BELOUSOV-ZHABOTINSKII OSCILLATION REACTION WITH GLYCERALDEHYDE

Milan MELICHERČÍK* and Ľudovít TREINDL**
Department of Physical Chemistry, Comenius University, 842 15 Bratislava

Received November 17, 1989
Accepted January 8, 1990

An oscillation system of Belousov–Zhabotinskii type with aldehyde as substrate is described for the first time. Oscillations of the concentration of Mn(III) ions can be followed spectrophotometrically or potentiometrically with a Pt electrode in a relatively narrow concentration range of the substrate. In contrast to the analogous reaction with malonic acid, no oscillations of the concentration of Br^- ions were detected by a bromide ion selective electrode. This together with the fact that the concentration of Mn(III) ions oscillates even at relatively high bromine concentrations suggests that oscillations of the concentration of the redox catalyst Mn(II)/Mn(III) are probably controlled by organic radicals rather than by Br^- ions.

The Belousov–Zhabotinskii oscillation reaction has for many years attracted the attention of workers both in the field of reaction kinetics and synergetics, which is concerned with time-spatial dissipative structures. Although its mechanism was principally proposed by Field. Körös and Noyes[1], and a generalized mathematical model Oregonator[2] was derived on its basis, there remains much to be elucidated, e.g. the influence of mechanical stirring, the role of Br^- ions and intermediate radicals, and the influence of the substrate and its structure on the main parameters of the BZ reaction.

The known substrates of the BZ reaction involve many ketones[3–5], some saccharides[6,7], but no aldehyde. The present paper describes a BZ reaction with glyceraldehyde and it may possibly start a systematic study of BZ reactions with aldehydes.

EXPERIMENTAL

The course of the BZ oscillation reaction and of the reaction of glyceraldehyde with bromine or sodium bromate was followed spectrophotometrically by using a Specord UV VIS spectrophotometer (Zeiss, Jena). The reaction system was placed in a 1 cm cuvette in a tempered block connected with a U10 ultrathermostat (Medingen, G.D.R.). The solution was stirred electromagnetically during the reaction[8]. The reaction course was also followed potentiometrically with a Pt redox or Br^- ion selective electrode against 1M Hg_2SO_4 electrode.

* Present address: Department of Biology and Chemistry, Pedagogical Faculty, 975 49 Banská Bystrica.
** Author to whom correspondence should be addressed.

The chemicals ($MnSO_4.4H_2O$, $NaBrO_3$, and H_2SO_4, Lachema, Brno) were of reagent grade. DL-glyceraldehyde (Fluka AG, Buchs SG, Switzerland) was also of reagent grade. Solutions were prepared from redistilled water.

RESULTS AND DISCUSSION

In a solution of $3.4 \cdot 10^{-3}$M $MnSO_4$, 0·14M $NaBrO_3$ and 1M H_2SO_4 at 20°C at a concentration of glyceraldehyde in the range from 0·026 to 0·067 mol dm^{-3}, we observed oscillations of the absorbancy at a wave number $\tilde{\nu}$ = 35 000 cm^{-1} corresponding to Mn(III) ions (Fig. 1). The course of the oscillation reaction can also be followed potentiometrically by measuring the time course of the redox potential of the system Mn(II)–Mn(III) with a Pt electrode. The dependence of the main parameters of the BZ reaction on the reactant concentrations was evaluated from spectrophotometric measurements. Oscillations appeared always after an induction period, whose length as well as the duration and number of the oscillations depend on the concentrations of the substrate and sodium bromate (Tables I and II). Although it is not possible to determine the activation parameters of the elementary steps of the BZ reaction, the temperature dependence of the characteristic parameters is interesting (Table III).

In contrast to the BZ reaction with malonic acid, we found no oscillations of Br^- ions in the studied system using a bromide ion selective electrode, although the oscillations of the redox potential of the Pt electrode and the oscillations of the absorbancy of Mn(III) ions were well reproducible. The course of the BZ reaction with glyceraldehyde is accompanied by production of bromine, whose absorbancy at a wave number $\tilde{\nu}$ = 25 000 cm^{-1} rises monotonically during the induction period and then periodically at the same frequency as the oscillations of Mn(III) ions. The

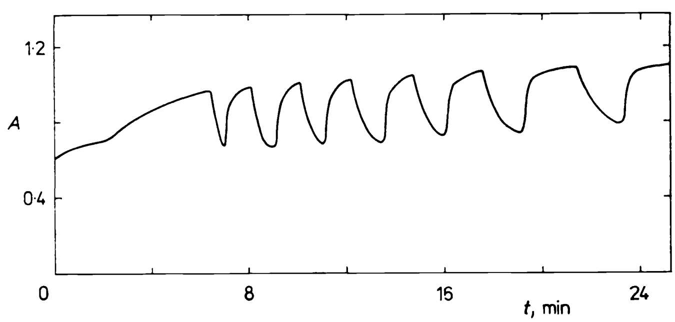

FIG. 1

Oscillations of absorbancy of Mn(III) ions. 1M H_2SO_4, $3.4 \cdot 10^{-3}$M $MnSO_4$, 0·14M $NaBrO_3$, $2.7 \cdot 10^{-2}$M $C_3H_6O_3$, 20°C, $\tilde{\nu}$ = 35 000 cm^{-1}

TABLE I

Dependence of parameters of the BZ reaction on substrate concentration. 1M H_2SO_4, 3·4 . 10^{-3}M $MnSO_4$, 0·14M $NaBrO_3$, 20°C

Concentr. of $C_3H_6O_3$ mol dm^{-3}	Induction period min	Duration of oscil. min	Number of oscil.
0·026	7·0	13·3	5
0·028	5·97	22	8–9
0·030	4·47	22	10
0·040	1·65	1·2	2
0·053	1·02	0·5	2–3
0·066	0·47	0·4	2

TABLE II

Dependence of parameters of BZ reaction on the concentration of $NaBrO_3$. 1M H_2SO_4, 3·4 . 10^{-3}M $MnSO_4$, 2·8 . 10^{-2}M $C_3H_6O_3$, 20°C

Concentr. of $NaBrO_3$ mol dm^{-3}	Induction period min	Duration of oscil. min	Number of oscil.
0·1	2·75	3·5	4
0·142	5·97	22	8–9
0·2	9·42	11	4

TABLE III

Dependence of parameters of BZ reaction on temperature. 1M H_2SO_4, 3·4 . 10^{-3}M $MnSO_4$, 0·14M $NaBrO_3$, 0·028M $C_3H_6O_3$

Temperature °C	Induction period min	Duration of oscil. min	Number of oscil.
15	17·3	30	9–10
20	5·6	23	9
25	3·7	18	9
30	2·5	12	9
35	1·6	9	9

periodic growth of the bromine concentration was evaluated in the range from $8 \cdot 7 . 10^{-3}$ to $1 \cdot 5 . 10^{-2}$ mol dm^{-3} Br_2. Even at these concentrations of bromine, the studied system oscillated.

The role of Br^- ions and bromine is still under discussion in connection with perfectioning the Field–Körös–Noyes mechanism. We therefore studied also the kinetics of the reaction of bromine with glyceraldehyde. The values of the rate constant were determined as $k = 8 \cdot 1 . 10^{-5}$ s^{-1} at 20°C and $3 \cdot 3 . 10^{-4}$ s^{-1} at 35°C in a solution of $5 . 10^{-2}$ mol dm^{-3} glyceraldehyde and $5 . 10^{-3}$ mol dm^{-3} bromine in one-molar sulphuric acid. From these values and the Eyring equation we found the activation enthalpy $\Delta H^{\ddagger} = 61 \cdot 3$ kJ mol^{-1} and the activation entropy $\Delta S^{\ddagger} = -114$ J K^{-1} mol^{-1}.

The reaction system under study is the first oscillation system of the BZ type with aldehyde as substrate. It is expected that similar BZ reactions with aldehydes will be found later. These systems, and especially the present one, may be interesting from the point of view of the role of aldehydes in the metabolism of saccharides[9]. With the related compounds, glycerol and glyceric acid, BZ type oscillation systems were already described[10,11].

The fact that in the present system the concentration of Br^- ions does not oscillate and the Mn(III) concentration oscillates even at relatively high bromine concentrations suggests that here the BZ type oscillation reaction is not controlled by Br^- ions[1] but probably by organic radicals, as supposed in similar cases by other authors[12,13].

In our case, the reaction probably involves the following steps:

$$\text{Mn(III)} + \text{RH} \rightarrow \text{Mn(II)} + \text{R}\cdot + \text{H}^+ \tag{A}$$

$$\text{HBrO}_2 + \text{R}\cdot \rightarrow \text{HOBr} + \text{RO}\cdot \,, \tag{B}$$

where RH denotes glyceraldehyde, R· and RO· are intermediate radicals. The relatively narrow concentration range of the reaction components in which the oscillations take place can be qualitatively elucidated by the important role of the mentioned radicals in switching over between autocatalytic oxidation of Mn(II) with BrO_3^- ions and reduction of Mn(III) ions with glyceraldehyde according to the FKN mechanism[1]. The optimum value of the stationary concentration of the radicals probably depends very markedly on the concentration ratio of the reaction components and on the concentration of radical scavengers. According to ref.[12], interaction of radicals R· with hypobromous acid leads to Br· radicals, which have a controlling function.

$$\text{HOBr} + \text{R}\cdot \rightarrow \text{ROH} + \text{Br}\cdot \tag{C}$$

$$\text{Br}\cdot + \text{HBrO}_2 \rightarrow \text{HOBr} + \cdot\text{OBr} \,. \tag{D}$$

According to Försterling[13], a feedback based on the reaction of organic radicals with $BrO_2^{\cdot}$ radicals can also play a role in oscillation systems of the BZ type.

REFERENCES

1. Field R. J., Körös E., Noyes R. M.: J. Am. Chem. Soc. *94*, 8649 (1972).
2. Field R. J., Noyes R. M.: J. Chem. Phys. *60*, 1877 (1974).
3. Bowers P. G., Caldwell K. E., Prendergast D. E.: J. Phys. Chem. *76*, 2185 (1972).
4. Farage V. J., Janjic D.: Helv. Chim. Acta *61*, 1539 (1978).
5. Treindl Ľ., Kaplan P.: Chem. Zvesti *35*, 145 (1981).
6. Rastogi R. P., Yadava R. D., Singh S., Sharma A.: Indian J. Chem., A *24*, 43 (1985).
7. Ševčík P., Adamčíková Ľ.: React. Kinet. Catal. Lett. *33*, 47 (1987).
8. Švec A., Rajec P., Mátel Ľ.: Chem. Listy *75*, 1734 (1981).
9. Huskey W. P., Epstein I. R.: J. Am. Chem. Soc. *111*, 3157 (1989).
10. Adamčíková Ľ., Ševčík P.: Collect. Czech. Chem. Commun. *52*, 2375 (1987).
11. Blume R., Bader H. J.: Z. Naturforsch., B *39*, 1795 (1984).
12. Ganapathisubramanian N., Noyes R. M.: J. Phys. Chem. *86*, 5155 (1982).
13. Försterling H. D.: *International Conference on Dynamics of Exotic Phenomena in Chemistry, Hajdúszoboszló, Hungary, August 22—25, 1989*; Preprints of Lectures, p. 33.

Translated by K. Micka.