Oscillating reaction of the Belousov—Zhabotinskii type with ninhydrin

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Received 1 September 1986

The topic of this paper is spectrophotometric and polarographic study of the oscillating reaction of the Belousov—Zhabotinskii type proceeding in the presence and absence of air oxygen with ninhydrin as substrate. A significant effect of stirring of the system on the course of the oscillating reaction at 15°C was observed. Owing to this effect, the time of duration of oscillations may increase even 17 times.

The thoroughly investigated dependence of the time of duration of the oscillation on concentration of bromates, ninhydrin, and initial concentration of the Br⁻ ions is discussed from the viewpoint of the Field—Köröš—Noyes (FKN) mechanism. In this connection, the key role of the intermediate HBrO₂ is corroborated.

The oscillating systems of the Belousov—Zhabotinskii type containing keto compounds have been given special attention because the stirring is not a necessary condition of oscillating course of a reaction in such systems. Janjic with his coworkers [1] was the first who observed that malonic acid in the Belousov—Zhabotinskii (BZ) system could be replaced by a simple keto compound, e.g., 2,4-pentanedione, fluorinated 2,4-pentanedione, 2,5-hexanedione, acetone [2, 3], cyclohexanone, and cyclopentanone [4—6]. The oscillating systems of this type are important also in reference with investigations of the influence of stirring, temperature, and oxygen on their oscillation behaviour [7, 8].
Recently, we investigated [9—18] the influence of oxygen and mechanical stirring on the modified BZ reaction in the presence of some keto compounds. As for the oscillating systems with keto compounds, a special attention should be paid to the oscillating system with the ethyl ester of 3-oxobutanoic acid [10, 12, 16—19] which exhibits the excitability induced by oxygen in the presence of ferroin [17, 18]. Besides the above keto compounds, the oxidation of 1,4-cyclohexanedione by bromate in the presence of the Mn(III) and Ce(IV) ions also exhibits an oscillating course [20, 21].

The influence of mechanical stirring on chemical oscillations in solutions has not hitherto been unambiguously elucidated. Farage and Janjic [7] assume that the mechanical stirring affects dissipative structures and thus violates the organization of system in space and time. They base their opinion on the observation that the oscillations vanish with increasing intensity of mechanical stirring. Sørensen [22] explains the suppression of oscillations at a certain critical rate of stirring as a result of turbulence. Patonay and Noszticzius [23] do not give agreement to the idea of a change in dissipative structure and turbulence and explain the effect of stirring by an increased supply of air oxygen. On the other hand, Habashi-Krayenbuhl and Janjic [24] have come on the basis of their observations to the conclusion that both the mentioned factors influence the number of oscillations and the length of induction period. According to Ruoff [25], the amplitude as well as the frequency of oscillations depends on intensity of stirring.

In this paper, we report on an oscillating reaction of the BZ type with further keto compound, i.e. ninhydrin in coherence with the outlined problems.

**Experimental**

The spectrophotometric measurements were carried out with a spectrophotometer Specord UV VIS (Zeiss, Jena) equipped with 10 mm cells which were placed in the thermostated block joined to an Ultrathermostat TM 150 (Medingen). The course of the oscillating reaction was investigated by the use of the time dependence of the absorbance at the wavenumber of $28 \times 10^3 \text{cm}^{-1}$ corresponding to the Ce(IV) ions.

A polarograph LP 7 (Laboratorní přístroje, Prague) was used for polarographic measurements. A rotating platinum electrode (Type M 22, Radiometer, Copenhagen) served for indication electrode. The reaction system was placed in a Kalousek vessel with separated mercurous sulfate electrode which was equipped with a thermostated jacket joined to the above-mentioned ultrathermostat. The polarographic measurements were performed in the presence of air oxygen or in the inert atmosphere of nitrogen (nitrogen of electric bulb industry). The flow of gas was controlled by a capillary flow-meter.

All chemicals used were anal. grade reagents. Redistilled water was used for preparing the solutions.
OSCILLATING REACTION WITH NINHYDRIN

Results

The reaction system consisting of $2 \text{M-H}_2\text{SO}_4$, $3 \times 10^{-2} \text{M-KBrO}_3$, $4 \times 10^{-4} \text{M-Ce(SO}_4)_2$, and $3 \times 10^{-2} \text{M ninhydrin}$ exhibits regular oscillations of absorbance after the lapse of the induction period even if the solution is not mechanically stirred. For instance, if the system is stirred immediately at the reaction start at $35^\circ\text{C}$ and the induction period goes by, the period of oscillations increases whereas their amplitude gradually decreases with time. If the system is also stirred at the expiration of the induction period, the time of

![Fig. 1](image1.png)

*Fig. 1.* Spectrophotometric record of the course of the oscillating reaction with ninhydrin. $2 \text{M-H}_2\text{SO}_4$, $3 \times 10^{-2} \text{M-KBrO}_3$, $4 \times 10^{-4} \text{M-Ce(SO}_4)_2$, $3 \times 10^{-2} \text{M ninhydrin}$, temperature $35^\circ\text{C}$, wavenumber $28 \times 10^3 \text{ cm}^{-1}$.

a) System stirred only at the beginning of reaction; b) system stirred at the start of oscillation regime, too.

![Fig. 2](image2.png)

*Fig. 2.* Influence of stirring of the system at the start of oscillation regime at $25^\circ\text{C}$. For composition of solution see *Fig. 1*, wavenumber $28 \times 10^3 \text{ cm}^{-1}$.

a) System stirred only at the beginning of reaction; b) system stirred at the start of oscillation regime, too.
Table 1
Dependence of characteristic quantities of the oscillating reaction on concentration of ninhydrin
2M-H$_2$SO$_4$, 3 x 10$^{-2}$ M-KBrO$_3$, 4 x 10$^{-4}$ M-Ce(SO$_4$)$_2$, temperature 20°C, air oxygen, potential of
Pt-electrode $E = 0.5$ V

<table>
<thead>
<tr>
<th>$c$(ninhydrin)$ \times 10^2$ mol dm$^{-3}$</th>
<th>$\delta$/s</th>
<th>$T$/s</th>
<th>Time of duration of oscillations</th>
<th>Number of oscillations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1810</td>
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<td>79.7</td>
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<tr>
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<td>4.5</td>
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<td>6.0</td>
<td>349</td>
<td>22</td>
<td>33.5</td>
<td>53</td>
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</table>

$\delta$ — induction period; $T$ — period of the first oscillation.

duration of oscillations decreases by 16 % (Fig. 1). At 25°C the mechanical
stirring of the solution before the end of the induction period brings about a
prolongation of the time of duration of oscillations as much as by 92 % (Fig. 2).
This effect is more conspicuous at 15°C. The mechanical stirring of the solution
at the beginning of the oscillation regime causes a 17-fold prolongation of this
regime and the overall time of duration of oscillations rises from 2.8 min to 49.8
min.

For the above composition of the system the dependence of the period of the
first oscillation on temperature was investigated in the temperature interval
5°C—45°C. The apparent activation parameters $E_0 = 31.7$ kJ mol$^{-1}$ and the
preexponential factor $A = 1.3 \times 10^4$ s$^{-1}$ were evaluated by means of the Ar-
henius equation.

The oscillating system of the above composition was also investigated po-
larographically on the basis of the time dependence of the polarographic dif-
fusion current at constant potential of the rotating Pt-electrode (from +0.2 V
to +0.65 V). It has been ascertained that the main parameters of the oscillation
reaction (induction period, period of the first oscillation, frequency and time of
duration of oscillations) do not depend on the value of potential in the inves-
tigated interval in the presence of air oxygen as well as in the inert atmosphere
of nitrogen. A part of the amplitude of oscillations passes from the cathodic to
anodic region at the values of potential of the indication electrode between
+0.6 V and 0.65 V. If the system is not bubbled through by nitrogen, we cannot
Dependence of characteristic quantities of the oscillating reaction on concentration of bromates

\[ 2M-H_2SO_4, 4 \times 10^{-4}\text{ M-Ce(SO}_4)_2, 3 \times 10^{-2}\text{ M ninhydrin, temperature 20°C, air oxygen, potential of Pt-electrode } E = 0.5\text{ V} \]

<table>
<thead>
<tr>
<th>(c(\text{BrO}_3^-) \cdot 10^2)</th>
<th>(\delta_i/s)</th>
<th>(T_i/s)</th>
<th>Time of duration of oscillations</th>
<th>Number of oscillations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td></td>
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<td></td>
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<tr>
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<td>23</td>
<td>3.4</td>
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<td>3.0</td>
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<td>54.5</td>
<td>43</td>
</tr>
<tr>
<td>4.0</td>
<td>723</td>
<td>50</td>
<td>41.4</td>
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<td>5.0</td>
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<td>70</td>
<td>26.7</td>
<td>15</td>
</tr>
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<td>6.0</td>
<td>1569</td>
<td>102</td>
<td>15.9</td>
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<tr>
<td>7.0</td>
<td>1560</td>
<td>121</td>
<td>15.5</td>
<td>7</td>
</tr>
</tbody>
</table>

\(\delta_i\) — induction period; \(T_i\) — period of the first oscillation.

reliably investigate the course of oscillations at potential values ranging from +0.2 V to +0.4 V because the oscillations are overlapped by the current of accumulating bromine.

Special attention was paid to investigation of the dependence of induction period, period of the first oscillation, time of duration of oscillations, and number of oscillations on concentration of ninhydrin (Table 1). The time of duration of oscillations decreases with increasing concentration of substrate from 79 min to 41 min. It passes through a minimum at the concentration of ninhydrin of \(10^{-2}\text{ mol dm}^{-3}\), afterwards it increases and passes through a maximum at the concentration of ninhydrin of \(2.5 \times 10^{-2}\text{ mol dm}^{-3}\) and subsequently it decreases nonlinearly. If we introduce the dimensionless parameter \(q\) as ratio of the initial concentration of bromates to the initial concentration of substrate, the maximum value of the time of duration of oscillations is attained at \(q = 1.2\) while the minimum is at \(q = 3\).

Similarly, we investigated the dependence of characteristic quantities of the oscillating system on concentration of bromates (Table 2). It is remarkable that the dependence of the time of duration of oscillations on concentration of bromates also passes through a maximum, namely at the value \(q = 0.83\).

As the \(\text{Br}^-\) ions play an important part in chemical oscillations of the BZ type, we investigated the dependence of characteristic quantities of the oscillation system on initial concentration of the \(\text{Br}^-\) ions (Table 3). It can be seen from Table 3 that the time of duration of oscillations almost linearly decreases with increasing concentration of the \(\text{Br}^-\) ions in contrast to the number of oscillations which first increases, passes through a maximum and then decreases.
Table 3
Dependence of characteristic quantities of the oscillating reaction on concentration of the Br⁻ ions

\[ 2\text{M-H}_2\text{SO}_4, 3 \times 10^{-2} \text{M-KBrO}_3, 4 \times 10^{-4} \text{M-Ce(SO}_4)_2, 3 \times 10^{-2} \text{M ninhydrin}, \text{temperature 20}^\circ\text{C, air oxygen, potential of Pt-electrode } E = 0.5 \text{ V} \]

<table>
<thead>
<tr>
<th>(c(\text{Br}^-)/(\text{mol dm}^{-3}))</th>
<th>(\delta_i/s)</th>
<th>(T_i/s)</th>
<th>Time of duration of oscillations</th>
<th>Number of oscillations</th>
</tr>
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<tr>
<td>0</td>
<td>370</td>
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<td>(10^{-5})</td>
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<td>(10^{-4})</td>
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<td>(10^{-3})</td>
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<tr>
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<tr>
<td>(10^{-2})</td>
<td>0</td>
<td>36</td>
<td>26.0</td>
<td>35</td>
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</tbody>
</table>

\(\delta_i\) — induction period; \(T_i\) — period of the first oscillation.

The oxidation of ninhydrin (2,2-dihydroxy-1,3-indandione) by potassium bromate in solution of sulfuric acid and in the absence of redox catalyst is governed by the first-order kinetics. The value of the rate constant measured in the solution containing \(\text{H}_2\text{SO}_4 (c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}), \text{ninhydrin} (c(\text{ninhydrin}) = 2.5 \times 10^{-2} \text{ mol dm}^{-3}), \) and potassium bromate \((c(\text{KBrO}_3) = 2.5 \times 10^{-1} \text{ mol dm}^{-3})\) at \(5^\circ\text{C and 25}^\circ\text{C was } k = 6.9 \times 10^{-4} \text{ s}^{-1} \) and \(k = 1.6 \times 10^{-2} \text{ s}^{-1}, \) respectively.

Discussion

The oscillating system of the BZ type with ninhydrin as well as the hitherto known oscillating systems with keto compounds is interesting by the fact that it exhibits oscillations of concentration of the redox catalyst even without mechanical stirring of the solution. On the other hand, an appreciable effect of stirring was observed in the temperature region \(15^\circ\text{C—25}^\circ\text{C if the system was stirred at the beginning of the oscillation regime. The cause may not consist in an increase in supply of air oxygen into the reaction system and the effect cannot be explained by an accidental concentration increase of ninhydrin owing to stirring of the maybe oversaturated system. The cause of this effect is to be seen in violation of some sort of “equilibrium” of temporal and spatial dissipative structure of the investigated system. Another alternative explanation could be based on the phenomenon of oxygen-induced excitability which was described by us recently [17, 18].
The results obtained by the use of spectrophotometry and polarography complete one another. The oscillations of polarographic current in the region of less positive potentials correspond predominantly to the Ce\(^{4+}\) ions while the oscillations recorded at more positive potentials in the anodic region may be attributed to the Br\(^{-}\) ions. The oscillations due to the Ce\(^{4+}\) ions as well as the oscillations due to the Br\(^{-}\) ions proceed with equal frequency but with a phase shift and, for this reason, the evaluated values concerning the BZ reaction are independent of potential of the indication electrode.

Considerable attention was given to the dependence of characteristic quantities of the oscillating reaction on concentration of the substrate in the presence of air oxygen. The dependence of the induction period on concentration of ninhydrin may be linearized if the induction period is plotted against inversion value of the concentration of substrate. The fact that the induction period as well as the period of the first oscillation nonlinearly decreases with increasing concentration of the substrate is in line with the FKN mechanism according to which the course of oscillations significantly depends on the rate of formation of the bromo derivative of substrate. The dependence of the time of duration of oscillations on concentration of ninhydrin and bromates indicates that the interval of the values of \(q\) between 0.83 and 1.2 represents the most favourable conditions for the time of duration of oscillations. If we take into account ninhydrin as a two-electron reducing agent and the parallel noncatalytic course of oxidation of the substrate by bromates, the value \(q \approx 1\) corresponds to the best conditions of origination of the intermediate HBrO\(_2\) which plays the main role in the oxidation course from the viewpoint of the FKN mechanism [26]. The competition between the Br\(^{-}\) and BrO\(_3^-\) ions for interaction with the intermediate HBrO\(_2\) is, from the viewpoint of the FKN mechanism, the principle of the alternation of process (B) and process (C) which controls the oscillation course and thus the time of duration of oscillations.

If we compare the results measured in nitrogen atmosphere with the results obtained in the presence of air oxygen, we can observe difference. The presence of air oxygen is an intervention into the reaction system in the sense that oxygen reacts most probably with the radical intermediates which arise in oxidation of ninhydrin by the Ce\(^{4+}\) ions.

The added Br\(^{-}\) ions have significant influence on the time of duration of oscillations. Table 3 shows that the time of duration of oscillations almost linearly decreases with increasing concentration of bromides which may be interpreted according to the FKN mechanism on the basis of process (A) [26]

\[
\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightarrow \text{HBrO}_2 + \text{HOBr} \quad (A)
\]

\[
\text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightarrow 2\text{HOBr} \quad (B)
\]
\[
\text{HOBr} + \text{Br}^- + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O} \quad (C)
\]
\[
\text{Br}_2 + \text{ninhydrin} \rightarrow \text{Br-ninhydrin} + \text{Br}^- + \text{H}^+ \quad (D)
\]

We have to deal with a system of consecutive reaction stages the reaction rate of which shall increase with concentration of the Br\(^-\) ions. This fact gives rise to reduction of the quasi-stationary concentrations of HBrO\(_2\) and HOBr the values of which have evidently decisive influence on the time of duration of oscillations, as stated earlier.

References


Translated by R. Domanský