STUDIA UBB CHEMIA, LVI, 1, 2011

THE EFFECT OF SALICYLIC ACID ON THE BRIGGS-RAUSCHER OSCILLATING REACTION

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ABSTRACT. Results concerning the effect of salicylic acid on the Briggs-Rauscher oscillating reaction in batch mode are presented. In contrast to the other phenolic and polyphenolic compounds studied before, this compound does not stop immediately the oscillations; however it reduces the amplitudes gradually. The time elapsed between the addition of the salicylic acid and the complete cessation of the oscillations is denominated as attenuation time. After the inhibition time the oscillations are restarted with low amplitude. The dependence of the amplitudes, attenuation time, inhibition time and period times on the salicylic acid is presented. Furthermore a new method for kinetic study of the unusual inhibitory effect is implemented. The reaction was followed potentiometrically, by means of an iodide ion selective electrode coupled to a double junction saturated calomel electrode. We derived the integrated rate equation that corresponds to the pseudo-first order reaction followed by a sensor with a nernstian transfer function. The hypothesis concerning the pseudo-first order kinetics of iodide ion production and consumption over a relatively long time within one period of oscillation is proven. The rate constants of iodide ion production and consumption are diminished gradually for the oscillations after the addition of salicylic acid. The fact that salicylic acid decreases the amplitudes and the rate constants of iodide ion formation and consumption during the attenuation period lead to the conclusion that this compound manifests a weak inhibitory effect in the attenuation period as well. However this inhibitory effect increases in time, until complete cessation of the oscillations.

Keywords: *Briggs-Rauscher oscillating reaction, salicylic acid, iodide ion selective electrode, Nernst equation, kinetics*

INTRODUCTION

The Briggs-Rauscher (BR) reaction is one of the most intensively investigated homogeneous phase oscillating reactions. It consists of oxidation and iodination of an organic substrate by hydrogen peroxide and iodate ion, catalyzed by Mn^{2+} and H^{+} ions [1]. The organic substrate is usually malonic acid, but other enolic hydrogen atom containing organic compounds (i.e. acetone, methylmalonic acid, iodomalonic acid, phenylmalonic acid) can be used [2].

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The early mechanistic studies revealed the existence of 30 pseudo-elementary steps involving various oxygen and iodine containing species (i.e.: HOO•, HO•, $Mn(OH)^{2+}$ HIO, HIO_2, I•, IO•, IO_2•, I^-, and I_2) as intermediates [3, 4]. A set of 11 steps, known as skeleton mechanism, was proposed, which described qualitatively the nonlinear behavior of the system [5, 6]. The further studies led to a better mechanistic understanding of the reaction [2, 7].

Cervellati et al. studied the effect of different polyphenolic free radical scavengers (antioxidants) on the BR reaction [8-10]. All the studied polyphenolic compounds stopped immediately the oscillations for a certain time, denominated as inhibition time. A linear correlation was found between the inhibition time and the concentration of the antioxidant added to the mixture. Relative antioxidant activities have been determined. The qualitative mechanistic interpretation of the inhibitory effect was given: the antioxidant consumes the HOO• from the mixture in a fast step. When the antioxidant is completely consumed, the HOO• concentration increases above a critical value and the oscillations reappear. Reactions of antioxidant with other species than HOO• were also accounted for (i.e. oxidation and iodination by various oxy-iodine species) [10]. This method was claimed to be a validated analytical method for antioxidant activity determinations [9, 10]. More recent studies revealed the complexities of the reactions steps involving polyphenolic compounds in the BR-mixture [11, 12]. The effect of polyphenol was tested also in case of the BR reaction performed under flow conditions [13]. The analyte pulse perturbation technique applied in a CSTR showed that in contrast to the batch experiments, the resorcinol does not stop the oscillations, but decreases the period time and amplitude. Parabolic and reciprocal relationships were found between the concentration of resorcinol and the amplitude and the period time, respectively.

In our previous studies we reported that salicylic acid does not stop immediately the oscillations of the BR reaction operated in batch mode, like all the other phenolic compounds did [14-16]. In this work we present a more detailed phenomenological and kinetic study on the effect of salicylic acid on the BR reaction.

RESULTS AND DISCUSSION

The uninhibited Briggs-Rauscher reaction

Here we present the features of the uninhibited BR-reaction under the conditions described in the Experimental section. The reaction was followed using the iodide ion selective electrode and the bright platinum electrode simultaneously. The potential variation in time of these electrodes versus the reference electrode is presented in the Figure 1. It can be seen that the initial amplitudes monitored by the iodide ion selective electrode are large, approximately 250 mV. However the amplitudes monitored by the bright platinum electrode are lower by a factor of 8, approximately 30 mV. In our previous studies we used exclusively a bright platinum electrode coupled to a reference electrode and we monitored only the redox potential change in time [14-15]. For the same composition of the BR-mixture we observed that the initial amplitudes were between 30 and 50 mV. The higher amplitude of the oscillations is a clear advantage of the application of the iodide-ion selective electrode. The second advantage and importance of the application of this electrode is related to the fact that it makes possible the kinetic study of iodide ion consumption and production [16]. This will be described in more detail in subsection entitled The potentiometric method for monitoring the BR-reaction.

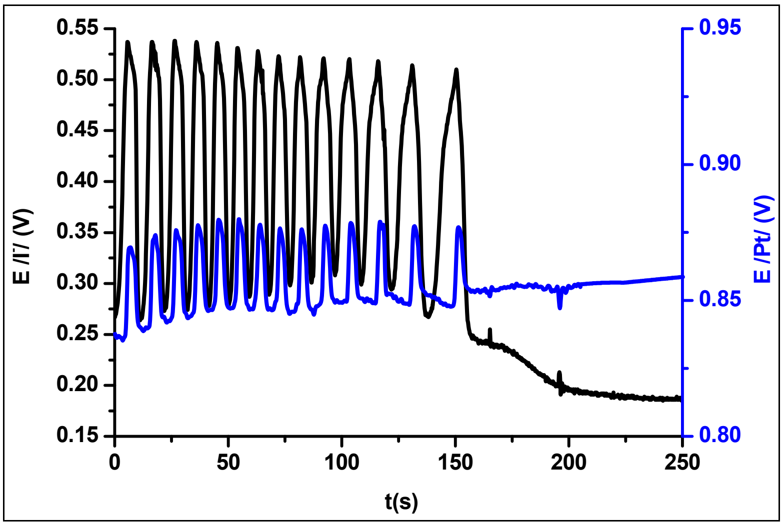

Figure 1. Simultaneous recording of the potentials of the iodide ion selective and the bright platinum electrodes versus the reference electrode immersed in the BR-mixture.

The shape of the first oscillations consists of four segments. The color changes observed during a single oscillation and the initial periods lengths are the same as reported previously [14, 15, 17]. Upon magnification it is notable that the peak maximum corresponding to the Pt-electrode is delayed in time by 0,6-1,0 s compared to the peak maximum on the iodide ion selective electrode. Szabó also reported a time-delay of 0,5-0,9 s between the peak maxima on the Pt-electrode and the iodide ion selective electrode for the first oscillations in the BR mixture [17].

The inhibition of the BR reaction with salicylic acid

When salicylic acid was added after the third oscillation in a relatively low concentration interval to the reacting BR mixture, the oscillations were not stopped at all (Figure 2).

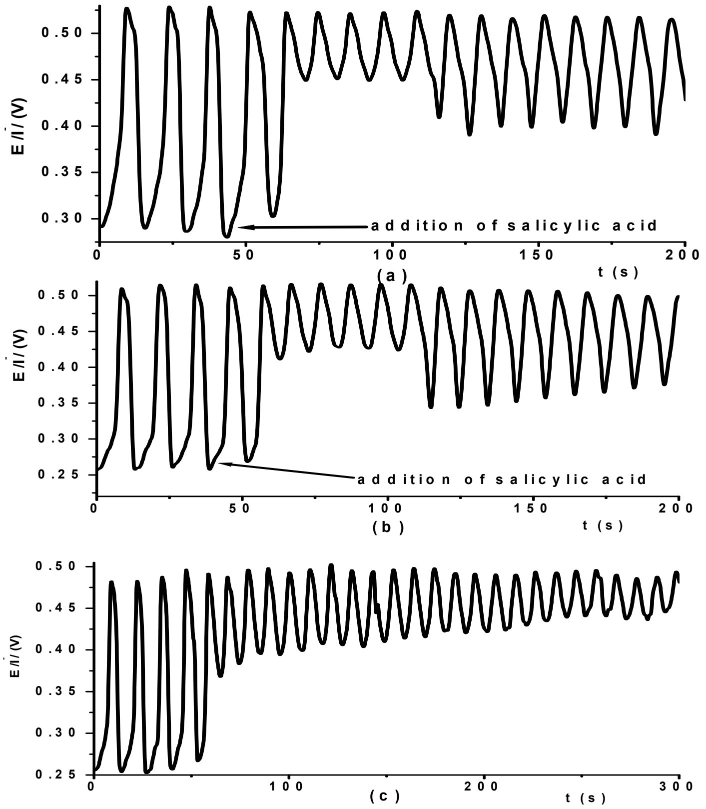

Figure 2. The effect of salicylic acid on the BR reaction in low concentrations, (a) - 0,28 mM, (b) - 0,31 mM, (c) - 0,34 mM.

The amplitude of the oscillation which appears right after the addition of the salicylic acid solution is not affected significantly. However the amplitude of the subsequent 5 and 6 oscillations are reduced considerably (Figure 2a and b, Figure 4), but then the amplitudes are increasing up to about half of the initial amplitudes.

When the salicylic acid concentration is higher than 0,34 mM, the amplitudes are reduced monotonically over the time (Figure 2.c, Figure 3. a-c and Figure 4). In accordance with the previous findings, the period times are not affected by the presence of salicylic acid [15]. It is also notable that after the addition of salicylic acid, the potential corresponding to the peak maxima are not changed significantly, however the minima are shifted considerably to more positive values. The shape of the oscillations after the addition of salicylic acid are also changed compared to the non-inhibited periods. In presence of salicylic acid, the shape of the oscillations resemble to sawtooth (when $c_{\text{salicylic acid}} \leq 0{,}31$ mM) and to damped sine wave (when $c_{\text{salicylic acid}} \geq 0{,}34$ mM).

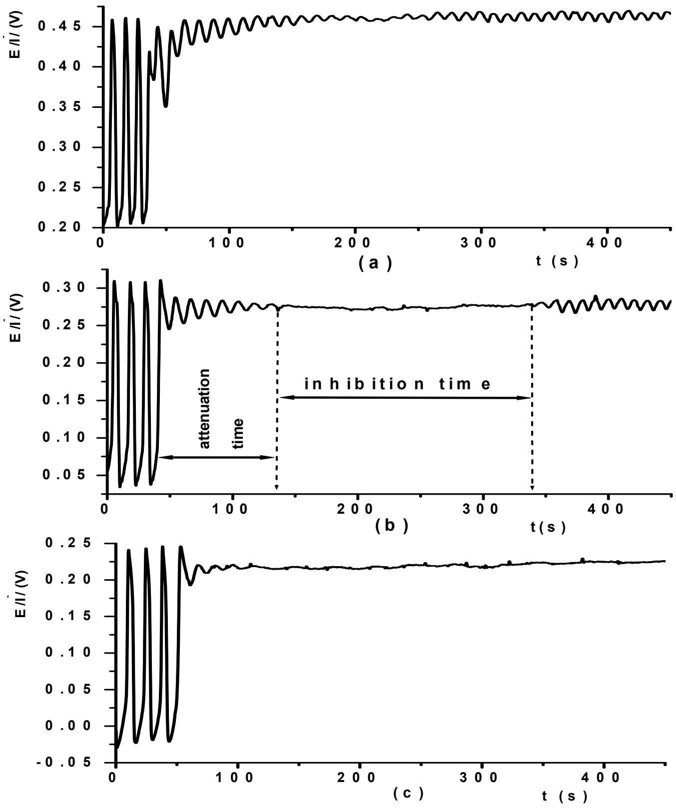

Figure 3. The effect of salicylic acid on the BR reaction in higher concentrations 0,69 mM, (b) - 0,85 mM, (c) - 1,16 mM.

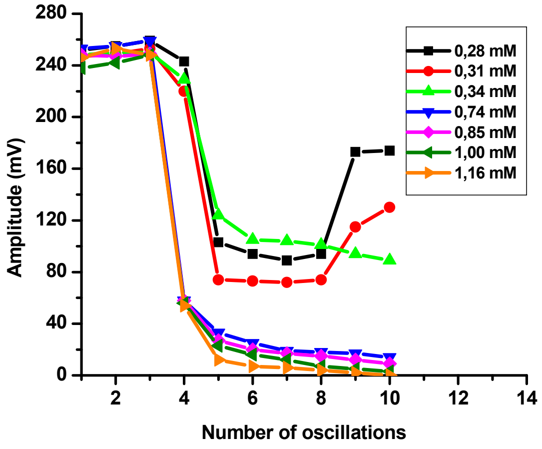

Figure 4. The effect of salicylic acid concentration on the amplitudes. The salicylic acid solution was injected after the third oscillation.

The mixture after the addition of salicylic acid was always transparent; therefore there was no indication that iodine was formed. The oscillatory time is longer than 700 seconds after addition of salicylic acid in low concentration. However the oscillatory time of the uninhibited BR-reaction is about 160 s, which is approximately 4,5 times shorter compared to the reaction inhibited by 0,28 mM salicylic acid.

We denominated the time elapsed between the addition of salicylic acid and the complete cessation of the oscillations as attenuation time [16]. The attenuation time decreases linearly with the concentration of salicylic acid (Figure 5). The equation of the straight line is the following:

$$t_{\mathrm{attenuation}} = (266 \pm 11) - (189 \pm 12) \cdot c_{\mathrm{salicylic\,acid}}, \quad R^2 = 0{,}9740, N = 8 \quad (\mathrm{eq.}1)$$

At higher salicylic acid concentrations than 0,69 mM the oscillations are stopped after the attenuation time. The inhibitory time increased linearly with the salicylic acid concentration (Figure 5 and eq. 2). However at a concentration of 1,16 mM, the oscillations are not regenerated after a long inhibition time (more than 900 seconds).

$$t_{\mathrm{inh}} = (-70 \pm 5) + (323 \pm 5) \cdot c_{\mathrm{salicylic\,acid}}, \qquad R^2 = 0{,}9986, N = 7 \quad (\mathrm{eq.}2)$$

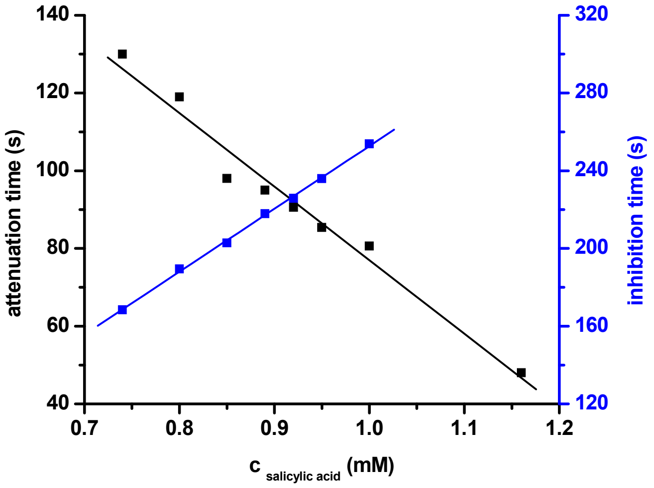

Figure 5. Plot of the attenuation time and inhibition time in function of the salicylic acid concentration.

Kinetic study on the BR-reaction inhibited by salicylic acid

Hypothesis

We assumed that one of the intermediates, the iodide ion presents pseudo-first order kinetics for a certain time interval, whithin one period of oscillation. To prove this assumption, it was necessary to monitor the iodide ion concentration changes during the BR-reaction by means of a iodide ion selective electrode [16]. We present a method to obtain the rate constant of the iodide ion formation and consumption, respectively, directly from the variation in time of the potential difference between the iodide ion selective electrode and the reference electrode.

Instrumental methods (including spectroscopy and conductometry) for obtaining kinetic data are described in the literature. The transfer function of these instruments is linear. Upon changing the concentration variable with the instrument response variable (noted with P), the kinetic equation of a first order reaction becomes the following [18, 19]:

$$\ln\frac{P_\infty - P_t}{P_\infty - P_0} = -k_{obs}\cdot t \qquad (eq.3)$$

The above method has extensively been used for kinetic study of simple reactions. However only a few quantitative reports appeared about the employment of instrumental methods for kinetic study of complex reaction networks such as oscillating reactions. Some of these studies are briefly reviewed below.

The BR reaction has been followed by means of EPR [20], resonance Raman [21] and UV-Vis spectroscopy [2, 22]. Most of these studies lead to qualitative information concerning the intermediates [20-22]. An extensive quantitative kinetic study was presented by Furrow, who monitored the reaction spectrophotometrically and determined the rate of iodine production and consumption. He found that the iodine is consumed mainly in the iodination of the enol form of the organic substrate [2].

A less conventional coupling of instrumental analytical methods was employed by Fujieda and Ogata [23]. They monitored the reaction potentiometrically, calorimetrically and gasometrically in the same time. Semi-quantitative correlations were reported between the iodide ion concentration change, the total heat production, the heat production rate and the volume of the oxygen gas formation rate during the reaction.

Noszticzius et al. employed an experimental setup for the quantitation of the evolved CO and CO_2 end-products. N_2 carrier gas was bubbled through the reacting mixture, removing the CO and CO_2. Hydrogen was added to the gas mixture and the CO+CO_2 content was converted to methane over nickel catalyst. The formed methane was analyzed by a flame ionization detector. It was found that both the CO and CO_2 are products with oscillatory behavior [24, 25].

The potentiometric method for monitoring the BR-reaction

Potentiometry is an easier and more convenient method for the monitoring of the Briggs-Rauscher reaction compared to the spectrophotometric method. The difficulties concerning the spectrophotometric method of monitoring are the following:

- the BR reaction is strongly exothermic [9, 23] and in order to maintain the mixture under isothermal conditions, it needs to be well thermostated,
- during the reaction oxygen gas is evolved. The appearence of oxygen bubbles influences the absorbance of the mixture. Moreover, the oxygen is a triplet diradical and there are evidences that it inhibits the BR reaction [2]. Therefore the mixture needs to be stirred in order to facilitate the removal of the oxygen gas,
- the intermediates of the BR-reactions are photosensitive [2, 21]. The light beam of the spectrophotometer alters the oscillations. Strong light irradiation may stop the oscillations.

The potentiometric method can be applied easily under thermostated and stirred conditions. The method consists of recording of the potential difference between an indicator electrode and a suitable reference electrode. Frequently bright platinum electrode is employed as indicator electrode. However the platinum is a redox electrode. The measured potential is a mixed potential which depends on all the redox couples (i.e. $Mn^{2+}/Mn(OH)^{2+}$, I_2/I^-, HIO_2/HOI, etc.) existing in the solution. Therefore it is not possible to follow the concentration of a single species in time with a platinum electrode.

On the other hand the potential of a iodide ion selective electrode depends on the iodide ion concentration or activity, respectively. This depedence is given by the Nernst-equation (eq. 4). The main difference between the spectroscopic, conductometric methods and the potentiometric method is that the transfer function of the electrochemical sensor is not linear, but logarithmic.

Hence, by employing an iodide ion selective electrode for monitoring the BR reaction, it is possible to follow the concentration changes of the iodide ion. The knowledge of iodide ion concentration is of great interest, because the BR reaction is a iodide ion controlled oscillator.

$$\varepsilon_{I^-} = \varepsilon^0 + \frac{RT}{zF}\ln a_{I^-} = \varepsilon^{01} + \frac{RT}{zF}\ln c_{I^-} \qquad \text{(eq.4)}$$

where: - ε_{I^-} is the potential of the ionselective electrode,

- a_{I^-} is the activity and c_{I^-} is the concentration of iodide ion, respectively,
- ε^0 standard potential,
- ε^{01} standard formal potential.

The logarithm of the iodide ion concentration was explicited Nernst equation for the initial conditions t=0 and t=t (equations 7-8). Then by substituting these equations in the integrated rate law of a first order reaction and after performing the algebraic operations, we got the equation 9 [16].

$$E = \varepsilon_{I^-} - \varepsilon_{ref} \qquad \text{(eq.5)}$$

$$\mathrm{E} = \varepsilon^{01} + \frac{RT}{zF}\ln c_{I^-} - \varepsilon_{ref} \qquad (eq.6)$$

$$\ln c_{I^-,0} = \frac{zF}{RT}(E_0 - \varepsilon^{01} + \varepsilon_{ref}) \qquad (eq.7)$$

$$\ln c_{I^-,t} = \frac{zF}{RT}(E_t - \varepsilon^{01} + \varepsilon_{ref}) \qquad (eq.8)$$

$$\mathrm{E_t} = \mathrm{E_0} \pm \frac{RT}{zF} \cdot k_{obs} \cdot t \qquad (eq.9)$$

This latter linear equation 9 describes the variation in time of the electromotive force of an ion selective electrode-reference electrode couple, when the ion concentation follows a (pseudo)-first order kinetics. The ± sign means that the equation 9 is applicable either for the consumption or for the formation of the given ionic species. The (pseudo)-first order rate constant can be determined from the slope (noted here with b) of the E−t plots:

$$k_{obs} = \frac{zF}{RT} \cdot b \qquad \text{(eq.10)}$$

It can be concluded that the electrode response linearizes the integrated exponential rate law corresponding to the pseudo-first order reactions. For the determination of the rate constant, only a simple linear regression and a multiplication are needed. Because of the fact that this method for determination of rate constant requires less mathematical operations (only a linear regression and a multiplication, respectively) than those presented in the previous section, the error propagation is also lower [18].

The rate constants are accessible also when the logarithm of the iodide ion concentration calculated from the potential and is plotted against the time. According to the conventional kinetics, the linear segment on this plot also indicates that the iodide ion is involved in pseudo-first order steps within one period os oscillations. However for the calculation of the iodide ion concentration the knowledge of the standard formal potential (ε^{01}) is needed (eq. 9). Nevertheless this potential may change in long term measurements [26] or due to the corroding effect of the highly reactive iodide containing intermediates [27]. In such cases frequent calibration is recommended [26]. Otherwise due to the potential drifting phenomenon, the calculated concentrations will be also shifted severly (by one order of magnitude per 59 mV of potential drift).

The drifting phenomenon can also be observed in the present study: during the measurement series the potential interval of the first three non-inhibited oscillations were shifted gradually from 0,27 − 0,55 V to -0,025 − 0,25V (Figure 2 and 3). Nevertheless, the amplitudes of the first three non-inhibited oscillations are satisfactorily reproducible within the measurement series (Figure 4). This suggests that the sensitivity of the electrode did not change; only the standard formal potential of the iodide ion selective electrode and/or the potential of the reference electrode (ε_{ref}) were drifting.

However if the rate constant is determined directly from the E-t plots according to the equation 9, neither the knowledge of the standard formal potential of the iodide ion selective electrode, nor the potential of the reference electrode is required. Since the sensitivity of the iodide ion selective electrode was found to be satisfactorily constant, we took the advantage of determining the rate constants according to the equation 9.

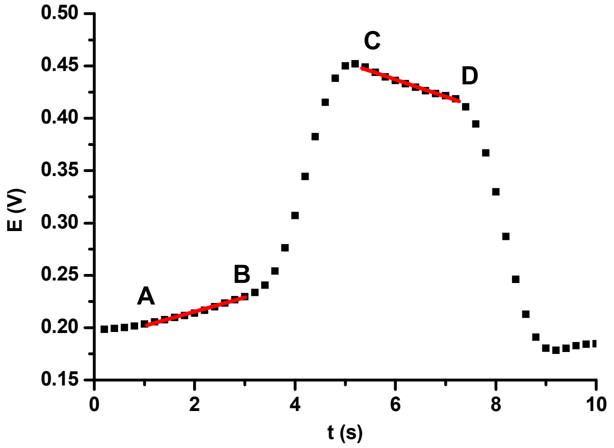

Figure 6. The variation of the electromotive force (E) during a single uninhibited oscillation.

Upon analyzing the shape of a single uninhibited oscillation, two relatively long linear segments can be observed (Figure 6). The AB segment with positive slope represents the iodide ion formation step. At the beginning of this segment the color of the mixture was brown due to the iodine. During the AB segment the brown color faded out gradually, the iodine was reacting with the enolic form of the organic substrate. The length of this segment was about 4,0 second, which represents 32-35% of the period time of the first oscillations. In order to determine the rate constant of iodine ion formation, a straight line was fitted to the most linear portion of the AB segment. The slope of the straight line was found to be 0,0132 ± 0,0006 V/s. The calculation of apparent rate constant and its standard deviation was done according to equation 11 and 12.

The potential increased rapidly between the B and C points, due to rapid reaction steps that are also producing iodide ions.

The decreasing CD segment represents the steps involving the consumption of the iodide ion.

$$k_{obs} = 0{,}01315 \cdot \frac{zF}{RT} = \frac{0{,}01315}{0{,}0257} = 0{,}51\,s^{-1} \qquad (eq.11)$$

$$\sigma_{kobs} = \sigma_b \cdot \frac{zF}{RT} = \frac{0{,}0006}{0{,}0257} = 0{,}02 s^{-1} \qquad (eq.12)$$

During the whole CD segment the mixture remained colorless. The length of this segment was about 2,0 seconds, which corresponds to approximately 16-18% of the period time. Linear fitting gave a slope of -0,01638±0,0006 V/s, therefore the apparent rate constant of iodide ion consumption was found to be k_{obs} = 0,64±0,02 s^{-1}.

After the CD segment the potential suddenly decreased due to fast reaction steps. The color of the mixture changed into brown and the cycle started again.

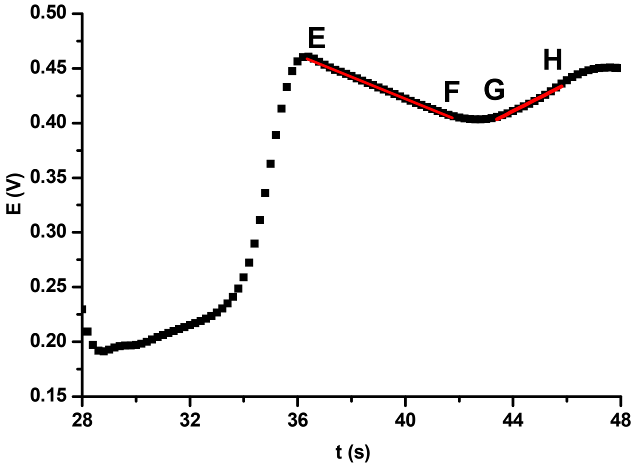

Figure 7. The segment where iodide ion is produced and consumed, respectively, in presence of 0,85 mM salicylic acid.

In the case of the inhibited reaction, the length of the straight line EF (see Figure 7) corresponding to the iodide ion consumption is increased significantly compared to the non-inhibited reaction. However the slope is smaller, consequently the observed rate constant of iodide ion consumption is also lower. Due to the fact that the shape of the oscillations in the attenuation period are different compared to the non-inhibited oscillations, the GH segment seems not to correspond to the AB segment of the first three non-inhibited oscillations.

The apparent rate constants corresponding to the iodide ion consumption and formation in the EF and GH portions are k_{obs} = 0,39±0,02 s^{-1} and k_{obs} = 0,41±0,02 s^{-1}, respectively.

The apparent rate constants of iodide ion formation and consumption corresponding to the successive periods of oscillations were represented in the Figure 8. It can be observed that after addition of the salicylic acid, the rate constant of iodide ion consumption is significantly reduced. Moreover, the rate constants decay in the successive periods until the oscillations are ceased. During the inhibitory time the potential is constant, therefore the concentration of iodide ions is also constant.

The salicylic acid also decreases progressively the rate constant of iodide ion formation in the attenuation period (Figure 8). The progressive decay of the iodide ion formation and consumption after salicylic acid addition suggests that this substance presents an inhibitory effect also during the attenuation period.

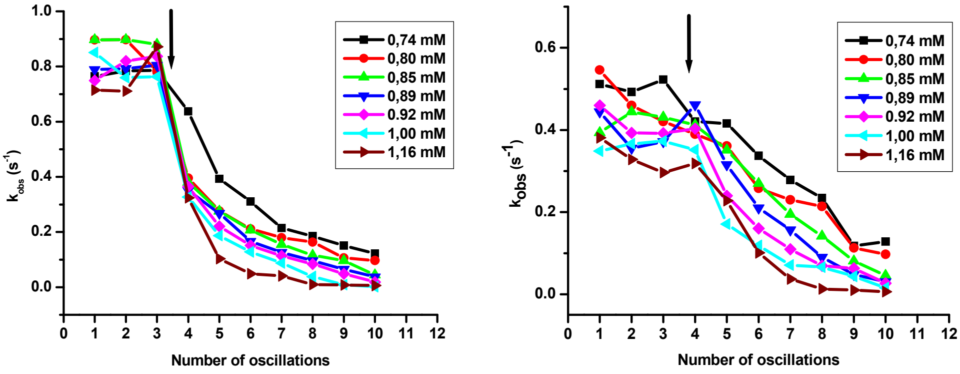

Figure 8. The effect of salicylic acid concentration on the apparent rate constants of iodide ion formation (top) and consumption (bottom) in the successive periods. The arrow indicated the addition of salicylic acid solution.

Up to our knowledge, the salicylic acid was the first organic compond reported which presents unusual inhibitory effect on the BR reaction operated in batch mode. The fact that this compound does not stop immediately the oscillations suggests that it is not a strong hydroperoxyl radical quencher. The antioxidant activity of salicylic acid determined by the TEAC method was found to be 0,04±0,01. This low value was explained by the steric hindrance and the electron withdrawing effect of the carboxylic group in the orto-position with respect to the hydroxyl-group [28].

However in presence of salicylic acid the oscillations are stopped after some time. A possible explanation is that some compound is formed in the reaction mixture, which is a more effective inhibitor of the BR reaction. The salicylic acid has been reported to be an effective hydroxyl radical quencher (spin trap). The hydroxyl radical is also an intermediate of the BR-reaction [2-4].

Upon hydroxylation of salicylic acid 2,3- and 2,5-dihydroxybenzoic acid isomers, catechol and hydroquinone are formed [29-31]. On the other hand, the dihydroxybenzoic acid isomers and catechol present a high antioxidant activity, i.e. they inhibit strongly the BR reaction even in micromolar concentration [9] (Table1).

Table 1. Comparison of the antioxidant activity of some polyphenols. Data collected from (a) Rice-Evans et al. [28], (b) Cervellati et al., relative antioxidant activity with respect to the slopes of the calibration graph, using resorcinol as stadard [9], and (c) this work. n.a.-data not available.

Compound	TEAC antioxidant Activity (a)	BR antioxidant Activity (b)
2-hydroxy-benzoic-acid	0,04±0,01	Unusual, low (c)
2,3-dihydroxy-benzoic-acid	1,46±0,01	n.a.
2,5-dihydroxy-benzoic-acid	1,04±0,03	0,092±0,003
o-catechol	n.a.	5,30±0,40

We did not find kinetic data concerning the hydroxylation of salicylic acid, but the cited literature data suggests that it is a relatively slow radical substitution reaction. The reaction time for the formation of well detectable amount of hydroxylated products spans from 30 seconds to 15 minutes, depending of the method of hydroxyl radical generation and the temperature. This would explain the observed attenuation period and the gradual decrease in the iodide formation and consumption rate constants as well.

It is also notable, that we also checked the effect of 4-sulfosalicylic acid on the BR-reaction. This derivative of the salicylic acid did not stop the oscillations, nor changed the amplitudes of the oscillations below 10 mM concentration. At a concentration of 20 mM the amplitudes were still unaffected, only the period time was slightly increased from 11-13 to about 14-15 seconds.

CONCLUSIONS

We studied the effect of salicylic acid on the Briggs-Rauscher oscillating reaction. This compound does not stop immediately the oscillations, in contrast to the other mono-and polyphenolic compounds which are effective inhibitors already in the micromolar concentration interval.

If the concentration of salicylic acid in the BR-mixture is lower than 0,69 mM, the oscillations are not stopped at all, only the amplitudes are reduced. However after a few periods of oscillations the amplitudes are increasing.

Added in higher concentration than 0.69 mM in the BR mixture, salicylic acid decreases the amplitudes gradually untill the oscillations are stopped. We denominated the time elapsed between the addition of salicylic acid and the cessation of the oscillations as attenuation time. The attenuation time decreases linearly, the inhibition time increases linearly over a relatively narrow concentration of salicylic acid. However the period time is not affected by the presence of salicylic acid.

For the kinetic study the reaction was monitored by iodide ion selective electrode coupled to a reference electrode. We assumed that the iodide ion concentration follows pseudo-first order kinetics over a given time within one period of oscillations. We derived the equation that corresponds to the case when a first order reaction is followed by a sensor with nernstian transfer function. Based on this equation we validated the assumption concerning the reaction order of iodide ion formation and consumption. The rate constants were found to be decreased gradually from period to period in presence of salicylic acid, similarly to the decay of the amplitudes of the oscillations. This fact suggested that the studied compound manifests a weak inhibitory effect in the attenuation period as well. However the inhibitory effect enhances with the concentration and the reaction time as well, until the oscillations are stopped temporarily. These observations lead to a hypothesis that after adding the salicylic acid in the BR mixture, some compound is formed which is a better inhibitor of the oscillations. Since the hydroxyl radical is also an intermediate of the BR-reaction, it was plausible to suppose that the salicylic acid is hydroxylated to dihydroxybenzoic acid isomers. These latter compounds were reported to be efficient inhibitors of the BR-reaction. However the hypothesis is yet to be proven.

EXPERIMENTAL SECTION

The following stock solutions have been prepared according to the procedure described earlier [14-16]. The stock solutions and the double-walled glass reactor were thermostated to 25,0±0,1 °C. Mixing of the stock solutions gave an oscillatory mixture with the following initial concentrations: $[H_2O_2]_0=9{,}20\cdot10^{-1}$ M, $[\text{malonic acid}]_0=5{,}00\cdot10^{-2}$ M, $[H_2SO_4]_0=2{,}50\cdot10^{-2}$ M, $[MnSO_4]_0=6{,}50\cdot10^{-3}$ M, $[KIO_3]_0= 6{,}75\cdot10^{-2}$ M. After the minimum of the third oscillation a given volume of the sodium salicilate was added to the reaction mixture using a Labsystems Finnpipette micropipette. Since the pH of the BR-mixture is sufficiently low (around 1,7), the salicilate ion was protonated quantitatively to salicylic acid.

The BR-reaction was monitored potentiometrically using an iodide ion selective electrode (Radelkis, Budapest) and a double junction saturated calomel reference electrode (Chemical Institute, Cluj-Napoca). For comparison a few experiments were performed using the iodide ion selective electrode and a bright platinum electrode simultaneously. A double junction calomel electrode was chosen as a reference electrode, because the conventional single junction electrodes contain saturated potassium-chloride electrolyte. When a single junction reference electrode is immersed into a solution, chloride ions diffuse out through the fritt of the electrode in the solution. The contamination rate is approximately $0{,}2\cdot10^{-3}$ M/min [26]. Because of the fact that already traces of chloride ions inhibit the BR-reaction; any contamination with chloride ions must be avoided. For this purpose we used a double junction saturated calomel electrode, which contained 1,0 M KNO_3 electrolyte in the outer compartment.

The variation in time of the potential of the iodide ion selective electrode versus the reference electrode was recorded using a computer equipped with a National Instruments® data acquisition card. The acquisition frequency has been set to 5 s^{-1}.

ACKNOWLEDGMENTS

The author acknowledges the scholarship awarded by the PROFIL Group for the Cluj-Szeged Student Exchange Program to the University of Szeged, Hungary, Faculty of Natural Sciences. The author thanks Prof. Dr. I. C. Popescu (Dept. of Physical Chemistry, Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University) for the iodide selective electrode.

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