

## Evaluation of Steric Effect of Hydroquinone, Tert-Butyl Hydroquinone and 2, 5-Ditert-Butyl Hydroquinone by using a Briggs-Rauscher Oscillator

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This article indicated a novel methodology of evaluation of steric effect of (hydroquinone (HQ), tert-Butyl hydroquinone (TBHQ) and 2, 5-ditert-butyl hydroquinone (DTBHQ)) by using a Briggs-Rauscher chemical oscillating system. The macro cyclic [NiL](ClO<sub>4</sub>)<sub>2</sub> complex catalyst with 5,7,7,12,14,14-hexamethyl-1,4,8,1,1-tetraazacyclotetradeca-4,1,1-diene as ligand is used. The calculated experimental data confirmed the diverse perturbation effects of all three additives towards the active Briggs-Rauscher oscillator in their concentration ranges from  $5.0 \times 10^{-7}$  M to  $1.25 \times 10^{-5}$  M. Hydroquinone generate inhibition time ( $t_{in}$ ) higher than t-BHQ, whereas, no influence of 2,5-DBHQ were observed in Briggs-Rauscher system. Our claim for such differences in perturbation is due to the strong steric hindrance effect of these additives. The presence of bulky group (tertiary butyl) reduces the reactivity of the antioxidants by covering the active sides (OH-group) from the attack of HOO• radical. Thus, Hydroquinone produced larger  $t_{in}$  because of absence of bulky group, the shorter  $t_{in}$  of t-BHQ due to the presence of one bulky group whereas, no  $t_{in}$  of 2, 5-DBHQ because of two bulky groups attached. The perturbation reaction mechanism was discussed on the basis of FCA (Furrow-Cervellati-Amadori) model. The explanation mechanism is that both HQ and t-BHQ is oxidized by HOO• into their respective Quinone.

**Keywords:** Antioxidant; Briggs-Rauscher; Antioxidants; Inhibitory effect; Steric effect

### 1. INTRODUCTION

Free radical (FR) and reactive oxygen species (ROS) have been shown to be accompanying with earlier ageing and several human diseases such as cancer, central nervous system injury, autoimmune diseases, ischemia anomia, reperfusion injury, inflammatory and degenerative diseases

[1-4]. The uses of antioxidants like vegetables, fruits and different kind of beverages for the prevention of such kind of free radical that is cause by the damaging cell and tissue in human body. Antioxidants classified into two kinds; natural and synthetic antioxidant. The natural antioxidants initiate in fruits and vegetables in the form of vitamins and polyphenols. However, the comparison of synthetic antioxidants, natural antioxidants have less number of side effect on the human body. The uses of natural antioxidants play an important role in the field of medicine and food industry [5,6].

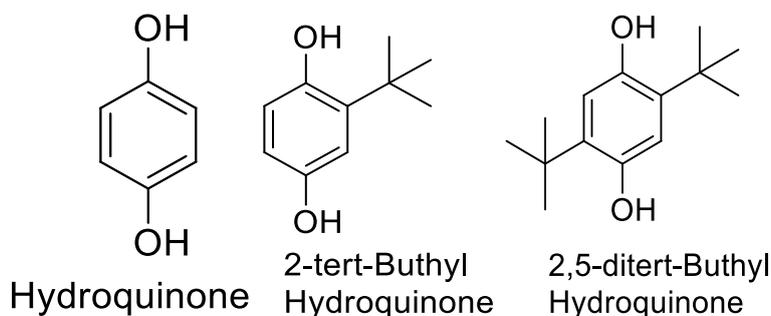
New analytical methods are proposed to measure the antioxidants capacity of free radical scavengers including (Trolox Equivalent Antioxidant Capacity/ TEAC), (Oxygen Radical Absorbance Capacity/ ORAC), (Total Oxidant Scavenging Capacity/ TOSC) and (Total Radical Trapping Parameter/ TRAP), which is based on scavenging of 2,2-azinobis-(3-ethylbenzothiazoline-6-sulphonate) radical anions [5,7-9].

Antioxidant activity to determining different kinds of tea, like black tea, green tea and also determines the foods content of antioxidant like beverages, vegetable and fruits were measured with different methods, Amperometric method (AM) it measuring the electric current in electric detector cell, during the oxidation of analyst working electrodes with potential are applied [10,11]. Evaluation of antioxidant of some natural polyphonic compounds are analyzing by different kind of oscillator, which used different kind of catalyst like Mn (II) catalyst [12], but we used our  $[\text{NiL}](\text{ClO}_4)_2$  complex catalyst (Briggs-Rauscher Oscillator) [13] for the purpose of evaluation of antioxidant of natural polyphonic compound, identification and determination, This method is quite good, sensitive, sample and easy to handle and highly accuracy [14].

Recently our group has successfully utilized Briggs-Rauscher oscillator for identification of isomers of compounds namely Ortho-vanillin and Para-vanillin [15], cyclohexane isomers [16],  $\alpha$  &  $\beta$  ketoglutaric acid [17] and aromatic isomers 3- & 4-hydroxy hydroxy benzoic acid [18].

The natural polyphonic compound including Hydroquinone (HQ), tert-buthyl hydroquinone (TBHQ) and 2,5-ditert-buthylhydroquinone (DTBHQ) evaluate steric effect by using macrocyclic nickel complex-catalyst in Briggs-Rauscher system. The  $\text{H}_2\text{SO}_4\text{-KIO}_3\text{-CH}_2(\text{-COOH})_2\text{-NiL}(\text{ClO}_4)_2$  this system create potentiometric oscillation, because of periodic difference of the quantity of  $\log \{[\text{Ni(III)}]/[\text{Ni(II)L}]\}$ . In macrocyclic nickel complex- catalyst Briggs-Rauscher system which involve radical species, such as  $(\text{HOO}^\bullet)$  in Briggs-Rauscher chemical oscillator.

For the first time we evaluate the steric effect of natural polyphonic compounds, (HQ, Tert-BHQ, and 2, 5-di tert-BHQ) by using a Briggs-Rauscher chemical oscillators involving macro cyclic Ni complex used as catalyst. Inhibition time is considered as a parameter to investigate the steric effect of the additives. The behavior of all of these antioxidants towards Briggs-Rauscher oscillator is quite differ because of the involvement of their steric hindrance. The HQ produced  $t_{in}$  larger than tert-BHQ whereas no influence caused by 2,5-ditert-BHQ. Thus a new method could expect to establish for investigation of antioxidant activity on the base of steric effect by using oscillating chemical system. Our proposed method is quite simpler with low cost and high sensitivity and was expected to investigate the phenomena of steric effect, antioxidant activity of synthesis or natural polyphonic compounds as well.



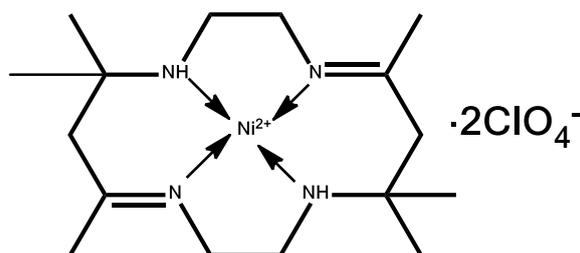
**Scheme 1.** Hydroquinone; 2-tert-Buthylhydroquinone; 2,5-ditert-Buthylhydroquinone.

## 2. EXPERIMENTAL SECTION

### 2.1. Reagents

All the Chemicals i.e. potassium iodate, malonic acid, hydrogen peroxide (30%),  $\text{H}_2\text{SO}_4$  (Aldrich, 98%), and HQ, tert-BHQ, 2, 5-DBHQ were used of analytical grade except macrocyclic Ni complex catalyst. According to literature [19,20] the tetraazamacrocyclic complex,  $[\text{NiL}](\text{ClO}_4)_2$  were synthesized and identified by elemental analysis and infrared spectrum. The structure of  $[\text{NiL}](\text{ClO}_4)_2$  are shown in Scheme 2.

The  $2.50 \times 10^{-2}$  M  $\text{H}_2\text{SO}_4$  was diluted from 98% of  $\text{H}_2\text{SO}_4$  and initial concentrations of other reagents i.e. 2.00 M malonic acid,  $1.40 \times 10^{-1}$  M  $\text{KIO}_3$ ,  $1.73 \times 10^{-2}$  M  $[\text{NiL}](\text{ClO}_4)_2$ , and 4.00 M  $\text{H}_2\text{O}_2$  were prepared within such  $2.50 \times 10^{-2}$  M  $\text{H}_2\text{SO}_4$  solution. Different concentrations of the HQ, tert-BHQ, 2, 5-DTBHQ were synthesized in ethyl alcohol. Double distilled water is used in all cases.



**Scheme 2.** Structure of  $[\text{NiL}](\text{ClO}_4)_2$

### 2.2. Apparatus

The Briggs-Rauscher instrumentation consists of two electrodes platinum (Pt) electrode and saturated calomel electrode (SCE) and potential measuring system. The Pt-electrode (model 213 Shanghai, China) served as working electrode while SCE (Model 217 Shanghai, China)) acts as reference electrode. The electrodes were dipped into oscillating mixture in a glass reactor, consisting magnetic bar (type 793, Jiangsu, China) which homogenized the solution at 700 rpm through magnetic stirrer (type 793, Jiangsu, China). Both the electrodes were connected to PC through potential

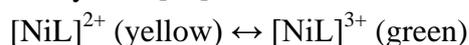
measuring system i.e. amplifier, Go-link sensor interfere (Vernier Software Technology, U.S.A.). The potential Vs time were recorded through Logger-Lite (Vernier Software Technology, U.S.A.) data collected software. The temperature of the reaction was kept at 5°C by thermostat modal (DZCS-IIC, Nanjing Dazhankejiao institute of instrument, China).

### 2.3. Procedure

The oscillating solutions were mixed into the following order: 3.5 ml of 2.00 M malonic acid, 14.5 ml of  $2.5 \times 10^{-2}$  M H<sub>2</sub>SO<sub>4</sub>, 6.5 ml of 0.14 M KIO<sub>3</sub>, 1.5 ml of 0.0173 M of [NiL](ClO<sub>4</sub>)<sub>2</sub>, 14 ml of 4.0 M of H<sub>2</sub>O<sub>2</sub> solution. When the last reagent (H<sub>2</sub>O<sub>2</sub>), were added into system the oscillation were began after a short induction time. The potential were recorded in PC through amplifier and Golink. Different concentrations of the additives (HQ, tert-BHQ, 2, 5-DTBHQ) were used to perturbed the oscillation at the bottom of 3<sup>rd</sup> cycle and were recorded the difference.

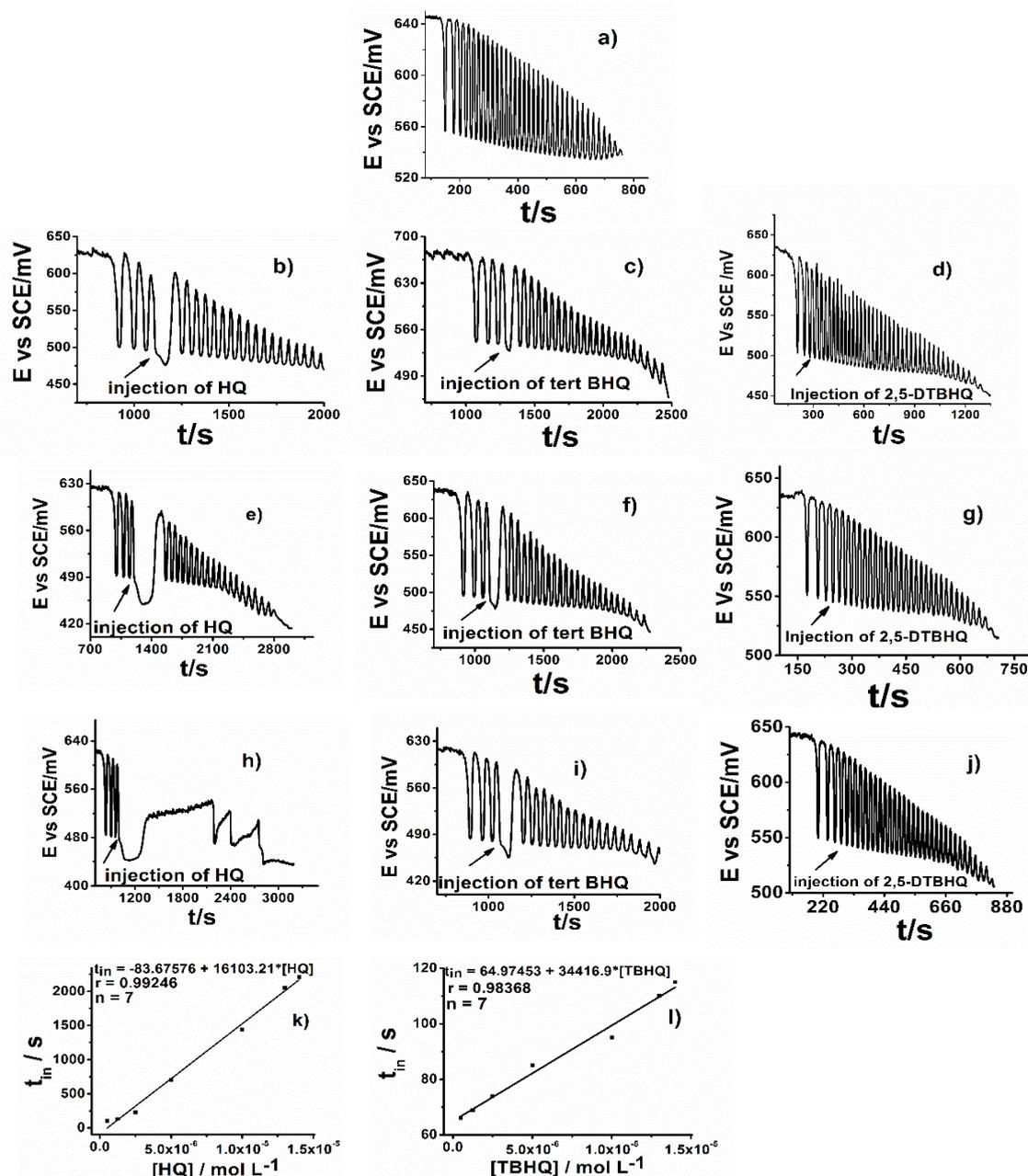
## 3. RESULTS AND DISCUSSIONS

The typical oscillation (as shown in the Figure 1a) was achieved by mixing the reagents on the above stated order. During oscillation, the color of solution was continuously interconverted between yellow to brown owing the single electron transfer between [NiL]<sup>2+</sup> (yellow) and [NiL]<sup>3+</sup> (brown). The expected color of [NiL]<sup>3+</sup> is green but experimentally observed brown. It is assumed, the formation of iodine and was dissolve into the system [21].



The typical Briggs-Rauscher oscillator was disturbed by adding the equal amount of the same concentrations of these three antioxidant (HQ, TBHQ and DTBHQ) in their concentrations range between  $5.0 \times 10^{-7}$  M to  $1.25 \times 10^{-5}$  M. Different perturbation effects of these additives were noticed. The HQ and the TBHQ produced the  $t_{\text{in}}$  but the  $t_{\text{in}}$  caused by the HQ is higher as compared to TBHQ. Whereas the DTBHQ didn't influence the oscillation. For example; when the concentration of  $5.0 \times 10^{-7}$  M of all the three additives were put separately into the system, HQ produced  $t_{\text{in}}$  of 95 sec (as shown in Figure 1b), 36 sec  $t_{\text{in}}$  caused by TBHQ (as shown in Figure 1c) but no  $t_{\text{in}}$  initiated by DTBHQ (as shown in Figure 1d). The interesting phenomenon is that as the concentrations of these additives (HQ and TBHQ) into the system were increased, their influences ( $t_{\text{in}}$ ) were increased. For example; the increase in the  $t_{\text{in}}$  were observed by the increasing concentrations ( $5.0 \times 10^{-7}$  or  $1.25 \times 10^{-5}$  M) of HQ or TBHQ into the system as shown in the Figures 1(e)(h) or Figures 1(f)(i) respectively. Whereas, the rising concentration amount of DTBHQ didn't show any influence the oscillation as shown in Figures 1(g)(j). The concentration versus inhibition time (HQ and TBHQ), two linear regression curves were plotting between the concentration range is ( $5.0 \times 10^{-7}$  to  $1.25 \times 10^{-5}$  M) with a correlation coefficient of HQ is 0.99 and TBHQ is 0.98 as shown in (Figures k and l), which clearly show the different behavior of HQ and TBHQ.

The different behavior of these three antioxidants are based on the  $t_{in}$ , DTBHQ do not show any change toward Briggs-Rauscher system, and the other two antioxidants shown  $t_{in}$  but their  $t_{in}$  is directly proportional to their concentrations as shown in the Figure 1 (k and l)



**Figure 1.** a) Typical oscillation profile for the proposed oscillation system; b). perturbation of HQ  $5.0 \times 10^{-7}$  M in the system; c) perturbation of TBHQ  $5.0 \times 10^{-7}$  M in the system; d) perturbation of 2,5-DTHQ  $5.0 \times 10^{-7}$  M in the system; e) perturbation of HQ  $5.0 \times 10^{-6}$  M in the system; f) perturbation of TBHQ  $5.0 \times 10^{-6}$  M in the system; g) perturbation of DTBHQ  $5.0 \times 10^{-6}$  M in the system; h) perturbation of HQ  $1.25 \times 10^{-5}$  M in the system; i) perturbation of TBHQ  $1.25 \times 10^{-5}$  M in the system; j) perturbation of 2,5-DBHQ  $1.25 \times 10^{-5}$  M in the system; k) Linear regression curve between  $t_{in}$  vs concentration of HQ; l) Linear regression curve between  $t_{in}$  vs concentration of TBHQ; Common condition:  $[H_2SO_4] = 2.50 \times 10^{-2}$  M,  $[KIO_3] = 2.275 \times 10^{-3}$  M,  $[MA] = 1.75 \times 10^{-1}$  M,  $[NiL](ClO_4)_2 = 6.487 \times 10^{-4}$  M,  $[H_2O_2] = 1.4$  M,  $T = 4 \pm 0.5$  °C

The assumption of such different behaviors caused by these additives was due to the involvements of steric hindrance. The HQ didn't have any bulky group (tertiary butyl) so no resistance towards oxidation of HQ in Briggs-Rauscher matrix that is why HQ produced a longer  $t_{in}$ . Whereas TBHQ possess one bulky group which resist the oxidation of TBHQ and result in lower  $t_{in}$  as compare to HQ. But due to the two bulky groups on DTBHQ completely block the oxidation reaction have no  $t_{in}$  in result. Thus, a novel technique for the investigation of steric hindrance in bulky compounds was introduced in this article by using Briggs-Rauscher oscillating matrix and such technique is also extended to investigate the steric effects in other bulky compounds as well.

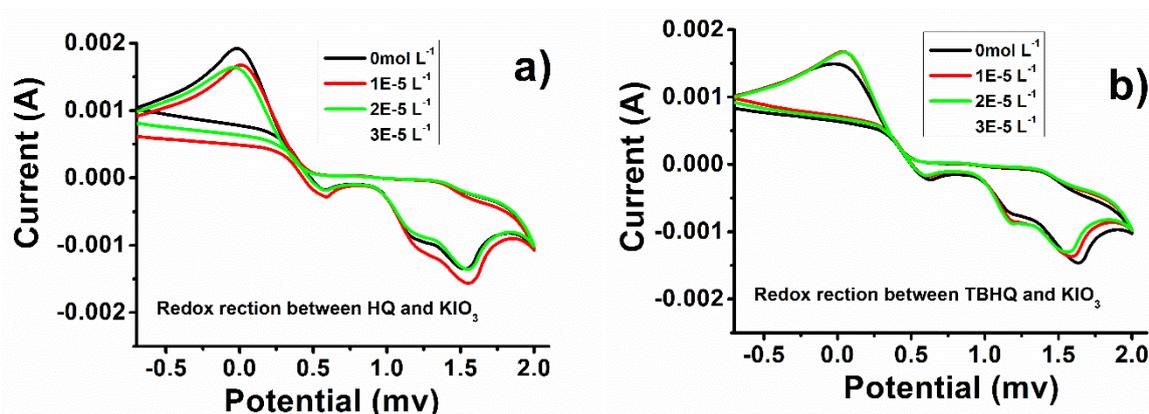
### 3.1 Mechanism

#### 3.1.1. Cyclic voltammetry

The redox reactions of the additives (HQ, TBHQ and 2,5-DTBHQ) with reagents or products or intermediate species has been confirmed from below listed solutions in the presence and absence of additives;



From the results of cyclic voltammograms shown that only HQ and TBHQ has the redox reaction with  $\text{KIO}_3$  but no reaction with 2,5-DTBHQ as shown the in Figure 2. Here the direct reaction between the additives with  $\text{KIO}_3$  has not been consider because the additives are in low concentrations as compared to the  $\text{KIO}_3$ . If we consider the direct reaction between additives with  $\text{KIO}_3$ , there will be no inhibition recorded.

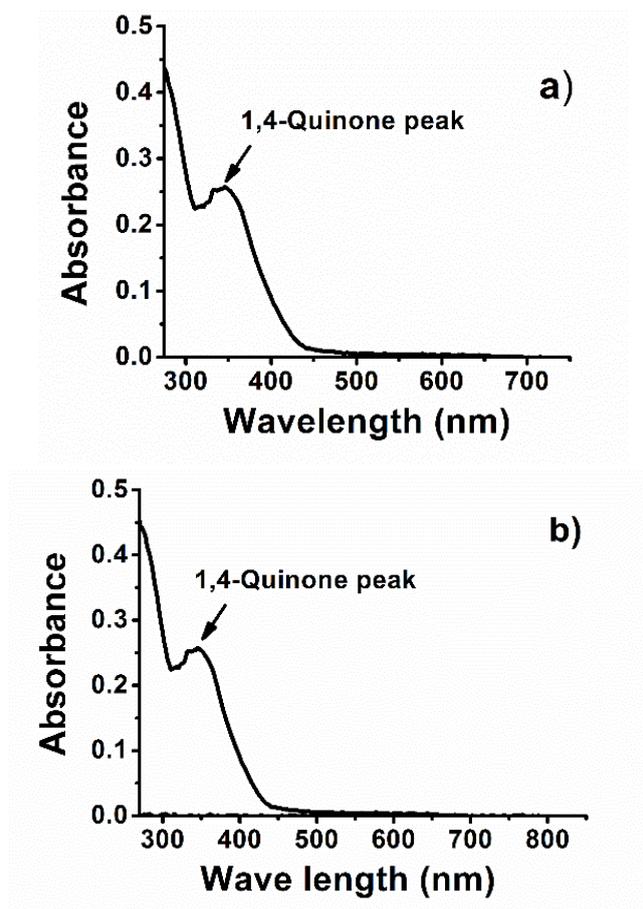


**Figure 2.** (a) Cyclic Voltammograms of the reaction between HQ and  $\text{KIO}_3$ ; (b) Cyclic Voltammogram of the reaction between tert-BHQ and  $\text{KIO}_3$ . Common Conditions:  $[\text{H}_2\text{SO}_4] = 2.50 \times 10^{-2} \text{ M}$ ,  $[\text{KIO}_3] = 2.275 \times 10^{-3} \text{ M}$ , Scan rate = 100 mV / s.

Thus we assume the involvement of intermediate species ( $\text{HOO}^\bullet$ ) that reacted with additives and produced  $t_{in}$ . For the first time, the  $t_{in}$  caused by  $\text{HOO}^\bullet$  radical was described by Franz [22]. Later, it also verified by Cervellati et al [23-25] and then numerous publications based on  $t_{in}$  caused by  $\text{HOO}^\bullet$  radical [5, 16, 26-31] were reported.

### 3.1.2. Product identification in Briggs-Rauscher system

For typical UV experiments, the analyzed mixtures were made by the following solutions: 45  $\mu\text{L}$  of 0.01 M solution of HQ or TBHQ, 33.5 ml of  $2.50 \times 10^{-2}$  M.  $\text{H}_2\text{SO}_4$  solution, and 6.5 ml of  $2.275 \times 10^{-3}$  M  $\text{KIO}_3$ . While  $[\text{NiL}] (\text{ClO}_4)_2$ , MA and  $\text{H}_2\text{O}_2$  were didn't used because they don't have a redox reactions with HQ and TBHQ in cyclic voltammetry (CV) experiments. The mixture of 1 ml solution poured into cuvette for measurement of UV experiment to identify products from both antioxidants. The maximum absorbance wavelength for the product is obtained approximately 350 nm as shown in Figure 3 which is the agreement with the absorbance peak for 1-4 Quinone in literature [32].

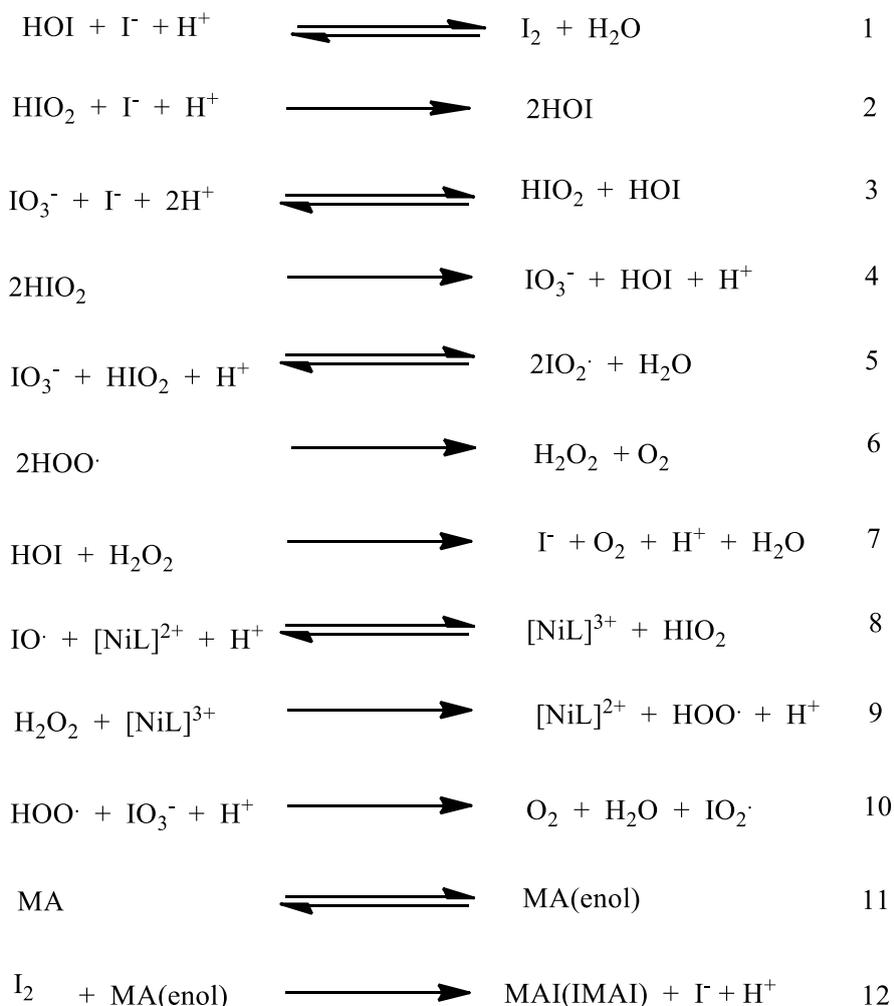


**Figure. 3** a) The UV spectrum of HQ in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{KIO}_3$ , Conditions:  $[\text{HQ}] = 1.12 \times 10^{-5}$  M,  $[\text{H}_2\text{SO}_4] = 2.50 \times 10^{-2}$  M,  $[\text{KIO}_3] = 2.275 \times 10^{-3}$  M, b) The UV-Visible absorbance spectrum of TBHQ in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{KIO}_3$ , Conditions:  $[\text{TBHQ}] = 1.12 \times 10^{-5}$  M,  $[\text{H}_2\text{SO}_4] = 2.50 \times 10^{-2}$  M,  $[\text{KIO}_3] = 2.275 \times 10^{-3}$  M.

### 3.1.3. Interpretation of Briggs-Rauscher mechanism

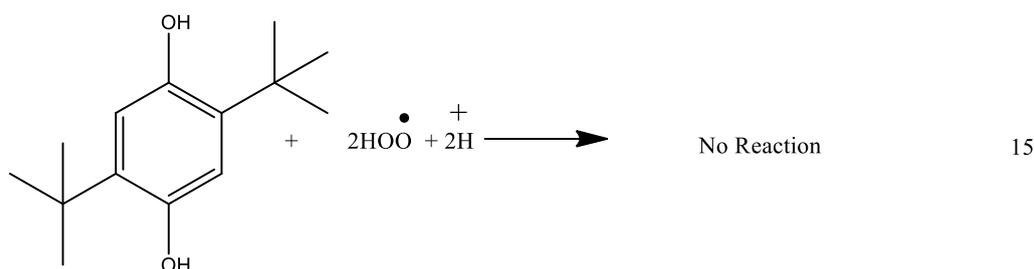
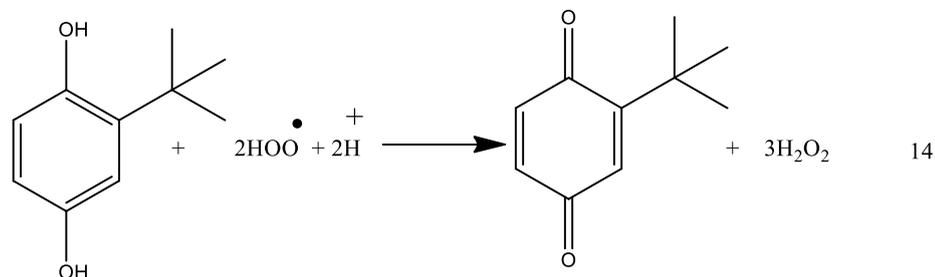
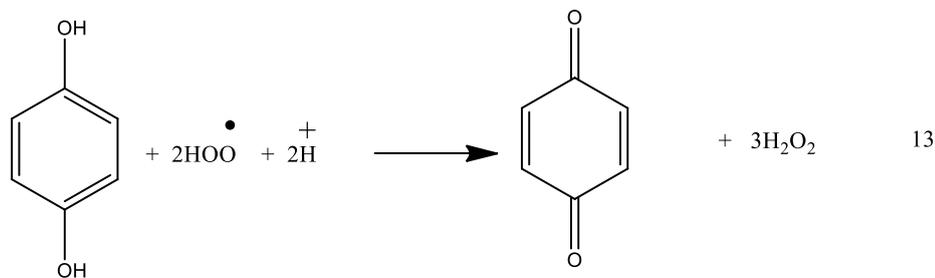
Briggs-Rauscher oscillating mechanism is extremely complex because of contamination of various species, intermediates ( $\text{HOO}\cdot$ ,  $\text{IO}_2\cdot$ ,  $\text{HOI}$ ,  $\text{HIO}_2$ ) [23,25] etc. Beside its complexity various attempt has been made to explain the Briggs-Rauscher mechanism. Recently, Furrow et al developed

the well-known FCA (Furrow-Cervellati-Amadori) mechanism [33] from the union combination of two famous models DE (De Kepper-Epstein) model [34] and NF (Noyes-Furrow) model [35]. Such mechanism consist the below 12 oscillatory reactions.



FCA mechanism is totally focus on the role played by hydroperoxyl radical ( $\text{HOO}^\cdot$ ). Such radical is responsible for temporary termination of oscillation by reacting it with additives. Such phenomenon was supported by Franz [22] and later successfully tested and agreed by Cervellati et al [23-25]. Recently a lot of publications [26-33] supported that  $t_{\text{in}}$  was due to the involvement of intermediate species ( $\text{HOO}^\cdot$ ). This reported work shown that the  $\text{HOO}^\cdot$  has oxidized the additives (HQ and TBHQ) into their respective quinone (reactions 13 and 14) and produced  $t_{\text{in}}$ . Whereas  $\text{HOO}^\cdot$  couldn't oxidized DTBHQ to produce  $t_{\text{in}}$  as shown in reaction 15.

The reactions 13, 14 and 10 consumed  $\text{HOO}^\cdot$  but the occurrence of  $t_{\text{in}}$  indicated that reaction 13 and 14 has faster in consuming  $\text{HOO}^\cdot$  radical. Such consumption of radical via reaction 13 and 14 reduce the amount in  $\text{IO}_2^\cdot$  via reaction 10. The decrease amount of  $\text{IO}_2^\cdot$  led to decrease the amount of  $[\text{NiL}]^{3+}$  via reaction 8 because  $\text{IO}_2^\cdot$  is accountable for the oxidation of  $[\text{NiL}]^{2+}$  into  $[\text{NiL}]^{3+}$ . The low concentration of  $[\text{NiL}]^{3+}$  led to slow down the reduction of  $[\text{NiL}]^{3+}$  into  $[\text{NiL}]^{2+}$  via reaction 9. Therefore the oscillation are temporary terminated and  $t_{\text{in}}$  was noticed. When the concentration of the additives are completely degraded via reaction 13 and 14 the oscillation was regime.



#### 4. CONCLUSION

In this paper, we used Briggs-Rauscher oscillator involving macro cyclic Ni-complex catalyst as a tool to investigate the steric effects of three antioxidants (HQ, TBHQ and 2,5-DTBHQ). It was confirmed that the inhibitory effects has been greatly influence by bulky group (tertiary butyl) attached to additives. For example, the HQ has no bulky group that is why it produced higher  $t_{in}$  with respect to TBHQ (having one bulky group) it produced smaller  $t_{in}$ , but no  $t_{in}$  was notice by DTBHQ because of having two bulky groups is attached. The redox reaction of HQ or TBHQ with  $\text{KIO}_3$  was confirmed through CV experiments. The reaction perturbation mechanism explained that the  $\text{HOO}\cdot$  radical has oxidized the HQ and TBHQ into their respective quinone's.

#### ACKNOWLEDGEMENTS

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