STUDIA UBB CHEMIA, LX, 2, Tom I, 2015 (p. 187-199)
(RECOMMENDED CITATION)

IS STARCH ONLY A VISUAL INDICATOR FOR IODINE IN THE BRIGGS-RAUSCHER OSCILLATING REACTION?

LÉNÁRD-ISTVÁN CSEPEI[a,b,*], CSABA BOLLA[a]

ABSTRACT. In this work we studied the effect of malonic acid concentration on the Briggs-Rauscher oscillating reaction both in absence and in presence of starch, which acts as indicator for the iodine intermediate. For the starch free mixtures, the number of oscillations and the oscillation time increased with the increase of initial malonic acid concentration, while the period time showed the opposite trend. When starch was also present in the Briggs-Rauscher mixture, the number of oscillations, the oscillation time and period length were higher in comparison with the starch free mixtures with the same initial malonic acid concentration. In presence of starch, within one oscillation period, the iodine consumption segment was also longer compared to those measured for the starch free mixtures. This suggests that the starch is not only a simple visual indicator for the iodine intermediate, but it probably acts as a reservoir for iodine due to the starch-triiodide equilibrium during each oscillation cycle. As such, the starch may influence the kinetics of the reaction steps involving the iodine intermediate. Finally, we present a simple method for the treatment of the residual Briggs-Rauscher mixture which enables the removal of the strong acid, the oxidizing agents and the quantitative recovery of the Mn^{2+} catalyst in form of MnO_2. Thereby, this method enables to minimize the environmental effect of the residual mixture before disposing it.

***Keywords**: Briggs-Rauscher oscillating reaction, malonic acid, iodine, starch, indicator, starch-triiodide complex, oscillation time, period time, apparent activation energy, nonlinear chemical dynamics, environmental awareness*

INTRODUCTION

The Briggs-Rauscher reaction is a prominent example of the liquid phase oscillating reactions. Although it was discovered more than four decades

---

[a] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Arany János Str., Nr. 11, RO-400084 Cluj-Napoca, Romania.*
[b] *Current adress: Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB, Bio-, Electro- and Chemocatalysis BioCat, Straubing Branch, Schulgasse 11a, 94315 Straubing, Germany.*
** Corresponding author: cslenard@gmail.com*

ago [1], an intensified interest towards this reaction could be observed since the early 2000s.

The net chemical reaction is the iodination of an organic substrate by iodate ion and hydrogen peroxide, catalyzed by Mn^{2+} ion in acidic media [2, 3, 4]. In the first years after its discovery, thirty elementary steps were identified [3, 4] and it was found that a set of thirteen steps - known as skeleton mechanism - describes qualitatively well the nonlinear behavior of the reaction [5, 6]. This mechanism was further refined over the past one and a half decade [7-11].

The intermediates of the reaction (e.g. I_2, I^-, HOI, HIO_2, $IO_2\cdot$, $HOO\cdot$) show more than one extreme point – maximum and minimum – in time. The periodic changes of the iodine concentration can be seen visually: during the reaction colorless-brown-pale yellowish-colorless cycles can be observed. A few reports described that in presence of starch indicator the oscillations of iodine concentration are more visible because of the formation of the starch-triiodide complex: the color of the reacting mixture changes within one period from colorless to deep blue then to brownish and colorless again [1, 12, 13, 14, 15, 16, 17]. In some of these studies spectroscopic methods were applied to learn more details about the involvement of the iodine or starch-triiodide complex in the BR-reaction [15, 16]. Nevertheless, besides the more dramatic color change, no other differences were documented between the oscillations of the starch containing and starch free BR mixtures in the above literature sources.

It is also interesting to mention that the inorganic subset of the Briggs-Rauscher reaction is very similar to the well studied Bray-Liebhafsky oscillating reaction. The Bray-Liebhafsky reaction involves only hydrogen-peroxide, iodate ions and mineral acid. Although the iodine is an intermediate also in this chemical oscillator, up to our best knowledge the effect of starch was not studied yet on the Bray-Liebhafsky reaction.

In our previous studies we also used starch for qualitative observations concerning the iodine formation and consumption upon addition of several substances (ascorbic acid, tartaric acid, pyrogallol and salicylic acid) to the oscillating Briggs-Rauscher mixture [18, 19]. During these experiments, however, we have already noticed some quantitative differences between the oscillations of a starch free and starch containing mixture. As it is known that some organic compounds (such as ascorbic acid and other hydroxyl-group containing organics) interfere strongly with starch-iodine reaction [20], based on our experiments reported in [18, 19] it was not possible to establish what the reason for the observed differences was. These observations triggered a more systematic study on the effect of starch on the reaction [21]. We also varied the malonic acid concentration, because the iodine consumption rate within one oscillation depends on the malonic acid concentration [13]. Therefore, our goal was also to check the complex interrelation between malonic acid, iodine and starch in this reaction. In the present work we report the phenomenological effect of starch on the oscillation parameters of Briggs-Rauscher reaction studied at different malonic acid concentrations. In the following paper we will report the effect of starch on the kinetics of iodine consumption within one period of oscillation.

RESULTS AND DISCUSSION

In the first series of experiment the initial concentration of malonic acid was varied from 0,031 to 0,199 M while keeping constant the initial concentration of potassium-iodate (0,0675 M), hydrogen peroxide (0,92 M), manganous sulfate (0,0065 M) and sulfuric acid (0,025 M) in absence of starch indicator. During the second series of measurement 0,48 mg/ml starch indicator was added, while keeping the other conditions the same as at the first series of runs. All these experiments were carried out at a temperature of 25ºC. Under every condition, the experiment was repeated typically three times in order to check for the reproducibility of the observed effects. More than that, the quantitative oscillating parameters were statistically analyzed.

The Figure 1 displays the reproducibility test at the lowest malonic acid concentration: three runs of the BR reaction recorded after each other using the same initial composition, in absence of starch. The reproducibility demonstrated on Figure 1 was typical also for measurements under every other condition.

The stock solutions A and B were mixed in the reactor; then the malonic acid and manganese sulfate containing solution C was injected by a rapid delivery piston pipette at the time indicated by the green arrow on Figure 1 (for the composition of the stock solutions A, B and C see the Experimental section).

The oscillation started immediately, without induction period after the injection of the solution C. However, the very first oscillation appearing right after the injection of the solution C was a first, incomplete oscillation, since it did not exhibit a minimum like the subsequent ones. In our previous studies [18, 19, 22, 23] we started to record the potential a few seconds after the mixing of all the three solutions, therefore the first, incomplete oscillation was not observable. After the first, incomplete oscillation there were regular oscillations, i.e. those three in the middle of the Figure 1, possessing well defined minima, maxima and similar shape. The very last oscillation was much broader and had significantly lower amplitude than the regular ones. However, when the malonic acid concentration was higher than 0,075 M, the last oscillation was also regular.

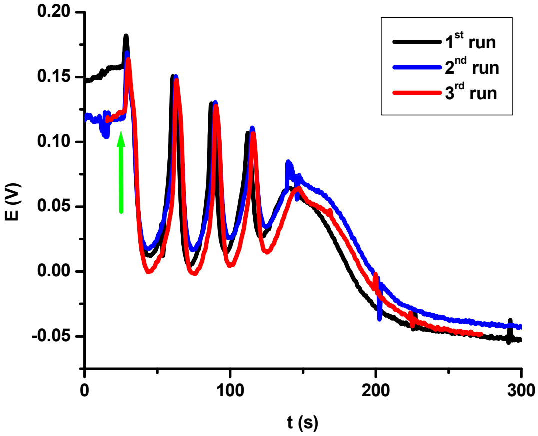

Figure 1. Reproducibility test of the oscillations in a starch free BR-mixture. The malonic acid concentration was 0,031 M.

The following oscillating parameters are considered here:

1) oscillation time (s): the time elapsed from the maximum of the first, incomplete oscillation until the minimum of the last regular oscillation. At malonic acid concentrations higher than 0,075 M the last oscillation was also included in the length of the oscillation time
2) period time (s): the time elapsed between two consecutive oscillatory maxima,
3) amplitude (V): the potential difference between a maximum and minimum,
4) number of oscillations: only the regular oscillations were counted. The last broad oscillation observed at low malonic acid concentrations and the „two-third oscillation” were not taken into account.

As the Figure 1 demonstrates, the peak shapes and parameters are well reproducible. The high frequency potential fluctuations with minor amplitude appeared due to electric noise in the electronic recording system.

Qualitative comparison of the oscillations of starch free and starch containing BR-mixtures

In the followings, the qualitative features of the BR reaction are compared in absence and in presence of starch while keeping constant the initial concentrations of malonic acid, hydrogen peroxide, sulfuric acid and iodate-, manganous ion (Figure 2). It is notable that in presence of starch, the number of oscillations and the oscillation time is much higher than in the starch free mixture. On the other hand, the period times are visibly longer and the amplitudes throughout the reaction are more uniform when starch is present in the reacting mixture.

As described earlier, one period of oscillation on the E(V) versus time plot consists of four distinct segments [19, 25]: two decreasing segments and two increasing segments with different slopes and lengths. The color changes of the oscillating mixture during one period are described below:

In the starch free mixture, brown coloration appeared during the steep decreasing segment, which indicates iodine formation. During the slightly increasing slope the brown color faded out gradually to pale yellow, indicating relatively slow reaction between iodine and the enolic form of the malonic acid. During the rapidly increasing segment, the mixture became transparent and remained transparent during the relatively slowly decreasing segment. Then the cycle repeated. After the last oscillation, the color of the mixture became deep brown, indicating strong iodine formation and accumulation.

In the starch containing mixture the color turned into deep blue during the fast decreasing segment and it faded out to slightly brownish during the slow increasing slope. During the fast increasing and the relatively slowly decreasing segment the mixture was colorless. At the end of the oscillations the mixture was deep blue because of the formed iodine.

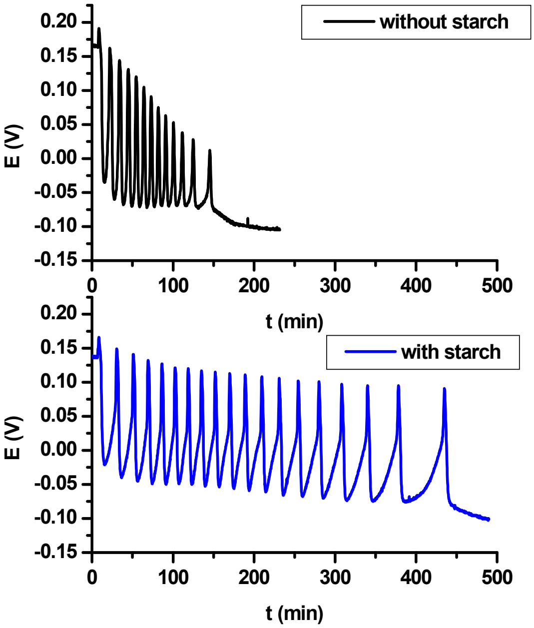

Figure 2. The oscillations recorded in a BR mixture containing 0,131 M malonic acid. The starch concentration: black – 0,00 mg/ml, blue – 0,48 mg/ml.

Quantitative comparison of the oscillations of starch free and starch containing BR-mixtures

The effect of malonic acid concentration on the quantitative parameters listed above is presented here.

First, the number of oscillations was plotted versus the initial malonic acid concentration for both the starch free and starch containing mixtures. A linear increase can be observed in each case (Figure 3, top). In presence of starch, the number of oscillations was approximately two times higher than in the case of starch free mixtures.

The oscillation time increased approximately linearly with the malonic acid concentration for the starch free mixture and apparently exponentially for the starch containing mixture (Figure 3, bottom).

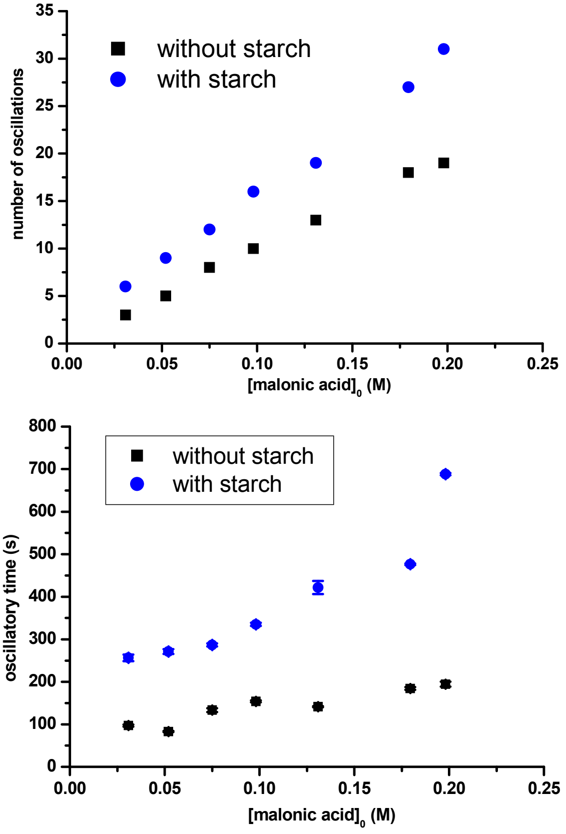

Figure 3. The effect of malonic acid concentration on the number of oscillations and the oscillation time.

In general, the length of the iodine consumption segment (which was evaluated by measuring the lenght of the slowly increasing segment after the potential minimum) was dominant within one cycle of oscillation. This observation is in agreement with the observation of Furrow [13]. In the case of starch free mixture, the iodine consumption segment was 38-45% of the period time. On the other hand, in presence of starch, the iodine consumption constitutes 48-60% of the period time.

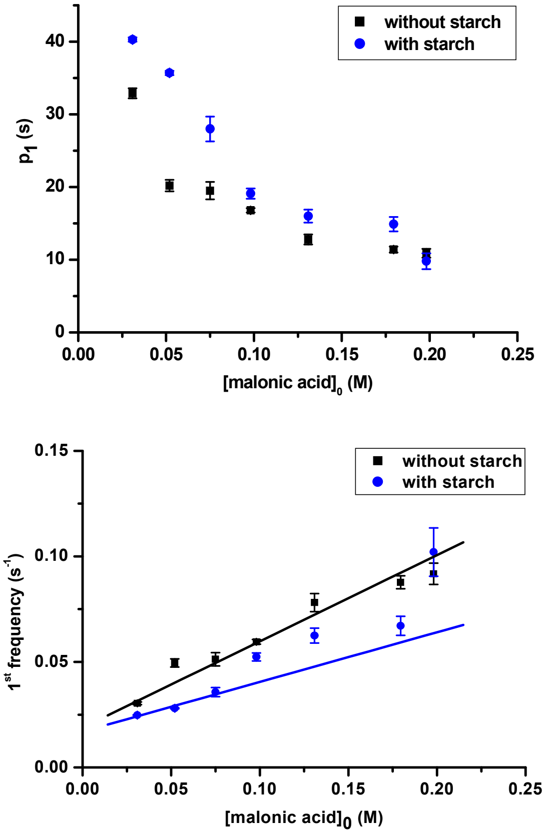

Figure 4. The effect of malonic acid concentration on the first period time and frequency, respectively.

The period time was decreasing with the increase of the malonic acid concentration. This trend was the same for both the starch free and starch containing mixture. However, in the starch containing the period times were higher (Figure 4, top).

Table 1. The dependence of the frequency (f) of the first oscillation on the initial malonic acid concentration.

c_{starch} (mg/mL)	Equation	R^2
0,00	$f = 0{,}02+0{,}41\cdot[\text{malonic acid}]_0$	0,9835
0,48	$f = 0{,}02+0{,}19\cdot[\text{malonic acid}]_0$	0,9090

Similarly to the observation of Furrow, the reciprocal period time (that is equal to the frequency) increases approximately linearly with the substrate concentration [13]. This linear dependence is given on Figure 4 bottom, while the equations of the straight lines are in the Table 1.

Finally, no trend was found between the amplitude of the first three oscillations and the initial concentration of the malonic acid, irrespectively whether starch was present or absent in the mixture.

Determination of the apparent activation energy for the starch containing BR-mixture

In the third series of measurements the reaction temperature was varied between 26 and 52ºC for a BR mixture with 0,199 M malonic acid and 0,48 mg/ml starch. The apparent activation energies were evaluated.

The apparent activation parameters of the BR reaction are usually determined from the temperature dependence of the oscillation time [26, 27] and the period time [12, 25]. In the literature it was noted that both of these quantities decrease exponentially with the temperature. The dimension of the reciprocal oscillation time and period time is the same as the dimension of a first-order rate constant (second^{-1}).

The Arrhenius plot of the reciprocal oscillation time and period time, respectively lead to straight lines (Figure 5 and 6). From the slope of these lines the apparent activation energy of the reaction was calculated corresponding to the starch containing mixture. The values are compiled in Table 2, among the apparent activation energies reported in the literature. Due to the fact that the reaction mechanism is very complex – it consists of at least 30 elementary steps in absence of starch – the determined activation energy does not correspond to any of the elementary steps of the BR reaction, but it is „global” or apparent activation energy. In the presence of starch, there is at least one additional equilibrium reaction corresponding to the formation of the starch-triiodide complex. Therefore, due to the above described complexity, it is very difficult to draw conclusions on the effect of starch on the apparent activation energy.

On the other hand, because the reaction mechanism is so complex and the compositions of the BR mixtures reported in the literature are different (Table 2), the apparent activation energies are not comparable directly [27].

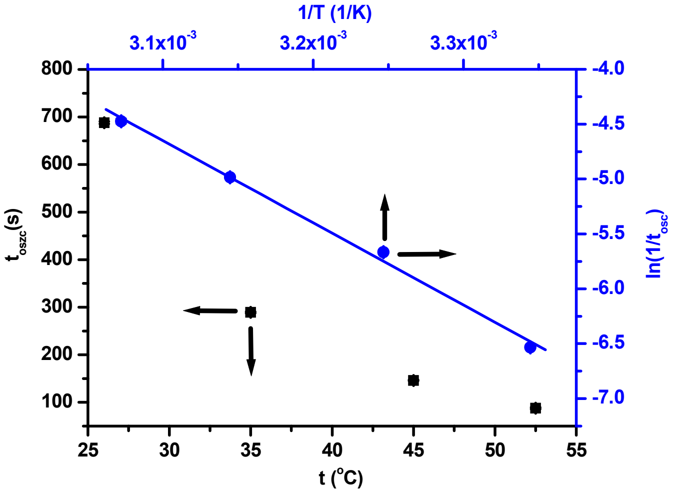

Figure 5. The effect of temperature on the oscillation time (black squares) and the corresponding Arrhenius-plot (blue dots). The malonic acid and starch concentration was 0,199 M and 0,48 mg/ml, respectively.

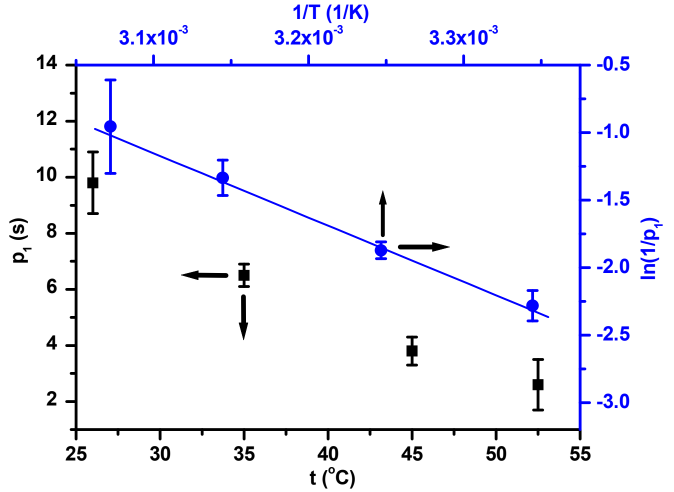

Figure 6. The effect of temperature on the first period time (black squares) and the corresponding Arrhenius-plot (blue dots). The malonic acid and starch concentration was 0,199 M and 0,48 mg/ml, respectively.

Table 2. The apparent activation energy of BR mixtures with different compositions. Ea (I.) – activation energy determined from the temperature dependence of the oscillation time. Ea (II.) – activation energy determined from the temperature dependence of the period time. (a) – this work, n.a. – data not available.

Ref. **Comp.**	**(a)**	**23**	**25**	**26**	**27**
$[H_2O_2]_0$ (M)	0,92	0,92	0,48	1,20	1,20
$[MA]_0$ (M)	$1{,}99\cdot10^{-1}$	$5{,}0\cdot10^{-2}$	$5{,}0\cdot10^{-2}$	$5{,}0\cdot10^{-2}$	$5{,}0\cdot10^{-2}$
$[KIO_3]_0$ (M)	$6{,}75\cdot10^{-2}$	$6{,}75\cdot10^{-2}$	$6{,}75\cdot10^{-2}$	$6{,}0\cdot10^{-2}$	$3{,}33\cdot10^{-2}$
$[H_2SO_4]_0$ (M)	$2{,}50\cdot10^{-2}$	$2{,}50\cdot10^{-2}$	$2{,}50\cdot10^{-2}$	$4{,}0\cdot10^{-2}$	$2{,}66\cdot10^{-2}$
$[MnSO_4]_0$ (M)	$6{,}50\cdot10^{-3}$	$6{,}50\cdot10^{-3}$	$6{,}50\cdot10^{-3}$	$6{,}0\cdot10^{-3}$	$6{,}67\cdot10^{-3}$
c_{starch} (mg/ml)	0,48	0,00	0,00	0,00	0,00
E_a(I.) (kJ/mol)	62±3	38±2	n.a.	57	68±2
E_a(II.) (kJ/mol)	42±1	51±1	61±7	n.a.	n.a.

CONCLUSIONS

The results of our experiments show that starch does not act only as a simple indicator of iodine intermediate in the oscillatory Briggs-Rauscher reaction. In the presence starch containing mixtures, the number of oscillations and also the period time of oscillations increased compared to the starch free mixture. Additionally, the reaction step involving the iodine and the malonic acid seems to be slowed down significantly in presence of starch in the reacting mixture. This may hint towards the fact the starch acts as a „reservoir" for iodine due to the starch-triiodide reaction, and it may change significantly the kinetics of the reaction steps in which the iodine (and in general, the triiodide anion) is involved. One of these steps is the iodination of the malonic acid, which produces the iodide ion. Another important step is the reaction of iodine with water which produces HOI, another key intermediate of the Briggs-Rauscher reaction. Last but not least, iodine may catalyze the decomposition of the diiodomalonic acid which accumulates gradually over the Briggs-Rauscher reaction [9]. Therefore, in presence of starch, the kinetics of the diiodomalonic acid decomposition step may also be slowed down.

EXPERIMENTAL SECTION

Two stock solutions were prepared according to the procedure described in our previous reports (solution A: 1,84 M hydrogen peroxide, and solution B: 0,27 M potassium iodate and 0,1 M sulfuric acid) [18, 19, 22, 23, 24]. The stock solution C contained 0,026 M manganese sulfate and different malonic acid concentrations (0,124, 0,208, 0,300, 0,392, 0,542, 0,720, 0,793 M). Starch solution was prepared by dissolution of starch in water at 60ºC and cooled down to room temperature. All chemicals were used without any further purification: H_2O_2 (Merck, p.a), KIO_3 (AnalytiCals, p.a), H_2SO_4 (Riedel de Haen, p.a), $CH_2(COOH)_2$ (Reachim, p.a), $MnSO_4$ (Reactivul, p.a), starch (Reactivul, p.a). Doubly distilled water was used for the preparation of all the solutions.

The stock solutions were mixed in a double walled glass reactor connected to a thermostat. After mixing, the composition of the BR reaction mixture was the following: $[H_2O_2]_0$=0,92 M, $[H_2SO_4]_0$=0,025 M, $[MnSO_4]_0$ = 0,0065 M, $[KIO_3]_0$ = 0,0675 M, whereas the concentration of malonic acid was 0,031; 0,052; 0,075; 0,098; 0,131; 0,180; 0,199 M. A magnetic stirrer and a submersible magnetic bar were used for the thorough stirring of the BR mixture. The reaction was monitored employing an iodide ion selective electrode (Radelkis, Budapest) and a double junction saturated calomel electrode as reference electrode. The variation of the potential in time has been registered using a computer eqipped with a National Instruments® data acquisition card. Then the E(V) vs time plots along with the further data analysis were made in Origin program.

The first series of measurements was carried out without addition of starch, while the second in presence of 0,48 mg/ml starch. Both measurement series were done at 25 ºC. The third series of measurement consisted of temperature variation in four steps between 26 and 52 ºC, using the following BR composition: $[H_2O_2]_0$ = 0,92 M, $[H_2SO_4]_0$ = 0,025 M, $[MnSO_4]_0$ = 0,0065 M, $[KIO_3]_0$ = 0,0675 M, $[\text{malonic acid}]_0$ = 0,199 M, and starch concentration of 0,48 mg/ml. Three measurements were carried out under every condition. The parameters (oscillation time, period time, number of oscillations, amplitude) were averaged over the three measurements, and the standard deviation was calculated. The standard deviation was used as weighting factor for linear regression.

We present here also the treatment method that we developed for decreasing significantly the environmental impact of the residual reaction mixture. The residual BR mixture contains always unreacted hydrogen peroxide, sulphuric acid, manganese- and iodate ions and sometimes significant amounts of iodine from the decomposition of iodo-malonic acid. Since all of these compounds are of environmental concern, all the residual BR-mixture was collected in a larger beaker and treated in the following way: first sodium-tiosulphate was added which transformed the iodine into iodide ion. The iodide ion reacted with the residual iodate ion and produced iodine. Therefore, the sodium-tiosulphate was added until the iodine formation completely ceased – this signaled that all the residual iodate ions were completely consumed from the mixture. Then sodium carbonate was added in order to reduce the acidity of the mixture. At slightly basic pH the Mn^{2+} ion was oxidized to MnO_2 by the dissolved O_2 (the oxygen being a product of the BR-reaction as well) [29].

$$2\,Mn^{2+} + 4HO^{-} + O_2 \rightarrow 2MnO_2 + 2H_2O \qquad (R1)$$

The formed MnO_2 decomposed catalytically the residual amounts of H_2O_2 to O_2 and H_2O. After sedimentation, the MnO_2 was separated by filtration. Therefore, by treating of the residual BR-mixture with two inexpensive chemicals such as sodium-tiosulphate and carbonate it was possible to remove all the strong oxidizing agents, the mineral acid and to recover quantitatively the heavy metal ion in form of MnO_2. At the end, the solution contained only sodium-, potassium-, iodide, sulphate- and residual tiosulphate ions which are environmentally much less harmful.

ACKNOWLEDGEMENT

L. I. Csepei 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. L.I. Csepei thanks Dr. G. Szabó for sharing part of her lab-equipments and for the valuable discussions; Prof. Dr. I.C. Popescu for the iodide ion selective electrode.

REFERENCES

1. T.S. Briggs, W.C. Rauscher, *J. Chem. Educ.*, **1973**, *50*, 496.
2. D.O. Cooke, *Int. J. Chem. Kinet.*, **1980**, *12*, 683.
3. S.D. Furrow, R.M. Noyes, *J. Am. Chem. Soc.*, **1982**, *104*, 38.
4. S.D. Furrow, R.M. Noyes, *J. Am. Chem. Soc.*, **1982**, *104,* 42.
5. S.D. Furrow, R.M. Noyes, *J. Am. Chem. Soc.*, **1982**, *104*, 45.
6. P. De Kepper, I.R. Epstein, *J. Am. Chem. Soc.*, **1982**, *104*, 49.
7. S.D. Furrow, R. Cervellati, G. Amadori, *J. Phys. Chem. A*, **2002**, *106*, 5841.
8. G. Szabo, A. Csavdari, L. Onel, G. Bourceanu, Z. Noszticzius, M. Wittmann, *J. Phys. Chem. A*, **2007**, *111*, 610.
9. R. Cervellati, E. Greco, S.D. Furrow, *J. Phys. Chem. A*, **2010**, *114*, 12888.
10. R. Cervellati, S.D. Furrow, *Russ. J. Phys. Chem. A*, **2013**, *87*, 13, 2121.
11. G. Holló, K. Kály-Kullai, T.B. Lawson, Z. Noszticzius, M. Wittmann, N. Muntean, S.D. Furrow, G. Schmitz, *J. Phys. Chem. A,* 2014, 118, 26, 4670.
12. A.K. Dutt, R.S. Banerjee, *Z. Phys. Chem. Leipzig*, **1982**, *263*, 2, 298-304.
13. S.D. Furrow, *J. Phys. Chem.*, **1995**, *99*, 11131.
14. R. Cervellati, S.D. Furrow, S. De Pompeis, *Int. J. Chem. Kinet.*, **2002**, *34* (6), 357.
15. M.J. Mahon, A.L. Smith, *J. Phys. Chem.*, **1985**, *89*, 1215.

16. B.Z. Chowdry, A.P. Mendham, J. Tetteh, R. Withnal, *ChemPhysChem*, **2002**, *5*, 443.
17. S.D. Furrow, *J. Chem. Ed.*, **2012**, *89*, 1421.
18. L.I. Csepei, A Briggs-Rauscher reakció oszcillációinak leállitása (The Cessation of the Oscillations of Briggs-Rauscher Reaction), Bachelor Diploma Thesis, Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, **2005**.
19. L.I. Csepei, Cs. Bolla, *Studia UBB Chemia*, **2009**, *54*, 4, II, 249.
20. S.S. Sharma, S. Sharma, V.K. Rai, *Annals of Botany*, **1990**, *65*, 281.
21. L.I. Csepei, Cs. Bolla, I. Pontos, The Effect of Malonic Acid Concentration on the Briggs-Rauscher Reaction in Presence and Absence of Starch, 13th International Conference of Chemistry, Hungarian Technical Scientific Society of Transylvania, Cluj-Napoca, 8-11 November **2007**.
22. L.I. Csepei, Inhibiţia reacţiei oscilante Briggs-Rauscher cu acid salicilic (Inhibition of Briggs-Rauscher Reaction with Salicylic Acid), Master Diploma Thesis, Thesis, Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, **2006**.
23. L.I. Csepei, A hőmérséklet hatása a Briggs-Rauscher reakcióra (The effect of Temperature upon the Briggs-Rauscher Oscillating Reaction), 8th Scientific Conference on Technical Sciences, 7-9 April **2006**.
24. L.I. Csepei, Cs. Bolla, *Studia UBB Chemia*, **2011**, *55*, I, 285.
25. I. Pontos, Bachelor Thesis, Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, **1999**.
26. R. Ramaswami, N. Ganapathisubramanian, *J. Chem. Educ.*, **1979**, *56*, 321-325.
27. R. Cervellati, K. Höner, S.D. Furrow, F. Mazzanati, S. Costa, *Helv.Chim. Acta*, **2004**, *87*, 133-155.
28. J.A. Thoma, D. French, The Starch-Iodine-Iodide Interaction. Part I. Spectrophotometric Investigations, *J. Am. Chem. Soc.*, **1960**, *82 (16)*, 4144-4147.
29. D. Harvey, Modern Analytical Chemistry, McGraw Hill, **2000**, 345-346.