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Pseudo-steady states in the model of the Bray-Liebhafsky oscillatory reaction

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The main pseudo-steady states in the process of catalytic hydrogen peroxide decomposition are analysed. The dominant steady states during the monotonic and oscillatory evolution, well known experimentally, are defined by stoichiometric network analysis of the model for this process. The trajectories for the evolution of the system in the phase space in the vicinity of the unstable pseudo-steady state where oscillatory behaviour is obtained, are also calculated. The adjustment of the phase trajectory to the corresponding oscillation is proposed as an additional criterion for the selection of the kinetic parameters necessary for numerical simulation. The calculation procedure is general, independent of the model under consideration.

The decomposition of hydrogen peroxide into water and oxygen,

\[ 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad \text{(D)} \]

in the presence of iodate and hydrogen ions, the so called Bray-Liebhafsky (BL) oscillatory reaction,\(^{1,2}\) is known to exhibit different forms of dynamic behaviour, generally divided into monotonic and oscillatory catalysis.\(^1\)\(^-\)\(^17\)

The oscillatory evolution of the concentration of iodine, one of the numerous intermediates such as I\(^-\), HIO, HIO\(_3\), I\(_2\) and others appearing in the mentioned reaction, was discovered at the beginning of this century by Coulkins and Bray and published by Bray\(^1\) in 1921. Already, at that time, two kinetically well separated steady-state pathways for hydrogen peroxide decomposition during the oscillatory evolution of the reaction were postulated. In the reduction pathway, iodate was reduced to iodine by hydrogen peroxide acting as a reducing agent.\(^1\)\(^8\)

\[ 2\text{IO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{I}_2 + 5\text{O}_2 + 6\text{H}_2\text{O} \quad \text{(R)} \]

and, in the oxidation pathway, the iodine was oxidized into iodate by hydrogen peroxide acting as an oxidizing agent.\(^1\)\(^8\)

\[ \text{I}_2 + 5\text{H}_2\text{O}_2 \rightarrow 2\text{IO}_3^- + 2\text{H}^+ + 4\text{H}_2\text{O} . \quad \text{(O)} \]

The decomposition of hydrogen peroxide into water and oxygen, given by reaction (D), was the straightforward result of the stoichiometric network of the last two equations in which the species \( \text{I}_2 \) and \( \text{IO}_3^- \) were introduced as one catalytic couple. Moreover, by analysing the reactions (R) and (O) and the evolved oxygen during the overall process, Bray concluded that these reactions had to be complex.

The above reaction pathways are encountered in all models of the overall process of hydrogen peroxide decomposition.\(^1\)\(^7\)\(^-\)\(^25\) They are not simple reactions but stoichiometric networks in the corresponding steady states and are explained in different ways.

Here, we examine the possible pseudo-steady states and, particularly, those characterizing the reduction and oxidation pathways during the oscillatory evolution, obtained in the proposed model,\(^22\)\(^-\)\(^24\) characterized by the instability condition yielding oscillatory behaviour as a function of the concentrations of the reactant species.\(^26\)

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**Model**

The model discussed here can be represented by the following reaction scheme:\(^\dagger\)

\[ \text{IO}_3^- + \text{I}^- + 2\text{H}^+ \rightleftharpoons \text{HIO} + \text{HIO}_2 \quad \text{(r1),} \quad (r - 1) \]

\[ \text{HIO}_2 + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2\text{O} + \text{H}_2\text{O} \quad \text{(r2)} \]

\[ \text{I}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{HIO} \quad \text{(r3),} \quad (r - 3) \]

\[ \text{HIO} + \text{I}^- + \text{H}^+ \rightleftharpoons \text{I}_2 + \text{H}_2\text{O} \quad \text{(r4),} \quad (r - 4) \]

\[ \text{HIO} + 2\text{H}_2\text{O}_2 \rightarrow \text{I}_2^- + \text{H}^+ + \text{O}_2 + \text{H}_2\text{O} \quad \text{(r5)} \]

\[ \text{I}_2\text{O} + 2\text{H}_2\text{O}_2 \rightarrow \text{HIO} + \text{HIO}_2 \quad \text{(r6)} \]

\[ \text{HIO}_2 + 2\text{H}_2\text{O}_2 \rightarrow \text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O} \quad \text{(r7)} \]

\[ \text{IO}_3^- + \text{H}^+ + 2\text{H}_2\text{O}_2 \rightarrow \text{HIO}_2 + \text{O}_2 + \text{H}_2\text{O} \quad \text{(r8)} \]

In general, the species involved can be divided into two groups, external and internal species,\(^9\)\(^-\)\(^27\) where external species are those appearing as reactants or products in the overall stoichiometry (the net reaction). The external species are \( \text{H}_2\text{O}_2, \text{H}_2\text{O} \) and \( \text{O}_2 \). In the present model, the internal species are \( \text{I}^-\), \( \text{HIO}, \text{HIO}_2\), \( \text{I}_2\), \( \text{I}_2\text{O}, \text{IO}_3^- \) and \( \text{H}^+ \). By means of the law of mass conservation it can be shown that only five of these internal species are independent.\(^2\) Therefore, two of these seven species ought to be dropped. Since the concentrations of \( \text{IO}_3^- \) and \( \text{H}^+ \), varying between \( 10^{-1} \) and \( 10^{-2} \) mol dm\(^{-3}\), are relatively large in comparison with the others and, consequently, do not undergo significant change during the reaction, they will be treated as constant and included in the corresponding rate constants. Hence, the model will be analysed with the use of five independent internal species, \( \text{I}^-\), \( \text{HIO}, \text{HIO}_2, \text{I}_2, \text{I}_2\text{O} \).
Dynamic behaviour

We mentioned at the outset that hydrogen peroxide decomposition in the BL system can occur through both monotonic [e.g., see Fig. 3 in ref. 22 and Fig. 2 in ref. 12(e)] and oscillatory catalysis [e.g., see Fig. 1 in ref. 22]. In the course of the monotonic evolution of hydrogen peroxide decomposition in a closed reactor, there exists one pseudo-steady-state pathway (the system tends to a stable non-equilibrium stationary state), whereas in the course of the oscillatory evolution this state is unstable and the system cycles around it along a stable limit cycle.\(^\text{§}\)

At the border between monotonic and oscillatory catalysis, monotonic hydrogen peroxide decomposition changes its trend to a stepwise form.\(^1,2,3,21\) The oscillograms have the form presented in Fig. 1 of ref. 22. The intermediate concentrations begin to oscillate around the unstable pseudo-steady state. However, there are differences between their concentrations and behaviour. Of the five independent internal species appearing in the model, viz. \(\Gamma^-, \text{HIO, HIO}_2, \text{I}_2\) and \(\text{I}_2\text{O}\), iodine has the largest concentration. The experimental measurements show that it ranges between \(10^{-4}\) and \(10^{-5}\) mol dm\(^{-3}\).\(^{1,4,17,22}\) The other four species have at least two orders of magnitude lower concentrations.\(^4,22\) The variables can be separated on the basis of the time scales. The concentration of \(\text{I}_2\) can be regarded as ‘slow’ variable, whereas the concentrations of \(\Gamma^-, \text{HIO, HIO}_2\) and \(\text{I}_2\text{O}\) can be regarded as ‘fast’ variables. In this case of ‘relaxation’ oscillations,\(^3,8\) the trajectory denotes the cyclic evolution of the system along the limit cycle, which consists of two stable branches of the folded nullcline separated by rapid jumps between them.

In the oscillatory region, the iodine concentration, which had similar evolution to that of hydrogen peroxide in the monotonic region (Fig. 3 in ref. 22), begins to decrease and increase alternately. During the increase in iodine concentration, the system follows one branch of the stable nullcline and the stoichiometric evolution is given by reaction (R). During the decrease in iodine concentration, the system follows the other branch of the stable nullcline and the stoichiometric evolution is given by reaction (O). The concentrations of ‘fast’ intermediates \(\Gamma^-, \text{HIO, HIO}_2\) and \(\text{I}_2\text{O}\), dependent on the \(\text{I}_2\) concentration as some kind of precursor in the oscillatory domain,\(^21\) have values characteristic of these two states. When the \(\text{I}_2\) concentration time derivatives change sign, their concentrations change from the values characteristic of one state to these characteristic of the other. These states will be called ‘reduction pseudo-steady state’ and ‘oxidation pseudo-steady state’ since the steady-state approximation for the ‘fast’ variables will be used in the following calculations. These reduction and oxidation pseudo-steady states must be carefully distinguished from the main pseudo-steady state which is stable in monotonic and unstable in oscillatory evolution of the system and which we call the catalytic pseudo-steady state. The first two steady states are not new ones for the decomposition of the hydrogen peroxide, but they are the steady states for the concentrations of the intermediate species in reactions (R) and (O).

Thus, when the overall process of hydrogen peroxide decomposition is in the stable catalytic pseudo-steady or pseudo-stationary state, depending on the hydrogen peroxide concentration, \(\text{I}_2\) is an internal species. In the unstable catalytic pseudo-stationary state, \(\text{I}_2\) is an external species. The species \(\text{I}^-, \text{HIO, HIO}_2\) and \(\text{I}_2\text{O}\) are, in both cases, internal species. Therefore, \(\text{I}_2\) alone appears in the stoichiometric equations (R) and (O).

The concentrations of \(\text{IO}_3^-\) and \(\text{H}^+\) also oscillate around the unstable pseudo-steady state,\(^22,31\) but the amplitudes of their oscillations are insignificant.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Steady-state stoichiometric networks</th>
</tr>
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<tbody>
<tr>
<td>(E_1)</td>
<td>((r1) + (r - 1))</td>
</tr>
<tr>
<td>(E_2)</td>
<td>((r3) + (r - 3))</td>
</tr>
<tr>
<td>(E_3)</td>
<td>((r4) + (r - 4))</td>
</tr>
<tr>
<td>(E_4)</td>
<td>((r2) + (r5) + (r6))</td>
</tr>
<tr>
<td>(E_5)</td>
<td>((r1) + (r5) + (r7))</td>
</tr>
<tr>
<td>(E_6)</td>
<td>((r - 1) + (r2) + (r6) + (r8))</td>
</tr>
<tr>
<td>(E_7)</td>
<td>((r7) + (r8))</td>
</tr>
<tr>
<td>(E_8)</td>
<td>(2 \times (r1) + 2 \times (r2) + 2 \times (r3) + (r4) + 5 \times (r5))</td>
</tr>
<tr>
<td>(E_9)</td>
<td>(3 \times (r - 1) + 2 \times (r2) + 2 \times (r3) + (r4) + 5 \times (r8))</td>
</tr>
<tr>
<td>(E_{10})</td>
<td>(2 \times (r2) + 2 \times (r3) + (r4) + 3 \times (r5) + 2 \times (r8))</td>
</tr>
<tr>
<td>(E_{11})</td>
<td>(2 \times (r - 1) + 3 \times (r2) + 2 \times (r - 3) + (r - 4) + 5 \times (r6))</td>
</tr>
<tr>
<td>(E_{12})</td>
<td>((r1) + 2 \times (r - 3) + (r - 4) + 2 \times (r6) + 3 \times (r7))</td>
</tr>
<tr>
<td>(E_{13})</td>
<td>((r2) + 2 \times (r - 3) + (r - 4) + 3 \times (r6) + 2 \times (r7))</td>
</tr>
</tbody>
</table>

\(\text{E} = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 & 0 & 2 & 0 & 0 & 1 & 0 \ 1 & 0 & 0 & 0 & 1 & 0 & 0 & 3 & 0 & 2 & 0 & 0 \ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 2 & 2 & 2 & 3 & 0 & 1 \ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 2 & 2 & 2 & 0 & 0 \ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 2 & 2 & 0 \ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 \ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 \ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 5 & 0 & 3 & 0 & 0 \ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 5 & 2 & 3 \ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 3 & 2 & 0 & 0 \ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 5 & 2 & 0 & 0 \ \end{bmatrix}\)

When the overall hydrogen peroxide decomposition is not a periodic reaction, the stable catalytic pseudo-steady state can be reached. Then, besides the currents due to equilibrations without any external mass balance (represented by the first three columns in the matrix \(E\)), the currents due to the stoichiometric networks summarized by reaction (D) are the only possible ones (columns 4–7 in matrix \(E\)).

When the overall hydrogen peroxide decomposition exhibits periodicity, the catalytic pseudo-steady state is

\(\text{§ The general theory can be found in ref. 28 and 29.}\)
unstable. Then, besides the currents mentioned above, new ones summarized by reactions (R) and (O) are possible. They are presented by columns 8–13 in the matrix E.

In particular, the reaction (R), in which iodate is reduced to iodide, can be obtained by the extreme currents E₁₂, E₁₉ and E₁₀ and the reaction (O), in which iodide is oxidized to iodate, by the extreme currents E₁₄, E₁₂ and E₁₃ (Table 1).

Thus, we can see one pseudo-steady state in the region of monotonic catalysis, described by reaction (D), and two well defined pseudo-steady states in the oscillatory region, described by reactions (R) and (O). The pseudo-steady states and transitions between them during the time evolution of the system (Fig. 1) are illustrated in Fig. 2 for the intermediate species I⁻ and HIO. The curves denoting d[I⁻]/dt = 0 and d[HIO]/dt = 0 are presented for fixed iodine concentration.

The intersections of these two curves in Fig. 2, give the pseudo-steady states. The corresponding, numerically evaluated, position of the system is represented by the point N. In Fig. 2(c), (f) and (h), the curves cross in three points giving three pseudo-steady states. The left one is related to reaction (R), the right to reaction (O) and the middle one is unstable. Fig. 2(e) and (g) show situations where a rapidly transition between the reduction and the oxidation state occurs.

Pseudo-steady state in the region of monotonic catalysis

If the catalytic steady state is stable, the rates of reactions (R) and (O) become equal. Iodide is an internal species, as already mentioned, so that pseudo-stationary of the concentrations of all five independent intermediates (I⁻, HIO, HIO₂, I₂, I₂O) can be assumed. Denoting the rates of reactions by

\[ r₁ = kₙ₁[HIO][HIO₂] = k₁[I⁻] \]

\[ r₂ = kₙ₂[HIO₂][H⁺][I⁻] = k₂[I⁺][I⁻] \]

\[ r₃ = kₙ₃[I₂O] = k₃[I₂] \]

\[ r₆ = kₙ₄[I₂][I₂O] = k₄[I₂][I₂O] \]

\[ r₇ = kₙ₅[I₂O][H₂O₂] = k₅[I₂O] \]

\[ r₈ = (k₆ + k₇[H⁺])[HIO][H₂O₂] = k₆ \]

in this catalytic steady state, the following equalities can be written:

\[ r_2 + r_3 = r_3 + r_6 \]  
\[ r_1 + r_6 + r_7 = r_7 + r_2 + r_3 \]  
\[ r_1 + 2r_3 + r_4 + r_6 = r_7 + r_2 + 2r_3 + r_4 + r_5 \]  
\[ r_7 + r₈ + r₉ = r_1 + r_2 + r_₈ \]  
\[ r_4 = r_₈ \]  

Solving these, the steady-state concentrations of the intermediates considered, in the stable catalytic steady state, can be obtained:

\[ \frac{k_3}{k_₈} \frac{[HIO]_₆}{[I⁻]_₆} (k_₇ + [I⁺]_₆) + k_₇ \]

\[ = k_₅[I₂][I₂O] + k₆ \]  
\[ \frac{k_₇}{k₈} \frac{[HIO]_₈}{[I⁻]_₈} \left(1 + \frac{k_₇}{k₈} \frac{[I⁻]_₈}{[I⁺]_₈} \right) = k₅[I₂][I₂O] + k₆ \]  
\[ \frac{[HIO₂]_₈}{[I⁻]_₈} = \frac{k₇}{k₈} \frac{[HIO]_₆}{[I⁺]_₆} \]  
\[ \frac{[I₂O]_₈}{[I₂]₈} = \frac{k₆}{k₇} \frac{[HIO₂]_₈}{[I⁻]_₈} \]  

The steady-state concentrations of intermediates for the model under consideration are presented in an explicit form in ref. 26.

Pseudo-steady states for reactions (R) and (O)

When the catalytic steady state is unstable and iodine is an external species, one cannot write eqn. (5) for the stationarity of iodine. Only the pseudo-stationarity of I⁻, HIO, HIO₂ and I₂O concentrations can be assumed, and eqns. (I)–(IV) hold. By linear combinations among these four equations some useful relations can be obtained:

\[ r₃ - r₈ = r_2 - r₆ = 2(r₆ - r₈) = r₁ - r₇ + r₈ \]

\[ = \frac{k₆}{k₇} (r₆ - r₇ + r₈) \]  

so that the time evolution of iodine can be expressed in different forms:

\[ \frac{d[I⁺]}{dt} = r₄ - r₈ = \frac{r₃ - r₈}{2} = \frac{r₂ - r₆}{2} \]  

The system cannot stay in the unstable catalytic steady state. Therefore, we ought to analyse its behaviour in the vicinity of the state mentioned. To this aim, we shall first
derive a relation, resulting from eqn. (I), (III) and (IV), which is more convenient for further calculation:

\[
\delta = \frac{k_3 k_8}{k_{-3} k_9 [\text{HIO}]_o} \beta
\]

The set of equations, consisting now of eqn. (I), (II), (XII) and (XIII), we shall transform to the dimensionless form using the following dimensionless concentrations

\[
X = [\Gamma_-]/[\Gamma_-]_o
\]

\[
Y = [\text{HIO}]/[\text{HIO}]_o
\]

\[
Z = [I_2]/[I_2]_o
\]

\[
U = [\text{HIO}_2]/[\text{HIO}_2]_o
\]

\[
V = [I_2O]/[I_2O]_o
\]

and the corresponding parameters

\[
\alpha = 1 + \frac{k_6}{k_3}
\]

\[
\beta = \frac{k_3 [\Gamma_-]_o}{k_{-1} [\text{HIO}]_o}
\]

\[
\gamma = \frac{k_7}{k_{-1} [\text{HIO}]_o}
\]

With these parameters we write the equation of the nullcline\textsuperscript{28} in the concentration phase space \((X, Y, Z, U, V)\) as follows

\[
(s - 1)UX + Y^2 = \alpha V
\]  \hspace{1cm} (XIV)

\[
(1 + \gamma - \delta)X + \beta V + \delta = (\beta X + Y + \gamma)U
\]  \hspace{1cm} (XV)

\[
UY + (\beta + \gamma - \delta)Y = (1 + \gamma - \delta)X + \beta UX
\]  \hspace{1cm} (XVI)

\[
\frac{dZ}{d\tau} = XY - Z = \frac{\beta Y}{2(\alpha - 1)} (V - Y^2)
\]  \hspace{1cm} (XVII)

where \(\tau = k_{-4} t\) is the dimensionless time.

It is easier to analyse the projections of this nullcline on the phase planes. Therefore, from eqn. (XIV) and (XV) we first calculate \(U\) and \(V\) as functions of \(X\) and \(Y\),

\[
U = \frac{\alpha \delta + \alpha (1 + \gamma - \delta)X + \beta Y^2}{\alpha Y + \alpha Y + \beta X}
\]  \hspace{1cm} (XVIII)
Replacing Eqn. (XX) expresses the nullcline in the \( XÈY \) and insert them into eqn. (16) and the second equality of eqn. (17)

\[
\beta(\alpha + 1.5)(1 + \gamma - \delta)X^2 + \beta^2XY^2 - (\beta + \gamma - \delta)\beta XY
+ [\alpha(1 + \gamma - \delta) + \beta\delta(\alpha + 0.5)]X
= 1.5\beta Y^2 + [\alpha(\beta + \gamma - \delta) + 0.5\beta\gamma]Y^2
+ \alpha(\delta + \gamma(\beta + \gamma - \delta))Y
\]

\[
Z = XY - \frac{\beta^2(\delta X + (1 + \gamma - \delta)X^2 - \gamma Y^2 - \gamma Y^2)}{2\mu(1 + \gamma - \delta(\alpha + \beta X))} \tag{XXI}
\]

Eqn. (XX) expresses the nullcline in the \( XÈY \) phase plane. Replacing \( X \) and \( Y \) from eqn. (XX) in eqn. (XXI), we obtain the equation of the nullcline in the \( XÈYÈZ \) phase space. The projections of this nullcline on \( XÈZ \) and \( YÈZ \) phase planes are presented in Fig. 3 and 4, respectively.

In Fig. 3(a) and 4(a), in particular, the projections of the nullcline in the \( XÈZ \) and \( YÈZ \) phase planes when the system

is in the stable catalytic steady state are presented. The time evolution of the system is then relatively simple. Starting from the state when \([I_{3}]\) is very low or zero, the system undergoes such changes that \([I_{2}]\) and \([I^{-}]\) increase, \([I^{-}]\) passes through its maximum and, eventually, the system reaches the stable catalytic steady state in which \([I_{2}]\) remains constant [Fig. 3(a)]. However, in the closed, well stirred reactor, \([I_{2}]\) decreases slowly, since \([I_{2}]_{\text{eq}}\) is a function of the hydrogen peroxide concentration which decreases with time by reaction (D). If the system starts its evolution from the right side of the point denoting the steady state, \([I_{2}]\) and \([I^{-}]\) decrease, \([I^{-}]\) passes through its minimum and, eventually, the system reaches the same stable catalytic steady state in which \([I_{2}]\) remains constant [Fig. 3(a)]. In Fig. 4(a), the corresponding evolution of \([HIO]\) can be seen.

In Fig. 3(b) and 4(b) the projections of the nullcline on the \( XÈZ \) and \( YÈZ \) phase planes when the catalytic steady-state is unstable, are presented. Then, starting from the state in which \([I_{2}]\) is very low or zero, the system changes so that \([I_{2}]\) and \([I^{-}]\) increase, \([I^{-}]\) passes through its maximum, and system reaches the point \( A \) [Fig. 3(b)]. At this point, \( dZ/dt \) is still positive but \( Z \) cannot increase along the nullcline. The system must leave this branch of the nullcline. The concentrations are

![Fig. 3](image-url)  
![Fig. 4](image-url)
no longer pseudo-stationary. (This point corresponds to point e of Fig. 1 and 2.) The iodide concentration decreases rapidly and the system jumps to the lower branch of the nullcline, where $I_2$ decreases (point f in Fig. 1 and 2). At the point B a situation similar to that at point A sets in. The derivative $dZ/dt$ is negative, but $Z$ cannot decrease along the nullcline. The iodide concentration increases rapidly (the point g in Fig. 1 and 2) and the jump onto the upper branch of the nullcline is the only possible way out for further evolution of the real system (point h in Fig. 1 and 2). In Fig. 4(b), the corresponding evolution of [HIO] can be seen. The real system follows the trajectory AA'BB' around the unstable steady state, producing one relaxation oscillation.28

During monotonic catalysis, the S-shaped curves presented in Fig. 3(b) and 4(b) cannot be obtained, which is in accordance with the calculations, on the grounds of the instability condition of the same model.24,26 Hence, the system converges to the stable catalytic steady state [Fig. 1 and 2(a)–(d)].

Thus, analysis of the evolution of the system in the stable and unstable catalytic pseudo-steady state by numerical integration [the point N in Figures 2(a)–(h)] shows that the system is almost permanently in the steady states, except during the transitions between the reduction (R) and oxidation (O) steady states in the oscillations.

**Conclusion**

The considered model (r1)–(r8) can predict all the main steady-state pathways [denoted by reactions (D), (R) and (O)], found during the experimental monitoring of the BL system, and proposed by Bray in 1921.1 The trajectories calculated by numerical integrations are in excellent agreement with those derived by the pseudo-steady state hypothesis. Hence, the approximations necessary to obtain the equation of the nullcline, eqn. (XIV)–(XVII), are verified. Consequently, as the numerical simulations have to give results close to the experimental ones, the analytical calculations presented here are very useful in selecting the values for the rate constants of the particular reactions. More specifically, not the rate constants, but the set of constants appearing in the normalized differential equations of the model and denoted here by $a$, $b$, $\gamma$ and $\delta$, which must be adjusted in such a way that the resulting form of particular phase trajectory is in accordance with the corresponding oscillation presented in the phase space. Moreover, the relations for the stationary state concentrations have to be satisfied and correlated with the experimentally ordered ones.

Closing the parameters in their narrow domains by the proposed selection procedure, numerical integration is simplified. This is much better than trying to guess the rate constants doing many numerical integrations without guidance. Although the calculations are carried out for one model of the BL reaction, the procedure is general, irrespective of the model and reaction under consideration.

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**References**