TEMPERATURE AND OXYGEN EFFECT ON OSCILLATIONS OF THE BELOUSOV–ZHABOTINSKY REACTION WITH 2-OXOPENTANEDIOIC ACID AS SUBSTRATE

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The temperature dependence of the influence of oxygen on the Belousov–Zhabotinsky (BZ) system with a Ce(IV)–Ce(III) redox catalyst and 2-oxopentanedioic acid as substrate and on the autocatalytic oxidation of Ce(III) ions with bromate was studied in detail. The influence of temperature on the induction period, the period of the second oscillation, duration and number of oscillations, and finally on the average frequency of oscillations, was investigated both in oxygen and in nitrogen. The corresponding activation parameters have been determined and discussed. The most pregnant effect of oxygen is observed on the temperature dependence of the duration and the number of oscillations. The value for enthalpy of activation is more than 50 kJ mol^{-1} higher in oxygen than in nitrogen. The presence of oxygen may generate chaotic behaviour or multi-mode oscillations since in the presence of oxygen, new intermediates in the BZ system are formed, thereby increasing its complexity.

Key words: Oxygen and temperature effect; Belousov–Zhabotinsky oscillations; Autocatalytic oxidation; Ce(III) ions; Bromate; Ce(IV) ions; 2-Oxopentanedioic acid; Chaotic behaviour.

Even though the Belousov–Zhabotinsky (BZ) oscillatory reaction became an archetype of the temporal and/or spatial dissipative structures and its mechanism is relatively well explained, some aspects are still incompletely understood, for example, the influence of oxygen. Oxygen effects on the BZ reaction and some of its component processes have been described by several authors[1–22]. The accelerating effect of oxygen on the oxidation of malonic acid (MA) with Ce(IV) has been studied in detail by Noyes and co-workers[7]. It has been explained by the formation of organic peroxy radicals that increase the rate of initial attack on MA. An evidence from electron paramagnetic resonance (EPR) has been presented by Neumann *et al.*[14] that peroxymalonyl radicals ($MAOO^{\bullet}$) are actually formed in the aerobic oxidation of MA with ceric ions.

For a long time, it has been believed that oxygen does not influence oxybromine chemistry of the BZ reaction[2–4]. Only recently, a significant influence of oxygen and organic substrate has also been found for the autocatalytic oxidation of the catalyst (Ce(III) ions) with bromate[22]. Both in the presence and the absence of an alkyl derivative of MA (RMA, where R = methyl, ethyl, *etc.*), oxygen always increases inflection times of the autocatalysis when compared with anaerobic conditions (argon atmosphere). According to the Noyes–Field–Thompson (NFT) mechanism[23], a sufficient number of BrO_2 radicals has to accumulate before the autocatalytic oxidation of the reduced form of the catalyst can start. Therefore, conditions that affect the lifetimes of the $RMA^{\bullet}$ and $RMAOO^{\bullet}$ radicals will play a significant role in the BrO_2 kinetics and inflection times.

Even though the phenomenology of the oxygen effects on the BZ reaction is now relatively rich, a number of additional experiments and computations are needed to understand completely this complex influence. A better insight into the role played by oxygen may also be helpful in understanding some of the phenomena associated with spatial pattern formation and with the phenomenon of excitability of non-linear systems.

The main goal of this work was to study the influence of temperature on the oxygen participation in the BZ reaction, using the Ce(IV)–Ce(III) redox catalyst and 2-oxopentanedionic acid (as substrate), as well as on the component processes, on the autocatalytic oxidation of Ce(III) ions with bromate[22], and on the reduction of Ce(IV) ions with substrate. In our previous studies of this kind of the BZ reaction we observed two kinds of oscillations[24,25]. The chosen substrate, 2-oxopentanedioic acid, plays an important role in metabolism of living systems (Krebs cycle, synthesis of hemoglobin, *etc.*) and, therefore, its participation in BZ oscillations may be of importance. The detailed study of the temperature effect on the BZ reaction becomes important also with regard to the possibility of the temperature-compensation in the BZ reaction[26]. The latter phenomenon in chemical and biological oscillators is now in the centre of interest for many chronobiologists[27]. Only recently, the effect of oxygen on the cerium-catalyzed BZ reaction, occurring only at low catalyst concentrations[28], and oxygen inhibition of the BZ oscillations were investigated[29] in detail.

EXPERIMENTAL

Sulfuric acid, $Ce(NO_3)_3$, $Ce(SO_4)_2$, $NaBrO_3$, and 2-oxopentanedioic acid were of commercial analytical quality (Fluka, Aldrich).

BZ reactions were followed potentiometrically (with a universal polarograph OH 105, Radelkis, Hungary) and/or amperometrically (with a Polariter polarograph, Radiometer, Copenhagen, Denmark) in a thermostated cell at various temperatures, with a platinum working electrode and a Hg/Hg_2SO_4 reference electrode. The solutions were stirred during measurements by bubbling of oxygen or nitrogen saturated with water by passing through distilled water in a washing bottle, at a constant flow-rate of 1 l min^{-1}. The data shown in the tables are averages of four independent measurements with a standard deviation of 8%. The values for enthalpy and entropy of activation, determined using the Eyring equation, are apparent or experimental values that do not correspond to any elementary reaction step, but do provide an information about the extent of the temperature-controlled oxygen influence.

RESULTS AND DISCUSSION

As a rule, the BZ reaction is preceded by an induction period which is necessary for accumulating a sufficient amount of brominated substrate, for example bromomalonic acid. It was observed earlier that oxygen may shorten or prolong induction and/or oscillation periods[2,4]. In the system under study, oxygen prolongs the induction period, but the oxygen effect is temperature- dependent (Fig. 1). In contrast to the temperature dependence of the induction period in nitrogen fitting to an Arrhenius plot, in the presence of oxygen, it is a non-Arrhenius dependence, indicating a very complex oxygen effect on bromination of 2-oxopentanedioic acid and the formation of bromide from bromate, as proposed by Ruoff *et al.*[30].

As far as the period of the second oscillation is concerned, it becomes shortened in the presence of oxygen compared to its duration in nitrogen.

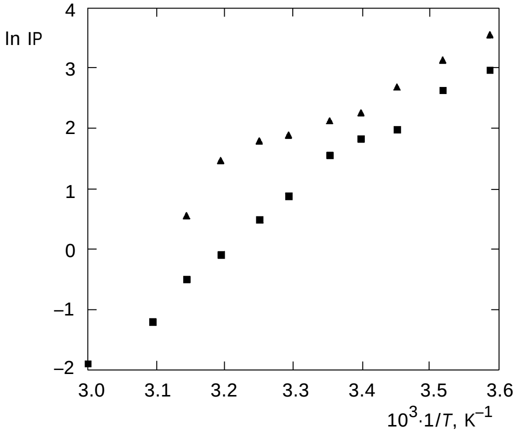


FIG. 1
Temperature dependence of the induction period (IP). $[Ce(SO_4)_2]_0 = 6.25 \cdot 10^{-5}$ mol l^{-1}, $[H_2SO_4]_0 = 1.5$ mol l^{-1}, $[NaBrO_3]_0 = 1.5 \cdot 10^{-2}$ mol l^{-1}, $[\text{2-oxopentanedioic acid}]_0 = 1.25 \cdot 10^{-1}$ mol l^{-1}; ▲ oxygen, ■ nitrogen

We investigated its temperature dependence both in oxygen and in nitrogen and observed an Arrhenius plot in both cases (Fig. 2). Having applied the Eyring equation, we evaluated both apparent activation parameters, enthalpy and entropy of activation (Table I). The value for enthalpy of activation in oxygen is about 4 kJ mol^{-1} higher than in nitrogen. The oxygen effect on the period of the second oscillation (T_2) also relates to entropy of activation; this is about 17 e.u. higher in oxygen than in nitrogen. As the oscillation originates from the reduction of Ce(IV) ion with reducing substrate and the subsequent autocatalytic oxidation of Ce(III) ion with bromate, we also studied the oxygen effect on these processes at variable temperatures. The effect of oxygen on the autocatalytic oxidation of Ce(III) with bromate has been proven by Treindl *et al.*[22]. Herein, we will report the temperature dependence of the oxygen effect on the inflection time values (Fig. 3) and on the derived activation parameters (Table I). One can see that enthalpy activation is responsible, rather than entropy of activation, for the oxygen effect on the inflection time. As BrO_2 radicals are probably partly scavenged by oxygen molecules (Eq. (*1*)), a longer inflection time is necessary for a sufficient amount to be accumulated.

$$BrO_2 + O_2 \rightarrow O_2 \cdots BrO_2 \qquad (1)$$

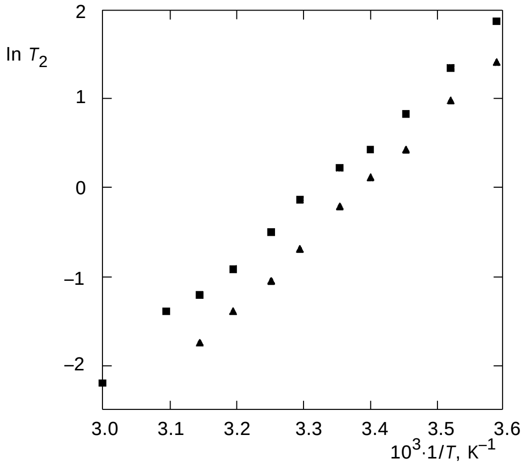


FIG. 2

Temperature dependence of the period of the second oscillation (T_2). $[Ce(SO_4)_2]_0$ = $6.25 \cdot 10^{-5}$ mol l^{-1}, $[H_2SO_4]_0$ = 1.5 mol l^{-1}, $[NaBrO_3]_0$ = $1.5 \cdot 10^{-2}$ mol l^{-1}, [2-oxopentanedioic acid]$_0$ = $1.25 \cdot 10^{-1}$ mol l^{-1}; ▲ oxygen, ■ nitrogen

Similarly to the RMA–BZ system[22], prolongation of the inflection time in the presence of substrate may be due to the interaction of BrO_2 with intermediate radicals (Eqs (*2*) and (*3*); PDA = 2-oxopentanedioic acid):

$$PDA^{\bullet} + BrO_2 \rightarrow P_1 \qquad (2)$$

$$PDAOO^{\bullet} + BrO_2 \rightarrow P_2 \qquad (3)$$

TABLE I
Activation parameters derived from the period of the second oscillation (T_2) and inflection time (t_i)

Parameter	T_2[a]		t_i[b]	
	N_2	O_2	N_2	O_2
ΔH^*, kJ mol^{-1}	57.8	61.6	67.5	69.8
ΔS^*, J mol^{-1} K^{-1}	441.5	458.3	456.0	461.8

[a] $[Ce(SO_4)_2]_0 = 6.25 \cdot 10^{-5}$ mol l^{-1}, $[H_2SO_4]_0 = 1.5$ mol l^{-1}, $[NaBrO_3]_0 = 1.5 \cdot 10^{-2}$ mol l^{-1}, $[\text{2-oxopentanedioic acid}]_0 = 1.25 \cdot 10^{-1}$ mol l^{-1}; [b] $[Ce_2(SO_4)_3]_0 = 2 \cdot 10^{-3}$ mol l^{-1}, $[H_2SO_4]_0 = 3.3 \cdot 10^{-1}$ mol l^{-1}, $[NaBrO_3]_0 = 1 \cdot 10^{-2}$ mol l^{-1}.

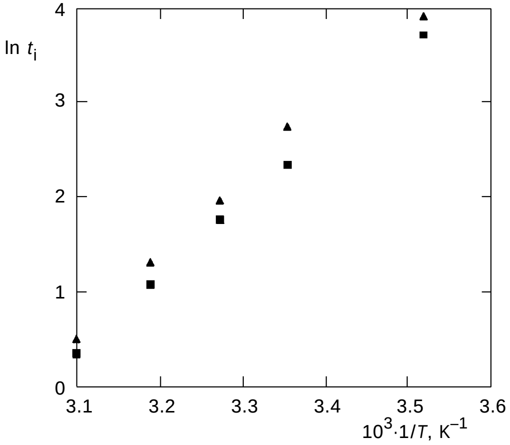


FIG. 3
Temperature dependence of the inflection time (t_i). $[Ce_2(SO_4)_3]_0 = 2 \cdot 10^{-3}$ mol l^{-1}, $[H_2SO_4]_0 = 3.3 \cdot 10^{-1}$ mol l^{-1}, $[NaBrO_3]_0 = 1 \cdot 10^{-2}$ mol l^{-1}; ▲ oxygen, ■ nitrogen

We were able to prove that also the temperature dependence of duration of oscillations (*D*), and of number of oscillations (*N*), possess an Arrhenius character. This also holds for the deduced temperature dependence of the average frequency of oscillations (*f*) (Figs 4a–4c and Table II). The most pregnant effect of oxygen is observed for the temperature dependence of the *D* and *N* parameters. With increasing temperature an inhibiting effect of oxygen on *D* increases, and no oscillations occur at 45 °C in oxygen (in contrast to nitrogen). The corresponding value of enthalpy of activation is more than 50 kJ mol^{-1} higher in oxygen than in nitrogen (Table II). This is in accordance with the observations of Ruoff and Noyes[13] that the bromide ion (inhibiting the oxidation of Ce(III) with bromate) is produced more quickly under aerobic than anaerobic conditions.

If we compare the oscillatory behaviour of the BZ system investigated in oxygen with that in nitrogen, we can see an essential difference. Chaotic behaviour can be observed after several minutes of regular oscillations if oxygen is bubbled through the solution. Analysis may indicate deterministic chaos starting *via* a period of doubling scenario. In the presence of oxygen in the BZ system, new intermediates are formed[22], thereby increasing the complexity of oscillations. This may indicate a more variable system where the phase space becomes at least three-dimensional and transition through a period-doubling bifurcation can be expected[31]. So far, we have not proclaimed that period-doubling cascades are found unequivocally, since further measurements are needed. We can at least say that multimode oscillations in the presence of oxygen are found with time series like

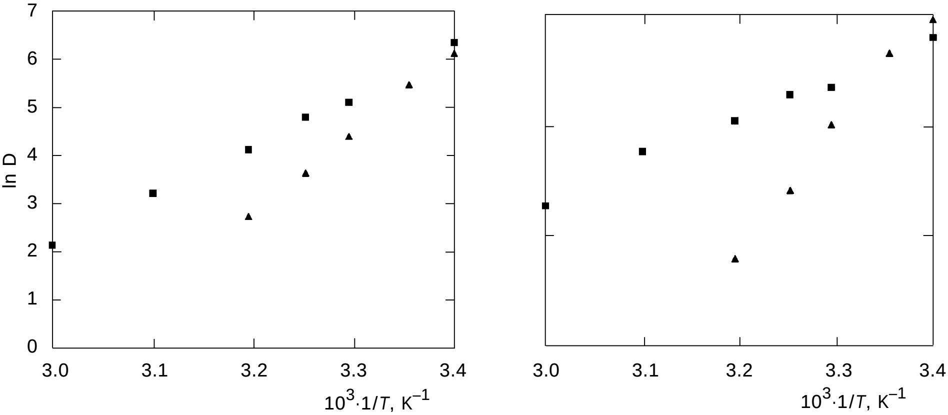
TABLE II
Activation parameters derived from the number (*N*), duration (*D*) and average frequency (*f*) of oscillations

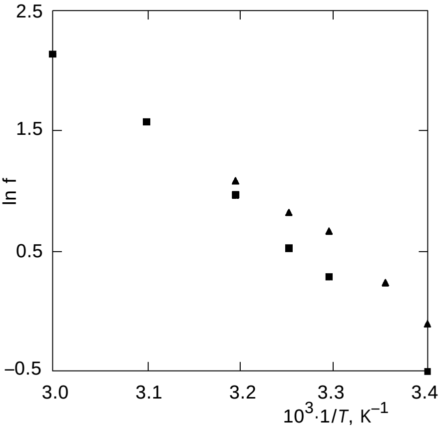
Parameter	*N*		*D*		*f*	
	N_2	O_2	N_2	O_2	N_2	O_2
ΔH^*, kJ mol^{-1}	33.3	93.2	87.3	140.5	51.4	44.8
ΔS^*, J mol^{-1} K^{-1}	314.1	515.8	494.4	676.2	77.8	97.0

$[Ce(SO_4)_2]_0 = 6.25 \cdot 10^{-5}$ mol l^{-1}, $[H_2SO_4]_0 = 1.5$ mol l^{-1}, $[NaBrO_3]_0 = 1.5 \cdot 10^{-2}$ mol l^{-1}, $[\text{2-oxopentanedioic acid}]_0 = 1.25 \cdot 10^{-1}$ mol l^{-1}.

AaaAaaaAaaaaAaaaaaA..., where *A* means a high oscillation amplitude and *a* means a low oscillation amplitude.

As to the possibility of temperature-compensation in the BZ reaction[26], we can say that almost all parameters (induction period, period of the second oscillation, the duration of oscillations, the number of oscillations, and the average frequency of oscillations) of the BZ reaction with the Ce(III)–Ce(IV) redox catalyst and 2-oxopentanedioic acid as substrate in nitrogen fulfill the Arrhenius and/or Eyring equations; we have not found the temperature compensation of its oscillatory behaviour. A non-Arrhenius plot of the induction period in oxygen (Fig. 1) may be due to a very complex influence of oxygen on bromination of substrate, this being usually determined by the rate of enolization of the substrate. Like in the malonic





Temperature dependences of: a duration of oscillations (*D*), $[Ce(SO_4)_2]_0 = 6.25 \cdot 10^{-5}$ mol l^{-1}, $[H_2SO_4]_0 = 1.5$ mol l^{-1}, $[NaBrO_3]_0 = 1.5 \cdot 10^{-2}$ mol l^{-1}, $[\text{2-oxopentanedioic acid}]_0 = 1.25 \cdot 10^{-1}$ mol l^{-1}; b number of oscillations (*N*), $[Ce(SO_4)_2]_0 = 6.25 \cdot 10^{-5}$ mol l^{-1}, $[H_2SO_4]_0 = 1.5$ mol l^{-1}, $[NaBrO_3]_0 = 1.5 \cdot 10^{-2}$ mol l^{-1}, $[\text{2-oxopentanedioic acid}]_0 = 1.25 \cdot 10^{-1}$ mol l^{-1}; c average frequency of oscillations (*f*), $[Ce(SO_4)_2]_0 = 6.25 \cdot 10^{-5}$ mol l^{-1}, $[H_2SO_4]_0 = 1.5$ mol l^{-1}, $[NaBrO_3]_0 = 1.5 \cdot 10^{-2}$ mol l^{-1}, $[\text{2-oxopentanedioic acid}]_0 = 1.25 \cdot 10^{-1}$ mol l^{-1}. ▲ Oxygen, ■ nitrogen acid BZ system, it has been proven[13,30,32], that within an induction period, also in the system under study, most bromide originates from bromate *via* inorganic intermediates (such as HOBr) attacked by intermediary radicals. The most dramatic effect of temperature on the oxygen effect on the induction period as well as on the oscillatory state can be observed in the temperature range of 45–60 °C, which is probably due to the high rate of the bromide production.

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REFERENCES

1. Field R. J. in: *Oscillations and Traveling Waves in Chemical Systems* (R. J. Field and M. Burger, Eds). Wiley, New York 1985.
2. Roux J. C., Rossi A. C.: *C. R. Acad. Sci., Ser. III* **1978**, *287*, 151.
3. Bar-Eli K., Haddad S.: *J. Phys. Chem.* **1979**, *83*, 2952.
4. Treindl Ľ., Fabian P.: *Collect. Czech. Chem. Commun.* **1980**, *45*, 1168.
5. Ruoff P.: *Chem. Phys. Lett.* **1982**, *92*, 1168.
6. Ganapathisubramanian N., Noyes R. M.: *J. Phys. Chem.* **1982**, *86*, 5158.
7. Barkin S., Bixon M., Noyes R. M., Bar-Eli K.: *Int. J. Chem. Kinet.* **1978**, *10*, 619.
8. Ruoff P.: *Z. Naturforsch., A* **1983**, *38*, 974.
9. Ruoff P., Schwitters B.: *Z. Phys. Chem.* **1983**, *135*, 171.
10. Tkáč I., Treindl Ľ.: *Chem. Pap.* **1985**, *39*, 175.
11. Treindl Ľ., Mrákavová M.: *Chem. Phys. Lett.* **1985**, *122*, 493.
12. Mrákavová M., Treindl Ľ.: *Collect. Czech. Chem. Commun.* **1986**, *51*, 2693.
13. Ruoff P., Noyes R. M.: *J. Phys. Chem.* **1989**, *93*, 7394.
14. Neumann B., Muller S. C., Hauser M. J. B., Steinbock O., Simoyi R. H., Dalal N. S.: *J. Am. Chem. Soc.* **1995**, *117*, 6372.
15. Neumann B., Steinbock O., Muller S. C., Dar N. S.: *J. Phys. Chem.* **1996**, *100*, 12342.
16. Chou Y., Lin H. P., Sun S. S., Jwo J. J.: *J. Phys. Chem.* **1993**, *97*, 8450.
17. Sun S., Lin H. P., Chen Y. F., Jwo J. J.: *J. Chin. Chem. Soc.* **1994**, *41*, 651.
18. Lin H. P., Jwo J. J.: *J. Phys. Chem.* **1995**, *99*, 6897.
19. Chen Y. F., Lin H. P., Sun S. S., Jwo J. J.: *Int. J. Chem. Kinet.* **1996**, *28*, 345.
20. Drummond A. Y., Waters W. A.: *J. Chem. Soc.* **1954**, 2456.
21. Wang J., Hynne F., Sorensen P. G., Nielsen F.: *J. Phys. Chem.* **1996**, *100*, 17593.
22. Treindl Ľ., Ruoff P., Kvernberg P. O.: *J. Phys. Chem. A* **1997**, *101*, 4606.
23. Noyes R. M., Field R. J., Thompson R. C.: *J. Am. Chem. Soc.* **1971**, *93*, 7315.
24. Treindl Ľ., Dorovský V.: *Z. Phys. Chem.* **1981**, *126*, 129.
25. Treindl Ľ., Dorovský V.: *Collect. Czech. Chem. Commun.* **1982**, *47*, 2831.
26. Ruoff P.: *Physica D (Amsterdam)* **1995**, *84*, 204.
27. Ruoff P., Rensing L., Kommedal R., Mohsenzadeh S.: *Chronobiol. Int.* **1997**, *14*, 499.
28. Petrascu A. M., Koch M. H. J., Forsterling H.-D.: *J. Phys. Chem. A* **1999**, *103*, 6757.
29. Steinbock O., Hamik Ch. D., Steinbock B.: *J. Phys. Chem. A* **2000**, *104*, 6411.

30. Ruoff P., Varga M., Koros E.: *Acc. Chem. Res.* **1988**, *21*, 326.
31. Scott S. K.: *Chemical Chaos*, p. 81. Clarendon Press, Oxford 1991.
32. Varga M., Gyorgyi L., Koros E.: *J. Am. Chem. Soc.* **1985**, *107*, 4780.