Electronic Supplementary Information

Time-periodic Oscillation Reaction in an Organic-Solvent Dominated Electrolyte

Yu Chang\textsuperscript{a,\#}, Nannan Zhang\textsuperscript{b,\#}, Yuxin Yang\textsuperscript{a}, Jun Du\textsuperscript{b}, Xing Fan\textsuperscript{a,*}, and Changyuan Tao\textsuperscript{b,*}

\textsuperscript{a}. College of Chemistry and Chemical Engineering, Chongqing University, Chongqing, 400044, P.R China, E-mail: foxcqdxcq@cqu.edu.cn

\textsuperscript{b}. Key Laboratory of Chemical Process for Clean Energy and Resource Utilization of Chongqing, Chongqing University, Chongqing 400044, P. R. China., E-mail: taocy@cqu.edu.cn

\# These authors have contributed equally.

Contents

\textbf{Note S1.} The reaction scheme according to FKN model.

\textbf{Note S2.} Electrode potential calculation based on Nernst equation.

\textbf{Note S3.} Detailed mathematical analysis on the mechanism

\textbf{Figure S1.} Periodic color change during the oscillation reaction in Ce(IV) catalyzed B-Z organic solution and corresponding potential oscillation scheme.

\textbf{Figure S2.} Potential oscillation scheme with different types of ionic liquids as oxidants.

\textbf{Figure S3.} Ce-catalyzed oscillation reaction with 1-ethylpyridinium iodate as the oxidant.
Note S1. The reaction scheme according to FKN model

For the following equations, either Ce(IV), or Ru(II) can be employed as the catalyst.

Process A (consumption of bromide ion)

\[ \text{Br}^- + \text{HBrO} + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (S1)

\[ \text{Br}^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2\text{HOBr} \]  \hspace{1cm} (S2)

\[ \text{Br}^- + \text{BrO}_3^- + 2\text{H}^+ \rightarrow \text{HOBr} + \text{HBrO}_2 \]  \hspace{1cm} (S3)

Process B (oxidation of catalyst(R), autocatalytic reaction)

\[ 2\text{HBrO}_2 \rightarrow \text{HOBr} + \text{BrO}_3^- + \text{H}^+ \]  \hspace{1cm} (S4)

\[ \text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \rightleftharpoons 2\text{BrO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (S5)

\[ \text{BrO}_2 + \text{catalyst (R)} + \text{H}^+ \rightleftharpoons \text{HBrO}_2 + \text{catalyst (O)} \]  \hspace{1cm} (S6)

Process C (reduction of catalyst(O), production of bromo malonic acid)

\[ \text{BrO}_2 + \text{Catalyst(O)} + \text{H}_2\text{O} \rightarrow \text{BrO}_3^- + \text{Catalyst(R)} + 2\text{H}^+ \]  \hspace{1cm} (S7)

\[ \text{Br}_2 + \text{CH}_2(\text{COOH})_2 \rightarrow \text{BrCH(CHOH)OH}_2 + \text{Br}^- + \text{H}^+ \]  \hspace{1cm} (S8)

\[ 6 \text{Catalyst(O)} + \text{CH}_2(\text{COOH})_2 + 2\text{H}_2\text{O} \rightarrow 6 \text{Catalyst(R)} + \text{HCOOH} + 2\text{CO}_2 + 6\text{H}^+ \]  \hspace{1cm} (S9)

\[ 4 \text{Catalyst(O)} + \text{BrCH(CHOH)OH}_2 + 2\text{H}_2\text{O} \rightarrow 4 \text{Catalyst (R)} + \text{HCOOH} + \text{Br}^- + 2\text{CO}_2 + 5\text{H}^+ \]  \hspace{1cm} (S10)

Reference

Note S2. Electrode potential calculation based on Nernst equation

\[ \varphi = \varphi^\theta + \frac{RT}{nF} \ln\left(\frac{[\text{Cat.}(O)]}{[\text{Cat.}(R)]}\right) \]

In which \( \varphi \) represents the electrode potential, \( \varphi^\theta \) represents the standard electrode potential at 298K, R represents the gas constant(8.31441J/(mol*K)), T represents the temperature, \( n \) represent the number of electron transferred in each electrode reaction step, F represent Faraday constant(96.487J/(V*mol)), \([\text{cat.}(R)]\), \([\text{cat.}(O)]\) represent the concentration of reductive and oxidative catalyst, respectively.

Reference
Note S3. Detailed mathematical analysis on the mechanism

The overall B–Z oscillation can be divided into three possible sub-processes: consumption of the bromide ion (sub-process A, Eqs. 1–3), autocatalytic redox reaction of bromous acid with the oxidation of the transition metal catalyst (sub-process B, Eqs. 4–6), and production of bromomalonic acid and the proton, accompanied by the re-reduction of the catalyst (sub-process C, Eqs. 7–10).

Which are included as follows.

Process A (consumption of bromide ion)

\[
\text{Br}^- + \text{HOBr} + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O} \quad \text{(R1)}
\]

\[
\text{Br}^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2\text{HOBr} \quad \text{(R2)}
\]

\[
\text{Br}^- + \text{BrO}_3^- + 2\text{H}^+ \rightarrow \text{HOBr} + \text{HBrO}_2 \quad \text{(R3)}
\]

Process B (oxidation of Catalyst(R), autocatalytic reaction)

\[
2\text{HBrO}_2 \rightarrow \text{HOBr} + \text{BrO}_3^- + \text{H}^+ \quad \text{(R4)}
\]

\[
\text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \rightleftharpoons 2\text{BrO}_2^- + \text{H}_2\text{O} \quad \text{(R5)}
\]

\[
\text{BrO}_2^- + \text{Catalyst(R)} + \text{H}^+ \rightleftharpoons \text{HBrO}_2 + \text{Catalyst(O)} \quad \text{(R6)}
\]

Process C (reduction of Catalyst(O), production of bromo malonic acid)

\[
\text{BrO}_2^- + \text{Catalyst(O)} + \text{H}_2\text{O} \rightarrow \text{BrO}_3^- + \text{Catalyst(R)} + 2\text{H}^+ \quad \text{(R7)}
\]

\[
\text{Br}_2 + \text{CH}_2(\text{COOH})_2 \rightarrow \text{BrCH(\text{COOH})}_2 + \text{Br}^- + \text{H}^+ \quad \text{(R8)}
\]

\[
6 \text{Catalyst(O)} + \text{CH}_2(\text{COOH})_2 + 2\text{H}_2\text{O} \rightarrow
\quad 6 \text{Catalyst(R)} + \text{HCOOH} + 2\text{CO}_2 + 6\text{H}^+ \quad \text{(R9)}
\]

\[
4 \text{Catalyst(O)} + \text{BrCH(\text{COOH})}_2 + 2\text{H}_2\text{O} \rightarrow
\quad 4 \text{Catalyst(R)} + \text{HCOOH} + \text{Br}^- + 2\text{CO}_2 + 5\text{H}^+ \quad \text{(R10)}
\]

Each step of the ten processes above is elementary or at least has clearly defined kinetics, with kinetics parameters as follows:\[1\]:

\[
\text{HOBr} + \text{Br}^- + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O} \quad \text{(R1)}
\]

\[
k_{1}^* = 8.0 \times 10^9 \text{M}^2 \text{sec}^{-1}
\]

\[
k_{1}^0 = 110 \text{sec}^{-1}
\]

\[
\text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightarrow 2\text{HOBr} \quad \text{(R2)}
\]

\[
k_{2}^* = 2.0 \times 10^9 \text{M}^2 \text{sec}^{-1}
\]

\[
k_{2}^0 = 5.0 \times 10^{-5} \text{M}^4 \text{sec}^{-1}
\]

\[
\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightarrow \text{HBrO}_2 + \text{HOBr} \quad \text{(R3)}
\]

\[
k_{3}^* = 2.1 \text{M}^{-3} \text{sec}^{-1}
\]
\[ k^0_{3} = 1.0 \times 10^{4} \text{ M}^2 \text{ sec}^{-1} \]

\[ 2\text{HBrO}_2 \rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+ \quad \text{(R4)} \]

\[ k^0_{4} = 4.0 \times 10^{7} \text{ M}^{-1} \text{ sec}^{-1} \]

\[ k'_{-4} = 2.0 \times 10^{10} \text{ M}^{-2} \text{ sec}^{-1} \]

\[ \text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightleftharpoons 2\text{BrO}_2^- + \text{H}_2\text{O} \quad \text{(R5)} \]

\[ k'_{3} = 1.0 \times 10^{4} \text{ M}^2 \text{ sec}^{-1} \]

\[ k^0_{5} = 2 \times 10^{7} \text{ M}^{-1} \text{ sec}^{-1} \]

\[ \text{BrO}_2^- + \text{Ce}^{3+} + \text{H}^+ \rightleftharpoons \text{HBrO}_2 + \text{Ce}^{4+} \quad \text{(R6)} \]

\[ k_{5}/k_{6} = K_{6} = 0.025 \text{ M}^{-1} \]

\[ \text{Br}_2 + \text{CH}_2(\text{COOH})_2 \rightarrow \text{BrCH( COOH)}_2 + \text{Br}^- + \text{H}^+ \quad \text{(R8)} \]

\[ k^0_{8} = 1.3 \times 10^{1} \text{ M}^{-1} \text{ sec}^{-1} \]

\[ 6\text{Ce}^{4+} + \text{CH}_2(\text{COOH})_2 + \text{H}_2\text{O} \rightarrow 6\text{Ce}^{3+} + \text{HCOOH} + 2\text{CO}_2 + 6\text{H}^+ \quad \text{(R9)} \]

An empirical rate equation for reaction 9 is

\[ v_9 = -\frac{d[MA]}{dt} = \frac{k_9'[\text{Ce}^{4+}][MA]}{K_9'' + [MA]} \]

The empirical constant \( K''_9 = 0.53 \text{ M} \)

\[ 4\text{Ce}^{4+} + \text{BrCH( COOH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{Br}^- + 4\text{Ce}^{3+} + \text{HCOOH} + 2\text{CO}_2 + 5\text{H}^+ \quad \text{(R10)} \]

An empirical rate equation for reaction 10 is:

\[ v_{10} = -\frac{d[BrMA]}{dt} = \frac{k_{10}'[\text{Ce}^{4+}][BrMA]}{K_{10}'' + [BrMA]} \]

The empirical constant \( K''_{10} = 0.2 \text{ M} \)

Where superscript zero (\(^0\)) designates a value extrapolated to infinite dilution with standard states of ideal 1 m solution or a value involving only neutral species so that activity coefficient effects are presumably minimal. A prime (\(^'\)) designates a rate constant for an ionic reaction measured directly in strongly acid medium. An asterisk (\(\ast\)) designates a value expected in acid medium and calculated from data for ideal standard states by assuming that neutral species have activity coefficients of unity and that singly charged ions have activity coefficients of 0.7.

Different from traditional FKN mechanism for aqueous system, the concentration of water in organic-solvent dominated system could not be simplified as a constant. Thus, certain reaction kinetic parameters in organic-solvent dominated system should be regarded as variations of \( k_i[H_2O] \).
BrO$_3^-$ + HBrO$_2$ + H$^+$ ⇌ 2BrO$_2^-$ + H$_2$O  \hspace{1cm} (R5)

$k_5 = k'_5 [H_2O]$

BrO$_2^-$ + Ce$^{4+}$ + H$_2$O → BrO$_3^-$ + Ce$^{3+}$ + 2H$^+$  \hspace{1cm} (R7)

$k_7 = k'_7 [H_2O]$

6Ce$^{4+}$ + CH$_2$(COOH)$_2$ + H$_2$O → 6Ce$^{4+}$ + HCOOH + 2CO$_2$ + 6H$^+$  \hspace{1cm} (R9)

A new empirical rate equation for reaction 9 could be supposed as:

$$v_9 = -\frac{d[MA]}{dt} = \frac{k_9 [Ce^{4+}] [MA][H2O]}{K'' + [MA]}$$

$k_{9} = k'_{9} [H_2O]$

4Ce$^{4+}$ + BrCH(COOH)$_2$ + 2 H$_2$O → Br$^-$ + 4Ce$^{3+}$ + HCOOH + 2CO$_2$ + 5H$^+$  \hspace{1cm} (R10)

A new empirical rate equation for reaction 10 could be supposed as:

$$v_{10} = -\frac{d[BrMA]}{dt} = \frac{k'_{10} [Ce^{4+}] [BrMA][H2O]}{K'' + [BrMA]}$$

$k_{10} = k'_{10} [H_2O]$

Besides, the value of other reaction kinetic parameters in organic-solvent dominated system ($k_{org}$) should be also different from that in water. For example, from the mechanism point of view, the activity of proton would be higher at the same concentration in the organic solvent, because a weaker interaction between the protons and organic solvent molecules would give protons more freedom to react with other reactants \cite{2}. Therefore, almost all the reaction kinetic parameters would be affected, resulting from the promotion of the reactive activity of H$^+$ in organic-solvent dominated system.

The above reaction scheme could be simplified using the Oregonator model \cite{3}. The Oregonator dynamics is an activator/inhibitor system containing both an autocatalytic step and a delayed negative feedback loop. It is composed of five coupled stoichiometries shown below.

\begin{align*}
A+Y &\rightarrow X+P \hspace{1cm} \text{Rate} = k_{M1}AY \hspace{1cm} (a) \\
X+Y &\rightarrow P \hspace{1cm} \text{Rate} = k_{M2}XY \hspace{1cm} (b) \\
B+X &\rightarrow 2X+Z \hspace{1cm} \text{Rate} = k_{M3}BX \hspace{1cm} (c) \\
X+X &\rightarrow Q \hspace{1cm} \text{Rate} = k_{M4}X^2 \hspace{1cm} (d) \\
Z &\rightarrow fY \hspace{1cm} \text{Rate} = f_{M5}Z \hspace{1cm} (e)
\end{align*}

Where, \(X = \text{HBrO}_2, Y = \text{Br}^-, Z = \text{Ce}(IV), A = \text{B} = \text{BrO}_3^-, P \) and \(Q \) represent reaction products like HOB or BrCH(COOH)$_2$. The reactant and product species BrO$_3^-$, MA, BrCH(COOH)$_2$ and HBrO are normally present in much higher concentrations than the
dynamic intermediate species X, Y and Z, and are assumed to be constant on the time scale of a few oscillations.

The Oregonator Mass-Action dynamics in a well-stirred, homogeneous system could be given by following equations.

\[
\frac{dX}{dt} = k_{M1}AY - k_{M2}XY + k_{M3}AX - 2k_{M4}X^2 \quad S1
\]

\[
\frac{dY}{dt} = -k_{M1}AY - k_{M2}XY + k_{M5}fBZ \quad S2
\]

\[
\frac{dZ}{dt} = k_{M4}AX - k_{M5}BZ \quad S3
\]

Its frequency and critical point of the bifurcation could be analyzed using the mathematical linear instability analysis \[4\]. However, their explicit expressions are usually very complicated. In order to understand the solvent effect on the oscillation, some simplification could be made at a place not far from the bifurcation during the initial period of the oscillation.

HBrO$_2$ is an important intermediate reactant in the process, and involved in autocatalytic process. The redox potential of the system should also increase with its concentration, as described by the Nernst equation.

In the aqueous system, its concentration ([HBrO$_2$]) at a state not far from the steady-state approximation could be calculated as follows \[1\].

\[
\frac{d[HBrO_2]}{dt} = -\alpha[HBrO_2]^2 - \beta[HBrO_2] + \gamma \quad S4
\]

Where,

\[
\alpha = 2k_4 \quad S5
\]

\[
\beta = k_2[Br^-][H^+] - k_5[BrO_3^-][H^+] + (2k_5[BrO_3^-][H^+] + k_{d5}[Ce^{4+}])k_7[Ce^{4+}] \quad / (k_{d5}[Ce^{3+}][H^+] + k_{d7}[Ce^{4+}]) \quad S6
\]

\[
\gamma = k_3[BrO_3^-][Br^-][H^+]^2 \quad S7
\]

\(\beta\) and \(\gamma\) should be considered as variations with time, because \([Br^-], [Ce^{3+}]\) and \([Ce^{4+}]\) would all vary with time at the same frequency as \([HBrO_2]\).

In the organic-solvent dominated system, the effects of H$^+$ and H$_2$O should be taken into consideration. Therefore, the kinetic equation S4 should be revised with a new set of \(\alpha, \beta\) and \(\gamma\).

\[
\alpha = 2k_4 \quad S8
\]

\[
\beta = k_2[Br^-][H^+] - k_5[BrO_3^-][H^+] + (2k_5[BrO_3^-][H^+] + k_{d5}[Ce^{4+}])k_7[Ce^{4+}][H_2O] \quad / (k_{d5}[Ce^{3+}][H^+] + k_{d7}[Ce^{4+}][H_2O]) \quad S9
\]

\[
\gamma = \delta^2k_3[BrO_3^-][Br^-][H^+]^2 \quad S10
\]

where, \(\delta\) indicates the solvent effects on the activity of H$^+$.

Then, the frequency and amplitude of the concentration oscillation could be
subsequently estimated based on above equations.

For the oscillation frequency,

Letting \([\text{HBrO}_2]=X=X_0+x\), \([\text{Br}^-]=Y=Y_0+y\) and \([\text{Ce}^{4+}]=Z=Z_0+z\), where \(X_0, Y_0\) and \(Z_0\) represents the steady concentration; \(x, y\) and \(z\) represents small perturbation around the steady state at a place not far from the bifurcation point. Thus, \(x, y\) and \(z\) can be simplified as \(\theta_x e^{i\omega t}\), \(\theta_y e^{i\omega t}\) and \(\theta_z e^{i\omega t}\). And, the linear perturbation equation around \(X_0\) could be derived from equation S4 as follows.

\[
\frac{dx}{dt} = -(2\alpha X_0 + \beta_0)x \quad S12
\]

Thus, \(|\omega| = |2\alpha X_0 + \beta_0|\), and period \(T=\frac{2\pi}{|\omega|}\)

According to previous researches by R. J. Field, E. Koros, and R. M. Noyes \([xxx]\), \(\beta^2 \gg 4\alpha\gamma\) is a good approximation for most of the anticipated finite values of \(\beta\). Besides, it is more rational to assume \(\beta < 0\), as for \([\text{Br}^-]\) in organic solvent-dominated system should be very small. By assuming that \(\frac{d[\text{HBrO}_2]}{dt}=0\), it could be solve out approximatively from equation S4 that,

\[
[\text{HBrO}_2]_0 = -\frac{\beta_0}{\alpha}. \quad S13
\]

Therefore,

\[
T^2 = \frac{4\pi^2}{\beta^2} \quad S14
\]

For the oscillation amplitude,

It is complicated to give a precise and explicit expression for the oscillation amplitude. Nevertheless, it could be approximately estimated from the concentration difference between the peak point and the valley point, according to the Nernst equation. The larger the concentration difference is, the larger the oscillation amplitude is. At both points, the slope of oscillation curve is zero.

\[
\frac{d[\text{HBrO}_2]}{dt} = 0 \quad S15
\]

The corresponding concentrations could be calculated as follows:

\[
[\text{HBrO}_2] = (\frac{\beta}{2\alpha}) \left(-1 \pm (1+4\alpha\gamma/\beta^2)^{0.5}\right) \quad S16
\]

\[
= \frac{\gamma}{\beta} \quad (\beta > 0)
\]

\[
= -\frac{\beta}{\alpha} \quad (\beta < 0)
\]

At the peak of the potential, the rate of reaction R6 should be very small. It could be assumed that, \(k_\delta [\text{Ce}^{3+}] [\text{H}^+] \ll k_\gamma [\text{Ce}^{4+}] [\text{H}_2\text{O}].\) Thus,
\[ k_7[Ce^{4+}][H_2O](k_6[Ce^{3+}]\delta[H^+]+k_9[Ce^{4+}][H_2O]) = 1. \] And,
\[ \beta_{\text{peak}} = k_2[Br^-]\delta[H^+]+k_5[BrO_3^-]\delta[H^+]k_6[Ce^{4+}]_{\text{peak}} > 0 \quad \text{S17} \]
\[ ([HBrO_3]/[Br^-])_{\text{peak}} = \delta k_9[BrO_3^-][H^+]^2/\beta_{\text{peak}} \quad \text{S18} \]

At the valley of the potential, the rate of reaction R7 should be very small. It could be assumed that, \( k_6[Ce^{3+}]\delta[H^+] \gg k_7[Ce^{4+}][H_2O] \). Thus,
\[ \delta k_7[Ce^{4+}][H_2O]/(k_6[Ce^{3+}]\delta[H^+]+k_7[Ce^{4+}][H_2O]) << 1. \]
\[ \beta_{\text{valley}} = k_2[Br^-]\delta[H^+]-k_5[BrO_3^-]\delta[H^+] < 0 \quad \text{S19} \]
\[ ([HBrO_3]/[Br^-])_{\text{valley}} = -\beta_{\text{valley}}/2k_4[Br^-]_{\text{valley}} \quad \text{S20} \]

Therefore, the oscillation amplitude (Amp) could be calculated via Nernst equation.
\[ Amp= -(RT/zF)\ln\left(\frac{[HBrO_2]_{\text{peak}}[Br^-]_{\text{valley}}/[HBrO_2]_{\text{valley}}[Br^-]_{\text{peak}}}{k_6[Ce^{4+}]_{\text{peak}}/\delta[H^+]}/2k_3[BrO_3^-][Br^-]\right) \quad \text{S21} \]

1) The influence of trace amount of water

It could be derived from S14 that, \( dT/d[H_2O] = (2\pi/\beta_0^2) d\beta/d[H_2O] \). Furthermore, it could also be derived from S9 that, \( d(\beta_0)/d[H_2O] > 0 \), and \( \beta_0 < 0 \). Thus, \( dT/d[H_2O] > 0 \). As the [H_2O] increases, oscillation frequency decreases, oscillation period increases, which matches well with the Fig.3b.

Besides, it could be judge from equation S17 and S18 that, the value of \( \beta \) would not related to [H_2O] in a certain range of [H_2O]. As is also indicated in Fig.3b, the oscillation amplitude would not vary with [H_2O] in a certain range of concentration. When [H_2O] continues to increase, The term of \( k_7[Ce^{4+}][H_2O]/(k_6[Ce^{3+}]\delta[H^+]+k_9[Ce^{4+}][H_2O]) \) could not be ignored as 0, and it will increases with [H_2O]. Therefore,
the absolute value of $\beta_{\text{valley}}$ will decrease with $[H_2O]$, resulting the decrease of oscillation amplitude.

2) The influence of $[H^+]$

It could be derived from $S14$ that, $dT/d[H^+]=\left(2\pi/\beta_0^2\right)d\beta/d[H^+]|_0$. Furthermore, it could also be derived from $S9$ that, when $\delta[H^+]$ is small enough, $d(\beta_0)/d[H^+]<0$ and $\beta_0<0$, therefore, $dT/d[H^+]<0$. As is indicated in Fig.3a, the oscillation period decreases with $[H^+]$ in a certain range of pH value. Furthermore, when $\delta[H^+]$ is large enough, $\beta$ could be simplified as $(k_2[Br^-]k_5[BrO_3^-]\delta[H^+]+2k_5[BrO_3^-]k_7[Ce^{4+}][H_2O]/(k_6[Ce^{3+}]+k_7[Ce^{4+}][H_2O]/\delta[H^+]))$, which would be large than 0 and increase with $\delta[H^+]$. Then, $T$ would increase with $\delta[H^+]$.

Besides, it could also be derived from equation $S19$ that, $d(\text{Amp})/d[H^+]<0$. As is also indicated in Fig.3b, the oscillation amplitude decreases with $[H^+]$ in a certain range of pH value. When $[H^+]$ is too small the oscillation would disappear.

3) The influence of $[Ce^{4+}]$

As is indicated in equation $S21$, the amplitude would increase with $[Ce^{4+}]_{\text{peak}}$. At the peak of the potential oscillation, $[Ce^{4+}]_{\text{peak}}$ approximately equals to the overall concentration of the Ce catalyst.

\[
\text{Amp} = -(RT/zF)\ln\left(\frac{[HBrO_2]_{\text{peak}}[Br^-]_{\text{valley}}/[HBrO_2]_{\text{valley}}[Br^-]_{\text{peak}}}{(k_5^2[BrO_3^-]^2-k_2[Br^-])+(k_5[BrO_3^-]-k_2[Br^-])}ight) \\
k_6[Ce^{4+}]_{\text{peak}}/\delta[H^+] / 2k_3k_4[BrO_5^-][Br^-]\]  

The influence of $[Ce]$ on the frequency is more complicated. According to equation $S20$ and $S9$, the period $T$ would decrease with the absolute value of $\beta$. 

10
\[ \beta = (k_2[Br^-] - k_3[BrO_3^-])\delta[H^+] + (2k_3[BrO_3^-]\delta[H^+] + k_6Ce^{4+}) \]
\[ k_7[Ce^{4+}][H_2O]/(k_6[Ce^{3+}]\delta[H^+] + k_7[Ce^{4+}][H_2O]) \]

At very low [Ce], \( \beta < 0 \), and \( \beta \) will increase with [Ce]. Thus, the absolute value of \( \beta \) would decrease as [Ce] increases, leading to an increase of the period.

At higher [Ce], \( \beta > 0 \), and \( \beta \) will increase [Ce]. Thus, the absolute value of \( \beta \) would increase as [Ce] increases, leading to a decrease of the period.

Therefore, there formed a turning point at the peak.

Reference:
Periodic color change during the oscillation reaction in Ce(IV) catalyzed B-Z organic solution

**Figure S1.** Color change between light yellow and orange yellow during the oscillation reaction.
Potential oscillation with different types of ionic liquids as oxidants

Figure S2. Potential oscillation with different types of oxidants: 1-ethylpyridinium bromate (0.06M, 0.19M), 1-ethylpyridinium iodate (0.06M, 0.19M), and 1-ethylpyridinium chlorate (0.06M, 0.19M). ([MA] = 0.36M, [Ce(NH₄)₂(NO₃)₆] = 3.6mM).

Figure S3. Potential oscillation profile for different oxidants: 1-ethylpyridinium bromate (0.06M), 1-butyl-3-methylimidazole bromate (0.06M), ([MA] = 0.36M, [Ce(NH₄)₂(NO₃)₆] = 3.6mM).
Ce-catalyzed oscillation reaction with 1-ethylpyridinium iodate as the oxidant

Figure S4. Ce(IV) catalyzed oscillation reaction at different concentration of oxidants (0.123M, 0.154M, 0.192M, 0.198M).