

## Oscillations in the bromate system with malic acid as the substrate

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**Abstract.** The oscillation characteristics, investigated by potentiometry, of the bromate-Mn(II)/Ce(III)-malic acid system are presented. The induction period characteristic of the oscillatory system is analysed. The results are compared with the malonic acid and citric acid systems and are correlated with the difference in the rate of bromide production, proposed as the control intermediate.

**Keywords.** Oscillatory reaction ; periodic reaction ; bromate-Mn(II)/Ce(III) system ; malic acid ; induction time.

### 1. Introduction

Oscillatory behaviour in chemical, biochemical and biological systems have been surveyed (Anon 1974; Franck 1978; Nicolis and Portnow 1973). Certain important aspects pertaining to the iodate and the bromate systems have been discussed (Ramaswamy *et al* 1978a). The present work deals with the bromate-Mn(II)/Ce(III)-malic acid oscillatory system.

### 2. Experimental

The concentration oscillations in  $Mn^{3+}/Mn^{2+}$  and  $Ce^{4+}/Ce^{3+}$  in these systems are followed as the varying potentials of a platinum indicator electrode using a Siemens  $x-t$  recorder. The platinum electrode is coupled with a SCE as reference electrode through a potassium nitrate salt bridge. Use of potassium chloride bridge is objectionable due to the inhibition of oscillations by chloride ions. Pre-treatment of the platinum electrode by immersing it in a solution containing bromate, sulphuric acid and manganous or cerous sulphate is found to be essential in order to obtain reproducible results.

### 3. Results and discussion

Standard conditions are chosen as 0.05 M potassium bromate, 2.23 M sulphuric acid, 0.05 M malic acid and 0.003 M/0.005 M of  $Mn^{2+}/Ce^{3+}$  at a temperature

of 40° C. All the constituents except potassium bromate are kept stirred magnetically in a polythene beaker thermostated at 40° C. Addition of the pre-thermostated bromate sets off the oscillations. Through repeated runs of the experiments under standard conditions, the reproducibility of the system is established and the oscillation characteristics are given in table 1.

In order to understand the role of each constituent in the oscillatory reaction, the effect of varying the concentration of the constituents taken one at a time, is considered.

The concentration of sulphuric acid is varied in the range 1.8 to 4.5 M. The minimum concentration used is 1M to avoid the possible hydrolysis of the higher valence metal ions. Concentrations  $\geq 3.6$  M lead to distortion and a decrease in the number of oscillations. Hence an optimum concentration of 2.23 M is chosen. Potassium bromate is varied in the range of 0.01 to 0.09 M. The induction period is practically a constant at 1.1 min in the  $Ce^{3+}$  system while an enormous increase from 1 to 15 min is observed in the  $Mn^{2+}$  system.

The metal ion is varied in the concentration range of 0.001 to 0.009 M. The induction period is found to increase with increasing concentrations of  $Mn^{2+}$  while in the  $Ce^{3+}$  system it remains constant (1.3 min). The significant decrease in the number of oscillations with increasing concentrations indicates the key role played by the metal ion. This is further exemplified by the dependence of the apparent energy of activation on the nature of the metal ion used. This dependence along with the temperature dependence of the oscillation parameters is discussed in detail (Ganapathisubramanian *et al* 1978; Ramaswamy *et al* 1979).

The effect of varying malic acid was studied in the range 0.03 to 0.15 M. The recordings for the  $Mn^{2+}$  system are presented in figure 1. The results obtained in the  $Ce^{3+}$  system are indicated in table 2.

The induction period decreases with increasing concentrations in both the systems. The total number of oscillations is found to increase with increasing concentrations of malic acid and reach a limiting value in the  $Mn^{2+}$  system while it remains constant over the whole range studied in the  $Ce^{3+}$  system.

Essentially, the oscillations in the above systems involve the oxidation of the metal ion by bromate through a number of elementary reactions followed by the reduction of the metal ion by the organic substrate. The reduction step is also a combination of elementary reactions involving free radicals. The oxidation of the metal ion is known to be inhibited by the presence of bromide (Barkin *et al*

Table 1. Oscillation characteristics under standard conditions.

Parameter	$Mn^{2+}$ system	$Ce^{3+}$ system
Induction period	4.7 min	1.1 min
Total number of oscillations	$26 \pm 1$	$12 \pm 1$
Total duration	24 min	6 min
Frequency of the oscillations	$0.022 \text{ sec}^{-1}$	$0.041 \text{ sec}^{-1}$

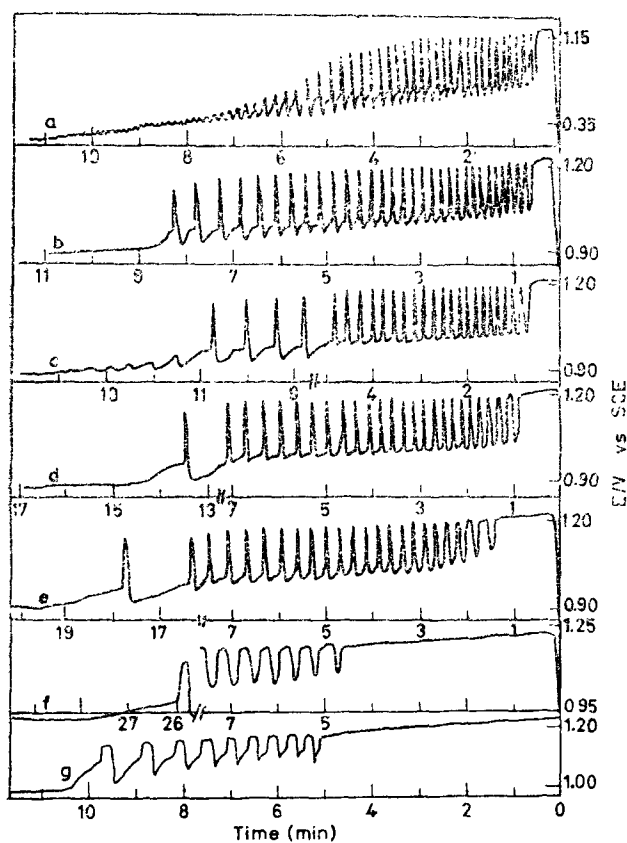
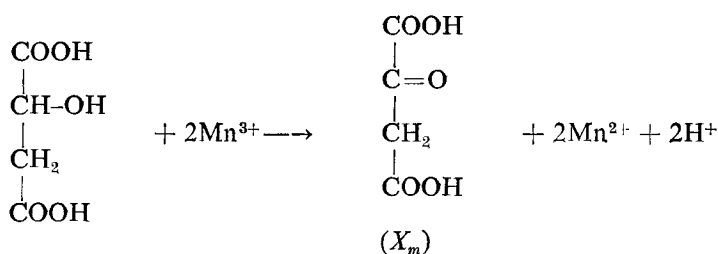


Figure 1. Effect of concentration of malic acid on the bromate system. Concentration conditions;  $\text{KBrO}_3$  0.05 M;  $\text{MnSO}_4$  0.005 M;  $\text{H}_2\text{SO}_4$  2.25 M; Temperature  $40^\circ\text{C}$ . Concentration of malic acid: (a) 0.15 M; (b) 0.12 M; (c) 0.1 M; (d) 0.09 M; (e) 0.07 M; (f) 0.05 M; (g) 0.03 M.

Table 2. Effect of the concentration of malic acid-Ce<sup>3+</sup> system.

Concn. of malic acid (M)	Induction time (sec)	Total duration (sec)	Oscillating time (sec)	Total No. of oscillations	Frequency of oscillations (sec <sup>-1</sup> )
0.03	116	502	386	11	0.029
0.05	66	380	314	13	0.041
0.07	50	374	324	12	0.037
0.09	42	364	322	13	0.084
0.11	30	286	256	12	0.047

1977). As a result, unless the concentration of bromide exceeds a critical value, the oxidation of the metal ion is not inhibited. During the period of induction (Edelson *et al* 1975) the concentration of bromide is low because its rate of formation is small resulting in a steady state concentration of the oxidised metal ion. The oxidation of malic acid by  $Mn^{3+}$  is found to be slow compared with citric and malonic acid (Ganapathisubramanian *et al* 1979) which results in a slow build-up of the oxidised product possibly oxaloacetic acid ( $X_m$ ).



The formation of oxaloacetic acid ( $X_m$ ) by the permanganate oxidation of malic acid has been reported (Blanchetiere 1916). This can undergo bromination due to the presence of active methylene group. But the bromination step resulting in the formation of  $Br^-$  is slow because of the slow build-up of oxaloacetic acid. This results in the slow build-up of  $Br^-$  leading to a large period of induction. This is further confirmed by the fact that the addition of  $Br^-$  ( $5 \times 10^{-4}$  M) reduces the induction period to one-third the original value. Thus the observations with malic acid support the suggestion that bromide is the controlling intermediate.

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