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Identification of Two Positional Isomers between Ortho-Vanillin and Para-Vanillin by their Inhibitory Effects on a Briggs-Rauscher Oscillator

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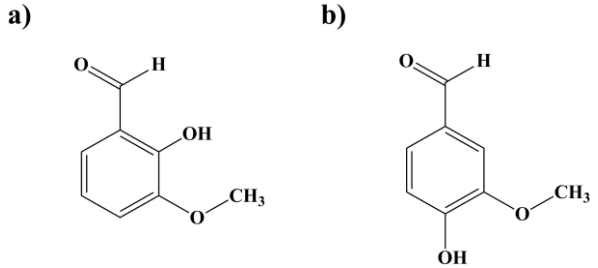
A suitable method by means of Briggs-Rauscher (BR) oscillating system as an analytical technique to identify the two positional isomers between ortho-vanillin (OV) and (para-)vanillin (PV) by their different perturbation effects has been proposed in this article. In BR system the macrocyclic Ni-complex, $[NiL](ClO_4)_2$ was used as catalyst, in which ligand L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The experimental data has proven that putting equal amount of same concentrations of these isomers (OV and PV) separately into the active BR system could cause the inhibition time (t_{in}). But the t_{in} initiated by OV is higher as compared to the t_{in} produced by PV. Our predication for such different inhibitory effects caused by these isomers may be due to their different existing strength of intermolecular hydrogen-bonding. Furthermore, by plotting t_{in} against the concentration of OV or PV, two linear regression curves were achieved for these two isomers in their concentrations range 2.5×10^{-6} mol L^{-1} to 4×10^{-5} mol L^{-1} with correlation coefficients of 0.98, which obviously illustrated the different behaviors of isomers. The perturbation reaction mechanism, involving hydroperoxyl radical ($HOO^{\bullet}$) on the basis of FCA has been proposed. The description of the proposed mechanism is that these isomers react with hydroperoxyl radical to form a dimeric product (divanillin).

Keywords: Briggs-Rauscher Oscillator; Inhibition time; Isomers Identification; Ortho Vanillin; Para Vanillin

1. INTRODUCTION

An isomer is a molecule with the same chemical formula but with a different chemical structure. It does not necessarily that isomers of a compound may have similar properties, although they have the same functional group. In medical point of view, isomers are a special concern because they may possess quite different biological activities. For instance, in the treatment of Parkinson's disease L-dopa is used while isomer D-dopa has never been used because it causes a deficiency of white cell and is thus susceptible to infections. Similarly isomer R-Naproxen is used for arthralgic pain while isomer S-Naproxen is teratogenic. Thus the desire of separation and identification of isomers is highly important. Various instrumental techniques like LC-MS [1, 2], GC-MS [3], MS [4, 5] and mass spectrometric-molecular statistic [6] were used for the identification of isomers. All of these techniques are well-defined and were have massive applications but a few disadvantages are associated with such techniques. First, all of these techniques were costly and secondly in each of these techniques may have different limitation factors e.g. selection of suitable mobile phase in LC-MS, higher operating temperature in GC-MS while the direct use of MS technique for identify sample may cause error, thus MS technique will be coupled with other techniques to identify samples. Therefore, new approaches are desirable for identification of organic isomers and avoid these costly techniques. Thus we developed a new chemical method (oscillating chemical system) which is advantageous over instrumental techniques with good detection limitations, recovery and being easy to setup.

The chemical oscillation is nonlinear chemical dynamics, which exhibits the periodic changes in the concentration of some species (usually a reaction intermediate) in a reaction. The first chemical oscillator [7] was discover in 1828 by Fechner and are so-called electrochemical oscillator. With passage of time many other electrochemical oscillators [8, 9] were published and the most important one is "beating heart mercury [10]. In 1921, 1961, 1972, the homogenous oscillators, Bray-Liebhafsky (BL reaction) [11, 12], Belousov-Zhabotinsky (BZ) [13-15], Briggs-Rauscher (BR) [16, 17] respectively were discovered. Among all oscillating reactions both BZ and BR involving metal ion catalysts (Ce^{4+}, Mn^{2+}, $Fe(phen)_3^{2+}$, or $Ru(bipy)_3^{2+}$) have been thoroughly studied. Later, 1982 the macrocyclic complex of Cu and Ni catalysts were reported by Yatimirskii [18]. Both BZ and BR chemical oscillators involving metal ions and macrocyclic complex of Cu and Ni were extensively used for determination of various compounds, antioxidants, species and ions [19-27]. The chemical oscillation has not only been used in determination techniques, but it has a vast application like wave propagation and pattern formation [28], chaos [29] etc as well. Thus, we extended the role of chemical oscillation toward identification of isomers of compound.



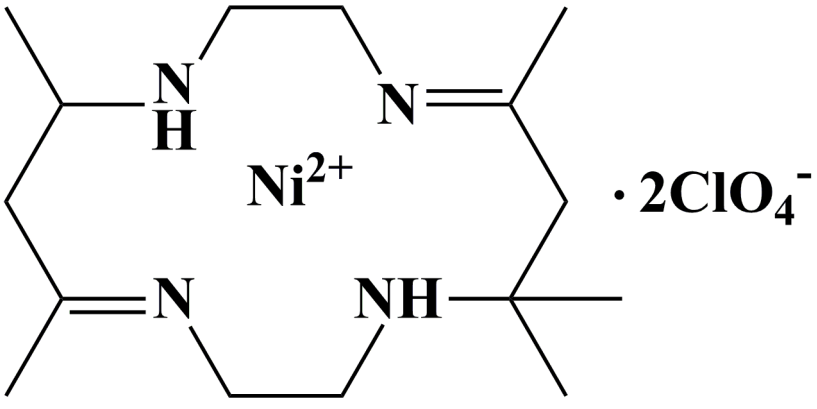
Scheme 1. (a) Structure of ortho-vanillin; (b) Structure of (para-)vanillin

In this paper, BR chemical oscillator was used as analytical tool for the identification of two isomers, ortho-vanillin (OV) and para-vanillin (PV), as shown in the Scheme 1. The macrocyclic Ni complex, $[NiL](ClO_4)_2$ was used as catalyst, where L in the complex is ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The reaction temperature was kept at 5 ^{0}C. When small amount (40 uL) of same concentrations ranging (2.5×10^{-6} mol L^{-1} to 4×10^{-5} mol L^{-1}) of these isomers were added separately into the active BR oscillator, the oscillations were temporary ceased and then regenerated after inhibition time (t_{in}). But t_{in} caused by OV is much higher as compared to the t_{in} caused by PV. Furthermore, the increase in concentrations of these isomers within the system results in increased t_{in} of the system. Thus, based on inhibitory effect as parameter, the different behaviors of these isomers were reported by using BR oscillator as a new analytical tool for identifying isomers.

(para-)Vanillin (PV) is considered a major component of food flavor and is extensively used for various purposes i.e. in cosmetics and medicines. The natural and synthetic PV, has also been utilized as a tracer substance in the dairy goods under a subsidy by the European Union. Vanillin can be merged in butter, pastry goods, ice creams, or with another kinds of foodstuff for trades at low costs by keeping its amount of 250 ppm for artificial vanilla or 100 ppm for natural vanilla [30]. Various publications have been reported to express the oxidation nature of PV in various medium: alkaline solution [31], chlorite [32,33], per-acetic acid [34], potassium bromate [35]. Baumgartner has reported the enzymatic oxidation of PV into divanillin in the presence of hydrogen peroxide [36] and very recently the similar statement that vanillin could be oxidized into divanillin in the presence of hydrogen peroxide was claimed by Elke Anklam et al [37]. In this article, we have not only conveyed the novel method for identification of isomers of vanillin but also possess the claim of dimeric product formation (divanillin) from the oxidation of these two functional group isomers (OV and PV) by hydroperoxyl radical ($HOO^{\bullet}$) radical. The $HOO^{\bullet}$ is the intermediate species generated from hydrogen peroxide during the course of reactions within BR system.

2. EXPERIMENTAL

2.1. Reagents



Scheme 2. Structure of $[NiL](ClO_4)_2$

All the chemical reagents, malonic acid, H_2SO_4, KIO_3, H_2O_2, OV and PV were of analytical grade without further purification except catalyst, $[NiL](ClO_4)_2$ which was synthesized according to literature [38, 39], and was identified by IR spectrum and elemental analysis. Its structure is shown in Scheme 2. Solution of 2.5×10^{-2} mol L^{-1} H_2SO_4 was prepared while 2.00 mol L^{-1} malonic acid, 1.4×10^{-1} mol L^{-1} KIO_3, 1.73×10^{-2} mol L^{-1} $[NiL](ClO_4)_2$, 4.00 mol L^{-1} H_2O_2 were prepared within such H_2SO_4 solution. Solutions of different concentrations of ortho-vanillin and para-vanillin were prepared in ethyl alcohol.

2.2. Apparatus

Two electrodes, a platinum electrode (model 213 Shanghai, China) which acts as working electrode and a saturated calomel electrode (SCE) (Model 217 Shanghai, China) which acts as reference electrode, were dipped into 50 ml glass reactor. The function of a magnetic stirrer (Jiangsu, China) is to homogenize the reaction solution in the glass reactor at stirring rate of 650 rmp. The glass reactor was placed into thermostat model (DZCS-IIC, Nanjing Dazhankejiao Institute of Instrument, China) and reaction temperature was kept at 5 ℃ with the help of temperature controller. Through an amplifier and a GO-Link sensor interface, these electrodes were finally connected to a PC. By using Logger Lite data-acquisition program the potential vs time were recorded.

2.3. Procedure

The 40 ml mixture were poured into 50 ml glass reactor in the following order, 14 ml of 2.5×10^{-2} H_2SO_4 solution, 5.5 ml of 1.4×10^{-1} mol L^{-1} KIO_3 solution, 2.5 ml of 1.85×10^{-2} mol L^{-1} $[NiL](ClO_4)_2$ solution, 3.5 ml of 2.00 mol L^{-1} MA solution and 14.5 ml of 4.00 mol L^{-1} H_2O_2 solution. When the electrodes were immersed into reactor and H_2O_2 was added into glass reactor, the oscillations began to start after a short induction time. Potential vs time were recorded in PC.

3. RESULT AND DISCUSSION

Typical oscillation were obtained (as shown in Figure 1a) by mixing the reagents in the above stated order. During oscillation it was noticed that, the color of solution was continuously change from yellow to brown and from brown to yellow, owing one electron transfer process between $[NiL]^{2+}$ and $[NiL]^{3+}$ as listed below. During a course of reaction, I_2 was generated and dissolved in solution that is why the appearance of solution color was observed brown rather than green.

$$[NiL]^{2+}(\text{yellow}) \Leftrightarrow [NiL]^{3+}(\text{green})$$

A small amount (40 uL) of same concentrations of both isomers, OV and PV was used to perturb the active BR system, and that resulted in temporary cease and succeeding regeneration oscillation after inhibition time (t_{in}). The concentration range of these two isomers was tested from 2.5×10^{-6} mol L^{-1} to 4×10^{-5} mol L^{-1}.

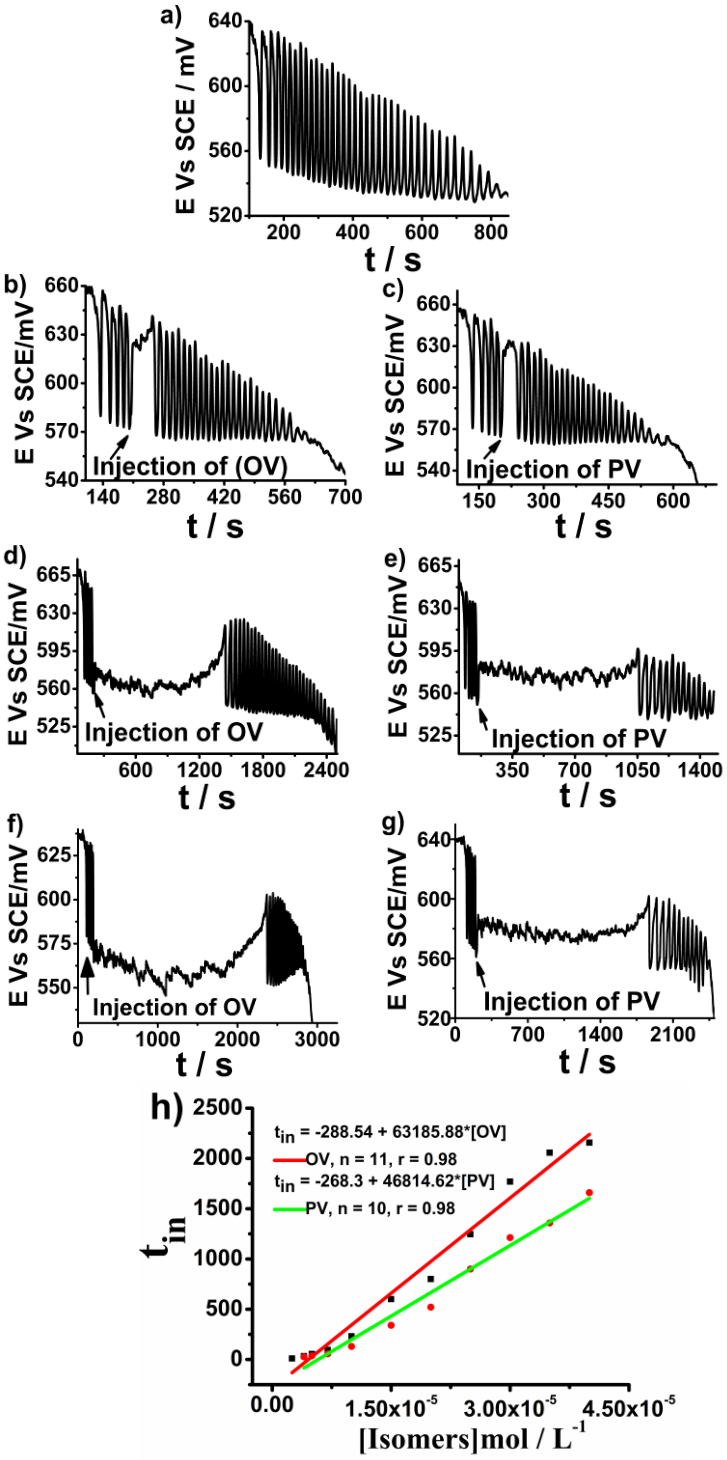


Figure 1. (a) Typical oscillation profile for the proposed oscillation system; (b). Perturb oscillation by Injection of 5×10^{-6} mol L^{-1} [OV]; (c). Perturb oscillation by Injection of 5×10^{-6} mol L^{-1} [PV]; (d). Perturb oscillation by Injection of 2.5×10^{-5} mol L^{-1} [OV]; (e). Perturb oscillation by Injection of 2.5×10^{-5} mol L^{-1} [PV]; (f). Perturb oscillation by Injection of 4×10^{-5} mol L^{-1} [OV]; (g). Perturb oscillation by Injection of 4×10^{-5} mol L^{-1} [PV]; (h) Linear regression curves for both isomerides; Common condition; $[H_2SO_4] = 8.75 \times 10^{-3}$ mol L^{-1}; $[KIO_3] = 1.9 \times 10^{-2}$ mol L^{-1}; $[[NiL](ClO_4)_2] = 1.16 \times 10^{-3}$ mol L^{-1}; $[MA] = 1.75 \times 10^{-1}$ mol L^{-1}; $[H_2O_2] = 1.45$ mol L^{-1}; t = 5 ℃.

The interesting features is that, when small amount (40uL) of 5×10^{-3} mol L^{-1} (final concentration in reaction is 5×10^{-6} mol L^{-1}) of OV or PV were used to perturb BR profile separately, the obtained t_{in} for both isomer were nearly similar i.e the t_{in} cause by OV was 54 sec as shown in Figure 1b whereas the t_{in} caused by PV is 36.5 sec as shown in Figure 1c.

As the concentration were raised to higher ranging (6×10^{-6} mol L^{-1} to 4×10^{-5} mol L^{-1}), the obtained t_{in} of the system due to injection of the OV was higher (as shown in Figure 1(d,f)) as compared to the t_{in} obtained by the injection of PV as shown in Figure 1(e,f). By plotting t_{in} against the concentration of OV or PV, two linear regression curves for both isomers were achieved in the range of (2.5×10^{-6} mol L^{-1} to 4×10^{-5} mol L^{-1}) with a correlation coefficients of 0.98 (Figure 1h), which clarify the different behaviors of OV and PV. Thus we design a new method for identification of two isomers of vanillin on the basis of their perturbation technique by BR chemical oscillator using macrocyclic Ni complex as catalyst. BR oscillating technique has not only suitable in parameters i.e. limits of detection, recovery, and simple in setup but also this analytical method could extended for the identification of others isomerides as well.

3.1. Interpretation of the proposed Mechanism

The mechanistic approach of oscillating system is exceedingly intricate because it has frequently kinetic steps and sovereign variables. The first oscillating mechanism was developed in 1982 by Noyes and Furrow (NF model) [40] was able to replicate few basic features of oscillation in the system. A quantitative similar mechanism, called DE model [41] was established by De Kepper and Epstein in the similar period. In 1996, Sorensen and co-workers [42] have obtained a thorough mechanism that well professes extensive series of experimental outcomes from flow and batch reactors. Later, Furrow et al [43, 44] derived a novel FCA mechanism from NF and DE models. This FCA mechanism is based on the significant function played by $HOO^{\bullet}$ radical. According to FCA model, the mechanism for such Ni-complex catalyzed BR oscillator consists of the following oscillatory reactions.

$$HOI + I^{-} + H^{+} \leftrightarrow I_2 + H_2O \quad (1)$$

$$HIO_2 + I^{-} + H^{+} \rightarrow 2HOI \quad (2)$$

$$IO_3^{-} + I^{-} + 2H^{+} \leftrightarrow HIO_2 + HOI \quad (3)$$

$$2HIO_2 \rightarrow IO_3^{-} + HOI + H^{+} \quad (4)$$

$$IO3^{-} + HIO_2 + H^{+} \leftrightarrow 2IO_2^{\bullet} + H_2O \quad (5)$$

$$2HOO^{\bullet} \rightarrow H_2O_2 + O_2 \quad (6)$$

$$HOI + H_2O_2 \rightarrow I{-} + O_2 + H^{+} + H_2O \quad (7)$$

$$IO_2^{\bullet} + [NiL]^{2+} + H^{+} \leftrightarrow [NiL]^{3+} + HIO_2 \quad (8)$$

$$H_2O_2 + [NiL]^{3+} \rightarrow [NiL]^{2+} + HOO^{\bullet} + H^{+} \quad (9)$$

$$HOO^{\bullet} + IO_3^{-} + H^{+} \rightarrow O_2 + H_2O + IO_2^{\bullet} \quad (10)$$

$$MA \leftrightarrow MA(enol) \quad (11)$$

$$I_2 + MA(enol) \rightarrow MAI(IMAI) + H_2O \quad (12)$$

In order to confirmed the redox reaction of additives with BR-reagents or intermediate species, the cyclic voltammetry (CV) experiments were applied to the below listed media in the present and absence of OV or PV.

1).H_2SO_4 + KIO_3, 2) H_2SO_4 + H_2O_2, 3) H_2SO_4 + M.A, 4) H_2SO_4 + $[NiL](CLO_4)_2$

It was concluded from cyclic voltammograms that both of these isomers (OV and PV) could have only possessed the redox reactions with KIO_3, the results were shown in Fig 2. In the oscillating system, a smaller amount of the additives (isomers) were trigger (from 2.5×10^{-6} mol L^{-1} to 4×10^{-5} mol L^{-1}) as compare with the concentration of KIO_3 (1.4×10^{-1} mol L^{-1}). If we consider the direct reaction between the additives and KIO_3, the amount of additives will be consumed rapidly and there will be no inhibition time recorded as yield. Thus we consider the intermediate species ($HOO^{\bullet}$) that was produced within the oscillatory reactions, and such a species reacts with additives to produce the t_{in}.

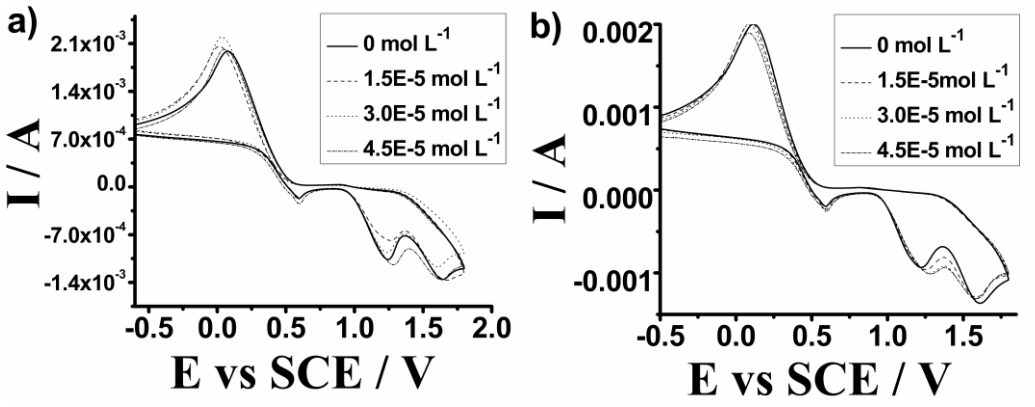
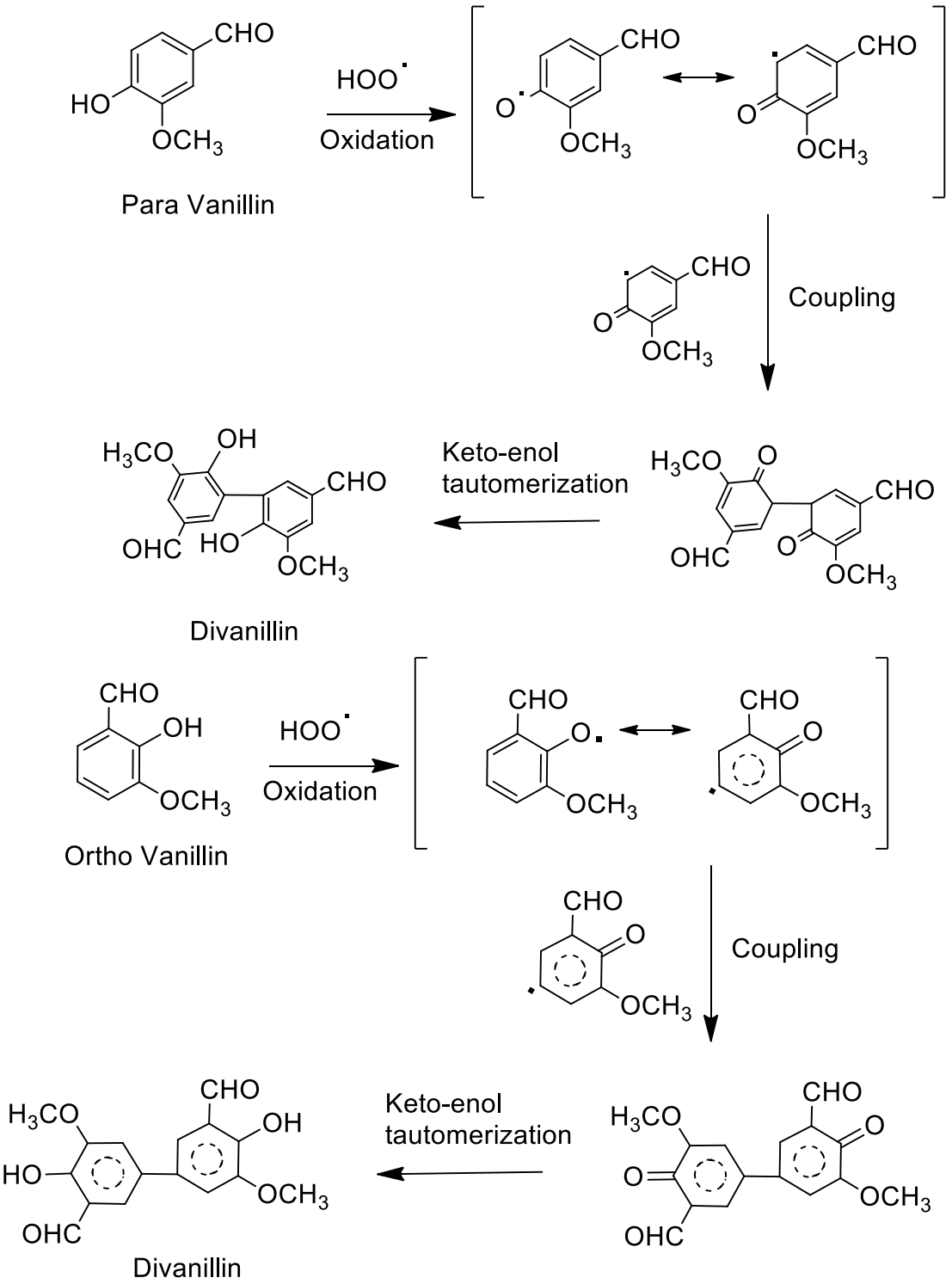


Figure 2. Cyclic Voltammogram of the reaction between OV or PV and the reactants obtained in the idant and prooxidant action of same concentration of OV and PV, (a). $[KIO_3] = 2 \times 10^{-2}$ mol L^{-1}, (b). $[KIO_3] = 2 \times 10^{-2}$ mol L^{-1}; Common condition; $[H_2SO_4] = 2.50 \times 10^{-2}$ mol L^{-1}. Scan rate = 100 mV / s

The inhibitory effect due to $HOO^{\bullet}$ radical on BR system was reported for the first time by Franz [45]. Later, the Franz's hypothesis was not only experimentally verified by R. Cervellati et al [43] but also contributed a huge publications regarding t_{in} caused by $HOO^{\bullet}$ radical [46,47, 48]. Beside this, various other authors including our group have been successfully able to explored the role played by $HOO^{\bullet}$ radical in producing t_{in} [49-57].

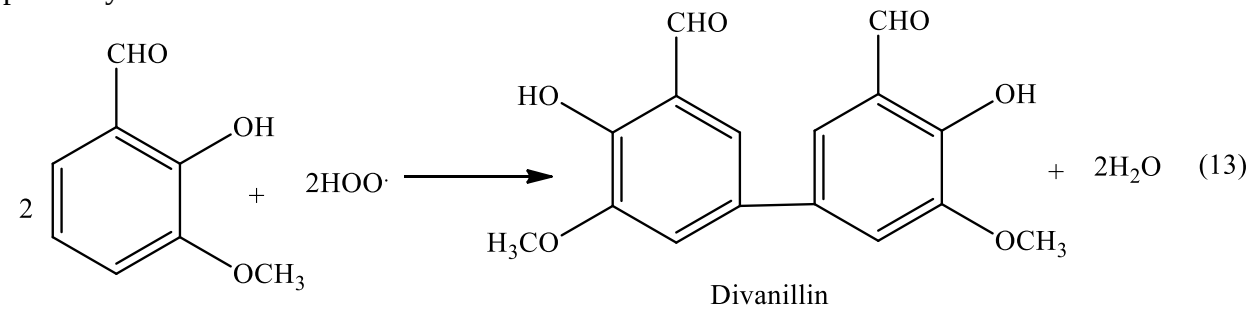
In this paper, we not only hold the claim that t_{in} were caused due to the reaction of OV or PV with $HOO^{\bullet}$ radical but have also a claim that both of these isomers converted into a dimeric product (divanillin) [36,37]. It is because the previous publications reported that $HOO^{\bullet}$ radical oxidized the additives into their respective radicals and then these "additives radicals" self-coupled to form product [43,44,46,56,57]. Due to this respect, we consider that the isomers of vanillin were first oxidized to their respective radicals (phenoxy radical, or called vanillin radical) by hydroperoxyl radical ($HOO^{\bullet}$), and then vanillin radical underwent the phenoxy radical coupling process and keto-enol tautomerization in the synthesis of Divanillin [59] (as indicated in the below Scheme 3),

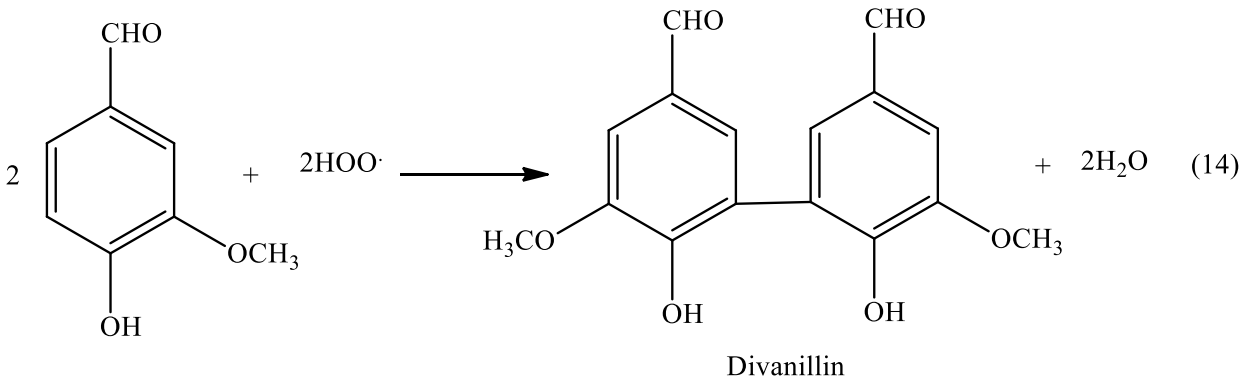


Scheme 3: Phenoxy radical coupling and keto-enol tautomerization in the synthesis of Divanillin

Beside this, we have a claim that longer t_{in} produced by the OV as compared to the shorter t_{in} caused by PV within the BR system may be due to the involvement of intramolecular hydrogen-bonding within these isomers. The H-bonding (O-H·····O=C-H) existing in OV has stronger then the H-bonding (O-H·····O-R) in PV [58], and due to this respect the OV become more stable during oscillatory reaction. Thus, in BR system the OV has slowly oxidized to divanillin and produced a

larger t_{in} as compared to PV. The below reactions (13) and (14) represent the oxidation of OV and PV respectively.





(Where m is an integer)

Both reactions (13) and (14) were competitive with reaction (10) [46] because all of these reactions can consume $HOO^{\bullet}$ radical, but both reactions (13) and (14) were faster. The consumption of $HOO^{\bullet}$ radicals in the reaction (13) and (14) leads to decrease in $IO_2^{\bullet}$ radical via reaction (10). The $IO_2^{\bullet}$ is responsible for the oxidizing $[NiL]^{2+}$ into $[NiL]^{3+}$. Such decrease in $IO_2^{\bullet}$ radical caused the reduce oxidizing of $[NiL]^{2+}$ into $[NiL]^{3+}$ in via reaction (8). The deficiency of $[NiL]^{3+}$ led to the decreased in $[NiL]^{2+}$ via reaction (9). Thus oscillation between $[NiL]^{2+}$ and $[NiL]^{3+}$ were terminated and t_{in} were observed. When the amount of OV or PV has completely reacted via reaction (13) or (14) respectively, the reaction (8), (9), and (10) become dominate again and the oscillation regenerated.

5. CONCLUSION

In this paper we verified that macrocyclic Ni- Complex catalyzed-BR oscillating system is a best analytical tool for identification between two isomers (OV and PV). Both of these isomers have the inhibitory effect on active BR system but t_{in} of OV was found much higher as compared to the t_{in} caused by PV. Our assumption for such difference in the inhibition time cause by these isomers are the involvement of intermolecular hydrogen bonding. Thus, these two isomers are identified as keeping inhibitory effect as parameter. Therefore, an analytical method was developed by using BR-oscillator for identifying these isomers. The detail perturbation mechanism is that, $HOO^{\bullet}$ radical has oxidized these two isomers into dimeric product (divanillin).

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