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Oxidation State of BZ Reaction Mixtures

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The unstirred, ferroin ($Fe(phen)_3^{2+}$)-catalyzed Belousov−Zhabotinsky (BZ) reaction[1−4] is the prototype oscillatory chemical system. After an induction period of several minutes, one sees “spontaneous” formation of “pacemaker” sites, which oscillate between a blue, oxidized state (high $[Fe(phen)_3^{3+}]$) and a red, reduced state (low $[Fe(phen)_3^{3+}]$). The reaction medium appears red (reduced) during the induction phase, and the pacemaker sites generate target patterns of concentric, outwardly moving waves of oxidation (blue). Auto-oscillatory behavior is also seen in the Oregonator model of Field, Kőrös, and Noyes (FKN), a robust, reduced model which captures qualitative BZ kinetics in the auto-oscillatory regime. However, the Oregonator model predicts a blue (oxidized) induction phase. Here, we show that including reaction R8 of the FKN mechanism, not incorporated in the original Oregonator, accounts for bromide release during the induction phase, thus producing the observed red oxidation state.

The unstirred, ferroin [$Fe(phen)_3^{2+}/Fe(phen)_3^{3+}$]-catalyzed Belousov−Zhabotinsky (BZ) reaction[1−4] is a prototype chemical system[1−8] exhibiting traveling waves of oxidation in an oscillatory or excitable medium. The BZ reagent may either oscillate between the red (reduced, high ferroin [$Fe(phen)_3^{2+}$]) and blue (oxidized, high ferriin [$Fe(phen)_3^{3+}$]) states of the catalyst or settle into a red steady state, which may remain excitable, leading to transient excursions through the blue state upon suitable perturbation. A blue steady state is possible in principle but is seldom seen experimentally. Instead, a typical thin-layer BZ medium (∼2 D) displays a red (reduced) induction phase lasting several minutes, followed by “spontaneous” formation of “pacemaker” centers[7,8] that oscillate between red and blue states and generate target patterns of concentric, outwardly moving waves of oxidation (blue) in the red medium. The origin of these pacemaker centers is not yet completely understood.[9−13]

Field, Kőrös, and Noyes (FKN)[5,6] rationalized the kinetics of the Ce(III)/Ce(IV)-catalyzed BZ reaction using ∼ 20 reactions involving ∼8 intermediate species. Considerably more detailed mechanisms have since been developed.[14] However, Field and Noyes[6] captured the qualitative dynamics with a skeleton model (the Oregonator), although there are clear differences in behavior and thus mechanism between the Ce(III)/Ce(IV)- and ferroin-catalyzed systems. The dynamics of the Oregonator is described by a system of three ordinary differential equations where $x = [HBrO_2]$, $y = [Br^-]$, and $z = 2[Ce(IV)]$ or $2[Fe(phen)_3^{3+}]$:

$$
\begin{aligned}
\mathrm{d}x/\mathrm{d}t &= k_3[\mathrm{BrO_3}^-][\mathrm{H}^+]^2 y - k_2[\mathrm{H}^+]xy + k_5[\mathrm{BrO_3}^-][\mathrm{H}^+]x - 2k_4x^2 \\
\mathrm{d}y/\mathrm{d}t &= -k_3[\mathrm{BrO_3}^-][\mathrm{H}^+]^2 y - k_2[\mathrm{H}^+]xy + (f/2)k_c[\mathrm{MA}]_0 z \qquad (1) \\
\mathrm{d}z/\mathrm{d}t &= 2k_5[\mathrm{BrO_3}^-][\mathrm{H}^+]x - k_c[\mathrm{MA}]_0 z
\end{aligned}
$$

Here, $[MA]_0$ denotes $[CH_2(COOH)_2]_0$ and k_2, k_3, k_4, and k_5 are rate constants from the FKN mechanism. The rate constant k_c and stoichiometric factor f are expendable quantities related to the reduction of ferriin and consequent release of bromide:

$$
2\mathrm{Fe(phen)_3}^{3+} + \mathrm{MA} + \mathrm{BrMA} \rightarrow f\,\mathrm{Br}^- + 2\mathrm{Fe(phen)_3}^{2+} + \text{other products} \qquad (2)
$$

Above, BrMA denotes bromomalonic acid ($BrCH(COOH)_2$). The stoichiometric factor f serves as a bifurcation parameter, with a blue, oxidized steady state (high [$Fe(phen)_3^{3+}$] and [$HBrO_2$] with low [Br^-]) for $f < f_{crit} \approx 0.5$, a red, reduced steady state (low [$Fe(phen)_3^{3+}$] and [$HBrO_2$] with high [Br^-]) for high f (> ∼2.414), and oscillatory dynamics (blue/red) for intermediate values of f. Transitions between steady state and oscillatory behavior occur at Hopf bifurcations, the first at $f = f_{crit}$.[7]

Typical BZ reagent mixtures initially contain little or no bromomalonic acid (BrMA),[7,8] making f near 0 at time 0. The value of f increases as MA is converted to BrMA. The oscillatory behavior in the simple Oregonator model, seen at target centers in experimental systems, requires that $f > f_{crit}$. However, in typical ferroin-catalyzed BZ reagent mixtures, especially with added bromide, the reaction medium is in a red,

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reduced steady state (after a rapid blue excursion upon mixing) through most of the initial induction period, not the blue, oxidized steady state for $f < f_{\mathrm{crit}}$. We reconcile this conflict by adding Br^- release from the bromination of MA to the Oregonator and explore qualitative consequences for oscillatory and excitable BZ systems.

The stoichiometric factor f increases with bromination of malonic acid, for example, by FKN reaction R8:[5,6]

$$\mathrm{MA} + \mathrm{Br_2} \rightarrow \mathrm{BrMA} + \mathrm{H^+} + \mathrm{Br^-} \qquad (3)$$

In the spirit of a skeleton mechanism, we extend the Oregonator to include two key consequences of R8: increases in f and bromide release beyond that of eq 2:

$$\begin{aligned}
\mathrm{d}x/\mathrm{d}t &= k_3[\mathrm{BrO_3}^-][\mathrm{H}^+]^2 y - k_2[\mathrm{H}^+]xy + k_5[\mathrm{BrO_3}^-][\mathrm{H}^+]x - 2k_4x^2\\
\mathrm{d}y/\mathrm{d}t &= -k_3[\mathrm{BrO_3}^-][\mathrm{H}^+]^2 y - k_2[\mathrm{H}^+]xy + (f/2)k_c[\mathrm{MA}]_0 z + c\,\mathrm{d}f/\mathrm{d}t \qquad (4)\\
\mathrm{d}z/\mathrm{d}t &= 2k_5[\mathrm{BrO_3}^-][\mathrm{H}^+]x - k_c[\mathrm{MA}]_0 z\\
\mathrm{d}f/\mathrm{d}t &= k_f(f_\infty - f)
\end{aligned}$$

The last equation above represents the evolution of f from its initial value of 0 through f_{crit} and finally approaching a limiting value of f_∞ in the oscillatory regime as MA is converted to BrMA.[9] Here, k_f is a "rate constant" for the evolution of f. This provides a mechanism for target nucleation (slow passage through a Hopf bifurcation[15] followed by a supercritical state sensitive to local fluctuations)[9] but still predicts an initial blue, oxidized induction period. Reproducing the observed red, reduced induction period requires an added source of Br^- to suppress the oxidation of ferroin while $f < f_{\mathrm{crit}}$. Reaction R8 provides Br^- release.

The rate of Br^- release in R8 is proportional to the rate of bromination of MA. Since f corresponds roughly to [BrMA]/[MA], we represent Br^- release by adding the term $c\,\mathrm{d}f/\mathrm{d}t$ to the second equation above. The parameter c is essentially expendable but is related to $[\mathrm{MA}]_0$. The term $c\,\mathrm{d}f/\mathrm{d}t$ approaches 0 as f approaches f_∞ and bromination of MA nearly ceases. Beyond this point, Br^- generation occurs via eq 2 according to the normal Oregonator dynamics. (We had previously considered the case $c = 0$.[9])

Our purpose here is only to demonstrate the qualitative role of Br^- release during the induction period. Thus, we do not include other possible mechanisms for Br^- production, for example,[7,16,17]

$$\begin{gathered}
\mathrm{H_2OBr^+} + \text{ferroin} \rightarrow \text{ferriin} + \bullet\mathrm{Br} + \mathrm{H_2O}\\
\bullet\mathrm{Br} + \mathrm{CH_2(COOH)_2} \rightarrow \bullet\mathrm{CH(COOH)_2} + \mathrm{Br^-} + \mathrm{H^+} \qquad (5)\\
\mathrm{Br^-} + \mathrm{HOBr} + \mathrm{H^+} \rightleftarrows \mathrm{Br_2}
\end{gathered}$$

The reactions of eq 5 may be of particular interest because they are not expected to occur in the Ce(III)/Ce(IV)-catalyzed system [$\mathrm{H_2OBr^+}$ is not expected to have the potential to oxidize Ce(III) to Ce(IV)] and thus may be related to some observed differences (mentioned above) between it and the ferroin-catalyzed system, especially in dynamics during the induction period.

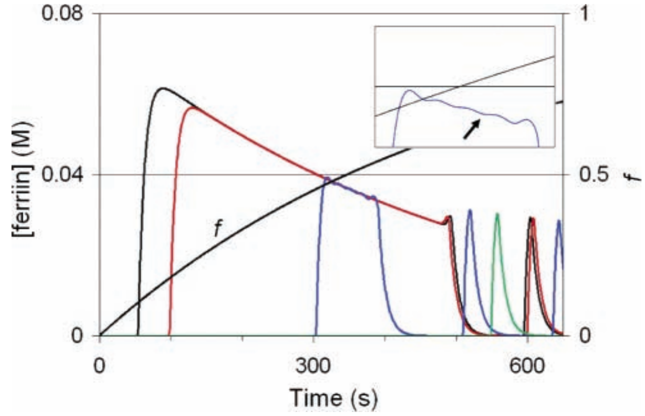

Figure 1. Dynamics of eq 4. Oregonator rate constants were assigned standard values,[6] except that k_4 was reduced by a factor of 1/2. $k_f = 2 \times 10^{-3}\ \mathrm{s^{-1}}$ and $f_\infty = 1$. $[\mathrm{H^+}] = 0.316$ M ($[\mathrm{H_2SO_4}] = 0.30$ M), $[\mathrm{MA}]_0 = 0.10$ M, $[\mathrm{KBrO_3}] = 0.25$ M. Initial conditions: $x = 0$, $y = 10^{-3}$ M, $z = 0$. Evolution of f is shown by a labeled black line (right axis); ferriin dynamics with no added Br^- release ($c = 0$) by a black line (not labeled, left axis). Red, blue, and green lines represent ferriin dynamics under successively higher rates of Br^- release: $c = 0.5$, 0.7, and 1 mM. For $c = 0.7$ mM, [ferriin] undergoes slowly increasing oscillations about a blue, oxidized state (inset, 300 s ≤ t ≤ 400 s) after slow passage of f through f_{crit} (arrow).[9]

Figure 2. Fluctuation-driven target formation in a thin 10 mm square with periodic boundary conditions, using our extended Oregonator model with similar parameter values. See ref 13 for details. Local ferriin concentration shown in blue; ferroin in red, arbitrary scale, to mimic experimental colors.

The extended Oregonator model (eq 4) was numerically integrated using winpp.[18] The observed red, reduced-induction-period local dynamics with a blue, oxidized clocking wave[7] are best matched at intermediate rates of bromide release as determined by an assumed value of c (Figure 1).

As c increases, the onset of an oxidized induction period (high ferriin) is delayed and its duration is shortened until it has disappeared at $c = 1$ mM, providing the experimentally observed reduced (red) induction period. For $c = 0.7$ mM, oscillations in [ferriin] about a relatively short-lived oxidized state (inset) correspond to a spiral approach to and departure from this state (clocking[7]) as f passes through f_{crit} (arrow).

We have previously reported spontaneous fluctuation-driven target formation in a stochastic partial differential equation version of eq 4 in a thin 2D system.[13] The system evolved into a red (reduced) steady state which became unstable as f increased through f_{crit}, leading to the formation of blue patterns in a red background,[9,14] as seen in experimental systems (Figure 2).

Including reaction R8 in an extended Oregonator model (eq 4) explains the transition from the observed red, reduced induction period to an unstable, oscillatory regime through a combination of slow increase of f through the critical value f_{crit} and consequent decreases in Br^- release ($c\,\mathrm{d}f/\mathrm{d}t$), allowing target formation. This Br^- release may explain why target formation is almost never seen in the excitable, nonoscillatory reaction, even if $[BrO_3^-][H_2SO_4]$ is only slightly less than the value (0.045 M^2) below which one sees nonoscillatory behavior.[19] Although the extended Oregonator becomes unstable for f sufficiently above f_{crit}, below the threshold of excitable, nonoscillatory behavior (∼2.414), targets will not form if Br^- release exceeds consumption by BrO_3^- in the FKN mechanism. Moreover, targets appear to form more quickly in 2D than in 3D experimental mixtures, possibly because loss of Br_2 by outgassing may retard bromination of MA, reducing Br^- release.

Finally, we speculate that the effects of Br^- release in delaying target initiation may play a critical role in determining whether one sees target formation or spontaneous bulk oscillations. For example, the CIMA reaction displays spontaneous target formation[20] but the chlorite−iodide reaction typically displays only bulk or stimulated oscillations.[21−23] In the absence of retarding mechanisms, the whole reaction medium might "flash" in bulk in response to microscopic fluctuations as triggers.

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