# **Complex Nonlinear Behavior in the Bromate–2-Aminophenol Reaction**

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ABSTRACT: The bromate–2-aminophenol reaction in a batch reactor was investigated in this research, in which both simple and sequential oscillations were observed. The occurrence of sequential oscillations were found to be very sensitive to changes of the initial concentrations, where decreasing the concentration of sulfuric acid or sodium bromate or increasing the 2-aminophenol concentration caused the two oscillation windows to coalesce. Lowering the reaction temperature from 30 to 5°C also caused the two oscillation windows to merge into one. A phase diagram in the bromate–sulfuric acid concentration plane demonstrates that sequential oscillations only occur within a narrow band of conditions. Mechanistic studies of the system through employing <sup>1</sup>H NMR and mass spectrometry suggest that a dibrominated ortho-benzoquinone is a major product. The oxidation of 2-aminophenol, on the other hand, can lead to the formation of pyrocatechol, which may be the substrate responsible for the second set of oscillations. © 2016 Wiley Periodicals, Inc. Int J Chem Kinet 1–7, 2016

#### INTRODUCTION

Chemical oscillations and wave formation have attracted a considerable amount of interest from researchers working in diverse areas such as mathematics, engineering, physics, and biology due to their fundamental connections in the emergence of similar nonlinear phenomena in those areas [1–14]. Arguably, the most extensively studied oscillatory chemical reaction is the Belousov–Zhabotinsky (BZ) reaction, which is the oxidation of an organic substrate by acidic bromate in the presence of metal catalysts such as cerium, ferroin, or ruthenium complexes [15–23]. In 1978, Orbán and Körös carried out an extensive search to study the oxidation of aromatic compounds by acidic bromate and reported that 23 phenol and aniline derivatives could produce oscillations without an addition of a metal catalyst to start the autocatalytic cycle [24]. Their investigation led to the establishment of a class of uncatalyzed bromate oscillators.

Ševčík and coworkers have discovered that using aniline and phenol as the organic substrate the uncatalyzed bromate oscillator could result in the occurrence of sequential oscillations, in which two oscillatory windows are separated by a long period of quiescent, nonoscillatory evolution of the reaction [25,26]. Computational investigations have illustrated that the

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coupling of two limit cycles (i.e., simple oscillations) may lead to the quench of the oscillatory behavior, depending on the frequency and magnitude of the two limit cycles. Working from such a theory, a chemical oscillator consisting of two suboscillators may temporally evolve into a nonoscillatory stage, where the stoppage of oscillation is due to the subtle balance of the two suboscillators. As a result, the phenomenon of sequential oscillation may take place in a closed chemical system, in which the continuous consumption or buildup of chemicals ensures that properties of suboscillators change in time. Several bromatebased oscillators consisting of coupled autocatalytic cycles have indeed been found to exhibit sequential oscillations [27-36]. For example, sequential oscillations have been reported when 1,4-cyclohexanedione (CHD) was added to the ferroin-catalyzed BZ oscillator, in which the minimum 1,4-CHD required for inducing complex oscillations depends on the parameter of the BZ reaction [34,35]. When ferroin was added to bromate-hydroquinone photochemical oscillators, two isolated oscillatory windows developed [36].

In spatially extended media, the temporal occurrence of nonoscillatory evolution may lead to spontaneous breakups of existing wave activity, resulting in the formation of spiral waves or turbulence [37]. To enrich the family of chemical oscillators exhibiting sequential oscillations, the uncatalyzed bromate oscillator using 2-aminophenol (2-AP) as the aromatic substrate has been systematically investigated here. The Wang research group have previously studied the reaction kinetics and wave patterns of bromate-4aminophenol (4-AP) oscillators [38]. Studying a system using an ortho substituted substrate may help gain new insights into such a system since the structures 4-AP and 2-AP only vary by the location of the functional groups; therefore, only the reaction rate of steps involving 4-AP are altered, allowing for further mechanistic understanding of the occurrence of complex behavior.

Different from the bromate–4-AP oscillator, the bromate–2-AP reaction has been found to exhibit sequential behavior without an addition of a metal catalyst. Another notable difference is that the oscillatory behavior is not photosensitive. After extensive studies in the concentration phase space were conducted, the phase diagram in the bromate–sulfuric acid concentration phase space demonstrates why finding sequential behavior in this uncatalyzed system is difficult. A possible mechanism has been suggested to explain the emergence of sequential behavior in this uncatalyzed bromate–2-AP system.

## **EXPERIMENTAL**

All reactions were carried out in a thermal-jacketed 50-mL glass beaker (ChemGlass; New Jersey, United States). A circulating water bath (Thermo NesLab RTE 7: Fisher Scientific: Ottawa, Canada) held the reaction temperature constant at  $25.0 \pm 0.1^{\circ}$ C unless stated differently. The reactions were monitored using a Hg|Hg<sub>2</sub>SO<sub>4</sub>|K<sub>2</sub>SO<sub>4</sub> reference electrode coupled with a platinum electrode (Radiometer Analytical, XR200 and M231 Pt-9; Villeurbanne Cedex, France). The volume for every reaction solution was fixed at 30.0 mL. The reaction was stirred with a magnetic stirring bar driven by a magnetic stirrer (Fischer Isotemp; Fisher Scientific; Ottawa, Canada) to ensure homogeneity. All measurements were recorded through a pH/potential meter (Radiometer PHM220; Villeurbanne Cedex, France) connected to a personal computer through a PowerLab/4SP data logger. All <sup>1</sup>H NMR studies were performed using either a Bruker Avance 300 or 500 MHz spectrometer, and the samples were dissolved in chloroform-d (Cambridge Isotope Laboratories: 99.8%: Montreal, Canada) or acetone $d_6$  (Cambridge Isotope Laboratories; 99.9%; Montreal, Canada). Mass spectrometry measurements were performed using a 1200-L single quadrupole MS (Varian) through a direct insertion probe, and using a Waters XEVO GS-XF Time-Of-Flight, with samples introduced via an Atmospheric Solids Analysis probe.

Stock solutions of sodium bromate (NaBrO<sub>3</sub>; Aldrich; 99%; Oakville, Canada), 0.06 M, and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>; Aldrich; 95%–98%; Oakville, Canada), 6.0 M, cerium(IV) sulfate (Ce(SO<sub>4</sub>)<sub>2</sub>; Aldrich; Oakville, Canada), 0.1 M, were prepared with double-distilled water. 2-AP (Aldrich; 99%; Oakville, Canada) was directly dissolved in the reaction mixture. Bromate solution was added to the reaction mixture, after 2-AP had dissolved completely. All chemicals were commercial grade and were used without further purification.

#### **RESULTS AND DISCUSSION**

Figure 1 shows five time series of the bromate–2-AP reaction conducted at different concentrations of 2-AP: (a) 0.0128 M, (b) 0.0112 M, (c) 0.0096 M, (d) 0.0064 M, and (e) 0.0032 M. In Fig. 1a, simple transient oscillations with a decreasing frequency were seen after a long induction time (ca. 4000 s). Phenomenologically, after mixing all reactants together the reaction solution slowly changes from a bright orange to a dark brown color; this corresponds to the long induction time that is



Figure 1 Time series of the bromate–2-AP reaction carried out at different 2-AP concentrations: (a) 0.0128 M, (b) 0.0112 M, (c) 0.0096 M, (d) 0.0064 M, and (e) 0.0032 M. Other reaction conditions were [H<sub>2</sub>SO<sub>4</sub>] = 1.3 M and [NaBrO<sub>3</sub>] = 0.03 M.

observed. This is then followed by a rapid color change to a bright yellow-orange solution as indicated by a sharp spike in the redox potential. Spontaneous oscillations in the bromate-2-AP system has been reported by Orbán and Körös in 1978; however, only simple oscillations were observed. [24] Once the concentration of 2-AP reaches above 0.0208 M, the oscillatory behavior disappears. As the 2-AP concentration was decreased to 0.0112 M in Fig. 1b, there was a noticeable change in the oscillatory behavior at about 6000 s after the start of the reaction, signaling the possible occurrence of complex oscillations. Upon further lowering 2-AP concentration to 0.0096 M in Fig. 1c, a period of quiescent nonoscillatory evolution became visible, forming two isolated oscillation windows. The frequency of oscillations in the first window was much higher than that in the second oscillation window. When the concentration of 2-AP was decreased from the sequential oscillation conditions, the second set of oscillations rapidly disappear as depicted in Figs. 1d and 1e. This would indicate that the concentration of the intermediates that start the second oscillatory regime was too low to induce an oscillatory cycle. The decrease of 2-AP concentration also resulted in the decrease in the number of oscillations until only one clock reaction is present at 0.0048 M 2-AP. The induction time of the potential excursion also continues to decrease, and



Figure 2 Time series of the bromate–2-AP reaction carried out at different  $H_2SO_4$  concentrations: (a) 1.4 M, (b) 1.3 M, (c) 1.2 M, and (d) 0.6 M. Other reaction conditions were [2-AP] = 0.008 M and  $[NaBrO_3] = 0.03$  M.

the excursion would occur almost instantaneously after mixing all reactants together as 2-AP concentration was decreased to 0.0016 M.

Figure 2 shows time series illustrating the effect of changing the concentration of sulfuric acid on the oscillatory behavior. Other conditions are kept constant at [2-AP] = 0.008 M and  $[NaBrO_3] = 0.03$  M. At the sulfuric acid concentration of 1.4 M, Fig. 2a shows that several oscillations took place about 2500 s after the start of the reaction. When the sulfuric acid concentration was increased to 1.7 M, only a single clock reaction could be observed. The second set of oscillations emerge in Fig. 2b as a result of decreasing sulfuric acid concentration to 1.3 M. When the acid concentration was decreased further, the nonoscillatory period slowly decreases until there was an overlap of the two sets leading to a single set of oscillations seen in Fig. 2c. Under the conditions employed in this figure, sequential behavior was observed to occur in the range of 1.2 M to 1.3 M H<sub>2</sub>SO<sub>4</sub>. At an acid concentration of 0.6 M, the initial excursion was less sudden and no oscillatory behavior could be observed.

Figure 3 presents five time series conducted at different bromate concentrations, while the 2-AP and



Figure 3 Time series of the bromate–2-AP reaction carried out at different NaBrO<sub>3</sub> concentrations: (a) 0.042 M, (b) 0.033 M, (c) 0.030 M, (d) 0.024 M, and (e) 0.012 M. Other reaction conditions were [2-AP] = 0.008 M and  $[H_2SO_4] = 1.3$  M.

H<sub>2</sub>SO<sub>4</sub> concentrations were kept constant at 0.008 M and 1.3 M, respectively. At NaBrO<sub>3</sub> concentration of 0.042 M, an excursion of redox potential took place at about 1000 s after the start of the reaction, followed by a few spontaneous oscillations (see Fig. 3a). The number of oscillations increased as the bromate concentration was decreased in Fig. 3b. As shown in Fig. 3c, sequential behavior could be observed at a bromate concentration near 0.030 M. Similar to decreasing the concentration of sulfuric acid, decreasing the bromate concentration resulted in a decrease in the nonoscillatory period until the two sets begin to merge. This disappearance occurs at a concentration of 0.024 M bromate in Fig. 3d. Notably, the remaining oscillatory behavior did not occur right after the excursion of the redox potential and their frequency resembles those of the second oscillation window seen in Fig. 1c or 2b. This leads us to suggest that the first oscillatory window was disfavored at the low bromate concentration. At 0.012 M NaBrO<sub>3</sub>, no oscillatory behavior can be observed, as depicted in Fig. 3e. Overall, sequential behavior is only observed within a narrow range of bromate concentration around 0.03 M, confirming the importance of bromate in both sets of oscil-



**Figure 4** Phase diagram of the bromate–2-AP reaction in the bromate–sulfuric acid concentration plane. 2-AP was kept at a constant concentration of 0.008 M.  $\circ$  Indicates the conditions under which the system exhibits simple oscillation,  $\blacktriangle$  indicates sequential behavior,  $\Box$  indicates a single peak behavior, and  $\times$  indicates the boundary at which no oscillatory behavior occurs.

lations since it produces the bromine dioxide radicals for the autocatalytic steps.

Figure 4 presents a phase diagram in the bromatesulfuric acid concentration phase plane while the concentration of 2-AP was kept constant at a concentration of 0.008 M. The circles represent conditions at which simple oscillations have been found, and the crosses represent the boundary at which no oscillatory behavior was observed. One can see that oscillatory behavior can occur over broad concentrations of bromate and sulfuric acid. However, sequential behavior can only be observed within a very narrow band of conditions as depicted by the triangles. Small increases in the concentrations of sulfuric acid or bromate would result in rapid disappearance of the second set of oscillations. A decrease in concentration results in the overlap of the two sets, making it impossible to see two individual sets of oscillations. This phase diagram also contains no upper boundaries in either the sulfuric acid or the bromate plane, meaning that oscillatory behavior will continue to be observed at high levels of bromate and sulfuric acid. However, only a single clock reaction can be observed at those conditions as depicted by the squares, while the induction period continues to decrease until it approaches zero.

Figure 5 illustrates the temperature dependence of the reaction behavior in the bromate–2-AP system. As to be expected, increasing the temperature results in an increase in the rate of reactions, leading to the increase of the oscillation frequency in both oscillatory windows. Sequential behavior was observed at temperatures above 25°C as shown in Figs. 5a and 5b. Please note that the x axis had to be changed to fit all the



**Figure 5** A time series of the bromate–2-AP reaction carried out at different temperatures: (a) 30°C, (b) 25°C, (c) 20°C, (d) 15°C, and (e) 5°C. Other reaction conditions were [2-AP] = 0.008 M,  $[H_2SO_4] = 1.24$  M, and  $[NaBrO_3] = 0.03$  M.

data in one figure, highlighting the significant influence of reaction temperature. As depicted in the figure, the majority of the reactions were out of the oscillatory window within a 5 h time span, but a temperature drop to  $15^{\circ}$ C caused the oscillatory period to last 7 h. When the temperature was further decreased to  $5^{\circ}$ C, no oscillatory behavior could be observed until the 15 h mark. An overall decrease in the number of simple oscillations were also observed as the temperature was decreased.

### **MECHANISTIC CHARACTERIZATION**

Similar to the bromate–4-AP reaction, precipitate was found to form in the 2-AP system after mixing the reactants together. To test whether the precipitate would affect the oscillatory behavior, the reaction was filtered during the oscillatory period. If the oscillatory behavior was a result of the precipitate, the oscillations would disappear after the reaction was filtered. However, the resulting behavior did not change which would indicate that the presence of precipitate does not affect the oscillatory behavior. Meanwhile, the observed oscillatory behavior is also not photosensitive, as opposed to what was seen in the 4-AP (para substituted benzene) system. To understand those differences, in particular the occurrence of sequential oscillations in this uncatalyzed system, <sup>1</sup>H NMR and mass spectrometry analyses were conducted at different stages throughout the reaction: (1) when the reaction was at about 10 min after mixing all reagents together while the reaction was still in its induction period, (2) a sample was obtained at about 50 min reaction time when the system was oscillating, and (3) a sample was obtained at around 180 min, when the oscillatory window had ended. In all three cases, the reaction solution was extracted by diethyl ether solvent and then analyzed using NMR and mass spectrometry.

The <sup>1</sup>H NMR and mass spectra for each sample contained many peaks which made it very difficult to identify all the compounds. However, a dominant intermediate giving resonances at  $\delta$  7.02 and 6.96 (2H, ABq, J = 10.5 Hz), which is indicative of the presence of a dibrominated ortho-benzoquinone can be seen at a reaction time of around 180 min (after sequential oscillations occur) as shown in Fig. 6. A series of peaks at 264/266/268 m/z in the mass spectrum also suggested the presence of this dibrominated species, which is most likely 3,4-dibromo orthobenzoquinone. <sup>1</sup>H NMR spectroscopy of the precipitate in acetone- $d_6$  revealed multiple resonances in the  $\delta$  6.3–7.6 and 9.0–9.1 regions, whereas peaks with high m/z in the mass spectrum suggest multiple 2-AP/quinone/catechol oligomers. The high-resolution mass spectrum of the precipitate also contained a series of peaks at 264/266 and 342/344/346 m/z, which indicated the presence of a dibrominated and tribrominated C<sub>11</sub> species, specifically with C<sub>11</sub>H<sub>6</sub>BrNO<sub>2</sub> and  $C_{11}H_5Br_2NO_2$  (as the M + H<sup>+</sup> ions), along with triand tetrabrominated  $C_{11}$  species.

Ce(IV) was reacted with a solution of 2-AP to determine the direct oxidation product of 2-AP as shown in Fig. 7. Ce(IV) was used as the oxidizing agent as opposed to  $BrO_3^-$  to prevent unwanted bromination of the aromatic sites. The resulting <sup>1</sup>H NMR spectra corresponded to the production of a significant amount of pyrocatechol ( $\delta$  6.82 and 6.88, 4H, AA'BB'). Scheme 1 presents a proposed mechanism for the production of pyrocatechol from 2-AP, where 2-AP is initially oxidized to produce an ortho-benzoquinone imine. This is then followed by a hydrolysis reaction to produce ortho-benzoquinone [39]. Finally, ortho-benzoquinone is reduced by residual 2-AP resulting in pyrocatechol.

Owing to the formation of pyrocatechol, this bromate–2-AP reaction may actually consist of two suboscillators, with the second one being the result from the formation of pyrocatechol from 2-AP oxidation.



**Figure 6** <sup>1</sup>H NMR (300 MHz) spectrum of the aromatic region of the bromate–2-AP reaction taken at 180 min when the oscillatory window had ended at the conditions [2-AP] = 0.008 M,  $[\text{H}_2\text{SO}_4] = 1.24 \text{ M}$ , and  $[\text{NaBrO}_3] = 0.03 \text{ M}$  using a CDCl<sub>3</sub> solvent.

There have been earlier reports on chemical oscillators being formed through the uncatalyzed oxidation of pyrocatechol by acidic bromate. [40–42] Competitions between the two suboscillators may lead to the occurrence of a long quiescent period in the middle of an oscillatory process, resulting in the behavior of sequential oscillations. We have examined this hypothesis by perturbing the system with 1/10 of 2-AP used in the system, and the first oscillatory window was indeed quenched.

#### CONCLUSIONS

This study demonstrated that the uncatalyzed bromate– 2-AP reaction in a batch reactor could exhibit sequential oscillations. The development of a quiescent, nonoscillatory evolution is likely the result of interactions between two suboscillators, in which the second suboscillator is being formed through acidic bromate



**Figure 7** <sup>1</sup>H NMR spectrum of the direct oxidation product 2-AP using Ce(IV) as an oxidant. Initial reaction conditions were [2-AP] = 0.008 M with excess Ce(IV) using CDCl<sub>3</sub> solvent.



Scheme 1 Proposed dominant pathway.

and the oxidation products of 2-AP. Preliminary mechanistic studies suggest that pyrocatechol could be the substance. Since this newly formed organic substrate, presumably pyrocatechol, is also subjected to the continuous consumption through reactions with acidic bromate, whether this intermediate substance can be built up in the system (i.e., its formation from 2-AP overwhelms its subsequent consumption) will be critical in the development of the second suboscillator as well as its competition with the bromate-2-AP oscillator. A decrease in the induction period of the potential excursion would cause the rapid disappearance of the second set, whereas an increase would result in the overlap of the two sets. This may indicate that the accumulation of the intermediate pyrocatechol needs to reach a certain level prior to the excursion to exhibit sequential behavior.

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