INFLUENCE OF TEMPERATURE AND REDOX COUPLE ON OSCILLATIONS IN THE BELOUSOV – ZHABOTINSKY REACTION

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The temperature dependence and the influence of catalyst effect on the Belousov – Zhabotinsky system with Ce(III)/Ce(IV) and Mn(II)/Mn(III) redox catalyst and malonic acid as organic substrate was studied. The influence of temperature on the induction period, the period of the second oscillation, number, duration and finally on the average frequency of the oscillations was investigated in nitrogen using spectrophotometric measurements. The corresponding activation parameters have been determined.

Introduction

The Belousov [1] – Zhabotinsky [2,3] (BZ) reaction is one of the most studied and best-understood chemical oscillating reactions. Even in a closed system the reaction exhibits an unexpected wealth of dynamic behaviors ranging from sustained oscillations [1÷5], excitabilities [6÷8] and chemical wave activity [9÷11] to bistability [7,12÷14]. In general, a BZ reaction is the simultaneous bromination and oxidation of an organic substrate by bromate in the presence of metal ion catalyst in aqueous media [15,16]. Malonic acid is the most common substrate used in the studies of the BZ reaction and it plays a dual role: the reduction of the metal ion catalyst and the removal of bromine. The basic mechanism was elucidated by Noyes and co-workers and is known as Field – Koros – Noyes (FKN) mechanism [5]. An important feature of the mechanism is that bromide ion acts as a control intermediate [5].

In this paper we made a comparison between BZ systems with different redox catalyst. The temperature dependence of a few parameters: induction period (IP), the period of the second oscillation (T_2), number (N), duration (D) and the average frequency of the oscillations (f) was followed in the range 30.8÷69.7^{0}C.

Spectrophotometric study of bromate driven oscillations was made before [17÷19].

Experimental

The experiments were carried out using a Pye Unicam SP 500 ultraviolet and visible spectrophotometer. The solutions were thermostated by means of a thermostat type Lauda K4R. Experimental curves were recorded with a Siemens Kompensograph X-Y. The scheme of this setup was described in an earlier paper [20]. The experiments were performed in a well-thermostated cuvette (diameter of 10 mm). The volume of the reaction

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mixture was 3.2 ml. The cuvette was closed with a rubber stopper through which a syringe needle was inserted into the solution. The stopper had one hole necessary for the elimination of the resulting gases from the reaction. Through the syringe needle, an inert gas (nitrogen) was bubbled. This was needed for the elimination of Br_2 (which results from the oscillating reaction and has an inhibitory effect) and other gases and for ensuring a proper stirring of the reaction mixture.

The following initial reactant concentrations were used: 4x10^{-3} M $Ce_2(SO4)_3$ / $MnSO_4{\cdot}H_2O$, 1.2 M malonic acid, 0.15 M $NaBrO_3$ and 2 M H_2SO_4. All reagents were of commercial analytical quality (Fluka, Aldrich) and were used without any further purification. Equal volumes (0.8 ml) from $Ce_2(SO4)_3$ / $MnSO_4$ and H_2SO_4 were added in the cuvette and nitrogen was bubbled through this solution. Malonic acid (0.8 ml) and $NaBrO_3$ (0.8 ml) were put in separate cuvettes into the thermostat. When the solutions reached the established temperature, malonic acid and sodium bromate were added (by means of a syringe) to the $Ce_2(SO4)_3$ / $MnSO_4$ solutions. All experiments were performed at λ = 323 nm or λ = 285 nm where Ce^{3+} or Mn^{2+} have a maximum of absorption. The results at each temperature are the average of at least four independent measurements.

Results and discussions

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. After this period, single oscillations in cerium / manganese concentrations begin to start.
The values of induction period (IP), the period of the second oscillation (T_2), number (N), duration (D) and the average frequency of the oscillations (f) are presented in Table 1.

Table 1. The values of induction period (IP), the period of the second oscillation (T_2), number (N), duration (D) and the average frequency of oscillations (f) for BZ systems with Ce (III) and Mn (II) ions

t (^{0}C)	IP (min)		T_2 (min)		N		D (min)		f (min^{-1})	
	Ce	Mn	Ce	Mn	Ce	Mn	Ce	Mn	Ce	Mn
30.8	3.16	2.87	1.08	1.04	414	15	313.0	16.8	1.3226	0.8933
40.0	1.71	1.31	0.58	0.44	302	15	144.7	6.2	2.0870	2.4325
49.8	1.01	0.79	0.31	0.25	247	16	54.4	3.3	4.5421	4.8302
54.0	0.98	0.71	0.27	0.16	228	15	37.6	2.3	6.0703	6.5217
60.0	0.61	0.53	0.18	0.11	122	14	13.3	1.6	9.1937	8.5926
69.7	0.41	-	0.09	-	18	-	1.6	-	11.548	-

$[Ce_2(SO_4)_3]$ = $[MnSO_4]$ = 1x10^{-3}M, $[NaBrO_3]$ = 3.75x10^{-2}M, $[H_2SO_4]$ = 5x10^{-1}M, $[CH_2(COOH)_2]$ = 3x10^{-1}M.

The values shown in the table are averages of four independent measurements with a standard deviation of 8%.

We can see that induction period, period of the second oscillation, number and duration of oscillations decrease when temperature increases (except N for BZ system with manganese). The average frequency of the oscillations increases with increasing temperature. The temperature dependence of IP, T_2, N, D and f are plotted in Figs. 1÷5.

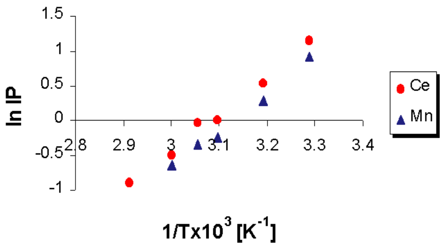

Fig. 1: *Temperature dependence of induction period*

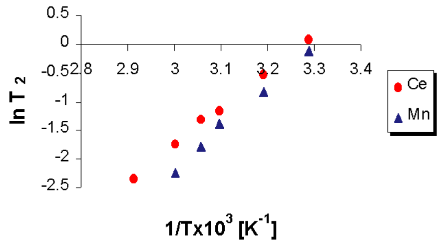

Fig. 2: *Temperature dependence of period of the second oscillation*

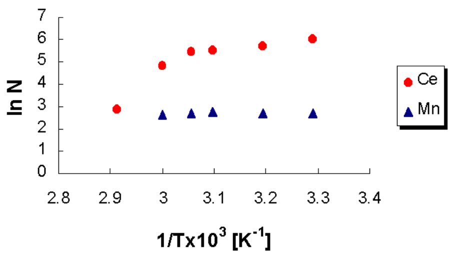

Fig. 3: Temperature dependence of number of oscillations

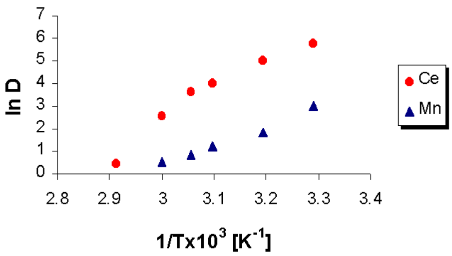

Fig. 4: Temperature dependence of duration of oscillations

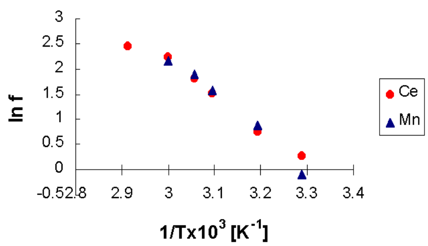

Fig. 5*: Temperature dependence of average frequency of oscillations*

Using Eyring equation we could calculate the activation parameters derived from IP, T_2, N, D and f.

Table 2. Values of enthalpy and entropy of activation for the BZ systems with cerium and manganese ions

	IP		T_2		D		f	
Activation parameter	Ce	Mn	Ce	Mn	Ce	Mn	Ce	Mn
$\Delta H^{\neq}$[kJ/mole]	51.64	52.57	55.27	63.43	114.09	69.47	49.04	62.69
$\Delta S^{\neq}$[J/moleK]	409.11	414.02	430.52	458.57	572.96	455.15	85.74	43.06

The values for enthalpy and entropy of activation are apparent or experimental values that do not correspond to any elementary reaction step, but provide an information about the extent of the temperature and catalyst influence on BZ oscillations.

From the Table 1 and Figs. 1÷5 we can observe that:

- the induction period is smaller in the case of BZ system with manganese;

- the periods of the second oscillation are comparable for these two BZ systems in the temperature interval 30.8÷60.0^{0}C;
- the temperature interval is shorter in the case of BZ system with manganese (at 69.7^{0}C no oscillation was recorded);
- in the temperature range 30.8÷60.0^{0}C, for the BZ system with manganese, the number of oscillations is almost constant;
- the most pregnant differences are observed for the temperature dependence of the N and D parameters, which are smaller for the BZ system with Mn^{2+} comparatively with the obtained values for the BZ system with Ce^{3+}.

Conclusions

Concerning the possibility of temperature compensation in the BZ reaction, we can say that almost all parameters (except N for BZ system with Mn) of the BZ systems with the Ce(III)-Ce(IV) and/or Mn(II)-Mn(III) redox catalyst and malonic acid as organic substrate in nitrogen fulfill the Arrhenius and/or Eyring equations and we have not found the temperature compensation of its oscillatory behavior.

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REFERENCES

1. Belousov, B. P. (1958) **Sb. Ref. Radiat. Med. Medgiz**, Moscow, 145.
2. Zhabotinsky, A. M. (1964) *Dokl. Akad. Nauk SSSR* **157**, 392.
3. Zhabotinsky, A. M. (1985) **Oscillations and Traveling Waves in Chemical Systems**, Field, R. J., Burger, M, Eds.; Wiley, New York.
4. Noyes, R. M., Field, R. J., Koros, E. (1972) *J. Am. Chem. Soc.* **94,** 1394.
5. Field, R. J., Koros, E., Noyes, R. M., (1972), *J. Am. Chem. Soc.* **94,** 8649.
6. Ruoff, P. (1982) *Chem. Phys. Lett.* **90**, 76. (b) Ibid. (1982) **92**, 239. (c) Ibid. (1983) **96**, 374.
7. Ruoff, P. (1983) *Z. Naturforsch. A:* Phys.*, Phys. Chem. Kosmophys.* **38A**, 974.
8. Ruoff, P. (1986) *J. Phys. Chem.* **90**, 6744
9. (a) Zaikin, A. N., Zhabotinsky, A. M. (1970) **225**, 535. (b) Winfree, A. T. (1972) *Science* **175**, 634, (c)Winfree, A. T. (1973) *Science* **185**, 937
10. Reusser, E. J., Field, R. J. (1979), *J. Am. Chem. Soc.* **101**, 1063.
11. Smoes, M. L. (1980) **Dynamics of Synergetic Systems**, Haken, H., Ed.; Springer-Verlag: Berlin, 80.
12. Geiseler, W., Follner, H. H. (1977) *Biophys. Chem.* **6**, 107.
13. (a) Geiseler, W., Bar-Eli, K. (1981) *J. Phys. Chem* **85**, 908. (b) Orban, M., De Kepper, P., Epstein, I. R. (1982) *J. Am. Chem. Soc.* **104**, 2657
14. (a) Ruoff, P., Noyes, R. M. (1985) *J. Phys. Chem.* **89**, 1339. B Ruoff, P., Varga, M., Koros, E. (1987) *J. Phys. Chem.* **91**, 5332.
15. Field, R. J. (1978) **Theoretical Chemistry***,* Eyring, H., Henderson, D., Eds.; Academic, New York vol. 4.
16. Field, R. J., 1985) **Oscillations and Traveling Waves in Chemical Systems**, Field, R. J., Burger, M, Eds.; Wiley, New York.
17. Treindl, L., Mrakavova, M. (1998) *J. Phys. Chem.* **92,** 1138.
18. Vîlcu, R. , Bala, D. *Revista de Chimie*, in press
19. Vîlcu, R. , Bala, D. (2001) *12th Romanian International Conference on Chemistry and Chemical Engeneering RICCCE* **12**, 97.
20. Vîlcu, R. , Danciu, T.; Bala, D. (1998) *Discrete Dynamics in Nature and Society* **2**, 195.