# INFLUENCE OF OXYGEN ON BELOUSOV-ZHABOTINSKII REACTION

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This work deals with the effect of oxygen on basic parameters of the Belousov–Zhabotinskii reaction in the presence of $Ce^{4+}/Ce^{3+}$ redox catalyst and malonic acid, citric acid, or 2,4-pentanedione as substrates. Oxygen lowers the duration of the induction period and the first oscillation period as well as the corresponding activation parameters. Oxygen lowers also rate constants and activation parameters for oxidation of malonic and citric acids with $Ce^{4+}$ ions. It is concluded that the effect of oxygen on the Belousov–Zhabotinskii reaction consists mainly in its catalytic influence on the oxidation of the substrate with $Ce^{4+}$ ions.

Oscillation reactions were already reviewed by us[1]. We studied the kinetics and mechanism of the Belousov-Zhabotinskii reaction using the rotating platinum electrode and we discussed the new kinetic data in terms of the Field–Körös–Noyes (F.K.N.) mechanism[2]. Recently we described[3] the influence of electrolytes on basic parameters of the B.–Zh. reaction, which we elucidated in terms of the more exact mechanism according to Edelson, Field and Noyes.

Blandamer and Roberts[4] analysed the influence of temperature on the oscillation frequency of the B.–Zh. reaction. The oscillation frequency is a linear function of the reciprocal absolute temperature. The authors calculated the corresponding activation parameters which they discussed in terms of their reaction schemes. According to them, the oscillation frequency is to a large extent limited by the rate of the reaction of $Br^-$ with $BrO_3^-$ ions under formation of HOBr and $HOBr_2$. Beck and Váradi[5] described a new variant of the B.–Zh. reaction; their reaction system consisted of a solution of sulphuric acid, potassium bromate, $Fe(phen)_3^{2+}$ ions, and acetylenedicarboxylic acid. Thus, they proved that the presence of an "active" methylene group is not a necessary condition for oscillation reactions with carboxylic acids. Tyson[6] presented a new mathematical analysis of the B.–Zh. reaction according to the F.K.N. mechanism referring to a relatively good agreement between calculated and observed oscillations. Recently Field and Noyes[7] studied anew the basic problems of the mechanism of chemical oscillations. According to them, the basic kinetic condition of chemical oscillations is that the system in the stationary state is unstable with respect to small fluctuations. Dynamic equations which describe oscillatory chemical systems are always nonlinear. Schmitz[8] discussed a new kinetic model of the B.–Zh. reaction on the basis of his results; he proved the existence of closed cycles also with the aid of an analogue computer for a set of chosen semiempirical kinetic parameters. Noyes and Bar-Eli[9] brought evidence for the F.K.N. mechanism and opposed the conclusions of Schmitz whose mechanism is at variance with several observations. Noyes and coworkers[10,11] studied anew the kinetics and mechanism of oxidation of $Ce^{3+}$ ions with bromate and supported the original F.K.N. mechanism through a mathematical treatment of their results. Orbán and Körös[12–14] referred recently about chemical oscillations taking place during a noncatalytic oxidation of several phenol and aniline derivatives with bromates.

In spite of the mentioned remarkable results, it seems that the kinetics and mechanism of the B.-Zh. reaction has not been sufficiently elucidated. The known effect of oxygen has not been studied in detail[15,16].

The subject of the present work is the study of the effect of molecular oxygen on the B.-Zh. reaction in the presence of $Ce^{4+}/Ce^{3+}$ redox catalyst and malonic acid or 2,4-pentanedione as substrate. Our intention was to compare the activation parameters corresponding to the induction period and the period of the first oscillation in the presence and absence of oxygen, and further to compare the activation parameters of the B.-Zh. reaction with those for the oxidation of the corresponding substrate with $Ce^{4+}$ ions.

## EXPERIMENTAL

Kinetic measurements of the B.-Zh. oscillating reaction with a rotating platinum electrode were described earlier[2]. All chemicals were of reagent grade. Chemical oscillations were studied at different temperatures in 1·5M-$H_2SO_4$, 6 . $10^{-2}$M-$NaBrO_3$, 2 . $10^{-3}$M-$Ce(SO_4)_2$ and 0·05M malonic or citric acid or 0·01M pentanedione. The solutions were either open to the air or in nitrogen atmosphere. Every measurement was repeated three times.

## RESULTS AND DISCUSSION

### *Kinetic Parameters of the B.-Zh. Reaction*

In the presence of malonic acid, citric acid or 2,4-pentanedione as substrate the induction period decreases exponentially with increasing temperature. The dependence of the logarithm of the induction period on reciprocal absolute temperature is linear and from this we found the activation energy and preexponential term in the Arrhenius equation (Table I).

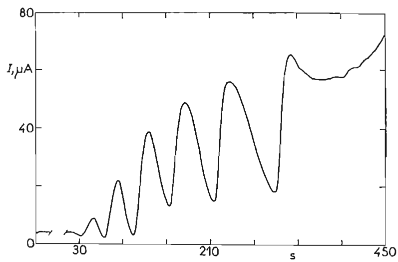


FIG. 1

Course of Belousov–Zhabotinskii Reaction with 2,4-Pentanedione

1·5M-$H_2SO_4$, 0·06M-$NaBrO_3$, 4 . $10^{-4}$M-$Ce(SO_4)_2$, 0·01M 2,4-pentanedione; 20°C.

The period of the first oscillation also decreases exponentially with increasing temperature; from its dependence on reciprocal absolute temperature the activation energy and preexponential term in the absence and presence of oxygen were determined (Table I).

In the presence of malonic or citric acid or 2,4-pentanedione, the effect of oxygen is to shorten the induction period of the oscillations, the period of the first oscillation, and the corresponding activation parameters. In addition, also the duration of the oscillations, their total number, and their frequency diminish (Tables II and III).

TABLE I

Influence of Oxygen on Activation Parameters of B.–Zh. Reaction (I.P.: Measured from Induction period; $T_1$: measured from the first oscillation period.)

| Substrate | Gas | I.P. | | $T_1$ | |
|---|---|---|---|---|---|
| | | $E$ kJ mol$^{-1}$ | $A$ s$^{-1}$ | $E$ kJ mol$^{-1}$ | $A$ s$^{-1}$ |
| Malonic acid | $N_2$ | 60·6 | $4·9 . 10^7$ | 58·9 | $2·1 . 10^8$ |
| | $O_2$ | 55·0 | $6·3 . 10^6$ | 55·6 | $6·2 . 10^7$ |
| Citric acid | $N_2$ | 108·3 | $3·8 . 10^{15}$ | 114·0 | $6·8 . 10^{16}$ |
| | $O_2$ | 76·3 | $2·7 . 10^{10}$ | 85·0 | $1·4 . 10^{12}$ |
| 2,4-Pentanedione | $N_2$ | 89·1 | $4·5 . 10^{12}$ | 26·5 | $3·8 . 10^3$ |
| | $O_2$ | 83·1 | $6·4 . 10^{11}$ | 20·9 | $5·0 . 10^2$ |

TABLE II

Influence of Oxygen on Duration and Number of Oscillations

| Duration of oscil. s | | Number of oscil. | |
|---|---|---|---|
| $N_2$ | $O_2$ | $N_2$ | $O_2$ |
| Malonic acid | | | |
| 5 358 | 5 100 | 69 | 66 |
| Citric acid | | | |
| 13 200 | 12 342 | 92 | 87 |

*Kinetics of Oxidation of Substrates with* $Ce^{4+}$ *Ions*

Since the oxidation of the substrate with $Ce^{4+}$ ions is one of the reaction steps of the B.–Zh. oscillating system, we checked the influence of oxygen on the corresponding activation parameters. The solution contained 0·05M malonic or citric acid, 2 . . $10^{-3}$M $Ce(SO_4)_2$ and 1·5M-$H_2SO_4$. The rate constants were determined by using a kinetic equation of the first order at 15, 20, 25, 30, 35, and 40°C in nitrogen or air atmosphere.

The temperature dependence of the rate constant and the Eyring equation led to the activation parameters given in Table IV. The activation enthalpy and entropy are lower in the presence of oxygen than in its absence. It can be concluded that the

TABLE III

Influence of Oxygen on Frequency of Oscillations at Various Temperatures, $10^3$ $s^{-1}$

| °C | Malonic acid | | Citric acid | | 2,4-Pentanedione | |
|---|---|---|---|---|---|---|
| | $N_2$ | $O_2$ | $N_2$ | $O_2$ | $N_2$ | $O_2$ |
| 15 | 6 | 7·6 | — | — | 50 | — |
| 20 | 10 | 12·2 | — | — | 40 | 56·6 |
| 25 | 15·5 | 17·1 | — | — | 60 | 60 |
| 30 | 22·7 | 24·3 | 5 | 6·7 | 76·7 | 83·3 |
| 35 | 31·8 | 32·7 | 10·8 | 12·5 | 105 | 103·3 |
| 40 | 44·3 | 44·5 | 19·7 | 20·3 | 133 | 146·7 |

TABLE IV

Influence of Oxygen on Activation Parameters for Oxidation of Substrates with $Ce^{4+}$ Ions

| $\Delta H^{\ddagger}$, kJ $mol^{-1}$ | | $\Delta S^{\ddagger}$, J $K^{-1}$ $mol^{-1}$ | |
|---|---|---|---|
| $N_2$ | $O_2$ | $N_2$ | $O_2$ |
| | Malonic acid | | |
| 46·6 | 38·3 | −103 | −124 |
| | Citric acid | | |
| 90·8 | 73·2 | 43 | − 12 |

described influence of oxygen on the parameters of the B.–Zh. reaction can be attributed to its influence on the activation parameters for oxidation of the corresponding substrates.

Oxidation of malonic acid with $Ce^{4+}$ ions was recently described in detail by Barkin with coworkers[17]. They studied also the effect of oxygen on this reaction. During oxidation of malonic acid with $Ce^{4+}$ ions an intermediary radical MA· is formed, which reacts in the presence of oxygen in the following steps:

$$\mathrm{MA\cdot} + \mathrm{O_2} = \mathrm{MAOO\cdot} \qquad (a)$$

$$\mathrm{MAOO\cdot} + \mathrm{MA} \rightarrow \mathrm{MA\cdot} + \mathrm{MAOOH} \qquad (b)$$

$$\mathrm{MAOOH} + \mathrm{Ce^{4+}} \rightarrow \mathrm{MAOO\cdot} + \mathrm{Ce^{3+}} + \mathrm{H^+}\,. \qquad (c)$$

This sequence of reaction steps is essential for the oxygen-catalysed oxidation of malonic acid with $Ce^{4+}$ ions. The analogous oxidation of citric acid and 2,4-pentanedione follows probably the same mechanism. The described influence of oxygen on the basic parameters of the B.–Zh. reaction can be elucidated mainly by the catalysis of the substrate oxidation with $Ce^{4+}$ ions by means of oxygen. The reaction steps $(a-c)$ can be assumed also in the F.K.N. mechanism if oxygen is present in the reaction system.

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