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Effect of Initial Reagent Concentrations on the Oscillatory Behavior of the BZ Reaction in a Batch Reactor

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ABSTRACT: A detailed investigation on resorcinol as the Belousov–Zhabotinsky (BZ) oscillator in manganese(II) ion catalyzed reaction system with inorganic bromate (oxidant) and acetone (cosubstrate) was carried out in aqueous sulfuric acid medium (1.3 M). The aforesaid reagents were mixed with various concentrations to evolve the effective concentrations at which the reaction system exhibited better oscillations. The various oscillatory parameters such as time period (t_p), induction period (t_{in}), frequency (v), amplitude (A), and number of oscillations (n) were derived, and the dependence of concentration of the reacting species on these oscillatory parameters was interpreted on the basis of the Field–Koros–Noyes mechanism. © 2009 Wiley Periodicals, Inc. Int J Chem Kinet 41: 650–657, 2009

INTRODUCTION

The Belousov–Zhabotinsky (BZ) reaction [1,2] has been a research subject of nonlinear dynamics including chemical, physical, and biological interest. The BZ reaction shows temporal and spatio-temporal structures such as redox oscillation of the catalyst and travelling waves [1–6]. The overall process of the BZ reaction is the oxidation of an organic substrate such as citric acid or malonic acid by an oxidizing agent (bromate) in the presence of metal ions as catalyst

under acidic conditions. Metal ions, such as cerium, iron, and manganese, are widely used as catalysts [7–13]. The mechanism of such reactions is explained in detail by Field, Koros, and Noyes (FKN) [3–5]. In the present work, resorcinol is chosen as BZ oscillator to study its oscillatory behavior in the reaction system, comprising inorganic bromate as the oxidant and manganese(II) ion as catalyst in 1.3 M sulfuric acid medium. The compound has sufficient solubility in aqueous acid medium and exhibits dynamic behavior over a wide range of concentrations. Moreover, owing to the presence of two phenolic OH groups, resorcinol has some similarity with biomolecules and, therefore, the present study can serve as a prototype example in understanding the behaviors possible in biology such as signal transmission and membrane transport in living organisms. The oscillations were also studied

in the presence of acetone as a mixed substrate system.

EXPERIMENTAL

Materials

All reagents used were either analytical grade chemicals or else of high purity. The reagents used were resorcinol 99% (Himedia Laboratories, Mumbai, India; AR), potassium bromate 99% (Merck, Mumbai, India), acetone 99% (Ranbaxy Fine Chemicals, New Delhi, India), manganese(II) sulfate monohydrate (s.d. fine, Biosar, India). All desired solutions of these reagents were prepared in 1.3 M sulfuric acid 98% (Merck; LR).

Procedure

The ion analyzer (ELICO LI-126) having pH as well as mV option was calibrated in the oxidation reduction potential (ORP) mode with the standard solutions, using a platinum electrode as the indicator and calomel (SCE) as the reference electrodes. The equipment was hooked to two half cells, one containing any one of the reaction systems under investigation into which the platinum electrode was dipped as an indicator electrode. Another half cell was filled with a 2.5×10^{-4} M solution of potassium chloride, and the calomel electrode was dipped into it as a reference electrode. The two half cells were connected through a salt bridge containing saturated solution of potassium nitrate (Merck) and kept immersed in a high precision water bath (Jindal SM Scientific Instruments, New Delhi, India) setup at a temperature of $30 \pm 0.1°C$. All the solutions used in the reaction system were first kept under thermostatic conditions at the desired temperature for about 10 min to acquire uniform temperature in the system. The reaction started by the addition

of a 2 mL 0.1 M solution of potassium bromate to a solution containing 2 mL 0.0225 M resorcinol and 2 mL 0.004 M manganese(II) sulfate monohydrate.

RESULTS AND DISCUSSION

Table I shows the variation in oscillatory parameters at different concentrations of resorcinol, keeping the concentrations of other reagents constant. From the data, it is apparent that with the increase in the concentration of resorcinol, the induction period decreases. The induction period is observed due to the accumulation of crucial concentration of the organic brominated species prior to the commencement of oscillations [3,6]. With the increase in the substrate concentration, the rate of formation of bromo-organic derivative increases and hence there is shortening of the induction period (Fig. 1). The dependence of the induction period on [resorcinol] fits well with the mechanistic explanations based on the FKN model. The time period of oscillations of the BZ reaction varies depending on the initial substrate concentrations [9,14]. The time period is an indicator for the overall BZ reaction. So, before seeing insight of the oscillation waveforms, the dependence of initial substrate concentrations on the time period was observed (Fig. 2). It is mentioned that the concentration of substrate at a certain measuring time may be approximated to its initial concentration, and in this study the average value of the time between the second and sixth oscillations was taken as the time period.

From the results shown in Figs. 1 and 3, it is clear that there are prominent variations in the time period of the BZ reaction with the increase in [resorcinol]$_0$. In all cases, the time period becomes shorter with increasing initial substrate concentration. The dependence of the initial substrate concentration on the oscillation period is justified on the basis of the FKN mechanism [3–5]. According to this mechanism, the overall BZ

Table I Variation in [Resorcinol] Having Other Species Such as $[Mn^{2+}] = 0.004$ M, $[BrO_3^-] = 0.1$ M, $[H_2SO_4] = 1.3$ M; Temperature $= 30 \pm 0.1°C$
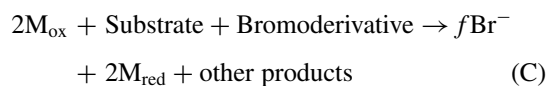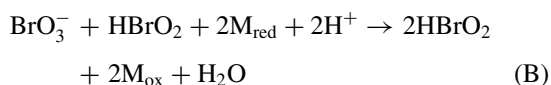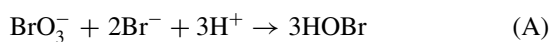
[Resorcinol] (M)	Induction Period t_{in} (s)	Time Period t_p (s)	Frequency v (s^{-1})	Amplitude (mV)	Number of Oscillations (n)
0.0100	190	280.0	0.0035	<30	<5
0.0150	170	150.0	0.0066	80	>10
0.0175	160	100.0	0.0100	75	>20
0.0200	140	85.0	0.0117	70	>30
0.0225	130	67.5	0.0148	65	>40
0.0250	110	60.0	0.0166	60	>30
0.0300	80	50.0	0.0200	34	>20
0.0400	60	20.0	0.0500	<20	>5
0.0600	**	**	**	**	**

** No oscillations are seen.
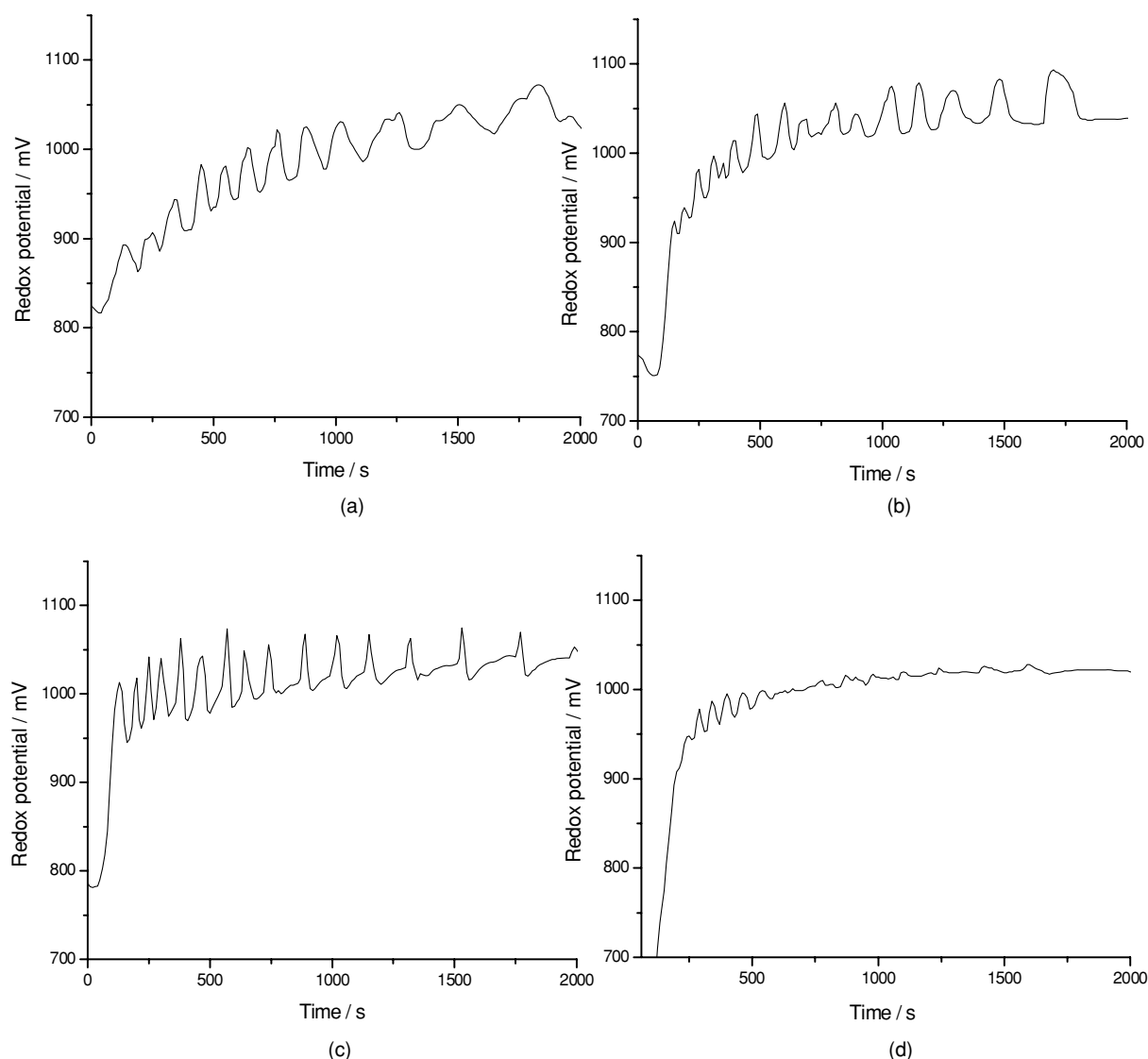
Figure 1 Potential (mV) verses time (s) plots showing variation of oscillatory characteristics for the system containing $[BrO_3{}^-] = 0.1$ M, $[Mn^{2+}] = 4 \times 10^{-3}$ M, and $[H_2SO_4] = 1.3$ M. [Resorcinol]: (a) 0.0100 M, (b) 0.0200 M, (c) 0.0225 M, and (d) 0.0300 M. Temperature $= 30 \pm 0.1°$C.

reaction may be divided into the following three main processes: consumption of bromide ion (process A), autocatalytic reaction of the bromous acid with oxidation of the catalyst (process B), and organic reaction with the reduction of the catalyst (process C).

$$BrO_3^- + 2Br^- + 3H^+ \rightarrow 3HOBr \qquad (A)$$

$$BrO_3^- + HBrO_2 + 2M_{red} + 2H^+ \rightarrow 2HBrO_2$$
$$+ 2M_{ox} + H_2O \qquad (B)$$

$$2M_{ox} + Substrate + Bromoderivative \rightarrow fBr^-$$
$$+ 2M_{red} + other\ products \qquad (C)$$

Following the FKN mechanism, we divided the wave-forms for one of the reaction systems involving 0.0225 M [resorcinol], 0.1 M $[BrO_3{}^-]$, 0.004 M $[Mn^{2+}]$ in 1.3 M H_2SO_4 into processes A, B, and C, signifying each process as follows:

- Process A represents the region where potential increases very slowly,
- Process B is the region where potential increases rapidly, and
- Process C is the region where potential decreases.

The dependence of the oscillation frequency and amplitude on [resorcinol]$_0$ is plotted in Fig. 3. With
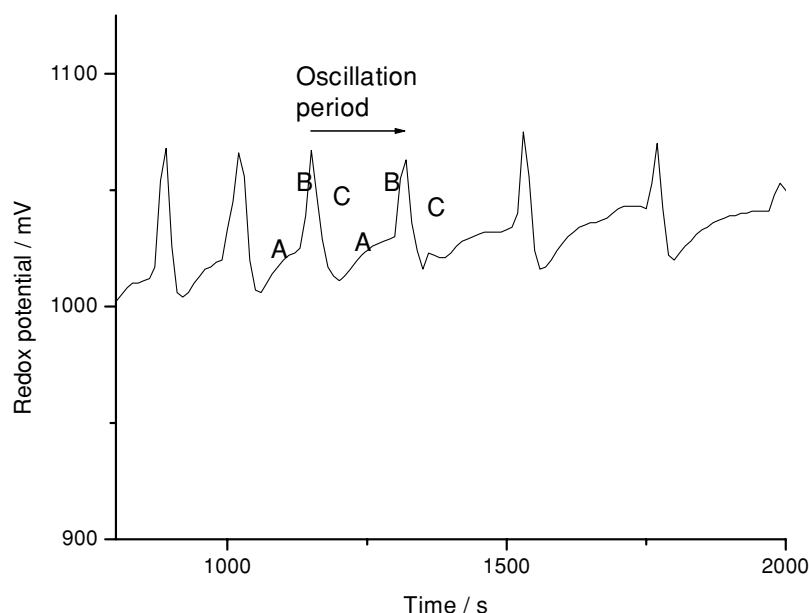
Figure 2 Typical oscillating profiles of the system containing $[Mn^{2+}] = 4 \times 10^{-3}$ M, $[BrO_3^-] = 0.1$ M, $[resorcinol] = 0.0225$ M at $30 \pm 0.1°C$.

increasing $[resorcinol]_0$, it was found that the frequency first increases rapidly up to 0.0175 M, then increases slowly up to 0.025 M, and afterward increases rapidly, until the concentration limit approaches, i.e. 0.04 M, after which no oscillation is observed. However, a good number of oscillations with better amplitude were observed at $[resorcinol] = 0.0225$ M.

Table II gives the variation of oscillatory parameters with varying $[BrO_3^-]_0$. With the increase in $[BrO_3^-]_0$, the induction period decreases first up to 0.1 M and then increases as seen in Fig. 4. This unusual trend can be

due to the inhibition effects of the $HBrO_2$ (autocatalysis process) where bromide competes with $HBrO_2$ for bromate, and the autocatalysis process would not start until the $[Br^-]$ drops to a certain critical value. We assume that the increase in the bromate concentration causes the faster accumulation of the bromoderivative of the substrate, and hence a shorter induction period is observed first and after certain concentration value demands longer time for the reduction of $[Br^-]$ to the threshold value [6]. In fact, the tendency for the longer induction period with increasing $[BrO_3^-]_0$ becomes stronger when $[Mn^{2+}]_0$ becomes limiting.
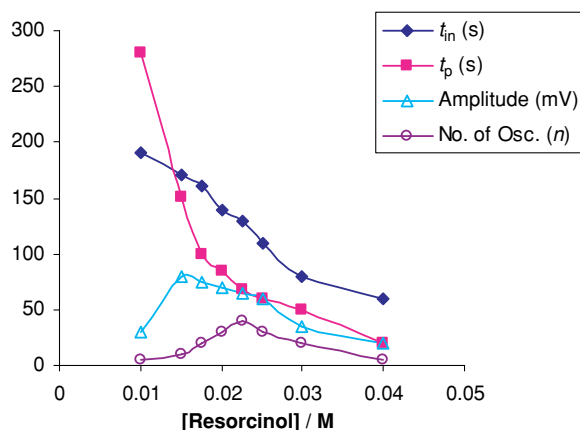
Figure 3 Effect of the initial substrate concentration on the induction period (t_{in}, s), time period (t_p, s), amplitude (mV), and number of oscillations (n) while keeping concentrations of other reagents constant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
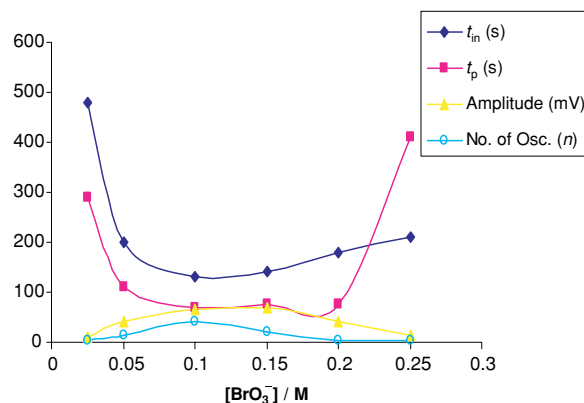
Figure 4 Effect of the initial bromate concentration on the induction period (t_{in}, s), time period (t_p, s), amplitude (mV) and number of oscillations (n) while keeping concentrations of other reagents constant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table II   Variation in $[BrO_3^-]_0$ Having Other Species Such as $[Mn^{2+}] = 0.004$ M, [Resorcinol] $= 0.0225$ M, $[H_2SO_4] = 1.3$ M; Temperature $= 30 \pm 0.1°C$

$[BrO_3^-]$ (M)	Induction Period t_{in} (s)	Time Period t_p (s)	Frequency v (s^{-1})	Amplitude (mV)	Number of Oscillations (n)
0.025	480	290.0	0.0034	>10	5
0.050	200	110.0	0.0091	40	>15
0.100	130	67.5	0.0148	65	>40
0.150	140	75.0	0.0133	70	>20
0.200	180	77.0	0.0129	40	>5
0.250	210	410.0	0.0024	>15	<5
0.300	**	**	**	**	**

** No oscillations are seen.

Accordingly, an increase in the bromate concentration would lead to first a decrease and then an increase in the induction time. At high [resorcinol]/$[BrO_3^-]$, the effect of another inhibitor, i.e., organic radical $C_6H_4(OH)O^\bullet$, generated by the catalyst becomes increasingly important, as noted by Field et al. [3]. The other oscillating parameters such as the time period, frequency, amplitude, and number of oscillations also vary with the increase in the concentration of $[BrO_3^-]$. The time period decreases up to 0.15 M $[BrO_3^-]$ and then increases until the limiting concentration value of 0.025 M $[BrO_3^-]$. The reason for this is similar to the induction period, where accumulation of bromo-derivative and reduction of $[Br^-]$ to the threshold value affects the processes A, B, and C and hence unusual variations of time period and frequency are observed. The trend for amplitude and the number of oscillations first show an increase and then decrease following the FKN mechanism (Fig. 4), although we cannot explain the particular reaction in detail due to the complexity of the BZ reaction.

Table III shows the oscillatory parameters for the varying $[Mn^{2+}]_0$. With the increase in the concentration of Mn^{2+} ion, the time period decreases following the FKN mechanism, whereas the induction period and frequency of oscillations first decrease and then increase (Fig. 5). This can be because of the com-
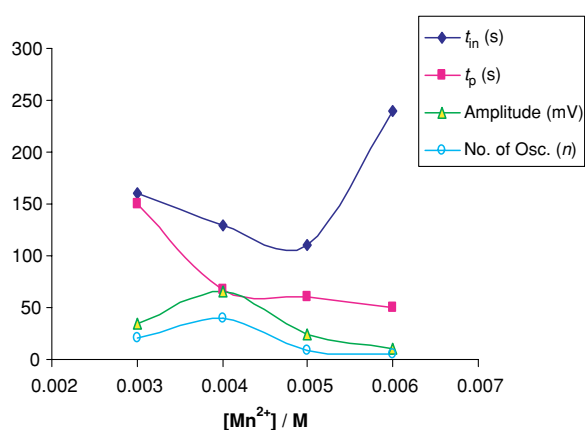
Figure 5   Effect of the initial Mn^{2+} ion concentration on the induction period (t_{in}, s), time period (t_p, s), amplitude (mV), and number of oscillations (n) while keeping concentrations of other reagents constant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

bined effect of the processes B and C, wherein the $[Mn^{2+}]/[Mn^{3+}]$ depends on the autocatalysis process, giving rise to the formation of $HBrO_2$. The amplitude and number of oscillations first increase and then decrease with the increase in $[Mn^{2+}]$ following the FKN mechanism.

Table III   Variation in $[Mn^{2+}]_0$ Having Other Species Such as [Resorcinol] $= 0.0225$ M, $[BrO_3^-] = 0.1$ M, $[H_2SO_4] = 1.3$ M; Temperature $= 30 \pm 0.1°C$

$[Mn^{2+}]$ (M)	Induction Period t_{in} (s)	Time Period t_p (s)	Frequency v (s^{-1})	Amplitude (mV)	Number of Oscillations (n)
0.001	**	**	**	**	**
0.003	160	150.0	0.0066	35	>20
0.004	130	67.5	0.0148	65	>40
0.005	110	60.0	0.0166	25	>9
0.006	240	50.0	0.0100	<10	>5
0.008	**	**	**	**	**

** No oscillations are seen.

Table IV Variation in $[H_2SO_4]_0$ Having Other Species Such as $[Mn^{2+}] = 0.004$ M, [Resorcinol] $= 0.0225$ M, $[BrO_3^-] = 0.1$ M; Temperature $= 30 \pm 0.1°C$

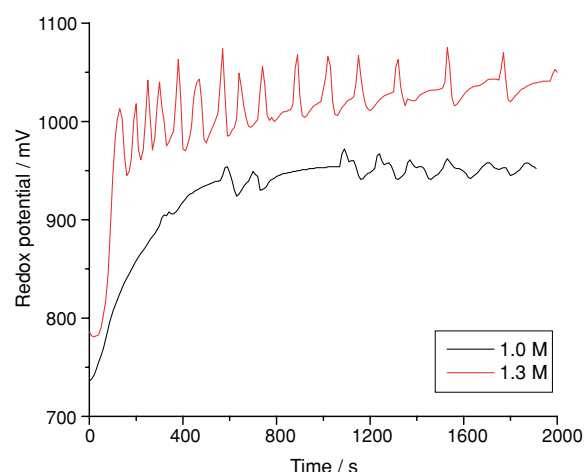| $[H_2SO_4]$ (M)	Induction Period t_{in} (s)	Time Period t_p (s)	Frequency v (s^{-1})	Amplitude (mV)	Number of Oscillations (n)
0.5	**	**	**	**	**
0.8	**	**	**	**	**
1.0	330	300.0	0.0033	25[a], 18[b]	>10
1.3	130	67.5	0.0148	65	>40
1.8	**	**	**	**	**

**No oscillations are seen.
[a]Large peak.
[b]Small peak.

Figure 6 Comparative potential (mV) verses time (s) plots showing mixed-mode oscillations for 1.0 M H_2SO_4 and 1.3 M H_2SO_4, [resorcinol] $= 0.0225$ M, $[BrO_3^-] = 0.1$ M, $[Mn^{2+}] = 4 \times 10^{-3}$ M, and temperature $= 30° \pm 0.1°C$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
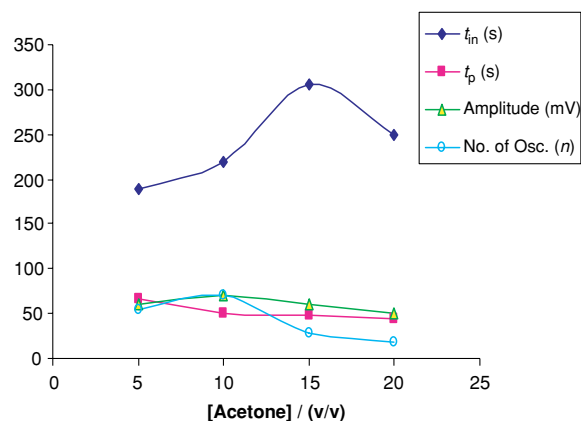
Table IV gives the variation of oscillatory parameters with varying $[H_2SO_4]_0$, keeping concentrations of other reagents constant. Good results were obtained in 1.3 M H_2SO_4, while as in 1.0 M H_2SO_4 mixed-mode oscillations with small and large peak amplitudes were observed (Fig. 6). The oscillations observed exhibit patterns of the type LS_n, where L denotes oscillations with large amplitudes and S means oscillations with substantially smaller amplitudes as compared to L, and $n = 0, 1, 2, \ldots$. In this system $n = 1$, so we can have only one small amplitude oscillation between two larger amplitude oscillations. Such behavior of periodic mixed-mode oscillations can be explained by considering the models [15,16] that qualitatively describe regularities observed in transients as well as asymptotic mixed-mode oscillations in the BZ reaction. The variables can be treated as the autocatalytic reagent, i.e., $HBrO_2$, Br^-, which is involved in negative feedback, $[Mn^{2+}]$, and concentration of acid, i.e., $[H^+]$ [17].

Table V shows the variation of oscillatory parameters with changing $[acetone]_0$ as cosubstrate. With the increase in the concentration of acetone (% v/v), there is first increase in the induction period [18] and then it decreases, showing a parabolic behavior, whereas the time period shows a gradual decrease (Fig. 7). However, the induction time is larger as compared to the values observed with changing concentrations of other reagents (as mentioned earlier). As suggested by the FKN mechanism, the bromoderivative acts as positive feedback for the bromination of resorcinol. As the mechanism suggests that the induction period corresponds to the saturation of the system with bromoderivative (autocatalyst), which is apparent in this experiment visually. The larger induction period is because of the bromination of acetone to give rise to bromoacetone in addition to the bromosubstrate derivative. The acetone hence competes with resorcinol

Table V Variation in $[Acetone]_0$ in % (v/v) Having Other Species Such as [Resorcinol] $= 0.0225$ M, $[Mn^{2+}] = 0.004$ M, $[BrO_3^-] = 0.1$ M, $[H_2SO_4] = 1.3$ M; Temperature $= 30 \pm 0.1°C$

[Acetone] % (v/v)	Induction Period t_{in} (s)	Time Period t_p (s)	Frequency v (s^{-1})	Number of Oscillations (n)	Amplitude (mV)
5	190	66.25	0.0151	>60	54
10	220	50.00	0.0200	>70	70
15	305	47.50	0.0211	>60	28
20	250	45.00	0.0222	>50	18

Figure 7 Effect of initial [acetone] as cosubstrate on the induction period (t_{in}, s), time period (t_p, s), amplitude (mV), and number of oscillations (n) while keeping concentrations of other reagents constant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in the bromination reaction and thus leads to the longer time for accumulation of the bromoderivative.
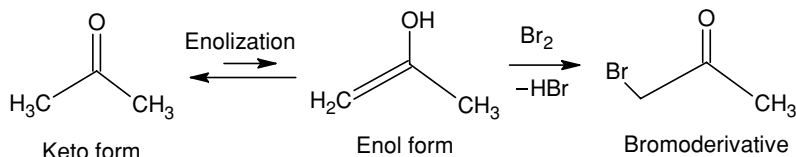
The enol form acts as a nucleophilic site for bromo attack and forms bromoacetone as a product intermediate [19]. The bromoacetone or the bromoketone derivative is responsible for the decrease in the time period and for higher [acetone]$_0$ in the induction period. Acetone has been found to increase the number as well as average amplitude of oscillations in our system. The increase in amplitude can be because of the increase in the [Mn^{2+}]/[Mn^{3+}] ratio, which can be due to involvement of acetone in processes B and C and thus competing with resorcinol in these reactions.

From the above discussion, it appears that the concentration dependence shows a prominent effect with respect to [resorcinol]$_0$ as compared to [BrO$_3^-$]$_0$ and [Mn^{2+}]$_0$. In addition, there are larger differences in the time period at low [resorcinol]$_0$ (i.e., 0.0175 M), low [Mn^{2+}]$_0$ (i.e., 0.003 M), low and high [BrO$_3^-$]$_0$ (i.e., 0.05 M and 0.25 M). However, the time period showed a gradual decrease for increasing [acetone]$_0$ as cosubstrate.

SUMMARY

The systematic study performed at various concentration ranges has revealed the effective concentrations

of the reagents at which better oscillations were exhibited by the reaction system. Furthermore, it is inferred that the increase in the bromate concentration enhances the reaction rate and lesser chances of negative feedback owing to the critical bromide ion concentration are seen. As such, either a few or no oscillations were observed. This holds good for the metal ion concentration as well. Moreover, mixed-mode oscillations are observed for the reaction system when studied in lower concentration of sulfuric acid medium. It is also observed that the single substrate system (without acetone) shows prominent oscillatory behavior as compared to the mixed substrate system with acetone, which is in cognizance with the fact that acetone also behaves as a bromide ion scavenger in such reactions [20].

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