Dual Control Mechanism in a Belousov−Zhabotinskii (B−Z) Oscillator with Glucose and Oxalic Acid as a Double Substrate

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Oscillations in a Belousov−Zhabotinskii (B−Z) system having oxalic acid (OA) and glucose (G) as a mixed organic substrate, neither of which acts as a bromine scavenger, have been investigated. Studies have been performed for (i) varying the concentration of G while keeping the OA concentration fixed and (ii) varying OA but keeping G fixed in a batch reactor. In both cases upper and lower critical limits occur, between which oscillations are observed. Both single and double frequency oscillations have been observed in a wide range of concentrations of G as well as of OA. The induction period in most of the cases was <1 min. When G is fixed and OA is varied, the time pause between the sequential oscillations increases with an increase in OA. On the other hand when OA is fixed and G is varied, the time-pause decreases with an increase in G. The first type of oscillation is Br^--controlled, whereas the second is non-Br^--controlled. The order of addition of G and OA in the last has no influence on the induction period. It influences, however, the oscillatory characteristics. Br_2 evolution in the $G + OA + Ce^{4+} + BrO_3^- + H_2SO_4$ reaction system has been investigated spectrophotometrically. ESR and polymerization studies indicate the important role of free radicals in influencing the reaction mechanism. A tentative dual control mechanism has been suggested involving autocatalysis of $HBrO_2$ and $BrO_2^\bullet$.

Introduction

Belousov−Zhabotinskii (B−Z) oscillators containing saccharides as organic substrates are interesting from many aspects. Ševčik and Adamčíkov'a[1] have reported oscillations in systems containing saccharides when nitrogen flow and Mn^{2+} as a catalyst were used. The systems behaved as bromine hydrolysis controlled (BHC) oscillators. Ou and Jwo[2] investigated primarily the kinetics of Mn(III)−saccharide, bromate−Mn(II), and bromate−saccharide reactions (glucose, galactose, xylose, arabinose, and ribose). Rastogi et al.[3] have reported oscillations in bromate-driven oscillators containing sucrose, fructose (F), glucose (G), maltose, and galactose along with acetone as a bromine scavanger. These also belong to the class of BHC oscillators. Oscillations in redox potential and Br^- concentration and the nature of the phase-plane plot have been reported for B−Z oscillators containing (i) G + acetone, (ii) G + cyclohexanone, (iii) F + acetone, and (iv) F + cyclohexanone as mixed substrates.[4] Both complex and periodic oscillations were observed. Limit cycle and folded limit cycles were obtained, and Hopf and Jug handle bifurcations occurring under different circumstances.[4]

Later, Srivastava[5] investigated the critical limits of acetone for (i) G, (ii) F, (iii) sucrose, and (iv) an equivalent mixture of G and F in the concentration range 0.01−0.075 M. The critical limits for (iii) and (iv) were found to be same. However, the most remarkable observation was that beyond [F] = 0.075 M, no acetone was needed and oscillations occurred in the B−Z oscillator. This is not so in the case of the glucose oscillator. At [G] = 0.075 M, the upper limit and lower limits are very close, further confirming that at higher [G] oscillations would not occur when it is used as a single substrate.[5] Rastogi et al.,[6] examined the behavior of the fructose oscillator in detail and found the critical limits of F in the range 0.04−0.6 M. Experiments have been performed to elucidate the control mechanism in the fructose oscillator, which appeared to be free radical controlled.[7] It may be noted that there are other oscillatory reactions where the role of free radicals has been found to be crucial.[8−15] It has been suggested that oscillatory aerial oxidation of propionaldehyde also involves free radical control mechanism.[16] In addition to use of ketones for Br_2 removal, the same has also been achieved by (i) partitioning in a two phase-oscillator[17] and (ii) nitrogen bubbling.[18]

Noszticzius and Bôdiss[18] have used carrier gas and recorded oscillations in the gas phase. The interpretation is complicated because there is the likelihood of formation of a supersaturated aqueous solution of Br_2 and of periodic release of supersaturation due to flux of the carrier gas. It has been reported that oscillations can be generated in the reaction system without bubbling the inert gas by only controlling the stirring rate.[19]

A novel-type of B−Z oscillator involving F + oxalic acid (OA) as double substrate has been reported, where F is below the critical limit.[20] It may be noted that no oscillations are observed when OA alone is used as the organic substrate. The F + OA oscillator is found to involve the dual control mechanism, i.e., both free radical- as well as Br^--controlled.[20]

Preliminary experiments revealed that when G + OA is used as a double substrate, oscillations also occurred. However, it may be noted that oscillations do not occur when G is used as substrate alone.

Because these were unexpected results, it prompted us to investigate thoroughly the $G + OA + Ce^{4+} + BrO_3^- + H_2SO_4$ reaction and to test the general dual-control mechanism, keeping in mind that glucose and free radicals produced from its

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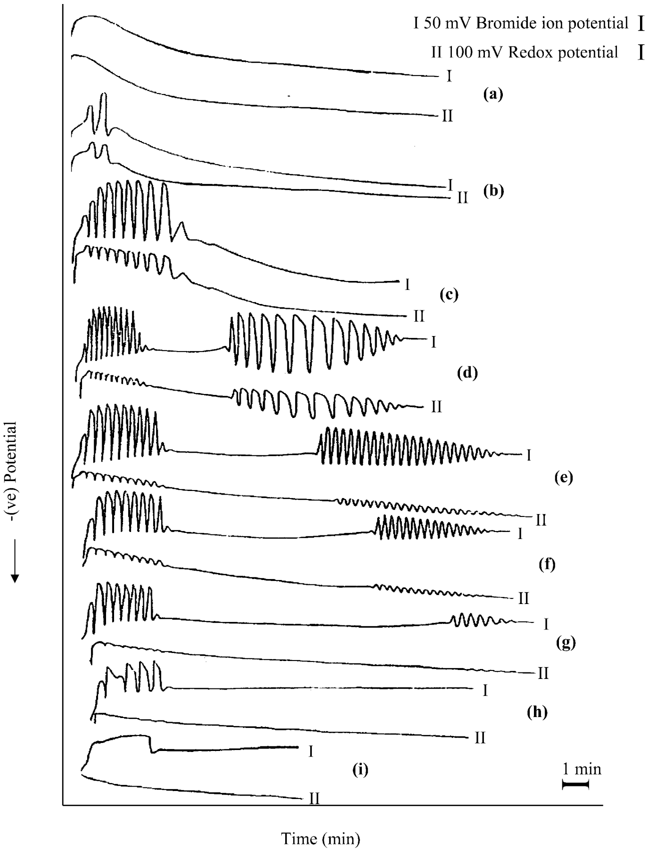

Figure 1. Oscillations in bromide ion potential (I) and redox potential (II), for the system H_2SO_4 (1.5 M) + BrO_3^- (0.06 M) + Ce^{4+} (1.45 × 10^{-3} M) + G (0.05 M) + (a) OA (0.007 M), (b) OA (0.01 M), (c) OA (0.02 M), (d) OA (0.03 M), (e) OA (0.045 M), (f) OA (0.05 M), (g) OA (0.09 M), (h) OA (0.2 M) and (i) OA (0.35 M), respectively. Temp: 26 ± 1 °C.

oxidation products are of considerable biological and physiological importance.[21] Detailed experimental results are reported in the present communication.

Experimental Procedure and Results

Materials. Glucose, sulfuric acid, KCl [E. Merck, India], cerium(IV) ammonium sulfate [AR, Thomas Baker & Co., Germany], potassium bromide [S. D. Fine Chem. Pvt. Ltd., India], potassium bromate [AR, Central Drug House, India], and acrylamide [LR, Koch-Light Ltd., Germany] were used. Ca−gluconate, Ca−glucarate, Ca−glucuronate, and bisacrylamide were procured from Sigma Chemical Co., USA. All solutions were prepared in 1.5 M sulfuric acid in double distilled water.

Monitoring of Oscillations. The oscillations were investigated for various concentrations of G and OA in OA + G + Ce^{4+} + BrO_3^- + H_2SO_4 system. Oxalic acid was added last. Experiments were performed in a closed batch reactor containing 50 cm^3 of the reaction mixture, which was stirred magnetically with moderate speed, as reported earlier.[7,20] First a mixture of BrO_3^- + Ce^{4+} + H_2SO_4 of desired concentration was introduced in the reactor. Two types of experiments were performed. Initially, G was kept constant (0.05 M) and OA was varied (0.007−0.35 M). In the second set of experiments, OA was kept constant (0.03 M) and G varied (0.005−0.55 M). Oscillations were recorded using a Br^--sensitive electrode and a Pt electrode in conjunction with a calomel electrode using an electronic recorder, as described in earlier communication.[7] Typical results are recorded in Figures 1 and 2 and Tables 1 and 2.

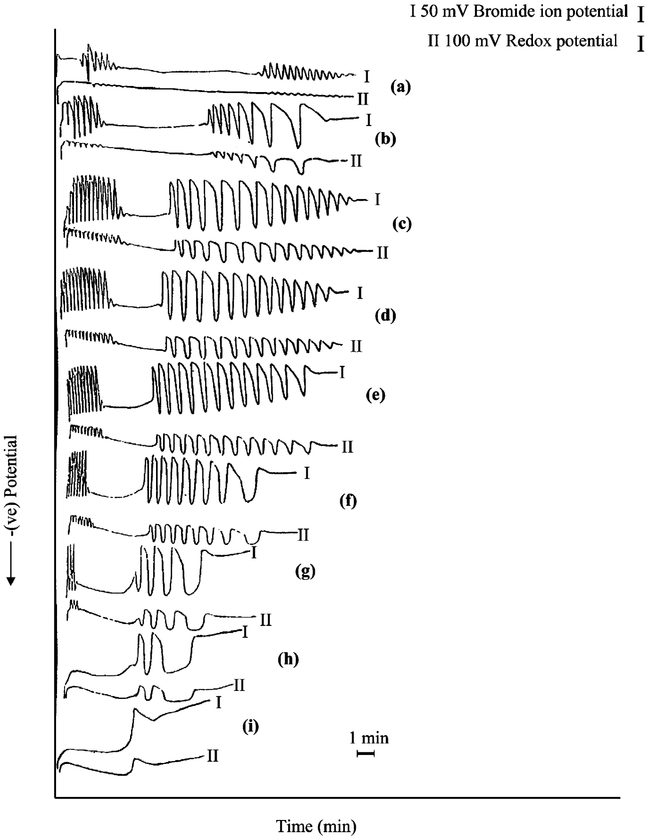

Figure 2. Oscillations in bromide ion potential (I) and redox potential (II), for the system H_2SO_4 (1.5 M) + BrO_3^- (0.06 M)+ Ce^{4+} (1.45 × 10^{-3} M)+ OA (0.03 M) + (a) G (0.01 M), (b) G (0.02 M), (c) G (0.07 M), (d) G (0.09 M), (e) G (0.15 M), (f) G (0.25 M), (g) G (0.35 M), (h) G (0.45 M), and (i) G (0.50 M), respectively. Temp: 26 ± 1 °C.

TABLE 1: Oscillatory Features in the System Ce^{4+} (1.45 × 10^{-3} M) + BrO_3^- (0.06 M) + H_2SO_4 (1.5 M) + G (0.05 M) + OA (as Variable) (Temp 26 ± 1 °C)

concn of OA (M)	induction period (min)	type I		time pause (min)	type II	
		no. of cycles	life time (min)		no. of cycles	life time (min)
0.007						
0.009						
0.010	0.7	3	1.5			
0.015	0.7	7	3.0			
0.020	0.3	10	3.8			
0.025		15	3.8			
0.030		13	3.0	2.5	13	9.5
0.035		13	3.3	3.8	18	12.0
0.040		11	2.8	7.5	20	7.5
0.045		12	3.5	5.6	24	7.5
0.050		10	3.3	7.5	20	5.0
0.055		10	3.3	7.5	23	6.0
0.060		10	3.0	7.5	17	4.0
0.065		10	3.0	8.0	19	5.0
0.070		10	3.3	7.8	14	3.8
0.075		10	2.3	6.0	16	3.5
0.080		9	3.0	9.0	12	3.5
0.090		9	3.0	10.5	7	2.8
0.100		9	4.0	8.0	5	1.8
0.150		8	3.8			
0.200		7	3.8			
0.250	1.8	3	1.5			
0.300	1.3	2	1.0			
0.350						

The effect of the order of addition of reagents on oscillatory behavior was also investigated. The first set of experiments was performed in the above manner where OA was added last. In the second set of experiment, G was added at the end. The effect of the order of addition on oscillatory features for a typical case is shown in Figure 3. In the first case both types of oscillations

TABLE 2: Oscillatory Features in the System Ce^{4+} (1.45 × 10^{-3} M) + BrO_3^- (0.06 M) + H_2SO_4 (1.5 M) + G (as Variable) + OA (0.03 M) (Temp 26 ± 1 °C)

concn of G (M)	induction period (min)	type I		time pause (min)	type II	
		no. of cycles	life time (min)		no. of cycles	life time (min)
0.005						
0.009	1.8	8	2.5			
0.010	1.8	8	2.5	8.5	15	5.5
0.015	1.8	6	2.5	7.5	15	8.0
0.020		9	3.5	6.0	10	8.0
0.025		10	3.5	4.5	12	10.0
0.030		13	3.0	4.5	12	9.5
0.035		13	4.5	2.5	14	12.0
0.040		15	5.0	2.5	15	13.5
0.050		13	2.8	2.5	13	9.5
0.060		15	4.0	1.8	15	9.5
0.065		14	3.3	1.8	16	9.5
0.070		14	3.8	2.3	15	11.5
0.075		13	3.0	2.0	15	10.0
0.080		14	4.0	2.3	15	11.5
0.090		14	3.5	2.5	14	10.5
0.100		14	2.8	2.5	16	8.5
0.150		12	2.5	2.0	13	9.8
0.200		9	1.8	2.5	11	10.0
0.250		9	1.8	2.8	9	7.5
0.300		6	1.3	3.0	6	5.0
0.350		4	1.0	3.3	5	5.0
0.400	3.8				5	3.0
0.450	4.0				4	4.3
0.500	4.0				1	1.0
0.550						

are obtained, whereas in the second case only type I oscillations are obtained.

Estimation of [Br^-]. Br^- during oscillations was monitored using a digital voltmeter as described in a previous communication.[7] Br^- was found to range between 10^{-5} and 10^{-6} M.

Br^- Sensitivity of the Reaction. To test whether oscillations are quenched at higher Br^- ion concentrations, varying amounts of potassium bromide in 1.5 M H_2SO_4 were added to the reaction mixture during oscillations. A typical result is recorded in Figure 4. The effective Br^- concentration in the total reaction mixture was ~2.0 × 10^{-2} M. A number of experiments were performed[22] with lower Br^- ion concentrations also. Type I oscillations are stopped at higher Br^- concentrations, whereas type II oscillation is unaffected. It may be noted that type I oscillations are unaffected at low Br^- concentrations.

Kinetics of Br_2 Evolution. Kinetics of bromine evolution in (a) G + BrO_3^- and (b) G + OA + BrO_3^- + Ce^{4+} + H_2SO_4 systems was studied by recording the absorbance at 530 nm with respect to time using Perkin-Elmer Lambda Bio 20 spectrophotometer and using the procedure described previously.[7] Results are recorded in Figure 5.

Product Analysis. The reaction products in the reaction systems (i) G + Ce^{4+} + H_2SO_4 and (ii) G + BrO_3^- + H_2SO_4 were analyzed by TLC and spot tests.[23] Results indicated the formation of gluconic acid (Q) and glucaric acid (P) but formation of glucuronic acid (S) was not observed.

Polymerization Study. Polymerization in the reaction systems was studied in a manner described earlier.[7] A saturated solution of acrylamide in 1.5 M H_2SO_4 was added to few cm^3 of the following reaction mixtures and the formation time of the thixotropic highly viscous fluid was noted:

$$G + Ce^{4+} + H_2SO_4 \tag{i}$$

$$G + BrO_3^- + H_2SO_4 \tag{ii}$$

The thixotropic viscous fluid formation time was <16 min.

For steady gel formation studies, a cross-linking agent bisacrylamide was used. The reaction mixture contained 5 mL of H_2SO_4 (1.5 M), 20% acrylamide and 0.8% bisacrylamide along with X = G, P, Q, S (0.05 M), BrO_3^- (0.06 M), Ce $^{4+}$ (1.45 × 10^{-3} mM), and the concentration of OA was 0.03 M.

The gel formation time of the following reaction mixtures was noted, which is indicated in parentheses:

(i) G + Ce^{4+} (122 min)
(ii) OA + Ce^{4+} (2 min)
(iii) gluconic acid + Ce^{4+} (2.25 min)
(iv) glucaric acid + Ce^{4+} (13.25min)
(v) glucuronic acid + Ce^{4+} (248 min)
(vi) G + OA + BrO_3^- + Ce^{4+} (<1 min)

The above results show that in case of (ii) and (iii) free radicals are rapidly formed as compared to (i) and (v).

ESR Studies. ESR spectra of the following reaction mixtures were investigated with the help of an ESR spectrometer (scan range = 3400 G, mild range = 500 G, RG = 5 × 10^4, MA = 1 G, power = 15 db/6.3 mw at room temperature): (i) γ-irradiated glucose; (ii) G + BrO_3^- + H_2SO_4; (iii) G + Ce^{4+} + H_2SO_4.

The ESR spectra indicate the formation of free radicals in all the three cases. In case (i) the free radical produced is likely to be $O{=}C^{\bullet}{-}(CHOH)_4{-}CH_2OH$. In cases (ii) and (iii) free radical is also indicated with a doublet in the ESR spectra, suggesting that the free radical is $HOOC{-}C^{\bullet}OH{-}(CHOH)_3CH_2\text{-}OH$ formed from gluconic acid.[22]

Discussion

Experimental data confirm that oscillations do not occur in OA + Ce^{4+}+ BrO_3^- + H_2SO_4 and G + Ce^{4+} + BrO_3^- + H_2SO_4. However, when both OA and G are present in the reaction system, oscillations appear. Both single frequency oscillations and dual frequency oscillations separated by time-pause are observed. We denote the first series of oscillations as type I and the second series as type II. Results on oscillatory features for a typical case are recorded in Figures 1 and 2.

Important features of the G + OA system are summarized in Tables 1 and 2.

The significant features are the following:

(i) The induction time is less than 1 min in most of the cases.

(ii) Lower and upper critical limits of OA as well as G are observed.

(iii) Type I oscillation is Br^- controlled whereas type II is non-bromide-ion-controlled. The behavior is in sharp contrast with F+OA oscillator.[6,7]

(iv) The order of addition influences the dual frequency oscillations only. When OA is added last, both types of oscillations are noticed; on the other hand, when G is added last, only type I oscillations are observed (Figure 3).

(v) [Br^-] during oscillations ranges between 10^{-5} and 10^{-6} M.

To elucidate the mechanism, the following additional experiments were undertaken. Br_2 production in different reaction systems has been studied, which shows that the initial rate of Br_2 production in the G + OA + BrO_3^- + Ce^{4+} + H_2SO_4 system is much faster as compared to the G + BrO_3^- + H_2SO_4 system. The Br_2 after 10 min is 8.66 × 10^{-3} M in the former case, whereas it is 1.14 × 10^{-3} M in the latter case, as shown in Figure 5. The maximum [Br_2] remains the same for ~1 h. This difference is evidently due to other reactions involving oxybromine species.

(vi) Both ESR and polymerization experiments provide a positive indication for the existence of free radicals. With Ce^{4+}, one-electron transfer during oxidation of G, gluconic acid,

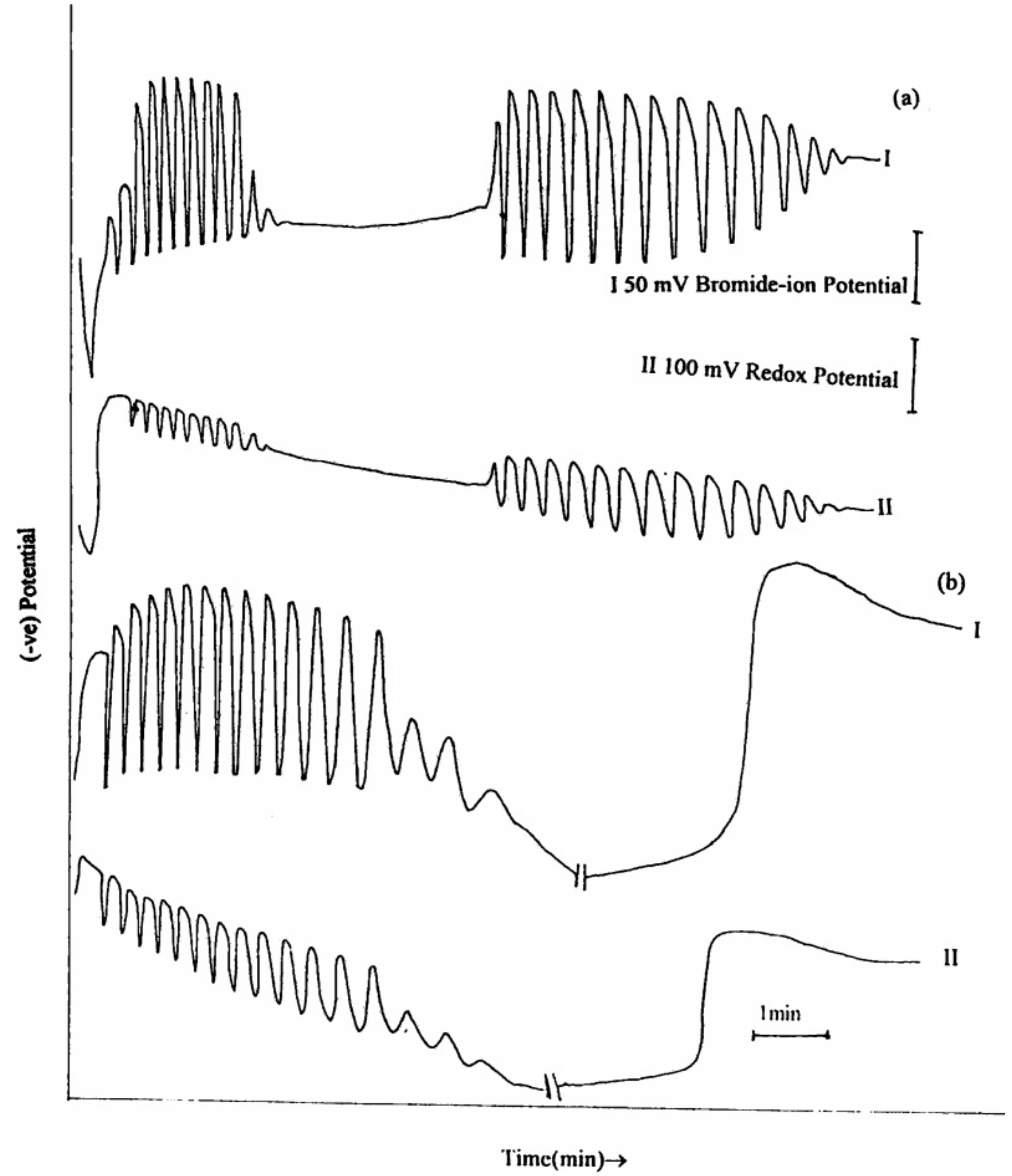

Figure 3. Effect of order of addition of organic substrate (G or OA) on the bromide ion potential (I) and redox potential (II), of the systems BrO_3^- (0.06 M) + Ce^{4+} (1.45×10^{-3} M) + H_2SO_4 (1.5 M) (a) OA (0.03 M) added after G (0.05 M) and (b) G (0.05 M) added after OA (0.03 M). Temp: 26 ± 1 °C.

glucaric acid, and oxalic acid would take place, which is easily detected by free radical chain polymerization of acrylamide.

The reaction mechanism in the present case is quite complex. However, a mechanism for the present oscillator with OA + G as substrate on the basis of the present experimental studies can be postulated using a modified version of the FKN mechanism,[24,25] which is as follows:

$$Br^- + BrO_3^- + 2H^+ \leftrightarrows HOBr + HBrO_2 \qquad (1)$$

$$Br^- + HBrO_2 + H^+ \leftrightarrows 2HOBr \qquad (2)$$

$$Br^- + HOBr + H^+ \leftrightarrows Br_2 + H_2O \qquad (3)$$

$$2HBrO_2 \leftrightarrows HOBr + BrO_3^- + H^+ \qquad (4)$$

$$HBrO_2 + BrO_3^- + H^+ \leftrightarrows Br_2O_4 + H_2O \qquad (5)$$

$$Br_2O_4 \leftrightarrows 2BrO_2^{\bullet} \qquad (6)$$

$$Ce^{3+} + BrO_2^{\bullet} + H^+ \leftrightarrows Ce^{4+} + HBrO_2 \qquad (7)$$

Reactions 1−7 are important steps of the FKN mechanism.

The network of reactions around G would involve a number of reactions involving oxidation products of G, i.e.

$$G + BrO_3^- + H^+ \rightarrow Q\text{ (gluconic acid)} + HBrO_2 \qquad (8)$$

$$G + HOBr \rightarrow Q + H^+ + Br^- \qquad (9)$$

$$Q + BrO_3^- + H^+ \rightarrow P\text{ (glucaric acid)} + HOBr + H_2O \qquad (10)$$

$$G + Br_2 + H_2O \rightarrow Q\text{ (gluconic acid)} + 2Br^- + 2H^+ \qquad (11)$$

$$G + Ce^{4+} \rightarrow G^{\bullet} + Ce^{3+} + H^+ \qquad (12)$$

$$G^{\bullet} + Ce^{4+} + H_2O \rightarrow P\text{ (glucaric acid)} + Ce^{3+} + H^+ \qquad (13)$$

The acids P and Q can generate free radicals by a one-electron-transfer reaction with Ce^{4+} as follows

$$Q + Ce^{4+} \rightarrow Q^{\bullet} + Ce^{3+} + H^+ \qquad (14)$$

$$P + Ce^{4+} \rightarrow P^{\bullet} + Ce^{3+} + H^+ \qquad (15)$$

The free radicals produced from P and Q can react with $BrO_2^{\bullet}$

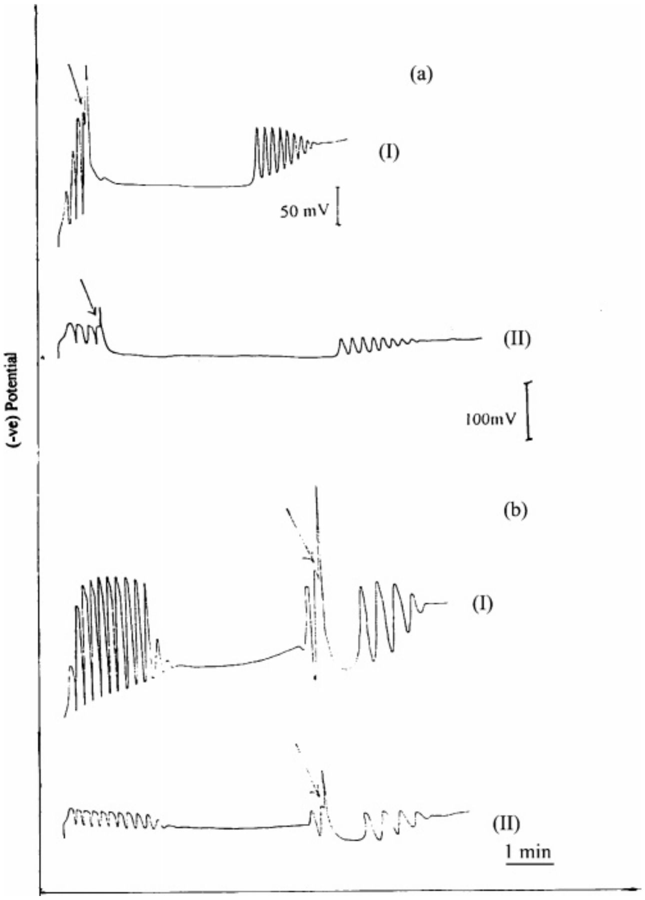

Figure 4. (a) Effect of Br^- ion on the oscillatory behavior of the Br^- ion potential by the bromide electrode (I) and the redox potential by the platinum electrode (II) in type I for the system BrO_3^- (0.06 M) + Ce^{4+} (1.45×10^{-3} M) + H_2SO_4 (1.5 M) + G (0.05 M) + OA (0.03 M). The concentration of added bromide ion is 2.0 mL of 0.5042 M KBr solution ($\sim 2.0 \times 10^{-2}$ M) in (I) and (II). (The arrow indicates the instant of addition of bromide ion in the reaction mixture.) Temp: 26 ± 1 °C. (b) Effect of Br^- ion on the oscillatory behavior of the Br^- ion potential (I) and the redox potential (II) in type II for the system BrO_3^- (0.06 M) + Ce^{4+} (1.45×10^{-3} M) + H_2SO_4 (1.5 M) + G (0.05 M) + OA (0.03 M). The concentration of added bromide ion is 2.0 mL of 0.5042 M KBr solution ($\sim 2.0 \times 10^{-2}$ M) in (I) and (II). (The arrow indicates the instant of addition of Bromide ion in the reaction mixture). Temp: 26 ± 1 °C.

in the following manner

$$P^\bullet + BrO_2^\bullet \rightarrow \text{product} + Br^- + H^+ \qquad (16)$$

$$Q^\bullet + BrO_2^\bullet \rightarrow P + HOBr \qquad (17)$$

Oxalic acid can undergo the following sequence of reactions,

$$Ce^{4+} + OA \rightarrow Ce^{3+} + {}^\bullet COOH + CO_2 + H^+ \qquad (18)$$

$$Ce^{4+} + {}^\bullet COOH \rightarrow Ce^{3+} + H^+ + CO_2 \qquad (19)$$

$$BrO_2^\bullet + {}^\bullet COOH \rightarrow HBrO_2 + CO_2 \qquad (20)$$

$$OA + BrO_3^- + H^+ \rightarrow HBrO_2 + 2CO_2 + H_2O \qquad (21)$$

Some other free radical reactions can take place as follows,

$$2{}^\bullet P \rightarrow \text{product} \qquad (22)$$

$${}^\bullet P + {}^\bullet Q \rightarrow \text{product} \qquad (23)$$

$$2{}^\bullet Q \rightarrow \text{product} \qquad (24)$$

Two types of autocatalytic reactions are involved in the above reaction scheme. On combining (5), (6), and twice the step (7) we get

$$HBrO_3 + BrO_3^- + Ce^{3+} + 3H^+ \leftrightarrows 2Ce^{4+} + 2HBrO_2 + H_2O \qquad (25)$$

which involves the autocatalysis of $HBrO_2$

On the other hand by adding (5), (6), and (7), we get

$$BrO_2^\bullet + BrO_3^- + Ce^{3+} + 2H^+ \leftrightarrows Ce^{4+} + 2BrO_2^\bullet + H_2O \qquad (26)$$

which involves autocatalysis of $BrO_2^\bullet$. As we can see, the autocatalytic process can be written in two alternative forms of (25) and (26). Thus both $HBrO_2$ and $BrO_2^\bullet$ are autocatalytic intermediates and any species reacting with them can inhibit the whole autocatalytic process. The usual control mechanism in B−Z reactions essentially involves step (25), which is inhibited by Br^- according to step (2). This is called the Br^- control mechanism. In the present case so far as type I oscillations are concerned, these are controlled by such a mechanism as supported by experimental data.

The second type of control mechanism would involve (i) autocatalysis of $BrO_2^\bullet$ (step 26) and (ii) the inhibitory reactions 16 and 17. Such a mechanism is called a free radical control mechanism, which controls type II oscillations as observed experimentally.

From the above study it is clear that the dual control mechanism is possible in the reaction system. Br^- control of type I oscillations can be explained as follows. Initially, in the presence of oxalic acid, a sufficient amount of $HBrO_2$ is produced and, in turn, by a sequence of reactions, Br^- is in greater excess than critically needed for balance of positive and negative feedback. However, when G is in the system, free radicals are generated from acids produced by oxidation of G, which reduce the concentration of $HBrO_2$ and Br^-. Thus, eventually, a situation is reached when autocatalytic production of $HBrO_2$ can be balanced by the inhibition through Br^-. Under such circumstances, the oscillations are Br^- controlled. During this process, interaction of G with BrO_3^- and other oxybromine species also generates Br^- and in a following stage oscillations stop.

Free radical control of type II oscillations can be explained as follows. After a time pause, sufficient amounts of free radicals are produced via interaction of Ce^{4+} with acids produced from oxidation of glucose. At a certain stage, autocatalytic production of $BrO_2^\bullet$ can be balanced by the negative feedback involving interaction of $BrO_2^\bullet$ and $P^\bullet$ and $Q^\bullet$. But the production of $P^\bullet$ and $Q^\bullet$ goes on increasing in the course of time and, when this exceeds the autocatalytic production of $BrO_2^\bullet$, even non-Br^--controlled oscillations stop.

At the upper limit of G, the concentration of free radicals is quite large even in the beginning so that autocatalysis of $HBrO_2$ becomes insignificant and only type II oscillations are observed.

The above mechanism can also explain the variation in oscillatory features when the order of addition of reagents is altered (Figure 3). When OA is added last, dual frequency oscillations are observed, as explained above. On the other hand, when G is added last, only type I oscillations are observed. This may be due to the fact that free radical control may be disturbed due to earlier larger consumption of $HBrO_2$ during type I oscillations and conditions may not be favorable for type II oscillations.

The above discussion provides a qualitative picture of the mechanism. It may be noted that, as reported by Adamčíkov'a et al.,[26] dual frequency oscillations are very sensitive to the stirring rate.

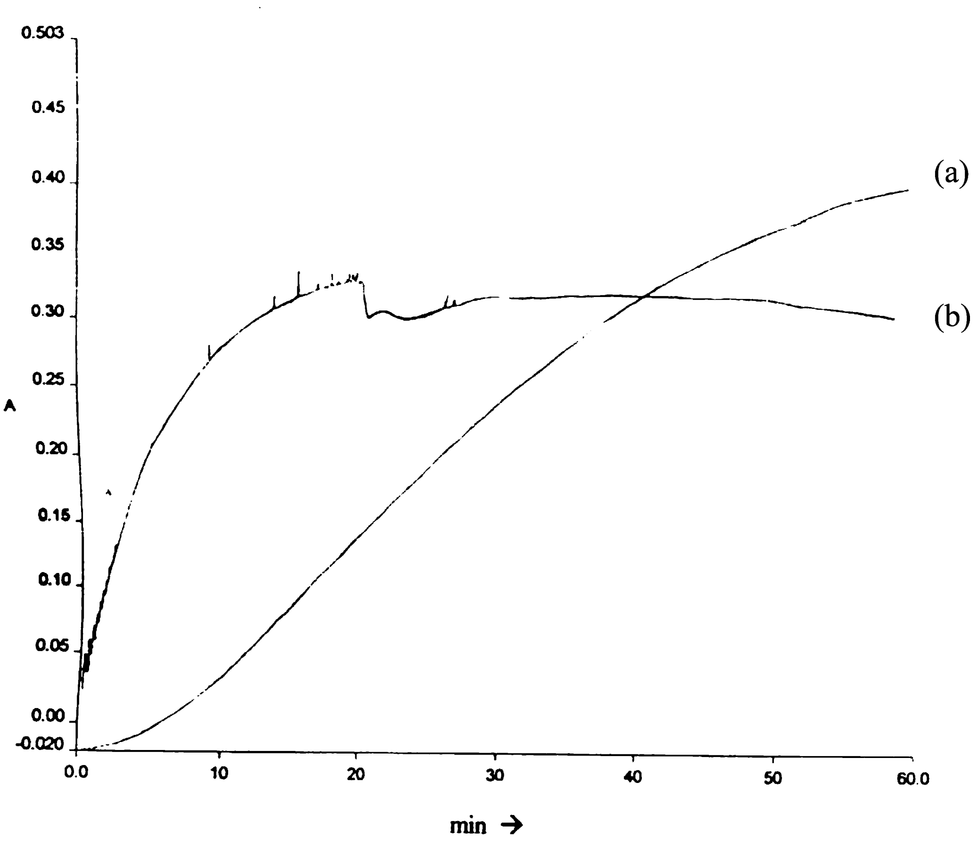

Figure 5. Absorbance *A* due to Br_2 evolution at 530 nm in the systems (a) G (0.05 M) + BrO_3^- (0.06 M) + H_2SO_4 (1.5 M) and (b) G (0.05 M) + OA (0.03 M) + BrO_3^- (0.06 M) + Ce^{4+} (1.45×10^{-3} M) + H_2SO_4 (1.5 M). Temp: 26 ± 1 °C.

In general, saccharide oscillators have the following unique features involving dual control mechanism.

(i) In the case of F + OA, type I oscillations are Br^- controlled, whereas type II oscillations are free radical controlled in most of the cases.[20]

(ii) For the G + OA oscillator, type I is Br^- controlled whereas type II is free radical controlled.

(iii) For xylose + OA, both types are Br^- controlled.[27]

In case (i) oscillations can occur even when F is used as a substrate alone. However, for oscillators (ii) and (iii), addition of OA is essential. Further, it may be noted that oscillations occur even when glucose + fructose are used as double substrate[28] where F is below the lower critical limit of oscillator or when F is used as substrate alone [Chand P., unpublished results]. Further work is in progress and would be reported in due course.

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