OSCILLATION SYSTEM OF BELOUSOV-ZHABOTINSKII TYPE IN PRESENCE OF Cl⁻ IONS

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Dedicated to Prof. A. Tockstein on the occasion of his 60th birthday.

A modified Belousov–Zhabotinskii oscillation system involving ethyl ester of 3-oxobutanoic acid and $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ as redox catalyst is remarkable in that it shows an oxygen-induced excitability. The oscillating state, involving 4–5 oscillations in the absorbancy of $Fe(phen)_3^{2+}$ ions, comes soon to its end but can be restored by shaking the reaction system, thus increasing the transport of oxygen from the air. This phenomenon is not influenced by Cl^- ions in a low concentration, but if this is equal to 10^{-3} mol dm^{-3} or higher, no oscillations are observed, the increase of the concentration of $Fe(phen)_3^{2+}$ ions is autocatalytic in character and can be reproduced several times by shaking or stirring the solution. These phenomena are discussed in terms of a probable reaction mechanism.

The inhibition of the Belousov–Zhabotinskii (BZ) oscillation reaction involving dicarboxylic acids by the action of Cl^- ions was already reported by Zhabotinskii[1]. Janjic and coworkers[2] described an inhibition effect of Cl^- ions on the BZ reaction, in which the dicarboxylic acid was replaced by a diketone, *e.g.* 2,4-pentanedione. Recently, we reported a modified BZ system with $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ as redox catalyst and ethyl ester of 3-oxobutanoic acid as substrate[3]. The use of the redox catalyst ferroine–ferriine is especially important in studies of space structures, so-called chemical waves[4]; the mechanism of the oscillation reaction based on ferroine-catalysed oxidation of bromomalonic acid with bromates corresponds better to the mathematical model "Oregonator" than systems with other catalysts[5], and the use of ethyl ester of 3-oxobutanoic acid ensures the homogeneity of the oscillation system[6]. Therefore, we studied the behaviour of the mentioned oscillation system in the presence of Cl^- ions.

From the point of view of the BZ oscillation reaction, the autocatalytic oxidation of $Fe(phen)_3^{2+}$ ions with bromates is of basic importance. Its kinetics and mechanism depend on the concentration ratio of the reactants[7]. For $[Fe(phen)_3^{2+}] \lessgtr [BrO_3^-]$, the rate-determining step is the dissociation of $Fe(phen)_3^{2+}$ ions. For $[Fe(phen)_3^{2+}] \ll [BrO_3^-]$ the reaction is autocatalytic. According to Rovinskii and Zhabotinskii[8], its kinetics may be described by the mechanism proposed for the analogous oxidation of Ce^{3+} ions with bromates[9]. The kinetics of the reaction of $Fe(phen)_3^{2+}$ ions with bromates were studied also by Yoshida and coworkers[10], according to whom the decrease of ferroine in acidic medium in the absence of bromates is caused by the dissociation of $Fe(phen)_3^{2+}$ to $Fe(phen)_2H_2O^{2+}$ and a phenanthroline molecule. Fösterling and coworkers[11] showed that a $BrO_2^{\bullet}$ radical is formed as intermediate product during oxidation of Ce^{3+} ions with bromates in a solution of sulphuric acid.

Differences between the Ce^{3+} and $Fe(phen)_3^{2+}$ catalysts in the BZ reaction were already pointed out by Smoes[4]. According to Noyes and coworkers[12,13], $Fe(phen)_3^{2+}$ ions participate in two steps of the original Field–Körös–Noyes mechanism, namely

$$Fe(phen)_3^{2+} + HOBr + H^+ \rightarrow Fe(phen)_3^{3+} + Br^{\bullet} + H_2O \qquad (A)$$

$$Fe(phen)_3^{3+} + ZH \rightarrow Fe(phen)_3^{2+} + Z^{\bullet} + H^+ , \qquad (B)$$

where ZH denotes an organic substrate. Since these steps are thermodynamically not favourable, the authors consider an alternate mechanism with the steps

$$2\,Fe(III) \rightleftarrows Fe(IV) + Fe(II) \qquad (C)$$

$$Fe(II) + HOBr + H^+ \rightarrow Fe(IV) + Br^- + H_2O \qquad (D)$$

$$Fe(IV) + ZH + H_2O \rightarrow Fe(II) + ZOH + 2\,H^+ . \qquad (E)$$

Since the value of E^0 for the Fe(IV)/Fe(II) system is equal to 1·2–1·3 V, the last two steps appear probable, although the equilibrium (*C*) is shifted too much to the left side for Fe(IV) to be observable. The mentioned interpretation of the catalytic action of $Fe(phen)_3^{2+}$ ions in the BZ reaction was not proved, and the kinetics of the reduction of $Fe(phen)_3^{3+}$ ions with ethyl ester of 3-oxobutanoic acid was hitherto not studied.

The inhibition effect of Cl^- ions on the BZ reaction with malonic acid was studied in detail by Jacobs and Epstein[14], according to whom these ions are oxidized to ClO_2^- ions, which in turn reduce Ce(IV) and thus prevent oscillations. The oscillations reappear as soon as the intermediate product $HClO_2$ is totally oxidized to $HClO_3$. Thus, the oxidation of chloride ions proceeds as

$$2\,Cl^- + 3\,H^+ + 3\,BrO_3^- \rightarrow 3\,HOBr + 2\,ClO_3^- . \qquad (F)$$

The present work deals with the modified BZ reaction system H_2SO_4–$KBrO_3$–$Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$–$CH_3COCH_2COOC_2H_5$ in the presence of Cl^- ions, which influence the kinetics of oxidation of $Fe(phen)_3^{2+}$ with BrO_3^- and reduction of $Fe(phen)_3^{3+}$ with the organic substrate.

EXPERIMENTAL

Chemical oscillations were followed spectrophotometrically by using a UV—VIS Spectrophotometer (Carl Zeiss, Jena) and measuring the absorbancy at a wavelength $\nu = 22\,000\ \text{cm}^{-1}$. The reaction system was in a cylindrical cuvette, which was 10 cm long. Another cuvette of the same dimensions and shape with 0·8—1·0 mol dm^{-3} H_2SO_4 served for comparison.

The time dependence of the absorption spectra was measured with the same apparatus and a 1 or 3 cm thick cuvette placed in a thermostated block, which was connected with an ultrathermostat TM 150 (Medingen, G.D.R.).

The kinetics of oxidation of ferroine with bromate ions in 0·8 mol dm^{-3} H_2SO_4 in the absence of Cl^- ions was followed by means of a Stopped-flow spectrophotometer (Aminco-Morrow, U.S.A.). The dependence of absorbancy on the time at a wave length of 520 nm was obtained on a storage oscilloscope Tektronix 5103 N with a time constant 0·1 s/cm. The voltage of the photomultiplier was 360 V.

Solutions were prepared from redistilled water and reagent grade chemicals.

RESULTS

Influence of Cl^- *Ions on the Oscillation System*

The modified BZ oscillation system with ethyl ester of 3-oxobutanoic acid and redox catalyst $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ is remarkable in that it shows oxygen-induced excitability[3]. Its optimum composition is 0·8 – 1·1 mol dm^{-3} H_2SO_4, 0·07 mol . . dm^{-3} $KBrO_3$, 6 . 10^{-4} mol dm^{-3} $Fe(phen)_3^{2+}$, 1·5 . 10^{-3} mol dm^{-3} ethyl 3-oxobutanoate. The oscillation state consists of 4 – 5 oscillations of absorbancy in the wavelength range 19 – 22 . 10^3 cm^{-1} corresponding to $Fe(phen)_3^{2+}$, and it can be restored by shaking the cuvette with the reaction solution when the oscillations come to their end. This can be repeated several times (Fig. 1).

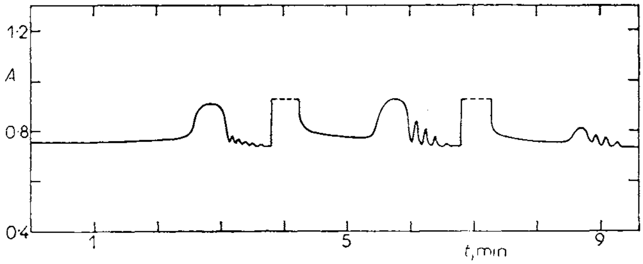

FIG. 1

Oscillations of absorbancy of $Fe(phen)_3^{2+}$ in presence of Cl^- ions. 0·8 mol dm^{-3} H_2SO_4, 0·07 mol dm^{-3} $KBrO_3$, 6 . 10^{-4} mol dm^{-3} ferroine, 1·5 . 10^{-3} mol dm^{-3} CH_3COCH_2. .$COOC_2H_5$, 10^{-4} mol dm^{-3} NaCl; 10 cm cylindrical cuvette, 25°C, $\nu = 22\,000\ \text{cm}^{-1}$. Dashed part corresponds to stirred system

This phenomenon is not influenced by the presence of Cl^- ions at low concentrations (from 10^{-5} to 10^{-4} mol dm^{-3}). With increasing concentration of Cl^- ions, the oscillations decrease until they disappear at $7{\cdot}5 \, . \, 10^{-4}$ mol dm^{-3}. At 10^{-3} mol . . dm^{-3} Cl^- the curve becomes monotonous: After an induction period of about 100 s the absorbancy at $\nu = 22\,000$ cm^{-1} corresponding to $Fe(phen)_3^{2+}$ ions increases in an S-like shape to a limiting value. By shaking or stirring the system returns into its initial state (or to a lower level of the stationary state), from which it spontaneously arrives at the higher stationary state (by an S-shaped curve, Fig. 2). This can be repeated many times.

The effect of shaking or stirring the BZ reaction system at higher concentrations of Cl^- ions (0·001 – 0·04 mol dm^{-3}) was also followed by visible absorption spectroscopy (Fig. 3). During the initial stage of the reaction, the absorbancy of $Fe(phen)_3^{3+}$ decreases and that of $Fe(phen)_3^{2+}$ increases to a maximum, after which it also decreases, as can be seen from Fig. 4 (here the wave number 19 300 cm^{-1} corresponds to maximum absorbancy). The time of attainment of the maximum, t_{max}, decreases with increasing concentration of Cl^- ions and temperature.The following values were obtained with the system 0·8 mol dm^{-3} H_2SO_4, 0·07 mol dm^{-3} $KBrO_3$, $6 \, . \, 10^{-4}$ mol dm^{-3} $Fe(phen)_3^{2+}$, and $1{\cdot}5 \, . \, 10^{-3}$ mol dm^{-3} $CH_3COCH_2.COOC_2H_5$ at 35°C; dependence on c_{NaCl}

10^3c, mol dm^{-3}	0·75	1·0	1·5	2·5	3·0	3·5
t_{max}, s	1 270	1 061	631	272	195	123

and dependence on the temperature (c_{NaCl} = 0·02 mol dm^{-3})

T, °C	5	15	25	35
t_{max}, s	5 325	2 708	965	408

If the reaction system is stirred for 1 – 2 min close to the maximum in absorbancy, the absorbancy of $Fe(phen)_3^{2+}$ ions decreases and that of $Fe(phen)_3^{3+}$ somewhat increases (Fig. 5).

In the absence of Cl^- ions, the dissociation

$$Fe(phen)_3^{3+} \rightleftarrows Fe(phen)_2H_2O^{3+} + phen \qquad (G)$$

is the rate-limiting step in reduction of $Fe(phen)_3^{3+}$ with ethyl 3-oxobutanoate, while no absorption band of $Fe(phen)_3^{2+}$ appears. From the time dependence of the absorbancy at 16 700 cm^{-1}, we evaluated the rate constant in 0·8 mol dm^{-3} H_2SO_4 at 35°C as $k = 3{\cdot}3 \, . \, 10^{-4}$ s^{-1}. The increase in the absorbancy at 22 000 cm^{-1} due to reduction of $Fe(phen)_3^{3+}$ ions with the ester in the presence of 0·01 mol dm^{-3} NaCl corresponds to increasing concentration of $Fe(phen)_3^{2+}$ ions. Their concentration in the reaction system in sensitive to oxygen. The transport of oxygen from the air is increased by stirring the system, resulting in oxidation of a part of the $Fe(phen)_3^{2+}$ ions to $Fe(phen)_3^{3+}$; this is, however, possible only in the presence of all the components (*i.e.* bromate, substrate, and Cl^- ions) (Fig. 5).

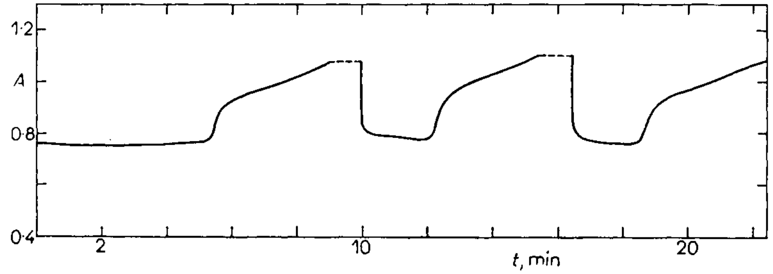

FIG. 2

Influence of stirring on the reaction course in presence of 10^{-3} mol dm^{-3} NaCl. Experimental conditions as in Fig. 1, dashed part corresponds to stirred system

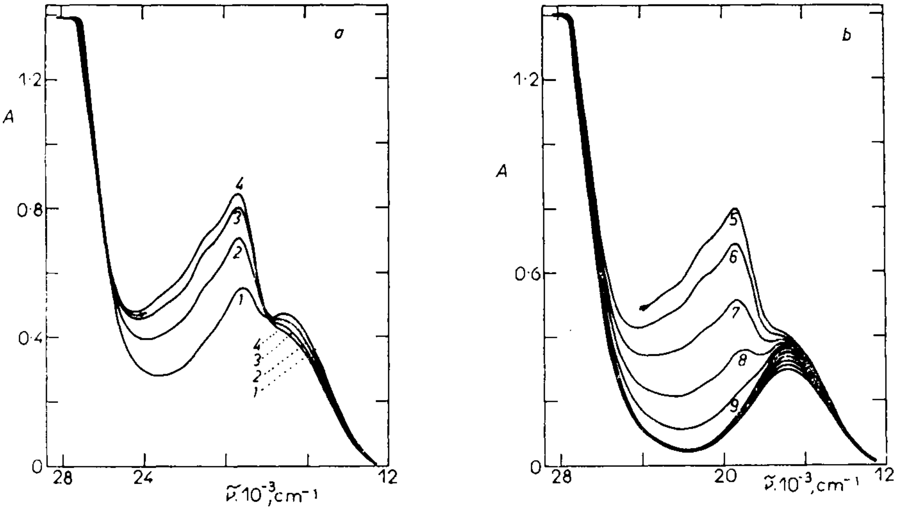

FIG. 3

Time dependence of absorption spectrum. Solution composition as in Fig. 1, but 0·01 mol dm^{-3} NaCl; 1 cm cuvette, 35°C. *a* Increasing absorption of $Fe(phen)_3^{2+}$; *b* decreasing absorption of $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$. Numbering of the curves denotes time sequence at 8 min intervals

Influence of Cl^- *ions on the Kinetics of Oxidation of* $Fe(phen)_3^{2+}$ *Ions with Bromate*

The oxidation of $Fe(phen)_3^{2+}$ with BrO_3^- ions in a solution of sulphuric acid was followed spectrophotometrically by measuring the time dependence of the absorbancy at a wave number 16 700 cm^{-1} corresponding to maximum absorption of $Fe(phen)_3^{3+}$ ions. The initial concentrations were 0·8 mol dm^{-3} H_2SO_4, 0·07 mol dm^{-3} $KBrO_3$ and $6 . 10^{-4}$ mol dm^{-3} ferroine. After an induction period of 20 – 30 s, the absorbancy increases linearly with the time, evidence for kinetics of the order zero. The cor-

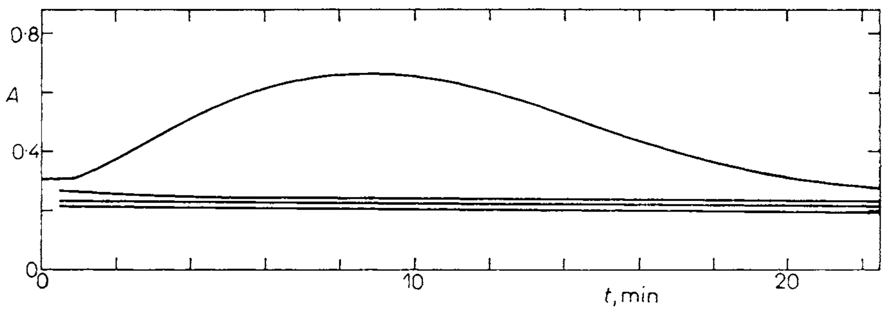

Fig. 4

Time dependence of absorbancy of $Fe(phen)_3^{2+}$ ions at $\nu = 19\,300\ cm^{-1}$. Experimental conditions as in Fig. 3

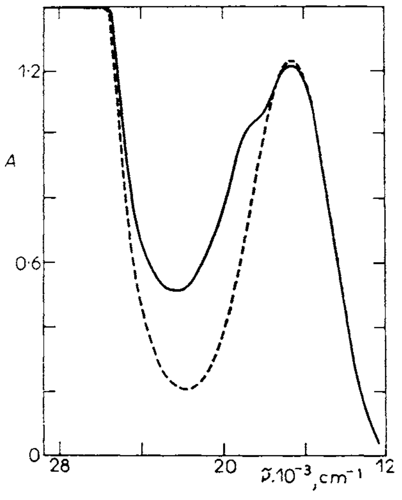

Fig. 5

Influence of stirring on absorption spectrum. Solution of 0·8 mol dm^{-3} H_2SO_4, 0·07 mol . dm^{-3} $KBrO_3$, $6 . 10^{-4}$ mol dm^{-3} ferroine, $1·5 . 10^{-3}$ mol dm^{-3} $CH_3COCH_2.COOC_2H_5$, $2 . 10^{-3}$ mol dm^{-3} NaCl; 3 cm cuvette, 25°C. Dashed curve was recorded after stirring responding rate constant, calculated from the slope of the linear dependence, depends on the concentration of Cl^- ions, c, as follows:

10^3c, mol dm^{-3}	1·0	1·5	2·0	3·0	5·0	7·5	10·0
10^7k, s^{-1} mol dm^{-3}	600	2·6	2·5	2·0	2·7	3·8	4·8

In the presence of 10^{-3} mol dm^{-3} NaCl, the value of k is relatively high, but it drops abruptly with increasing concentration, attains a minimum at $3 \,.\, 10^{-3}$ mol . . dm^{-3}, and then slightly increases.

DISCUSSION

The inhibition effect of Cl^- ions on the BZ reaction is important for the derivation of the reaction mechanism. According to Jacobs and Epstein[14], Cl^- ions disturb the autocatalysis in reaction (B) of the Field–Körös–Noyes mechanism[12,13] by the following reaction steps:

$$\mathrm{H}^+ + \mathrm{Cl}^- + \mathrm{HBrO}_2 \rightarrow \mathrm{HOBr} + \mathrm{HOCl} \qquad (H)$$

$$\mathrm{HOCl} + \mathrm{BrO}_3^- + \mathrm{H}^+ \rightarrow \mathrm{HBrO}_2 + \mathrm{HClO}_2 \qquad (I)$$

$$\mathrm{HClO}_2 + \mathrm{Ce(IV)} \rightarrow \mathrm{ClO}_2^{\bullet} + \mathrm{Ce(III)} + \mathrm{H}^+ \qquad (J)$$

$$\mathrm{BrO}_3^- + \mathrm{HBrO}_2 + \mathrm{H}^+ \rightarrow 2\,\mathrm{BrO}_2^{\bullet} + \mathrm{H}_2\mathrm{O} \qquad (K)$$

$$\mathrm{BrO}_2^{\bullet} + \mathrm{ClO}_2^{\bullet} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{H}^+ + \mathrm{HBrO}_2 + \mathrm{ClO}_3^- \,. \qquad (L)$$

By adding the reaction steps (H) through (L) we obtain

$$\mathrm{Cl}^- + 2\,\mathrm{BrO}_3^- + \mathrm{H}^+ + \mathrm{Ce(IV)} \rightarrow \mathrm{HOBr} + \mathrm{BrO}_2^{\bullet} + \mathrm{ClO}_3^- + \mathrm{Ce(III)}\,, \qquad (M)$$

and further by adding the oxidation step of Ce(III) with $\mathrm{BrO}_2^{\bullet}$ and disproportionation of HBrO_2, we obtain the resulting reaction (F).

Our BZ oscillation system, which shows oxygen-induced excitability[3], is less sensitive to Cl^- ions than the classical BZ system with malonic acid as substrate: the oscillations were suppressed when the concentration of Cl^- ions reached $7{\cdot}5 \,.\, 10^{-4}$ mol dm^{-3}. The relatively smaller inhibition effect may be due to the fact that some Cl^- ions are consumed in the reaction

$$\mathrm{Fe(phen)}_3^{2+} + 2\,\mathrm{Cl}^- \rightleftarrows \mathrm{Fe(phen)}_3^{2+}\,,\ 2\,\mathrm{Cl}^- \rightleftarrows$$

$$\rightleftarrows \mathrm{Fe(phen)_2Cl_2} + \mathrm{phen}\,, \qquad (N)$$

where the formation of the uncharged complex is preceded by the transitory ion pair $\mathrm{Fe(phen)_3^{2+}}$, 2 $\mathrm{Cl^-}$. Interaction of $\mathrm{Fe(phen)_3^{3+}}$ with $\mathrm{Cl^-}$ ions may be considered analogously. The unreacted $\mathrm{Cl^-}$ ions cause inhibition in the concentration range as in the BZ reaction with malonic acid.

The formation of ion pairs and/or chloride complexes apparently has a marked effect on the kinetics and mechanism of oxidation of $\mathrm{Fe(phen)_3^{2+}}$ ions with bromate or oxygen and reduction of $\mathrm{Fe(phen)_3^{3+}}$ with the ester. The mentioned inhibiting effect of $\mathrm{Cl^-}$ ions on the rate of oxidation of $\mathrm{Fe(phen)_3^{2+}}$ with bromate may be attributed to the fact the rate-determining step involves interaction of two uncharged particles and a proton according to the scheme

$$\mathrm{Fe(phen)_3^{2+}, 2\,Cl^-} \;\text{ or }\; \mathrm{Fe(phen)_2Cl_2} + \mathrm{HOBr} + \mathrm{H^+} \rightarrow$$
$$\rightarrow \text{ferriine} + \mathrm{Br^{\bullet}} + \mathrm{H_2O}\,. \qquad (O)$$

The zeroth order is in agreement with the concept that the step (O) is preceded by the reversible formation of the ion pair or uncharged complex in step (N). Such a scheme is also supported by the experimental fact that the $\mathrm{Fe(phen)_3^{2+}}$ ions are generated by reduction of $\mathrm{Fe(phen)_3^{3+}}$ ions with the ester only if the concentration of $\mathrm{Cl^-}$ ions is high enough.

The described return from the higher to the lower stationary state caused by stirring is due to repeated supply of atmospheric oxygen, which is consumed in the reaction. Recently, we proposed a more exact reaction scheme elucidating the influence of oxygen on the BZ reaction in the presence of the redox catalyst Mn(II)/ /Mn(III) and malonic acid as substrate[15]. This is based on the effect of oxygen on the oxidation of the substrate with Mn(III) ions, where the following concurrent reaction steps of peroxomalonic acid (MAOOH) play an important role:

$$\mathrm{MAOOH} + \mathrm{Mn^{3+}} \rightarrow \mathrm{MAOO^{\bullet}} + \mathrm{Mn^{2+}} + \mathrm{H^+} \qquad (P)$$

$$\mathrm{MAOOH} + \mathrm{Mn^{2+}} + \mathrm{H^+} \rightarrow \mathrm{MAO^{\bullet}} + \mathrm{Mn^{3+}} + \mathrm{H_2O}\,. \qquad (Q)$$

Analogous reaction steps are likely to play a role also in the system studied in the present work. The oxidation of $\mathrm{Fe(phen)_3^{2+}}$ with oxygen proceeds in a reaction step analogous to (Q) and the influence of $\mathrm{Cl^-}$ ions is taken into account by step (N).

The oxygen-induced excitability of our BZ system[3] can be elucidated by assuming that even in the absence of $\mathrm{Cl^-}$ ions the oscillations are conditioned by a sufficient concentration of oxygen which is restored by stirring the system after the oxygen is exhausted, *i.e.* by increasing its transport from the gas phase.

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