

Bursting in the Belousov-Zhabotinsky Reaction Added with Phenol in a Batch Reactor

Ariel Cadena,^a Daniel Barragán^b and Jesús Ágreda^{*,a}

^aDepartamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Cra 30 No. 45-03, Bogotá, Colombia

^bEscuela de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Calle 59A No. 63-20, Oficina 16-413, Medellín, Colombia

A reação de Belousov-Zhabotinsky clássica foi modificada pela adição de fenol como um segundo substrato orgânico que compete cineticamente com o ácido malônico na redução de Ce^{4+} para Ce^{3+} e na remoção de bromo molecular da reação. A reação oscilante de dois substratos exibiu oscilações abruptas e período oscilatório de longa duração. A análise de dados experimentais mostra um aumento do fenômeno abrupto, com pico maior e estado quiescente mais longo, como função do aumento da concentração de fenol inicial. Hipotetizou-se que o fenômeno de oscilação abrupta pode ser explicado pela introdução de um ciclo redox entre as espécies fenólicas reduzidas (hidroxifenóis) e as oxidadas onas (quinonas). A hipótese foi testada experimentalmente e numericamente e dos resultados concluiu-se que o fenômeno oscilatório abrupto exibido pela reação oscilante de dois substratos é impulsionado principalmente por um ciclo redox *p*-di-hidroxi-benzeno/*p*-benzoquinona.

The classic Belousov-Zhabotinsky reaction was modified by adding phenol as a second organic substrate that kinetically competes with the malonic acid in the reduction of Ce^{4+} to Ce^{3+} and in the removal of molecular bromine of the reaction mixture. The oscillating reaction of two substrates exhibited burst firing and an oscillatory period of long duration. Analysis of experimental data shows an increasing of the bursting phenomenon, with a greater spiking in the burst firing and with a longer quiescent state, as a function of the initial phenol concentration increase. It was hypothesized that the bursting phenomenon can be explained introducing a redox cycle between the reduced phenolic species (hydroxyphenols) and the oxidized ones (quinones). The hypothesis was experimentally and numerically tested and from the results it is possible to conclude that the bursting phenomenon exhibited by the oscillating reaction of two substrates is mainly driven by a *p*-di-hydroxy-benzene/*p*-benzoquinone redox cycle.

Keywords: reaction kinetics, mechanisms, phenolic compounds, BZ reaction, bursting phenomenon

Introduction

The Belousov-Zhabotinsky (BZ) and uncatalyzed bromate oscillator (UBO) reactions have been studied in a wide of experimental conditions in both batch and continuous stirred tank (CSTR) reactors.¹⁻⁵ Complex dynamic behaviors in oscillating reactions have been found in non-stirred batch reactors and in CSTR and electrochemical setups.⁶⁻¹² These amazing reactions have become relevant in science, and particularly in biochemistry, due to their similarity with the dynamic activity of many cellular control processes.¹³

On the other hand, travelling waves, Turing patterns, burst firing, sequential oscillations and chaotic phenomena are some of the more common spatio-temporal dynamics studied in oscillating reactions.¹⁴⁻¹⁸ Looking for a better understanding of the reaction mechanism and dynamics of oscillating reactions, researchers have employed several substrates, individually or mixed, in the study of BZ reaction. The induction period, frequency, amplitude, shape and periodicity of oscillations change by the presence of a new organic or inorganic substance in the reaction mixture of BZ reaction.¹⁹⁻²⁹

In the present work, the oscillatory dynamics of the classic BZ reaction^{30,31} (a mixture of malonic acid, Ce^{4+} and

*e-mail: jaagredab@unal.edu.co

bromated in sulfuric acidic) were studied in a batch reactor in the presence of phenol as a second organic substrate that kinetically competes with the malonic acid in the reduction of Ce^{4+} to Ce^{3+} and in the removal of molecular bromine. With the two substrates (malonic acid-phenol), BZ reaction shows an astonishing variation of its dynamics as a function of the initial concentration of phenol, exhibiting enhanced periods of oscillations and bursting phenomenon. At first glance, the malonic acid-phenol BZ oscillator was thought as a system of coupled oscillators because the bromate-phenol-sulfuric acidic is a well-known oscillating chemical reaction (UBO). In order to test this idea of coupled oscillators, a set of numerical simulations by using an extended reaction mechanism based on the Marburg-Budapest-Missoula (MBM)³² and Gyorgyi, Varga, Körös, Field and Ruoff (GVKFR)³³ reaction schemes was carried out. The MBM mechanism for the cerium-catalyzed BZ reaction is a complete reaction scheme that includes both negative feedback loops and radical-radical recombination reactions of organic species.³² Whereas the GVKFR model is a mechanism to explain the oscillations observed in the *p*-hydroxyphenol-bromate-acidic media reaction,³³ the closer and complete mechanism available in the literature to UBO that uses phenol as organic substrate. As a result of these numerical simulations, some interesting behaviors were obtained, but there was nothing to indicate the possibility of burst firing.

In order to address the experimental evidence of that burst firing obtained in this work for the malonic acid-phenol BZ reaction, a second hypothesis is that the subproducts of phenol oxidation (hydroxyphenols-quinones) are involved in a novel redox cycle coupled to the main catalytic cycle of cerium ions. A series of experiments using 1,4-benzoquinone, 2-hydroxyphenol and 4-hydroxyphenol instead of phenol as a second organic substrate were carried out to test this hypothesis. The experimental results obtained by adding benzoquinone and hydroxyphenols to the BZ reaction suggest that the hypothesized hydroxyphenol-quinone redox cycle can be accepted as plausible. This hypothesis was materialized as a set of reaction steps, and they were incorporated into an extended MBM-GVKFR mechanism. The numerical simulation results of this new model (MBM-GVKFR-hydroxyphenols-quinones redox cycle) support the idea of the hydroxyphenols-quinones redox cycle.

Experimental

Sulfuric acid (Merck 95-98% extra pure), KBrO_3 (Carlo Erba Milano ACS Titolo min 99.8%), $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Merck zur Analyse > 98%), malonic

acid (Merck zur Synthese), phenol (JT Baker Chemicals B. V. "Baker Grade"), 2-hydroxyphenol (Fisher Scientific Company), 4-hydroxyphenol (Merck zur Synthese) and *p*-benzoquinone (Hopkin and Williams, LTD.) were used as received. All solutions were prepared in deionized water. The initial concentration of phenol used in the experiments were: a. 0.00, b. 0.05347, c. 0.1337, d. 0.2673, e. 0.5347, f. 1.069, g. 1.337, h. 1.604, i. 1.871, j. 2.272, k. 2.673, l. 3.074, m. 3.476, n. 3.877, o. 4.278, p. 4.679, q. 5.347, and r. 10.69 mmol L^{-1} . The initial concentrations of classic BZ reagents were: 28.90 mmol L^{-1} KBrO_3 , 26.06 mmol L^{-1} malonic acid, 0.5606 mmol L^{-1} $\text{Ce}(\text{SO}_4)_2$ and 1.00 mol L^{-1} H_2SO_4 . A thermostated (25.0 ± 0.1 °C) 100 mL double jacket cylindrical cell, with magnetic stirring at 500 rpm, was used to obtain the potentiometric measurements, using a platinum electrode Mettler-Toledo Pt4805-60-88TE-S7/120 combination ORP/Redox with Ag/AgCl reference (movable PTFE reference junction). All the experiments were made at least by duplicate.

Results and Discussion

The malonic acid-phenol BZ reaction exhibits a striking alteration of its temporal oscillatory dynamics as a function of the initial concentration of phenol. An enlargement of the oscillatory regime and the onset of bursting phenomenon are the more important observed effects by the addition of phenol to BZ reaction. The length of the induction time, the amplitude of sustained oscillations and the increasing of the total oscillatory reaction time are closely correlated with the initial concentration of phenol, and the burst firing appears when the malonic acid-phenol concentration ratio ranges between 25 and 6. Figure 1 shows the temporal redox potentiometric measurements of BZ reaction in the presence of an initial concentration of phenol (curves a to r). The BZ reaction (Figure 1 curve a) has an oscillatory reaction time of around 2 h, while at the same initial concentrations but in the presence of 3.074 mmol L^{-1} phenol (Figure 1 curve l), the oscillatory reaction time extends to almost 30 h.

Figure 1 also shows other highlighting features of this BZ oscillating reaction of two substrates. When the initial concentration of phenol is lower than 2.0 mmol L^{-1} (Figure 1 curves from a to i), the reaction mixture exhibits sustained oscillatory phase, and the period and the amplitude of the oscillations remain constant before a sudden ending. If the initial concentration of phenol, ranges between 2.0 and 10 mmol L^{-1} (Figure 1 curves j to q), the BZ reaction mixture shows a transition from sustained to damped oscillations during its temporal evolution. But the most astonishing observed effect of phenol on the dynamics

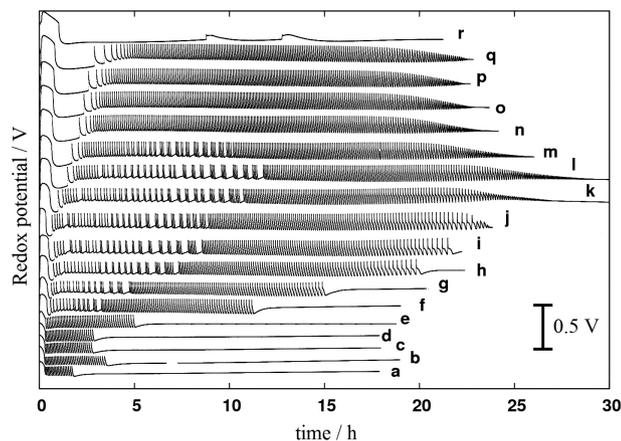


Figure 1. Redox potentiometric signal against time for the BZ oscillating reaction of two substrates. Initial concentrations for BZ reagents and initial concentration of phenol (curves a to r) are given in the experimental section.

of BZ reaction was the bursting phenomenon. If the initial concentration of phenol ranges between 1.069 and 3.476 mmol L⁻¹ (Figure 1 curves f to m), the reaction mixture exhibits a complex temporal transition from burst firing and sustained oscillations (ended suddenly), to still burst firing but damped oscillations. This means that the malonic acid-phenol BZ reaction in a batch reactor evolves in time through different attractors: period-*n* bursting attractor, limit cycle and stable focus.

In order to explain the experimental results showed in Figure 1, a new redox cycle is proposed: the Ce⁴⁺ oxidation of phenol to *p*-quinones^{34,37} followed by the reduction of *p*-quinones to phenolic compounds mediated by transient reactive organic free radicals in solution,³⁸ like carboxyl (COOH[•]) or tartronyl (TA[•]).^{31,32,39} If this aromatic redox cycle is plausible, then the Ce⁴⁺/Ce³⁺ catalytic cycle of BZ reaction is involved in a kinetic competition, the reduction of BrO₂[•] by Ce³⁺ or phenol. In a typical antioxidation action, common in phenols, the oxidation of Ce³⁺ is diminished, and because of this, the consumption of malonic acid is slower, whereas the phenol consumption is higher. These facts together increase the oscillation time of the BZ reaction of two substrates. Now, at low concentration of phenolic compounds, the Ce⁴⁺ concentration rises, and the Ce⁴⁺/Ce³⁺ catalytic cycle drives the BZ reaction while quinone type compounds are reduced to phenolic compounds by some reactive free radicals, like the carboxyl (COOH[•]) or the tartronyl (TA[•]) radicals. When the concentration of phenolic compounds increases, the aromatic cycle (phenol-quinone) restarts and drives the oscillating reaction. In this way, it is proposed that the two catalytic cycles alternate to drive the reaction until the oscillatory period ends. It is important to take into account that the polymerization of the quinones takes place at the reaction mixture conditions,

as it is well-known from the UBO chemical oscillator.^{33,34} The polymers of quinone are almost insoluble and their reduction by free radicals is not a viable process and we suppose that they are involved in the burst firing by way of a non-synchronized action between catalytic processes. It is also important to remark that at high enough concentration of phenol, the Ce⁴⁺ oxidation of phenolic compounds is a kinetically preferred process, instead of the Ce⁴⁺ oxidation of aliphatic species of the BZ reaction.⁴⁰

All the above ideas have the aim to help to understand, from a mechanistic point of view, the complex behavior exhibited by the malonic acid-phenol BZ oscillating reaction, and those ideas are summarized in the next way: at the beginning of reaction, the oxidation of phenol by Ce⁴⁺ is the kinetically favored process with a slow consumption of bromate and malonic acid; in this way, whereas the concentration of phenolic compounds is over a critical value, the aromatic catalytic cycle drives BZ oscillations; and when the phenol concentration is high enough, insoluble polymers of quinone are produced and an irregular oscillatory dynamic appears, the bursting phenomenon. At long times, the phenolic compounds are decreased in the reaction mixture, and a sequential train of sustained oscillations, driven by the consumption of malonic acid by the Ce⁴⁺/Ce³⁺ catalytic cycle, leads the oscillations to its end.

In order to get some experimental clues about the participation of phenol in the malonic acid BZ reaction, the classic experiment was tested in the presence of some key aromatic compounds, 2-hydroxyphenol, 4-hydroxyphenol and *p*-benzoquinone. The results are in Figure 2, in which curves c and e show that the BZ reaction of two substrates (malonic acid with *p*-benzoquinone and malonic acid with 4-hydroxyphenol, respectively) exhibits a dynamic behavior of a similar type that the malonic acid with phenol, curve b. On the contrary, the 2-hydroxyphenol, curve d, does not modify, to an appreciable extent, the malonic acid BZ reaction, curve a. The main result in Figure 2 is the evidence suggesting that the proposal, about the oxidation-reduction cycle, among phenol and quinone compounds, is capable to explain the experimental results. Also, it says that the main compound in the phenol-quinone process is a *para* compound and not an *ortho* compound, as could be inferred from UBO oscillators.³³

Numerical simulations

Numerical simulations were used as a tool to treat the fully nonlinear dynamics of the complex chemical BZ reaction and to test the validity of the previously presented hypothesis. The following set of reactions 1 to 9

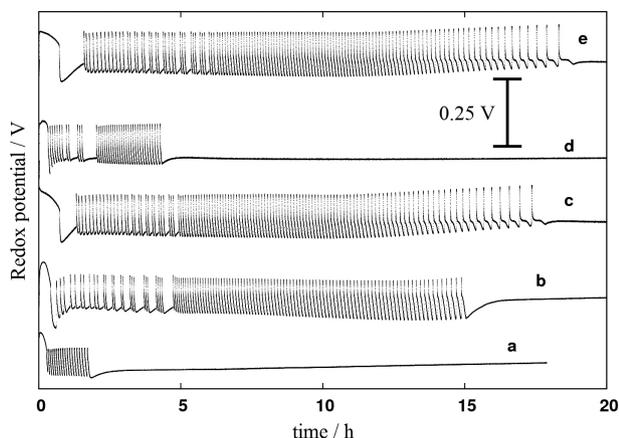
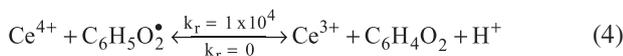
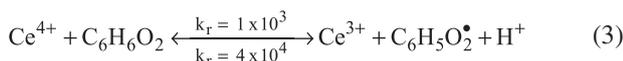
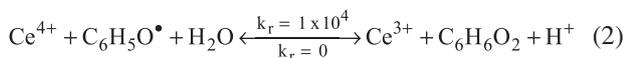
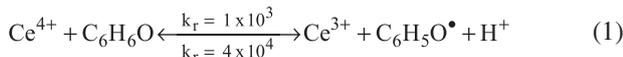


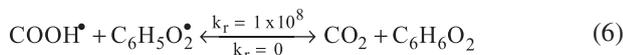
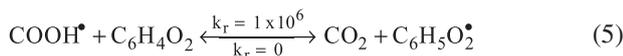
Figure 2. Redox potentiometric signal against time for the BZ oscillating reaction of two substrates. a: malonic acid alone, b: malonic acid with phenol, c: malonic acid with 1,4-benzoquinone, d: malonic acid with 2-hydroxyphenol, and e: malonic acid with 4-hydroxyphenol. The phenolic species were added in concentration of 1.3 mmol L^{-1} . The other concentrations were the same as in Figure 1.

was added to the complete set of reactions of MBM plus the GVKFR mechanisms (the complete set of reaction rates, kinetic constants and the fortran source code used for these simulations are presented in the Supplementary Information (SI) section).

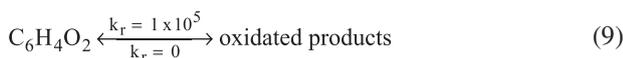
Phenol oxidation reactions:



Quinone reduction reactions:



Quinone consumption:



In these reactions, TA is for tartronic acid and MOA is for meso-oxalic acid.³⁰⁻³² The rate constants were estimated based on similar reactions of the MBM and GVKFR mechanisms. Reactions 1 to 4 describe a sequential electron

transfer for the Ce^{4+} and the resulting oxidation of phenol to the corresponding quinone. Reactions 5 to 8 indicate a plausible sequential reduction of quinone, by reactive organic free radicals, to phenolic like compounds. The selection of free radical species involved in reactions 5 to 8 was based on redox potentials. The carboxyl radical (COOH^\bullet) has a standard redox potential of -1.82 V vs. NHE .³⁸ On the other hand, the tartronyl radical (TA^\bullet) was chosen as a representative free radical that has been found in the BZ reaction (like the malonyl and bromomalonyl free radicals).³⁰⁻³² Finally, the reaction 9 describes the irreversible degradation or polymerization of quinones. Figure 3 shows the results obtained for simulations.

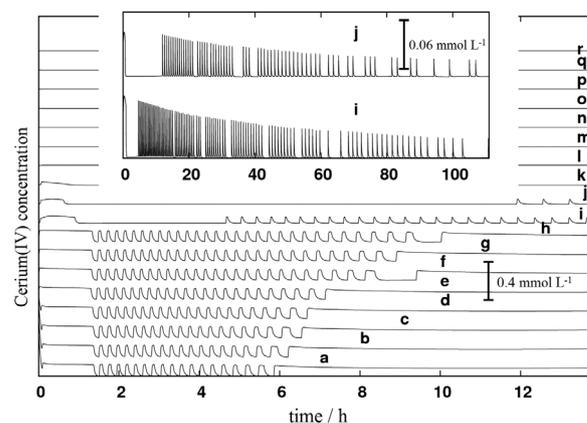


Figure 3. Numerical simulations of the two substrates, malonic acid and phenol, BZ reaction. Curves a to r are for the same initial concentrations used for Figure 1.

The numerical simulations have some of the experimental observed characteristics of the malonic acid-phenol BZ oscillating reaction, like an induction time enlargement and an increasing oscillatory reaction time as the initial phenol concentration increases. Also, the burst firing appears, and it is the most interesting result (inset in Figure 3). This qualitative agreement, between the experiments and the numerical simulations, is in favor of the hypothesized phenol-quinone redox cycle. However, it is necessary to confirm these ideas, in future works, by determining the experimental rate constant values, and by including, or deleting, some reactions. Also, a chromatographic and electron paramagnetic resonance (EPR) spectroscopy studies would be particularly useful to find the specific intermediaries.

Conclusions

The results presented in this work show the dynamic behavior of the malonic acid-phenol BZ reaction. It is interesting the appearance of bursting phenomenon in a

closed system. The burst firing origin was explained as a complex process that involves a kinetic competition between an aromatic redox cycle of phenolic compounds and the Ce^{4+}/Ce^{3+} catalytic cycle of the BZ classic oscillator. In this way, the presence of phenol in the malonic acid BZ reaction plays a role as an antioxidant agent preventing the oxidation of the malonic acid, and its derivatives, by Ce^{4+} ions.

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

Acknowledgment

This project has been supported by the DIB of the Universidad Nacional de Colombia under the code 803638.

Reference

1. Sagués, F.; Epstein, I. R.; *Dalton Trans.* **2003**, 7, 1201.
2. Báscangi, T.; Leda, M. Jr.; Toiya, M.; Zhabotinsky, A. M.; Epstein, I. R.; *J. Phys. Chem. A* **2009**, *113*, 5644.
3. Gentili, P. L.; Horvath, V.; Vanag, V. K.; Epstein, I. R.; *Int. J. Unconv. Comput.* **2012**, *8*, 177.
4. Adamciková, L.; Misičák, D.; Sevcik, P.; *React. Kinet. Catal. Lett.* **2005**, *85*, 215.
5. Szabo, E.; Adamciková, L.; Sevcik, P.; *J. Phys. Chem. A* **2011**, *115*, 6518.
6. Ruoff, P.; *J. Phys. Chem.* **1992**, *96*, 9104.
7. Grancicova, O.; Olexova, A.; *Z. Phys. Chem.* **2009**, *223*, 1451.
8. Rachwalska, M.; Kawczynski, A. L.; *J. Phys. Chem. A* **2001**, *105*, 7885.
9. Badola, P.; Rajani, P.; Ravi-Kumar, V.; Kulkarni, B. D.; *J. Phys. Chem.* **1991**, *9*, 2939.
10. Bronnikova, T. V.; Schaffer, W. M.; Olsen, L. F.; *J. Phys. Chem. B* **2001**, *105*, 310.
11. Kiss, I. Z.; Lv, Q.; Organ, L.; Hudson, J. L.; *Phys. Chem. Chem. Phys.* **2006**, *8*, 2707.
12. Simo, H.; Wofo, P.; *Mech. Res. Comm.* **2011**, *38*, 537.
13. Izhikevich, E. M.; *Int. J. Bifurcation Chaos* **2000**, *10*, 1171.
14. Lengyel, I.; Epstein, I. R.; *Acc. Chem. Res.* **1993**, *26*, 235.
15. Epstein, I. R.; Showalter, K.; *J. Phys. Chem.* **1996**, *100*, 13132.
16. Epstein, I. R.; Pojman, J. A.; *An Introduction to Nonlinear Chemical Dynamics*; Oxford University Press: New York, USA, 1998.
17. Rastogi, R. P.; *Introduction to Non-Equilibrium Physical Chemistry*; Elsevier: Amsterdam, The Netherlands, 2008.
18. Pojman, J. A.; Tran-Cong-Miyata, Q.; *Nonlinear Dynamics with Polymers*; Wiley-VCH Verlag: Weinheim, Germany, 2010.
19. Heilweil, E. J.; Henchman, M. J.; Epstein, I. R.; *J. Am. Chem. Soc.* **1979**, *101*, 3698.
20. Treindl, L.; Ruoff, P.; Kvernberg, P. O.; *J. Phys. Chem. A* **1997**, *101*, 4606.
21. Rastogi, R. P.; Chand, P.; Pandey, M. K.; Das, M.; *J. Phys. Chem. A* **2005**, *109*, 4562.
22. Shah, S.; Wang, J.; *J. Phys. Chem. C* **2007**, *111*, 10639.
23. Zeyer, K.-P.; Schneider, F. W.; *J. Phys. Chem. A* **1998**, *102*, 9702.
24. Chen, Y.; Wang, J.; *J. Phys. Chem. A* **2005**, *109*, 3950.
25. Amemiya, T.; Wang, J.; *J. Phys. Chem. A* **2010**, *114*, 13347.
26. Schwarz, H. A.; Dodson, R. W.; *J. Phys. Chem.* **1989**, *93*, 409.
27. Li, N.; Wang, J.; *J. Phys. Chem. A* **2008**, *112*, 6281.
28. Biossa, G.; Ristori, S.; Spalla, O.; Rustici, M.; Hauser, M. J. B.; *J. Phys. Chem. A* **2011**, *115*, 3227.
29. Asakura, K.; Konishi, R.; Nakatani, T.; Nakano, T.; Kamata, M.; *J. Phys. Chem. B* **2011**, *115*, 3959.
30. Gyorgyi, L.; Turányi, T.; Field, R. J.; *J. Phys. Chem.* **1990**, *94*, 7162.
31. Gyorgyi, L.; Turányi, T.; Field, R. J.; *J. Phys. Chem.* **1993**, *97*, 1931.
32. Hegedeus, L.; Wittman, M.; Noszticzius, Z.; Yan, S.; Sirimungkala, A.; Försterling, H. D.; Field, R. J.; *Faraday Discuss.* **2002**, *120*, 21.
33. Györgyi, L.; Varga, M.; Körös, E.; Field, R. J.; Ruoff, P.; *J. Phys. Chem.* **1989**, *93*, 2836.
34. Spence, W. R.; Duke, F. R.; *Anal. Chem.* **1954**, *26*, 919.
35. Dixon, W. T.; Murphy, D.; *J. Chem. Soc., Perkin Trans.* **1975**, *2*, 850.
36. Domagała, S.; Stegłńska, V.; Dziegieć, J.; *Monatsh. Chem. Chem. Mon.* **1998**, *129*, 761.
37. Simon, A.; Ballai, C.; Lente, G.; Fábíán, I.; *New J. Chem.* **2011**, *35*, 235.
38. Wardman, P.; *Reduction Potentials of One-Electron Couples Involving Free Radicals in Aqueous Solution*; American Chemical Society and the American Institute of Physics for the National Institute of Standards and Technology: USA, 1989, p. 1637.
39. Blagojevic, S. M.; Anic, S. R.; Cupic, Z. D.; *Russ. J. Phys. Chem. A* **2011**, *85*, 2274.
40. Singh, M. P.; Singh, H. S.; Verma, M.; *J. Phys. Chem.* **1980**, *84*, 256.

Submitted: July 27, 2013

Published online: October 16, 2013