Experimentally observable transitions between dynamical states in complex reaction systems

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Abstract

Identification of trends and their correspondence with dynamical state transitions are briefly discussed on several reaction network models. The influence of different threshold values on the trend analysis and dynamical state analysis results is examined. Both methods are applied here to the results of the numerical simulation. For this purpose the models of three reaction systems are used: simple model of consecutive, first order, equilibrium reactions, partial oxidation of cyclohexane, and model of the oscillatory reaction Bray Liebhafsky.

Detailed kinetic analysis confirmed that transient dynamical states may be identified through the symbolic representation of the sequence of trend episodes in experimentally obtainable time series. Stoichiometric Network Analysis of possible dynamical states was used to identify reaction pathways responsible for the sequences of trend episodes. Some technical problems were also addressed, connected with selection of the threshold value and dynamical state notion.

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Keywords: Dynamical states; Trend analysis; Non-linear reaction kinetics; Reaction pathways; Non-linear chemical dynamics; Chemical oscillations

1. Introduction

Complex reaction systems are very common in nature, as well as, in human made environments (Nicolis & Prigogine, 1990) Atmosphere chemistry (Clapp & Jenkin, 2001; Finlayson-Pitts & Pitts, 1997; Prinn, 2003) and realistic industrial catalytic processes (Berezin, Denisov, & Emanuel, 1969; Coppens & Froment, 1996; Quiceno, Perez-Ramirez, Warnatz, & Deutschmann, 2006) are examples of very complex systems. Also, biochemical reaction networks with hundreds of different reaction species and elementary reactions are subject of recent investigation (Cox et al., 2006; Palsson, Price, & Papin, 2003) Without a doubt, in complex reaction systems one can find fascinating kinetic phenomena, like multi-stability, excitability, oscillations, traveling waves and chaos (Field & Burger, 1985; Gray & Scott, 1990; Kolar-Anić, Stanisavljev, Krnajski Belovljev, Peeters, & Anić, 1990; Schmitz, 1990; Schmitz, Kolar-Anić, Anić, & Čupić, 2000; Schmitz, Kolar-Anić, Anić, Grozdić, & Vukojević, 2006; Scott, 1991). Moreover, variety of different shapes in the signal time sequences may occur in almost any chemical reaction, during the transition periods. Any reaction system starting from some arbitrary initial conditions and traveling to final steady or equilibrium state has to pass through the distant regions of phase space while number of different chemical species is simultaneously transformed through the reaction network (Higgins, 1965; Schmitz, 1990).

On the other hand, it is rarely necessary to know all details of the reaction mechanism of most processes proceeding under well controlled and only slightly variable reaction conditions. In most cases, reaction dynamics is reduced to lower dimensional attractors, simplifying the underlying mathematical models. According to (Higgins, 1965), who did early systematic study of the oscillatory reactions (Higgins, 1967), especially in biochemical systems, the reaction dynamics, in general, can be reduced to transitions between different dynamical states. In order to illustrate the changes in the reaction system regimes Higgins developed a concept of dynamical state level diagrams, based on the general description of the dynamical systems with different time scales (Fig. 1). Motion of the dynamical system in phase space, was depicted in Higgins’s work through the transition between distinct states – special states in the state space, where the motion of the dynamical system obeys a reduced set...
of equations – dynamical states. Moreover, system moves from one to another dynamical state within a characteristic time, more specifically half-life period of the dynamical state.

Higgins (1965) used terms of new species, defined as equilibrated fast species. In the Higgins’s paper (1965) this new hypothetical species corresponds to some specific dynamical state of the system. For example, in the case of two consecutive reversible reactions illustrated in Fig. 1, the symbol A(eq)B stands for the new hypothetical species, corresponding to equilibrated A and B, and A(eq)B(eq)C corresponds to the equilibrium.

Fig. 1. Dynamical state level diagram for the reaction A ⇌ B ⇌ C.

Higgins used dynamical state transitions to explain the control mechanism in cellular reactions with complex reaction kinetics, and further to develop the theory of oscillatory reactions (Higgins, 1967). He defined three kinds of species which differ in respect to the level of the corresponding dynamical state. Variables “well below” the level of the actual dynamical state (at frequency scale) can be approximated as constant and classified as structural control variables (SCV). Variables “well above” given level can be referred as hidden variables, since they will not generally be excited and they have no effect. These are the fast, dependent variables which do not enter reduced differential equations. Finally, between these extremes there are independent dynamical variables (Higgins, 1965, 1967). Obviously, the choice of the dynamic variables is dependent on actual dynamical state and further on the time scale of interest.

Although the concept of dynamical state level diagrams is not widely accepted, reaction systems with multiple time scales are studied extensively. Schmitz defined criterion for quasi-steady states, that can also be useful for choice of dynamical variables and hence, for identification of actual dynamical states (Schmitz, 1983). It is based on the ratio between the values of net-flux and one-direction-flux through the particular species of the reaction network. In the equilibrium state net fluxes are identical to zero for all species, since the rates of formation are equal to the rates of the destruction:

\[ r_+ = r_- \]

where \( r_+ \) is the rate of formation, and \( r_- \) is the rate of destruction for some species.

However, in non-equilibrium systems there is always non-zero net reaction in which some reactants are spent and some products are formed. Therefore, the rate of concentration changes of these external species is also non-zero. There is usually other kind of species which are formed and destroyed by the reaction network processes, and they will be called internal ones. The rate of change of the internal species concentration is then:

\[ \dot{x} = \sum r_+ - \sum r_- \]

where the summation is over all the reactions in which the specified species are formed or destroyed, respectively. If internal species is formed and destroyed with equal rates, steady state approximation is applicable:

\[ \sum r_+ = \sum r_- \]

If the reaction rates are dependent on slowly changing concentrations of the external species (reactants and products), then the steady state concentrations of the internal species also depend on time. Therefore, the rates of formation or destruction of the internal species will not be exactly equal and we have quasi-steady-state approximation:

\[ r_{\text{net}} = \left| \sum r_+ - \sum r_- \right| \approx 0. \]

The choice of internal species in this case depends on the time scale of interest. According to Schmitz criterion (Schmitz, 1983), we can say that some species is in quasi-steady-state if the rate of its concentration change is much lower than both, the sum of the rates of its formation and the sum of the rates of its destruction:

\[ r_{\text{net}} \ll \sum r_+ \wedge (r_{\text{net}} \ll \sum r_-) \]

We can use Schmitz criterion (5) to define which species are the equilibrated ones, according to Higgins terminology, and hence to identify dynamical state of the system.

Also, other forms of transitions between different dynamical states were studied in the multiple time scale systems (Gray & Scott, 1990). It seems that the transition between dynamical states or quasi-steady states in chemical reaction systems is connected with changes in dominating reaction pathways. Moreover, different reaction pathways can sometimes be ascribed to different kinetic behavior of the reaction systems at different time scales. Bray already noticed in the first description of a homogeneous oscillatory reaction (Bray, 1921), that during the oscillations, sequence of periods can be observed, where the domination is exchanged between the reduction of iodate and the oxidation of iodine by hydrogen peroxide. This oscillatory reaction, now known as the Bray–Liebhafsky (BL) reaction, is hydrogen peroxide decomposition to water and oxygen with iodate ions as a catalyst, present in acid medium (Anić, Mitić, & Kolar-Anić, 1985; Bray, 1921; Bray & Liebhafsky, 1931; Matsuzaki, Alexander, & Liebhafsky, 1970; Woodson & Liebhafsky, 1969). In their papers (Kolar-Anić, Čupić, Anić, & Schmitz, 1997; Schmitz, 1998) the authors described BL oscillatory reaction dynamics as a dynamical system with multiple
The progress of the reaction system in state space during the oscillations was described as a sequence of changes in dominating reaction pathways. Different reaction pathways in oscillatory reactions were also studied by Clark, Schmitz, Schreiber, Anić, Kolar-Anić, using the Stoichiometric Network Analysis (Clarke, 1980, 1988; Schmitz, 1991; Schreiber, Hung, & Ross, 1996; Strasser, Stemwedel, & Ross, 1993). In further investigation of the BL system, activation energies were evaluated, corresponding to different reaction pathways and characterizing different segments of time series data (Anić, Kolar-Anić, & Koros, 1997; Ćirić, Anić, Ćupić, & Kolar-Anić, 2000). Small differences in the reaction pathways would be added: “0,” “+,” and “−,” corresponding to kinetic curves with minimum and maximum values. However, it is usually more convenient to divide kinetic curve in separate trend episodes ending at these easily identifiable points.

It can be postulated that different trends are somehow connected with some sort of dynamical states. Due to possible importance of trend analysis for the detection of dynamical states and for the detection of transitions between them, a brief review of recent achievements in the area is given below.

Various approaches were used for trend detection in time series, from simple regression to fuzzy logic (Melek et al., 2005). Several problems arose in application of trend analysis, such as, numerical problems in treating noisy data, non-linearity detection, or model identification.

On-line extraction of semi-qualitative temporal episodes from any univariate time-series was developed in (Charbonnier et al., 2005). Only three primitives were used here to describe the episodes: Increasing, Decreasing and Steady. The method acts on noisy data, without prefiltering. It consists of several steps, including: (1) on-line segmentation of data into linear segments, (2) classification of the last segment into semi-quantitative episode, using three primitives, and (3) aggregation of the current episode to the previous one to form the trend. The method was designed to be useful engineering tool in control of the end product quality, depending on variations in raw materials as input (Charbonnier et al., 2005).

Another simple but effective approach was proposed (Zaliapin et al., 2004), based on piecewise linear approximation of time series. Computationally effective algorithm was constructed for the decomposition of a time series into a hierarchy of trends at different scales. This approach was particularly appropriate for self-affine analysis and obtaining of local fractal properties of the processes. It also allows detection of the non-linear correlations in non-linear, long-term trends (Zaliapin et al., 2004).

Automatic detection of trends was proposed (Dash et al., 2004) based on polynomial-fit based interval-halving technique, with wavelet based denoising. The least-order (among constant, first-order and quadratic) polynomial with fit-error statistically insignificant compared to noise (as dictated by F-test) is used to represent the segment. If the fit error is large even for the quadratic polynomial, then the length is halved and the process is repeated on the segments. Finally, a unique assignment of qualitative shape is made to each of the identified segments (Dash et al., 2004).

Finally, trend analysis was also the underlying method in a tool (TAM-C) developed for the automatic identification of mathematical models of chemical reaction systems (Schaich et al., 2001). The software imitates human ability to reason about system structure and system behavior at a qualitative level. Temporal shape of a continuous variable was described by a

Table 1
Types of the episodes

<table>
<thead>
<tr>
<th>Type</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>x(t)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dx/dt</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>0</td>
</tr>
<tr>
<td>d²x/dt²</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
sequence of, so called, episodes, and this sequence is called history. Episode is a time interval in which signs of the first and the second time derivative of the variable are not changed. Each episode is described by the +, 0 or - sign combination for the two derivatives.

To overcome measurement noise which is usually present in real data, the obtained time series is smoothed by cubic splines here (Schaich et al., 2001). At the end, the authors sought for a model which gives the same qualitative history with transitions somewhere in the intervals determined by the experiments. Therefore, the so-called, interacting interval simulation was used here, for the interval identification in specific cases. Finally, the procedure was used to identify model parameters of the industrial process (Schaich et al., 2001).

In the present paper, identification of trends and their correspondence with dynamical state transitions are briefly discussed on several reaction network models. The influence of different threshold values on the trend analysis and dynamical state analysis results is examined. Both methods are applied here to the results of the numerical simulation, because, only in this case the actual dynamical states of the system are known. For this purpose the models of three reaction systems are used: simple model of consecutive, first order, equilibrium reactions, already discussed by Higgins (1965), partial oxidation of cyclohexane (Khar’kova, Arest-Yakubovich, & Lipes, 1989), and model M(1-8) of the oscillatory reaction Bray–Liebhafsky (Kolar-ANIć, Mišlenović, Anić, & Nicolis, 1995a; Kolar-ANIć, Vukelić, Mišlenović, & Anić, 1995b).

2. Procedures and models

2.1. Numerical simulations

The numerical simulation was performed with the Gear algorithm (Gear, 1971), suitable for the integration of stiff differential equations.

2.2. Dynamical state analysis

Dynamical states were determined for every point of the time sequence, according to the slightly changed Schmitz criterion function:

$$\frac{r_{\text{net}}}{r_{\text{tot}}} = \frac{\sum r_+ - \sum r_-}{\sum r_+ + \sum r_-} < \varepsilon,$$

where $\varepsilon$ is a threshold value. We found criterion (6) more efficient in computing then (5), since it contains only one inequality. It is also applicable in systems arbitrarily far from equilibrium, either if the species are produced or destroyed in net reaction. Therefore, the condition (6) is checked in every point of the numerical simulation, for each of the selected internal variables, and dynamical states are identified as a combination of the variables fulfilling the condition (6). Higgins notion was used for the dynamical states, where it was applicable (Models M 1 and M 2) since it clearly indicates dynamics in simple models. However, in complex cases with several possible reaction pathways (Model M 3) only the stoichiometry of the net reaction was indicated.

2.3. Trend analysis

For the purpose of trend analysis, the formulas of the first and the second derivative of the concentrations were evaluated analytically as a function of the concentrations and their values were calculated along the numerical simulation. Obtained values of the derivatives were compared with chosen threshold value and appropriate combination of $-\; 0\; +$ signs was ascribed to the episode. Sequences of episodes (with notion explained in Table 1 of Section 1) are obtained as the result of this method.

2.4. Transitions between dynamical states

As mentioned before, in the most complex case with several possible reaction pathways (Model M 3) only the stoichiometry of the net reaction was used to indicate dynamical state, in order to keep the continuity with Higgins approach. However, the complete Stoichiometric Network Analysis (Clarke, 1980, 1988) was applied on the model with different combinations of quasy-steady species to identify transitions between dynamical states—transient states. Stoichiometry of the slow-species steady state pathways was easily connected with the first derivative of their concentration changes over time. Information contained in the second derivative changes was correlated with stoichiometry of the pathways corresponding to different combinations of quasy-steady species. Therefore, more detailed kinetic consideration of the feedbacks in the reaction network was necessary for other possible pathways in transient dynamical states.

2.4.1. Model 1

The first example is simple model of consecutive, first order, reversible reactions M 1 (Table 2). This is the same example which Higgins (1965) used to illustrate systems with different dynamics in weak excitation and strong excitation. Also, the same example was used for the illustration of the linear systems in (Kolar-ANIć, Anić, & ˇCupić, 2005). This simple example can show us the importance of the appropriate choice of the threshold values in both dynamical state analysis and trend analysis.

Writing the rate equation with respect to the intermediate B in the form

$$\frac{d[B]}{dt} = k_1[A] + k_{-2}[C] - (k_{-1} + k_2)[B],$$

we can see the linear terms with respect to exponents on the concentrations in all three terms at the right hand side. The last three terms contain contributions of the species B, C, and A, respectively.
equation can be rewritten in the form

\[
d[B] = \lambda - k[B]
\]

(8)

where \( k = k_{-1} + k_2 \) is a constant, whereas \( \lambda = k_{1}[A] + k_{-2}[C] \) is a parameter that varies in time as a function of time dependent concentrations of species A and C. Such parameter that defines the state of the system is control parameter. The non-equilibrium stationary state (steady state) is satisfied always when \( d[B]/dt \) is equal to zero. Consequently, the stationary state concentration of intermediate B, as the only function of state of considered reaction system,

\[
[B]_{ss} = \frac{\lambda}{k}
\]

(9)

is a linear function of \( \lambda \). However, \( \lambda \) depends on the concentrations of A and C, and consequently on time. Therefore, we can only quasi-steady state approximation (Eq. (5)) and it is a non-trivial problem to define the conditions where it is applicable.

### 2.4.2. Model 2

Our second example M 2 (Table 3) is the Model of Khar’kova et al. (1989) for the non-catalytic partial oxidation of cyclohexane. This model should demonstrate the richness of the information obtainable from the trend analysis, and to confirm their correspondence with dynamical state analysis in multi-variable systems. Rate constants listed with model M 2 are from the original paper.

The partial oxidation of cyclohexane (Ch) to a mixture of cyclohexanol (ChOH) and cyclohexanone (ChO) is an important homogeneous catalytic industrial process with soluble cobalt catalyst. Usually some quantity of cyclohexyl hydroperoxide (COOH) is also obtained, as an intermediary of the main products ChOH and ChO. Homogeneous catalytic process is usually stopped at conversion values of 3–8 mol%, and at selectivity of 70–80 percent with the ChO/ChOH ratio below one (Berezin et al., 1969; Schuchardt, Carvalho, & Spinacé, 1993; Schuchardt et al., 2001).

The reaction kinetics of the Ch oxidation depends on the mechanism of the heterogeneously or homogeneously catalyzed reaction, but also on the influence of the reactor walls, the mechanism of the uncatalyzed thermal oxidation process and the mass transport limitations. There is a general agreement in the literature that cyclohexane is oxidized in a radical-initiated reaction (Berezin et al., 1969; Khar’kova et al., 1989; Pohorecki et al., 2001). Recent kinetic and thermochemical analyses of the catalytic oxidation of lower alkanes confirmed that the formation of free alkyl radicals is the most energetically feasible process of the initial molecule activation (Sinev, 2003).

At temperatures higher than 150°C, the cyclohexane oxidation also occurs as a thermal, non-catalytic process (Khar’kova et al., 1989). The mechanism of the non-catalytic cyclohexane oxidation is important since it also gives a significant contribution to the catalytic process. The simplified reaction scheme of Khar’kova et al. (1989) with 19 reactions was reported to give a good correlation with experiments. The application of this model is limited to conversion levels lower than 8 percent.

The intermediary role of ChOOH in this complex multi-variable system with many reactions is a good example for the study of possible correspondence between dynamical states and kinetic trends. In many simplified models of the process the ChOOH appears as the unstable product, or as the stable intermediary species, while the free radicals are usually treated as fast variables (hidden variables in Higgins terminology). These simplified models can be recognized as special dynamical state representations of the full model. It was accepted in these simplified models that ChOH and ChO are produced from ChOOH through independent pathways, but also that ChOH is further oxidized to ChO, which is further oxidized to the deep oxidation products (Pohorecki et al., 2001; Schuchardt et al., 1993, 2001).

### 2.4.3. Model 3

Our last example, the famous BL reaction (Bray, 1921; Bray & Liebhafsky, 1931) should ensure us that dynamical state analysis and trend analysis are useful for the understanding of the complex reaction mechanisms and corresponding reaction dynamics. The BL reaction is a decomposition of hydrogen peroxide into water and oxygen in the presence of iodate and hydrogen ions, according to the following stoichiometry:

\[
2\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + 2\text{H}_2\text{O} + \text{O}_2.
\]

(D)

This apparently simple reaction comprises a complex homogeneous catalytic oscillatory process involving numerous iodine intermediates (Bray, 1921; Charma & Noyes, 1976; Degn, 1967; Liebhafsky, Furuichi, & Roe, 1981; Peard & Cullis, 1951; Schmitz, 1999). The global reaction (D) is the result of the reduction (R) of iodate to iodine and the oxidation (O) of iodine to...
The decomposition of hydrogen peroxide in the presence of hydrogen and iodate ions is a complex process catalyzed by iodate and iodine as a catalytic couple. All three reactions (D), (R) and (O) that we mentioned until now to explain possible mechanism, are the net ones. Besides, it is well known (Bray, 1921) that the rate of oxygen production during the domination of the reaction (O) is several times higher than during the domination of the reaction (R), although oxygen is not a product of the reaction (O). Hence, some other reaction steps ought to be included in the model of mechanism, having (D), (R) and (O) as the net reactions of corresponding pathways. At present, there is one such model with its different variants (Čupić & Kolar-Anić, 1999a,b; Schmitz, 1987; Kolar-Anić et al., 1995a,b). Although all variants, including the core of a model consisted of the first six reactions proposed by Schmitz (1987), are able to describe the oscillatory evolution, the version with the following eight reactions (Table 4) has been found as the most successful in simulating the lot of experimentally observed phenomena in a closed and open reactor:

Extreme currents of the model determined in previous work, by the Stoichiometric Network Analysis, have the overall net reaction (D). In this case, iodate ion was not explicitly treated as internal one, but it is linearly dependent on other, internal iodine species through the conservation law. However, if the iodine, as dynamically slow species, is treated as the external one, new reaction pathways are generated with net reactions (R) and (O).

Oscillations in this model are of the relaxation type. The BL system is moving along the nullcline corresponding to the steadiness of the fast variables $I^-$, HIO, HIO$_2$ and I$_2$O, which has three branches near the steady state. Middle one is unstable and it repels the system toward the other two, between which system oscillate. More or less smooth moving along the two stable branches corresponds to (R) and (O) pathways stoichiometries, involving the I$_2$ as the slow species. At the ends of the two stable branches system jumps between them, revert direction and alternate the stoichiometry between (R) and (O) (Kolar-Anić et al., 1997).

### 3. Results and discussion

#### 3.1. Model 1

Rate constants and initial concentrations in the Model 1 (equations in Section 2.4.1) simulation were chosen so that maximum occurred in concentration of intermediary B, after short time and dynamical system remains in quasi-steady state for a long time, as it is illustrated in Fig. 2, corresponding to the case when $k_1 + k_{-1} > k_2 + k_{-2}$ in Higgins’s paper (1965). However, picture looks different on different time scales (Fig. 2).

The cross points with several threshold values used in dynamical state analysis are indicated in Fig. 3, for all three species in M 1. Like the dynamical states, the episodes obtained by the trend analysis of the time sequence for the B species, also depend on the threshold value.

Several different thresholds $s$ were used for the derivatives and $r_{\text{tot}}/r_{\text{tot}}$ ratio. Sequences of dynamical states were detected depending on the threshold value, chosen for the criterion (Tables 5–7). There is no quantitative match between critical

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### Table 4

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$IO_3^- + I^- + 2H^+ \rightleftharpoons HIO + HIO_2$</td>
<td>$r_1 = k_1^0[HIO] \cdot [H^+] \cdot [I^-], r_{-1} = k_{-1}^0[HIO_2]$</td>
</tr>
<tr>
<td>$HIO_2 + I^- + H^+ \rightleftharpoons I_2O + H_2O$</td>
<td>$r_2 = k_2^0[HIO_2] \cdot [H^+] \cdot [I^-]$</td>
</tr>
<tr>
<td>$I_2O + H_2O \rightleftharpoons 2HIO$</td>
<td>$r_3 = k_3^0[H_2O], r_{-3} = k_{-3}^0[HIO]^2$</td>
</tr>
<tr>
<td>$HIO + H^+ + I^- \rightleftharpoons I_2 + H_2O$</td>
<td>$r_4 = k_4^0[HIO] \cdot [I^-] \cdot [H^+] - r_{-4} = k_{-4}^0[I_2][H^+]$</td>
</tr>
<tr>
<td>$HIO_2 + H_2O \rightleftharpoons I_2O + H_2O + 2H^+$</td>
<td>$r_5 = (k_5^0 + k_5^1[H^+])[HIO] \cdot [I_2O]$</td>
</tr>
<tr>
<td>$I_2O + H_2O \rightleftharpoons HIO + HIO_2$</td>
<td>$r_6 = k_6^0[I_2O] \cdot [H_2O]$</td>
</tr>
<tr>
<td>$HIO_2 + H_2O \rightleftharpoons I_2O + H^+ + H_2O$</td>
<td>$r_7 = k_7^0[HIO_2] \cdot [H_2O]$</td>
</tr>
<tr>
<td>$IO_3^- + H + H_2O_2 \rightleftharpoons HIO_2 + O_2 + 2H_2O$</td>
<td>$r_8 = (k_8^0 + k_8^1[H^+])[IO_3^-] \cdot [H_2O_2]$</td>
</tr>
</tbody>
</table>
Fig. 2. Initial part of the numerical simulation of Model 1 (two consecutive equilibrium reactions) \([B]_0 = 1 \times 10^{-8} \text{ mol dm}^{-3}, [C]_0 = 1 \times 10^{-8} \text{ mol dm}^{-3}\) and rate constants given in Table 2. Small figure inside shows the same system evolution on extended time scale.

Table 5
Dynamical states and trend episodes of Model 1 with threshold value \(\varepsilon\) equal to 1/3

<table>
<thead>
<tr>
<th>Time interval</th>
<th>Type</th>
<th>Trend episodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–57</td>
<td>A (\rightarrow) B, A (\rightarrow) C</td>
<td>0–49 +, −</td>
</tr>
<tr>
<td>57–58</td>
<td>A\textsuperscript{B\textsubscript{eq}} (\rightarrow) C</td>
<td>≥ 49 0, −</td>
</tr>
<tr>
<td>58–23,289</td>
<td>(A\textsuperscript{eq}B) (\rightarrow) C</td>
<td>≥ 23,289 0, 0</td>
</tr>
</tbody>
</table>

Table 6
Dynamical states and trend episodes of Model 1 with threshold value \(\varepsilon\) equal to 1/10

<table>
<thead>
<tr>
<th>Time interval</th>
<th>Type</th>
<th>Trend episodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–92</td>
<td>A (\rightarrow) B, A (\rightarrow) C</td>
<td>0–80 +, −</td>
</tr>
<tr>
<td>92–97</td>
<td>A\textsuperscript{B\textsubscript{eq}} (\rightarrow) C</td>
<td>80–82 0, −</td>
</tr>
<tr>
<td>≥ 97</td>
<td>(A\textsuperscript{eq}B) (\rightarrow) C</td>
<td>≥ 82 0, 0</td>
</tr>
</tbody>
</table>

Table 7
Dynamical states and trend episodes of Model 1 with threshold value \(\varepsilon\) equal to 1/100

<table>
<thead>
<tr>
<th>Time interval</th>
<th>Type</th>
<th>Trend episodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–134</td>
<td>A (\rightarrow) B, A (\rightarrow) C</td>
<td>0–127 +, −</td>
</tr>
<tr>
<td>134–170</td>
<td>A\textsuperscript{B\textsubscript{eq}} (\rightarrow) C</td>
<td>127–144 0, −</td>
</tr>
<tr>
<td>170–171</td>
<td>(A\textsuperscript{eq}B) (\rightarrow) C</td>
<td>≥ 144 0, 0</td>
</tr>
<tr>
<td>≥ 171</td>
<td>(A\textsuperscript{eq}B) (\rightarrow) C</td>
<td>(A\textsuperscript{eq}B) (\rightarrow) C</td>
</tr>
</tbody>
</table>

With the highest threshold value in dynamical state analysis, the transition from zero state to the first dynamical state A\textsuperscript{B\textsubscript{eq}} \(\rightarrow\) C, was observed in the 57th minute. Since it lasts only a minute, we can consider it as meta-stable state which is soon subjected to new transition to stable dynamical state (A\textsuperscript{eq}B) \(\rightarrow\) C, in the 58th minute. The new state lasts for a long time, before the system goes to its final state—equilibrium (A\textsuperscript{eq}B\textsuperscript{eq}C).

Furthermore, when we used lower threshold value (\(\varepsilon = 0.1\)), the trend analysis was more sensitive and short living meta-stable state was detected as the episode “0, −,” between the 80th and the 82nd minute. In this short episode, negative sign of the second derivative of the B concentration over time is caused by the decreasing concentration of A, corresponding to dynamical state A\textsuperscript{B\textsubscript{eq}} \(\rightarrow\) C. At selected, same, threshold value, only two episodes were observed in the trend analysis of the evolution of the intermediary B concentration. The episode “+,” corresponds to zero state, and the episode “0, 0,” occurred in the 49th minute and lasted until the end of the simulation, corresponds to stable dynamical state, rather then to the meta-stable one, or to the final equilibrium state.

Finally, the same episodes were observed in the trend analysis with, even, ten times smaller threshold value (\(\varepsilon = 0.01\)). Only their position in time was changed. On the other side, picture is in this case changed in the dynamical state analysis. After the same beginning, dynamical state (A\textsuperscript{eq}B) \(\rightarrow\) C, appears to be meta-stable, with fast transition to new stable dynamical state B\textsuperscript{A\textsubscript{eq}} \(\rightarrow\) C. Equilibrium state was not detected here since numerical simulation was interrupted before the system reached new, lower threshold value (Fig. 3).
Table 8
Dynamical states and trend episodes of Model 2 obtained with respect to cyclohexylhydroperoxide, with threshold value $\varepsilon$ equal to 1/3 for dynamical states, $1 \times 10^{-5}$ for the first and $1 \times 10^{-8}$ for the second derivative of $[\text{ChOOH}]$

<table>
<thead>
<tr>
<th>Time interval</th>
<th>Type</th>
<th>Trend episodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>No significant amounts of ChOOH are produced during this period</td>
<td>0–5.12 $\times 10^{-12}$</td>
<td>0,0</td>
</tr>
<tr>
<td></td>
<td>5.12 $\times 10^{-12}$–3.95</td>
<td>0,–</td>
</tr>
<tr>
<td></td>
<td>3.95–8.737</td>
<td>0,0</td>
</tr>
<tr>
<td>0–4.15 $\times 10^3$</td>
<td>Ch + O$_2$ $\rightarrow$ ChOOH</td>
<td>8.737–4277</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4277–5062</td>
</tr>
<tr>
<td>$\geq 4.15 \times 10^3$</td>
<td>$4\text{Ch} + 3\text{O}_2 \xrightarrow{\text{CChOOH}} 2\text{ChOH} + 2\text{H}_2\text{O}$</td>
<td>5062–5129</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5129–5927</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5927–6126</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6126–7617</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\geq 7617$</td>
</tr>
</tbody>
</table>

as the points where these criterion functions are crossing with horizontal threshold value lines.

According to our results (Tables 5–7) different threshold values should be used for the two methods. Also, different threshold values should be used for the first and second derivative. Appropriate choice should be maid with trial-and-error method.

3.2. Model 2

**Dynamical state analysis and trend analysis** were performed with respect to cyclohexylhydroperoxide (ChOOH), as the main intermediary species.

The results of the **dynamical state analysis** of the full set of the variables show several fast transitions in the first several minutes. If we consider only ChOOH (Table 8) in the first five minutes we also have sharp jumps connected with fast free radical processes, but only two distinct stable states and one transition between them occurred after 4150 s. The first of them is the state of the system with (constant rate or decelerated) production of the ChOOH, and second stable state corresponds to quasi-steady-state approximation. As we saw before the results do depend on the threshold values used. Many other states are detected also corresponding to other intermediary species, but ChOOH was chosen as an example, which can be connected with real experiments.

In the **trend analysis** of this system, a long sequence of episodes was detected. Each episode corresponds to real changes in the curve shape and characteristic values of the derivatives (Fig. 4). At the early beginning of the reaction few episodes were detected connected with fast changes of free radical concentrations. Other episodes should also possibly be connected with the changes in the concentrations of other kinetically important species involved in the model, but it was not the purpose of the example. Our aim was to illustrate number of episodes occurring in simple kinetic data series of the classical intermediary species.

![Fig. 4. Concentration of ChOOH and its derivatives with time. Vertical lines are limits of the trend episodes and horizontal lines indicate threshold values.](image-url)
Inspection of Fig. 4 is persuasive in proving that the observed episodes are real and logical and not some numerical error. Curves of the first and the second derivative are typical for the wide peak shape of ChOOH kinetics. Observed episodes should be expected in any similar experiment. The decrease of the threshold value can only improve our ability to detect episode. On the other side, the increase of the threshold value may be necessary if data with noise is used, for example, when data from real experiment is analyzed. In this case, which will be discussed in future, too low threshold values can lead to a number of obscure episodes, not connected with underlying reaction mechanism.

3.3. Model 3

For the Numerical simulation of the BL reaction, rate constants and initial concentrations are chosen, giving typical oscillatory evolution of the iodine species concentrations (Fig. 5).

Long sequence of changes in trend episodes and dynamical states are determined from IO₃⁻ concentration data. Only repeating sequence in the oscillation train is analyzed here. One typical oscillation, shown in Fig. 6, was selected near the central point of the oscillatory period and used for the analysis. Corresponding episodes and dynamical states are listed in Table 9.

At the highest threshold value, only the status of IO₃⁻ changes during the oscillations. Therefore, the iodate is chosen here for the dynamical state analysis, although it is not one of the typical internal species of the BL reaction system. Namely, the steady state concentration of iodate is much higher than any other iodine species, and therefore it is usually treated as the external one. However, there is clear and strict linear dependence between the iodate concentration and other internal species, caused by the conservation law. Therefore, the iodate is treated here as the one of the internal species, for the purpose of dynamical state analysis, only.
In the trend analysis, lower threshold values had to be used for the derivatives of the time sequence of the IO$_3^-$ species (Table 9).

Correspondence between the episodes and dynamical states was established, based on the stoichiometry of the reaction pathways (D), (O) and (R), and on the sign of the first derivative of the IO$_3^-$ concentration only. To be precise, episodes with negative sign of the first derivative were assigned to the stoichiometry (R), those with positive sign of the first derivative to the stoichiometry (O), and those which are equal and iodate and iodine concentrations stopped changing, for a short time period corresponding to the stoichiometry (D)

The sign of the second derivative should correspond to the stoichiometry of other dynamical states and to the stoichiometry of other sub-processes. For example, Fig. 6(b) illustrates the changes of the HIO $r_{net}/r_{tot}$ values, which might be responsible for the observed change in the second derivative over IO$_3^-$ concentration with time. At least, the position of the peaks and its sign are in good correlation with the episodes. The observed sequence of the episodes, which can also be experimentally observed, corresponds to the sequence of the transitions between dynamical states.

We can start from the (R) dynamical state, corresponding to the one stable branch of the nullcline. It leads to the decrease of the iodate and the increase of the iodine concentration. Such a stoichiometry is a result of the net-summation of the pseudo-steady state currents for the case when iodate and iodine are slow species—they correspond to slow component of the dynamical system with different time scales. When the iodate concentration became low enough the rates of the (R) and (O) pathways became equal and iodate and iodine concentrations stopped changing, for a short time period corresponding to the stoichiometry (D), as it is traditionally interpreted.

Nevertheless, during this short time period, the rates of changes of other species concentrations became dominant. For example, HIO species have a sudden jump in production rate (Fig. 6), while the iodide suffers the opposite changes. If we search for the stoichiometry, responsible for the changes in HIO and iodide concentrations, than we must treat the HIO and iodide species as the external ones.

Thus, simple currents can be obtained corresponding to the oxidation or the reduction, (o) and (r).

\[
\begin{align*}
\text{(o):} & \quad I^- + H_2O_2 + H^+ \rightarrow HIO + H_2O \\
\text{(r):} & \quad HIO + H_2O_2 \rightarrow I^- + H^+ + O_2 + H_2O
\end{align*}
\]

Extreme currents responsible for the net reaction (o) are obtained combining reactions R$_2$ and R$_6$ or reactions R$_1$ and R$_7$. On the other side, extreme currents responsible for the net reaction (r) are obtained combining reactions R$_{-1}$ and R$_8$ or reaction R$_5$ alone.

During a period of the (o) process, occurring during the low iodate values after the (R) branch, HIO is generated (we do not know why—maybe because the iodate is now less important for the consumption of the iodide, then HIO$_2$). Hence, due to the process (o), the dynamical equilibrium of the reversible reaction R$_1$R$_{-1}$ is moved to a new position from which the R$_{-1}$ direction is favored and the process turns direction toward the (O) dynamical state and corresponding stable branch of the nullcline. Process (o) acts here as a trigger. After the (O) branch the opposite process happened, while the iodate concentration is high (we do not know why, again—maybe because high iodate concentration values can promote the (r) reaction through the R$_8$R$_{-1}$ extreme current, or, maybe more probably, because the low iodine values cannot compensate R$_5$ through the R$_{-4}$. This (r) process acts as a trigger for the R branch. The increase of the iodide concentration favored R$_1$ direction of the reversible process.

Definite answer on the question of the role of particular species cannot be given since there is no unambiguous decomposition of the steady state rates in contributions of its extreme currents.

This way, the (r) triggering process consisting from R$_5$ mainly, dominates at high values of the iodate concentrations. During this initiation of the reduction, high quantity of oxygen is liberated, which can be the wanted explanation for the experimental facts. If we use higher threshold value for the (r) and (o) dynamical states, we can get good agreement with obtained results for the trend analysis (Fig. 6a). On the other hand, if we use slightly lower threshold value the (r) branch can be spread far back in the region of the (O) branch, explaining the evolution of the oxygen even better (Fig. 6b). Therefore it seems that the model M(1–8) has the functional ability to explain the phenomena, but the rate constants should probably be adapted.

The qualitative trend analysis occurred here as the method to make an additional insight in the reaction mechanism of a complex chemical reaction.

4. Conclusions

The existence of the qualitative correspondence between dynamical state transitions and sequences of trend episodes is generally confirmed on all three analyzed reaction network models. Hence, it was clearly shown in the most complex case of the oscillatory reaction BL, Model 3, how transient dynamical states may be identified through the symbolic representation.

<table>
<thead>
<tr>
<th>Time interval</th>
<th>Type</th>
<th>Trend episodes</th>
<th>Time interval</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤314.6912</td>
<td>R</td>
<td>≤315.0702−315.0989</td>
<td>≤315.0702</td>
<td>−,0</td>
</tr>
<tr>
<td>314.6912−315.1564</td>
<td>D</td>
<td>315.0989−315.1175</td>
<td>0,+</td>
<td></td>
</tr>
<tr>
<td>315.1564−315.776</td>
<td>O</td>
<td>315.1175−315.2695</td>
<td>+,+</td>
<td></td>
</tr>
<tr>
<td>315.2695−315.2725</td>
<td>O</td>
<td>315.2725−315.8019</td>
<td>+,−</td>
<td></td>
</tr>
<tr>
<td>315.776−315.8246</td>
<td>D</td>
<td>315.8019−315.8064</td>
<td>0,−</td>
<td></td>
</tr>
<tr>
<td>≥315.8246</td>
<td>R</td>
<td>≥315.8064−315.854</td>
<td>≥315.854</td>
<td>−,0</td>
</tr>
</tbody>
</table>
of the sequence of trend episodes in concentration time series. Application of the Stoichiometric Network Analysis on different possible dynamical states, resulted here in the set of reaction pathways alternating their domination during the concentration oscillations. Detailed kinetic analysis of these reaction pathways enabled the identification of possible transitions between dynamical states with observed trend episode sequences.

In any reaction system detected episodes and dynamical states will depend on the threshold value, as shown in the analysis of the Model 1. According to our results different threshold values should be used for the two methods. In addition, different threshold values should be used for the first and the second derivative. Appropriate choice should be made with trial-and-error method. The new criterion function (6) was defined and successfully used in the dynamical state analysis.

Series of episodes are detected in a simple model of \( \text{O}_2 \) oxidation. It was shown that detected episodes are typical for any system with intermediary species whose concentration at the beginning increases and then decreases. The decrease of the threshold value can improve our ability to detect episode.

The observed sequence of the episodes in BL reaction model, which can also be experimentally observed, corresponds to the sequence of the transitions between dynamical states. The qualitative trend analysis occurred here as the method to make an additional insight in the reaction mechanism of the complex chemical reaction. Possible explanation for the oxygen evolution during the oxidation branch of the reaction is proposed.

Higgins notion is proved to be useful although not completely appropriate for complex reaction mechanisms with more then one reaction pathway. Dominating reaction pathways should also be specified for each dynamical state.

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References


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