thus the system investigated here is an example of entrainment oscillations, in which citric acid is responsible for oscillations and the presence of malic acid increases the amplitude of oscillations.

The oscillatory behaviour of the system with 0.1 M of the individual substrate (malic acid or citric acid) leads to an increase in the frequency of oscillations due to an enhancement in the formation and consumption of bromine as well as of Mn(III). The solution containing a total concentration of 0.05 M of malic and citric acid (0.025 M each) gives an oscillatory behaviour that is identical with that of citric acid (0.05 M) for a duration of 15 min followed by an additional 24 oscillations in 40 min. Such an oscillatory behaviour can be termed as independent and persistent.

(ii) Malic acid and malonic acid
The oscillatory behaviour of this system under the concentration conditions indicated in Table 2 is presented in Fig. 3. The oscillatory profile observed with mixed substrate is identical to that of malonic acid in almost all aspects of the wave form, namely, potential range, frequency, and the alternation between a pink and a colourless solution. This clearly indi-

Fig. 1. Oscillatory behaviour of bromate–Mn(II) system at $30 \pm 0.1°C$. Concentration conditions: $[H_2SO_4] = 2.0$ M; $[MnSO_4] = 0.005$ M; $[KBrO_3] = 0.05$ M. (a) Citric acid (0.05 M); (b) malic acid (0.05 M) + citric acid (0.05 M).
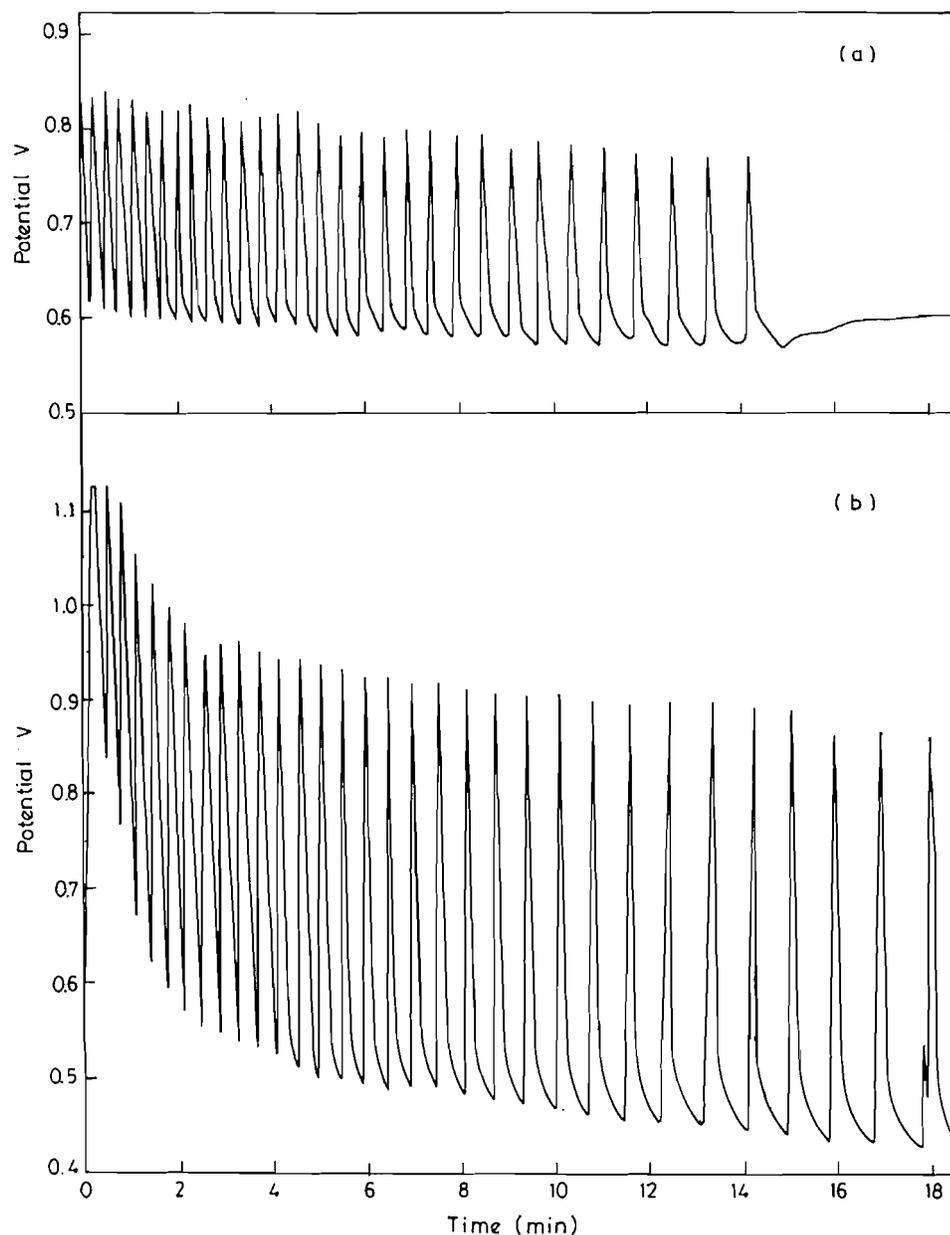
cates that the oscillations are of malonic acid type. The only difference between these two systems is in the number of oscillations. The presence of malic acid decreases the number of oscillations of the malonic acid system. Here, though the oscillations are controlled predominantly by malonic acid as the substrate, malic acid also participates in the reaction under the concentration conditions employed. This results in a decrease in the concentration of bromate, leading to an unfavourable concentration ratio of bromate to substrate at 9.5 min duration and a premature termination of oscillations. These observations can be substantiated on the basis of the relevant steps of the overall reaction involving the formation of Mn(III) and bromine (steps [1] and [2]) as well as their con-

sumption (steps [3] and [4]). The unfavourable ratio of bromate to substrate disfavours steps [1] and [2], which would otherwise have resulted in the up reaction. This is further supported by the restart of oscillation by the addition of bromate at the 9.5 min mark. Thus this system represents an example of interrupted independent oscillations, where malonic acid mainly controls the nature of oscillations and the interruption is due to an effective decrease in the relative concentration of bromate.
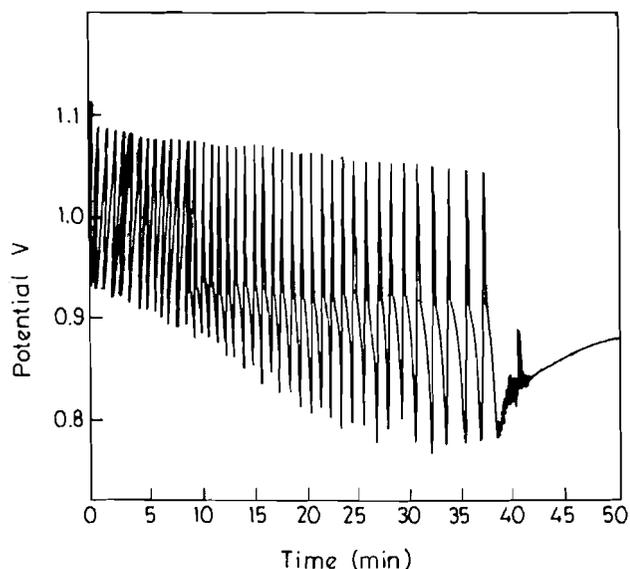
The oscillatory behaviour of the system with 0.1 M malonic acid alone is characterized by a smaller time per oscillation due to an enhancement in the formation and consumption of bromine as well as of Mn(III). The solution containing 0.05 M

Table 2. Oscillatory characteristics with malic acid and malonic acid.[a]

| Substrate | [S] M | Number of oscillations | Potential (V vs. SCE) | | Amplitude (V) | Time per oscillation (min) | Duration (min) |
			Base value	Peak value			
Malic acid	0.05	40	0.775	1.050	0.275	1.00	40.0
Malonic acid	0.05	39	0.825	1.010	0.185	0.45	17.5
Malic acid + malonic acid	0.05 + 0.05	22	0.825	1.010	0.185	0.45	9.5
	0.025 + 0.025	39	0.825	1.020	0.195	0.45	17.5

[a]$[KBrO_3]$ = 0.05 M; $[H_2SO_4]$ = 2 M; $[MnSO_4]$ = 0.005 M; temperature = 30 ± 0.1°C.

Fig. 2. Oscillatory behaviour of bromate–Mn(II) system at 30 ± 0.1°C. Concentration conditions: [Malic acid] = 0.05 M; $[KBrO_3]$ = 0.05 M; $[MnSO_4]$ = 0.005 M; $[H_2SO_4]$ = 2.0 M.

of the mixed substrate (0.025 M each) leads to an oscillatory behaviour identical with that of 0.05 M malonic acid alone. This behaviour can be termed as independent. The system behaves as if it contains only malonic acid.

(iii) Malic acid and cyanoacetic acid/maleic acid/acetic acid
In this set of experiments the second constituent, unlike malic acid, does not act as a substrate under the concentration conditions indicated in Table 3 and presented in Fig. 4. In all three systems the presence of the second substrate introduces an induction period, and decreases the duration and the number of oscillations. The second constituent is presumably involved in the following steps of the overall reaction.

[5] $BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2^{\bullet} + H_2O$

[6] $BrO_2^{\bullet} + S \rightleftharpoons HBrO_2 + S_{ox}$
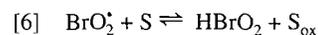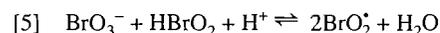
(S = substrate or added constituent; S_{ox} = oxidized product)

The course of the reaction involves steps [1]–[4] when malic acid is a single substrate. The inclusion of any one of the second constituents leads to a predominance of step [6] over steps [3] and [4]. This leads to a delay in the onset of oscillations and is manifest as an increase in the induction time as well as a decrease in the number of oscillations and in duration, resulting in partial inhibition. The reaction involving the second substrate in step [6] leads to a depletion in the bromate concentration in a non-oscillatory reaction as a result of which there is premature cessation of oscillations with smaller number and duration. This is confirmed by the restart of oscillation on addition of potassium bromate after the oscillations cease.

The system employing 0.1 M of the second substrate does not show oscillatory behaviour as with 0.05 M. Further, the system containing 0.05 M of the mixed substrate (0.025 M each) does not exhibit oscillatory behaviour. This is presumably due to high concentration of potassium bromate leading to consumption of substrate in a non-oscillatory reaction. This is substantiated by the fact that the system oscillates when the concentration of potassium bromate is reduced to 0.025 M.

(iv) Malic acid and tartaric acid/oxalic acid
The addition of either tartaric or oxalic acid to malic acid results in a total inhibition of oscillations. The potential remains constant at 1.01 V (vs. SCE) corresponding to the peak potential region. In these instances step [6], involving the consumption of substrate/added constituent, is totally overwhelming. The extent of reactions [3] and [4] is quite insignificant under these conditions, resulting in complete inhibition of oscillations.

It is interesting to note that the system exhibits oscillatory behaviour in a solution containing 0.05 M potassium bromate and 0.05 M mixed substrate (0.025 M each). The system changes from one of complete inhibition at 0.1 M mixed substrate to one of partial inhibition at a concentration of 0.05 M of mixed substrate resulting from a favourable concentration ratio of bromate to substrate.

Conclusion

A study of the B–Z reaction with mixed substrates provides valuable information regarding the key role of the substrate in the overall reaction. Different combinations of the substrates,

Fig. 3. Oscillatory behaviour of bromate–Mn(II) system at $30 \pm 0.1°C$. Concentration conditions:
$[H_2SO_4] = 2.0$ M; $[MnSO_4] = 0.005$ M; $[KBrO_3] = 0.05$ M. (a) Malonic acid (0.05 M); (b) malic acid
(0.05 M) + malonic acid (0.05 M).
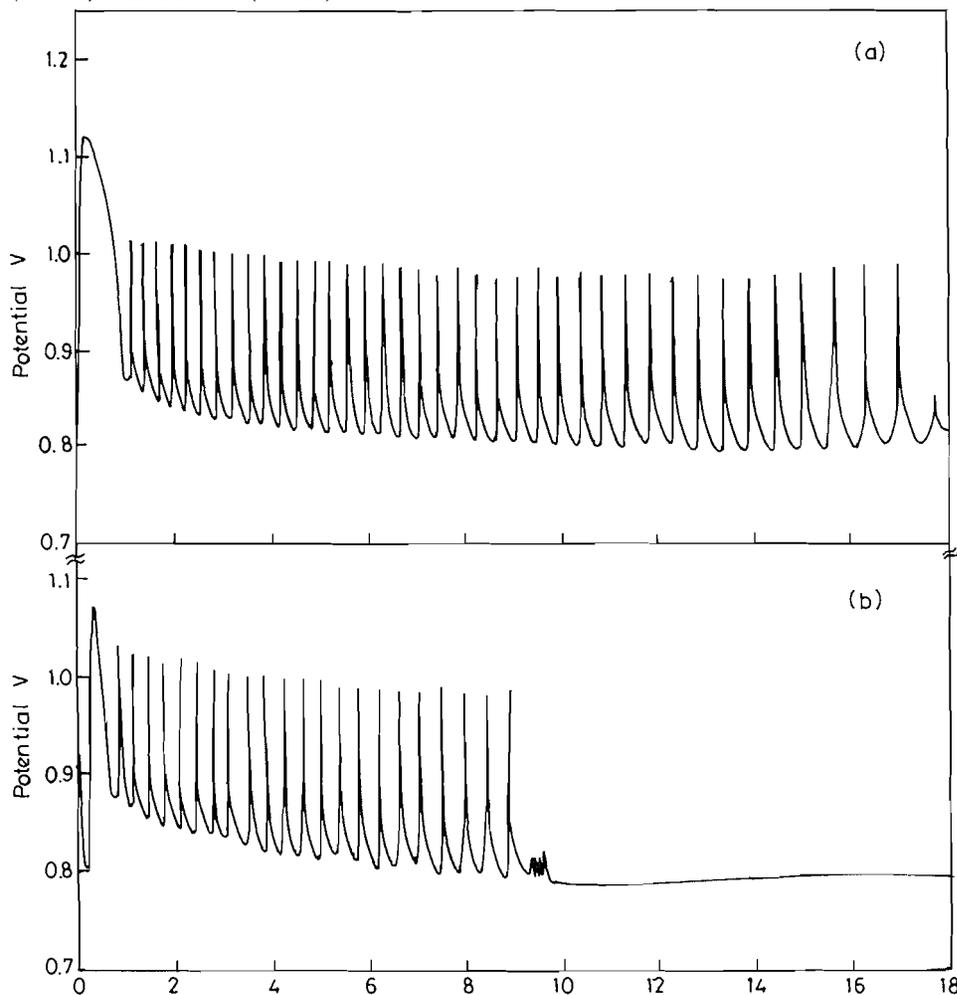
Table 3. Oscillatory characteristics with malic acid, cyanoacetic acid, maleic acid, and acetic acid.[a]

			Potential (V vs. SCE)					
Substrate	[S] M	Number of oscillations	Base value	Peak value	Amplitude (V)	Time per oscillation (min)	Duration (min)	Induction period (min)
Malic acid	0.05	40	0.775	1.050	0.275	1.00	40	0
Cyanoacetic acid	0.05	—	—	—	—	—	—	—
Malic acid + cyanoacetic acid	0.05 + 0.05	18	0.850	1.025	0.175	0.88	24.6	8.6
Maleic acid	—	—	—	—	—	—	—	—
Malic acid + maleic acid	0.05 + 0.05	10	0.840	1.050	0.210	1.40	26.5	12.5
Acetic acid	0.05	—	—	—	—	—	—	—
Malic acid + acetic acid	0.05 + 0.05	31	0.900	1.050	0.150	1.04	36.5	4.2

[a]$[KBrO_3] = 0.05$ M; $[H_2SO_4] = 2$ M; $[MnSO_4] = 0.005$ M; temperature $= 30 \pm 0.1°C$.

Fig. 4. Oscillatory behaviour of bromate–Mn(II) system at $30 \pm 0.1°C$. Concentration conditions: $[H_2SO_4] = 2.0$ M; $[MnSO_4] = 0.005$ M; $[KBrO_3] = 0.05$ M. (*a*) Malic acid (0.05 M) + cyano acetic acid (0.05 M); (*b*) malic acid (0.05 M) + maleic acid (0.05 M).
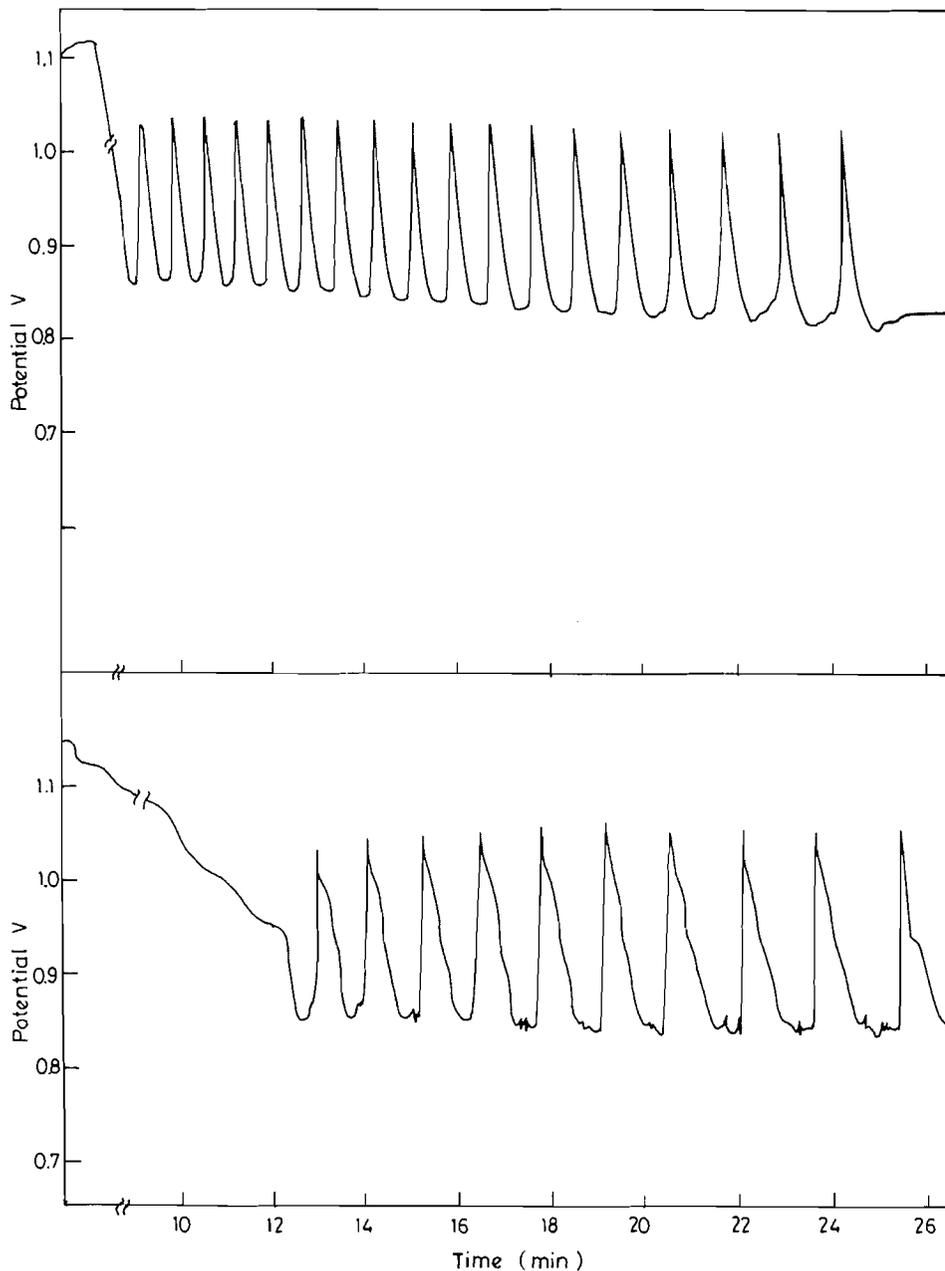
malic acid being common, provide different types of oscillatory behaviour of the system. The resultant pattern of behaviour is mainly governed by the reactivity of the second substrate in relation to malic acid. The behaviour of these systems can be well understood in the light of the relevant steps involved in the overall reaction.

References

1. R.J. Field and M. Burger (*Editors*). Oscillations and travelling waves in chemical systems. John Wiley and Sons, New York. 1987.

2. P.V. Lalitha and R. Ramaswamy. React. Kinet. Catal. Lett. **47**, 133 (1992).

3. V. Jayalakshmi and R. Ramaswamy. Int. J. Chem. Kinet. **27**, 197 (1995).

4. J. Heilweil, M.J. Henchman, and I.R. Epstein. J. Am. Chem. Soc. **98**, 3698 (1979).

5. R.P. Rastogi, R.D. Yadav, S. Singh, and A. Sharma. Indian J. Chem. **24A**, 43 (1985).

6. M.K. Ramreddy, K.C. Rajanna, and P.K. Saiprakash. Proc. Indian Acad. Sci. **98**, 333 (1987).