THE AUTOCATALYTIC OXIDATION OF IODINE WITH HYDROGEN PEROXIDE IN RELATION TO THE BRAY–LIEBHAFSKY OSCILLATORY REACTION

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The oxidation of iodine with hydrogen peroxide was studied spectrophotometrically and potentiometrically. At low concentrations of $HClO_4$, after induction period (IP), the iodine concentration decreases sigmoidally and IP decreases with decreasing surface area of the solution interphase. We assume that $^{\bullet}OH$ radicals are produced via the oxidation of iodide with H_2O_2 and, by their subsequent reaction with H_2O_2, the $HO_2^{\bullet}$ radicals are formed. By their disproportionation, $2\ HO_2^{\bullet} \rightleftharpoons H_2O_2 + {}^1O_2$, very reactive singlet oxygen is produced and the oxidation of iodine can start. The described experimental results are consistent with the Noyes–Treindl mechanism.

Keywords: Autocatalytic reaction; Oxidation of iodine; Bray–Liebhafsky reaction; Singlet oxygen intermediate; Oxidation with hydrogen peroxide; Noyes–Treindl reaction scheme.

The Bray–Liebhafsky (BL) reaction is based on the disproportionation of aqueous solution of hydrogen peroxide catalyzed by iodates. After an induction period, oscillations in iodine and/or iodide concentration can be observed and hydrogen peroxide is periodically consumed[1–10]. One- and two-dimensional traveling wave fronts have been observed in acidic mixtures of iodine, hydrogen peroxide, and starch[6]. Despite a large number of papers devoted to the mechanism of the BL reaction, almost 80 years after its discovery, no agreement about its mechanism has been reached.

In 1993 one of us was honored to collaborate with Prof. R. M. Noyes at the University of Oregon and, on the basis of this collaboration, a new ex-

planation of the oscillations in the BL reaction has been proposed[8]. According to the proposed skeleton reaction mechanism, H_2O_2 is oxidized only with HOI, the real oxidant is O_2, and H_2O_2 itself can oxidize no other iodine-containing species than iodide ion, even though H_2O_2 is the only oxidant in the overall stoichiometry for one of the two main processes of the BL reaction. The influence of MoO_4^{2-} ions on the BL oscillatory reaction as well as on the oxidation of iodine with hydrogen peroxide[11,12] have been qualitatively explained by the mentioned skeleton mechanism and the production of singlet oxygen ($^1O_2$) by disproportionation of hydrogen peroxide catalyzed by molybdate[13–16] has been also taken into account. The kinetics of autoxidation of iodine in acidic solutions has been studied and its autocatalytic character has been observed[17]. The proposed reaction scheme seems to be in accordance with the mentioned skeleton mechanism[8].

Schmitz[18] has considered the reactions of oxygen not to be a necessary part of the explanation of oscillations in the BL reaction. According to him[18], the chemical effects of oxygen result mainly from the oxidation of iodide by radical processes and the release of oxygen has also a physical effect, loss of iodine in the gas phase. Recently, the kinetics of the oxidation of iodine to iodate with hydrogen peroxide was studied also by Schmitz[19], and the results were discussed from the viewpoint of his model previously proposed for the BL reaction. In the meantime, it has been pointed out that chemical processes may couple with both oxygen and iodine nucleation and evolution causing enhancement or suppression of oscillations in the BL system[20]. Agreda et al.[21] have reported stopped-flow kinetic evidence for both the participation and accumulation of a stoichiometrically significant amount of $H_2I_2O_3$ in the Dushman reaction when $[KIO_3]_0 >> [KI]_0/5$, which may be also important in the discussion of the BL reaction. Very recently, Láňová et al.[22] studied the BL reaction by on-line mass spectrometry and found the sequence of species O_2, HOI, HIO_2 and I_2, which appear during the oscillations. Kéki et al.[23] devoted their attention to the effect of light on the BL reaction. They extended the reaction scheme proposed by Schmitz to a direct reaction of I_2 with H_2O_2.

In this paper, we have proved the autocatalytic character of the iodine oxidation with hydrogen peroxide, due to the formation of sufficient amount of oxygen and especially of singlet oxygen, which takes part in the reaction as an autocatalyst[8,11,12].

EXPERIMENTAL

Materials and Methods

Stock solutions of the components were prepared from commercially available chemicals, H_2O_2 p.a. (30%, Merck, Germany), $HClO_4$ p.a. (60%, Merck, Germany), I_2 p.a. (Centralchem, Slovakia), NaI p.a. (Centralchem, Slovakia), acrylamide for electrophoresis (Merck, Germany). All other reagents were of analytical grade. The H_2O_2 concentration was determined by iodometric titration and that of $HClO_4$ by alkalimetric titration. The iodine concentration was checked by thiosulfate titration. Fresh solutions of iodine and of hydrogen peroxide were prepared every day. Double-distilled water was used in all experiments. Heavy water (99.86%) (Institute for Research and Utilization of Radioisotopes, Prague, Czech Republic) was used for the preparation of binary mixtures.

Spectrophotometric measurements were performed using a Specord M 40 spectrophotometer (Carl Zeiss, Jena, Germany). Kinetic measurements were based on the measurements of absorbance (460 nm) corresponding to iodine and the absorbance (350 nm) corresponding to the I_3^- ions. A thermostatted 1-cm quartz cell with the orifice of 1 cm × 1 cm, or with the circle orifice ($r = 0.35$ cm), completely filled with solution, was placed in spectrophotometer. The measurements under illumination were carried out using a small lamp (2.4 V, 0.5 A). To avoid warming the reaction solution during illumination, the light passed through a glass filter.

The reaction course was followed also potentiometrically, by recording the time dependence of the I^-/I_2 redox potential (platinum electrode) against the potential of the saturated $Hg/Hg_2SO_4/K_2SO_4$ reference electrode. The concentration of the dissolved oxygen was determined using an oxygen-sensitive combined electrode RA-0950P (Radelkis, Hungary).

A cylindric vessel (height 5 cm, diameter 3 or 4 cm) was closed using a rubber plug with small tube (diameter 2 mm) to reduce pressure difference, with both electrodes and with a glass mantle connected to an ultra-thermostat. Reaction mixtures were kept in the dark as much as possible. The dependences were monitored with a digital multimeter Metex, M 4650CR connected to a PC. The collected data were worked up using the programs Gnuplot and Excel.

The measurements were performed mostly at 30 °C. The reaction system was intensively stirred ca. 10 s before the start of spectrophotometric or potentiometric recording. The value of induction period (IP) was determined with an accuracy of ±10%. The values of IP are averages of four independent measurements.

RESULTS AND DISCUSSION

Spectrophotometric Measurements

The oxidation of iodine with hydrogen peroxide was measured by monitoring the iodine absorption (*A*) at 460 nm. In mildly acidic solutions it proceeds very slowly in the absence of a catalyst and in an open cell (Fig. 1, curve *1*). If the reaction proceeds in a cell with a circular orifice, after IP, a sigmoidal decrease in absorbance can be observed, which indicates an auto-

catalytic process (Fig. 1, curve *2*). The value of IP decreases with decreasing surface area of the interphase (Fig. 1, curve *3*).

The observed effect is really striking and cannot be explained by the evaporation of iodine, which is insignificant under the applied conditions. If in the absence of H_2O_2 only iodine is present, its concentration decreases following just the first-order kinetics. The larger is the surface of the solution, the higher is the experimental first-order rate constant (Table I).

Comparing the $A = f(t)$ curves at two different initial concentrations of iodine with the same surface of solution (0.385 cm^2), the curves at 460 nm with a sigmoidal shape are almost identical. The decrease in the concentration of iodine has only a small effect on IP (Fig. 2, curves *1* and *2*). During IP, the absorbance at 350 nm corresponding to the I_3^- ions decreases exponentially with time to a certain critical concentration before the auto-

TABLE I
The dependence of the k_{exp} values on the surface of the solution[a]

Interphase area, cm^2	1	0.38	0.19
$10^3 k_{exp}$, min^{-1}	4.2	1.6	1.2

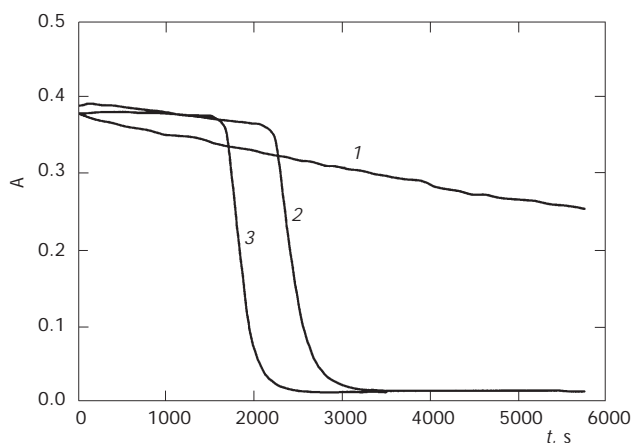[a] $[I_2]_0 = 5 \times 10^{-4}$ mol/l, $[HClO_4]_0 = 0.07$ mol/l, 30 °C.

FIG. 1
Influence of the interphase area on the I_2 oxidation with H_2O_2, studied by monitoring the iodine absorption, A, at 460 nm as a function of time. Conditions: 30 °C, no stirring, $[HClO_4]_0 = 0.07$ mol/l, $[I_2]_0 = 5 \times 10^{-4}$ mol/l, $[H_2O_2]_0 = 0.05$ mol/l; interface area (cm^2): 1 (*1*), 0.38 (*2*), 0.19 (*3*)

catalytic process can start (Fig. 2, curves *3* and *4*). The fact that after the oxidation there is still an appreciable absorbance (ca. 0.02) at both 350 and 460 nm can be explained by steady-state concentrations of I_3^- and I_2 species when the rate of the iodine oxidation is equal to the rate of the iodate reduction. The oxidation of iodine to iodate cannot occur unless the $HClO_4$ concentration is sufficiently high (at least 0.025 mol/l).

Our observations can be explained by the assumption that oxygen, forming slowly via a complex redox process of iodine with hydrogen peroxide, accumulates step by step, and when its sufficient concentration is attained, the oxidation of iodine with oxygen can start, as Treindl and Noyes[8] have proposed for the Bray–Liebhafsky oscillatory reaction:
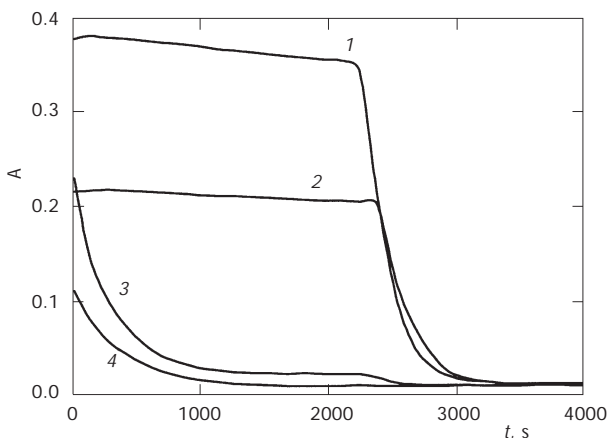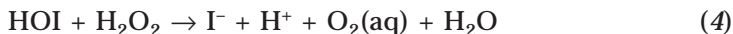
$$IO_3^- + I^- + 2\ H^+ \rightarrow HIO_2 + HOI \tag{1}$$

$$HIO_2 + I^- + H^+ \rightarrow 2\ HOI \tag{2}$$

$$HOI + I^- + H^+ \rightleftharpoons I_2 + H_2O \tag{3}$$

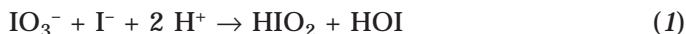$$HOI + H_2O_2 \rightarrow I^- + H^+ + O_2(aq) + H_2O \tag{4}$$
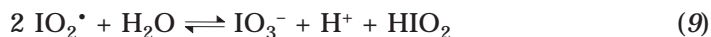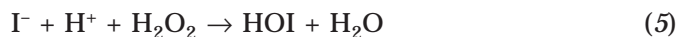

FIG. 2

$A = f(t)$ curves for four different initial concentrations of iodine. Conditions: 30 °C, no stirring, interphase area 0.38 cm^2, $[HClO_4]_0 = 0.07$ mol/l, $[H_2O_2]_0 = 0.05$ mol/l; $[I_2]_0 = 5 \times 10^{-4}$ mol/l, 460 nm (*1*); $[I_2]_0 = 3 \times 10^{-4}$ mol/l, 460 nm (*2*); $[I_2]_0 = 5 \times 10^{-4}$ mol/l, 350 nm (*3*); $[I_2]_0 = 3 \times 10^{-4}$ mol/l, 350 nm (*4*)

$$I^- + H^+ + H_2O_2 \rightarrow HOI + H_2O \tag{5}$$

$$I_2 \rightleftharpoons 2\ I^{\bullet} \tag{6}$$

$$I^{\bullet} + O_2(aq) \rightleftharpoons IOO^{\bullet} \tag{7}$$

$$IOO^{\bullet} \rightleftharpoons IO_2^{\bullet} \tag{8}$$

$$2\ IO_2^{\bullet} + H_2O \rightleftharpoons IO_3^- + H^+ + HIO_2 \tag{9}$$

$$O_2(aq) \rightleftharpoons O_2(g) \tag{10}$$

and finally, as Kaholek and Treindl[17] have observed during the auto-oxidation of iodine

$$I_2 + 2\ O_2(aq) + H_2O \rightarrow IO_3^- + H^+ + HIO_2\ . \tag{11}$$
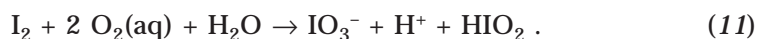
In our papers[11,12] describing the influence of molybdate ions on the BL reaction, an important role of singlet oxygen has been suggested since the $^1O_2$ molecules form during the disproportionation of hydrogen peroxide catalyzed by molybdate ions[13–16].

Stanisavljev et al.[24] studying the influence of heavy water on the BL oscillatory reaction concluded that the oxidation and reduction of the iodine species in the BL reaction do not proceed through the same intermediates. The D_2O effect on the oxidation of iodine with H_2O_2 is really very significant, especially at high H_2O_2 concentrations. In the presence of 10% D_2O, the induction period as well as the rate of the iodine oxidation increase (Fig. 3).

If we assume that in the reaction of iodide and hydrogen peroxide, besides step (5), also a parallel one-electron step (12) proceeds, it can be concluded that the $^{\bullet}OH$ radicals are produced via the oxidation of iodide with hydrogen peroxide

$$I^- + H_2O_2 + H^+ \rightarrow I + {}^{\bullet}OH + H_2O\ . \tag{12}$$
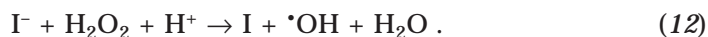
The produced $^{\bullet}OH$ radicals react with H_2O_2 and form $HO_2^{\bullet}$ radicals:

$$\cdot OH + H_2O_2 \rightarrow HO_2^\cdot + H_2O \tag{13}$$
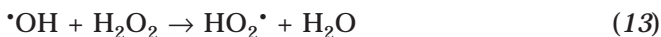
and finally, singlet oxygen is produced by disproportionation of $HO_2^\cdot$ radicals[25,26]

$$2\ HO_2^\cdot \rightarrow H_2O_2 + {}^1O_2\ . \tag{14}$$

Singlet oxygen as a strong oxidation agent can attack the I atom in step (7) producing $IO_2^\cdot$ in step (8). A sufficient amount of ${}^1O_2$ has to be formed during IP, before steps (7) and (8) can start.

The D_2O effect described above can be explained as follows. According to Parker et al.[27], an unambiguous test for the presence of singlet oxygen (${}^1O_2$) in aqueous systems is based on the increase in the lifetime in D_2O with that in H_2O. Thus the reactions mediated by ${}^1O_2$ are accelerated in per-deuterated solvents. An increase in the steady state concentration of singlet oxygen leads to a higher rate of the iodine oxidation. On the other hand, the effect of stirring on the reaction system can be understood as a decrease in the lifetime of singlet oxygen due to its enhanced physical deactivation. The prolongation of IP in the presence of D_2O can be explained by the decrease in the experimental rate constant of the iodide I_3^- oxidation (Table II)
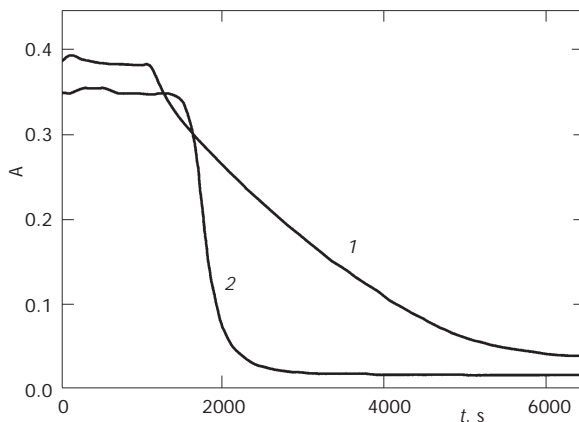

FIG. 3
The D_2O effect on the $A = f(t)$ curves corresponding to the I_2 oxidation with H_2O_2. Conditions: 30 °C, no stirring, interphase area 0.38 cm^2, $[HClO_4]_0 = 0.07$ mol/l, $[I_2]_0 = 5 \times 10^{-4}$ mol/l, $[H_2O_2]_0 = 0.15$ mol/l; $[D_2O]_0$ (%): 0 (1), 10 (2)

that is caused by the primary D_2O effect. The values of experimental rate constants were determined from the time dependence of the I_3^- absorbance at 350 nm assuming the first-order kinetics. Thus, the iodide concentration attains its critical value in the presence of D_2O later than in H_2O.

The effect of light on the course of the reaction is very significant (Fig. 4). If one compares curves *1* and *3*, the inhibiting effect of light can be clearly seen. By comparing curve *2* with *4*, one can see that the I_3^- concentration does not drop to a critical value under the influence of light, which can be explained by steps (*16*), (*17*) and (*18*) as can be seen later.

TABLE II
The influence of D_2O on the value of the experimental rate constant of the I_3^- oxidation with H_2O_2 [a]

D_2O, %	0	10	20	30	40
$10^3 k_{exp}$, s^{-1}	3.0	2.3	2.1	1.8	1.7

[a] $[HClO_4]_0 = 0.07$ mol/l, $[I_2]_0 = 5 \times 10^{-4}$ mol/l, $[H_2O_2]_0 = 0.15$ mol/l, 30 °C, no stirring, interphase area 0.38 cm^2.
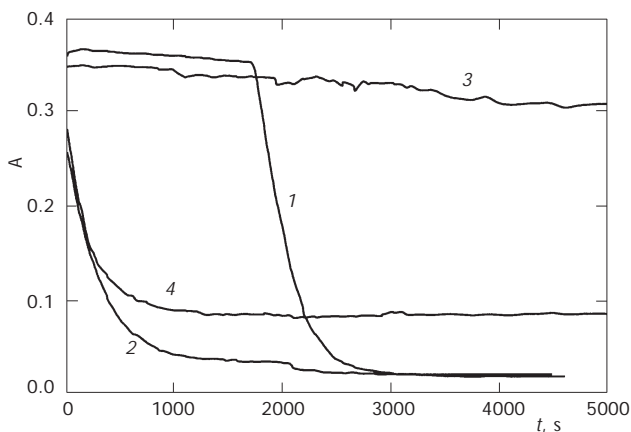

FIG. 4
The effect of light on the $A = f(t)$ curves during the I_2 oxidation with H_2O_2. Conditions: 30 °C, no stirring, interphase area 0.19 cm^2, $[HClO_4]_0 = 0.07$ mol/l, $[H_2O_2]_0 = 0.05$ mol/l, $[I_2]_0 = 5 \times 10^{-4}$ mol/l. Without illumination: wavelength 460 nm (*1*), 350 nm (*2*); with illumination: wavelength 460 nm (*3*), 350 nm (*4*)

Potentiometric Measurements

If the oxidation of iodine with H_2O_2 is studied potentiometrically in the dark, a maximum of the potential (corresponding to the redox potential $E = 0.38$ V) appears on the $E = f(t)$ curve after the induction period (Fig. 5,
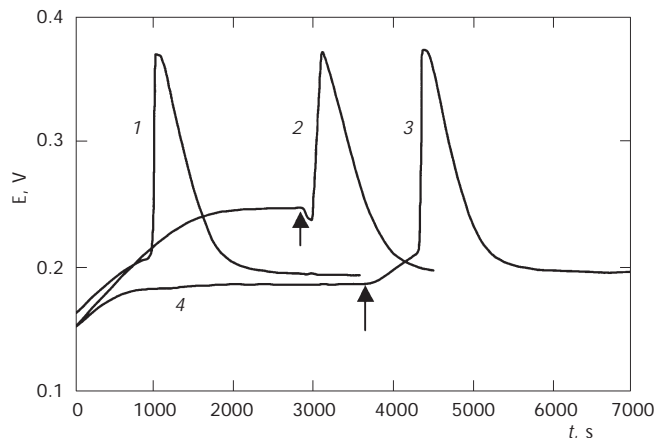

Fig. 5

The effect of light and stirring on the $E = f(t)$ curves during the I_2 oxidation with H_2O_2. Conditions: 30 °C, interphase area 10.2 cm^2, $[I_2]_0 = 9 \times 10^{-4}$ mol/l, $[H_2O_2]_0 = 0.05$ mol/l, $[HClO_4]_0 = 0.07$ mol/l; no stirring, in the dark (*1*); 50 rpm, in the dark (*2*); no stirring, daylight (*3*)
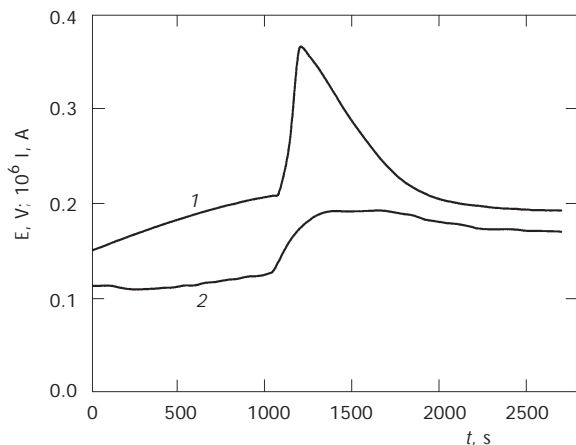

Fig. 6

The $E = f(t)$ curve (*1*) and $[O_2] = f(t)$ curve (*2*) during the I_2 oxidation with H_2O_2. Conditions: 30 °C, no stirring, in the dark, interphase area 10.2 cm^2, $[I_2]_0 = 9 \times 10^{-4}$ mol/l, $[H_2O_2]_0 = 0.05$ mol/l, $[HClO_4]_0 = 0.07$ mol/l

curve *1*). If the solution is exposed to light and stirred continuously (Fig. 5, curve *2*) the maximum is not observed. After stirring has been stopped (first arrow) and the reaction system has been protected against light (second arrow), the oxidation of iodine does proceed. If the maximum of the potential is compared with the dissolved oxygen content, measured as a function of time, autocatalytic production of oxygen is observed after a shorter IP than that manifesting itself by maximum potential (Fig. 6). The latter maximum exhibits a "clock behavior" and a sudden increase in the potential cannot start, unless oxygen is formed to a sufficient extent. The IP of this maximum decreases when the surface area of the interphase decreases. The height of the maximum increases and its IP decreases with increasing concentration of iodine (Fig. 7). With increasing concentration of hydrogen peroxide, IP decreases and its maximum slightly diminishes (Fig. 8). The presence of acrylamide as a scavenger of radicals may play an important role. With increasing acrylamide concentration, the height of the maximum decreases, but IP increases (Fig. 9). On the one hand, acrylamide is not only a radical scavenger, it may also react with HOI. On the other hand, from the temperature dependence of the 1/IP in the absence of acrylamide, the value of the experimental activation energy E_a = 50.2 ± 2.8 kJ/mol was determined (Table III). According to Anic et al.[28], the activation energy of the oxidation pathway of the BL reaction is between 75 and 78 kJ/mol. In
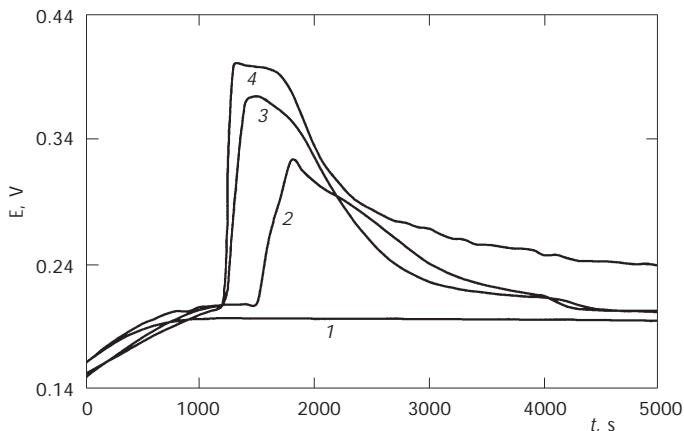

FIG. 7

The $E = f(t)$ dependence during the I_2 oxidation with H_2O_2 on the initial concentration of iodine. Conditions: 30 °C, no stirring, in the dark, interphase area 10.2 cm^2, $[H_2O_2]_0$ = 0.05 mol/l, $[HClO_4]_0$ = 0.07 mol/l; $[I_2]_0$ = 9 × 10^{-5} mol/l (*1*), 1 × 10^{-4} mol/l (*2*), 3 × 10^{-4} mol/l (*3*), 8.9 × 10^{-4} mol/l (*4*)
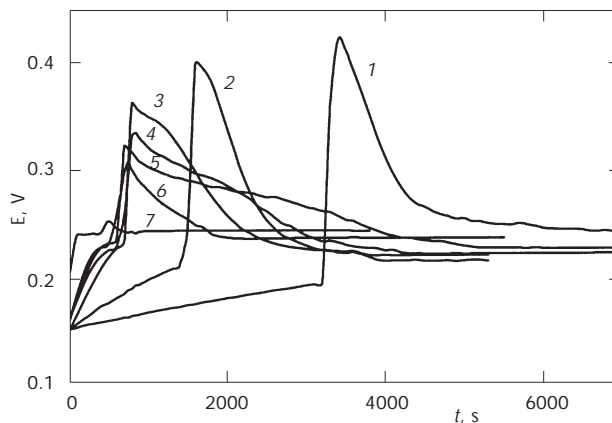
FIG. 8
The $E = f(t)$ dependence during the I_2 oxidation with H_2O_2 on the initial concentration of hydrogen peroxide. Conditions: 30 °C, no stirring, in the dark, interphase area 4.8 cm^2, $[I_2]_0 = 5 \times 10^{-4}$ mol/l, $[HClO_4]_0 = 0.07$ mol/l; $[H_2O_2]_0 = 0.01$ mol/l (*1*), 0.03 mol/l (*2*), 0.09 mol/l (*3*), 0.12 mol/l (*4*), 0.14 mol/l (*5*), 0.17 mol/l (*6*), 1 mol/l (*7*)
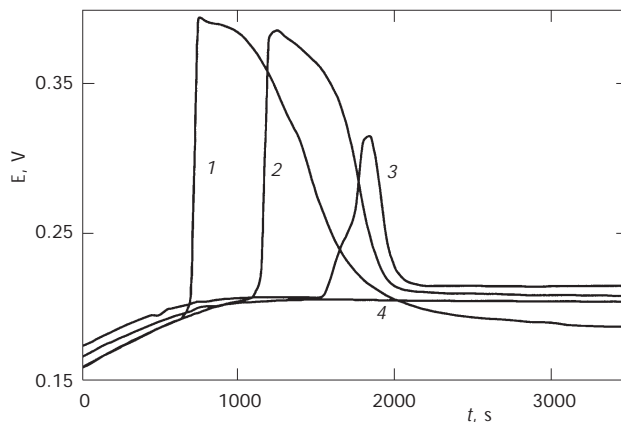
FIG. 9
Influence of acrylamide concentration on the $E = f(t)$ curves during the I_2 oxidation with H_2O_2. Conditions: 30 °C, no stirring, in the dark, interphase area 4.8 cm^2, $[I_2]_0 = 5 \times 10^{-4}$ mol/l, $[H_2O_2]_0 = 0.05$ mol/l, $[HClO_4]_0 = 0.07$ mol/l; $[CH_2=CH–CONH_2]_0 = 0$ (*1*), 1×10^{-3} mol/l (*2*), 2×10^{-3} mol/l (*3*), 2.5×10^{-3} mol/l (*4*)

our opinion, the results described above, in particular the relatively low value of the activation energy, indicate the formation of intermediary radicals during IP. The $HO_2^\bullet$ radicals formed during the iodide oxidation with H_2O_2 can either react with iodine according to Schwarz et al.[29]

$$HO_2^\bullet + I_2 \rightleftharpoons I_2^- + O_2 + H^+ \tag{15}$$
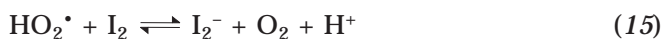
or are consumed by disproportionation (*14*) according to Kearns[30].

The equilibrium constant for reaction step (*15*) was measured and found to be 30 mol/l at 25 °C [29]. With increasing concentration of oxygen and of H^+ ions, the equilibrium in (*15*) shifts in favor of $HO_2^\bullet$ radicals which can produce singlet oxygen $^1O_2$ by disproportionation (*14*). The very reactive singlet oxygen $^1O_2$ then can start the oxidation of iodine as proposed by Treindl and Noyes[8] (reaction steps (*1*)–(*10*)).

The crucial role of singlet oxygen may be confirmed by the effect of N_3^- ions on the $E = f(t)$ and $A = f(t)$ curves during the oxidation of iodine with hydrogen peroxide (Figs 10a and 10b). In the presence of $3–6 \times 10^{-3}$ M NaN$_3$, IP increases with increasing concentration of N_3^- ions; at 7×10^{-3} M NaN$_3$, only a very low sigmoidal curve occurs, and finally at the 7.5×10^{-3} M concentration of N_3^- ions, the oxidation of iodine does not proceed at all. Azide reacts with $^1O_2$ obviously as a scavenger[26], and inhibits the oxidation of iodine in such a way.

The inhibiting effect of light on the iodine oxidation with H_2O_2 can be explained by interaction of I atoms with I^- ions:

$$I^\bullet + I^- \rightleftharpoons I_2^- \tag{16}$$

which are consumed at a low concentration of oxygen by the disproportionation[31]

$$2\ I_2^- \rightleftharpoons I_3^- + I^- \tag{17}$$

TABLE III
The temperature dependence of the length of induction period[a]

T, °C	20	25	30	40	50
IP, s	1667	1222	733	463	241

[a] $[I_2]_0 = 5 \times 10^{-4}$ mol/l, $[H_2O_2]_0 = 0.05$ mol/l, $[HClO_4]_0 = 0.07$ mol/l, 30 °C, in the dark, no stirring, interphase area 10.2 cm^2.

and in the reaction step[32]

$$I_2^- + HO_2^\bullet \rightarrow H^+ + 2\ I^- + O_2 \ . \tag{18}$$

According to Stanisavljev et al.[33], the oxidation pathway of the BL reaction is more effectively accelerated than its reduction pathway by replacing ordinary water with heavy water. We have also observed the influence of
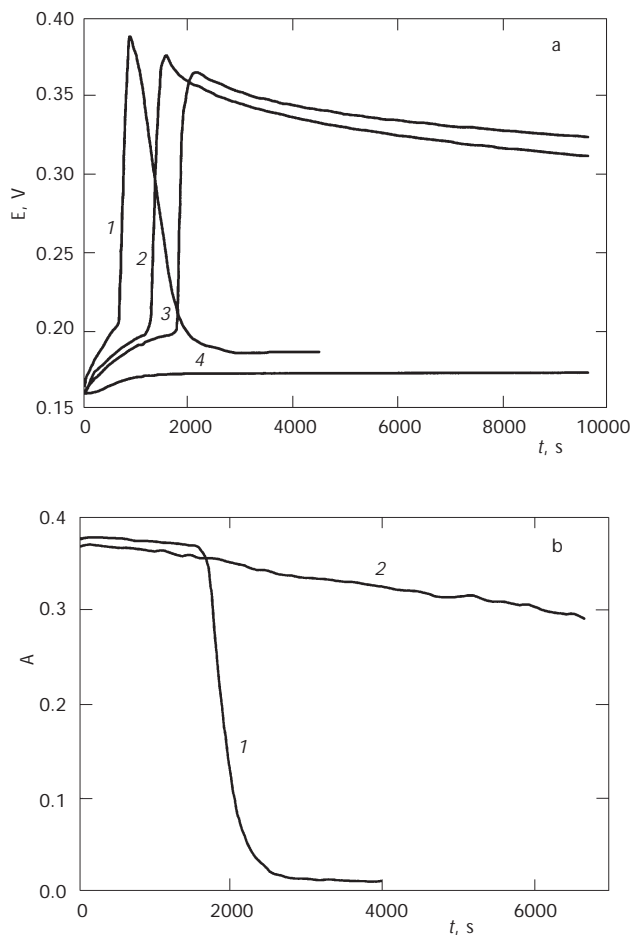

Fig. 10

The inhibiting effect of N_3^- ions on the I_2 oxidation with H_2O_2. Conditions: 30 °C, no stirring, in the dark, $[I_2]_0 = 5 \times 10^{-4}$ mol/l, $[H_2O_2]_0 = 0.05$ mol/l, $[HClO_4]_0 = 0.07$ mol/l; a: $E = f(t)$ curves, interphase area 4.8 cm^2, $[NaN_3]_0 = 0$ (1), 5×10^{-3} mol/l (2), 6×10^{-3} mol/l (3), 7×10^{-3} mol/l (4); b: $A = f(t)$ curves, interphase area 0.19 cm^2, $[NaN_3]_0 = 0$ (1), 5×10^{-3} mol/l (2)

D_2O on the value of IP corresponding to the oxidation of iodide with H_2O_2 including reaction steps (*12*)–(*15*) (Fig. 11). The value of IP increases with the concentration of D_2O. According to Aubry[31] and Ameta et al.[25] the lifetime of singlet oxygen is ten times higher in D_2O than in H_2O, which may explain the D_2O effect mentioned above. This means that the steady state concentration of singlet oxygen as well as the rate of the following steps of the iodine oxidation increase (Fig. 3). These facts are in favor of reaction steps (*7*) and (*8*) in the model of Noyes and Treindl[8] and also they indicate[24] that both the processes do proceed via different intermediates, which is also in agreement with the model mentioned above[8]. Their explanation of the oscillations in the BL reaction emphasizes the necessity of taking into account the transport of oxygen from supersaturated solution to surrounding atmosphere. Although we have stressed that the stirring of solution probably decreases the lifetime of singlet oxygen due to its enhanced physical deactivation, the stirring can also destroy the accumulation of oxygen in solution. These two effects can cause that the iodine oxidation does not proceed.

The reciprocal value of IP, corresponding to the value of the rate constant of the iodine oxidation with H_2O_2, depends on the concentration of perchloric acid. The oxidation does not proceed until $HClO_4$ attains 25 mM concentration, the value of k_{exp} drops to a minimum at 30 mM concentration, and then it increases with the $HClO_4$ concentration.
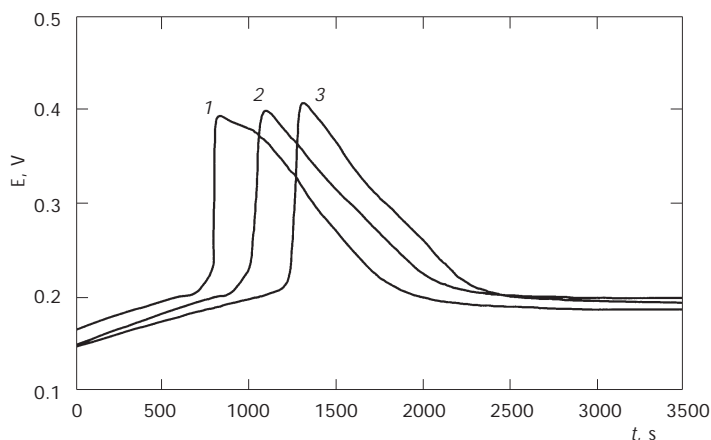

Fig. 11

The D_2O effect on the $E = f(t)$ curves during the I_2 oxidation with H_2O_2. Conditions: 30 °C, no stirring, in the dark, interphase area 4.8 cm^2, $[I_2]_0 = 5 \times 10^{-4}$ mol/l, $[H_2O_2]_0 = 0.05$ mol/l, $[HClO_4]_0 = 0.07$ mol/l; D_2O (%): 0 (*1*), 10 (*2*), 15 (*3*)

Finally, we would like to express that we are convinced that the described experimental observations are in favor of the mechanism which takes into account the important role of oxygen[8], especially of singlet oxygen, rather than the mechanism of Schmitz neglecting the essential participation of oxygen[18] in the mechanism of the BL oscillations.

Field et al.[10] showed using their mathematical model based on the proposed mechanism[8] that $[I_2]$ and $[O_2]$ oscillate around an unstable steady state. However, while these oscillations can be quite long-lived, they take place around a stable or unstable focus and do not involve a true limit cycle. We would like to modify their skeleton model by taking into account also the two competitive steps (*14*) and (*15*) and in particular the role of the singlet oxygen. This will be the aim of our project in the next future in the hope to get oscillations with a true limit cycle.

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