pH Oscillations in the Bromate-Sulfite-Perchloric Acid Reaction

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Abstract: The dynamics of oscillations in chemical reactions has stimulated a wide research interest and produced thousands of studies on about 70 known chemical oscillators, notably over the past 50 years. Oscillating chemical reactions find many applications in Physics, Biology, Geology, Physiology and Medicine.
The dynamics of the bromate-sulfite-perchloric acid (BSH) reaction is investigated in a continuous-flow stirred tank reactor (CSTR), with Mn^{2+} as a proton-consuming (or negative feedback) species. This reaction is known to exhibit periodic oscillations in $[H^+]$, and it thus belongs to a sub-category of chemical oscillators, called pH oscillators.
The reaction is carried out at 45°C, and a flow rate of 1.59 mL/min. The oscillations are monitored in the $[Mn^{2+}]$-$[BrO_3^-]$ phase space, wherein a bifurcation diagram is constructed to delineate the regions of the various behavior regimes. Under our prevailing conditions, a shorter period and higher amplitude of oscillation than those reported in the Literature were obtained. A decrease in the period of oscillations from 40 minutes to 10 minutes in our system under newly imposed $[BrO_3^-]_0$ conditions renders the system more feasible and practical for study. A variation in the flow rate and residence time was also conducted. Decreasing the flow rate from 1.59 mL/min to 1.35 mL/min caused a doubling of the period of oscillations. Yet, over the entire spanned range, no chaotic behavior was observed.
Keywords: Chemical oscillations, BSH reaction, Period doubling, Chaos monitoring, pH oscillations
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1 Introduction

Oscillating reactions [1] have garnished the chemical literature with rich dynamical behavior encompassing temporal concentration oscillations, and notably fascinating visual spatio-temporal structures. A large number of oscillating reactions is known nowadays, such as the Bray-Liebhafsky (H_2O_2-IO_3^- system) [2], Briggs-Rauscher [3], CIMA (chlorite-iodide-malonic acid) [4] and the Belousov-Zhabotinskii (BZ) [5-7] reactions. Of particular interest to us here, is a subclass of oscillating reactions where the oscillating species is the hydrogen ion (H^+), thus known as pH oscillators [8-10]. The first pH-regulated oscillator was reported by M. Orban, and I. Epstein [11], in the reaction of sulfide ion with hydrogen peroxide. The latter was shown to yield both periodic

oscillations and bi-stability in the H^+ potential/pH, in addition to the bi-stability and periodic oscillations in the potentials of Pt redox and sulfide ion-selective electrodes. Afterwards, the field of pH oscillations started growing rapidly spanning reactions with sulfur- or nitrogen- containing species or the ferrocyanide ion as reductants, and basically IO_3^-, IO_4^-, BrO_3^-, and H_2O_2 as oxidants. In constructing a pH-oscillator, the reductant is normally a species that is able to be oxidized to another species that produces H^+, often autocatalytically, or to another species that consumes H^+ by some oxidant. Furthermore, the proper combination of two reductants in a pH-oscillator is often a necessity to control high– or low– pH states. Several pH-oscillators have been characterized mechanistically [12-14]. The most systematically studied pH-oscillators include the reaction of iodate with sulfite and ferrocyanide [10,12], and its bromate [14] analogue. Essentially, designing a pH oscillator is based on having two main composite pathways, the positive feedback pathway that produces H^+, and a negative feedback pathway that removes H^+ from the system.

In this paper we study the bromate-sulfite-perchloric acid (BSH) reaction in a CSTR, and monitor oscillations while varying two main concentration parameters: $[BrO_3^-]_0$ and $[Mn^{2+}]_0$ (one at a time), maintaining all other parameters constant, and then construct the corresponding bifurcation diagrams. The overall reaction in acidic medium is as follows:

$$BrO_3^- + 3\,HSO_3^- \longrightarrow 3\,SO_4^{2-} + Br^- + 3\,H^+ \quad (1)$$

The waveform of the temporal pH oscillations for various values of $[BrO_3^-]_0$ at fixed $[Mn^{2+}]_0$, $[SO_3^{2-}]_0$ and $[H^+]_0$ shows large-amplitude pH oscillations of typically 4.5 pH units (range 2.8-7.3), as obtained in earlier studies [8]. Whereas the period of oscillations remains constant (39 min) while $[BrO_3^-]_0$ is being varied, it was found to decrease with gradual increase in the concentration of negative feedback species $[Mn^{2+}]_0$. The reaction was also studied at different flow rates, and the possibility of detecting a chaotic behavior was explored.

2 Experimental Procedure

Reagent-grade chemicals Na_2SO_3, $HClO_4$, $MnSO_4.H_2O$ and $NaBrO_3$ were used for the daily preparation of the needed solutions. A CSTR configuration was set as described by Okazaki and Hanazaki [15]. A water-jacketed quartz-glass beaker (double-walled) was employed as the reactor. Four stock solutions placed in three different beakers (one containing both SO_3^{2-} and H^+, another Mn^{2+} and the third one BrO_3^-) were brought into the reactor through glass capillary tubes connected by bendable Teflon tubes using regulated peristaltic pumps. SO_3^{2-} and H^+ were placed in one reservoir because their concentrations were held constant throughout the different runs, while Mn^{2+} and BrO_3^- were being varied. The flow rate of all the pumps was controlled by the voltage generated using a National Instruments toolkit interface with the *Labview software*. The pumps were connected to separate channels. The flow rate of each pump was then calibrated separately, as a function of the voltage. A schematic representation of the setup is shown in Fig. 1.
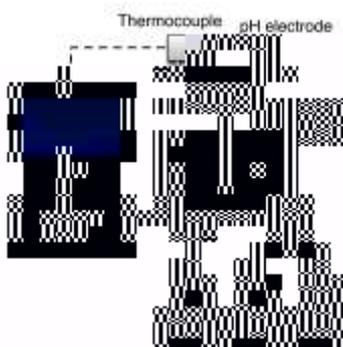
Figure 1: Experimental setup showing the CSTR, the reagent sources (flasks) and the corresponding pumps. Flask A: Mn^{2+}; Flask B: BrO_3^-; Flask C; H^+ and SO_3^{2-}.

The reaction mixture was vigorously stirred by a Teflon coated magnetic stirrer bar. As soon as the volume of the mixture reaches 9.0 mL, aspiration from the top of the reactor is operated in a way to maintain this volume constant throughout the remainder of the experiment. A thermostat bath providing water circulation to the reactor was used to maintain the reaction temperature at 45.0 ± 0.1 ºC. The pH of the mixture was monitored by continuous measurement using a calibrated glass/combination electrode, vertically inserted in the reaction mixture and connected to the NI interface. A thermocouple was also connected to monitor the temperature of the reactor. The sampling rate was 2 Hz, which yields a rate of 2 pH readings/sec.

3   Results and Discussion

Within the settings and configuration of our CSTR, we use a range of bromate concentrations notably higher than the one used by Okazaki *et al.* [8]**,** but we keep the concentrations of the other species essentially similar, i.e. $[Mn^{2+}]_0 = 9.0$ mM, $[SO_3^{2-}]_0 = 118$ mM and $[H^+]_0 = 16.5$ mM. The inlet flow rate is regulated at $k_{in} = 1.59$ mL/ min. This corresponds to a residence time of 5.66 min for a fixed CSTR volume of 9.00 mL ($t_{res.} = V_{CSTR}/k_{in}$). Note that in our experiments, the outlet flow rate k_{out} is threefold larger, that is, $k_{out} = 4.77$ mL/min, since the solutions in the *three* reservoirs are pumped in separately, while they are drained out of the reactor at once.
We explored the range $[BrO_3^-]_0 = 250$ to 1500 mM, with $[Mn^{2+}]_0$, $[SO_3^{2-}]_0$ and $[H^+]_0$ held constant as specified above, and according to Ref. [8]. Some of these concentrations exhibited oscillations and others did not. Over the $[BrO_3^-]_0$ range 90 – 300 mM, no oscillations were observed within the frame of our experimental CSTR settings. We jumped to higher $[BrO_3^-]_0$, starting particularly with $[BrO_3^-]_0 = 590$ mM. The first important result is the large-amplitude oscillations ranging from $pH_{lo} = 2.00$ to $pH_{hi} = 7.46$, with a pH amplitude 5.46.

This value exceeds the amplitude reported by Okazaki *et al.* [8] (4.5 pH units) by about 1 pH unit (0.96). In addition, the period is 10.9 min, compared to 39.1
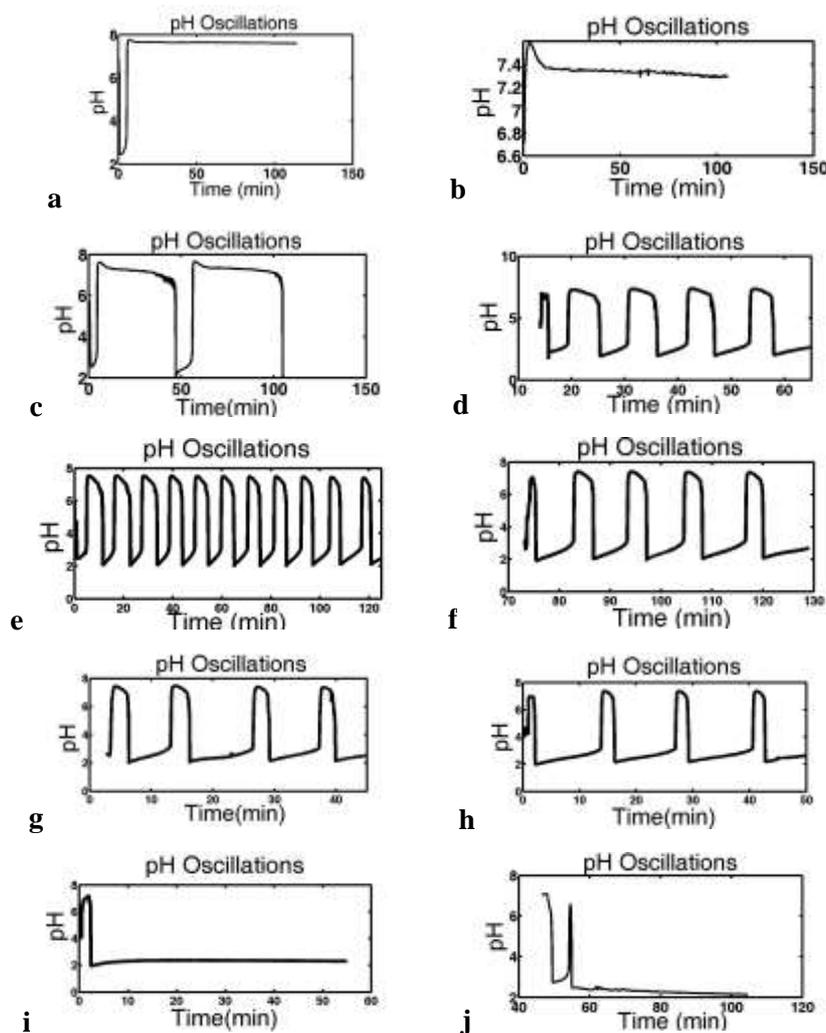

Figure 2: Oscillations obtained in the BSH reaction with $[Mn^{2+}]_0 = 9.0$ mM used a negative feedback; $[H^+]_0 = 16.5$ mM, $[SO_3^{2-}]_0 = 118$ mM, with $[BrO_3^-]_0 =$ (a) 350, (b) 385, (c) 450, (d) 560, (e) 590, (f) 620, (g) 730, (h) 800, (i) 1000, and (j)1500 mM.

min. reported by Okazaki *et al.* [8]. So we continue to vary $[BrO_3^-]_0$ throughout the rest of the study, i.e. explore the region 300-590 mM and then above 590 mM (the first $[BrO_3^-]_0$ with satisfactory oscillations). The obtained behavior for some relevant chosen BrO_3^- concentrations is displayed in Fig. 2. This wide range of BrO_3^- concentrations enables us to construct a bifurcation diagram in the pH $-$ $[BrO_3^-]_0$ space, delineating the various regions with different

characteristic behaviors. Such a bifurcation diagram is depicted in Fig. 3. It highlights the high steady state region (SSH), low steady state region (SSL) and the oscillatory regime (OR). At low $[BrO_3^-]_0$ values, only SSH is stable.
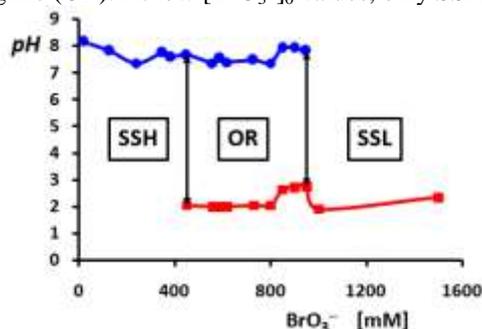

Figure 3: Bifurcation diagram in the Mn^{2+}- BrO_3^-- SO_3^{2-}-H^+ system with $[Mn^{2+}]_0 = 9.0$ mM. One (steady-state) or two (oscillatory region) pH values are plotted for each $[BrO_3^-]_0$ run. The framed labels read as follows: SSH (Steady-State High); OR (Oscillatory Region); SSL (Steady-State Low).

Upon increasing $[BrO_3^-]_0$ through the concentration 385 mM (among our tested values), the system experiences a transition (bifurcation) to an onset of oscillations (OR region). At $[BrO_3^-]_0 \geq 1000$ mM, as shown in Fig. 2 (frames **i** and **j**), the system is stable in the low pH regime. This is illustrated in the bifurcation diagram, and appears in the region labeled SSL (low pH steady state).

The variation of the amplitude and period of oscillation with the initial bromate concentration $[BrO_3^-]_0$ is shown in Fig. 4. We can see that the amplitude, and period of oscillations (beyond 450 mM) remain essentially constant (the range in Figure 4.a spans only about 0.5 pH unit).
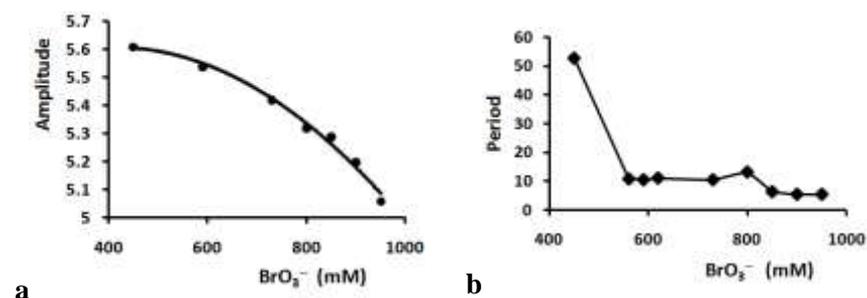

a   **b**

Figure 4: a. Variation of the amplitude of pH oscillations with bromate concentration $[BrO_3^-]_0$. b. Variation of the period of oscillations with bromate concentration $[BrO_3^-]_0$.

Among all the experiments done, $[BrO_3^-]_0 = 590$ mM is selected for the variation of flow rate, achieved by changing the voltages on the pumps.

Upon decreasing the flow rate to 1.35 mL/min, the period increased to 26.4 min, almost twice the value measured for k_{in} = 1.59 mL/min, as clearly shown in Fig. 5.
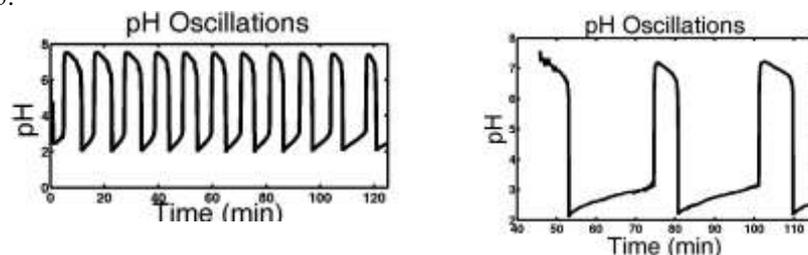

Figure 5: Effect of decreasing the flow rate from 1.59 to 1.35 mL/min for constant $[BrO_3^-]_0$ = 590 mM. The figure shows the pH oscillation at two different flow rates. a. $[BrO_3^-]_0$ = 590 mM, with k = 1.59 mL/min. b. $[BrO_3^-]_0$ = 590 mM, with k = 1.35 mL/min.

This can be considered as a period-doubling effect. Since the route to chaos starts with period-doubling and then followed by further increase (period-quadrupling etc.), we tried decreasing the flow rate further. We carried out runs at flow rates 1.260, 0.686 and 0.502 mL/min. No further ascent in the period of oscillation was obtained. As a second alternative, instead of decreasing the flow rate, we increased k_{in} to 1.89, 2.64 and 3.26 mL/min respectively. However none of the runs exhibited any noticeable change of interest, in particular the anticipated chaos.

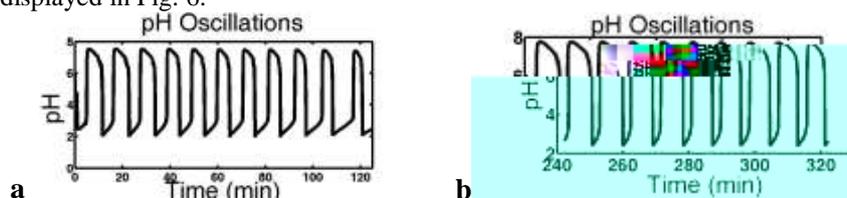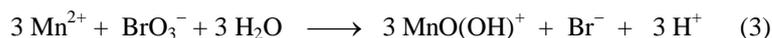We now vary $[Mn^{2+}]_0$, keeping the other concentrations constant. The results are displayed in Fig. 6.

Figure 6: BSH runs at fixed $[BrO_3^-]_0$ = 590 mM, $[H^+]$ = 16.5 mM, $[SO_3^{2-}]$ = 118 mM, but with $[Mn^{2+}]$ = 9.0 (a), and 13.0 mM (b). The period of oscillations decreases here from 10.9 to 8.7 min.

Upon increasing $[Mn^{2+}]_0$ from 7.2 to 9.0 to 13.0 mM, the period decreased from 11.76 min to 10.86 min to 8.66 minutes respectively. In the absence of $[Mn^{2+}]_0$, no oscillations were found indicating that Mn^{2+} plays an important role in the reaction mechanism, under the prevailing experimental conditions. It is worth noting that here again, the variation of $[Mn^{2+}]_0$ did not show any transition to chaotic behavior. Another interesting observation is that the duration of the low-pH stage decreases from 5.2 to 2.7 min. as $[Mn^{2+}]_0$ increases from 9.0 mM to 13.0 mM respectively, while that of the high pH stage remains constant (5.7 min.) as seen in Fig. 6. The latter trend agrees with the results of Okazaki et al. [8]. At very low $[Mn^{2+}]_0$, Mn^{2+} becomes insufficient for consuming protons, and

thus the low pH regime lasts gradually longer, until the transition to high pH is suppressed (oscillations cease). According to Okazaki et al. [8], among the stable Mn^{2+} species in the pH range 3-4 ($Mn(OH)^{2+}$, $Mn(OH)_2^{2+}$, and $MnO(OH)^+$), $MnO(OH)^+$ plays the most important role, and undergoes the reaction:

$$MnO(OH)^+ + 2\,HSO_3^- + 2\,H^+ \longrightarrow Mn^{2+} + HS_2O_6^- + 2\,H_2O \quad (2)$$
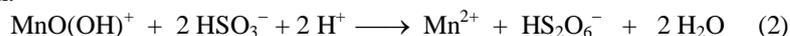
$MnO(OH)^+$ is readily produced from Mn^{2+} according to:

$$3\,Mn^{2+} + BrO_3^- + 3\,H_2O \longrightarrow 3\,MnO(OH)^+ + Br^- + 3\,H^+ \quad (3)$$

The predominance of $MnO(OH)^+$, coupled to the dependence on $[BrO_3^-]_0$, suggest that reaction (2) is the relevant process for the negative feedback scheme, contributed by the presence of Mn^{2+}. Finally, it is quite interesting to realize that the $[BrO_3^-]_0 = 590$ mM/$[Mn^{2+}]_0 = 9.0$ mM conditions produce oscillations with essentially equal durations of low and high pH stages (5.2 and 5.7 min. respectively).

It was further suggested [8] that the employment of two negative feedback species could produce chaotic pH-oscillations. To test this possibility, Mn^{2+} was combined with MnO_4^-, another known negative feedback species.
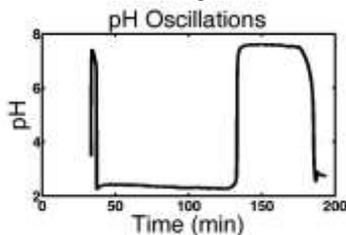

Figure 7: BSH run with two negative feedback species. $[Mn^{2+}] = 9.0$ mM and $[MnO_4^-] = 1.5$ mM, with $[BrO_3^-] = 590$ mM.

The result is shown in Fig. 7, without any noticeable sign of chaos. So with all those explored possibilities (variation in flow rate, $[Mn^{2+}]_0$ or use of two negative feedback species), no chaotic oscillations were observed.

4   Conclusions

The $[BrO_3^-]_0$ regime used here resulted in a *larger amplitude* and a *shorter period* than the values obtained in Ref. [8]. Furthermore, the system exhibited a period-doubling upon only one variation of flow rate. However, as discussed earlier, this system did not display any chaotic behavior in the whole range of BrO_3^- and Mn^{2+} concentrations explored, flow rate domains, or through the use of two negative feedback species. A *bifurcation diagram* was constructed, delineating the steady-state and oscillatory regimes.

Other suggested attempts to reach chaos in future studies on this system are, to name but a few, changing parameters such as the stirring rate and the temperature of the CSTR, in addition to variations in $[SO_3^{2-}]$ and $[H^+]$.

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