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Oscillatory Carbonylation of Poly(Ethylene Glycol)Methyl Ether Acetylene. Modelling of Reaction Mechanism and Stoichiometric Network Stability Analysis

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Abstract

The reaction mechanism of palladium-catalysed oscillatory carbonylation of poly(ethylene glycol)methyl ether acetylene (PEGA) was examined by stoichiometric network analysis (SNA) of the stability of the dynamic states. The previously published simplified reaction network proposed to account for the experimentally observed results was modified in order to obtain a more realistic reaction network for the investigated process. In

the modified reaction network, the direct autocatalytic steps were replaced with autocatalytic loops. In this procedure some complex net reactions had to be resolved, while some new reactions had to be taken into account, altering the reaction mechanism responsible for the appearance of oscillation. Moreover, in the modified reaction network, the expressions for reaction rates correspond formally to their stoichiometry in accordance to mass action kinetics. The SNA identified the instability condition which was further tested and confirmed by numerical simulation.

Nomenclature

CH_3OH – methanol

CO – carbon monoxide

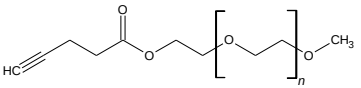
O_2 - oxygen

HI – hydroiodic acid

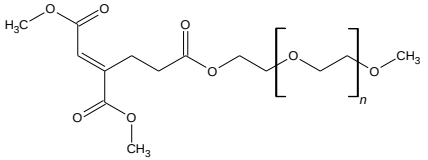
I_2 – iodine

Pd – palladium

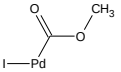
PEGA– poly(ethylene glycol)methyl ether acetylene,



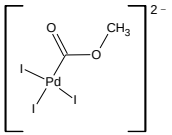
PEGP – poly(ethylene glycol)methyl ether (Z)-5-methoxy-3-(methoxycarbonyl)-5-oxopent-3-enoate; ester product,



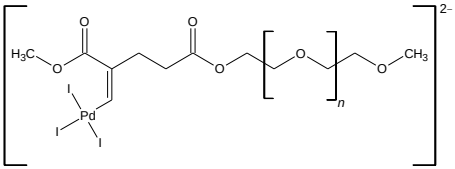
Int = $IPdCOOCH_3$ – Methoxycarbonylpalladium(II) iodide,



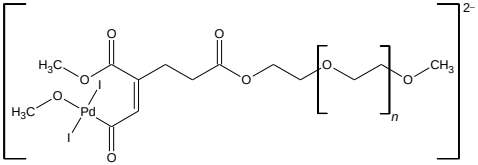
$Int_1 = (I_3PdCOOCH_3)^{2-}$ – Triiodo(methoxycarbonyl)palladate(II) anion,



Int_2 = $(I_3Pd(H)C=C(PEG)COOCH_3)^{2-}$ –(2-(poly(ethylene glycol)methyl ether)-3-methoxy-3-oxoprop-1-en-1-yl)triiodopalladate(II) anion



Int_3 = $((H_3CO(I_2Pd)(CO))(H)C=C(PEG)COOCH_3)^{2-}$ – (3-(poly(ethylene glycol)methyl ether)-4-methoxy-4-oxobut-2-enoyl)diiodo(methoxy)palladate(II) anion



1. Introduction

Oscillatory chemical reactions continue to draw attention and spark imagination. Ever since the Belousov-Zhabotinsky (BZ) reaction[1,2] firmly set the scene for what is now known as the area of Nonlinear Dynamics in Chemical Systems, the broad variety of spatiotemporal phenomena in solution, developed understanding and associated research directions continue to astonish.[3] The past five decades have brought to light numerous variations of oscillatory chemical reactions initially discovered by chance [1,2,4] as well as greater recognition of such phenomena with biological origins.[5] It is now readily accepted that some nonlinear chemical, physicochemical and biochemical reactions can exhibit different dynamic states from non-oscillatory to oscillatory and chaotic ones.[6–14] Therefore, in these nonequilibrium states their time evolutions are different which influences their net reactions and response to perturbations.[15] This is particularly important for all catalytic processes whether in living or non-living systems. Among more recent additions to the growing family of known oscillatory chemical reactions, oscillatory carbonylation reactions stand out in numerous ways. Firstly reported by Temkin and co-workers employing phenylacetylene as substrate, it has been shown that, in addition to oscillations in pH, this reaction system exhibits correlated oscillations in turbidity as well as the pulsatile release of reaction heat.[16–23] Further studies

of the oxidative carbonylation of phenylacetylene demonstrated that the presence or absence of oscillations has an effect on product selectivity with reaction temperature playing a major role.[22,24] In addition to the oscillatory phenomena captured when the reaction employed methanol as both reactant and solvent, it has been recently shown that pH oscillations prevail when a significant volume percent of methanol is replaced with water (up to 30 vol% under conditions reported.[23] An exciting step forward in oscillatory carbonylation reactions was made when the small phenylacetylene molecule was substituted with mono-alkyne-terminated poly(ethylene glycol) methyl ether (PEGA) and subsequently with di-alkyne-terminated poly(ethylene glycol) methyl ether (PEGDA).[25,26] The most recent advances have used polymeric catalysts in place of PdI_2.[27] The PEGA and PEGDA systems are the only reported polymeric substrates oscillatory chemical reactions under laboratory conditions so far. Linking these results together with the BZ reaction employing p(NIPAAm-r-Ru(bpy)$_3$) gels as catalysts[28–33], it can be seen that 20th century oscillatory chemical reactions studied in solution have paved the way for new research avenues. While the BZ reaction system and variants have been extensively studied and widely published for over 60 years, oscillatory carbonylation reactions have more recent origins and only a few dozen publications.

Aiming to further enhance our understanding of oscillatory carbonylation reactions, and in particular polymeric substrate oscillatory systems, the reaction network previously proposed to account for the oscillatory dynamics in the poly(ethylene glycol)methyl ether acetylene (PEGA) reaction system[25] has been examined in this study. Stability analysis was done by using Stoichiometric Network Analysis (SNA)[34] with the aim of confirming the reported oscillatory dynamics and obtaining a better understanding of the instabilities in this system. Firstly, as explained in Section 2, we examine the reaction network of palladium-catalysed oscillatory carbonylation of PEGA proposed by Donlon and [25] by SNA. This reaction network is approached in two ways: a) using the stoichiometry proposed by Donlon and Novaković but with the rate equations that follow the mass action law (Section 2.1) and b) using the rate equations Donlon and Novaković based on their interpretation of phenomena experimentally observed (Section 2.2). As a result of these analyses, a new, more realistic reaction network is proposed (Section 3) and subsequently examined by SNA (Section 3.1).

The reaction mixture consisting of PEGA as substrate, PdI_2/KI as a catalyst and methanol as both reactant and solvent, when purged with CO and air (semibatch configuration) under certain initial conditions is reported to yield several hours of oscillatory dynamics [25] A simplified reaction network was proposed to account for the experimentally

observed results (Table 1) and a simulation using this network is presented in Donlon and .[25] The reaction network is composed of six reactions. Reactions R1.1 and R1.4 are postulated to be autocatalytic. Reaction R1.1 is postulated to be autocatalytic in hydrogen iodide species which is considered to be the source of oscillations in hydrogen ions and therefore oscillations in pH in this system. It should be noted that the standard pH scale is based on measurements in water, therefore pH values experimentally recorded in methanol solution need to be adjusted prior to being converted to hydrogen ion concentration. It has been reported that in neat methanol, pH values can be adjusted by adding 2.3 to the observed pH measurements to obtain the equivalent pH value in water.[35] Reaction R1.1 also accounts for catalyst reduction (from PdI_2 to Pd) and product (PEGP) formation where PEGP denotes all molecules that form from PEGA in the oscillatory carbonylation reaction. Reaction R1.2 describes formation of iodine, which is subsequently considered to be responsible for regeneration of the palladium catalyst (Reactions R1.3 and R1.4). Reaction R1.2 also accounts for consumption of hydrogen iodide. Catalyst recycling is postulated to proceed in both a non-catalytic and autocatalytic manner in reactions R1.3 and R1.4, respectively. They are introduced in the proposed forms to support the experimentally recorded oscillatory behaviour of solution turbidity attributed to autocatalytic changes in the oxidation state of the palladium (from soluble Pd^{2+} to insoluble Pd^0) during the course of the reaction. Reactions R1.5 and R1.6 form one reversible reaction. Reaction R1.5, experimentally confirmed as a slow process[36], is included to account for the initial formation of hydrogen iodide required to initiate Reaction R1.1. Due to the excess of CH_3OH, and purging by O_2 and CO, their concentrations were considered constant[20,36–39] and were not included in the reaction rates associated with the proposed reaction network but were incorporated in the rate constants k_i. Thus, in some steps, the rate equations do not follow the mass action law. PEGA is consumed by the reaction R1.1 and hence, its concentration decreases with time, but it happens much slower than other reactions in the overall process.

Structural formulae for intermediate Int, and other, more complex structures mentioned later on are shown in Nomenclature.

$[\mathrm{PEGA}] + \mathrm{PdI_2} + \{2\mathrm{CH_3OH} + 2\mathrm{CO}\} \xrightarrow{\mathrm{HI}} \mathrm{PEGP} + \mathrm{Pd} + 2\,\mathrm{HI}$	$r_1 = k_1[c_6]c_1c_3^2$	(R1.1)
$2\,\mathrm{HI} + \{0.5\,\mathrm{O_2}\} \longrightarrow \mathrm{I_2} + \mathrm{H_2O}$	$r_2 = k_2c_3^2$	(R1.2)
$\mathrm{Pd} + \mathrm{I_2} \longrightarrow \mathrm{PdI_2}$	$r_3 = k_3c_2c_4$	(R1.3)
$\mathrm{Pd} + \mathrm{I_2} \xrightarrow{\mathrm{PdI_2}} \mathrm{PdI_2}$	$r_4 = k_4c_1c_2c_4$	(R1.4)
$\mathrm{PdI_2} + \{\mathrm{CH_3OH} + \mathrm{CO}\} \longrightarrow \mathrm{Int} + \mathrm{HI}$	$r_5 = k_5c_1$	(R1.5)
$\mathrm{Int} + \mathrm{HI} \longrightarrow \mathrm{PdI_2} + \{\mathrm{CH_3OH} + \mathrm{CO}\}$	$r_6 = k_6c_3c_5$	(R1.6)

Table 1. Reaction network associated with the palladium-catalysed oscillatory carbonylation of PEGA. Adopted from Donlon and Novakovic [25] Concentrations of species *j* denoted in the subscript with values 1 - 6 correspond to the species PdI_2, Pd, HI, I_2, Int and PEGA, respectively. Rate equations in several steps of this Model do not follow the mass action law.

Although the reaction network presented in Table 1 could produce oscillatory dynamics it can be noted that the associated expressions for the reaction rates of reactions R1.1 and R1.4 do not correspond to their stoichiometry in accordance with the mass action kinetics. For that reason, two cases, as detailed in Table 2 and Table 3, were considered and analysed using SNA with the aim to determine if the oscillatory dynamics can be obtained by either of them. In Table 2 the reaction network consisting of chemical reactions as proposed by Donlon and Novakovic[25] (Table 1) is given, but with the kinetic equations that follow the mass action law. Table 3 contains the kinetic equations used by Donlon and Novakovic[25] based on their interpretation of experimentally observed phenomena together with chemical reactions adapted to them. In other words, in Table 2 reactions R2.3 and R2.4 are now identical, while in Table 3 two molecules of HI are added to both sides of reaction R3.1, whereas in reaction R3.4 one molecule of PdI_2 is added to both sides.

$[\mathrm{PEGA}] + \mathrm{PdI_2} + \{2\mathrm{CH_3OH} + 2\mathrm{CO}\} \longrightarrow \mathrm{PEGP} + \mathrm{Pd} + 2\,\mathrm{HI}$	$r_1 = k_1[c_6]c_1$	(R2.1)
$2\,\mathrm{HI} + \{0.5\,\mathrm{O_2}\} \rightarrow \mathrm{I_2} + \mathrm{H_2O}$	$r_2 = k_2c_3^2$	(R2.2)
$\mathrm{Pd} + \mathrm{I_2} \rightarrow \mathrm{PdI_2}$	$r_3 = k_3c_2c_4$	(R2.3)
$\mathrm{Pd} + \mathrm{I_2} \rightarrow \mathrm{PdI_2}$	$r_4 = k_4c_2c_4$	(R2.4)
$\mathrm{PdI_2} + \{\mathrm{CH_3OH} + \mathrm{CO}\} \rightarrow \mathrm{Int} + \mathrm{HI}$	$r_5 = k_5c_1$	(R2.5)
$\mathrm{Int} + \mathrm{HI} \rightarrow \mathrm{PdI_2} + \{\mathrm{CH_3OH} + \mathrm{CO}\}$	$r_6 = k_6c_3c_5$	(R2.6)

Table 2. Palladium-catalysed oscillatory carbonylation of PEGA. Reaction network consists of chemical reactions as proposed by Donlon and Novakovic[25] (Table 1) but with the rate equations that follow the mass action law.

$$[\mathrm{PEGA}] + \mathrm{PdI_2} + 2\,\mathrm{HI} + \{2\mathrm{CH_3OH} + 2\mathrm{CO}\} \rightarrow \mathrm{PEGP} + \mathrm{Pd} + 4\,\mathrm{HI} \qquad r_1 = k_1[c_6]c_1c_3^2 \qquad \text{(R3.1)}$$

$$2\,\mathrm{HI} + \{0.5\,\mathrm{O_2}\} \rightarrow \mathrm{I_2} + \mathrm{H_2O} \qquad r_2 = k_2c_3^2 \qquad \text{(R3.2)}$$

$$\mathrm{Pd} + \mathrm{I_2} \rightarrow \mathrm{PdI_2} \qquad r_3 = k_3c_2c_4 \qquad \text{(R3.3)}$$

$$\mathrm{Pd} + \mathrm{I_2} + \mathrm{PdI_2} \rightarrow 2\,\mathrm{PdI_2} \qquad r_4 = k_4c_1c_2c_4 \qquad \text{(R3.4)}$$

$$\mathrm{PdI_2} + \{\mathrm{CH_3OH} + \mathrm{CO}\} \rightarrow \mathrm{Int} + \mathrm{HI} \qquad r_5 = k_5c_1 \qquad \text{(R3.5)}$$

$$\mathrm{Int} + \mathrm{HI} \rightarrow \mathrm{PdI_2} + \{\mathrm{CH_3OH} + \mathrm{CO}\} \qquad r_6 = k_6c_3c_5 \qquad \text{(R3.6)}$$

Table 3. Palladium-catalysed oscillatory carbonylation of PEGA. Reaction network consists of chemical reactions adapted to fit the rate equations as proposed by Donlon and Novakovic[25] (Table 1)

2. Stoichiometric network analysis (SNA) of reaction network of oscillatory PEGA carbonylation

SNA is a powerful mathematical method for steady-state-stability analysis and, consequently, for the examination of the oscillatory dynamic states of reaction systems.[40–42] In this Section, SNA will be briefly explained in general and applied to the reaction networks of PEGA carbonylation given in Tables 2 and 3.

Dynamic states of the reaction systems must be analysed through the reaction kinetics. The kinetic equations associated with any reaction network given in the form of a stoichiometric model can be presented by the set of the following differential equations,

$$\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t} = \mathbf{S}\,\boldsymbol{r} \qquad (1)$$

where d$\boldsymbol{c}$/dt is the time derivative of the concentration vector $\boldsymbol{c}$, $\boldsymbol{r}$ is the reaction rate vector and **S** the matrix of the stoichiometric coefficients that can be taken directly from the reaction networks (See Eq. 2).[14,43–45] Moreover, in the reaction networks presented in Tables 2 and 3 there are 11 chemical species: CH_3OH, CO, PEGP, O_2, H_2O, PEGA, PdI_2, Pd, HI, I_2 and Int. Some of these species are only present as products that are not involved in further reactions, and therefore do not influence reaction rates and dynamic states of the system. In the reaction networks analysed here such species are H_2O and PEGP. Furthermore, some species are present in nearly constant concentrations. Most often this is the case with reactants added in large surplus at the beginning of the reaction, like PEGA and CH_3OH, or reactants continuously fed in excess to the reaction mixture, like CO and O_2. Dynamic states depend on

such reactants only in a weak, parametrical sense. Only intermediate species are truly dynamical variables and state functions. The intermediate species in the reaction networks are Pd, HI, I_2, and Int. PdI_2 is one of the basic constituents of the reaction system, *i.e.* reactants, but since the main iodine intermediate species are not included in this abbreviated reaction mechanism, it was chosen to depict autocatalysis in the present reaction network. Therefore, PdI_2, may be essential for the instability of the steady state and hence, it is also taken as intermediate in SNA and variable species in numerical simulations. Thus, for the intermediate species of both reaction networks (Tables 2 and 3) PdI_2, Pd, HI, I_2, and Int are taken into account and the corresponding matrix **S** has the form:

$$\begin{array}{c} \begin{matrix} \text{R.1} & \text{R.2} & \text{R.3} & \text{R.4} & \text{R.5} & \text{R.6} \end{matrix} \\ \mathbf{S} = \begin{bmatrix} -1 & 0 & 1 & 1 & -1 & 1 \\ 1 & 0 & -1 & -1 & 0 & 0 \\ 2 & -2 & 0 & 0 & 1 & -1 \\ 0 & 1 & -1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 \end{bmatrix} \begin{matrix} PdI_2 \\ \text{Pd} \\ \text{HI} \\ I_2 \\ \text{Int} \end{matrix} \end{array} \tag{2}$$

Here, the species on the right-hand side and reactions above the matrix are added for clarity and they are not part of this matrix.

The corresponding kinetic equations for both reaction networks that will be used in SNA are then given by Eq. 3, although reaction rates are different for the cases given in Tables 2 and 3.

$$\begin{bmatrix} \frac{dc_1}{dt} \\ \frac{dc_2}{dt} \\ \frac{dc_3}{dt} \\ \frac{dc_4}{dt} \\ \frac{dc_5}{dt} \end{bmatrix} = \begin{bmatrix} -1 & 0 & 1 & 1 & -1 & 1 \\ 1 & 0 & -1 & -1 & 0 & 0 \\ 2 & -2 & 0 & 0 & 1 & -1 \\ 0 & 1 & -1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \\ r_6 \end{bmatrix} \tag{3}$$

Here c_j is the concentration of species j denoted in the subscript with values 1 - 5 corresponding to the species PdI_2, Pd, HI, I_2 and Int, respectively.

For stability analysis of the reaction network, the basic steady state must be defined. Therefore, the reaction rates in the steady state, $\boldsymbol{r}_{ss}$, are necessary. They are solutions of the relation

$$\mathbf{S}\,\boldsymbol{r}_{ss} = 0 \tag{4}$$

These rates at a steady state $\boldsymbol{r}_{ss}$ can be expressed by means of the current rates j_i, which are the contributions of the elementary reaction pathways with non-negative coefficients.[40,46,47] So, the overall process can be represented as a linear combination of several elementary reaction pathways with non-negative coefficients, known as extreme currents E_i and they all contribute to the steady state values of reaction rates. The contributions of the extreme currents E_i, denoted as the current rates j_i, are the components of the corresponding current rate vector $\boldsymbol{j}$, whereas the extreme currents E_i are the columns of the extreme current matrix.[14,34,40,43,44,46–50]

Since the matrix S is the same in the considered cases (Tables 2 and 3), the common matrix **E** is

$$\mathbf{E} = \begin{array}{c} \begin{matrix} E_1 & E_2 & E_3 \end{matrix} \\ \begin{bmatrix} 0 & 1 & 1 \\ 0 & 1 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \end{array} \begin{matrix} \text{R.1} \\ \text{R.2} \\ \text{R.3} \\ \text{R.4} \\ \text{R.5} \\ \text{R.6} \end{matrix} \tag{5}$$

By analyzing the extreme current matrix **E** the following net reactions were obtained:

E_1: (R.5) + (R.6) $\Rightarrow$

$$0 \rightarrow 0 \tag{6}$$

E_2: (R.1) + (R.2) + (R.3) $\Rightarrow$

$$\mathrm{PEGA} + 2\mathrm{CH_3OH} + 2\mathrm{CO} + 0.5\ \mathrm{O_2} \rightarrow \mathrm{PEGP} + \mathrm{H_2O} \tag{7}$$

E_3: (R.1) + (R.2) + (R.4) $\Rightarrow$

$$\mathrm{PEGA} + 2\mathrm{CH_3OH} + 2\mathrm{CO} + 0.5\ \mathrm{O_2} \rightarrow \mathrm{PEGP} + \mathrm{H_2O} \tag{8}$$

From Eq. 6-8 it can be noted that the first net reaction denotes the equilibrium between reactions R.5 and R.6 and that there are two possible reaction pathways besides this chemical equilibrium which allows the same transformation of the reactants into the products. Further details on calculation of all extreme currents can be found elsewhere.[40,46,47,51,52]

The extreme currents are essential for finding the relation between steady-state reaction rates and current rates using the basic equation of SNA

$$\boldsymbol{r}_{ss} = \mathbf{E}\,\boldsymbol{j} \tag{9}$$

Using Eq. 9, $\boldsymbol{r}_{ss}$ can be represented as following linear combinations of current rates j_i, where i = 1, 2, 3. These relations have the form:

$$\begin{aligned} r_{1,ss} &= j_2 + j_3 \\ r_{2,ss} &= j_2 + j_3 \\ r_{3,ss} &= j_2 \\ r_{4,ss} &= j_3 \\ r_{5,ss} &= j_1 \\ r_{6,ss} &= j_1 \end{aligned} \tag{10}$$

Moreover, the significance of extreme currents lies in their role in analysis of stability of the basic steady state. The stability of a steady state is usually examined through the response of the reaction system to some arbitrary small perturbation.

The time evolution of small concentration perturbations $\Delta\boldsymbol{c} = \boldsymbol{c} - \boldsymbol{c}_{ss}$ near a steady state $\boldsymbol{c}_{ss}$ is given by the equation

$$\mathrm{d}\Delta c / \mathrm{d}t = \mathbf{M}\Delta c \tag{11}$$

obtained by linearization of the general equation of motion about the steady state, where matrix **M** is the Jacobian of the system given by the following equation:

$$\mathbf{M}(\boldsymbol{r}_{ss}) = \mathbf{S}\left(\operatorname{diag} \boldsymbol{r}_{ss}\right)\mathbf{K}^{\mathrm{T}}\left(\operatorname{diag} c_{ss}^{-1}\right) = \mathbf{S}\left(\operatorname{diag} \boldsymbol{r}_{ss}\right)\mathbf{K}^{\mathrm{T}}\operatorname{diag} h \tag{12}$$

where ***h*** stands for a vector of reciprocal steady-state concentrations of the intermediate species and diag ***h*** is its diagonal matrix, while **K** is the matrix of the orders of reactions and $\mathbf{K}^{\mathrm{T}}$ is its transpose. If we assume the mass action law for the reaction rates, the elements of matrix **K** are stoichiometric coefficients of a species standing on the left side of the particular reaction step (See Eq. 15).

The Jacobian matrix **M,** written in SNA (Clarke 1980)[40], as a function of the SNA parameters j_i and h_i has particular advantages for the stability analysis since the parameters j_i and h_i are non-negative, which is an essential feature of SNA. The steady-state stability is determined by the eigenvalues of **M**, which are the roots λ of the characteristic polynomial

$$Det\left[\lambda\,\mathbf{I}\ -\mathbf{M}\right]=\sum_{i=0}^{n}\alpha_i\lambda^{n-i}=\lambda^{\mathrm{n}}+\alpha_1\lambda^{\mathrm{n}-1}+\alpha_2\lambda^{\mathrm{n}-2}+\ldots+\alpha_{\mathrm{n}}=0 \qquad (13)$$

where n is the number of independent intermediate species and coefficients α_i are the sums of all diagonal minors of dimensions i of matrix **M** multiplied by the product of the corresponding h_i values. Each diagonal minor of the matrix **M**, as the determinant of square matrix having dimension i, can be formed of any combination of i independent intermediate species. In one α_i the number of minors is equal to the number of different combinations of i intermediates.

If the real parts of all eigenvalues are negative, a steady state is stable. If one or more eigenvalues have positive real parts the steady state is unstable. The sign of the real part of the eigenvalues of the Jacobian matrix can be evaluated by using several criteria such as Hurwitz determinants [53,54] or α-approximation. According to the α-approximation, the eigenvalue with positive real part occurs when some coefficient α of the characteristic polynomial is negative.[40,53,54] Moreover, if we find negative minors in one coefficient α_i and we want to discuss its sign, then we ask if the sum of negative terms can be larger than the sum of positive terms in the same α_i. The applicability of each approach depends on the model complexity.

Since the matrix **K** in the reaction networks given in Tables 2 and 3 are different, we can expect different results with respect to their network stability. Corresponding results for the reaction network given in Table 2 are presented in Section 2.1., and for the reaction network given in Table 3 see Section 2.2.

2.1. Stability analysis with matrix K obtained from the reaction network given in Table 2

For the full set of intermediary species in the reaction network given in Table 2, the **K** matrix is:

$$\mathbf{K} = \begin{array}{c} \begin{matrix} R.1 & R.2 & R.3 & R.4 & R.5 & R.6 \end{matrix} \\ \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \begin{matrix} PdI_2 \\ Pd \\ HI \\ I_2 \\ Int \end{matrix} \tag{14}$$

while the calculated matrix **M**(***j***) is:

$$\mathbf{M}(\boldsymbol{j}) = -\begin{bmatrix} -(j_1+j_2+j_3)h_1 & (j_2+j_3)h_2 & j_1h_3 & (j_2+j_3)h_4 & j_1h_5 \\ (j_2+j_3)h_1 & -(j_2+j_3)h_2 & 0 & -(j_2+j_3)h_4 & 0 \\ (j_1+2j_2+2j_3)h_1 & 0 & -(j_1+4j_2+4j_3)h_3 & 0 & -j_1h_5 \\ 0 & -(j_2+j_3)h_2 & (2j_2+2j_3)h_3 & -(j_2+j_3)h_4 & 0 \\ j_1h_1 & 0 & -j_1h_3 & 0 & -j_1h_5 \end{bmatrix} \tag{15}$$

where $\boldsymbol{h}(h_1, h_2, h_3, h_4, h_5) = \boldsymbol{h}\,(1/c_1, 1/c_2, 1/c_3, 1/c_4, 1/c_5)$.

The obtained coefficients of the corresponding characteristic polynomial are given in Eq. 16-20.

$$\alpha_1 = h_1j_1 + h_1j_2 + h_1j_3 + h_2j_2 + h_3j_1 + h_2j_3 + 4h_3j_2 + 4h_3j_3 + h_4j_2 + h_5j_1 + h_4j_3 \tag{16}$$

$$\alpha_2 = (j_2+j_3)\begin{pmatrix} h_1h_2j_1 + 3h_1h_3j_1 + 4h_1h_3j_2 + h_1h_4j_1 + h_2h_3j_1 + 4h_1h_3j_3 + h_1h_4j_2 \\ +h_1h_5j_1 + 4h_2h_3j_2 + h_1h_4j_3 + 4h_2h_3j_3 + h_2h_5j_1 + h_3h_4j_1 + 4h_3h_4j_2 \\ +4h_3h_5j_1 + 4h_3h_4j_3 + h_4h_5j_1 \end{pmatrix} \tag{17}$$

$$\alpha_3 = j_1(j_2+j_3)^2(2h_1h_2h_3 + h_1h_3h_4 + 4h_1h_3h_5 + h_1h_4h_5 + 4h_2h_3h_5 + 4h_3h_4h_5) \tag{18}$$

$$\alpha_4 = 0 \tag{19}$$

$$\alpha_5 = 0 \tag{20}$$

Coefficients α_4 and α_5 are equal to zero since matrix **S** has a rank 3 due to the law of conservation of total concentration of palladium (c_{tot}(Pd)) and iodine (c_{tot}(I)) species, and consequently the linear dependence among the corresponding kinetic equations. If c_1, ... c_5, are the concentrations of PdI_2, Pd, HI, I_2, and Int respectively, it is easy to show that $c_1 + c_2 + c_5 = \text{const} = c_{tot}(\text{Pd})$, whereas $2\,c_1 + c_3 + 2\,c_4 + c_5 = \text{const} = c_{tot}(\text{I})$. Therefore, for stability evaluation we have used only the coefficients α_i where $i \leq 3$ and Hurwitz determinants Δ_i where $i \leq 3$, which are always positive. Thus the basic state of the reaction network given in Table 2 cannot be unstable and a sustained oscillatory dynamic state of this reaction system is impossible.

2.2. Stability analysis with matrix K obtained from the reaction network given in Table 3

For the full set of intermediary species in the reaction network given in Table 3, the **K** matrix is:

$$\begin{array}{c} \quad \text{R.1}\ \text{R.2}\ \text{R.3}\ \text{R.4}\ \text{R.5}\ \text{R.6} \\ \mathbf{K} = \begin{bmatrix} 1 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 \\ 2 & 2 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{array}{l} PdI_2 \\ \text{Pd} \\ \text{HI} \\ I_2 \\ \text{Int} \end{array} \end{array} \tag{21}$$

while the calculated matrix $\mathbf{M}(\boldsymbol{j})$ is:

$$\mathbf{M}(\boldsymbol{j}) = \begin{bmatrix} -(j_1 + j_2)h_1 & (j_2 + j_3)h_2 & -(-j_1 + 2j_2 + 2j_3)h_3 & (j_2 j_3)h_4 & j_1 h_5 \\ j_2 h_1 & -(j_2 + j_3)h_2 & (2j_2 + 2j_3)h_3 & -(j_2 + j_3)h_4 & 0 \\ (j_1 + 2j_2 + 2j_3)h_1 & 0 & -j_1 h_3 & 0 & j_1 h_5 \\ -j_3 h_1 & -(j_2 + j_3)h_2 & (2j_2 + 2j_3)h_3 & -(j_2 + j_3)h_4 & 0 \\ j_1 h_1 & 0 & -j_1 h_3 & 0 & -j_1 h_5 \end{bmatrix} \tag{22}$$

The coefficients of the corresponding characteristic polynomial are given in the following equations:

$$\alpha_1 = h_1 j_1 + h_1 j_2 + h_2 j_2 + h_3 j_1 + h_2 j_3 + h_4 j_2 + h_5 j_1 + h_4 j_3 \tag{23}$$

$$\begin{aligned}\alpha_2 = {} & 4h_1 h_3 {j_2}^2 + 4h_1 h_3 {j_3}^2 + h_1 h_4 {j_2}^2 + h_1 h_4 {j_3}^2 + h_1 h_2 j_1 j_2 + h_1 h_2 j_1 j_3 + h_1 h_3 j_1 j_2 \\ & + h_1 h_4 j_1 j_2 + h_2 h_3 j_1 j_2 + 8 h_1 h_3 j_2 j_3 + h_1 h_4 j_1 j_3 + h_1 h_5 j_1 j_2 + h_2 h_3 j_1 j_3 + 2 h_1 h_4 j_2 j_3 \\ & + h_2 h_5 j_1 j_2 + h_3 h_4 j_1 j_2 + h_2 h_5 j_1 j_3 + h_3 h_4 j_1 j_3 + h_4 h_5 j_1 j_2 + h_4 h_5 j_1 j_3\end{aligned} \tag{24}$$

$$\alpha_3 = -h_1 j_1 (j_2 + j_3)^2 (2h_2 h_3 + h_3 h_4 - 4h_3 h_5 - h_4 h_5) \tag{25}$$

$$\alpha_4 = 0 \tag{26}$$

$$\alpha_5 = 0 \tag{27}$$

As expected, coefficients α_4 and α_5 are equal to 0. As can be seen from Eq. 23-27, negative terms can only be found in α_3. Therefore, in the reaction network presented in Table 3, an instability region was obtained, and some type of oscillatory dynamics can be found.

Thus, the oscillatory dynamic states can be generated by the rate equations given in Donlon and Novakovic[25] (Tables 1 and Table 3). However, since the expressions for the reaction rates in reactions R1.1 and R1.4 do not correspond formally to their stoichiometry in accordance to mass action kinetics, whereas chemical reactions R3.1 and R3.4 adapted to the rate equations used in numerical simulations are obviously net reactions of a more complex mechanism, further modifications were desired in order to obtain a more realistic model of the investigated process. To reach this goal two things had to be resolved: the reaction network's stoichiometry and the mechanism responsible for the appearance of oscillations. Hence, the first step was to modify the reaction network (Table 1) in such a way that all reaction rates follow mass action kinetics corresponding to the reaction stoichiometry and, at the same time, produce oscillatory dynamic states.

3. Modified reaction network of oscillatory PEGA carbonylation

In the reaction network (Table 1), instabilities, and hence oscillatory dynamics, are the result of direct autocatalytic steps, which, although a very useful mechanism for the modelling of oscillatory chemical reactions are not a realistic representation of the investigated process. Hence, to make the reaction network more convincing, direct autocatalytic steps were replaced by feedback loops as an alternative source of instabilities which are the result of

interactions between several species. By doing so, new species with the related chemical reactions which are recognised to occur had to be added to the initial reaction network of the reaction mechanism. As a result of these modifications the new reaction network was proposed.

The modified reaction network based on results of SNA analysis of reaction networks presented in Tables 2 and 3, and experimental observations [22] is given in Table 4. New intermediary species, Int_1, Int_2 and Int_3 (see Nomenclature), were added to the model instead of one intermediate, Int, aiming to explain the stoichiometry and kinetics of the complex reaction step R1.1. Reaction steps R1.5 and R1.6 from Table 1 represent the initial step of the more complex mechanism given here, and roughly correspond to the new reactions R4.1 and R4.-1. Concentrations of the remaining species are denoted by c_j.

$PdI_4^{2-} + \{CH_3OH + CO\} \rightleftarrows Int_1 + HI$	$r_1 = k_1 c_{PdI_4^{2-}}$	(R4.1)
	$r_{-1} = k_{-1} c_{Int_1} c_{HI}$	(R4.-1)
$Int_1 + PEGA \rightarrow Int_2$	$r_2 = k_2 \left[c_{PEGA}\right] c_{Int_1}$	(R4.2)
$Int_2 + \{CH_3OH + CO\} \rightarrow Int_3 + HI$	$r_3 = k_3 c_{Int_2}$	(R4.3)
$Int_3 \rightarrow PEGP + Pd + 2I^-$	$r_4 = k_4 c_{Int_3}$	(R4.4)
$Pd + I_2 \rightarrow PdI_2$	$r_5 = k_5 c_{Pd} c_{I_2}$	(R4.5)
$PdI_2 + 2I^- \rightarrow PdI_4^{2-}$	$r_6 = k_6 c_{PdI_2} c_{I^-}^2$	(R4.6)
$PdI_4^{2-} + Pd \rightarrow Pd_2I_4^{2-}$	$r_7 = k_7 c_{PdI_4^{2-}} c_{Pd}$	(R4.7)
$Pd_2I_4^{2-} + I_2 \rightarrow Pd_2I_6^{2-}$	$r_8 = k_8 c_{Pd_2I_4^{2-}} c_{I_2}$	(R4.8)
$Pd_2I_6^{2-} + 2HI \rightarrow 2PdI_4^{2-} + 2H^+$	$r_9 = k_9 c_{Pd_2I_6^{2-}} c_{HI}^2$	(R4.9)
$2HI + \{0.5O_2\} \rightarrow I_2 + H_2O$	$r_{10} = k_{10} c_{HI}^2$	(R4.10)
$I_2 + H_2O \rightleftarrows HIO + HI$	$r_{11} = k_{11} \left[c_{H_2O}\right] c_{I_2}$	(R4.11)
	$r_{-11} = k_{-11} c_{HIO} c_{HI}$	(R4.-11)
$HI \rightleftarrows H^+ + I^-$	$r_{12} = k_{12} c_{HI}$	(R4.12)
	$r_{-12} = k_{-12} c_{H^+} c_{I^-}$	(R4.-12)
$HI + CH_3OH \rightleftarrows CH_3I + H_2O$	$r_{13} = k_{13} c_{HI}$	(R4.13)
	$r_{-13} = k_{-13} \left[c_{H_2O}\right] c_{CH_3I}$	(R4.-13)

Table 4. Modified reaction network of the palladium-catalysed oscillatory carbonylation of PEGA.

This reaction network, consisting of thirteen chemical reactions, four of which are reversible (R4.1, R4.11, R4.12 and R4.13), is proposed to explain the complex reaction in which PEGA, in the presence of methanol, oxygen and carbon monoxide, and PdI_2/KI as a catalytic mixture transforms to several products denoted as PEGP. In particular, the proposed reaction scheme acknowledges (See R4.6) that PdI_2 in the presence of KI reacts to form K_2PdI_4 which in dissociated form exists as the species PdI_4^{2-}. Reaction R4.1 represents the process in which PdI_4^{2-} reacts with methanol and CO to form Int_1 and HI [38,55,56]. The following reaction (R4.2) takes into account the insertion of substrate (PEGA) into the Pd−C bond in Int_1, to form Int_2.[55,56] In the next step (R4.3), further addition of CO and methanol takes place enabling formation of the diester Int_3, seen as a major product in this type of carbonylation reaction [22,57]. It can be noted that this reaction occurs with the release of HI. Subsequently, reaction R4.4 leads to product formation with the release of catalyst in the reduced form (Pd). Reactions R4.5-R4.9 are proposed to explain recycling of the catalytic species to PdI_4^{2-} through binuclear complexes. The palladium has strong affinity to form binuclear complexes and, although the existence of $Pd_2I_4^{2-}$ is not confirmed, we use reactions R4.7 and R4.8 to bridge the gap between known species in the mechanism which are all probable intermediates. The existence of $Pd_2I_6^{2-}$ has been experimentally determined using UV-Vis. After mixing Pd with CH_3OH, KI and I_2 a peak at 340 nm is noted, suggesting formation of $Pd_2I_6^{2-}$ species, as suggested by the literature. [58] While the reaction network is not to be treated as a proven mechanism, it represents a possible pathway which explains the oscillations in a simplified manner. Reactions R4.10-R4.12 acknowledge a route to form water in the system, subsequent reaction of the water and iodine and existence of the acid dissociation process. It should be noted that the reaction pathway formed by the reaction steps R4.7-R4.9 actually forms the autocatalytic loop which results from the net reaction:

$$PdI_4^{2-} + Pd + I_2 + 2HI \xrightarrow{k_7} 2PdI_4^{2-} + 2H^+ \qquad \text{(R4.14)}$$

3.1. Stoichiometric network analysis of the modified reaction network

Reaction network given in Table 4. describes interactions between 20 chemical species: CH_3OH, CO, PEGA, H_2O, H^+, O_2, PEGP, PdI_4^{2-}, Int_1, HI, Int_2, Int_3, Pd, I^-, I_2, PdI_2, $Pd_2I_4^{2-}$, $Pd_2I_6^{2-}$, HIO, CH_3I. As we already mentioned, PEGA is the reactant which transforms to the products denoted by PEGP in the presence of CH_3OH, CO, O_2 and catalytic mixture PdI_2/KI.

The concentrations of CH_3OH, CO and O_2 are in excess, whereas concentration of PdI_2, quickly decreases such that we have to consider it as intermediate species when the reaction system under consideration is in the oscillatory dynamic state. Moreover, although H_2O is a product as well as a reactant the concentration of H_2O is approximately zero at the beginning and quickly increases such that it ought to be considered as a product although reaction rates do parametrically depend on it. The remaining species together with PdI_2 will be considered in SNA as the intermediate ones. They are: H^+, PdI_4^{2-}, Int_1, HI, Int_2, Int_3, Pd, I^-, I_2, PdI_2, $Pd_2I_4^{2-}$, $Pd_2I_6^{2-}$, HIO and CH_3I.

For the reaction network given in Table 4 matrix **S** has the following form

$$\mathbf{S} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -2 & -2 & 1 & -1 & -1 & 1 & -1 & 1 \\ 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 1 & -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \end{bmatrix} \begin{matrix} H^+ \\ PdI_4^{2-} \\ Int_1 \\ HI \\ Int_2 \\ Int_3 \\ Pd \\ I^- \\ I_2 \\ PdI_2 \\ Pd_2I_4^{2-} \\ Pd_2I_6^{2-} \\ HIO \\ CH_3I \end{matrix} \tag{28}$$

The rank of the matrix **S** is 11. This means that there are 11 independent intermediate species and three conservation constraints between these species. However, we have shown [59] that we can calculate the **E** matrix with all 14 species. The result for stability will be equal to the one obtained with 11 species and three conservation equations, but the mathematical procedure is simpler in the first case which will be applied here. Thus, by means of the matrix **S** given in Eq. 28, the following matrix **E** is obtained:

$$\mathbf{E} = \begin{array}{c} \begin{matrix} E_1 & E_2 & E_3 & E_4 & E_5 & E_6 \end{matrix} \\ \left[\begin{array}{cccccc} 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 2 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{array}\right] \end{array} \begin{array}{l} \text{R4.1} \\ \text{R4.-1} \\ \text{R4.2} \\ \text{R4.3} \\ \text{R4.4} \\ \text{R4.5} \\ \text{R4.6} \\ \text{R4.7} \\ \text{R4.8} \\ \text{R4.9} \\ \text{R4.10} \\ \text{R4.11} \\ \text{R4.-11} \\ \text{R4.12} \\ \text{R4.-12} \\ \text{R4.13} \\ \text{R4.-13} \end{array} \tag{29}$$

By analyzing the elementary reaction pathways in the extreme current matrix **E** the following net reactions are obtained:

E_1: (R4.1) + (R4.-1) $\Rightarrow$
$0 \rightarrow 0$ (30)

E_2: (R4.11) + (R4.-11) $\Rightarrow$
$0 \rightarrow 0$ (31)

E_3: (R4.12) + (R4.-12) $\Rightarrow$
$0 \rightarrow 0$ (32)

E_4: (R4.13) + (R4.-13) $\Rightarrow$
$0 \rightarrow 0$ (33)

E_5: (R4.1) + (R4.2) + (R4.3) + (R4.4) + (R4.5) + (R4.6) + (R4.10)
$\mathrm{PEGA} + 2\mathrm{CH_3OH} + 2\mathrm{CO} + 0.5\ \mathrm{O_2} \rightarrow \mathrm{PEGP} + \mathrm{H_2O}$ (34)

E_6: (R4.1) + (R4.2) + (R4.3) + (R4.4) + (R4.7) + (R4.8) + (R4.9) + (R4.10)
+ 2(R4.-12)
$\mathrm{PEGA} + 2\mathrm{CH_3OH} + 2\mathrm{CO} + 0.5\ \mathrm{O_2} \rightarrow \mathrm{PEGP} + \mathrm{H_2O}$ (35)

Analyzing the extreme currents E_1 - E_6 or the corresponding Eq. 30-35, it can be noted that the first four net reactions denote the equilibrium between related reactions and that there are two possible reaction pathways given in Eq. 34 and 35 which allow same transformation of the reactants into the products. Besides, these net reactions are equal to the ones obtained analysing the reaction networks given in Tables 2 and 3. This result confirms that the new reaction network in Table 4 is a properly extended variant of the previous one given in Table 1.

Using relation (9), $\boldsymbol{r}_{ss}$ can be represented as following linear combinations of current rates j_i, where i = 1, 2, 3, 4, 5:

$$
\begin{aligned}
r_{1,ss} &= j_1 + j_5 + j_6 \\
r_{-1,ss} &= j_1 \\
r_{2,ss} &= j_5 + j_6 \\
r_{3,ss} &= j_5 + j_6 \\
r_{4,ss} &= j_5 + j_6 \\
r_{5,ss} &= j_5 \\
r_{6,ss} &= j_5 \\
r_{7,ss} &= j_6 \\
r_{8,ss} &= j_6 \\
r_{9,ss} &= j_6 \\
r_{10,ss} &= j_5 + j_6 \\
r_{11,ss} &= j_2 \\
r_{-11,ss} &= j_2 \\
r_{12,ss} &= j_3 \\
r_{-12,ss} &= j_3 + 2\,j_6 \\
r_{13,ss} &= j_4 \\
r_{-13,ss} &= j_4
\end{aligned}
\qquad (36)
$$

As explained in Section 2, besides the matrices **S** and **E** calculated above, for the examination of the dynamic state stability we need the matrix of the orders of reactions **K**:

$$\mathbf{K} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 2 & 0 & 1 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{matrix} H^+ \\ PdI_4^{2-} \\ Int_1 \\ HI \\ Int_2 \\ Int_3 \\ Pd \\ I^- \\ I_2 \\ PdI_2 \\ Pd_2I_4^{2-} \\ Pd_2I_6^{2-} \\ HIO \\ CH_3I \end{matrix} \tag{37}$$

Theoretically, we could now calculate the Jacobian matrix **M**(***j***,***h***).

$$\mathbf{M}(\boldsymbol{j},\boldsymbol{h}) = \mathbf{S}\left[\operatorname{diag}\left(\mathbf{E}\,\boldsymbol{j}\right)\right]\mathbf{K}^{\mathrm{T}}\operatorname{diag}\boldsymbol{h} \tag{38}$$

As here we consider fourteen intermediate species, we need to use a much simpler method to examine the steady-state stability based on the fact that diag ***h*** in matrix **M** introduces only scaling factors. Hence, Eq. 38 can be written as a function of the matrix of current rates **V**(***j***) given by the expression:

$$\mathbf{M}(\boldsymbol{j},\boldsymbol{h}) = -\,\mathbf{V}\left(\boldsymbol{j}\right)\ \left(\operatorname{diag}\boldsymbol{h}\right) \tag{39}$$

where

$$\mathbf{V}(\boldsymbol{j}) = -\,\mathbf{S}\left(\operatorname{diag}\boldsymbol{r}_{\mathrm{ss}}\right)\mathbf{K}^{\mathrm{T}} = -\,\mathbf{S}\left[\operatorname{diag}\left(\mathbf{E}\,\boldsymbol{j}\right)\right]\mathbf{K}^{\mathrm{T}} \tag{40}$$

Since any α_i is the sum of minors of **V**(***j***) with dimension *i* multiplied by the product of the corresponding h_i values, we look for negative diagonal minors of **V**(***j***). The steady state is considered unstable if there is at least one negative diagonal minor of **V**(***j***).[40] It is possible

only if a polynomial corresponding to the determinant of the aforementioned negative diagonal minor contains at least one negative term, and if the sum of negative terms is larger than the sum of positive terms. A negative minor actually represents a destabilizing term since all the coefficients of the current rates in the **V**(***j***) matrix are positive numbers. Although it is an approximation, this SNA criterion often gives very good results. [41,42,60–65]

In the case considered here matrix **V** is given by the next equation:

$$\mathbf{V}(\boldsymbol{j}) = \begin{bmatrix} V_{1,1} & \cdots & V_{1,q} \\ \vdots & \ddots & \vdots \\ V_{p,1} & \cdots & V_{p,q} \end{bmatrix} \tag{41}$$

with coefficients $V_{p,q}$ equal to

$V_{1,1} = V_{1,8} = -V_{4,1} = -V_{4,8} = V_{8,1} = j_3 + 2j_6$
$V_{1,4} = -j_3 - 4j_6$
$V_{1,12} = V_{2,12} = -V_{4,12} = -V_{12,4} = -2j_6$
$V_{2,2} = j_1 + j_5 + 2j_6$
$V_{2,3} = -V_{3,4} = -V_{4,3} = -j_1$
$V_{2,4} = -j_1 - 4j_6$
$V_{2,7} = V_{7,2} = V_{9,11} = -V_{11,2} = -V_{11,7} = V_{11,9} = V_{11,11} = -V_{12,9} = -V_{12,11} = V_{12,12} = j_6$
$V_{2,8} = -V_{8,10} = -V_{10,8} = -2j_5$
$V_{2,10} = -V_{7,9} = -V_{9,7} = V_{10,7} = V_{10,9} = -V_{10,10} = -j_5$
$V_{3,2} = -V_{3,3} = V_{4,2} = -j_1 - j_5 - j_6$
$V_{4,4} = j_1 + j_2 + j_3 + j_4 + 4j_5 + 8j_6$
$V_{4,5} = V_{5,3} = -V_{5,5} = V_{6,5} = -V_{6,6} = V_{7,6} = -V_{7,7} = -j_5 - j_6$
$V_{4,9} = -V_{4,13} = V_{9,13} = -V_{13,4} = V_{13,9} = -V_{13,13} = -j_2$
$V_{4,14} = V_{14,4} = -V_{14,14} = -j_4$
$V_{8,4} = -j_3$
$V_{8,6} = -2j_5 - 2j_6$
$V_{8,8} = j_3 + 4j_5 + 2j_6$
$V_{9,4} = -j_2 - 2j_5 - 2j_6$
$V_{9,9} = j_2 + j_5 + j_6$

The other coefficients are equal to zero.

The minimal negative diagonal minor of **V**(***j***) has dimension 5×5. In fact, there are three of them. They are:

$$M_{H^+,\,PdI_4^{2-},\,HI,\,Pd,\,I_2} = (j_3+2j_6)(2j_2j_5^3 - j_2j_6^3 + j_4j_6^3 + 6j_5j_6^3 + 6j_5^3j_6 + 12j_5^2j_6^2 + 2j_1j_2j_5^2 - j_1j_2j_6^2 + j_1j_4j_6^2 + j_2j_4j_5^2 + 3j_1j_5j_6^2 + 6j_1j_5^2j_6 + j_2j_4j_6^2 - j_2j_5j_6^2 + 5j_2j_5^2j_6 + 4j_4j_5j_6^2 + 2j_4j_5^2j_6 + j_1j_2j_4j_5 + j_1j_2j_4j_6 + j_1j_2j_5j_6 + 2j_1j_4j_5j_6 + 3j_2j_4j_5j_6) \tag{42}$$

$$M_{PdI_4^{2-},\,HI,\,Pd,\,I_2,\,Pd_2I_4^{2-}} = j_6(2j_2j_5^3 + 2j_2j_6^3 - 2j_5j_6^3 - 2j_5^3j_6 - 4j_5^2j_6^2 + 2j_1j_2j_5^2 + 2j_1j_2j_6^2 + j_2j_3j_5^2 + j_2j_3j_6^2 + j_2j_4j_5^2 - 2j_1j_5j_6^2 - 2j_1j_5^2j_6 + j_2j_4j_6^2 + 11j_2j_5j_6^2 + 7j_2j_5^2j_6 + j_1j_2j_3j_5 + j_1j_2j_3j_6 + j_1j_2j_4j_5 + j_1j_2j_4j_6 + 4j_1j_2j_5j_6 + 3j_2j_3j_5j_6 + 3j_2j_4j_5j_6) \tag{43}$$

$$M_{HI,\,Pd,\,I_2,\,Pd_2I_4^{2-},\,Pd_2I_6^{2-}} = j_6^2(2j_2j_5^2 + 2j_2j_6^2 - 4j_5j_6^2 - 4j_5^2j_6 + j_1j_2j_5 + j_1j_2j_6 + j_2j_3j_5 + j_2j_3j_6 + j_2j_4j_5 + j_2j_4j_6 + 2j_2j_5j_6) \tag{44}$$

By using Eq 36, Eq. 42-44 can be presented as a function of $\boldsymbol{r}_{ss}$ Eq. 45-47. The "ss" in the subscript is not written with the aim of shortening the expressions.

$$M_{H^+,\,PdI_4^{2-},\,HI,\,Pd,\,I_2} = r_{-12}(2r_1r_5r_7r_{10} - 4r_1r_5r_7r_9 - 4r_1r_5r_8r_9 + 4r_1r_5r_8r_{10} - 4r_1r_7r_8r_9 + r_1r_5r_7r_{13} - 4r_1r_5r_9r_{11} + 4r_1r_7r_8r_{10} + r_1r_5r_8r_{13} + 2r_1r_5r_{10}r_{11} - 4r_1r_7r_9r_{11} + r_1r_7r_8r_{13} + 2r_1r_7r_{10}r_{11} + r_1r_5r_{11}r_{13} + 4r_5r_7r_8r_{10} + r_1r_7r_{11}r_{13} - 4r_5r_7r_9r_{11} + r_5r_7r_8r_{13} + 2r_5r_7r_{10}r_{11} + r_5r_7r_{11}r_{13} + r_5r_7r_8r_{-1} + r_1r_5r_8r_{-11} + r_1r_7r_8r_{-11} + r_5r_7r_8r_{-11}) \tag{45}$$

$$M_{PdI_4^{2-},\,HI,\,Pd,\,I_2,\,Pd_2I_4^{2-}} = r_8(2r_1r_5r_{10}r_{11} - 2r_1r_5r_7r_{10} + r_1r_5r_{11}r_{12} + 2r_1r_7r_{10}r_{11} + r_1r_5r_{11}r_{13} + r_1r_7r_{11}r_{12} + r_1r_7r_{11}r_{13} + 4r_5r_7r_9r_{11} + 2r_5r_7r_{10}r_{11} + r_5r_7r_{11}r_{12} + r_5r_7r_{11}r_{13} - r_1r_5r_7r_{-11} + r_5r_7r_{11}r_{-1}) \tag{46}$$

$$M_{HI,\,Pd,\,I_2,\,Pd_2I_4^{2-},\,Pd_2I_6^{2-}} = r_8r_9(2r_5r_{10}r_{11} - 4r_5r_7r_{10} + r_5r_{11}r_{12} + 2r_7r_{10}r_{11} + r_5r_{11}r_{13} + r_7r_{11}r_{12} + r_7r_{11}r_{13} + r_5r_{11}r_{-1} + r_7r_{11}r_{-1} - 2r_5r_7r_{-11}) \tag{47}$$

The basic steady state can be unstable if the polynomial corresponding to the only one of these three diagonal minors satisfies the condition that the sum of negative terms is larger than the sum of positive terms, for selected values of the parameters. In the case considered here, the mentioned instability condition can be satisfied which is presented in the next section.

Hence, instability of the steady state, and consequently oscillations, may occur for the reaction network given in Table 4, if any of expressions in Eqs. 45-47 passes through the zero and become negative.

3.2. Numerical simulation

In order to validate the results of the SNA we carried out numerical simulations of the reaction network presented in Table 4. Essential part of this analysis was to find an example set of rate constants which produces oscillatory dynamics and to test if any of the conditions (Eq 45-47) are satisfied and consequently detect feedback loop responsible for oscillations. Numerical simulations were carried out by solving kinetic equations associated with the reaction network given in Table 4 which is represented by the set of differential equations Eq 48-63.

$$\frac{\mathrm{d}c_{\mathrm{H^+}}}{\mathrm{d}t} = 2r_9 + r_{12} - r_{-12} \tag{48}$$

$$\frac{\mathrm{d}c_{\mathrm{PdI_4^{2-}}}}{\mathrm{d}t} = -r_1 + r_{-1} + r_6 - r_7 + 2r_9 \tag{49}$$

$$\frac{\mathrm{d}c_{\mathrm{Int_1}}}{\mathrm{d}t} = r_1 - r_{-1} - r_2 \tag{50}$$

$$\frac{\mathrm{d}c_{\mathrm{HI}}}{\mathrm{d}t} = r_1 - r_{-1} + r_3 - 2r_9 - 2r_{10} + r_{11} - r_{-11} - r_{12} + r_{-12} - r_{13} + r_{-13} \tag{51}$$

$$\frac{\mathrm{d}c_{\mathrm{Int_2}}}{\mathrm{d}t} = r_2 - r_3 \tag{52}$$

$$\frac{\mathrm{d}c_{\mathrm{Int_3}}}{\mathrm{d}t} = r_3 - r_4 \tag{53}$$

$$\frac{\mathrm{d}c_{\mathrm{Pd}}}{\mathrm{d}t} = r_4 - r_5 - r_7 \tag{54}$$

$$\frac{\mathrm{d}c_{\mathrm{I_2}}}{\mathrm{d}t} = -r_5 - r_8 + r_{10} - r_{11} + r_{-11} \tag{55}$$

$$\frac{\mathrm{d}c_{\mathrm{PdI_2}}}{\mathrm{d}t} = r_5 - r_6 \tag{56}$$

$$\frac{dc_{Pd_2I_4^{2-}}}{dt} = r_7 - r_8 \tag{57}$$

$$\frac{dc_{Pd_2I_6^{2-}}}{dt} = r_8 - r_9 \tag{58}$$

$$\frac{dc_{HIO}}{dt} = r_{11} - r_{-11} \tag{59}$$

$$\frac{dc_{I^-}}{dt} = 2r_4 - 2r_6 + r_{12} - r_{-12} \tag{60}$$

$$\frac{dc_{CH_3I}}{dt} = r_{13} - r_{-13} \tag{61}$$

$$\frac{dc_{H_2O}}{dt} = r_{10} - r_{11} + r_{-11} + r_{13} - r_{-13} \tag{62}$$

$$\frac{dc_{PEGA}}{dt} = -r_2 \tag{63}$$

Although there are 20 chemical species in the considered model (Eq. 48-63) not all of them are necessary for performing numerical simulations. Since the concentrations of CH_3OH, CO and O_2 are in excess they were considered to be constant and consequently incorporated in the appropriate rate constants. On the other hand, PEGP is a typical product and does not affect kinetics since its concentration does not participate in any expressions for the reaction rates. Therefore, it is not required for performing numerical simulations while its concentration can be calculated from conservation relations.

As can be seen from Figure 1, numerical simulations of the reaction network given in Table 4 have shown that the modified reaction network can reproduce the anticipated oscillatory dynamics and therefore, our primary goal was reached. Dampened oscillations of [Pd] (Fig.1a) and $[H^+]$ (Fig.1b) are consequence of slow and approximately continuous depletion of the [PEGA] from nearly $2\ 10^{-3}$ M to about $0.5\ 10^{-3}$ M within the time interval used in this simulation.

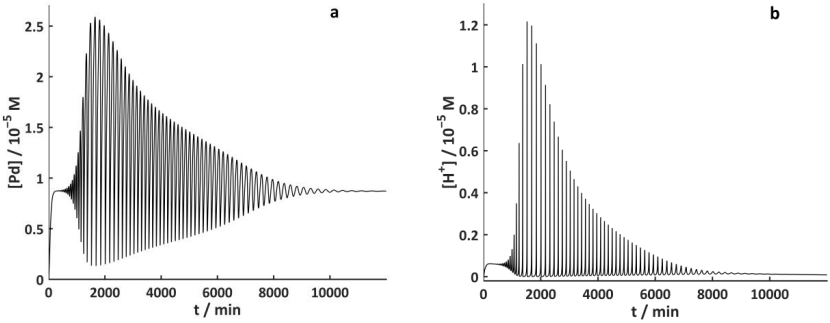


Figure 1. Result of the numerical simulations of the model presented in Table 4. **a)** [Pd] *vs* time **b)** [H+] *vs* time). Values of the rate constants and initial conditions are following: k_1 = 40.3704 min^{-1}, k_{-1} = 9.5288 × 10^2 mol^{-1} dm^3 min^{-1}, k_2 = 6.0089 mol^{-1} dm^3 min^{-1}, k_3 = 1.1992 × 10^8 min^{-1}, k_4 = 2.3984 × 10^8 min^{-1}, k_5 = 0.20000 mol^{-1} dm^3 min^{-1}, k_6 = 5.2008 × 10^3 mol^{-2} dm^6 min^{-1}, k_7 = 4.6080 × 10^6 mol^{-1} dm^3 min^{-1}, k_8 =9.6000 × 10^5 mol^{-1} dm^3 min^{-1}, k_9 = 4.7220 × 10^{14} mol^{-2} dm^6 min^{-1}, k_{10} = 4.7220 × 10^8 mol^{-1} dm^3 min^{-1}, k_{11} = 2.8000 mol^{-1} dm^3 min^{-1}, k_{-11} = 2.4874 × 10^4 mol^{-1} dm^3 min^{-1}, k_{12} = 3.7637 × 10^{-4} min^{-1}, k_{-12} = 5.1072 × 10^2 mol^{-1} dm^3 min^{-1}, k_{13} = 18.8192 min^{-1}, k_{-13} = 3.1165 × 10^3 mol^{-1} dm^3 min^{-1}, $[PEGA]_0$ = 2.03 × 10^{-3} mol dm^{-3}, $[PdI_2]_0$= 4.05 × 10^{-5} mol dm^{-3}, $[I^-]_0$ = 2.28 × 10^{-3} mol dm^{-3}.

Additionally, our numerical calculations confirmed that minor $M_{H^+,\,PdI_4^{2-},\,HI,\,Pd,\,I_2}$, given by Eq. 45 becomes negative under the conditions where oscillations occur in numerical simulations, while other two (Eq. 46 and Eq. 47) remain positive. Therefore, we may conclude that feedback loop responsible for oscillations in this model, is contained in reactions between the species H^+, PdI_4^{2-}, HI, Pd and I_2.

4. Conclusion

The previously modelled reaction mechanism of the palladium-catalysed oscillatory carbonylation of PEGA was represented by two reaction networks, Tables 2 and 3. The first one, Table 2, consisted of chemical reactions as proposed by Donlon and Novakovic (Table 1)[25], whereas the second one, presented in Table 3, consisted of chemical reactions adapted to fit the rate equations used by Donlon and (Table 1) in numerical simulations of the experimentally observed phenomena. Their stabilities were both examined by stoichiometric network analysis. It was found that the basic steady state can be unstable and consequently oscillations may occur only in the second variant of the reaction network (Table 3). However,

since in this reaction network, which consists of chemical reactions adapted to fit in the rate equations given in Table 3, there were several details that had to be resolved, a more realistic reaction network was proposed. In the modified reaction network the direct autocatalytic steps were replaced with autocatalytic loops. In this procedure some complex net reactions were resolved and some new ones were added, in other words, the reaction network's stoichiometry and the mechanism responsible for the appearance of oscillations was changed. Moreover, in the modified reaction network, the expressions for reaction rates corresponds formally to their stoichiometry in accordance with mass action kinetics. The instability condition, obtained by SNA, was further tested and confirmed by numerical simulation.

Finally, we would like to highlight that, besides all the modifications of the initial reaction networks (Table 2 and 3), the obtained net reaction of the new reaction network (Table 4), that is (Eq.35) is equivalent to the initial one (Eq.8). Thus, the new reaction network in Table 4 is a suitably extended variant of the previous one given in Table 1. In this context, the direct autocatalytic steps are replaced in the new variant of the reaction network by a reaction loop including reactions R4.7, R4.8, and R4.9 with the net reaction R4.14.

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