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Limit cycle behaviour in the Belousov-Zhabotinskii oscillatory reaction

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Abstract. Oscillations in the bromate-Mn(II)-organic substrate system are studied by following the concentrations of Mn(III) and Br_2 spectrophotometrically, apart from monitoring the concentration of Br^- by potentiometry. Limit cycles for the Mn(III)-Br_2 combination are constructed experimentally and theoretically. The experimental results agree with the theoretical expectations based on a suggested mechanism.

Keywords. Belousov-Zhabotinskii reaction; oscillatory reaction; periodic reaction; limit cycles; spectrophotometry.

1. Introduction

Oscillatory chemical reactions (Nicolis and Fortnow 1973; Noyes and Field 1974; Franck 1978) have gained considerable importance in recent years. One of the reasons for such an interest stems from the fact that some of the vital biological processes are oscillatory in nature (Pavlidis 1973). In general oscillating phenomena are characterised by several consecutive steps, at least one feedback process and limit cycles. Of all the oscillating systems, the Belousov-Zhabotinskii (BZ) reaction, viz, the oxidation of malonic acid by bromate with Ce(III) or Mn(II) has been the one most widely studied (Anon 1974; Noyes and Field 1977; Field and Noyes 1977). The BZ system consisting of BrO_3^- - Mn(II)/Ce(III)-organic substrate (*e.g.* malonic acid, citric acid or malic acid) in H_2SO_4 medium has been investigated in this laboratory (Ramaswamy *et al* 1977) by potentiometry (a platinum electrode for Mn(III)/Mn(II) couple and a Ag/AgBr electrode for Br^-) and by spectrophotometry. Concentrations of Mn(III) and Br_2 have been monitored at 480 nm and 390 nm respectively and the limit cycles obtained experimentally for the first time.

For such a system (BrO_3^--Ce(III)-malonic acid) a model called Oregonator was suggested (Noyes and Field 1974) and the deterministic reaction rate equations derived from that model were solved by numerical integration using appropriate initial conditions. Oscillations in the concentrations of the intermediates Br^-,

$HBrO_2$ and Ce(IV) with time were obtained by this analysis. Although Br_2 is considered as a possible intermediate in the reaction scheme, the Oregonator model does not take it into consideration.

Concentrations of the intermediates, when plotted against each other, yield limit cycles which are closed curves and stable to perturbations (Minorsky 1962). They are otherwise called periodic trajectories (Pavlidis 1973). Limit cycles are useful visual aids in the analysis of these systems. Oscillating systems can easily be characterised by their limit cycles as well as by the temporal profiles of the concentration of the intermediates. Theoretical limit cycles for the various combinations of the intermediates have been reported (Noyes and Field 1974). Although Br_2 was also considered as an intermediate in an improved model (Edelson *et al* 1975), the limit cycle for the Mn(III)/Ce(IV)–Br_2 has not been obtained. In the present investigation a mechanism is proposed and the limit cycles obtained theoretically are compared with experimental ones.

2. Experimental

All constituents except $KBrO_3$ were taken in a cell provided with a Pt electrode in combination with a saturated calomel reference electrode, thermostated and kept agitated by a magnetic stirrer. The oscillations were triggered off by adding thermostated $KBrO_3$ and the potential plotted using an X–*t* recorder. An Ag/AgBr electrode was used to monitor Br^-. Spectrophotometric recordings were taken in a 2 cm cell at a fixed wavelength using a Carl–Zeiss spectrophotometer. The concentration conditions employed for various experiments are given in the legend to figures.

3. Results and discussion

Since the Pt electrode is subjected to a certain interference due to mixed potentials, potentiometry could not be used for monitoring the exact concentration of Mn(III). A fairly wide separation of the values of λ_{max} for Mn(III) and Br_2 (480 nm and 390 nm respectively) enabled a fairly accurate spectrophotometric estimation of Mn(III) and Br_2. These recordings with malonic acid as the substrate are shown in figure 1. These values were first normalised and used for the construc-

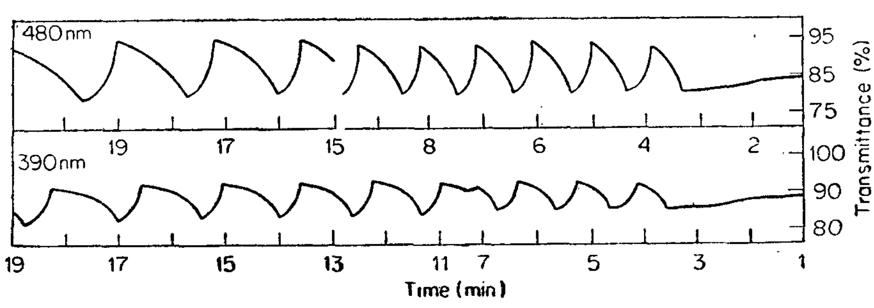

Figure 1. Spectrophotometric oscillations in the bromate system. Concentration conditions : $KBrO_3$ 0·05 M; $MnSO_4$ 0·005 M; H_2SO_4 1·0 M; malonic acid 0·02 M; T 27° C.

tion of the limit cycle for the above combination. The normalisation was necessary because no two oscillations at these wavelengths had the same duration, probably due to slight variations in experimental conditions. This is expected not to alter the relationships as the phase relationships of all the intermediates especially Br^- and Mn(III)/Mn(II), were found to be maintained the same throughout all the oscillations.

The limit cycle, obtained experimentally, is of a characteristic shape (a cross type), as shown in figure 2. The different stages in the oscillatory reaction are governed by a number of intermediates. It is quite possible that two of them have the same set of concentration values at two different stages of an oscillation, while the course of the reaction is determined by the other intermediates as well.

A model consisting of eight reactions (table 1) involving five intermediates (Br^-, $HBrO_2$, HOBr, Mn(III) and Br_2) is suggested and the differential equations are subjected to numerical integration analysis using the method of Gear (1971). The values of the rate constants used are taken from literature (Edelson *et al* 1975).

This gives rise to oscillations in the concentration of the above intermediates as well as the limit cycles. The limit cycle for the Mn(III)–Br_2 combination was similar in shape to the experimentally observed one. Furthermore, the limit cycle for the Ce(IV)–Br_2 combination was constructed from the results of Edelson *et al* (1975) which was also similar in shape to these two limit cycles (figure 2). These observations substantiate that the limit cycles (especially for the combination Mn(III)–Br_2) are characteristic of this oscillating system, providing vital information regarding the mechanistic pathway.

The model could not be modified suitably for the citric and malic acid systems, because the products and kinetics of their reactions with Mn(III) are not yet established. However, the limit cycle for the above combination in these two substrate systems were obtained experimentally (figure 3) which are simple closed curves, in contrast to the cross-type curve for Mn(III)–malonic acid. This suggests that

Table 1. Suggested mechanism: consecutive reactions in each cycle leading to oscillations in the BZ system.

1.	$Br^- + BrO_3^- + 2H^+ \rightarrow HBrO_2 + HOBr$	$1 \cdot 34\ M^{-1}\,sec^{-1}$
2.	$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr$	$1 \cdot 6 \times 10^9\ M^{-1}\,sec^{-1}$
3.	$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$	$8 \cdot 0 \times 10^9\ M^{-1}\,sec^{-1}$
4.	$Br_2 + CH_2\,(COOH)_2 \rightarrow BrCH\,(COOH)_2 + H^+ + Br^-$	$6 \cdot 0\ M^{-1}\,sec^{-1}$
5.	$BrO_3^- + HBrO_2 + 2Mn\,(II) + 3H^+ \rightarrow 2HBrO_2 + 2Mn\,(III) + H_2O$	$8 \cdot 0 \times 10^3\ M^{-1}\,sec^{-1}$
6.	$2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$	$4 \times 10^{+7}\ M^{-1}\,sec^{-1}$
7.	$Mn\,(III) + CH_2\,(COOH)_2 \rightarrow Mn\,(II)$ + Products*	$1 \cdot 0\ M^{-1}\,sec^{-1}$
8.	$Mn\,(III) + BrCH\,(COOH)_2 \rightarrow Mn\,(II) + Br^-$ + Products*	$1 \cdot 0\ M^{-1}\,sec^{-1}$

*Products refer to CO_2 and HCOOH.

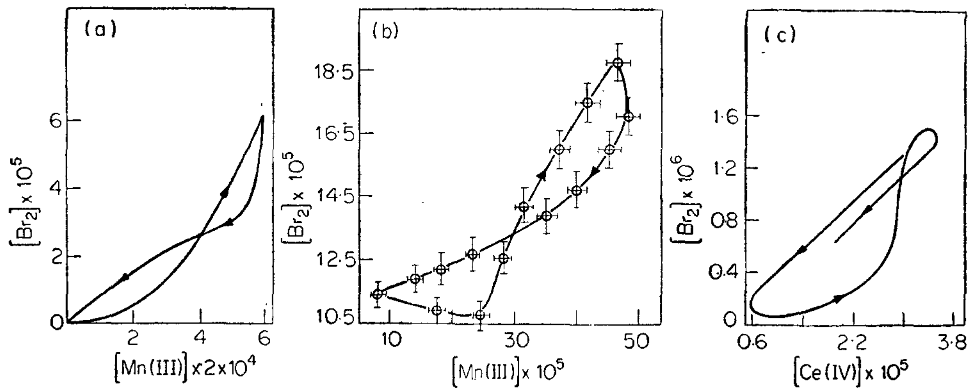

Figure 2. Limit cycles: (a) computed limit cycles from the suggested mechanism; (b) experimental limit cycle. Concentration conditions: $KBrO_3$ 0·05 M; $MnSO_4$ 0·005M; H_2SO_4 1·0 M; malonic acid 0·02 M; T 27° C; (c) limit cycle constructed from Edelson's work.

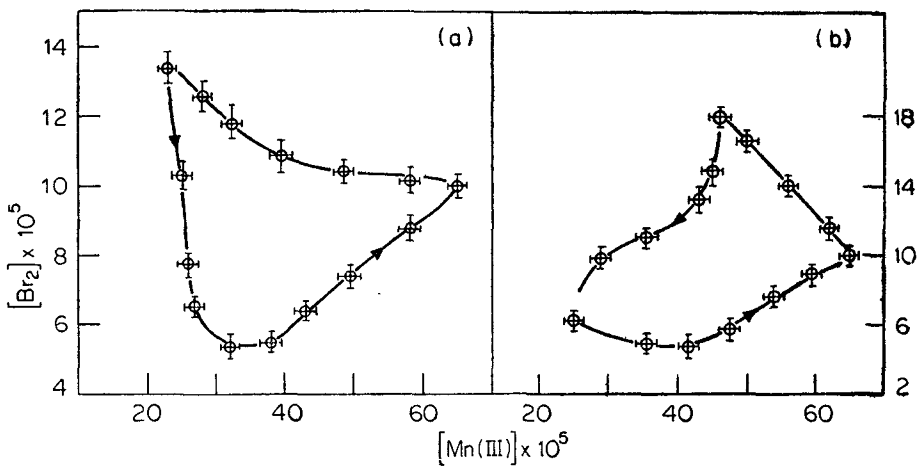

Figure 3. Experimental limit cycles: concentration conditions: $KBrO_3$ 0·05 M; $MnSO_4$ 0·005 M; H_2SO_4 1·0 M; T 27° C (a) citric acid 0·05 M, (b) malic acid 0·1 M.

some of the reaction steps in the overall mechanism which involve these substrates are different from those of malonic acid. Such a behaviour could be traced to the rates of oxidation of the substrate by Mn(III) and the bromination of the substrate or its oxidised product. Because of this, the rate of production of Br^- which is called the control intermediate is different in these cases resulting in different kinds of limit cycles (Ganapathisubramanian *et al* 1979). In conclusion the results support the view that limit cycles are characteristic of the nature of the oscillating system.

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