

## Exchange current density as control for oscillatory reactions

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**Abstract.** The oscillation characteristics of the iodate systems (Briggs-Rauscher reaction) and the bromate system (Belousov-Zhabotinskii reaction) with ethylacetoacetate show that the species responsible for the oscillations in these two systems are different. This arises from a large value of the exchange current density for  $\text{Pt}/\text{I}_2/\text{I}^-$ . The inclusion of ferroin in an uncatalysed bromate system (UBS) leads to a switchover to a new oscillatory phase, catalysed bromate system (CBS). Oscillation in UBS is caused by a periodic change in the concentration of bromine. The switchover in oscillation characteristics on the addition of ferroin results from the value of the exchange current density for  $\text{Pt}/\text{Fe(III)}/\text{Fe(II)}$  being larger than  $\text{Pt}/\text{Br}_2/\text{Br}^-$ .

**Keywords.** Oscillatory reaction; uncatalysed bromate system; exchange current density; oscillatory species; oscillatory control.

### 1. Introduction

The present work deals with the basic features relating to oscillatory control in the iodate and bromate systems. The range of potential, the oscillatory pattern and the static potential measurements relevant to the different systems establish that the oscillatory control in the Briggs-Rauscher (BR) and Belousov-Zhabotinskii (BZ) reactions are different.

### 2. Experimental

Requisite volumes of sulphuric acid, ferroin and pyrogallol were drawn from the stock solutions and kept well-stirred and thermostated in a polythene beaker. Ferroin, tris(1,10 phenanthroline) iron(II) sulphate, was prepared by mixing solutions of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 1,10 phenanthroline in 1:3 molar ratio. The addition of thermostated potassium bromate triggered off the oscillations. The indicator electrode (Pt and  $\text{Br}^-$  selective) was coupled to a saturated calomel electrode through a potassium nitrate salt bridge. The potential changes were continuously recorded using a  $x-t$  recorder.

### 3. Results and discussion

Ethylacetoacetate (EAA) was employed as the substrate in the bromate and iodate systems (Savithri 1981; Ramaswamy *et al* 1982) in the presence of Mn(II). The oscillating potential range in the bromate system is 0.9–1.1 V (vs SCE) while it is 0.5–0.7 V (vs SCE) in the iodate system. Increase in the concentration of manganese(II)

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sulphate or sulphuric acid leads to a flattening of the peak potential region in the bromate system but not in the iodate system. This could be further confirmed by the flattening of the peak region in the bromate system alone with the addition of tetra sodium pyrophosphate (Ramaswamy and Ramanathan 1983a) as the complexing agent. This could be traced to the value of the exchange current density of Pt/I<sub>2</sub>/I<sup>-</sup> being larger (10<sup>-2</sup> A/cm<sup>2</sup>) compared to that of Pt/Mn(III)/Mn(II) (10<sup>-5</sup> A/cm<sup>2</sup>) (Tanaka and Tamamushi 1964; Parsons 1959). Thus the former causes oscillations in the iodate system while in the bromate-Mn(II) system, there is a mixed control by Mn(III)/Mn(II) as well as Br<sub>2</sub>, the exchange current density of Pt/Br<sub>2</sub>/Br<sup>-</sup> being 10<sup>-5</sup> A/cm<sup>2</sup>.

The uncatalysed bromate-pyrogallol system oscillates in the potential range 0.7 to 1.1 V (vs SCE) with nine oscillations in 3.5 min. Addition of ferroin has been reported to inhibit (Koros *et al* 1980) the oscillations. However the inclusion of ferroin has led to a switchover (Ramanathan and Ramaswamy 1981) to a new oscillatory phase in the region 0.95 to 1.05 V (vs SCE). Such a switchover arises because of the larger exchange current density (10<sup>-3</sup> A/cm<sup>2</sup>) for Pt/Fe(III)/Fe(II) (Ramaswamy 1982) compared to that of Pt/Br<sub>2</sub>/Br<sup>-</sup>. Oscillations in Br<sup>-</sup> in the uncatalysed bromate system could be established by employing a calibrated bromide selective indicator electrode. The concentration of Br<sup>-</sup> at the peak and base region is about 10<sup>-6</sup> M and 10<sup>-5</sup> M respectively.

A direct confirmation of the fact that oscillations on a platinum electrode are caused by periodic change in the concentration of bromine is provided by the experimental simulation (Ramaswamy and Ramanathan 1983b,c) of the oscillations. Dropwise addition of bromine to a solution of acid-pyrogallol brings about a change in the potential of the platinum electrode (figure 1a). The pattern bears a striking resemblance to the self-oscillating uncatalysed bromate pyrogallol system (figure 1b). The potential variation of a platinum electrode being several times larger than the expected value can be traced to the partial misibility of the bromine-water system.

Oscillations in Br<sup>-</sup> concentration are observed in the catalysed system as well (figure 2). The temporal behaviour of the system in Br<sup>-</sup> is followed by a Br<sup>-</sup> selective electrode while that of Br<sub>2</sub> is followed by a Pt electrode. The Pt electrode responds to changes in Br<sub>2</sub> and not Br<sup>-</sup> and *vice-versa* with a Br<sup>-</sup> selective electrode. Based on the various experimental observations, schemes of reaction for both the UBS and CBS are suggested (table 1). When Br<sup>-</sup> concentration is large reactions (1), (2) and (3) take place and the sudden upshoot in the potential of Pt indicator electrode is seen with a corresponding decrease in Br<sup>-</sup> (figure 2). Br<sup>-</sup> is regenerated by steps (5) and (6) and the downtrend in the potential is due to the bromine consumption and Br<sup>-</sup> production. Step (4) takes care of the autocatalytic production of HBrO<sub>2</sub> and step (7) the disproportionation of HBrO<sub>2</sub>. Thus the system switches back and forth between two steady states—low Br<sup>-</sup>, high Br<sub>2</sub> and high Br<sup>-</sup>, low Br<sub>2</sub>.

The inclusion of ferroin in the UBS modifies the scheme of reactions as indicated in steps (8) and (9). When ferroin is added reaction (8) takes place instead of (4). Fe(II) is regenerated by reaction (9) and the cycle continues.

#### 4. Conclusion

The oscillatory pattern in any uncatalysed bromate system with a Pt electrode is due to a periodic change in the concentration of Br<sub>2</sub>. The inclusion of a metal ion (Mn(II),

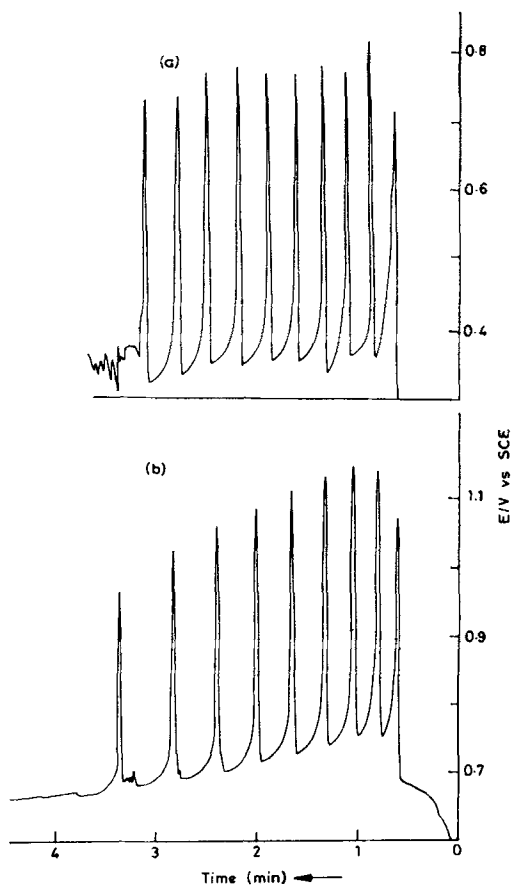


Figure 1. a. Simulated b. self-oscillating (UBS) concentration conditions in a. [Pyrogallol] =  $8 \times 10^{-3}$  M [H<sub>2</sub>SO<sub>4</sub>] = 0.8 M; [Br<sub>2</sub>] =  $10^{-3}$  M one drop at a time in b. [Pyrogallol] = 0.05 M; [H<sub>2</sub>SO<sub>4</sub>] = 2M; [KBrO<sub>3</sub>] = 0.1 M; temperature 35°C

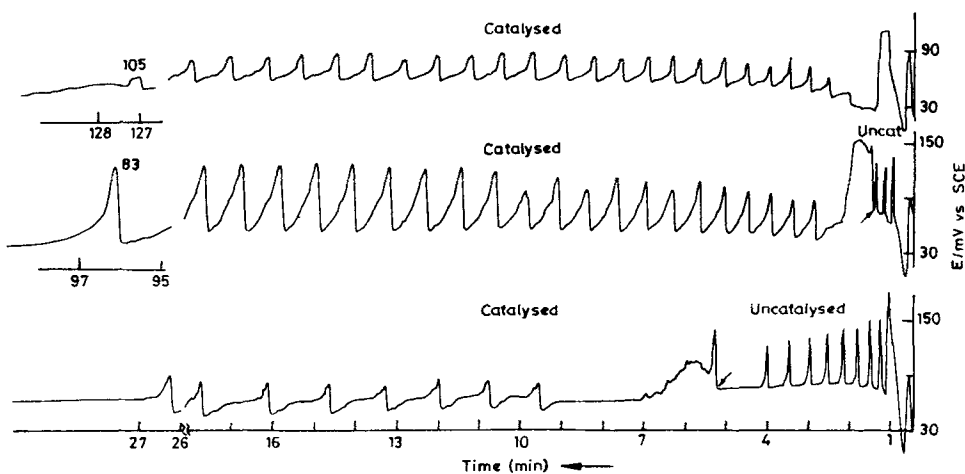


Figure 2. Oscillations in UBS and CBS with a Br<sup>-</sup> selective electrode concentration conditions [Pyrogallol] = 0.05 M; [H<sub>2</sub>SO<sub>4</sub>] = 2M; [KBrO<sub>3</sub>] = 0.1 M; [ferroin] = 0.022 M; Temperature = 33°C → indicates the point of addition of ferroin.

**Table 1.** Suggested mechanism for the UBS with pyrogallol and CBS with ferroin.

	UBS
(1) $\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+$	$\rightarrow \text{HBrO}_2 + \text{HOBr}$
(2) $\text{HBrO}_2 + \text{Br}^- + \text{H}^+$	$\rightarrow 2\text{HOBr}$
(3) $\text{HOBr} + \text{Br}^- + \text{H}^+$	$\rightarrow \text{Br}_2 + \text{H}_2\text{O}$
(4) $\text{BrO}_3^- + \text{H}^+ + \text{HBrO}_2 + \text{PG}$	$\rightarrow \text{PGQ} + 2\text{HBrO}_2 + \text{H}_2\text{O}$
(5) $2\text{Br}_2 + \text{PG}$	$\rightarrow \text{Br}_3\text{PG} + \text{Br}^- + \text{H}^+$
(6) $\text{Br}_2 + \text{PG}$	$\rightarrow \text{BrPG} + \text{Br}^- + \text{H}^+$
(7) $2\text{HBrO}_2$	$\rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+$
	CBS
(8) $2\text{Fe}^{2+} + \text{BrO}_3^- + 3\text{H}^+ + \text{HBrO}_2$	$\rightarrow 2\text{Fe}^{3+} + 2\text{HBrO}_2 + \text{H}_2\text{O}$
(9) $2\text{Fe}^{3+} \xrightarrow{\text{Organics}} 2\text{Fe}^{2+} + 2\text{H}^+$	

PG = pyrogallol; PGQ = pyrogalloquinone; BrPG = Bromopyrogallol (mono, di or tri); Br<sub>3</sub>PG = tribromopyrogallol.

Ce(III), Fe(II)) would lead to a switchover to a new oscillatory phase if the added couple has a larger value of exchange current density. The inclusion of species with comparable value of exchange current density would lead to a mixed control. The oscillatory pattern in any system would be that of the species possessing the largest value of exchange current density at the indicator electrode.

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