Long-Lasting Complex Reaction Behavior in a Closed Ferroin– Bromate–Hydroxybenzenesulfonate System

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ABSTRACT: The bromate-phenolsulfonate reaction was found to exhibit spontaneous oscillations in a batch reactor, where the addition of small amounts of ferroin would result in nonoscillatory behavior. As the ferroin concentration was increased, the system produced very rich nonlinear behavior, including three isolated oscillatory regimes that were separated by as long as 48 h nonoscillatory period. The long-lasting nonlinear behavior may be attributed to the slow desulfonation of phenolsulfonate in an acidic solution, forming phenol-like intermediates. However, unlike the bromate-phenol oscillator, oxygen was found to greatly influence the reaction, and various complex oscillations could be observed by tuning the oxygen concentration. Mechanistic studies performed through employ-



ing ¹H NMR spectroscopy and mass spectrometry to measure intermediate species at different stages of the reaction were able to identify 1,4-benzoquinone, 2-bromo-1,4-benzoquinone, 2,6-dibromo-1,4-benzoquinone, and 2,4,6-tribromophenol as major components during the reaction.

1. INTRODUCTION

The study of chemical oscillators has made significant contributions to advancing the theory of nonlinear dynamics, which has been incorporated into a diverse array of scientific disciplines ranging from computer science to molecular biology.¹⁻⁵ Dynamic control parameters of a chemical system such as the flow rate in a continuous flow stirred tank reactor (CSTR), reaction temperature, reactant concentrations, etc., can be conveniently manipulated, which makes the study of chemical oscillations excellent for gaining insights into related nonlinear behavior seen in nature. In comparison to CSTR experiments, reactions in a closed batch reactor are much easier to operate. Unfortunately, oscillations in a closed chemical system are transient, lasting only from a few minutes to a few hours,⁶⁻⁹ as opposed to the reaction dynamics in a CSTR, which can be kept permanently at a far from a thermodynamic equilibrium state via the continuous supply of fresh chemicals. This transient feature severely hinders the utilization of closed chemical systems to explore complex reaction phenomena and perturbed nonlinear dynamics.¹⁰ Finding ways to prolong the oscillatory window of existing chemical oscillators or developing new chemical oscillators that yield long-lasting oscillations in a closed system remains an important and challenging task.

In this research, sodium 4-hydroxybenzenesulfonate (PSA) was selected to react with acidic bromate in a closed system, in which the PSA is thermodynamically unstable in acidic media and may undergo desulfonation to produce aromatic compounds that can form bromate oscillators.¹⁴ Arguably, bromate-based reaction systems are the most extensively investigated and best understood chemical oscillators,^{15–17}

which involve the oxidation and bromination of an organic substrate by acidic bromate. In the past two decades, a host of aromatic compounds have been found to be capable of reacting with acidic bromate to exhibit spontaneous oscillations even in the absence of metal catalysts¹⁸⁻²¹ and have seen increasing use due to the lack of the formation of gas molecules, which is a desired property when the system is employed to explore pattern formation in reaction-diffusion media.^{22,23} The reaction of phenol with acidic bromate, for example, has been found to give rich nonlinear behavior, and derivatives of phenol such as 4-aminophenol have also been found to result in oscillatory behavior when reacting in acidic bromate solution, although some cases require the presence of external illumination. $^{26-28}$ The continuous supply of organic substrate through desulfonation of PSA makes the proposed chemical system similar to a semiopen bromate-aromatic compounds oscillator.^{24,25} Such a dynamic property provides opportunities of significantly prolonging the oscillatory window and discovering new phenomena.

Sulfonated aromatics are also important intermediates in the chemical industry, and understanding their reaction kinetics could have far-reaching impacts, far beyond nonlinear phenomena. For example, phenolsulfonate has been used as an antistress additive during the Ferrostan process that is the most commonly used method for electroplating tin.^{29,30} Nylon could acquire a stain resistance if it is treated with the condensation products of phenolsulfonate, formaldehyde, and

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sulfonates of dihydroxydiphenyl sulfones,³¹ and such compounds have also been used to produce a resin that acts as a cation exchanger to catalyze esterification reactions.³² Sulfonated aromatic compounds have also been found as constituents of many detergents, dyes, cosmetics, and agrochemicals.^{33,34} A pink dye can be produced, for example, by reacting hydrogen peroxide released from sucrose with phenolsulfonate and 4-aminoantipyrine in the presence of peroxidase enzyme, which can be used to determine the relative concentration of sucrose within food samples.³⁵

As shown in the following, the bromate–PSA system was uncovered to exhibit three isolated oscillatory regimes that were separated by as long as 48 h of nonoscillatory evolution. Such a result complements the earlier observation of sequential oscillations in the bromate–phenol reaction.^{24,25} A preliminary mechanistic study indicates that 1,4-benzoquinone, 2-bromo-1,4-benzoquinone, 2,6-dibromo-1,4-benzoquinone, and 2,4,6tribromophenol are major components during the reaction.

2. EXPERIMENTAL SECTION

All reactions were performed in a thermal-jacketed 50 mL glass beaker (ChemGlass). A circulating water bath (Thermo NesLab RTE 7) held the reaction temperature constant at 25.0 ± 0.1 °C. The reactions were monitored using a Hgl Hg₂SO₄|K₂SO₄ reference electrode coupled with a platinum electrode (Radiometer Analytical, XR200 and M231 Pt-9). 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) to ensure homogeneity. All measurements were recorded through a potential meter (Radiometer PHM220) connected to a personal computer through a PowerLab/4SP data logger. Mass spectrometry measurements were performed using a Waters XEVO GS-XF time-of-flight spectrometer with samples introduced via an Atmospheric Solids Analysis Probe. All ¹H NMR studies were performed using a Bruker Avance 500 MHz spectrometer, and the samples were dissolved in deuterated chloroform (Cambridge Isotope Laboratories, 99.8%).

Absorption spectra were measured with a UV-vis spectrophotometer (Ocean Optics, 2000 USB). A quartz cuvette (10 mm light path, HELLMA) containing 2.5 mL sample mixture was placed in a CUV sample holder. The cuvette was stirred with a small magnetic bar. Electrochemical experiments were performed on a CHI 760E electrochemical station (CHI Instruments, Bee Cave, TX). A glassy carbon electrode with a diameter of 3.0 mm was used as the working electrode. Platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Prior to each experiment, the working electrode was polished with 1 μ m, 0.3 μ m, and then 0.05 μ m fine alumina powder and cleaned using an ultrasonic cleaner (Branson 1510, USA) for 10 min in double-distilled water.

Stock solutions of analytical grade sodium bromate (NaBrO₃, Aldrich, 99%), 0.1 M, and sulfuric acid (Aldrich, 95–98%), 6.0 M, were prepared with double-distilled water. Ferroin (Fe(phen)₃²⁺), 0.030 M, was prepared with FeSO₄. 7H₂O (Aldrich) and 1,10-phenanthroline (Aldrich, 98%) according to a 1:3 stoichiometric relationship. The sodium 4-hydroxybenzenesulfonate (Aldrich, 98+%) was directly dissolved in the reaction mixture. Bromate solution was added to the reaction mixture after sodium 4-hydroxybenzenesulfonate had dissolved completely. All chemicals were commercial grade and were used without further

purification. A Teflon cap was placed on top of the thermaljacketed beaker to hold the electrodes.

3. RESULTS AND DISCUSSION

Figure 1 presents the time series of the bromate–PSA reaction with the presence of (a) 0.0, (b) 1.0×10^{-6} , (c) 1.0×10^{-5} ,



Figure 1. Time series of the bromate–PSA reaction performed at different ferroin concentrations: (a) 0.0, (b) 1.0×10^{-6} , (c) 1.0×10^{-5} , (d) 2.4×10^{-3} , (e) 2.9×10^{-3} , and (f) 4.3×10^{-3} M. Other reaction conditions were [PSA] = 0.0150 M, [H₂SO₄] = 1.4 M, and [NaBrO₃] = 0.040 M.

(d) 2.4×10^{-3} , (e) 2.9×10^{-3} , and (f) 4.3×10^{-3} M ferroin, while the other conditions were held constant at [PSA] = $0.0150 \text{ M}, [H_2SO_4] = 1.4 \text{ M}, \text{ and } [NaBrO_3] = 0.040 \text{ M}.$ The redox potential of the ferroin-free system in Figure 1a gradually decreased within the first 3000 s, which was followed by a group of spontaneous oscillations toward a lower potential. Here, the autocatalytic nonlinear feedback is formed through the oxidation of PSA intermediates by the bromine dioxide radicals. Upon the termination of the oscillatory behavior, the redox potential started to increase again. Notably, after the inclusion of 1.0×10^{-6} M ferroin, the oscillatory behavior disappeared, where the redox potential began to increase after the initial decrease within the first 1600 s. The inclusion of ferroin introduced a second autocatalytic feedback through the oxidation of ferroin by bromine dioxide radicals, which therefore created a system consisting of two suboscillators. The result in Figure 1b clearly demonstrates that interactions of two oscillators can annihilate spontaneous oscillations. In Figure 1c, the oscillatory behavior re-emerged after the ferroin concentration was increased to 1.0 \times 10^{-5} M. Here, the oscillations had a much longer induction period and lasted a significantly longer time.

Phenomenologically, the reaction mixture rapidly changes from a bright red solution to a clear blue solution upon the addition of bromate, which indicates the formation of ferriin from ferroin. After that, the solution gradually developed an opaque dark green color. While no periodic color change was apparent to the naked eye, about 1-7 oscillations in the redox potential could be seen after an induction time of around 40 min, forming the first oscillatory window. This was then followed by a quiescent period of ~100 min, leading to the

second oscillatory window. As shown in Figure 1e, when the ferroin concentration was close to 2.9×10^{-3} M, a third oscillatory window occurred after an extremely long quiescent period of around 40 h. The increase of ferroin concentration also led to an increase in the number of observable oscillations within the second and third oscillatory windows. Further increasing ferroin concentration, however, caused the disappearance of the third oscillatory window, as seen in Figure 1f.

Although no visible color change could be identified by the naked eye, with the aid of UV/vis absorption measurements, the color changes could be monitored by following ferroin which absorbs at a wavelength of 508 nm. Here, the reaction began at the regular reactor until spontaneous oscillations emerged, and then 2.0 mL of the solution was transferred to a cuvette for the absorption measurements. The reaction solution was stirred during the measurement. As shown in Figure 2a, spontaneous oscillations could be observed within



Figure 2. UV/vis absorption time series recorded during the (a) first, (b) second, and (c) third oscillatory windows. The concentrations are [PSA] = 0.0150 M, $[H_2SO_4] = 1.4 M$, $[NaBrO_3] = 0.040 M$, and [ferroin] = $3.0 \times 10^{-3} M$.

the first and second oscillatory windows. The amplitude of the oscillatory behavior in the third window was very low. Results in Figures 1a and 2a together suggest that both autocatalytic cycles play an essential role in the occurrence of spontaneous oscillations in the first oscillatory window. The time series in Figure 1a illustrates that the uncatalyzed oscillator only survives for several thousand seconds; therefore, oscillations in the second and third oscillatory windows are likely arising from autocatalytic reactions between ferroin—bromine dioxide radicals. The detection of ferroin oscillations in Figure 2b,c supports the above conclusion.

Figure 3 shows six time series conducted at different concentrations of sulfuric acid: (a) 0.8, (b) 1.0, (c) 1.3, (d) 1.4, and (e) 1.8 M. Other reaction conditions were [PSA] = 0.0150 M, [NaBrO₃] = 0.040 M, and [ferroin] = 3.0×10^{-3} M. At a low acid concentration, there were no spontaneous oscillations, although a very broad plateau with a high redox potential could be seen in Figure 3a. Sequential behavior was observed within the first 4 h of the reaction when the acid concentration was increased above 1.0 M. Notably, within a range of moderate acid concentration (between 1.3 and 1.5 M), a third oscillatory window also became visible. The results presented in Figure 3 also illustrate that the increase of acid concentration resulted in an increase in the frequency of oscillations.



Figure 3. Time series of the ferroin-bromate-PSA reaction performed at different H_2SO_4 concentrations: (a) 0.8, (b) 1.0, (c) 1.3, (d) 1.4, and (e) 1.8 M.

In Figure 4, time series conducted at different bromate concentrations are shown, where the PSA, ferroin, and sulfuric



Figure 4. Time series of the ferroin-catalyzed bromate–PSA reaction carried out at different NaBrO₃ concentrations: (a) 0.020, (b) 0.035, (c) 0.040, (d) 0.045, and (e) 0.075 M. Other reaction conditions were [PSA] = 0.0150 M, [H₂SO₄] = 1.4 M, and [ferroin] = 3.0×10^{-3} M.

acid concentrations were kept constant at 0.0150, 3.0×10^{-3} , and 1.4 M, respectively. Similar to that observed while changing the ferroin or sulfuric acid concentrations, the third oscillatory window could only be observed within a narrow range of conditions around a bromate concentration of 0.040 M, as depicted in Figure 4c. A deviation of 0.0050 M in either direction resulted in the disappearance of the third window. When the bromate concentration was lowered from 0.045 M, the number of observable oscillations in the first two oscillatory windows began to decrease until only the initial autocatalytic excursion could be observed, as shown in Figure 4a. Similarly, when bromate was increased past a concentration of 0.075 M, it resulted in all oscillatory behavior being quenched.

The dependence on PSA was tested and summarized in Figure 5, where other reaction conditions were $[H_2SO_4] = 1.4$ M, $[NaBrO_3] = 0.040$ M, and $[ferroin] = 3.0 \times 10^{-3}$ M. It was observed that at high concentrations of PSA (e.g., 0.0225 M in Figure 5e) only a couple of very low frequency oscillations could be observed. As the concentration was decreased, the frequency and number of oscillations began to increase along with the emergence of the two isolated oscillatory windows.



Figure 5. Time series of the ferroin-catalyzed bromate–PSA reaction carried out at different PSA concentrations: (a) 0.0120, (b) 0.0135, (c) 0.0150, (d) 0.0158, and (e) 0.0225 M.

Further decrease to a concentration of 0.0150 M resulted in the emergence of the third oscillatory window. This window could be observed until the concentration fell below 0.0135 M, as shown in Figure 5b.

The reaction behavior of several uncatalyzed bromate oscillators including the bromate-phenol system has been reported to exhibit great dependence on stirring.^{24,25,36} Such a dependence may arise from its influences on the extremely fast reaction steps or the influence on the diffusion of volatile species as well as oxygen out/into the reaction solution. It has previously been shown that oxygen can increase the induction period as well as gradually decrease the amplitude of the oscillatory behavior in the BZ oscillator.^{31,32} To shed light on the effects of oxygen on this reaction, the reaction solution was first purged with nitrogen gas to remove any excess oxygen. After the addition of bromate to initiate the reaction, a constant stream of nitrogen at a low flow rate was applied to the space above the solution surface. Low flow rates were used since elevated flow rates may have led to the significant removal of the volatile species such as bromine. As shown in Figure 6a, the second oscillatory window lasted substantially longer when compared to the conditions run in air. The duration of this oscillatory window was similar to the combination of both second and third oscillatory windows of the reaction in air (see Figure 5c). This suggests the long



Figure 6. Time series of the ferroin-catalyzed bromate–PSA reaction carried out in the presence of different gases: (a) N_2 , (b) 1:20 mixture of O_2 and N_2 , (c) O_2 , and (d) with O_2 introduced at 100000 s. Other reaction conditions were [PSA] = 0.0150 M, [H₂SO₄] = 1.4 M, [NaBrO₃], and [ferroin] = 3.0×10^{-3} M.

quiescent period observed in the presence of air may be due to the oxygen quenching the oscillatory behavior. Here, transient complex oscillations like burst and mixed mode patterns could be observed.

Using the same conditions as in Figure 6a, the reaction was repeated in Figure 6b under the flow of 1:20 (v/v) mixture of O₂ and N₂, in which the long quiescent period occurred, which led to the formation of two isolated oscillatory windows. When pure oxygen was allowed to flow in Figure 6c, the quiescent window became even longer, indicating the inhibitory effect of oxygen here. Earlier studies have reported that no oxygen effect was detected in the bromate-phenol system.^{24,25} The strong oxygen influence seen here suggests that phenol is less likely a major product from PSA desulfonation. Such a postulation is consistent with the UV/vis and NMR spectroscopic measurements. To further confirm the oxygen influence, the reaction was repeated under nitrogen conditions but with oxygen being introduced at 100000 s and resulted in the immediate quenching of oscillatory behavior as indicated by the arrow shown in Figure 6d.

In Figure 7 the influence of bromate concentration on complex behavior was further explored in a nitrogen



Figure 7. Time series of the ferroin–bromate–PSA reaction carried out at different NaBrO₃ concentrations: (a) 0.036, (b) 0.040, and (c) 0.044 M. Other reaction conditions were [PSA] = 0.0150 M, [H₂SO₄] = 1.4 M, and [ferroin] = 3.0×10^{-3} M. These reactions were run under nitrogen protection.

atmosphere, where the PSA, ferroin, and sulfuric acid concentrations were kept constant at 0.0150, 3.0×10^{-3} , and 1.4 M, respectively. Here, the reactor was sealed with parafilm, while nitrogen was slowly flowed into the empty space above the reaction solution. Clearly, increasing bromate concentration from 0.036 to 0.044 M greatly prolonged the oscillation window. Transient period-doubling and mixed mode oscillations could be seen at the bromate concentrations of 0.036 M (Figure 7a) and 0.040 M (Figure 7b). A phenomenon of three isolated oscillatory windows was seen at a bromate concentration of 0.044 M, where within each oscillatory window only simple oscillations occurred.

Figure 8 presents the cyclic voltammograms measured with a glassy carbon electrode in two solutions containing (a) 0.0200 M PSA + 2.0 M H_2SO_4 and (b) 0.0200 M PSA + 0.1 M KCl. In the acidic solution, a new oxidation peak emerged at around 1.2 V, while the anodic peak at 0.85 V also became more pronounced. The qualitative and quantitative changes in the cyclic voltammogram suggest that PSA might have decomposed. The UV/vis absorption method and NMR spectroscopic technique were deployed to examine the decomposition products of PSA and showed there was no convincing evidence on the formation of substantial amounts of phenol, contrary to expectations. However, small amounts of phenol could be



Figure 8. CVs measured with a glassy carbon electrode in solutions containing (a) $0.0200 \text{ M PSA} + 2.0 \text{ M H}_2\text{SO}_4$ and (b) 0.0200 M PSA + 0.1 M KCl.

detected when the concentrations of PSA and H_2SO_4 were much higher. This explains why this PSA system exhibited a very different response to oxygen.^{24,25} Notably, the presence of two well-separated anodic peaks in Figure 8 suggests that the oxidation of PSA in acidic solution is likely occurring in two distinct steps with very different rate constants, creating a chemically coupled system in which the subsystems are coupled through chemical reactions between their products or intermediates.^{24,25}

To gain insight into the intermediates and final products of the ferroin-bromate-PSA oscillatory reaction, ¹H NMR spectroscopic measurements were performed. Samples were collected approximately halfway through each of the three oscillatory windows and were extracted twice with diethyl ether. After concentrating the diethyl ether solution under a reduced pressure, ¹H NMR samples were prepared with deuterated chloroform. The ¹H NMR throughout all three samples showed resonances which correspond to the presence of benzoquinone (δ = 6.80, 4H, s), 2-bromobenzoquinone (δ = 7.32, 1H, d, J = 2.4 Hz; 6.98, 1H, d, J = 10.2 Hz; 6.84, 1H, dd, J = 2.4, 10.2 Hz), 2,6-dibromobenzoquinone ($\delta = 7.34, 2H$, s), and 2.4.6-tribromophenol (δ = 7.60, 2H, s) as indicated by the letters a-d, respectively, in Figure 9. As the reaction time progressed from the first to the second window, the emergence of two peaks at δ = 7.01 (2H, s) and δ = 7.41 ppm (2H, s) could be observed, which possibly correspond to 2,3- and 2,5dibrominated derivatives of benzoquinone as indicated by the letters e and f in Figure 9, respectively. The relative peak intensity of the 2,3-dibrominated derivative continued to grow during the third window, and due to the reaction being run for around 50 h, the resulting spectra contained a multitude of compounds as shown in Figure 9. The presence of these compounds was confirmed as the mass spectrometry measurements gave a series of peaks at 108, 186/188, 264/266/268, and 320/330/332/334 m/z which correspond the benzoquinone, 2-bromobenzoquinone, 2,6-dibromobenzoquinone, and 2,4,6-tribromophenol, respectively.

A plausible reaction pathway demonstrating the formation of benzoquinone and bromobenzoquinones is proposed as the following: the starting material PSA undergoes oxidation and bromination reactions in the presence of acidic bromate. Because of the presence of the sulfonate group in the paraposition, the phenol-like reagents may also participate in oxidation reactions in the ortho-position in ways similar to that reported earlier.^{24,39} With the presence of ferroin, a second autocatalytic cycle was introduced through a reaction between ferroin and bromine dioxide radicals. The competition



Figure 9. ¹H NMR (300 MHz) spectrum of the aromatic region of the ferroin-catalyzed bromate–PSA taken at different times: (bottom) during the first, (middle) second, and (top) third oscillatory windows.

between the two autocatalytic cycles led to the quiescent period between the first two oscillatory windows in the form of sequential oscillations.

4. CONCLUSIONS

The presence of two well-isolated anodic peaks in the cyclic voltammogram of PSA suggests that its oxidations are likely taking place through two stages with very different reaction kinetics. The variation of CVs seen in Figure 8 is also indicative on the decomposition of PSA in an acidic solution. UV/vis absorption measurement of PSA-H₂SO₄ solution at the wavelength of 275 nm confirms the slow decomposition of PSA. Such a chemical property allows the ferroin-bromate-PSA reaction to exhibit long-lasting oscillatory behavior (>2 days) in a batch reactor, making this new oscillatory system an excellent candidate for investigating self-powered oscillating gels.⁴⁰ Notably, when only a small amount of ferroin was introduced into the system, the system became nonoscillatory, providing an experimental example on an earlier theoretical prediction that the coupling of two oscillators may lead to amplitude death and oscillation death.⁴¹

Different from the bromate-phenol oscillator, in which oxygen was reported to have no effect on its oscillatory phenomena,²⁵ oxygen was found to have strong inhibitory effects in the ferroin-bromate-PSA system. Oscillations that occurred within the earlier or near the end of the reaction were not quenched by oxygen. On the other hand, spontaneous oscillations were completely quenched by oxygen during the intermediate stage of the reaction, which led to the development of a very long nonoscillatory region and three isolated oscillatory regimes. The observed inhibitory influence of oxygen is likely through its interactions with organic substrate radicals such as 1,4-semiquinone, which would otherwise undergo autocatalytic reactions with bromine dioxide radicals. It is similar to the BZ reaction, in which oxygen influence has been attributed to the interactions between oxygen and malonyl radicals.^{42–45} Benzoquinone and several brominated benzoquinones have been detected with

NMR spectroscopy and mass spectrometry as major components during the reaction. Indeed, benzoquinone, monobromobenzoquinone, and tribromobenzoquinone could be found in a sample that was prepared at 10 min after the start of the reaction.

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Notes

The authors declare no competing financial interest.

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