Mapping Sequential Oscillations in the Bromate–Oxalic Acid–Acetone–Ce(IV) Reaction

Michael S. Chem†* and Roberto B. Faria*†

Instituto de Química, Universidade Federal do Rio de Janeiro, Avenida Athos da Silveira Ramos, 149, CT, Bloco A, Rio de Janeiro, RJ 21941-909, Brazil

ABSTRACT: Oscillating reactions are reactions in which it is possible to observe oscillations in the concentrations of some reaction intermediates. The reaction studied here is composed of acetone, sulfuric acid, bromate, oxalic acid, and Ce(IV). Chemical oscillators may have different behaviors in batch, for example, the presence of an induction period and change of oscillations’ pattern. A much rarer event is the presence of a break, or pause, between two groups of oscillations, which is shown by this system. To better determine the conditions under which this behavior occurs, we built several phase diagrams for the initial concentrations of reactants. These phase diagrams show that there is a well-defined range of concentrations that produce a pause in the oscillations. The initial bromate concentration is special because increasing this concentration eliminates the pause in the oscillations, but a further increase can make a pause appear again. These results can be interpreted considering that the reaction mechanism is controlled by at least two intermediates. In addition, this work presents a representative set of data that must be acknowledged by any detailed proposal of mechanism for this oscillating reaction.

INTRODUCTION

Oscillating reaction is a kind of nonlinear behavior observed in chemical systems in both batch and flow regimes.1,2 In the last case, several different behaviors have been well characterized, but in the batch regime, the situation is more difficult because the concentration of reactants decreases all the time, until the oscillations die. A very special behavior in batch is the sudden interruption of the oscillations for a while, followed by their resumption, without any external interference. In other words, there is a pause in the oscillations. This remarkable behavior has been reported for the first time in the Belousov–Zhabotinsky (BZ) modified system iodide–bromate–malonic acid–Ce(IV) by Kaner and Epstein.3 Following this article, Heilweil et al. reported the presence of different kinds of oscillations, separated in time, in a BZ system containing three different organic substrates (malonic acid, acetylacetone, and ethyl acetoacetate).4 These authors concluded that each isolated sequence of oscillations was due to a different oscillation reaction with one of the three organic substrates and because of this they coined the name sequential oscillations.

Several other authors also observed a pause in oscillations. Cooke investigated the Briggs–Rauscher oscillating reaction modified by addition of acetone and observed a pause in oscillations, which he called double-barreled oscillations.5 Wittmann et al.6 called the pause observed in the bromate–oxalic acid–acetone–Ce(IV) system a temporary nonoscillatory state. However, the name sequential oscillations is almost settled by now to indicate the presence of a pause between a group of oscillations, in batch.7–12 The systems that present sequential oscillations may include a metal catalyst or can be uncatalyzed.9,10,13 Concentration of oxygen over the solution can also determine the emergence of sequential oscillations, as in the case of a BZ system catalyzed by ferroin.14 For oscillating reactions in micellar systems produced by the presence of a surfactant, the concentration of the surfactant can also determine the occurrence of sequential oscillations.15 Photochemical systems, as bromate–(4-aminophenol)–Ce(IV) and bromate–(2-methyl-1,4-benzoquinone)–Ce(IV), can also present sequential oscillations.12,16

Only for a few systems that present sequential oscillations in batch, there are detailed phase diagrams indicating the simultaneous range of concentrations for two reactants.5,14 In this work, we present five two-dimension phase diagrams for sequential oscillations observed in the system bromate–oxalic acid–acetone–Ce(IV).6,17 These phase diagrams show that the emergence of sequential oscillations is more sensible to some reactants than others, and the use of special mathematical functions in some axes produces linear boundaries between the regions for sequential oscillations and regular oscillations or nonoscillatory behavior. The effects of the concentrations of reactants over the length of the pause and the induction period were also investigated.

Bromate–Oxalic Acid–Acetone–Ce(IV) Oscillating Reaction and Its Mechanism. In 1971, Kasper and Bruce failed to obtain oscillations using oxalic acid as an organic reductor.18 In 1979, Noszticzius et al.19 observed oscillations bubbling H2 to remove Br2 and later by addition of
acetone with the same purpose.\textsuperscript{17} Bromine is removed by its reaction with the enol of acetone (see eqs 15 and 16 below).\textsuperscript{20}

The bromate–oxalic acid–acetone–Ce(IV) oscillating reaction is considered simpler than the BZ reaction, which uses malonic acid, because the first forms less different organic products and intermediates. Moreover, the Br\textsuperscript{−} source cannot be a brominated organic compound, like bromomalonic in the Field–Körös–Noyes (FKN)\textsuperscript{31} mechanism, because oxalic acid does not form any brominated product, and bromoacetone does not react at a significant speed with Ce(IV).\textsuperscript{20,22} The Br\textsuperscript{−} is mainly formed by bromine hydrolysis (eq 3 below).

A detailed mechanism for the bromate–oxalic acid–acetone–Ce(IV) oscillating reaction, containing 24 reactions, was proposed, in 1985, by Field and Boyd (FB), as shown below.\textsuperscript{20} To make the presentation of this mechanism simpler than in the original article, the reactions that do not contribute to the mechanism, reaction FB-19 can also be deleted. In addition, reaction 17 (FB-26), between bromate and oxalic acid, was corrected by the addition of one H\textsuperscript{+} in the left side. The deleted reactions are indicated below, following the FB mechanism’s reactions. The labels for reactions 1–10 are the same as in the FB mechanism.

\[
\begin{align*}
\text{Br}^- + \text{BrO}_3^- + 2 \text{H}^+ &\rightleftharpoons \text{HOBr} + \text{HBrO}_2 \quad (1) \\
\text{Br}^- + \text{HBrO}_2 + \text{H}^+ &\rightarrow 2 \text{HOBr} \quad (2) \\
\text{Br}^- + \text{HOBr} + \text{H}^+ &\rightleftharpoons \text{Br}_2 + \text{H}_2\text{O} \quad (3) \\
\text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ &\rightleftharpoons 2 \text{BrO}_2^- + \text{H}_2\text{O} \quad (4) \\
\text{BrO}_2^- + \text{Ce}^{3+} + \text{H}^+ &\rightleftharpoons \text{Ce}^{4+} + \text{HBrO}_2 \quad (5) \\
\text{BrO}_2^- + (\text{COOH})_2 &\rightarrow \text{HBrO}_2 + \text{CO}_2 + \text{HCO}_2^- \quad (6) \\
\text{HBrO}_2 + \text{HBrO}_2 &\rightleftharpoons \text{HOBr} + \text{BrO}_3^- + \text{H}^+ \quad (7) \\
\text{Ce}^{4+} + \text{BrO}_2^- + \text{H}_2\text{O} &\rightleftharpoons \text{Ce}^{3+} + \text{BrO}_3^- + 2 \text{H}^+ \quad (8) \\
\text{HOBr} + (\text{COOH})_2 &\rightarrow \text{H}_2\text{O} + \text{H}^+ + \text{CO}_2 + \text{HCO}_2^- + \text{Br}^+ \quad (9) \\
\text{Br}^+ + \text{Br}^+ &\rightarrow \text{Br}_2 \quad (10) \\
\text{HCO}_2^- + \text{HCO}_2^- &\rightarrow (\text{COOH})_2 \quad (FB-12) \quad (11) \\
\text{Ce}^{3+} + (\text{COOH})_2 &\rightarrow \text{Ce}^{3+} + \text{CO}_2 + \text{HCO}_2^- + \text{H}^+ \quad (FB-14) \quad (12) \\
\text{Ce}^{3+} + \text{HCO}_2^- &\rightarrow \text{Ce}^{3+} + \text{CO}_2 + \text{H}^+ \quad (FB-15) \quad (13) \\
\text{Br}^+ + (\text{COOH})_2 &\rightarrow \text{Br}^- + \text{H}^+ + \text{HCO}_2^- + \text{CO}_2 \quad (FB-16) \quad (14) \\
\text{CH}_3\text{COCH}_3 + \text{H}^+ &\rightleftharpoons \text{CH}_2=\text{C(OH)CH}_3 + \text{H}^+ \quad (FB-20) \quad (15) \\
\text{CH}_2=\text{C(OH)CH}_3 + \text{Br}_2 &\rightarrow \text{BrCH}_2\text{COCH}_3 + \text{Br}^- + \text{H}^+ \quad (FB-21) \quad (16) \\
\text{BrO}_3^- + (\text{COOH})_2 &\rightarrow \text{BrO}_2^- + \text{H}_2\text{O} + \text{CO}_2 + \text{HCO}_2^- \quad (FB-26) \quad (17) \\
\text{HBrO} + \text{HCO}_2^- &\rightarrow \text{H}_2\text{O} + \text{Br}^- + \text{CO}_2 \quad (FB-28) \quad (18) \\
\text{Br}^- + \text{Br}_2 &\rightleftharpoons \text{Br}_3^- \quad (FB-29) \quad (19) \\
\text{HCO}_2^- + \text{H}^+ + \text{BrO}_3^- &\rightarrow \text{BrO}_2^- + \text{CO}_2 + \text{H}_2\text{O} \quad (FB-31) \quad (20) \\
\text{Br}_3^- + \text{CH}_2=\text{C(OH)CH}_3 &\rightarrow \text{BrCH}_2\text{COCH}_3 + 2 \text{Br}^- + \text{H}^+ \quad (F-32) \quad (21) \\
\text{Br}_2 + \text{BrCH}_2\text{COCH}_3 &\rightarrow \text{BrCH}_2\text{COCH}_3 + \text{Br}^- + \text{H}^+ \quad (FB-34) \quad (22) \\
\text{Br}_3^- + \text{BrCH}_2\text{COCH}_3 &\rightarrow \text{BrCH}_2\text{COCH}_3 + 2 \text{Br}^- + \text{H}^+ \quad (FB-35) \quad (23) \\
\text{Br}^+ + \text{HCO}_2^- &\rightarrow \text{Br}^- + \text{H}^+ + \text{CO}_2 \quad (FB-11) \quad (24) \\
\text{HCO}_2^- + \text{HCO}_2^- &\rightarrow \text{HCOOH} + \text{CO}_2 \quad (FB-13) \quad (25) \\
\text{Br}^- + \text{CH}_3\text{COCH}_3 &\rightarrow \text{Br}^- + \text{CH}_3\text{COCH}_2^- + \text{H}^+ \quad (FB-17) \quad (26) \\
\text{CH}_3\text{COCH}_2^- + \text{Br}_2 &\rightarrow \text{BrCH}_2\text{COCH}_3 + \text{Br}^- \quad (FB-18) \quad (27) \\
\text{CH}_3\text{COCH}_2^- + \text{CH}_3\text{COCH}_2^- &\rightarrow \text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3 \quad (FB-19) \quad (28) \\
\text{BrO}_2^- + \text{CH}_3\text{COCH}_3 &\rightarrow \text{CH}_3\text{COCH}_2^- + \text{HBrO}_2 \quad (FB-27) \quad (29) \\
\text{HCO}_2^- + \text{BrO}_2^- &\rightarrow \text{HBrO}_2 + \text{CO}_2 \quad (FB-30) \quad (30) \\
\text{Br}^- + \text{Br}^- + \text{BrO}_3^- &\rightarrow 3 \text{HOBr} \quad (FB-33) \quad (31) \\
\text{HCO}_2^- + \text{Br}_2 &\rightarrow \text{H}^+ + \text{CO}_2 + \text{Br}^- + \text{Br}^- \quad (FB-36) \quad (32)
\end{align*}
\]

The reactions involving only bromine and cerium chemistry are the same as in the FKN mechanism.\textsuperscript{21} Reactions 1–3 form what is called the first process (P1), which is a set of nonradical reactions that keeps the system in a reduced state because of a low [Ce\textsuperscript{4+}] and low absorbance at 318 nm) in the FKN mechanism for the BZ reaction. Reactions 4, 5, and 7 form the second process (P2), which is a set of radical reactions that keeps the system in an oxidized state because of a high [Ce\textsuperscript{4+}] and high absorbance at 318 nm). The third process in the FKN mechanism includes reaction 8, but the other reactions are different in the FB mechanism because oxalic acid cannot be brominated. In this way, the production of Br\textsuperscript{−}, which changes the control of the reaction from the set of reactions P2 to P1, is made by the reaction between acetone (and their brominated products) and bromine (reactions 16 and 21–23). Oxalic acid is responsible
for the reduction of Ce⁴⁺ to Ce³⁺ (reactions 12 and 13), together with reaction 8.

Using this mechanism, Pereira and Faria observed several complex behaviors for this system by computer modeling, some of them not observed experimentally yet. Experimental work on this system has shown that for the oscillations to start, it is necessary for some Ce⁴⁺ to be changed to Ce³⁺. This can be obtained by the slow reaction between acetone and Ce⁴⁺ in a reactant solution or using directly a Ce³⁺ salt as a catalyst.²⁴,²⁵ Bubbling an inert gas is also used to remove Br₂, without the use of acetone. In this case, a more recent mechanism considers that Br₂ can also be removed by reaction with HCO₂⁻. This mechanism considers several radical reactions that were not included in the FB mechanism and also the formation of the Br₂⁻⁻ species.

It can be said that, until now, there is only one proposed mechanism for the bromate–oxalic acid–acetone–Ce(IV) oscillating reaction, and there is no realistic mechanism that explains the emergence of sequential oscillations in batch. In the present work, the FB mechanism is used to explain the formation of sequential oscillations. In addition, a more general topological approach is also presented.

**METHODS**

The solutions were prepared using chemicals of analytical grade without further purification. Water was purified through distillation followed by deionization. All solutions were produced and stored for up to 2 months, except for the acetone solution, which was prepared on the day it was used. Initial concentrations of the stock solutions were as follows: acetone 1.0 mol L⁻¹ (95%, Merck), oxalic acid 0.50 mol L⁻¹ (Quimbras), sulfuric acid 8.71 mol L⁻¹ (95%, Vetec), sodium bromate 0.25 mol L⁻¹ (99.5%, Vetec), and cerium sulfate 0.015 mol L⁻¹ (85%, Vetec). Sulfuric acid concentration on the stock solution was measured by titration using sodium hydroxide 0.1 mol L⁻¹ (97%, Grupo Química Industrial Ltda). The sodium hydroxide was titrated with potassium hydrogen phthalate (99.95%, Grupo Química Industrial Ltda). The reaction was held in a 3 mL quartz cell with an optic path of 1 cm and a Teflon lid. The spectrophotometer (Agilent 8435) was equipped with a deuterium lamp. The spectra from 200 to 800 nm were acquired every 0.5 s (cycle time) for at least 30 min. Due to the short cycle time, the cell was continuously irradiated by the deuterium lamp throughout the reaction. The Ce(IV) peak at 318 nm was used to follow the oscillations. We assumed that the ultraviolet light does not significantly affect the reaction because our data is in agreement with previous reports on this system.⁶ Temperature was kept at 24.1 ± 0.3 °C using a thermostatic bath (ETICA S21) connected to a thermostatted cell holder, which can also perform magnetic stirring. The 0.3 mm × 0.9 mm magnetic stirrer is Teflon coated.

Reactants’ solutions were added to the quartz cell in the following order: water, sulfuric acid, acetone, oxalic acid, bromate, and Ce(IV). Spectrum acquisition started immediately after addition of the Ce(IV) solution. The stirring rate was kept at, approximately, 200 rpm.

**RESULTS**

Sequential oscillations are known for several chemical systems, as indicated in the Introduction section, but the reports in the literature, usually, only indicate a few ranges of reactants’ concentration for which this behavior occurs. One exception is the work by Cooke,⁵ which describes the effect of the
reactant’s concentrations in the length of the pause for the Briggs–Rauscher oscillating reaction. In this work, we determined several phase diagrams for the bromate–oxalic acid–acetone–Ce(IV) oscillating reaction, which can help understand in more detail the mechanism of this reaction.

**Acetone vs Sulfuric Acid Phase Diagram.** Fixing the initial concentrations of bromate, oxalic acid, and Ce(IV), the initial concentrations of sulfuric acid and acetone were changed in the range of 1.0–3.0 and 0.06–0.45 mol L\(^{-1}\), respectively. Depending on the initial acetone concentration, three different behaviors were observed, as shown in Figure 1: (d) regular oscillations, which start immediately; (b,c) sequential oscillations; and (a) regular oscillations, which start after an induction period. These behaviors are indicated in Figure 2 by different colors. In addition, the length of the pause between two oscillating regimes and the length of the induction period are indicated by the size of the dots.

![Figure 2. Phase diagram ln[acetone]\(_0\) vs [H\(_2\)SO\(_4\)]\(_0\). Regular oscillations (Figure 1d) are indicated in blue; sequential oscillations (Figure 1b,c) are indicated in magenta. The size of magenta dots indicates the length of the pause. Regular oscillations preceded by an induction period (Figure 1a) are indicated in brown. The size of the brown dots indicates the length of the induction period. Other concentrations are the same as in Figure 1.](Image)

As can be observed in Figure 2, sequential oscillations occur in a narrow range of [H\(_2\)SO\(_4\)]\(_0\) and [acetone]\(_0\). Inside this region, as [acetone]\(_0\) increases, the number of oscillations before the pause decreases and the length of the pause increases, until it becomes an induction period (Figure 1). The length of the induction period tends to be greater at higher [H\(_2\)SO\(_4\)]\(_0\). This phase diagram also indicates that if one of these initial concentrations is reduced, the other must be increased to allow the observation of the sequential oscillations. In addition, the lowest value of [H\(_2\)SO\(_4\)]\(_0\) is, approximately, 33% of the highest value, but the lowest value of [acetone]\(_0\) is 12.5% of the highest value, indicating that [H\(_2\)SO\(_4\)]\(_0\) is more critical for the emergence of sequential oscillations than [acetone]\(_0\). Figure 3 shows that the borders of the sequential oscillations’ region can be turned linear using ln[acetone] in the abscissa axis.

**Other Behaviors Observed.** In the middle range of [H\(_2\)SO\(_4\)]\(_0\), the use of low [acetone]\(_0\) produces mixed-mode oscillations, preceded by an induction period, displaying low absorbance (low [Ce(IV)], reduced state), instead of regular oscillations, as shown in Figure 4.

At low concentrations, [H\(_2\)SO\(_4\)]\(_0\) = 1.0 mol L\(^{-1}\), and at [acetone]\(_0\) = 0.040 mol L\(^{-1}\), there is no induction period and the second group of oscillations in the sequential oscillations starts gradually (Figure 5). In this case, we can say that after the pause, the system crosses a supercritical Hopf bifurcation, differently as observed in Figure 1b,c, in which, after the pause, we can consider that the system crosses a subcritical Hopf bifurcation.27,28

At high [H\(_2\)SO\(_4\)]\(_0\) above 2.50 mol L\(^{-1}\), the oscillation patterns start becoming more complex, presenting irregular small amplitude oscillations (low absorbance; low [Ce(IV)], reduced state) during the “pause” and other irregularities, as shown in Figure 6. In this way, it can be considered that no regular oscillations occur at these high [H\(_2\)SO\(_4\)]\(_0\). However, although irregular, the total duration of the oscillations is the longest we observed, especially at low [acetone]\(_0\), as can be seen in Figure 7.

**Bromate vs Sulfuric Acid and Bromate vs Acetone Phase Diagrams.** Figures 8 and 9 present the phase diagrams describing the relations between the initial concentrations of bromate and sulfuric acid and bromate and acetone, respectively. As can be seen in both diagrams, the effect of the initial concentration of bromate is opposite to the effect of the initial concentration of acetone in Figures 2 and 3. If the initial concentration of bromate is increased, the concentrations of sulfuric acid or acetone must also be increased to allow the observation of sequential oscillations. Similarly, as in Figures 2 and 3, the region for sequential oscillations is between the region for regular oscillations and the region for regular oscillations preceded by an induction period. It can also be observed that the pause increases as [acetone]\(_0\) is increased. **Other Behaviors Observed.** At intermediate initial concentrations of acetone and sulfuric acid ([acetone]\(_0\) = 0.200 mol L\(^{-1}\), [H\(_2\)SO\(_4\)]\(_0\) = 1.50 mol L\(^{-1}\)) several different behaviors are observed at low bromate initial concentration. (i) Reduction of [BrO\(_3^−\)] from 0.0175 to 0.010 mol L\(^{-1}\) produces only one set of regular oscillations because the second group of oscillations disappears, as shown in Figure 10. This behavior is different from that observed at higher initial bromate concentrations, when reduction of [BrO\(_3^−\)] changes the sequential oscillations to regular oscillations preceded by an induction period, as indicated in the phase diagrams shown in Figures 8 and 9. (ii) On increasing [BrO\(_3^−\)] from 0.030 to 0.050 mol L\(^{-1}\), we
observe a sequence of behaviors, as shown in Figure 11: (a) sequential oscillations; (b) regular oscillations; (c) sequential oscillations again; and (d) sequential oscillations with a large pause and a small number of oscillations after the pause. The behavior observed in Figure 11 is remarkable (mostly Figure 11a−c), which suggests that there are two oscillating regimes separated by a pause: the first with lower frequency and the second with higher frequency. In addition, the first regime goes directly to the second regime without going through a pause (Figure 11b).

**Acetone vs Oxalic Acid Phase Diagram.** The effect of changing the initial concentration of acetone and oxalic acid is shown in Figure 12. As in other phase diagrams, the region for sequential oscillations is between the regions of regular oscillations and regular oscillations preceded by an induction period. At [acetone]₀ = 0.20 mol L⁻¹, decreasing [(COOH)₂]₀ goes through regular oscillations, sequential oscillations, and regular oscillations with an induction period. At [(COOH)₂]₀ as low as 0.021 mol L⁻¹, the system does not oscillate anymore. In addition, low [(COOH)₂]₀ favors longer pauses.

**Acetone vs Ce(IV) Phase Diagram.** The effect of changing the initial concentration of acetone and Ce(IV) is shown in Figure 13. One consequence of changing [Ce⁴⁺]₀ is the change of the amplitude of oscillations (not shown) because the wavelength used to follow the reaction corresponds to the [Ce⁴⁺]₀. As shown in Figure 13, decreasing [Ce⁴⁺]₀ goes through regular oscillations, sequential oscillations, and regular oscillations with an induction period. Decreasing [Ce⁴⁺]₀ also increases the length of the pause or the induction period.

### DISCUSSION

**Induction Period.** Induction periods usually appear due to a growth of the pause period on sequential oscillations (Figures 1 and 2). They start with a short and fast decrease of Ce⁴⁺ absorbance followed by a slow, long, and almost horizontal decrease of this absorbance, until the system starts to oscillate with high amplitude oscillations (subcritical Hopf bifurcation). Ce⁴⁺ has a greater absorbance in sulfuric acid than in water. This might happen due to the formation of complexes with water or OH⁻ ions (eqs 33 and 34), which would absorb at wavelengths different from 318 nm. On the other hand, at high [H₂SO₄]₀, the interaction with other ions such as SO₄²⁻ forms complexes that absorb at 318 nm (eqs 35−38). Complexation of Ce⁴⁺ with SO₄²⁻ and OH⁻ has already been described, and the proposed reactions by these authors are shown below.
The formation of a stable complex between Ce$^{4+}$ and SO$_4^{2-}$ would decrease the availability of Ce$^{4+}$ to oxidize oxalic acid, forming an induction period. This induction period would represent the time needed for intermediates to accumulate and start an autocatalytic process that would start the oscillations. Although the complexation of Ce$^{4+}$ by sulfate has been recognized since the first model for oscillating reactions,$^{21}$ as it is a key step to stabilize this ion and change the potential of the redox pair Ce$^{3+}$/Ce$^{4+}$, until now, no mechanism for oscillating reactions has considered the formation of these complexes.

### Sequential Oscillations

The phase diagrams presented in Figures 2, 3, 8, 9, 12, and 13 show that sequential oscillations occur in a narrow range between regular oscillations and the induction period. Sequential oscillations may appear by increasing [H$_2$SO$_4$]$_0$ or [acetone]$_0$ (Figures 2 and 3). To keep inside the sequential oscillations’ region, if [H$_2$SO$_4$]$_0$ is

\[
[\text{Ce(OH)}_2]^{4+} \rightleftharpoons [\text{Ce(OH)}_2]^{3+} + \text{H}^+ \quad (33)
\]

\[
[\text{Ce(OH)}_2]^{3+} + \text{HSO}_4^- \rightleftharpoons [\text{Ce(OH)}_2]^{2+} + 2 \text{H}_2\text{O} + \text{H}^+ \quad (34)
\]

\[
[\text{Ce(OH)}_2]^{4+} + \text{HSO}_4^- \rightleftharpoons [\text{Ce(OH)}_2]^{2+} + 2 \text{H}_2\text{O} + \text{H}^+ \quad (35)
\]

\[
[\text{Ce(OH)}_2]^{3+} + \text{HSO}_4^- \rightleftharpoons [\text{Ce(OH)}_2]^{3+} + 2 \text{H}_2\text{O} + \text{H}^+ \quad (36)
\]

\[
[\text{Ce(OH)}_2]^{2+} + \text{HSO}_4^- \rightleftharpoons [\text{Ce(OH)}_2]^{2+} + 2 \text{H}_2\text{O} + \text{H}^+ \quad (37)
\]

\[
[\text{Ce(OH)}_2]^{3+} + \text{HSO}_4^- \rightleftharpoons [\text{Ce(OH)}_2]^{3+} + 2 \text{H}_2\text{O} + \text{H}^+ \quad (38)
\]

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from the first group. As [acetone]₀ increases, oscillations near the border between the two groups start to enlarge until they completely merge, giving rise to the pause period that characterizes the sequential oscillations. If [acetone]₀ is increased even higher, the pause period grows in the direction of short times until it becomes an induction period (Figure 1a).

Figure 11a,b shows that increasing [BrO₃⁻]₀ initially, suppresses the pause, which is the opposite effect of increasing [acetone]₀ (compare with Figure 1d,c). However, as shown in Figure 11b,c, a new pause period appears by increasing [BrO₃⁻]₀. Notice that this new pause period occurs at the same time where the previous pause period used to end. Additional increase of [BrO₃⁻]₀ makes the pause period longer and occurs at higher times, and the second group of oscillations presents few oscillations, and the reaction ends in an oxidized state. Such differences in the pattern of oscillations and the pause periods as a consequence of changing the initial concentration of reactants suggest that this system is controlled by more than one intermediate. In other words, another species, besides Br⁻, might be controlling the oscillations. This control can be due to one or more radicals, as a recent mechanism has suggested. If it is the case, the pause period can be a result of the transition between these two controls.

**First Group of Oscillations.** The main role of acetone is to remove Br₂ (eqs 16 and 21−23). To react with bromine, acetone must first become an enol (eq 15). An explanation for the relation between [H₂SO₄]₀ and [acetone]₀ (Figures 2 and 3) is that changes in the concentrations of any of these reactants can affect the rate of enol formation (eq 15). Halogenation of enol is so fast that it is pointless to consider the reverse of eq 15. Consequently, an increase in acid concentration would also increase the enol formation. Moreover, the combination of the enolization reaction with the halogenation reaction results in an autocatalytic process because halogenation generates H⁺ (eq 16), which accelerates the enolization. In addition, SO₄²⁻ could also be acting as a base, accelerating the second step of the enolization, which is the rate-determining step of this reaction (Scheme 1). As a result, Br₂ would be removed even faster from the system if [H₂SO₄]₀ and [acetone]₀ are increased. Therefore, the induction period and the pause period can be related to Br₂ concentration, a known inhibitor of oscillations, or they can be related to a product from the halogenation. As the reaction between Br₂ and enol yields Br⁻ and bromoacetone (eq 16), this production of Br⁻ would help process P3 to supply Br⁻ to make the system switch to process P1.

Ce⁴⁺ absorbance is high during the induction period and the pause, and Br⁻ concentration is low. This would require processes P2 and P3 to be in equilibrium, oxidizing and reducing cerium, keeping [Ce³⁺] and [Ce⁴⁺] almost constant. However, process P1 inhibits P2 by consuming HBF₄⁻. A possible explanation for an equilibrium between P2 and P3 is that process P3 and halogenation of acetone supply Br⁻ in such a way to keep P1 at an almost constant rate. Consequently, [Br⁻] would be kept in a range where P1 and P2 are in equilibrium.

When [acetone]₀ is low, the first group of oscillations tends to stay at a reduced state. There is a noticeable separation in the first group of oscillations if [H₂SO₄]₀ is high or moderate. At high [H₂SO₄]₀ (Figure 6), after the first small group of oscillations, there is a kind of pause, which is indeed a period of irregular and small amplitude oscillations. However, at

### Figure 8. Phase diagram [bromate]₀ vs [H₂SO₄]₀. Regular oscillations (Figure 1d) are indicated in blue; sequential oscillations (Figure 1b,c) are indicated in magenta. The size of magenta dots indicates the length of the pause. Regular oscillations preceded by an induction period (Figure 1a) are indicated in brown. The size of the brown dots indicates the length of the induction period. Other constraints: [acetone]₀ = 0.20; [(COOH)₂]₀ = 0.050; [Ce(IV)]₀ = 0.0010 mol L⁻¹.

### Figure 9. Phase diagram [bromate]₀ vs [acetone]₀. Regular oscillations are indicated in blue (Figure 1d); sequential oscillations (Figure 1b,c) are indicated in magenta. The size of magenta dots indicates the length of the induction period. Other constraints: [(COOH)₂]₀ = 0.050; [Ce(IV)]₀ = 0.0010; [H₂SO₄]₀ = 1.50 mol L⁻¹.
$[\text{H}_2\text{SO}_4]_0 = 1.53 \text{ mol L}^{-1}$ (Figure 4), the first small group of regular oscillations completely disappears, but the period of irregular oscillations is kept with oscillations with even lower amplitudes.

At high $[\text{H}_2\text{SO}_4]_0$, the period of irregular and small amplitude oscillations between the two groups of regular oscillations (Figure 6) can be caused by an inhibition of process P2 by P1. The fact that the system stays mostly in the reduced state implies that this period has high $\text{Br}^-$.
concentration. This favors reaction 2 and inhibits P2, which is responsible for Ce³⁺ oxidation. Because P1 is a fast process, after almost complete consumption of Br⁻, P2 can be ignited again. However, due to a fast renewal of Br⁻ through P3 and other reactions, P1 would be promptly activated and the amplitude of oscillations would be small and, eventually, irregular, as it was observed.

The short initial period of oscillations at high [H₂SO₄]₀ (Figure 6) may happen due to eq 1, which is favored by H⁺. As a result, P1 would also be accelerated and Br⁻ readily consumed. Then, eq 1 would be able to produce HBrO₂ faster and favor P2, which does not happen during the period of irregular oscillations.

At moderate [H₂SO₄]₀, HBrO₂ production would be slower. As such, it would probably not be able to suppress Br⁻ production and P2 would stay inhibited, resulting in a longer period at a reduced state without oscillations (Figure 4). Irregular oscillations may occur due to the accumulation of an intermediate followed by a sequence of fast reactions involving radical species, which may favor P2.

Second Group of Oscillations. Regardless of [H₂SO₄]₀, a decrease of oscillations’ frequency was observed as [acetone]₀ was reduced (see, e.g., Figure 6). In addition, when compared with Figure 1, the amplitude was also increased. With this reduction of oscillations’ frequencies, the system is kept longer in a reduced state, implying that P2 is being inhibited for longer. According to the FB mechanism, P2 is inhibited by P1, and P1 needs Br⁻ to operate, which can be produced by reactions 21–23. In addition, Br⁻ can be formed from Br₂ by the reverse of eq 3. Because of this, this mechanism can be considered an oscillator controlled by Br₂. Accumulation of Br₂ can dislocate the equilibrium of eq 3 to the left side. Such change would reduce Br⁻ consumption by P1, and this process would be able to prevail for longer, increasing the interval between oscillations.

As [H₂SO₄]₀ is reduced, the second group of oscillations tends to disappear (not shown). This behavior may be due to a variety of factors. An explanation is that processes P1 and P2 and also acetone enolization are dependent on H₂SO₄ concentration. Process P1 is probably the most directly affected because it requires four H⁺. However, P1 is also responsible for HBrO₂, which is the species that is controlled by Br⁻ to determine the prevalent process. Because many factors are involved, it is hard to explain the sequential oscillations considering a specific reaction or process based only on H₂SO₄ concentration. The reaction begins oscillating, and as it proceeds, the concentration of intermediates increases and starts to interfere with the equilibriums, possibly involving reactions 4 and 8. The lower the [H₂SO₄]₀ is, the more sensible to these intermediates the system would be, and because of that, oscillations would end earlier. However, decreasing [BrO₃⁻]₀ also shows a similar behavior (Figure 10). The reactions that directly rely on BrO₃⁻ and H₂SO₄ concentrations are 1, 4, and 20. Reaction 1 needs two H⁺ to produce HBrO₂, which is consumed by 4. Reactions 4 and 20 generate BrO₂⁺, responsible for Ce³⁺ oxidation. Then, the second group of oscillations could disappear if the concentrations of HBrO₂, Br⁺, and BrO₂⁺ do not favor P2 and slow down P1. Therefore, the system would slowly exit the oxidized state after the last oscillation. In both cases shown in Figure 10,
no induction period was observed. In this case, the reduction of \([\text{BrO}_3^-]_0\) stretched the pause and dislocated it to higher times. When the second group of oscillations is not present (Figure 10b; \([\text{BrO}_3^-]_0 = 0.010 \text{ mol L}^{-1}\)), the first group of oscillations ends at the same time of the pause period in Figure 10a (\([\text{BrO}_3^-]_0 = 0.0175 \text{ mol L}^{-1}\)).

Some authors believe that sequential oscillations may happen due to a change in the reducing agent. It can be added as a starting reactant\(^5\),\(^38\) or formed by the oxidation of the initial reducing agent.\(^8\),\(^11\),\(^39\) These explanations, however, hardly apply to the system studied in this work. First is because acetone does not reduce \(\text{Ce}^{4+}\) in the time scale of the oscillations.\(^{40}\) Second, according to a recent mechanism,\(^{26}\) the only species generated by oxalic acid, which is able to reduce \(\text{Ce}^{3+}\) is the radical \(\text{COOH}\) through the reaction \(\text{COOH} + \text{Ce}^{4+} \rightarrow \text{CO}_2 + \text{Ce}^{3+} + \text{H}^+\). Because \(\text{COOH}\) is an unstable species, it would not be able to accumulate enough to be responsible for the second group of oscillations. Instead of a change in the mechanism of reduction, the system might be going through a change in the oxidation mechanism. The mechanism proposed by Pelle et al.\(^{26}\) considers a series of reactions between \(\text{Ce}^{3+}\) and radicals from bromine. Some of the reactions are as follows

\[
\text{Br}^* + \text{Br}^- \rightarrow \text{Br}_2^*\quad \text{(40)}
\]

\[
\text{Br}_2^* + \text{Ce}^{3+} \rightarrow 2 \text{Br}^- + \text{Ce}^{4+}\quad \text{(41)}
\]

These reactions may be an alternative to P2 on \(\text{Ce}^{3+}\) oxidation, even at high Br\(^-\), since they rely on Br\(^*\) instead of HBrO\(_2\). They could be the reason why the system oscillates when Br\(_2\) is accumulated. However, these reactions do not explain the low-frequency oscillations at lower \([\text{H}_2\text{SO}_4]_0\) which removes Br\(_2\). If Br\(^*\) is the limiting reactant of reaction 40 and Br\(^-\) is in excess, this reaction would not make an autocatalytic process with reaction 41, and they may explain the second group of oscillations in Figure 11c,d. Oscillations from the second group in these figures have a curvature typical of an autocatalytic process on the left side. Such reactions would happen until almost all \(\text{Ce}^{3+}\) is consumed. At high \(\text{Ce}^{4+}\), an autocatalytic process faster than eqs 40 and 41 would take place. This process would renew \(\text{Br}^*\) and \(\text{Ce}^{3+}\) through reactions with oxalic acid, acetone, and derivatives. Then, \(\text{Br}^*\) or \(\text{Ce}^{3+}\) would have concentration ranges where they can induce oscillations. As the behaviors from Figure 11c,d are observed at high \([\text{BrO}_3^-]_0\), it is possible that the second group of oscillations is indeed due to the formation of a \(\text{BrO}_3^-\) derivative. Moreover, Figure 11c,d also shows a pause period that grows from lower to higher times as \([\text{BrO}_3^-]_0\) is increased. At medium \([\text{BrO}_3^-]_0\) the pause disappears. However, at high \([\text{BrO}_3^-]_0\) a new pause period appears at the frontier of the two groups of oscillations. This new pause period is different. It takes place at times where oscillations from the second group were observed. Reactions 40 and 41 might be responsible for this curious behavior. These reactions could happen due to an accumulation of \(\text{Br}_2^*\), and together with P2, they would compensate the reduction of \(\text{Ce}^{4+}\) by oxalic acid. Then, the system would be able to oscillate again because of \(\text{Br}^-\) accumulation. \(\text{Br}^-\) can inhibit P2, and oxalic acid would reduce a significant amount of \(\text{Ce}^{4+}\). As \(\text{Ce}^{3+}\) is increased, reaction 41 would be favored again, and the process is to be repeated until oxalic acid concentration is low enough to not be able to compete with eq 41.

**Phase Diagrams.** Figure 2 shows that \([\text{H}_2\text{SO}_4]_0\) and \([\text{acetone}]_0\) do not have a linear relationship with reaction behavior because the graphic is slightly curved. Also, the interval between the first and second sets of oscillations increases as \([\text{acetone}]_0\) decreases. This diagram can be linearized, as shown in Figure 3. At concentrations beyond the ones shown in Figure 2, the system has irregular behaviors. Figure 3 shows two lines with almost the same slope and a good correlation coefficient \((R^2 \approx 0.990)\), which is high considering the irregularities on the frontiers in Figure 1. Therefore, Figure 3 implies that sequential oscillations may appear if a mathematical relation between \([\text{H}_2\text{SO}_4]_0\) and \([\ln(\text{acetone})]_0\) is kept.

The diagram in Figure 8 has a different behavior from that in Figure 2 as the same behavior is observed if both reactants are

![Image](148x547 to 459x740)

**Figure 14.** Topological diagram of sequential oscillations. The axes \(\mu\) and \(\nu\) represent two nonidentified parameters, which can be reactants that are consumed during the reaction, in batch, or can be any other parameters. The system does not oscillate in the white region and oscillates inside the gray region. The frontiers between these two behaviors are Hopf bifurcations. The solid line represents subcritical bifurcations, and the dashed line represents supercritical bifurcations. The colored arrows indicate the direction of the time. The red line represents the path for oscillations preceded by an induction period. The green line is the path for sequential oscillations. The blue line is the path for regular oscillations without an induction period. The insets exemplify the behaviors observed when following each path as shown in Figure 1.
increased. In addition, for concentrations in the frontiers between two kinds of behavior, the system is very sensible to the stirring, especially in the ranges $1.70 \text{ mol L}^{-1} < [\text{H}_2\text{SO}_4]_0 < 1.75 \text{ mol L}^{-1}$ and $0.0325 \text{ mol L}^{-1} < [\text{BrO}_3^-]_0 < 0.0375 \text{ mol L}^{-1}$. The relation between $[\text{acetone}]_0$ and $[\text{BrO}_3^-]_0$ which is shown in Figure 9, is similar to that observed in Figure 8.

Even though Figures 12 and 13 have fewer data than the former diagrams, they show that decreasing $[(\text{COOH})_2]_0$ or $[\text{Ce}^{4+}]_0$ goes through regular oscillations, sequential oscillations, and later to regular oscillations after an induction period.

Hopf Bifurcation. Oscillations can start when a system crosses a critical point called a Hopf bifurcation, which can be supercritical, with a gradual change between stable and unstable states, or subcritical, showing an abrupt transition between them. In the present study, because it was made in batch, we cannot say that the system crosses a true Hopf bifurcation, as there is no well-defined steady state and the system does not follow a closed limit cycle and only damped oscillations are observed. In this case, we must consider that the system crosses a pseudo-Hopf bifurcation. Despite this, we will use the terms supercritical and subcritical Hopf bifurcations to indicate a gradual or abrupt transition between nonoscillatory and oscillatory states, respectively. In addition, there are other kinds of bifurcations (saddle-node bifurcation, infinite-period bifurcation, saddle-loop bifurcation), called global bifurcations, that explain the emergence of a limit cycle (oscillations), but which are also difficult to characterize in batch. In this way, we choose to use in the following the terms supercritical and subcritical Hopf bifurcations, even if they are not the most accurate terms.

Our results show that a pause period is always preceded by a subcritical bifurcation, and, in general, it is also followed by another subcritical bifurcation. Figure 1b shows a pause period between two subcritical bifurcations, and Figure 5 shows a pause period followed by a supercritical bifurcation. Every induction period observed was followed by a subcritical bifurcation. In most of the experiments, oscillations ceased with a supercritical bifurcation with the system in a reduced state (low absorbance at 318 nm, low $[\text{Ce}^{4+}]$). One exception is shown in Figure 11d, which ends in an oxidized state (high absorbance at 318 nm, high $[\text{Ce}^{4+}]$).

Figure 14 is an attempt to elaborate a topological description for sequential oscillations. This figure relates two nonidentified parameters ($\mu$ and $\nu$), which can be the reactants’ concentrations that are consumed during the reaction in batch. These parameters can also be any combination of reactants’ and intermediates’ concentrations. In this figure, there are two regions: in the white region, the system does not oscillate, and in the gray region, the system oscillates. These regions are separated by frontiers, which can be subcritical or supercritical Hopf bifurcations. The colored arrows indicate the time direction for different behaviors. The time in which the system stays in a state, which is oscillatory or nonoscillating, is proportional to the distance it goes through inside the white or gray areas.

An induction period (Figure 14, red line) happens when the system starts in the white area (nonoscillating region) and, as the time goes, starts to oscillate when it crosses the solid line (subcritical Hopf bifurcation). It continues oscillating while it is in the gray area, and the oscillations gradually lose amplitude until the system crosses the dashed line (supercritical Hopf bifurcation) and enters the nonoscillatory region again.

Sequential oscillations, without an induction period (Figure 14, green line), are observed when the system starts in the gray area. It oscillates until crossing a subcritical bifurcation, entering the white area and stopping to oscillate. After some time, the system starts to oscillate again, when it enters the gray area, after crossing another subcritical bifurcation. This second group of oscillations would gradually lose amplitude until the system crosses a supercritical bifurcation and completely stops oscillating. Finally, the blue path shows a system that starts to oscillate without an induction period and shows regular oscillations while it is inside the gray region. After some time, the amplitude of oscillations gradually decreases until a supercritical bifurcation is crossed and the system does not oscillate anymore.

### CONCLUSIONS

This study scrutinized the concentration range of all reactants of the system bromate–oxalic acid–acetone–Ce(IV), which produces sequential oscillations and other behaviors. The results are presented in five phase diagrams, which show that keeping some kind of relation between the concentrations is more important than the concentration itself. In addition, the range of reactants’ concentrations that produce sequential oscillations is always between the concentrations that produce regular oscillations without an induction period and regular oscillations preceded by an induction period.

Some new behaviors for this system were observed, which include a short induction period at high $[\text{H}_2\text{SO}_4]_0$, a low-amplitude group of irregular oscillations, and an induction period at a reduced state.

Based on current mechanisms, the experimental data implies that one additional control should be operating in this system, besides the accepted Br$^-$ control, to explain the variety of behaviors observed. The full set of experimental results presented in this work is a good challenge for any mechanism to be proposed for this system, which intends to be an improvement to the Field and Boyd mechanism.

### AUTHOR INFORMATION

Corresponding Author

*E-mail: faria@iq.ufrj.br.

ORCID ©

Michael S. Chern: 0000-0003-3701-1080

Roberto B. Faria: 0000-0001-9337-4324

Present Address

1Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan (E-mail: mscar@cheng.es.osaka-u.ac.jp) (M.S.C.).

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