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# Insight into the origin of pyrocatechol inhibition on oscillating Bray-Liebafsky reactions: combined experimental and theoretical study

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Maja C. Pagnacco (maiden name Milenković) received her B.Sc (2008), and Ph.D (2013) in physical chemistry from the University of Belgrade, Serbia. As Associate Research Professor (2019), M. P. participates in many National basic research projects funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia. She is an active member of the Society of Physical Chemists of Serbia. Main fields of interest: halogen chemistry, oscillatory reactions, catalysis, kinetics, mechanism, and model investigation.

## Abstract

The pyrocatechol inhibitory effect on the oscillatory Bray-Liebafsky (BL) reaction is reported. Obtained results are compared with those available in the literature (R. Cervellati et al, *Helvetica Chimica Acta* 2001) for Briggs-Rauscher (BR) reaction with pyrocatechol addition. The two orders of magnitude larger calibration curve slope obtained in BR in comparison to BL reaction, suggests that different reactions are responsible for inhibitory effects in these systems. The potential explanation of pyrocatechol behavior is given by employing the ultraviolet-visible (UV/VIS) spectroscopy, density functional theory, and coupled cluster computational methods. The last two were employed for the first time to discover potential candidates among unstable chemical species HIO, HIO<sub>2</sub>, I<sub>2</sub>O, HOO<sup>•</sup>, HO<sup>•</sup>, IO<sup>•</sup>, IO<sub>2</sub><sup>•</sup>, and I<sup>•</sup> of the BL (and BR) system for reaction with pyrocatechol. The calculated reaction rate constants for the hydrogen atom transfer reactions between pyrocatechol and free radical intermediates indicate the following order of reactivity: HO<sup>•</sup>>IO<sup>•</sup>>HOO<sup>•</sup>>IO<sub>2</sub><sup>•</sup>. The same order of reactivity is also observed in the case of a thermodynamic investigation. In addition, kinetic insight indicates that the inhibitory behavior of pyrocatechol could not be explained with one particular chemical reaction in BL (or in BR) oscillatory system.

**Keywords:** oscillatory reaction; pyrocatechol; computational methods.

## 1. Introduction

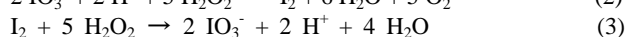
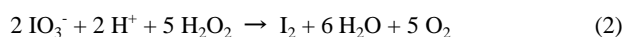
Bray-Liebafsky (BL)<sup>1</sup> reaction is the oldest known oscillating reaction. Since it was discovered, the BL system has attracted a high interest for both, mechanistic<sup>2-4</sup> and exotic dynamics point of view.<sup>5-8</sup>

The BL reaction represents the catalytic decomposition of the hydrogen peroxide into oxygen and water, in the presence of iodate (IO<sub>3</sub><sup>-</sup>) and hydrogen ions (H<sup>+</sup>):



Although it seems simple since it includes only three reactants, this reaction has a very complex and unexplained mechanism which may involve numerous stable and unstable

intermediate species, such as non-radicals: I<sub>2</sub>, I, HIO, HIO<sub>2</sub>, I<sub>2</sub>O,<sup>2,3,9,10</sup> and several free radical species: IO<sub>2</sub><sup>•</sup>, HOO<sup>•</sup>, HO<sup>•</sup>, I<sup>•</sup>.<sup>2,4,11-14</sup> The problem is further complicated because it does not mean that all these intermediates are crucial for the BL reaction core model. Generally, in the BL reaction (1), hydrogen-peroxide decomposition is the result of two complex pathways in which hydrogen peroxide acts either as a reducing (2) or as an oxidizing (3) agent:



Therefore, the sum of reactions (2) and (3) gives the reaction (1). When the rates of the mentioned two pathways are equal, the smooth decomposition of hydrogen peroxide is observed. However, under certain conditions, pathways (1) and (2) will alternately dominate one over the other, resulting in a cascading consumption of hydrogen peroxide concentration and an oscillatory evolution of intermediate concentrations.<sup>15</sup>

Beside wide scientific interest from the aspects of their unusual dynamics and mechanism, thanks to their great sensitivity to external perturbations, chemical oscillators have also become very popular for analytic determination of "reactive" analyte, usually antioxidant or radical scavenger.<sup>16-21</sup> It is well-known that iodate-based oscillatory Briggs-Rauscher (BR) reaction,<sup>22</sup> which is the hybrid of two oscillatory reactions Bray-Liebafsky (BL) and Belousov-Zhabotinsky<sup>23</sup> (BZ), can be inhibited by small amounts of different perturbants.<sup>19-21</sup> Based on this observation, the BR reaction was successfully applied as a test tool for measuring the concentration of different analytes and their potential antioxidative/antiradical activity.<sup>19-21,24</sup> Our recently published results<sup>25</sup> indicate that the same concentrations of analyte give a completely different influence on the dynamics of the BL and BR system. Even though UV/VIS spectroscopy determined that analyte interacts in both BL and BR reactions with respective stable chemical species, changes of dynamical states after analyte (adrenaline) addition (for applied experimental conditions) have occurred only for BR system.<sup>25</sup> The recent results point out the importance of examination of analyte interaction in both iodate based oscillators, in order to potentially clarify the mechanism of analyte acting.

The influence of the pyrocatechol addition was already examined in the BR reaction by Cervellati and coworkers.<sup>19</sup>

Thus, the main idea of this paper is an examination of the pyrocatechol influence on Bray-Liebafsky reaction and the comparison of obtained results with those found in Briggs-Rauscher reaction. The results of Cervellati et al.<sup>19</sup> showed that pyrocatechol has an inhibitory effect on BR dynamics. The authors explained that this inhibitory effect arises as a result of pyrocatechol scavenging of hydroperoxyl radicals (HOO<sup>•</sup>), produced in BR reaction. Because hydroperoxyl radical is not the only reactive species present in iodate-based oscillators we focus on elucidating which BL and BR reaction intermediate species are most likely to react with pyrocatechol. Since the potential intermediates (HIO, HIO<sub>2</sub>, I<sub>2</sub>O, HOO<sup>•</sup>, HO<sup>•</sup>, IO<sup>•</sup>, IO<sub>2</sub><sup>•</sup>, and I<sup>•</sup>) are usually unstable the computational approach is used to complement the presented results. This approach includes reaction energy predictions using different computational methods and is applied in this work to investigate interactions between unstable reactive species involved in BL and BR system and pyrocatechol.

In addition to nonlinear phenomena and iodate-based oscillators, the theoretical and experimental consideration applied in this work could find potential applications in environmental chemistry, particularly in the removal of phenolic compounds and the possible application of reactive halogen species in water treatment.<sup>26,27</sup>

## 2. Experimental

**Bray-Liebafsky reaction experimental setup and conditions.** All experiments were carried out in a closed well-stirred (with stirring rate,  $\sigma = 900$  rpm) reactor and thermostated at  $T = (60.0 \pm 0.2)$  °C. The reaction volume was 55 ml. The initial concentrations of reactants were:  $[KIO_3]_0 = 7.35 \times 10^{-2}$  mol dm<sup>-3</sup>,  $[H_2SO_4]_0 = 4.79 \times 10^{-2}$  mol dm<sup>-3</sup>,  $[H_2O_2]_0 = 7 \times 10^{-3}$  mol dm<sup>-3</sup>. All stock reactants solutions were pro analysis grade and prepared in deionized water. The substances were added to the reaction vessel in the following order: 27 ml KIO<sub>3</sub>, 27 ml H<sub>2</sub>SO<sub>4</sub> and when the temperature and potential were stabilized 1 ml H<sub>2</sub>O<sub>2</sub> was added. The moment when H<sub>2</sub>O<sub>2</sub> was added to the vessel was taken as the beginning of the reaction. Different concentrations of the pyrocatechol were added (100  $\mu$ l aliquot) into the reaction after the second oscillation. The time evolution of the BL reaction was followed by the iodide ion-selective electrode as a working electrode and a double junction Ag/AgCl electrode as a reference electrode.

**UV-VIS measurements.** In order to investigate potential interactions between pyrocatechol and stable species of the BL system Agilent 8453 UV/VIS Diode Array Spectrophotometer was used. The UV/VIS spectra were recorded for the following combinations of reacting species in 3 ml reaction volume:

- Pure pyrocatechol at room temperature and at  $T = 60$  °C (concentration of pyrocatechol in cuvette was  $5 \times 10^{-4}$  M),
- Pyrocatechol with iodate in acidic media (concentrations in cuvette:  $[C_6H_6O_2]_0 = 5 \times 10^{-4}$  M,  $[KIO_3]_0 = 3.6 \times 10^{-2}$  M and  $[H_2SO_4]_0 = 4.8 \times 10^{-2}$  M),
- Pyrocatechol with iodine in acidic medium (concentrations in cuvette:  $[C_6H_6O_2]_0 = 5 \times 10^{-4}$  M,  $[I_2]_0 = 2.7 \times 10^{-4}$  M and  $[H_2SO_4]_0 = 4.8 \times 10^{-2}$  M),
- Pyrocatechol with iodide in acidic medium (concentrations in cuvette:  $[C_6H_6O_2]_0 = 5 \times 10^{-4}$  M,  $[I^-]_0 = 1 \times 10^{-3}$  M and  $[H_2SO_4]_0 = 4.8 \times 10^{-2}$  M) and
- Pyrocatechol with hydrogen peroxide (concentrations in cuvette:  $[C_6H_6O_2]_0 = 5 \times 10^{-4}$  M and  $[H_2O_2]_0 = 3.9 \times 10^{-3}$  M).

In order to observe all peaks in UV/VIS spectra, except pyrocatechol and sulfuric acid, concentrations of all species in

cuvette were smaller than in experiments in batch BL reactor. Time-based measurements of absorbance were collected for 600 s at a characteristic wavelength for pyrocatechol (at 276 nm), triiodide complex (at 287 nm, 353 nm), iodine (at 460 nm) and o-Quinone (390 nm).

## 3. Theoretical background

**General details.** All calculations were carried out by the Gaussian 09 program package.<sup>28</sup> The equilibrium geometries of reactants and products were fully optimized and frequency calculations were performed utilizing two density functionals: M06-2X<sup>29</sup> and B3LYP-D3.<sup>30,31</sup> To obtain more accurate energy values the coupled cluster CCSD method was applied.<sup>32</sup> Moreover, starting from the CCSD optimized geometries, the single-point energy calculations were performed using the CCSD(T) method. In addition, to give better insight into the mechanisms of investigated reactions, the transition states (TS) were calculated using the B3LYP-D3 level of theory. The TS structures were additionally studied by performing the IRC (intrinsic reaction coordinate) calculations. These calculations show that each transition state connects two corresponding energy minima: reactant complex (RC) and product complex (PC). The 6-311++G(d,p) basis set for carbon, oxygen and hydrogen atoms and def2-TZVPD for iodine atom were utilized.<sup>33</sup> All calculations refer to water solution at  $P = 101325$  Pa and  $T = 333.15$  K, in agreement with experimental conditions. To mimic water solution the SMD continuum solvation model was used.<sup>34</sup>

**Calculation of the reaction rate constants.** The Eyring equation, often called the transition state theory (TST) equation, is the most convenient way to interpret the thermal rate constants in contemporary solution-phase kinetics. For monomolecular reactions this equation is as follows:

$$k_{TST} = k_B T / h \exp(-\Delta G_a^\ddagger / RT) \quad (4)$$

In Eq. (4)  $k_B$  and  $h$  stand for the Boltzmann and Planck constants respectively, and  $\Delta G_a^\ddagger$  is the reaction free energy of activation.

The Eyring equation can be transformed into:

$$k_{ZCT-0} = \sigma \gamma(T) \frac{k_B T}{h} \exp(-\Delta G_a^\ddagger / RT) \quad (5)$$

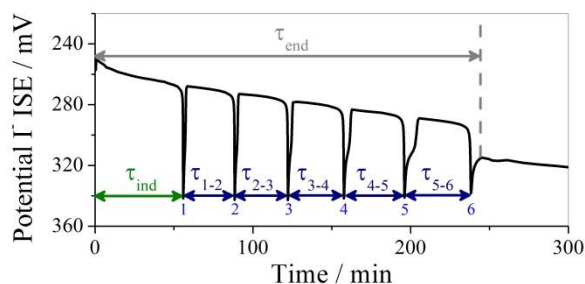
where  $\sigma$  and  $\gamma(T)$  denote reaction path degeneracy and transmission coefficient, respectively. The reaction path degeneracy accounts for the number of equivalent reaction paths. The transmission coefficient corrects for tunneling effects (defined as the Boltzmann average of the ratio between the quantum and classical probabilities), the nonseparability of the reaction coordinate, and nonequilibrium reactants.

In this work all examined reactions are bimolecular, implying that Eqs (4) and (5) become significantly more complex.<sup>35, 36</sup>

For this reason, the reaction rate constants were calculated using the TheRate program,<sup>36</sup> in which these equations are incorporated. This program has been successfully applied for calculation and reproduction of the experimentally obtained reaction rate constants of bimolecular reactions.<sup>37-39</sup> The  $k_{ZCT-0}$  values were calculated using the Eckart method,<sup>40</sup> also referred to as ZCT-0. The energy values and partition functions were taken from the quantum mechanical calculations.

## 4. Results and Discussion

**The inhibitory effects of pyrocatechol addition in Bray-Liebafsky reaction.** The recorded I<sup>-</sup> ISE-potential vs. time series (or oscillogram) of the BL reaction without pyrocatechol is shown in Figure 1. From the presented oscillogram, it can be seen that without pyrocatechol and under mentioned conditions (see Experimental part), the duration of the BL reaction is  $\tau_{end} = 245$  min. For that time system initially passes through induction period,  $\tau_{ind} = 55$  min, after which oscillatory behavior (six oscillations) takes place.

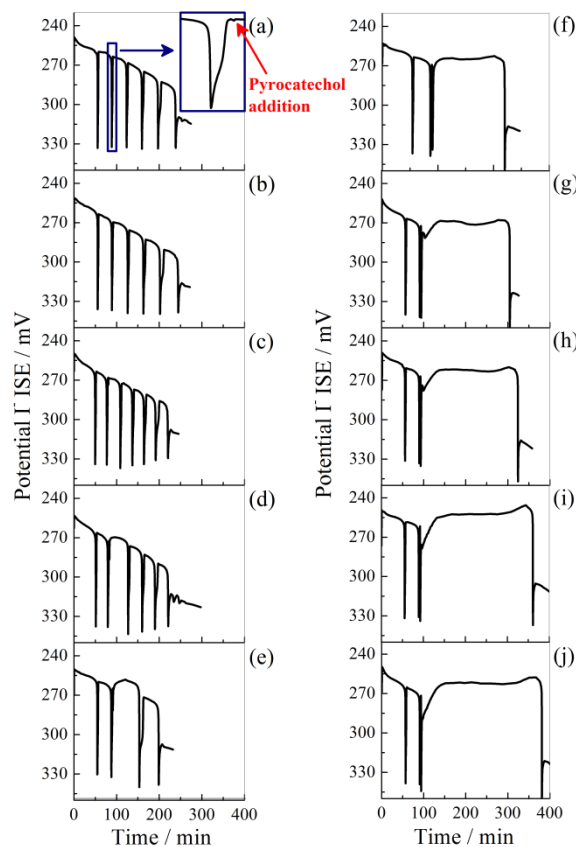


**Figure 1.** Potential I SE time series (oscillogram) of the Bray-Liebafsky reaction obtained under batch reactor under following conditions  $[KIO_3]_0 = 7.35 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[H_2SO_4]_0 = 4.79 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[H_2O_2]_0 = 7 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $T = (60.0 \pm 0.2 \text{ } ^\circ\text{C})$  and  $\sigma = 900 \text{ rpm}$ , with marked oscillogram properties such as: induction period,  $\tau_{\text{ind}}$ , periods between oscillations,  $\tau_{1-2}$ ,  $\tau_{2-3}$ ,  $\tau_{3-4}$ ,  $\tau_{4-5}$ ,  $\tau_{5-6}$ , number of oscillations and duration of the oscillogram,  $\tau_{\text{end}}$ .

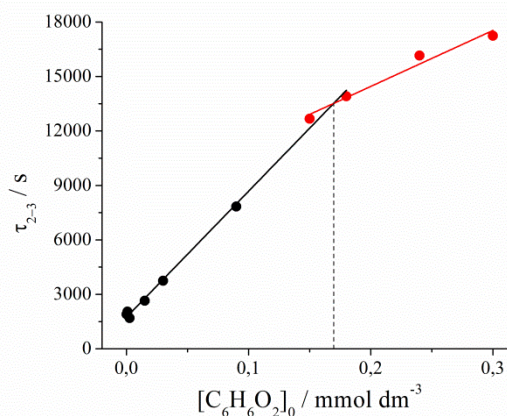
In this paper, the influence of the pyrocatechol, in the wide range of its concentrations from  $9.0 \times 10^{-8} \text{ mol dm}^{-3}$  to  $3.0 \times 10^{-4} \text{ mol dm}^{-3}$ , on Bray-Liebafsky reaction dynamics was investigated. The pyrocatechol is added immediately after the second oscillation was completed. The moment of addition is also important regarding previously reported<sup>13</sup> different TEMPONE radical signal before and after BL oscillation. The TEMPONE radical signal was always lower before the oscillation than after it, suggesting an intensified production of radicals or other strong oxidizing agents before the oscillation. Therefore, the pyrocatechol is added after the oscillation due to the presence of analyte-pyrocatechol at the “beginning” of the production of potential strong oxidation agents, as well as to have better experimental control of the addition. The oscillograms of the BL reaction with different pyrocatechol concentrations are given in Figure 2. It is noticeable, from Figure 2, that the addition of pyrocatechol changes the evolution of the BL system. Namely, it can be seen that the addition of pyrocatechol inhibits oscillatory behavior and therefore, prolong the time of the emergence of the third oscillation (Figure 2). Furthermore, it can be seen that small concentration ( $< 3 \times 10^{-5} \text{ M}$ ) of added pyrocatechol after inhibition period provokes regular BL oscillations (Figure 2 a-e), while higher pyrocatechol concentration ( $> 9 \times 10^{-5} \text{ M}$ ) quench oscillatory behavior with the characteristic appearance of the one oscillation when the system exits oscillatory mode (Figure 2 f-j).

The influence of different pyrocatechol concentrations on the time between the second and third oscillation is shown in Figure 3. As it can be seen from BL oscillograms presented in Figure 2 and confirmed in Figure 3., there are two different pyrocatechol behavior in BL reaction depending on pyrocatechol concentration added. It is demonstrated that in a range of pyrocatechol concentration from  $9.0 \times 10^{-8} \text{ M}$  to  $1.8 \times 10^{-4} \text{ M}$ , the period between second and third oscillation shows linearity with the regression equation, obtained for investigated experimental conditions:  $\tau_{2-3} = 6.94 \times 10^4 \times C_{\text{pyrocatechol}} + 1736$ , (concentration presented in  $\text{mmol dm}^{-3}$  and  $\tau$  denoted in s, due to easier comparison of results with pyrocatechol addition in Briggs-Rauscher oscillatory reaction). Furthermore, for the pyrocatechol concentration above  $1.8 \times 10^{-4} \text{ M}$  system also shows linearity with the regression equation:  $\tau_{2-3} = 3.08 \times 10^4 \times C_{\text{pyrocatechol}} + 8284$ . The slopes of these two regression equations are different, and the larger slope is obtained for the smaller concentration of pyrocatechol, indicating better sensitivity of

the BL system toward low pyrocatechol concentration ( $< 1.8 \times 10^{-4} \text{ M}$ ). The intersection of these two curves shows the critical concentration of pyrocatechol ( $1.7 \times 10^{-4} \text{ M}$ ) at which „both kinetics“ are present for the experimental conditions used here (Figure 3.).



**Figure 2.** Oscillograms of the BL reaction with different concentrations of pyrocatechol, added after second oscillation:  $9 \times 10^{-8} \text{ mol dm}^{-3}$  (a),  $9 \times 10^{-7} \text{ mol dm}^{-3}$  (b),  $2.7 \times 10^{-6} \text{ mol dm}^{-3}$  (c),  $1.5 \times 10^{-5} \text{ mol dm}^{-3}$  (d),  $3 \times 10^{-5} \text{ mol dm}^{-3}$  (e),  $9 \times 10^{-5} \text{ mol dm}^{-3}$  (f),  $1.5 \times 10^{-4} \text{ mol dm}^{-3}$  (g),  $1.8 \times 10^{-4} \text{ mol dm}^{-3}$  (h),  $2.4 \times 10^{-4} \text{ mol dm}^{-3}$  (i),  $3 \times 10^{-4} \text{ mol dm}^{-3}$  (j)



**Figure 3.** Dependence of the period between second and third oscillation on pyrocatechol concentration

In comparison to previously published results in the BR system with pyrocatechol,<sup>19</sup> it can be concluded that BR reaction is more sensitive to pyrocatechol addition than BL reaction. This conclusion can be made based on the larger slope (two orders of magnitude) obtained in BR reaction system ( $\tau_{inh} = 1.58 \times 10^6 \times C_{\text{pyrocatechol}} - 5482$ , where  $C$  is in  $\text{mmol dm}^{-3}$ , and  $\tau_{inh}$  is in seconds from ref.<sup>19</sup>) compared to the slope of the linear dependence of  $\tau_{2,3}$  on pyrocatechol concentration in BL reaction ( $\tau_{2,3} = 6.94 \times 10^4 \times C_{\text{pyrocatechol}} + 1736$ ). Although the pyrocatechol added in both reactions in the oscillatory regime, it is difficult to make a precise comparison, because the sensitivity of any dynamics state depends on its vicinity to the bifurcation point for applied experimental conditions.<sup>5-7</sup> Hypothetically, if dynamical states of both oscillators were in the same vicinity of their bifurcation points (which cannot be known without transient bifurcation diagrams for Bray-Liebhaufsky and Briggs-Rauscher reaction in closed reactor) the two orders of magnitude larger slope obtained in BR could also suggest that the same reaction (or reactions) is not responsible for obtained pyrocatechol behavior in BL and BR system. The hypothesis of different reactions responsible for inhibitory behavior of pyrocatechol obtained in BL and BR system is further supported by the work of Schmitz and Furrow<sup>41</sup> and it is addressed to two different pathways of iodate reduction by hydrogen peroxide depending on hydrogen peroxide concentration, related to BL and BR reaction.

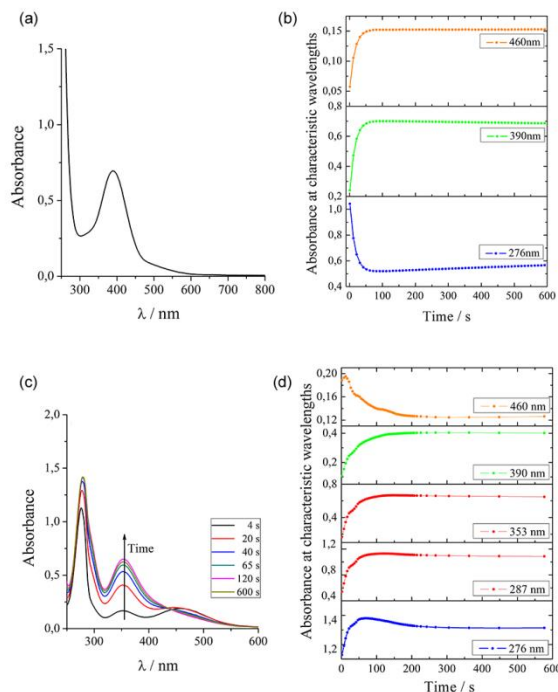
**The UV/VIS spectroscopy study of potential pyrocatechol reactions with stable BL species ( $\text{H}_2\text{O}_2$ ,  $\text{KIO}_3$ ,  $\text{I}_2$ ,  $\text{I}^-$ ) in acidic solution.** Since pyrocatechol addition showed an influence on the dynamics of the BL reaction, we wanted to examine potential interactions between pyrocatechol and stable species of BL (and BR) oscillator. For this purpose, UV/VIS spectroscopy was used. It is well known that the BL reaction takes place at high temperature ( $60^\circ\text{C}$ ) while the BR reaction takes place at room temperature. Therefore, the UV/VIS spectra of pure pyrocatechol were recorded at room and the temperature of the BL reaction system ( $T = 60^\circ\text{C}$ , for 1h), to exclude the possible thermal degradation of pyrocatechol. Both recorded spectra overlap and had a typical peak from pyrocatechol at  $\lambda = 276\text{ nm}$ , so it could be concluded that pyrocatechol remained stable at  $T = 60^\circ\text{C}$ .

The UV/VIS spectrum of pyrocatechol with hydrogen peroxide was recorded, and it showed that pyrocatechol does not interact with hydrogen peroxide. Besides, the same conclusion emerged from UV/VIS spectra pyrocatechol with iodide in acidic medium.

Unlike the previous combinations of the pyrocatechol with hydrogen peroxide and iodide in acidic medium, recorded UV/VIS spectra of the pyrocatechol with iodate in acidic media showed that pyrocatechol interacts with iodate. A new peak was observed at  $\lambda = 390\text{ nm}$ . The UV/VIS spectra of the pyrocatechol with iodate in acidic media is given in Figure 4 a, while the behavior of absorbance at 276 nm, 390 nm and 460 nm vs. time is given in Figure 4 b. Moreover, UV/VIS spectra of the pyrocatechol with iodine in acidic media showed that besides iodate, pyrocatechol interacts with iodine as well (see Figure 4 c, while the behavior of absorbance at 276 nm, 287 nm, 353 nm, 390 nm, 460 nm vs. time are presented at Figure 4 d). All spectra were collected for 600 s.

The peak around  $\lambda = 390\text{ nm}$  in the reaction between iodate and pyrocatechol in acidic solution originated from o-Quinone.<sup>42</sup> The UV/VIS spectra of the iodine-pyrocatechol system are completely masked with peaks originating from triiodide  $\text{I}_3^-$  complex (it has large molar absorption coefficients at 287 nm and 353 nm)<sup>43,44</sup>. The reaction between iodine (460 nm) and pyrocatechol (276 nm) may produce o-quinone, as

well as some iodination products. In this reaction, the iodine is reduced to iodide in two-electron processes. The formed iodide produces a triiodide complex when reacting with iodine:  $\text{I}^- + \text{I}_2 \leftrightarrow \text{I}_3^-$ . It is noticeable that the reaction between pyrocatechol and iodate has been finished in 50 s (it enters the thermodynamic equilibrium after 50 s) (see Figure 4 b). The reaction with iodine and pyrocatechol is significantly slower (Figure 4 c and d) and it enters the thermodynamic equilibrium after 200 s. The obtained UV/VIS results are not surprising. Similar conclusions about phenolic compounds reactivity have been made by Cervellati et al.<sup>42</sup>



**Figure 4.** Recorded UV/VIS spectra of pyrocatechol and iodate reaction in acidic media a), and related behavior of absorbance at 276 nm, 390 nm and 460 nm vs. time b), reaction between pyrocatechol and iodine in acidic media c), related behavior of absorbance at 276 nm, 287 nm, 353 nm, 390 nm and 460 nm vs. time d).

It should be mentioned that our attempts to simultaneously monitor the BL reaction using spectrophotometric quartz fiber optic probe (Hellma 662.000-UV, Z.12) and the iodide ion-selective electrode, and therefore further clarify reaction mechanism with pyrocatechol, were unsuccessful (see Supplementary Material). This can be explained by the fact that during the BL reaction a large amount of oxygen (bubbles) was produced which blocked the optical path and consequently produced large noise (see Figure S1 and a brief discussion).

#### Results of the computational approach:

**Thermodynamic considerations.** The concentration of pyrocatechol above  $9 \times 10^{-5}\text{ M}$ , totally quenched Bray-Liebhaufsky oscillatory behavior (Figure 2. from (f) to (j)). It is important to emphasize that pyrocatechol concentration ( $\geq 3 \times 10^{-5}\text{ mol dm}^{-3}$ ) which quenched BL oscillogram is more than three orders of magnitude smaller than iodate concentrations ( $\sim 7 \times 10^{-2}\text{ mol dm}^{-3}$ ), while the iodine concentration in both iodate-based oscillators is about  $10^{-4}\text{ M}$ . The concentration of other possible non-radical and some radical intermediates is certainly lower. What happens to the reactivity towards pyrocatechol? To elucidate this question, the computational approach was applied.

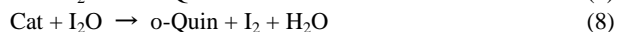
**Table 1.** Energies of the reactions (6) - (11) in kJ mol<sup>-1</sup>.

Intermediates	HO <sup>•</sup>	HOO <sup>•</sup>	I <sup>•</sup>	IO <sup>•</sup>	IO <sub>2</sub> <sup>•</sup>	I <sub>2</sub> O	I <sub>2</sub> O	HIO	HIO <sub>2</sub>	
Equation	(6)	(6)	(6)	(6)	(6)	(7)	(8)	(9)	(10)	(11)
B3LYP-D3										
$\Delta rH$	-171.6	-34.3	5.8	-71.6	-16.4	15.0	-133.9	10.4	-93.6	110.7
M06-2X										
$\Delta rH$	-155.3	-24.0	56.5	-74.8	-18.4	43.2	-120.4	36.9	-88.3	118.8
CCSD										
$\Delta rE$	-147.5	-23.7	40.4	-73.0	-18.1	17.9	-155.6	8.7	-126.3	82.2
CCSD(T)										
$\Delta rE$	-148.0	-21.1	46.4	-67.2	-2.7	24.4	-148.3	11.9	-114.1	94.0

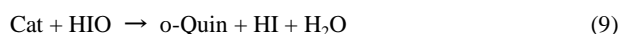
Therefore, it is necessary to investigate the reaction between pyrocatechol and non-radical intermediates such as HIO, I<sub>2</sub>O and, HIO<sub>2</sub>,<sup>2,3,9,10,45</sup> as well as with recently detected and potentially obtainable radical species in both iodate-based oscillators, such as HO<sup>•</sup>, HOO<sup>•</sup>, I<sup>•</sup>, IO<sup>•</sup>, and IO<sub>2</sub><sup>•</sup> radicals.<sup>2,4,11-14,41,46,47</sup> Based on the nature of the proposed intermediates, two types of reactions were examined. The first ones are the free radical reactions:



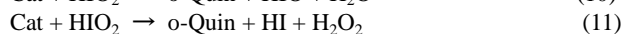
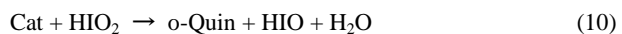
The second ones are redox reactions. In the reaction of pyrocatechol with I<sub>2</sub>O we propose the two following reaction pathways:



whereas in the case of the reaction with HIO we assumed the following reaction pathway:



In the case of the reaction with HIO<sub>2</sub> we have investigated two possible reactions:



In reactions (6) – (11) Cat stands for pyrocatechol, CatO<sup>•</sup> stands for the free radical formed from pyrocatechol, o-Quin stands for o-benzoquinone, and R<sup>•</sup> stands for HO<sup>•</sup>, HOO<sup>•</sup>, IO<sup>•</sup>, I<sup>•</sup> or IO<sub>2</sub><sup>•</sup>.

The reaction energies related to the proposed reaction pathways are summarized in Table 1.

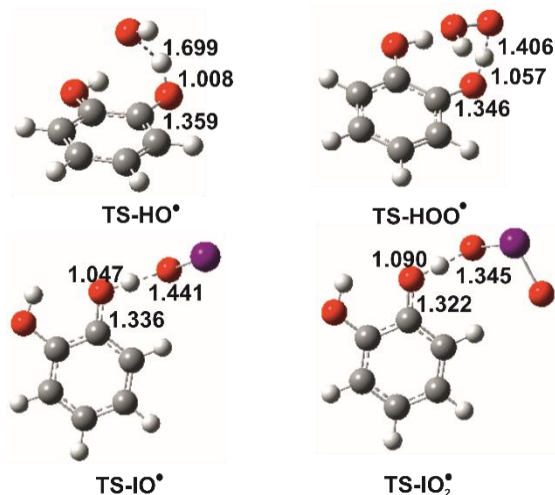
Despite some numerical differences, all four theoretical models show equal trends. An inspection of Table 1 reveals that the most favorable radical reaction of pyrocatechol is with HO<sup>•</sup>, as expected. The radical reactions with IO<sup>•</sup>, HOO<sup>•</sup>, and IO<sub>2</sub><sup>•</sup> are also characterized by negative reaction energy values, but they are much less negative than that of the reaction with HO<sup>•</sup>. When the reactions between pyrocatechol and nonradical intermediates are considered, calculated reaction energies

indicate that reaction with HIO is not thermodynamically feasible. However, the situation with I<sub>2</sub>O and HIO<sub>2</sub> molecules is rather different. Namely, the energies of the reactions described with Eqs (6) and (8) are much more favorable, than those of the reactions presented as Eqs (5) and (9) of I<sub>2</sub>O and HIO<sub>2</sub>, respectively

Considering that the most negative reaction energy values are obtained for the reactions with HO<sup>•</sup> radicals and oxyiodine species I<sub>2</sub>O, it can be concluded that these two reaction pathways, could be competitive from a thermodynamic point of view. Consequently, they could be responsible separately (or together) for observed pyrocatechol behavior in BL or BR system.

The results obtained utilizing the thermodynamic approach suggest the following order of reactivity of potential intermediates in BL and BR towards pyrocatechol: HO<sup>•</sup> > I<sub>2</sub>O > HIO<sub>2</sub> > IO<sup>•</sup> >> HOO<sup>•</sup> ≈ IO<sub>2</sub><sup>•</sup>; whereas the reactions with HIO and I<sup>•</sup> intermediates are thermodynamically unfavorable.

**Kinetic considerations.** The mechanisms of inhibition of oscillatory reactions by organic compounds are either hypothesized or completely unknown. The difficulty of studying these mechanisms is increased by the fact that some intermediates have only been recently detected (for example, before mentioned I<sub>2</sub>O).<sup>45</sup> One can assume that the mechanisms of the redox reactions are particularly complex. On the other hand, it has been lately reported that the oxidation reactions between organic compounds and free radical intermediates occur via hydrogen atom transfer (HAT) mechanism.<sup>48,49</sup> Considering this fact, the HAT mechanism for all thermodynamically favorable reactions involving free radicals were further investigated. The TSs for the HAT reactions between Cat and HO<sup>•</sup>, IO<sup>•</sup>, HOO<sup>•</sup>, and IO<sub>2</sub><sup>•</sup> radicals were successfully revealed (Figure 5.; Cartesian coordinates of all TSs are provided in the Supplementary data). The results of the IRC calculations for two representative TSs are presented in Figures S2 and S3. In all TSs, the planarity of the system is preserved. Moreover, in all cases, the reaction center is stabilized with a hydrogen bond between the oxygen of the reactive hydroxyl group and a vicinal hydroxyl group. The results for the activation energies and both reaction rate constants  $k_{\text{TST}}$  and  $k_{\text{ZCT}_0}$  for the investigated reactions are summarized in Table 2.



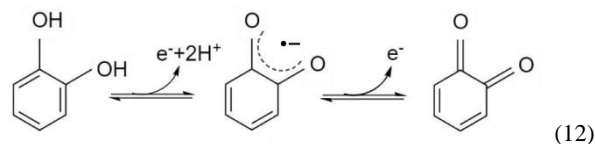
**Figure 5.** Optimized geometries of transition states for the HAT reaction pathways of pyrocatechol with HO<sup>•</sup>, IO<sup>•</sup>, HOO<sup>•</sup>, and IO<sub>2</sub><sup>•</sup> radicals. All distances are reported in Å. Carbon atoms are depicted in gray, oxygen atoms in red, iodine atoms in violet, and hydrogen atoms in white color.

**Table 2.** Gibbs free energies of activation  $\Delta G_a^\ddagger$  (kJ mol<sup>-1</sup>) and rate constants (M<sup>-1</sup> s<sup>-1</sup>) for the reactions of Cat with HO<sup>•</sup>, IO<sup>•</sup>, HOO<sup>•</sup>, and IO<sub>2</sub><sup>•</sup> radicals via the HAT mechanism.  $k_{TST}$  and  $k_{ZCT-0}$  denote the rate constants calculated using TST and Eckart methods.

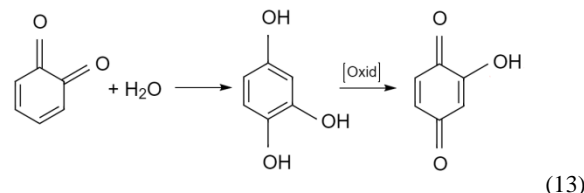
Free radicals	$\Delta G_a^\ddagger$	$k_{TST}$	$k_{ZCT-0}$
HO <sup>•</sup>	16.0	$4.40 \times 10^{11}$	$5.60 \times 10^7$
IO <sup>•</sup>	20.2	$2.02 \times 10^{11}$	$3.81 \times 10^7$
HOO <sup>•</sup>	48.4	$3.64 \times 10^6$	$4.27 \times 10^6$
IO <sub>2</sub> <sup>•</sup>	45.6	$2.11 \times 10^7$	$1.59 \times 10^6$

A comparison of  $k_{TST}$  and  $k_{ZCT-0}$  values shows that the two rate constants for reactions of pyrocatechol with HOO<sup>•</sup> and IO<sub>2</sub><sup>•</sup> are comparable (Table 2) indicating that both TST (Eq. 3) and Eckart (Eq. 4) methods are suitable for assessing the rates of these reactions. On the other hand, a significant discrepancy between the two values is observed in the case of the reactions with HO<sup>•</sup> and IO<sup>•</sup> radicals. Namely,  $k_{ZCT-0}$  values are considerably smaller. In rare cases, such as these two reactions  $k_{TST}$  decreases with increasing temperature, and  $k_{ZCT-0}$  values are significantly smaller at all temperatures (Figure S4.). It is evident that conventional TST is not adequate for evaluating the rates of such HAT pathways. Bearing in mind that the reactions with HO<sup>•</sup> and IO<sup>•</sup> are characterized with extremely small activation energy, the failure of TST can be attributed to the flat potential energy surface.<sup>37-39</sup> The obtained  $k_{ZCT-0}$  values indicate the following order of reactivity: HO<sup>•</sup>>IO<sup>•</sup>>HOO<sup>•</sup>>IO<sub>2</sub><sup>•</sup>. It is worth pointing out that the obtained order of reactivity of the free radical intermediates is the same as the order observed in thermodynamic investigation.

**Additional remarks.** Both oscillating systems can support the production of o-quinone generated by the potentially fast reaction of iodate and pyrocatechol. However, the pyrocatechol concentration ( $\geq 3 \times 10^{-5}$  mol dm<sup>-3</sup>) which quenched the BL oscillogram is more than three orders of magnitude smaller than iodate concentration ( $\sim 7 \times 10^{-2}$  mol dm<sup>-3</sup>), thus small changes in iodate concentration will *not* directly affect BL (or BR) oscillogram. The oxidation reaction of pyrocatechol with iodate should also be two electron-process, which passes through a first step in which the radical semiquinone is formed (Eq. 12):



The problem is more complex because the potentially formed o-quinone (in pyrocatechol-iodate reaction or other possible reactions Eqs 7-11) is unstable species in aqueous solution:<sup>50,51</sup>



Furthermore, the obtained C<sub>6</sub>H<sub>3</sub>(OH)<sub>3</sub> can also be further oxidized (Eq 13) or iodinated.<sup>51</sup>

From a kinetic point of view, the rate constant of pyrocatechol and iodate reaction could be smaller than the rate constant for the reaction between pyrocatechol and HIO<sub>2</sub>, but the concentration of IO<sub>3</sub><sup>-</sup> is several orders of magnitude higher, which could certainly influence the overall rate of reaction. Although the reaction between pyrocatechol and HIO<sub>2</sub> is exergonic and therefore thermodynamically favorable, many studies on the mechanism of BL and BR reactions have shown that other reactions of HIO<sub>2</sub> (for example with H<sub>2</sub>O<sub>2</sub> or I<sup>-</sup>) are also fast in BL (and BR) system. This brings into question the importance of HIO<sub>2</sub> reaction with pyrocatechol producing inhibitory effect in BL (or in BR) reaction. On the other hand, recently detected and potentially key intermediate in BL reaction<sup>10</sup>, I<sub>2</sub>O, exhibits thermodynamically favorable reaction with pyrocatechol. This fact indicates that, besides iodate-pyrocatechol reaction, I<sub>2</sub>O-pyrocatechol reaction could be considered as a dominantly responsible reaction for inhibitory effect obtained in BL reaction.

Additionally, there is no doubt that the HO<sup>•</sup> radical is very reactive, which is also reflected through highly exergonic reaction energy value in the reaction between pyrocatechol and HO<sup>•</sup>. However, the reaction between HO<sup>•</sup> radical and hydrogen peroxide:



is also very fast ( $k = 4.5 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>).<sup>52,53</sup> Moreover, the concentration of H<sub>2</sub>O<sub>2</sub> is about  $\sim 10^5$  times greater than the concentration of pyrocatechol, taking into account the experimental condition applied in this work. Thus, every HO<sup>•</sup> that is formed would quickly be converted to HOO<sup>•</sup>.<sup>54</sup> It is well known that HOO<sup>•</sup> radical exhibits slow reaction with H<sub>2</sub>O<sub>2</sub>,<sup>55</sup> and therefore the HOO<sup>•</sup> radical could be considered as an important intermediate causing an inhibitory effect in oscillatory reactions with pyrocatechol. Regarding HOO<sup>•</sup> radical, it should be stressed that because of higher hydrogen peroxide concentration present in the BR in comparison to BL system, the BR is certainly better ROS (reactive oxygen species, such as HO<sup>•</sup>, HOO<sup>•</sup>) generator. Thus, the reaction between pyrocatechol and HOO<sup>•</sup> radical is more likely in BR, than in the BL system.

Consequently, what is the impact of obtained results on Bray-Liebafsky (and Briggs-Rauscher) reaction with pyrocatechol?

Regarding significantly different slope obtained in these

two oscillatory systems (two orders of magnitude higher in BR than in BL system), it could be concluded that the same reaction (or reactions) are not responsible for the inhibitory effect of pyrocatechol addition in Bray-Liebhafsky and Briggs-Rauscher reactions.

Obtained results also indicated that, depending on pyrocatechol concentration, two kinetics exist in the BL reaction. The critical pyrocatechol concentration at which complex behavior is present (for investigated experimental conditions) is  $1.7 \times 10^{-4}$  M. Interestingly, this concentration is the same order of magnitude ( $\sim 10^{-4}$  M) as one of the key intermediates in BL (and BR) reaction - iodine. This can mean that at very small pyrocatechol concentration ( $\ll 1.7 \times 10^{-4}$  M) very fast pyrocatechol reaction proportional to [Cat] dominates in BL system, while at higher pyrocatechol concentration ( $\gg 3 \times 10^{-4}$  M) reactions with lower rate constant which is proportional to [Cat] or to the square of pyrocatechol concentration (possible dimerizing reaction) can also occur so that the net result depends on [Cat]. Thus, at lower [Cat] reactions with iodate or  $I_2O$  probably dominate, in addition to the reactions of their oxidation/iodination products (Eqs 12, 13). When the concentration of added pyrocatechol is higher ( $> 1.7 \times 10^{-4}$  M), the reactions with lower rate constants (probably with  $I_2$  or  $HIO_2$ ) could also occur in the BL system because of the overall rate of reaction increases. Therefore, we assume that the curve in Figure 2 obtained for low pyrocatechol concentration represents fast pyrocatechol reaction(s) in the BL system. When pyrocatechol concentration increase, the fast reactions exists as well, but additional reactions with lower rate constants could also take part in BL mechanism with pyrocatechol at concentration  $> 1.7 \times 10^{-4}$  M. All the above-mentioned facts result in slightly lower slope obtained for higher pyrocatechol concentration. The possible explanations for slightly lower slope and, consequently, different kinetic obtained at higher pyrocatechol concentration could be:

- i) kinetically less active organic products of these side pyrocatechol reactions,
- ii) the BL system's lower sensitivity toward changing intermediate concentration which additionally reacts at higher pyrocatechol concentration, and more likely
- iii) changing the oxidation/iodination reaction pathway due to the change of the overall rate of oxidation/iodination reactions involving pyrocatechol.

Regarding hydrogen peroxide concentration used in these two oscillatory systems, there is no doubt that the BR system is the better generator of reactive oxyradical species ( $HO^\bullet$  and  $HOO^\bullet$ ) due to significantly higher hydrogen peroxide concentration. Therefore, pyrocatechol almost certainly reacts with  $HOO^\bullet$  in BR system, but also possibly has side reactions with iodate when present in high access.

## 5. Conclusion

In this paper, usage of batch Bray-Liebhafsky reaction system for determination of pyrocatechol concentration was investigated. A wide range of pyrocatechol concentrations from  $9.0 \times 10^{-8}$  mol  $dm^{-3}$  to  $3.0 \times 10^{-4}$  mol  $dm^{-3}$  was used for the perturbations of the oscillatory BL system. The addition of pyrocatechol between second and third oscillation influenced BL dynamics in a way that inhibits oscillatory behavior. Results obtained suggest "two kinetics" in the BL reaction depending on pyrocatechol concentration. The critical pyrocatechol concentration which exists between these two kinetics is  $1.7 \times 10^{-4}$  M.

Obtained results for the BL system were compared with

previously published results for Briggs-Rauscher reaction with pyrocatechol addition. In both systems, pyrocatechol exhibited the inhibitory behavior, but it can be concluded that BR reaction is more sensitive to pyrocatechol addition than BL reaction. The two orders of magnitude larger calibration curve slope obtained in BR in comparison to BL could also suggest that the same reaction (or reactions) is not responsible for observed pyrocatechol behavior in BL and BR system.

The recorded UV/VIS spectra of the pyrocatechol reaction with stable BL species ( $H_2O_2$ ,  $IO_3^-$ ,  $I_2$ ,  $I^-$ ) in acidic media have shown that pyrocatechol interacts with iodate and iodine, but the pyrocatechol-iodate reaction is kinetically more preferable. Moreover, the reactivity of pyrocatechol towards unstable and potentially present BL and BR intermediates ( $HIO_2$ ,  $HIO$ ,  $I_2O$ ,  $IO_2^\bullet$ ,  $I^\bullet$ ,  $IO^\bullet$ ,  $HO^\bullet$ ,  $HOO^\bullet$ ) was examined using density functional theory and coupled cluster computational calculations. According to the calculated thermodynamic parameters, the order of reactivity of potential intermediates in BL and BR towards pyrocatechol should be as follows:  $HO^\bullet \approx I_2O > HIO_2 > IO^\bullet \gg HOO^\bullet \approx IO_2^\bullet$ . On the other hand, the reactions with  $HIO$  and  $I^\bullet$  intermediates are thermodynamically unfavorable. In addition, the HAT mechanism between Cat and  $HO^\bullet$ ,  $IO^\bullet$ ,  $HOO^\bullet$ , and  $IO_2^\bullet$  radicals was examined. The obtained reaction rate constant ( $k_{ZCT,0}$ ) values suggest the following order of reactivity:  $HO^\bullet > IO^\bullet > HOO^\bullet > IO_2^\bullet$ . It should be pointed out that the obtained order of reactivity of the free radical intermediates is identical as the order observed in thermodynamic investigation. Finally, it can be inferred that kinetical consideration implies a more complex situation. Namely, chemical kinetics is full of traps and the inhibitory behavior of pyrocatechol could not be addressed to only one chemical reaction in BL (or in BR) oscillatory system.

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