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New Experimental and Mechanistic Investigation on the KSCN-H₂O₂-NaOH-Cu(II)-Catalyzed Oscillating System (Orbàn–Epstein Reaction): Inhibitory Effects by Diphenols

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ABSTRACT: The KSCN-H₂O₂-NaOH-Cu(II)-catalyzed system is one of the few reactions in which chemical oscillations can be observed in batch conditions. In the present paper, this oscillating reaction was revisited in a wide range of initial concentrations of all components in batch. A mixture with a long lasting oscillation time (1 h 34 min) and a great number of oscillations (24) was found and used to investigate the effect of temperature. An Arrhenius-type temperature dependence was observed from which an apparent “average activation energy” $E_{av} = 76 \pm 5$ kJ for the overall oscillatory reaction was observed. A mechanistic study based on a modified model analyzed by the stoichiometric network analysis approach gave a satisfactory agreement between calculated and experimental oscillating behaviors and temperature dependence. The addition of the three diphenols (catechol, resorcinol, and hydroquinone) causes perturbations similar to those observed in the Briggs-Rauscher oscillating system, i.e., an inhibition of the

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oscillatory regime. These inhibitory effects were described in detail, and a reasonable qualitative interpretation is given. © 2014 Wiley Periodicals, Inc. *Int J Chem Kinet* 47: 82–92, 2015

INTRODUCTION

The system KSCN-H₂O₂-CuSO₄-NaOH, also known as the Orbán–Epstein reaction (OE) [1,2], together with the Bray–Liebhafsky (BL) [3], Belousov–Zhabotinsky (BZ) [4], and Briggs–Rauscher (BR) [5] reactions, are the few systems in which chemical oscillations can be observed in batch conditions, as well as, in flow conditions. These systems belong to different families of chemical oscillators, the first to the sulfur family, the others to the halate–halide one, as defined by Epstein [6]. However, a common feature of BL, BR, and OE oscillating reactions is hydrogen peroxide which acts as a reagent. The presence of oxygen-centered radicals such as •OH and •OOH as intermediates has been postulated in the mechanisms of these reactions [2,7,8]. Even if the debate on the effective role of these radicals is still open [9,10], some experimental evidence of their presence has been recently reported in a subsystem of BL and BR reactions [11,12]. Indirect experimental evidence of •OOH radicals involvement in the BR reaction mechanism comes by investigation of perturbations provoked by the addition of diphenols to active BR mixtures [13]. A detailed mechanism for the OE reaction involving 30 steps and 26 independent variables was first presented in 1989 by Luo *et al.* [2]; this mechanism was satisfactorily checked comparing some experimental and simulated behaviors both in batch and flow conditions [2]. In this mechanism, HOO• radicals play an important role, but since the pK_a for the couple HOO•/O₂•⁻ is 4.8 [14], and the reaction takes place between about pH 10 and 12, most HOO• would be in the form of O₂•⁻. Thus, Luo *et al.* [2] used a rate constant that is appropriate for about pH 10–12 for disproportionation of HOO•. The same mechanism has been reported in a paper by Orbán *et al.* about mechanistic studies on oxidation of several inorganic sulfur compounds by H₂O₂ with the copper ion as a catalyst that induces exotic phenomena as periodic oscillations [15]. More recently, the different potentiometric responses of various inert electrodes were successfully interpreted using a simplified model involving 12 steps and 9 intermediates for the OE reaction [16]. Other studies on the OE reaction have regarded new pulsating sensors to monitor oscillations [17], a conductometry technique for analytical applications [18], and a study of oscillating chemiluminescence induced by the addition of 1,10-phenanthroline to the system [19].

In the present paper, we report a revised study of the effects of component concentration variations on the oscillation parameters over a wide concentration range and the effect of the temperature in batch conditions. A mechanistic model using the stoichiometric network analysis (SNA) approach is presented and discussed. Another aim of the present research work is to present inhibitory effects by three diphenols on the oscillations of the OE reaction which take place in strong alkaline environment (pH 10–12), together with a reasonable qualitative molecular interpretation.

EXPERIMENTAL

Materials and Apparatus. KSCN (potassium thiocyanate; reagent grade, 99% minimum; Merck), hydrogen peroxide (H₂O₂; reagent grade, 30% w/w; Sigma Aldrich) CuSO₄·5H₂O (copper(II) sulfate pentahydrate; reagent grade, 99.0–100.5%; Merck), sodium hydroxide (NaOH; reagent grade, 99% minimum; Merck) were of analytical grade and used without further purification. All stock solutions were prepared from doubly distilled deionized water. Sodium hydroxide solution was analyzed by titration versus standard HCl 0.1 M (Carlo Erba). The H₂O₂ was standardized daily by manganometric analysis.

Diphenols. Catechol (1,2-dihydroxybenzene; reagent grade, ≥99%; Sigma-Aldrich), resorcinol (1,3-dihydroxybenzene; reagent grade, ≥98%; Fluka), hydroquinone (1,4-dihydroxybenzene; reagent grade, 99%; Carlo Erba) were used.

Oscillations in the OE mixtures were followed potentiometrically by recording the potential of the solution using a couple bright platinum electrode (model P/N 238 945; Hamilton) —reference electrode (double-junction Ag/AgCl electrode; model 373–90-WTE-ISE-S7; Ingold). Electrodes were connected to a pH multimeter (model pH 540 GLP; WTW) controlled by an IBM-compatible PC. The accuracy of the multimeter was ±1 mV. The data-acquisition program Multi Achat II (WTW) was used. The multimeter was equipped with a temperature sensor with an accuracy of ±0.1°C. OE mixtures were prepared by mixing the appropriate amounts of stock solutions of reagents using pipettes or burettes in a 100-mL beaker to a total volume of 30 mL. The order of addition was KSCN, NaOH, H₂O₂, and CuSO₄. Oscillations start after the addition of CuSO₄. All solutions and

Table I Effect on the OE Oscillator of X = KSCN, NaOH, H₂O₂, CuSO₄ Variations

[X] (M)	Induction (s)	Oscillation Time (t_{osc}) (s)	Number of Oscillations
X = KSCN, [H ₂ O ₂] = 0.25, [NaOH] = 0.025, [CuSO ₄] = 1.5×10^{-4}			
0.0188	N/A	N/A	N/A
0.0262	116	1910	12
0.0300	N/A	1863	13
0.0375	36	1458	10
X = NaOH, [H ₂ O ₂] = 0.25, [KSCN] = 0.0262, [CuSO ₄] = 1.5×10^{-4}			
0.015	108	1034	11
0.020	49	1676	13
X = NaOH, [H ₂ O ₂] = 0.5, [KSCN] = 0.06, [CuSO ₄] = 3×10^{-4}			
0.040	5	975	12
X = H ₂ O ₂ , [NaOH] = 0.050, [KSCN] = 0.060, [CuSO ₄] = 3.0×10^{-4}			
0.20	65	5635	24
0.30	13	2738	17
0.40	6	1753	15
0.50	6	1294	14
X = CuSO ₄ , [NaOH] = 0.050, [KSCN] = 0.060, [H ₂ O ₂] = 0.2			
2.4×10^{-4}	42	4882	20
1.8×10^{-4}	11	4675	19
1.2×10^{-4}	28	4287	10
0.6×10^{-4}	0	3320	1

reaction mixtures were maintained at constant temperature by means of a suitable thermostating system (accuracy $\pm 0.1^\circ\text{C}$). Inhibitory effects by diphenols were studied by adding 1.0 mL of a suitable diluted solution of each compound to 30 mL of an active OE mixture after the second or third oscillation.

RESULTS

The OE Reaction Revisited. Following the indications by Orbán [1], we performed a systematic series of experiments by varying the concentration of the components one at a time to find conditions in which it has a high number of oscillations and a long oscillation time (t_{osc}). A summary of the performed experiments together with some oscillation parameters is reported in Table I.

From data reported in Table I, it can be seen that in the mixture with [KSCN]₀ = 0.06 M; [NaOH]₀ = 0.050 M; [H₂O₂]₀ = 0.20 M; [CuSO₄]₀ = 3.0×10^{-4} M, oscillations last for 5635 s (ca. 1 h 34 min) and their number is 24, as shown in Fig. 1. Some other experimental recordings taken from data in Table I are reported in the Supporting Information (Supplement 1).

Effect of Temperature. The specified mixture was used to study the temperature effect on the oscillation time, not previously reported. We made potentiometric

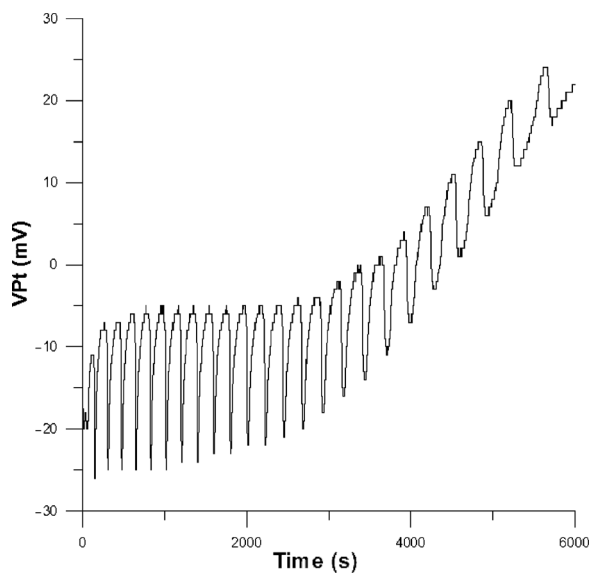


Figure 1 Long last recording of V(Pt) versus time. For the initial composition of mixture, see the text. $T = 25^\circ\text{C}$.

recordings at 5°C intervals, starting from 20 up to 45°C when oscillations lasted for only 729 s. Figure 2a shows the plot of the inverse of oscillatory time $1/t_{osc}$ (s^{-1}) versus temperature (K). As can be seen, the trend well approximates an Arrhenius-type temperature dependence.

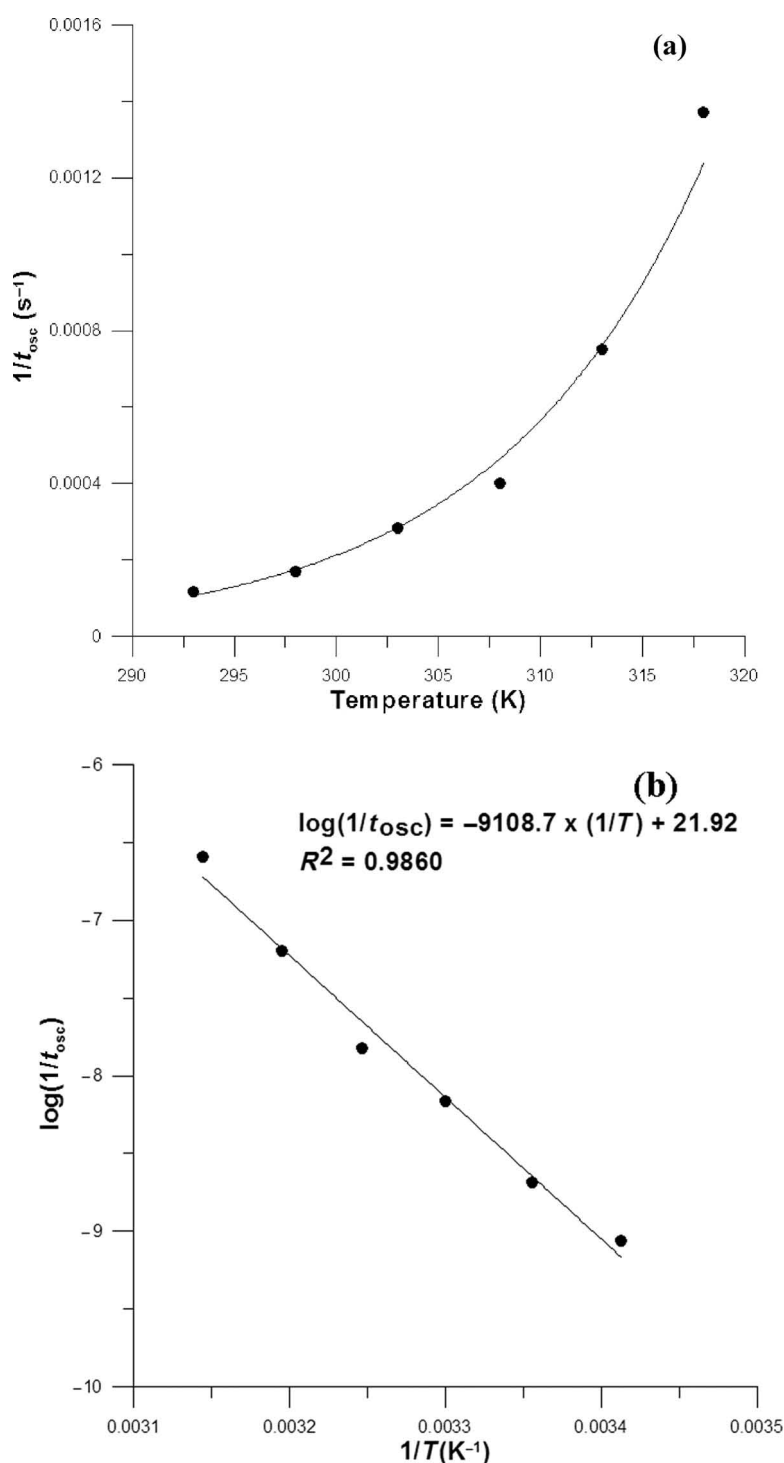


Figure 2 (a) An inverse of oscillatory time (s⁻¹) plotted as a function of temperature (K). (b) Plot of $\log(1/t_{osc})$ against $(1/T)$. For the initial composition of the mixture, see the text.

Plots of the logarithm of rate constants versus $1/T$ are frequently used to obtain values of the activation energy, but in the case of a OE reaction there is no basis for expecting the temperature coefficient to be

related to a well-established activation energy. However, a plot of $\log(1/t_{osc})$ against $(1/T)$ yields a straight line (Fig. 2b), from whose slope an approximate apparent “average activation energy” (E_{av}) value of

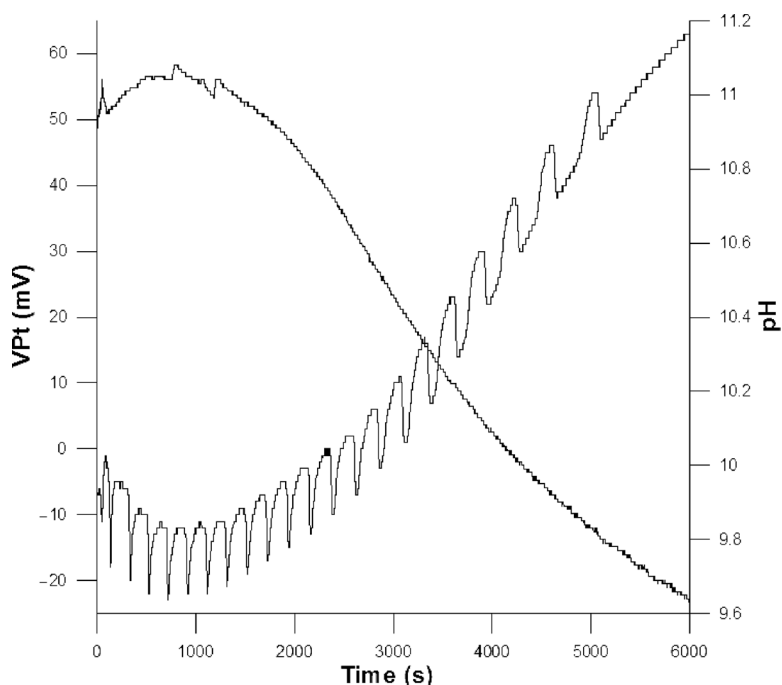


Figure 3 Behavior of $V(\text{Pt})$ and pH versus time. For initial composition of the mixture, see the text.

76 ± 5 kJ for the overall oscillatory regime is found.

Behavior of pH. The H^+ concentration does not show oscillatory behavior; in the example mixture reported by Orbán [1], the pH decreases monotonically from 10.5 to 6 in 6.5 in 50 min. A similar trend can be seen in our mixture as shown in Fig. 3 for $[\text{KSCN}]_0 = 0.06$ M; $[\text{NaOH}]_0 = 0.050$ M; $[\text{H}_2\text{O}_2]_0 = 0.20$ M; $[\text{CuSO}_4]_0 = 3.0 \times 10^{-4}$ M at 25.0°C .

Inhibitory Effects by Diphenols. The three compounds tested (resorcinol, catechol, and hydroquinone) show inhibitory effects similar to those observed in the BR reaction [13]: an immediate quenching of oscillations, an inhibitory time (t_{inhib}) that linearly depends on the concentration of the compound added in a narrow range of concentration, followed by a resumption of oscillations. A typical recording of an inhibited OE mixture is shown in Fig. 4a, whereas in Fig. 4b the linear relationship between t_{inhib} and the concentration of inhibitor (resorcinol in this example) is reported.

At low concentrations of substance added (different for each substance), the inhibition times become too low to be measured. There is a threshold under which inhibition time cannot be detected. We believe that below this threshold the straight line curves toward the period of oscillation. At high concentrations of inhibitor added, the amplitude of the resumed oscillations becomes too low, so that at a given value (different for each inhibitor) oscillations do not resume. This means

that the oscillating reaction reached its end. The main results obtained by experiments on the diphenols tested are summarized in Table II.

The last column reports the “potency” of inhibitors with respect to resorcinol chosen as a standard. The potency was calculated as an average of ratios $[\text{Re}]/[\text{smp}]$, where $[\text{Re}]$ and $[\text{smp}]$ are the concentrations of resorcinol and sample that give the same inhibition time. $[\text{Re}]$ at a given time is obtained from the straight line t_{inhib} versus $[\text{Re}]$ (Fig. 4b).

Even if a comparison between perturbations in OE and BR systems by phenols is arbitrary because the only common feature between the two systems is H_2O_2 , the inhibitor concentrations for the first system fall at the mM level, for the second at the μM level. This could be an indication that the perturbation effects by phenolics are more effective at acidic pH. As can be seen, hydroquinone shows the high potency whereas catechol the less.

Mechanistic Interpretation

Mechanistic modeling of the reaction was subject of the paper [2], where Luo et al. suggested a mechanism with 30 reactions and 26 species to explain the dynamic behavior of the reaction. With huge success, the model described most observed effects, including dependence of the reaction dynamics on the NaOH concentration. However, some discrepancies were

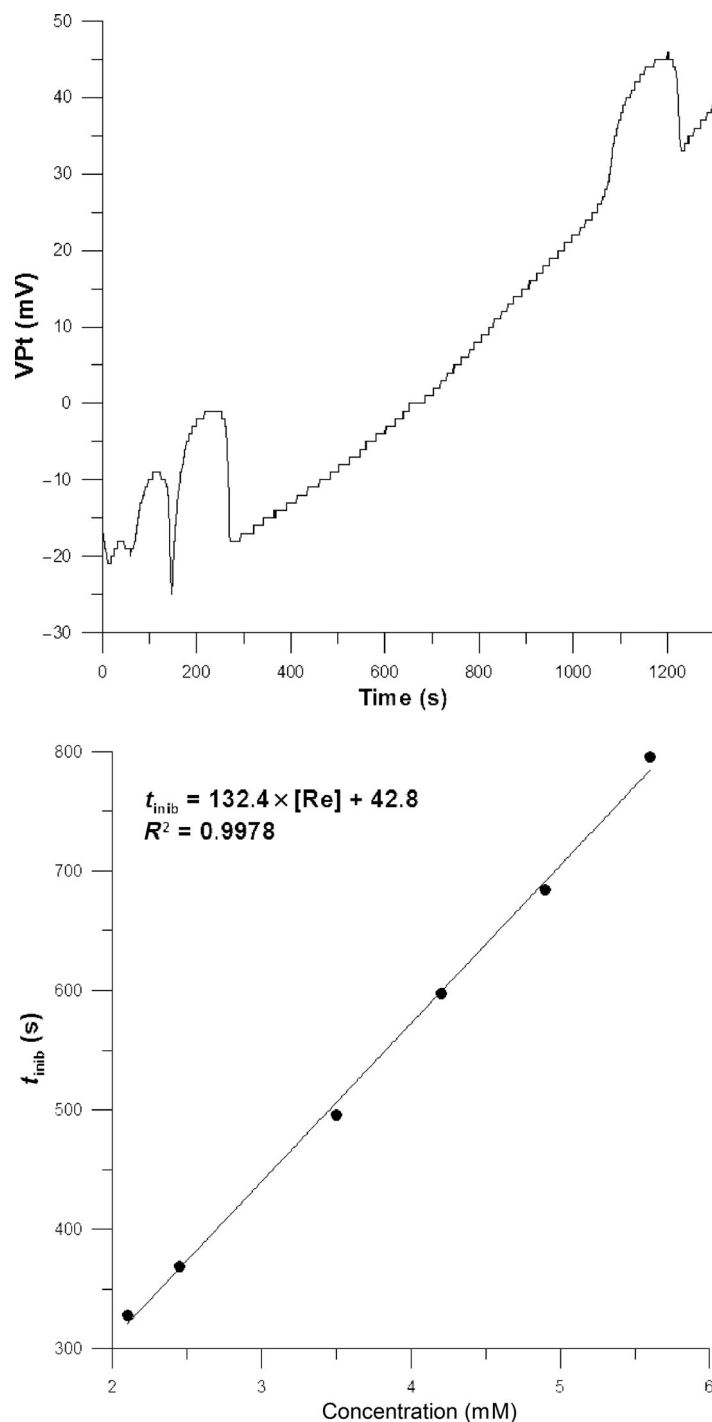


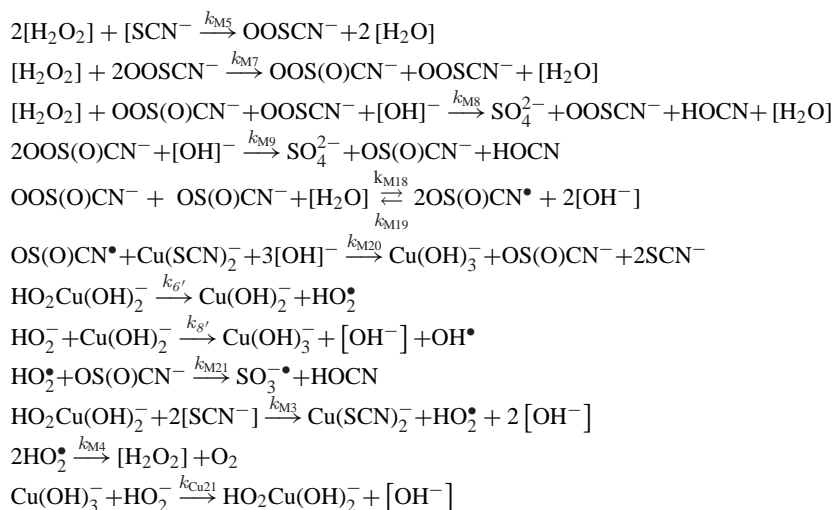
Figure 4 (a) Recording of the potential of the mixture (for the initial composition, see Fig. 1) versus time when 1.0 mL of a suitably diluted solution of resorcinol (Re) was added to 30 mL of the mixture after the second oscillation; the initial concentration of Re in the mixture, $[Re] = 5.60$ mM. (b) Graph of the inhibition time versus the concentration of resorcinol added to the mixture.

observed when other reactant concentrations were varied. Moreover, the large model was not practical for a brief description of the dynamical states and, hence, Orbàn et al. [15] used a short scheme for this purpose.

Based on this reduced representation, Wiśniewski et al. [16] developed an effective reaction model of the OE process with only 13 reactions and 10 species. The proposed model was able to oscillate. In present paper,

Table II Summary of the Inhibitory Effects by Diphenols

Compound	Number of Experiments	Concentration Range (mM)	Parameters of the Straight Line ^a m q R^2	Potency
Resorcinol	6	2.10–5.60	$t_{\text{inib}} = 132 \times [\text{Re}] + 43$ $R^2 = 0.9978$	1
Catechol	4	4.90–7.00	$t_{\text{inib}} = 259 \times [\text{Ca}] - 1031$ $R^2 = 0.9942$	0.57 ± 0.09
Hydroquinone	7	0.70–4.90	$t_{\text{inib}} = 599 \times [\text{Hy}] - 237$ $R^2 = 0.9932$	± 0.3

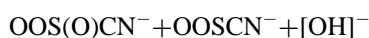
^a m = slope (mM^{-1}s); q = intercept (s); R^2 = coefficient of determination.**Table III** Model of the OE Reaction**Table IV** Reaction Rates and Rate Constants at 25°C for the Model Presented in Table III

$R_{\text{M5}} = k_{\text{M5}}[\text{H}_2\text{O}_2][\text{SCN}^-]$	$k_{\text{M5}} = 7.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$
$R_{\text{M7}} = k_{\text{M7}}[\text{OOSCN}^-]^2$	$k_{\text{M7}} = 5.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$
$R_{\text{M8}} = k_{\text{M8}}[\text{SCN}^-][\text{S(O)CN}^-]$	$k_{\text{M8}} = 1.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
$R_{\text{M9}} = k_{\text{M9}}[\text{S(O)CN}^-]^2$	$k_{\text{M9}} = 1.0 \text{ M}^{-1} \text{ s}^{-1}$
$R_{\text{M18}} = k_{\text{M18}}[\text{S(O)CN}^-][\text{S(O)CN}^-]$	$k_{\text{M18}} = 2.25 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
$R_{\text{M19}} = k_{\text{M19}}[\text{S(O)CN}^\bullet]^2$	$k_{\text{M19}} = 2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
$R_{\text{M20}} = k_{\text{M20}}[\text{S(O)CN}^\bullet][\text{Cu}(\text{SCN})_2^-]$	$k_{\text{M20}} = 1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
$R_{6'} = k_{6'}[\text{HO}_2\text{Cu}(\text{OH})_2^-]$	$k_{6'} = 6.93 \times 10^{-3} \text{ s}^{-1}$
$R_{8'} = k_{8'}[\text{HO}_2^\bullet][\text{Cu}(\text{OH})_2^-]$	$k_{8'} = 5.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
$R_{\text{M21}} = k_{\text{M21}}[\text{HO}_2^\bullet][\text{OS(O)CN}^-]$	$k_{\text{M21}} = 2.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
$R_{\text{M3}} = k_{\text{M3}}[\text{HO}_2\text{Cu}(\text{OH})_2^-]$	$k_{\text{M3}} = 1.0 \times 10^{-2} \text{ s}^{-1}$
$R_{\text{M4}} = k_{\text{M4}}[\text{HO}_2^\bullet]$	$k_{\text{M4}} = 2.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$
$R_{\text{Cu21}} = k_{\text{Cu21}}[\text{Cu}(\text{OH})_3^-][\text{HO}_2^-]$	$k_{\text{Cu21}} = 1.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$

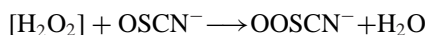
we further develop reduced model given by Wiśniewski et al. [16] to simulate different dynamic states achievable in the batch reactor. Our model is given in Table III. Reaction rates for each reaction step are given in Table IV with the corresponding rate constant.

The first three reactions [2] in Table III are synthetic steps, representing initial sequence:





followed by rapid stoichiometric transformation [16]:



Therefore, they are represented by the net reactions given in Table III, but governed by the kinetic laws corresponding to the rate-determining steps given above:

$$R_{M5} = k_{M5}[\text{H}_2\text{O}_2][\text{SCN}^-]$$

$$R_{M7} = k_{M7}[\text{OOSCN}^-]^2$$

$$R_{M8} = k_{M8}[\text{OOS(O)CN}^-][\text{OOSCN}^-]$$

Moreover, like in the previous model [16], species in square brackets within stoichiometric expressions are considered to be important only for the reaction stoichiometry and are not involved in the rate-determining steps. These are considered to be external species in the context of SNA.

Almost all rate constants are the same as the ones from the previous paper. Rate constant k_{M18} is just slightly decreased (the previous value was $k_{M18} = 3.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) and k_{M4} is increased by one order of magnitude to get better agreement with our experimental results. Other rate constants are taken from Wiśniewski et al. [16]. As O₂ was already considered only as an final product in the original model, here it was not considered as a variable. To make a model convenient for simulations of the batch experiments, concentrations of H₂O₂, HO₂[−], and SCN[−] are here allowed to change according to the stoichiometry of corresponding reactions. However, neither of these species was considered as independent intermediate one (usually called internal species) in the sense of the SNA. Moreover, since OH[−] does not influence the reaction rate of any reaction in the model, it was considered as a constant, although it is known and confirmed by our experiments that its concentration decreases with time. The attempts were done to include the concentration of OH[−] in our simulations, but it came out that the present model gives a too strong decrease, which resulted in premature iteration break. Our intention was to make just minimal necessary changes to the original model. Hence, the complete list of intermediary species calculated in our simulations is

Cu(OH)₂[−], Cu(OH)₃[−], HO₂Cu(OH)₂[−], Cu(SCN)₂[−], HO₂[•], OOSCN[−], OOS(O)CN[−], OS(O)CN[−], OS(O)CN[•], H₂O₂, HO₂[−], and SCN[−].

All numerical simulations were performed by employing the MATLAB ode15s solver based on the Gear algorithm for integration of stiff differential equations [20]. Initial concentrations for simulations are given in Table V. The concentration of the OH[−] in numerical simulations was fixed and included in rate constants.

Instability condition is evaluated by the SNA [21].

RESULTS

The steady-state stability is determined by the sign of eigenvalues of linearized operator **M**:

$$\begin{aligned} \mathbf{M}(\mathbf{h}, \mathbf{r}_{ss}) &= \mathbf{S} \cdot \text{diag}(\mathbf{r}_{ss}) \cdot \mathbf{K}^T \cdot \text{diag}(\mathbf{h}) \\ &= \mathbf{S} \cdot \text{diag}(\mathbf{E} \cdot \mathbf{j}) \cdot \mathbf{K}^T \cdot \text{diag}(\mathbf{h}) \end{aligned}$$

where **S** is the matrix of the net stoichiometric coefficients, **diag**(**r**_{ss}) is diagonal matrix of steady-state reaction rates, **K**^T is transpose of the matrix of reaction orders, and **diag**(**h**) is the diagonal matrix of reciprocal steady-state concentrations. According to SNA practice, steady-state reaction rates are expressed as combinations of the current rates **j** with coefficients in the extreme current matrix **E**. Extreme currents are irreducible reaction pathways, represented by the columns of the matrix **E**.

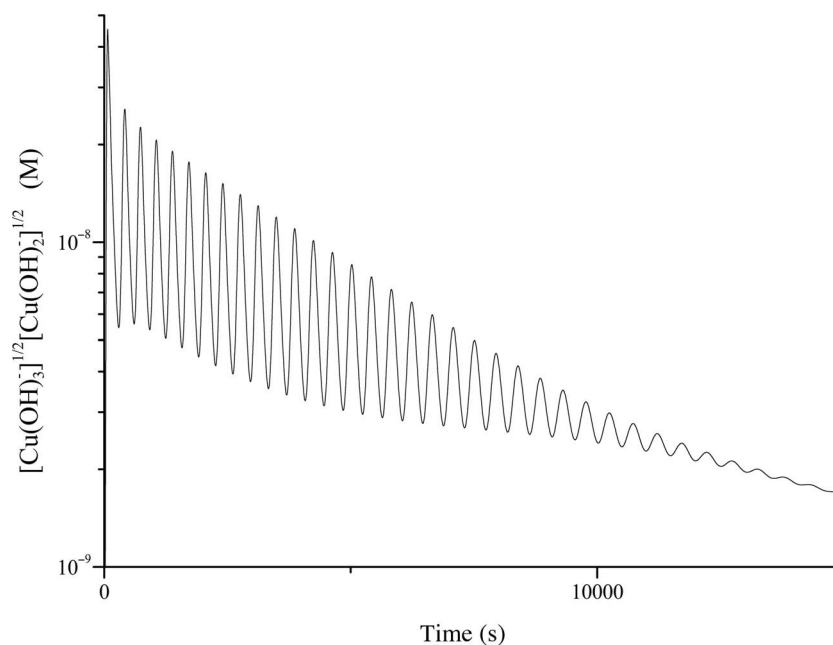
For the model presented in Table III, independent intermediate species are Cu(OH)₃[−], HO₂Cu(OH)₃[−], Cu(SCN)₂[−], HO₂[•], OOSCN[−], OOS(O)CN[−], OS(O)CN[−], and OS(O)CN[•]; reactants are H₂O₂, HO₂[−], and SCN[−]; and Cu(OH)₂[−] is a dependent species. The concentration of Cu(OH)₂[−] in any moment can be expressed as

$$\begin{aligned} [\text{Cu(OH)}_2^-] &= [\text{Cu}]_{\text{tot}} - ([\text{HO}_2\text{Cu(OH)}_2^-] \\ &\quad + [\text{Cu(OH)}_3^-] + [\text{Cu(SCN)}_2^-]) \end{aligned}$$

where [Cu]_{tot} is the conservation constant. Exact treatment of the conservation among Cu species would require the replacing of reaction (8') with several pseudoreactions for each of the independent Cu species and one more for the conservation constant. This would result in many additional extreme currents, which are actually only pseudocurrents. Instead, we just restricted our analysis to reaction (8') with a dependent concentration expressed approximately as

Table V Initial Concentrations (mol dm⁻³) in Simulations with the Model Presented in Table III

Species X	Cu(OH) ₂ ⁻	Cu(OH) ₃ ⁻	HO ₂ Cu(OH) ₂ ⁻	Cu(SCN) ₂ ⁻	HO ₂ [•]
[X] ₀	1 × 10 ⁻⁸	1 × 10 ⁻⁸	1 × 10 ⁻⁸	3.00 × 10 ⁻⁴	1 × 10 ⁻⁸
Species X	OOSCN ⁻	OOS(O)CN ⁻	OS(O)CN ⁻	OS(O)CN [•]	O ₂
[X] ₀	1 × 10 ⁻⁸	1 × 10 ⁻⁸	1 × 10 ⁻⁶	1 × 10 ⁻⁸	1 × 10 ⁻⁸
Species X	H ₂ O ₂	HO ₂ ⁻	OH ⁻	SCN ⁻	
[X] ₀	0.2	0.0375	0.001	0.06	

**Figure 5** Simulated product $[\text{Cu}(\text{OH})_3^-]^{1/2}[\text{Cu}(\text{OH})_2^-]^{1/2}$ (M) versus time (s).

$[\text{Cu}(\text{OH})_2^-] \simeq [\text{Cu}]_{\text{tot}}$ and an included conservation constant into the rate constant.

The stoichiometric matrix \mathbf{S} , kinetic reaction order matrix \mathbf{K} , and extreme current matrix \mathbf{E} are given in the Supporting Information (Supplement 2).

Thus, we obtained six extreme currents, and the minimal instability condition is satisfied if the minor of the \mathbf{M} operator, corresponding to species HO_2^\bullet , $\text{OS}(\text{O})\text{CN}^-$ and $\text{OS}(\text{O})\text{CN}^\bullet$:

$$\begin{aligned}
 &16j_2j_3j_4 - 2j_2j_3j_5 + 12j_2j_3j_6 + 24j_2j_4j_5 \\
 &+ 16j_2j_4j_6 - 4j_2j_5^2 + 12j_2j_5j_6 + 8j_2j_6^2 + 8j_3j_4j_5 \\
 &+ 16j_3j_4j_6 - 2j_3j_5^2 + 8j_3j_6^2 + 8j_4j_5^2 \\
 &+ 16j_4j_5j_6 - 4j_5^3 - 12j_5^2j_6 - 16j_5j_6^2 - 16j_6^3
 \end{aligned}$$

is negative. Analyzing adjacent vertices in exponential polytope of that minor, we found that the simplest

instability condition may be $j_2 > 2j_4$ and this could be approximated by $R_{M19} > 2R_{M4}$. Details of derivation of the instability conditions are also given in the Supporting Information (Supplement 2). Hence, rate constants of these two reactions were adapted to fit simulation results to experimental results.

Since Wiśniewski et al. [16] found that the Pt electrode in $\text{KSCN-H}_2\text{O}_2\text{-CuSO}_4\text{-NaOH}$ system mostly measures the product $[\text{Cu}(\text{OH})_3^-]^{1/2}[\text{Cu}(\text{OH})_2^-]^{1/2}$, we plotted its value in simulations against time (Fig. 5) to compare with our experimental measurements in Fig. 1.

Qualitative agreement is obviously achieved—oscillations are damped with time and disappear after some finite period, typically for a batch reactor. The same agreement was obtained for all mixtures reported in Table I. However, the characteristic time of the oscillations is still too long and the number of oscillations is too large for quantitative comparison.

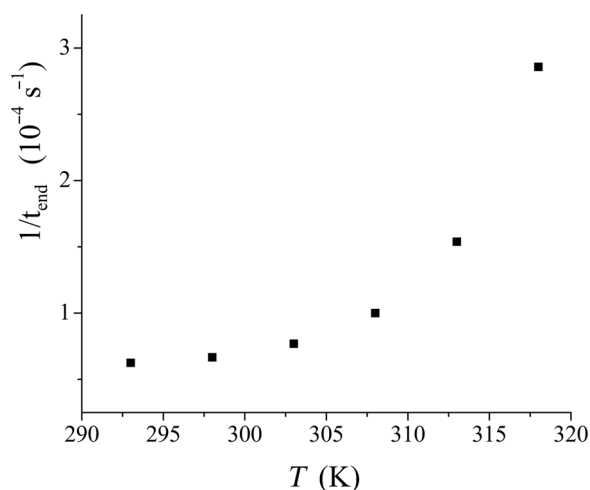
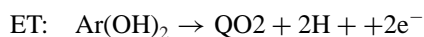


Figure 6 Inverse of oscillatory time (s⁻¹) plotted as a function of temperature (K). The initial composition of the mixture is same as in Fig. 1.

Yet, the general trend of dynamic state transformation with temperature variation could be analyzed. We assumed that the limiting step is reaction (M9) with activation energy $E_a = 76$ kJ/mol, and the Arrhenius factor recalculated from the rate constant for 25°C, is equal to $A = 2.065 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$. Hence, an inverse of oscillatory time is plotted in Fig. 6 as a function of temperature for a sequence of simulations at various temperatures. We used an experimentally determined value of the activation energy from Fig. 2 to calculate the rate constant k_9 at different temperatures and to plot Fig. 6. However, simulated result is not completely equivalent to the experiment, and hence the apparent activation energy in Figs. 2 and 6 is not the same.

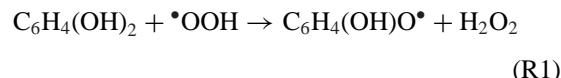
Interpretation of Diphenols Inhibitory Effect

In the reaction model considered here, reactions (RM3) and (RM4) involve the peroxyradical $\bullet\text{OOH}$ as an important intermediate. It is well known that phenols act as antioxidants either via an HAT (hydrogen atom transfer) mechanism or an ET (electronic atom transfer) mechanism, i.e.,

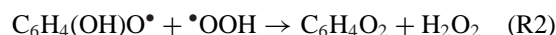


in acidic medium. In alkaline medium, the extraction of an hydrogen atom from catechol or hydroquinone by $\bullet\text{OOH}$ is highly exothermic and

very fast [22], giving the corresponding semiquinone radical)*:



subsequently, the products further react (diffusion control) with $\bullet\text{OOH}$

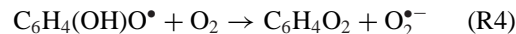


where $\text{C}_6\text{H}_4(\text{OH})_2$ represents 1,2- or 1,4-dihydroxybenzene, $\text{C}_6\text{H}_4(\text{OH})\text{O}^\bullet$ the corresponding semiquinone, and $\text{C}_6\text{H}_4\text{O}_2$ the corresponding quinone.

If the radical flow is slow, the 1,4-semiquinone can dismutate to quinone and hydroquinone:

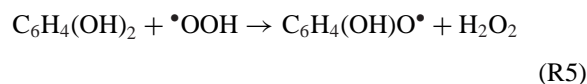


For the 1,4-semiquinone, in alkaline medium the reaction with O_2 is also possible:



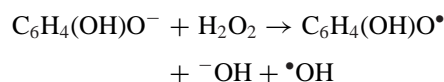
That is very difficult with the 1,2-isomer.

Resorcinol (1,3-dihydroxybenzene) can transfer an H atom to radicals, but it is unable to be further oxidized to quinone (in fact *m*-quinones do not exist):



where $\text{C}_6\text{H}_4(\text{OH})_2$ represents 1,3-dihydroxybenzene.

It is known that diphenols can be oxidized by hydrogen peroxide [23,24]. The reactions of catechol and hydroquinone are fast and exothermic and in alkaline medium the oxidation reactions are faster than in acidic medium. The first reaction is an electronic transfer from phenolate anion to H_2O_2 that reduces to ^-OH and $\bullet\text{OH}$:



*In alkaline medium, diphenols are present as phenolate anions, i.e., $\text{C}_6\text{H}_4(\text{OH})\text{O}^-$, but since the final products are the same here we used the simpler $\text{C}_6\text{H}_4(\text{OH})_2$ formula.

then *o*- and *p*-semiquinone radicals are oxidized to respective quinones and $\bullet\text{OH}$ turns to H_2O :



For resorcinol that cannot form the quinone, after reaction (R5) the semiquinone presumably adds $\bullet\text{OH}$ in the ring, finally leading to *o*-quinone (see Scheme 1 in the Supporting Information (Supplement 3)).

The interpretation of the results reported in Table II is given in the Supporting Information taking into account the bond dissociation enthalpy theory proposed by Wright et al. [25], and the rate of the parallel oxidation of diphenols by H_2O_2 .

Some Final Remarks

The oscillatory $\text{KSCN-H}_2\text{O}_2\text{-NaOH-Cu(II)}$ -catalyzed system (OE reaction) was revisited in a wide concentration range of all components, and the temperature dependence showing an Arrhenius-type behavior was detected. These features are satisfactorily described by a modified simplified model. The OE system is perturbed by the addition of diphenols. The perturbation effect consists of an immediate quenching of oscillations, an inhibitory time that linearly depends on the concentration of the diphenol added, and a subsequent regeneration of oscillations. The effect (similar to that observed in the BR oscillating reaction) is qualitatively interpreted in terms of interaction among diphenols, hydroperoxyl radical, and hydrogen peroxide. A further study will include the effects of several polyphenols and a mechanistic study of the observed perturbations.

Ž. Čupić stayed in Bologna as a visiting professor, as part of a bilateral project between the Universities of Bologna and Belgrade during October 2013.

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