

# Effect of temperature and associated bifurcation in the oscillatory Belousov–Zhabotinskii reaction in a flow reactor

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Oscillatory characteristics of the Belousov–Zhabotinskii reaction as a function of temperature have been investigated in a continuous flow stirred tank reactor. Oscillations are not observed above a critical temperature limit. The limit is found to be associated with a Hopf bifurcation. Numerical computations show that the results can be qualitatively interpreted on the basis of the Oregonator model.

## 1. Introduction

The oscillatory Belousov–Zhabotinskii (BZ) reaction system has been the subject of considerable current interest [1–3]. Efforts have been made to understand the complex dynamics of the system. Physical perturbations of the BZ reactions by temperature [4–7], ultraviolet, visible and cobalt-60  $\gamma$  radiations [8–12] have been investigated. Körös [4] reported the dependence of the oscillatory frequency on temperature. The apparent energy of activation was reported to be of the order of 65 kJ/mol both for Ce and Mn catalyzed BZ systems. It has been pointed out [5,6] that the oscillatory frequency depends on the reaction



which is a rate determining step for the  $\text{Br}^-$  consumption process in the Field, Körös and Noyes (FKN) mechanism [13]. The effect of radiation has been reported to be associated with the catalyst while uncatalyzed oscillators were found to be unaffected by the radiation. Upper and lower temperature limits of instability have also been reported [14] in uncatalyzed BZ systems.

Since temperature can markedly influence the dy-

namics of the BZ reaction system, and only a few studies have been made, we have investigated the bifurcation behaviour of the catalyzed BZ system containing malonic acid +  $\text{Ce}^{4+}$  +  $\text{BrO}_3^-$  +  $\text{H}_2\text{SO}_4$  at different temperatures in a continuous flow stirred tank reactor (CSTR). Difficulty arises in explaining the temperature-related result since the activation energies of most of the reactions are not known. Rastogi and Misra [15] have shown that the bond breaking and bond formation reactions are greatly affected by the temperature. Since the Oregonator [16] adequately describes most of the dynamic features of the malonic acid containing BZ system, we have examined the Oregonator in the present situation.

## 2. Experimental

Potassium bromate (A.R., J.T. Baker), malonic acid (A.R., C.D.H.), ceric ammonium sulphate (A.R., Wilson Laboratory, Bombay) and sulphuric acid (G.R., E. Merck) were used as such without further purification. Oscillations were monitored with a bright platinum electrode and a bromide-selective electrode (Orion, 94-35) in conjunction with a calomel electrode as a reference using a double pen electronic recorder (Digital Electronics Ltd., Bombay, Omniscrite series 5000). Experiments were

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done in a continuous flow stirred tank reactor (CSTR) as used earlier [17].

Oscillations in the redox potential and  $\text{Br}^-$  potential for the system malonic acid +  $\text{Ce}^{4+}$  +  $\text{BrO}_3^-$  +  $\text{H}_2\text{SO}_4$  were recorded at different temperatures. The results are recorded in fig. 1.

### 3. Results and discussion

Results recorded in fig. 1 show that there is an upper temperature limit beyond which no oscillations are observed. Oscillations are again generated when temperature is decreased below the critical value (bifurcation point). The interesting behaviour is that when the temperature approaches the critical value, the amplitude of the oscillations tends to zero while the time period remains finite, which indicates the occurrence of a supercritical Hopf bifurcation. Both

the amplitude and time period as a function of temperature are plotted in fig. 2, supporting the above contention. Further, fig. 2 shows that the amplitude decreases sharply near the bifurcation point.

The nature of the bifurcation can be tested by using the scaling laws, as pointed out by Argoul et al. [18]. According to them, for a non-degenerate Hopf bifurcation (super critical), the following power laws should be satisfied:

- (i)  $\tau \sim |\lambda - \lambda_c|^\alpha$ ,
- (ii)  $A \sim |\lambda - \lambda_c|^\beta$ , and
- (iii)  $\alpha = 1$ ;  $\beta = \frac{1}{2}$ ,

where  $\tau$  is the time period,  $A$  is the amplitude,  $\lambda$  is the bifurcation parameter and  $\lambda_c$  the bifurcation point.

Experimental data plotted in fig. 3 give  $\alpha = 1.09$  and  $\beta = 2.82$ , showing the possibility of the occurrence of a degenerate Hopf bifurcation near the end of oscillation. The high value of  $\beta$  may be due to the non-availability of enough data close to the bifurcation point. It should be noted that the bifurcation would be degenerate for any value of  $\beta$  not equal to  $\frac{1}{2}$ , and that  $\beta$  equal to  $\frac{1}{4}$  would be the case of the simplest type of degenerate Hopf bifurcation.

We have attempted to explain the observed be-

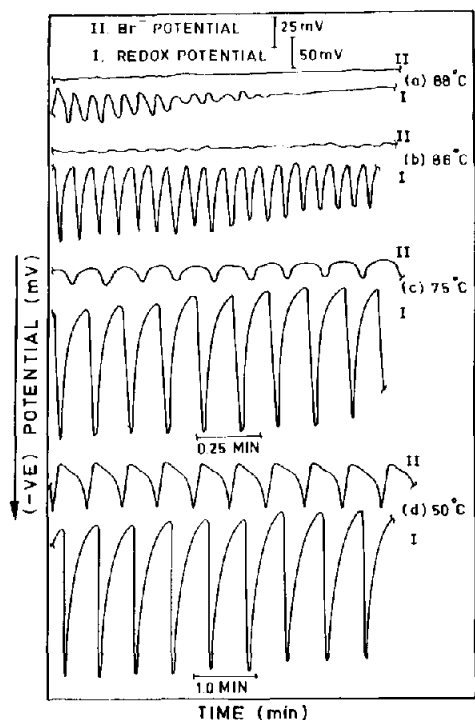


Fig. 1. Oscillations in redox potential and  $\text{Br}^-$  potential in a CSTR:  $\text{H}_2\text{SO}_4$  (1.5 M) +  $\text{Ce}^{4+}$  ( $5.0 \times 10^{-4}$  M) + malonic acid ( $3.66 \times 10^{-2}$  M) +  $\text{KBrO}_3$  ( $2.0 \times 10^{-2}$  M). Values within parentheses denote the feed concentrations.  $k_0 = 8.33 \times 10^{-4} \text{ s}^{-1}$  and rate of increase of temperature =  $0.5\text{--}1.0^\circ\text{C/min}$ .

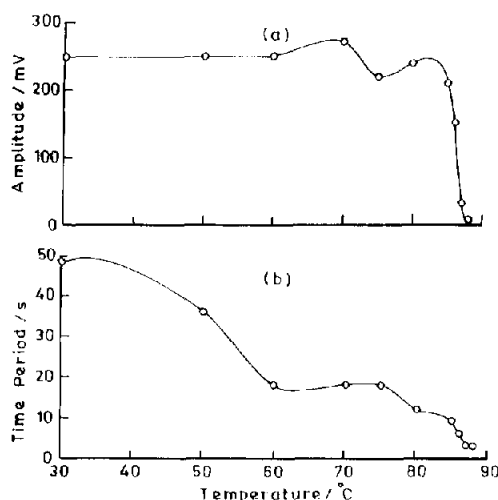


Fig. 2. (a) Plot of amplitude of redox potential oscillations versus temperature. Other conditions are the same as in fig. 1. (b) Plot of time period of redox potential oscillations versus temperature (time period of both redox potential and  $\text{Br}^-$  potential oscillations were the same). Other conditions are the same as in fig. 1.

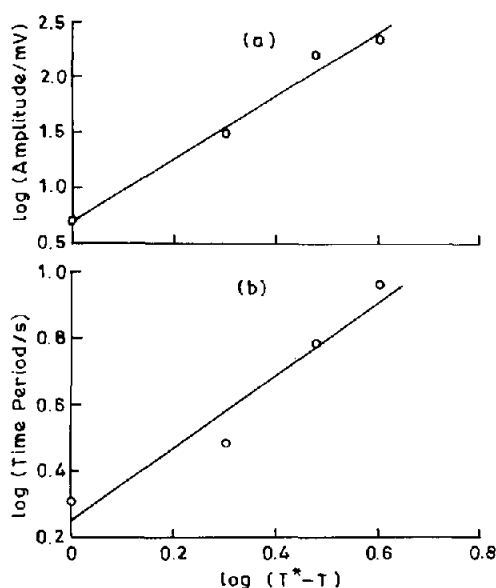
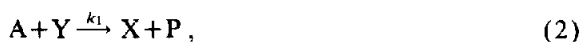


Fig. 3. Plot of (a) log(amplitude) (b) log(time period) versus  $\log(T^* - T)$ .  $T^*$  is the critical temperature at which oscillation stops and  $T$  is the temperature. Solid lines are the least-squares fit which give  $\alpha = 1.09$  and  $\beta = 2.82$ . Other conditions are the same as in fig. 1.

haviour by numerical computations using the Orongator [16], which envisages the following steps:



where  $A = \text{BrO}_3^-$ ,  $X = \text{HBrO}_2$ ,  $Y = \text{Br}^-$ ,  $Z = 2\text{Ce}^{4+}$  and  $MA = \text{malonic acid}$ .

Step (6) involves bromination of malonic acid by  $\text{HOBr}$  and  $\text{Br}_2$  and oxidation of malonic acid by  $\text{Ce}^{4+}$  and subsequent reaction of brominated organics of malonic acid with  $\text{Ce}^{4+}$  and other species which produce free radicals and  $\text{Br}^-$ . Since these reactions involve oxidation and bromination and it has been pointed out [15] that the oxidation reaction becomes more prominent at higher temperatures, the

rate constant of step (6) can be taken as the bifurcation parameter. Although the rate constants of the other steps (2)–(5) which involve reaction of mainly ionic species would also be affected with the increase of temperature, it may be assumed that the variation of the rate constant of step (6) with temperature would dominate over the others, since the energies of activation of bond formation and bond breaking reactions are usually higher than for reactions involving ionic species. Computer results can be compared qualitatively with the experimental observations by computing the amplitude and time period for varying values of  $k_5$ , although there is no exact similarity.

The above arguments are supported by the activation energy data for the steps (2) and (3) reported earlier by Kshirsagar and Field [19]: energy of activation is 54 and 26.4 kJ/mol for steps (2) and (3), respectively.

Activation energy data for the other steps (4)–(6) are not available. It should be noted that step (6) is the slowest reaction and its energy of activation may be higher compared to the others.

Computations have been made for CSTR conditions by including inflow and outflow of  $\text{BrO}_3^-$ ,  $\text{Ce}^{4+}$  and malonic acid and outflow of  $\text{HBrO}_2$  and  $\text{Br}^-$  and using the latest values of rate constants due to Field and Försterling [20] (FF set). Calculations have been performed with an HCL PC/AT computer and using the subroutine [21] STIFF3. Conservation of [cerium(IV)] has also been taken into account.

The following rate expression was used for the step (6):

$$\text{rate} = k_5 [\text{malonic acid}] [2\text{Ce}^{4+}].$$

Computed results for the amplitude and time period for different  $k_5$  are plotted in fig. 4. The amplitude was calculated by taking the ratio of  $[\text{Ce}^{4+}]_{\text{maximum}}$  and  $[\text{Ce}^{4+}]_{\text{minimum}}$ . The value of  $k_0$  (where  $k_0$  is the inverse of the residence time) used in the calculations, has been taken to be  $1.0 \times 10^{-5} \text{ s}^{-1}$ . However, it may be argued that this value is lower by a factor  $10^2$  than the corresponding experimental value. Calculations reveal that no oscillations are obtained when the experimental value of  $k_0$  is used. Oscillations of low amplitude are obtained at high values of  $k_5$ . Computed results (amplitude versus  $k_5$  and time period versus  $k_5$ ) show similar

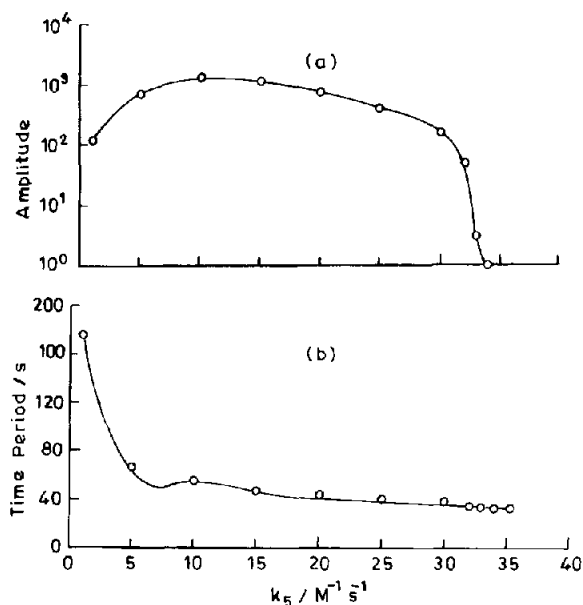


Fig. 4. (a) Plot of computed amplitude ( $Ce^{4+}_{\text{maximum}}/Ce^{4+}_{\text{minimum}}$ ) versus  $k_5$ . Total [cerium(IV)] =  $5.0 \times 10^{-4}$  M. Initial  $[BrO_3^-]$  =  $2.0 \times 10^{-2}$  M and [malonic acid] =  $3.66 \times 10^{-2}$  M.  $k_0$  was taken to be equal to  $1.0 \times 10^{-5} \text{ s}^{-1}$ . (b) Plot of computed time period versus  $k_5$ . Other conditions are the same as in (a).

behaviour to those obtained experimentally (fig. 2). Both experimental and computed results show a sharp decrease in the amplitude near the end of the oscillations. However, the time period decreases gradually and remains finite. It should be noted that a rich dynamic behaviour [22–24] is associated with the step (6) when the stoichiometric factor  $f$  of the Oregonator [16] becomes the bifurcation parameter. Bar-Eli and Brons [24] have reported that in a subcritical Hopf bifurcation (or loop-loop bifurcation) there is a sharp increase of the period when  $f$  was varied.

Although most Oregonator studies [22,23] give subcritical Hopf bifurcations, the apparent occurrence of a supercritical Hopf bifurcation in the present case is not surprising. The difference may arise for the following reasons:

(1) Nielsen et al. [25] reported that in the Oregonator with flow the bifurcation from the thermodynamic branch is always supercritical while bifurcation from the flow branch is supercritical at higher values of  $f$  and subcritical at lower values of  $f$  with the FF set of rate constants. These are always sub-

critical with the FKN [13] set of rate constants. Similar bifurcations in the Oregonator with flow with the FF and FKN sets of rate constants have been obtained [25] in the case when the rate constant of the step associated with the stoichiometric factor  $f$  (i.e. step (6)) was varied while  $f$  was held constant. It should be noted that in previous studies [22,23] the FKN set of rate constants was used while in the present work the latest set of rate constants (the FF set) has been used.

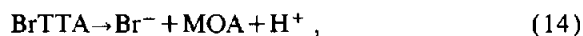
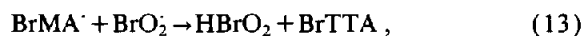
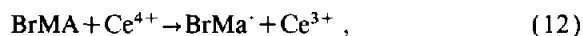
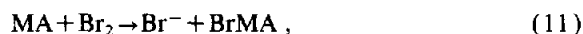
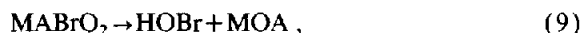
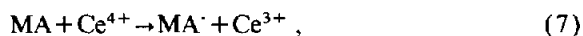
(2) In the present case, bifurcation analysis is based on the amplitude and time period of oscillations obtained directly from the numerical integration of the differential equations resulting from the Oregonator, while in other studies [22,23] the analyses are based on analytical methods using steady-state approximations.

(3) A three-variable Oregonator has been used in the present case while in the previous cases [22,23] the steady-state concentration of  $HBrO_2$  has been assumed and a two-variable Oregonator has been used. Since  $HBrO_2$  is an important species in the BZ reaction mechanism and an important dynamic variable of the Oregonator, it may be that the steady-state approximation of  $[HBrO_2]$  gives different results.

(4) It has been pointed out [23] that a continuous increase in amplitude is expected following supercritical bifurcation while fully developed oscillations appear following a subcritical bifurcation. These points are further strengthened by the fact that "appearance of full blown oscillations at the end of the induction period in the BZ reaction is usually explained by a subcritical Hopf bifurcation" [26]. In the present case, the system moves from an oscillatory state to a non-oscillatory state which is just the reverse of the case where the system moves from a steady state to the full blown oscillatory state.

Stoppage of oscillations at higher temperatures can be explained as follows: since the BZ reaction involves complicated [3,27,28] organic chemistry and there is a possibility of inhibition of the autocatalytic reaction by organic radicals which are produced by  $Ce^{4+}$  oxidation of malonic acid, it seems that oscillations at higher temperatures are controlled by a radical. Further, in view of the recent studies, a question arises whether it is due to the malonyl radical ( $MA^{\cdot}$ ) [27,28] or to  $BrMA^{\cdot}$  [3]. The important reactions associated with the production of these two

radicals and inhibition of autocatalysis are:



where BrTTA = bromohydroxymalonic acid and MOA = mesoxalic acid.

The primary sources of the production of  $\text{MA}^{\cdot}$  and  $\text{BrMA}^{\cdot}$  are the reactions (7) and (12), respectively. Since reaction (7) is fast enough ( $\approx 2.5$  times) compared to (12), and since  $\text{MA}^{\cdot}$  seems to be more reactive compared to  $\text{BrMA}^{\cdot}$ , it is possible that the autocatalytic inhibition due to  $\text{MA}^{\cdot}$  predominates over the inhibition due to  $\text{BrMA}^{\cdot}$  at higher temperatures. Further, at higher temperatures, there is a possibility of production of more and more free radicals as compared to  $\text{Br}^-$  and inhibitory action seems to be more effective than the corresponding inhibition by  $\text{Br}^-$ .

It should be noted that there is no controversy over the inhibitory role (control intermediate) of organic radicals in the BZ reaction, particularly when the substrate is malonic acid. The possibility of radical control in other BZ systems can not be ruled out, although the role of  $\text{Br}^-$  is equally important since it appears that it is the experimental conditions which determine the role of the effective control intermediate. In view of the above, it seems reasonable to consider the role of radicals in explaining the spectacular dynamic behaviour of the BZ reaction.

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