

## The iodate-hydrogen peroxide system: An oscillatory chemical reaction

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**Abstract.** Certain salient features of the oscillatory reaction in the iodate-hydrogen peroxide-manganese sulphate-malonic acid system are presented. Oscillations were followed by recording the potential developed at a platinum electrode. Reproducibility of the results in such a complicated system is established. Evidence is provided for the periodic formation of  $Mn^{3+}$  in the system. Effect of the concentration of the constituents as well as the effect of temperature are discussed.

**Keywords.** Oscillatory reaction; periodic reaction; oscillation reproducibility; iodate-hydrogen peroxide— $Mn^{3+}$  system.

### 1. Introduction

Chemical oscillations involving periodic concentration changes of chemical species were first reported (Bray 1921) in the iodate-hydrogen peroxide system. Following this several biological and a few chemical systems where concentration changes of an oscillating nature take place have been reported (Nicolis and Portnow 1973; Noyes and Field 1974). The reaction reported by Bray (1921) was followed either by measuring the volume of gas evolved (Peard and Cullis 1951) or by the measurement of light absorption by iodine (Degn 1967). The addition of malonic acid and manganese sulphate was reported (Briggs and Rauscher 1973) to accentuate the oscillations.

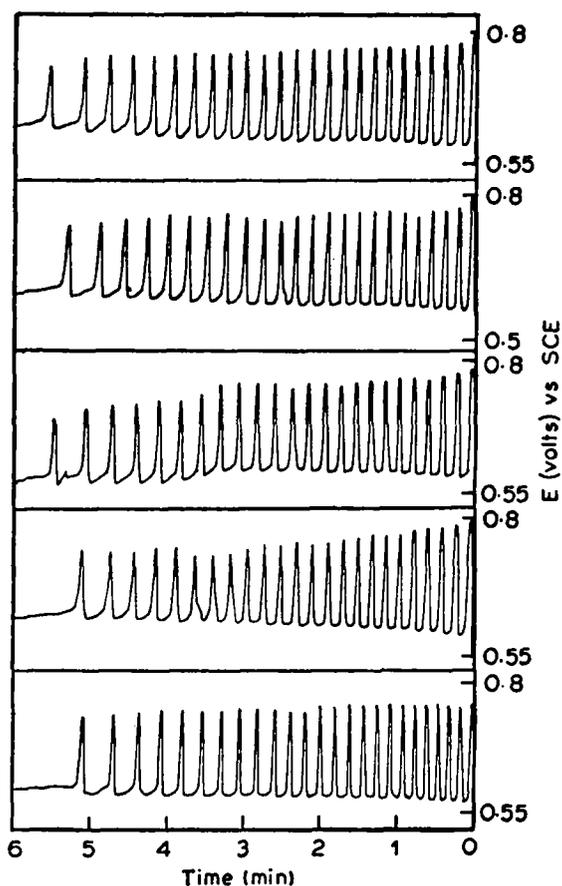
### 2. Experimental

The reaction system employed in the present investigation contained hydrogen peroxide, potassium iodate, manganese sulphate, malonic acid, perchloric acid and starch. The composition of the solution for a representative experiment is given in the table 1. Requisite amounts of the stock solutions of the various constituents are mixed in a polythene beaker and the temperature maintained at 27°C. The system commences to oscillate immediately after the addition of the last constituent, usually hydrogen peroxide. The presence of starch enables visual observation of the oscillations with the periodic appearance and disappearance of the blue colour of the

starch-iodine complex. The oscillations are followed by a continuous recording of the e.m.f. between a platinum indicator electrode and a saturated calomel electrode connected through a potassium nitrate bridge to a suitable recorder. Stirring with a magnetic stirrer ensured homogeneity of the solution. In the earlier part of the investigation it was found that the behaviour of the oscillating system was totally irreproducible. This was traced to the glass walls interfering with the reaction. The use of a polythene container is a very important factor in ensuring reproducibility of the observations so that one could investigate with confidence the effect of varying the

**Table 1.** Solution composition

	Concentration (M)
Potassium iodate	0.06
Hydrogen peroxide	1.20
Malonic acid	0.05
Manganous sulphate	0.006
Perchloric acid	0.05
Starch	0.01 %



**Figure 1.** Reproducibility (temperature 27°C).

different parameters. The high degree of reproducibility is illustrated by the recordings of five different experiments under identical conditions (table 1) presented in figure 1. The solution develops a blue colour characteristic of the starch-iodine complex as the base potential is approached. The blue colour disappears when the potential reaches the peak value. One could discern a pale pink colour in the solution near the peak potential.

### 3. Results and discussion

The formation of iodine near the base potential region is evident from the characteristic blue colour. The rise of potential leading to the formation of each wave is probably due to the promotion of manganese to the higher valence state. The pale pink colour near the peak potential region suggests the possibility that trivalent manganese formed periodically is responsible for the rise of potential. The formation of tetravalent manganese is unlikely since no green colour is observed. A series of solutions were made with concentrations corresponding to the representative experimental solution but excluding one of the constituents each time. In all cases the static potential was close to the base potential value, making it difficult to isolate the constituent responsible for the base potential. In the instance when trivalent manganese salt prepared separately was added to a solution containing all other constituents, the potential corresponded to the peak value.

Further evidence for the presence of trivalent manganese in the system was sought through spectroscopic measurement. While studying the effect of change in the hydrogen peroxide concentration, it was observed that no oscillation resulted at 0.17 M  $H_2O_2$ ; instead a more or less steady potential corresponding to the peak value was recorded, possibly due to a near steady concentration of trivalent manganese being maintained. A spectrum was taken for this solution in the range 500 to 300 nm. This was compared with the standard curves obtained in this range using known concentrations of  $Mn^{3+}$  in the concentration region 1 to 5 mM. In both instances a maximum in the absorbance occurred at 480 nm and the spectra were similar.

A spectrophotometric recording was made for the iodate-hydrogen peroxide system at two wave lengths (600 and 480 nm) for the purpose of comparing them with the spectra with known concentration of trivalent manganese or iodine. However, there was difficulty in resolution because of interference due to absorbance by iodine. Spectroscopic evidence for the presence of trivalent manganese was therefore sought in the bromate-manganese system. A series of spectra for bromine in the concentration range 1 to 5 mM was recorded in the region 500 to 300 nm. For bromine the absorbance at 390 nm is greater than at 300 nm whereas for trivalent manganese it is the other way round. For the bromate-manganese system the oscillations were recorded at fixed wave lengths of 300 and 390 nm. The absorbance amplitude at 300 nm was much greater than at 390 nm thereby providing evidence for the formation of trivalent manganese in the system. The fact that the manganese ion is playing a key role in the oscillatory reaction is evident from the remarkable influence of the concentration of manganese sulphate on the reaction. For a variation of  $MnSO_4$  concentration in the range 0.008 M to 0.001 M, the number of oscillations for complete reaction increased from 15 in 2.5 minutes at 0.008 M to 266 in 26.3 minutes at 0.001 M. At the lower concentration of  $MnSO_4$ , the amplitude of the oscillation is however smaller.

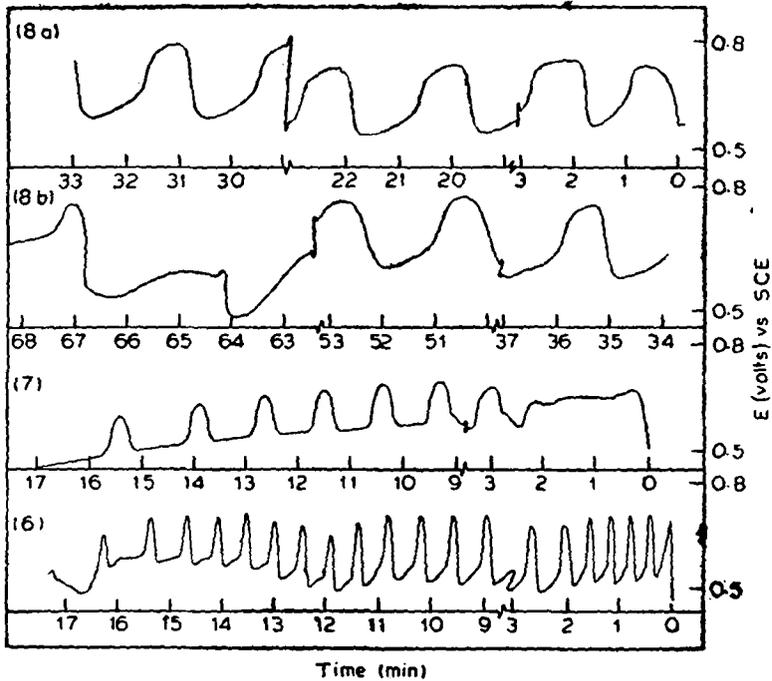
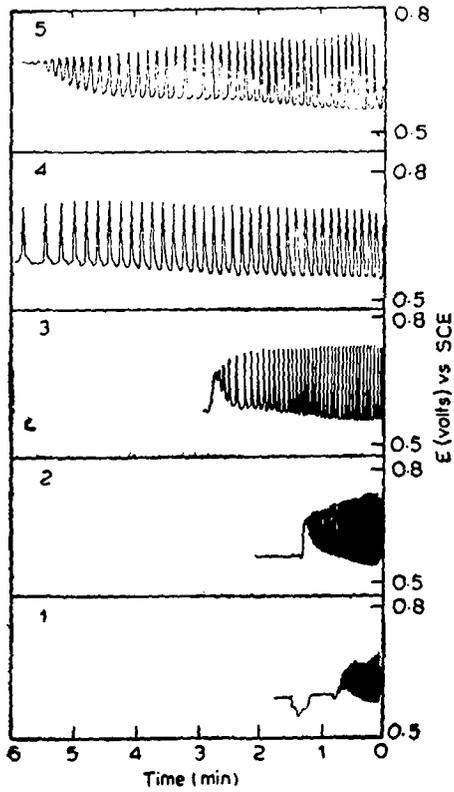


Figure 2. Effect of temperature a. 1-61°C; 2-50°C; 3-40°C; 4-33°C; 5-27°C; b. 6-17°C; 7-10°C; 8a and 8b-0°C.

The role of perchloric acid is essentially to provide hydrogen ions. Oscillations could be obtained with  $\text{H}_2\text{SO}_4$  as well as with a slight increase in the number of oscillations under identical conditions. When the concentration of perchloric acid was varied in the region of 0.0375 M to 0.125 M the number of oscillations and time for complete reaction decreased from 42 in 7.3 min to 10 in 3.1 min. At the higher concentrations of perchloric acid (0.1 M and 0.125 M) the peak was found to be blunt possibly indicating the greater stability of manganese ion in its higher valence state. The concentration of hydrogen peroxide has a very pronounced influence in the range 0.17 to 1.0 M. There is a gradual decrease in the number of oscillations from 23 in 4.7 min at 1.0 M to 4 in 2.7 min at 0.17 M. At a concentration of 0.68 M there is an induction time which increases with decrease in concentration to a value of 1.1 min at 0.34 M. At the lower concentrations of  $\text{H}_2\text{O}_2$  the peak is blunt. At a concentration of 0.17 M no oscillation occurs and the potential recorded corresponds nearly to the peak value.

Malonic acid acts as the iodine consumer. Iodine is decolourised by malonic acid when the two solutions are mixed. The reaction occurs probably by the replacement of the methylenic hydrogen in malonic acid by iodine. The use of acetic, oxalic or succinic acid in the place of malonic acid failed to produce oscillations. However, compounds like acetyl acetone and ethyl aceto acetate could be employed instead of malonic acid.

The concentration of malonic acid influences the oscillating reaction considerably. The number of oscillations increased from 12 in 3.3 min at 0.03 M to 63 in the same duration at 0.15 M. At 0.2 M, no oscillation occurs; instead the potential corresponding to the peak value was recorded.

The influence of the concentration of potassium iodate was observed in the range 0.02 M to 0.08 M. The oscillations increased from 16 in 2.5 min to 84 in 10.5 min. With the higher concentration of potassium iodate (0.08 M to 0.05 M) precipitation of iodine occurred at the end. However, when the concentration of potassium iodate was lower (0.04 M and 0.02 M) compared to that of malonic acid (0.05 M), there was no precipitation of iodine.

The periodic rise in potential during the reaction is probably due to the formation of trivalent manganese followed by its involvement in a reaction leading to the generation of molecular iodine from iodate. The iodine does not accumulate due to its reaction with malonic acid when a critical concentration is reached. The influence of temperature on the oscillatory reaction is considerable. The composition of the solution corresponds to that given in the table except that  $\text{H}_2\text{SO}_4$  of the same concentration was used instead of  $\text{HClO}_4$ . The temperature was varied in the range  $0^\circ$  to  $61^\circ\text{C}$ . In all cases the number of oscillations remained constant (37). However, the duration increased from 0.7 min at  $61^\circ\text{C}$  to 68 min at  $0^\circ\text{C}$  (figures 2a, and 2b).

The oscillations appear to be brought about by an overshooting of the reaction either due to a necessity of a nucleation step for formation of a new phase or some other cause. Further investigations are in progress to isolate the steps in the consecutive reactions taking place in this system in order to elucidate the mechanism of the oscillations.

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