Electronic Supplementary Information

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

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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)

$Br^- + HBrO + H^+ \rightleftharpoons Br_2 + H_2O$	(S1)
$Br^+ + HBrO_2 + H^+ \rightarrow 2HOBr$	(S2)

$$Br^{-} + BrO_{3^{-}} + 2H^{+} \rightarrow HOBr + HBrO_{2}$$
(S3)

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

 $2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$ (S4)

$$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2 + H_2O$$
(S5)

$$BrO_2 + catalyst (R) + H^+ \rightleftharpoons HBrO_2 + catalyst (O)$$
(S6)

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

BrO_2 +Catalyst(O) + $H_2O \rightarrow BrO_3^-$ + Catalyst(R) + $2H^+$	(S7)
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$Br_2 + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+$	(S8)

 $6 \text{ Catalyst}(O) + CH_2(COOH)_2 + 2H_2O \rightarrow 6 \text{ Catalyst}(R) + HCOOH + 2CO_2 + 6H^+$ (S9)

 $4 \text{ Catalyst}(O) + BrCH(COOH)_2 + 2H_2O \rightarrow 4 \text{ Catalyst } (R) + HCOOH + Br + 2CO_2 + 5H^+$ (S10)

Reference

[1] T. Ueki, M. Watanabe, R. Yoshida, Angew. Chem. Int. Ed. 2012, 51, 11991.

[2] R. J. Field, E. Koros, R. M. Noyes, J. Am. Chem. Soc. 1972, 94,8649.

Note S2. Electrode potential calculation based on Nernst equation

$\varphi = \varphi^{\theta} + RT/nF \ln([Cat.(O)]/[Cat.(R)])$

In which φ represents the electrode potential, φ^{θ} 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)), [cat.(R)], [cat.(O)] represent the concentration of reductive and oxidative catalyst,respectively.

Reference

[1] G. Ertl , Angew. Chem. Int. Ed. 2015, 54,5828-5835

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)
Br + HOBr + H⁺
$$\rightleftharpoons$$
 Br₂ + H₂O (R1)
Br + HBrO₂ + H⁺ \rightarrow 2HOBr (R2)
Br + BrO₃⁻ + 2H⁺ \rightarrow HOBr + HBrO₂ (R3)
Process B (oxidation of Catalyst(R), autocatalytic reaction)
2HBrO₂ \rightarrow HOBr + BrO₃⁻ + H⁺ (R4)
HBrO₂ + BrO₃⁻ + H⁺ \rightleftharpoons 2BrO₂ + H₂O (R5)
BrO₂ + Catalyst(R) + H⁺ \rightleftharpoons HBrO₂ + Catalyst(O) (R6)
Process C (reduction of Catalyst(O), production of bromo malonic acid)
BrO₂ + Catalyst(O)+ H₂O \rightarrow BrO₃⁻ + Catalyst(R)+ 2H⁺ (R7)
Br₂ + CH₂(COOH)₂ \rightarrow BrCH(COOH)₂ + Br⁻ + H⁺ (R8)
6 Catalyst(O)+ CH₂(COOH)₂ + 2H₂O \rightarrow
6 Catalyst(R) + HCOOH + 2CO₂ + 6H⁺ (R9)
4 Catalyst(O)+ BrCH(COOH)₂ + 2H₂O \rightarrow
4 Catalyst(R) + HCOOH + Br⁻ + 2CO₂ + 5H⁺ (R10)

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

HOBr + Br⁻ + H⁺
$$\rightleftharpoons$$
 Br₂ + H₂O (R1)
 $k_{I}^{*} = 8.0 * l0^{9} M^{-2} sec^{-1}$
 $k_{-1}^{0} = 110 sec^{-1}$
HBrO₂ + Br⁻ + H⁺ \rightarrow 2HOBr (R2)
 $k_{2}^{*} = 2.0 * l0^{9} M^{-2} sec^{-1}$
 $k_{-2}^{0} = 5.0 * 10^{-5} M^{-1} sec^{-1}$
BrO₃⁻ + Br⁻ + 2H⁺ \rightarrow HBrO₂ + HOBr (R3)
 $k_{3}^{'} = 2.1 M^{-3} sec^{-1}$

$$k^{0}_{-3} = 1.0 * l0^{4} M^{-2} \sec^{-1}$$

$$2HBrO_{2} \rightarrow BrO_{3}^{-} + HOBr + H^{+}$$
(R4)
$$k^{0}_{4} = 4.0 * 10^{7} M^{-1} \sec^{-1}$$

$$k^{*}_{-4} = 2.0 * 10^{l0} M^{-2} \sec^{-1}$$
BrO_{3}^{-} + HBrO_{2} + H^{+} \rightleftharpoons 2BrO_{2}^{-} + H_{2}O
(R5)
$$k'_{5} = 1.0 * l0^{4} M^{-2} \sec^{-1}$$

$$k^{0}_{-5} = 2 * l0^{7} M^{-1} \sec^{-1}$$
BrO_{2}^{-} + Ce^{3+} + H^{+} \rightleftharpoons HBrO_{2} + Ce^{4+}
(R6)
$$k_{6} / k_{-6} = K_{6} = 0.025 M^{-1}$$
Br_{2} + CH_{2}(COOH)_{2} \rightarrow BrCH(COOH)_{2} + Br^{-} + H^{+}
(R8)
$$k^{0}_{8} = 1.3 * M^{-1} \sec^{-1}$$

$$6Ce^{4+} + CH_2(COOH)_2 + H_2O \rightarrow 6Ce^{4+} + HCOOH + 2CO_2 + 6H^+$$
 (R9)

$$v_{9} = -\frac{d[MA]}{dt} = \frac{k_{9}'[Ce^{4+}][MA]}{K_{9}'' + [MA]}$$

An empirical rate equation for reaction 9 is

$$k'_9 = 8.8 * l0^{-2} sec^{-1}$$

The empirical constant $K''_{g} = 0.53 M$

$$4Ce^{4+} + BrCH(COOH)_{2} + 2 H_{2}O \rightarrow Br^{+} + 4Ce^{3+} + HCOOH + 2CO_{2} + 5H^{+}$$
(R10)
$$v_{10} = -\frac{d[BrMA]}{dt} = \frac{k_{10}^{'}[Ce^{4+}][BrMA]}{K_{10}^{''} + [BrMA]}$$
An empirical rate equation for reaction 10 is:

$$k'_{10} = 1.7 * l0^{-2} sec^{-1}$$

The empirical constant $K''_{10} = 0.2 M$

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 (*) 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 $k_i[H_2O]$.

$$BrO_{3}^{-} + HBrO_{2} + H^{+} \rightleftharpoons 2BrO_{2}^{-} + H_{2}O$$
(R5)

$$k_{-5} = k'_{-5} [H_2 O]$$

BrO₂· + Ce⁴⁺ + H₂O \rightarrow BrO₃⁻ + Ce³⁺ + 2H⁺ (R7)

$$k_7 = k'_7 [H_2 O]$$

$$6Ce^{4+} + CH_2(COOH)_2 + H_2O \rightarrow 6Ce^{4+} + HCOOH + 2CO_2 + 6H^+$$
(R9)

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

$$v_9 = -\frac{d[MA]}{dt} = \frac{k_9' [Ce^{4+}][MA][H2O]}{K_9' + [MA]}$$

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

 $4Ce^{4+} + BrCH(COOH)_2 + 2 H_2O \rightarrow Br^- + 4Ce^{3+} + HCOOH + 2CO_2 + 5H^+$ (R10) A new empirical rate equation for reaction 10 could be supposed as:

$$v_{10} = -\frac{d[BrMA]}{dt} = \frac{k_{10}[Ce^{4+}][BrMA][H2O]}{K_{10} + [BrMA]}$$

 $k_{10} = k'_{10} [H_2 O]$

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 ^[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 ^[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.

$A+Y \rightarrow X+P$ F	Rate = $k_{M1}AY$	(a)
$X + Y \rightarrow P$	Rate = $k_{M2}XY$	(b)
$B + X \rightarrow 2X + Z$	Rate = $k_{M3}BX$	(c)
$X + X \rightarrow Q$ F	Rate = $k_{M4}X^2$	(d)
$Z \rightarrow fY$ F	Rate = $fk_{M5}Z$	(e)

Where, $X = HBrO_2$, Y = Br, Z = Ce(IV), $A = B = BrO_3^-$, P and Q represent reaction products like HOBr 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.

$$dX/dt = k_{M1}AY - k_{M2}XY + k_{M3}AX - 2k_{M4}X^2$$
 S1

$$dY/dt = -k_{M1}AY - k_{M2}XY + k_{M5}fBZ$$
 S2

$$dZ/dt = k_{M3}AX - k_{M5}BZ$$
 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].

$$d[HBrO_2]/dt = -\alpha[HBrO_2]^2 - \beta[HBrO_2] + \gamma$$
 S4

Where,

$$\alpha = 2k_4$$
 S5

$$B = k_{2}[Br][H^{+}] - k_{5}[BrO_{3}^{-}][H^{+}] + (2k_{5}[BrO_{3}^{-}][H^{+}] + k_{-6}[Ce^{4+}])k_{7}[Ce^{4+}]$$

$$/(k_{6}[Ce^{3+}][H^{+}] + k_{7}[Ce^{4+}])$$
S6

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

 β and γ 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 H₂O should be taken into consideration. Therefore, the kinetic equation S4 should be revised with a new set of α , β and γ .

$$\alpha = 2k_4$$

$$\beta = k_2[Br^{-}]\delta[H^{+}] - k_5[BrO_3 -]\delta[H^{+}] + (2k_5[BrO_3 -]\delta[H^{+}] + k_{-6}[Ce^{4+}])k_7[Ce^{4+}][H_2O]$$

$$/(k_6[Ce^{3+}]\delta[H^{+}] + k_7[Ce^{4+}][H_2O])$$
S9

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

where, δ indicates the solvent effects on the activity of H⁺.

Then, the frequency and amplitude of the concentration oscillation could be

subsequently estimeted based on above equations.

For the oscillation frequency,

Letting [HBrO₂]=X=X₀+x, [Br]=Y=Y₀+y and [Ce⁴⁺]=Z=Z₀+z, where X₀, Y₀ and Z₀ 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.

$$dx/dt = -(2\alpha X_0 + \beta_0)x$$
S12
Thus, $|\omega| = |2\alpha X_0 + \beta_0|$, and period T= $|2\pi/\omega|$

According to previous researches by R. J. Field, E. Koros, and R. M. Noyes ^[xxx], $\beta^2 >> 4\alpha\gamma$ is a good approximation for most of the anticipated finite values of β . Besides, it is more rational to assume $\beta < 0$, as for [Br⁻] in organic solvent-dominated system should be very small. By assuming that $d[HBrO_2]/dt=0$, it could be solve out approximatively from equation S4 that,

$$[HBrO_2]_0 = -\beta_0/\alpha.$$

Therefore,

$$T^2 = 4\pi^2 / \beta_0^2 \qquad \qquad S14$$

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.

$$d[HBrO_2]/dt = 0$$
 S15

The corresponding concentrations could be calculated as follows:

$$[HBrO_2] = (\beta/2\alpha) (-1 \pm (1 \pm 4\alpha\gamma/\beta^2)^{0.5})$$

$$= \gamma/\beta \qquad (\beta > 0)$$

$$= -\beta/\alpha \qquad (\beta < 0)$$

S16

At the peak of the potential, the rate of reaction R6 should be very small. It could be assumed that, $k_6[Ce^{3+}]\delta[H^+] \ll k_7[Ce^{4+}][H_2O]$. Thus,

$$k_{7}[Ce^{4+}][H_{2}O]/(k_{6}[Ce^{3+}]\delta[H^{+}]+k_{7}[Ce^{4+}][H_{2}O]) = 1. \text{ And},$$

$$\beta_{\text{peak}} = k_{2}[Br^{-}]\delta[H^{+}]+k_{5}[BrO_{3}^{-}]\delta[H^{+}]+k_{-6}[Ce^{4+}]_{\text{peak}} > 0$$
 S17

$$([HBrO_2]/[Br^-])_{peak} = \delta k_3 [BrO_3^-][H^+]^2 / \beta_{peak}$$
 S18

At the valley of the potential, the rate of reaction R7 should be very small. It could be assumed that, $k_6[Ce^{3+}]\delta[H^+] >> k_7[Ce^{4+}][H_2O]$. Thus, $\delta k_7[Ce^{4+}][H_2O]/(k_6[Ce^{3+}]\delta[H^+] + k_7[Ce^{4+}][H_2O]) << 1$. And,

$$\beta_{\text{valley}} = k_2 [Br^-] \delta[H^+] - k_5 [BrO_3 -] \delta[H^+] < 0$$
 S19

$$([HBrO_2]/[Br^-])_{\text{valley}} = -\beta_{valley}/2k_4[Br^-]_{\text{valley}}$$
 S20

Therefore, the oscillation amplitude (*Amp*) could be calculated via Nernst equation.

$$Amp = -(RT/zF)ln([HBrO_2]_{peak}[Br^{-}]_{valley}/[HBrO_2]_{valley}[Br^{-}]_{peak})$$

=(RT/zF)ln{(k₅²[BrO_3^{-}]² - k₂²[Br^{-}]²)+(k₅[BrO_3^{-}]-k₂[Br^{-}])
k₋₆[Ce⁴⁺]_{peak}/\delta[H^{+}])/2k_3k_4[BrO_3^{-}][Br^{-}]} S21

1) The influence of trace amount of water

It could be derived from S14 that, $dT/d[H_2O]=(2\pi/\beta_0^2) d\beta/d[H_2O]|_0$. 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 β 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 $k_7[Ce^{4+}][H_2O]/(k_6[Ce^{3+}]\delta[H^+]+$ $k_7[Ce^{4+}][H_2O])$ could not be ignored as 0, and it will increases with $[H_2O]$. Therefore, the absolute value of β_{valley} will decrease with $[H_2O]$, resulting the decrease of oscillation amplitude.

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

It could be derived from S14 that, $dT/d[H^+]=(2\pi/\beta_0^2)d\beta/d[H^+]|_0$. 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, β 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, $d(Amp)/d[H^+] < 0$. 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 $[Ce^{4+}]_{peak}$. At the peak of the potential oscillation, $[Ce^{4+}]_{peak}$ approximately equals to the overall concentration of the Ce catalyst.

$$Amp = -(RT/zF)ln([HBrO_2]_{peak}[Br^-]_{valley}/[HBrO_2]_{valley}[Br^-]_{peak})$$

=(RT/zF)ln{(k₅²[BrO_3-]²-k₂²[Br^-]²)+(k₅[BrO_3-]-k₂[Br^-])
k₋₆[Ce⁴⁺]_{peak}/\delta[H⁺])/2k₃k₄[BrO_3⁻][Br⁻]} S21

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 β .

 $\beta = (k_2[Br^-] - k_5[BrO_3 -])\delta[H^+] + (2k_5[BrO_3 -]\delta[H^+] + k_{-6}[Ce^{4+}])$ $k_7[Ce^{4+}][H_2O]/(k_6[Ce^{3+}]\delta[H^+] + k_7[Ce^{4+}][H_2O])$

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

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

Therefore, there formed a turning point at the peak.

Reference:

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[4] R.J. Field , F. W. Schneider, Oscillating chemical reactions and nonlinear dynamics, *J. Chem. Educ.*, 1989, **66 (3)**, 195-204.

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, $[Ce(NH_4)_2(NO_3)_6] = 3.6mM$).



Figure S3. Potential oscillation profile for different oxidants: 1-ethylpyridinium bromate (0.06M), 1-butyl-3methylimidazole 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).