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Investigation of the Influence of Heavy Water on Kinetic Pathways in the Bray−Liebhafsky Reaction

Dragomir R. Stanisavljev* and Vladana B. Vukojević

Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, P.O. Box 137,
YU-11001 Belgrade, Yugoslavia

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A more detailed investigation of the influence of heavy water on the two main kinetic pathways underlying the mechanism of the Bray−Liebhafsky (BL) reaction is performed. The course of the BL reaction at four temperatures was monitored with an improved experimental setup, enabling simultaneous recordings of the potential of the platinum electrode, the concentration of I_2, and the oxygen production rate. It is confirmed that by replacing ordinary water with heavy water, the oxidation pathway is more effectively accelerated than the reduction pathway. Influence of the isotopic substitution on the acidity of the BL system, VIS spectra of iodine in D_2O, and the reaction between iodine and deuterated peroxide are investigated in separate experiments. It is concluded that the observed enhancement of the oxidation pathway cannot be simply explained by the isotopic effect. Hence, the possible role of bulk water in the process of shifting the whole reaction mechanism toward the oxidation pathway is discussed.

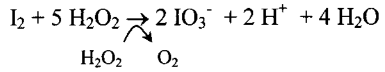
1. Introduction

In a previous paper,[1] we initiated investigations concerning the influence of heavy water on the dynamics of the Bray−Liebhafsky (BL) reaction.[2,3] In these investigations we noticed that the two main kinetic pathways, the reduction of iodate to iodine (A) and its subsequent oxidation back to iodate (B), are differently affected when light water is replaced with heavy water.

As a reminder, the two main kinetic pathways underlying the mechanism of the BL reaction are usually described by the following summary reactions:

$$\text{(A)} \qquad 2\,IO_3^- + 5\,H_2O_2 + 2H^+ \rightarrow I_2 + 5\,O_2 + 6\,H_2O$$

(B)



$$I_2 + 5\,H_2O_2 \xrightarrow[H_2O_2 \;\rightarrow\; O_2]{} 2\,IO_3^- + 2\,H^+ + 4\,H_2O$$

Pathways A and B dominate over each other alternately in the oscillatory mode, and a catalytic decomposition of hydrogen peroxide (C) is occurring in the system:

$$\text{(C)} \qquad n\,H_2O_2 \rightarrow n\,H_2O + n/2\;\,O_2$$

The amount of hydrogen peroxide decomposed during the course of the BL reaction, as presented by the summarized reaction (C), differs from the value predicted by a simple sum of (A) and (B) because process (B) itself is additionally accompanied by a catalytic decomposition of hydrogen peroxide to oxygen, which is not shown by the summarized stoichiometry.[3−5]

The least understood part of the whole mechanism of the BL reaction is the process of oxidation of iodine (B). Namely, it is well-known that the oxidation of iodine by hydrogen peroxide, as presented by (B), is a kinetically unfavorable process and that these two components can stay together for days without an appreciable change in the iodine concentration.[6] Contrary to this, in the BL reaction the rate of the oxidation process (B) may exceed the rate of the reduction process (A) by 20−30 times during some intervals.[7] However, the actual mechanism by which this is accomplished is not yet fully revealed.

The purpose of the present study is to refine and extend the previous investigations with heavy water.[1] Namely, in the previous experiments the production of oxygen and iodine are measured in separate experiments, whereas the new experimental setup enables us to monitor these quantities simultaneously and to establish more precisely the phase correlation between them. Also, a more sensitive measurement of the oxygen production is achieved, revealing the oscillatory evolution of oxygen as well.

To be able to give a more elaborate consideration of the effect of D_2O on the course of the BL reaction, we performed pH and pD measurements in the BL reaction mixture with light and heavy water, respectively, and compared the activities of H^+ and D^+.

Further, we investigated in separate experiments whether the observed decrease of iodine concentration in the BL reaction in the presence of heavy water can arise as a consequence of a grossly enhanced hydrolysis. Namely, this complex reaction[8−11] has an important role in the mechanism of the BL reaction, and it is necessary to establish to what extent it is affected in the presence of D_2O. Since hydrolysis may also be enhanced by a more efficient oxidation of its products by the deuterated H_2O_2, the reaction between iodine and D_2O_2 is investigated too.

Finally, in our previous experiments with heavy water[1] and the study of the BL reaction by ^{1}H NMR,[12] we have contemplated the possibility that bulk water may be important for shifting the whole reaction mechanism toward the oxidation pathway, i.e., for the initiation and the subsequent prevalence of the oxidation pathway during certain intervals. Here, we pursue this concept further and give a more elaborate discussion to substantiate it. We consider that the idea of introducing bulk

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* Corresponding author. E-mail: dragisa@ffh.bg.ac.yu.

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water as a possible reactant in the BL reaction may be of more general interest, since water is a usual solvent in many reacting systems.

2. Experimental Section

The BL reaction was conducted under batch conditions in a rectangular spectrophotometric glass cuvette (with an optical path length of 1 cm), at four different temperatures: $T = 50.0$, 55.0, 64.0, and 73.2 °C. The temperature is controlled within ±0.1 deg by a circulating water bath. The initial concentrations of the reactants were: $[KIO_3]_0 = 7.34 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4]_0 = 4.89 \times 10^{-2}$ mol dm^{-3}, and $[H_2O_2]_0 = 2.22 \times 10^{-1}$ mol dm^{-3}. Different volume fractions of heavy water, V_{D_2O}/V, where V_{D_2O} is the volume of D_2O and V is the entire volume of the reaction mixture ($V = 2.55$ mL), were achieved by mixing appropriate volumes of the stock solutions of KIO_3 and H_2SO_4 in H_2O and D_2O. The reaction commences by mixing appropriate volumes of the reactant solutions at room temperature. Thereafter the reaction mixture is heated, until the required temperature is reached.

The reaction dynamics is followed by simultaneously measuring the potential of a platinum microelectrode versus an Ag/AgCl reference electrode,[1,12] the I_2 concentration spectrophotometrically at $\lambda = 460$ nm, and the evolution rate of gaseous oxygen over the reaction mixture by an oxygen microelectrode. The rate of the oxygen evolution was monitored just above the surface of the reaction mixture and is regarded to be proportional to the concentration of oxygen in the reaction mixture. Such an experimental procedure is adopted to prevent sticking of the oxygen bubbles to the electrode membrane, which causes unreliable measurements when the oxygen concentration is measured directly in the reaction mixture.

Measurements of the pH and pD values were performed by a glass electrode, versus an Ag/AgCl electrode as a reference. The pH and pD values were measured in separate experiments, because a larger reaction vessel (volume of the reaction mixture was 10.1 mL) had to be applied since it was not possible to fit the glass electrode into the spectrophotometric cuvette. Beforehand, it was checked that these modifications of the experimental setup have no observable influence on the BL reaction dynamics. The pH meter was calibrated against buffering solutions pH = 1.00 ± 0.05 and pH = 2.00 ± 0.05. The acidity measurements were performed under conditions that are slightly modified: $[KIO_3]_0 = 7.42 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4]_0 = 4.95 \times 10^{-2}$ mol dm^{-3}, and $[H_2O_2]_0 = 8.80 \times 10^{-2}$ mol dm^{-3}, at temperatures $T = 58.0$ °C and $T = 19.8$ °C. The initial concentration of peroxide was deliberately decreased because here the frequency of the oscillations is lower, compared to the oscillations frequency under the original conditions. Hence, it would have been easier to monitor any oscillations in the pH and pD values should they appear.

It was tested spectrophotometrically whether there are differences in the VIS spectra of iodine in saturated solutions of H_2O and D_2O. The saturated solutions of iodine in H_2O and D_2O were prepared by equilibrating the same weights of solid iodine ($m = 0.05$ g) with 25 mL of light and heavy water for 2 weeks, in well-fitted glass flasks. VIS spectra of the equilibrated solutions were then compared. Further, aliquots of the saturated solutions were diluted with equal amounts of (a) H_2O, (b) a solution of 0.1 mol dm^{-3} H_2SO_4 in H_2O, and (c) a solution of 0.1 mol dm^{-3} H_2SO_4 in D_2O. The effects after dilution were followed spectrophotometrically.

Oxidation of iodine by deuterated peroxide is investigated at $T = 67.0$ °C. A sample of the saturated iodine solution in 0.1 mol dm^{-3} H_2SO_4 in D_2O is diluted with an equal volume of D_2O. Thereafter, 0.050 mL of 8.90 mol dm^{-3} H_2O_2 is added to an aliquot of 2.50 mL of this solution. In this way, we prepared a solution in which the initial stoichiometric concentrations of the acid and peroxide are similar, as in other experiments. VIS spectra of the above mixture were recorded immediately after mixing and in regular intervals for 6 h thereafter.

All experiments were conducted without stirring in order to be comparable with the previous results.[1,12] We underline that, under the investigated conditions, stirring is not an essential reaction parameter and that all crucial properties of the reaction dynamics are preserved though the reaction is conducted without stirring.

All chemicals are used without further purification: KIO_3, H_2SO_4, H_2O_2, and I_2 from Merck; D_2O from Fluka (99.8% D), Cambridge Isotope Laboratories (99.96% D), and Norsk Hydro 99.8% D).

Deionized ordinary water of specific resistance $\rho = 18$ MΩ cm^{-1} is used.

3. Results

3.1. Effect of D_2O on the Dynamics of the BL Reaction. Typical time series showing the simultaneously recorded potential of the platinum electrode (first column), the iodine concentration (second column), and the oxygen production rate (third column) are given in Figure 1. The recordings are obtained for various contents of D_2O at $T = 55.0$ °C. Similar changes in the reaction's dynamics caused by different amounts of D_2O, are observed at all investigated temperatures.

We note from the time series given in Figure 1 and in Figure 1 of ref 1 that general features of the BL reaction dynamics in the presence of D_2O are the same and are not affected by the small discrepancies in the experimental setup.

In pure H_2O ($V_{D_2O}/V = 0.00$) as well as for smaller contents of D_2O, the oscillatory evolution commences right after the first preoscillatory period, τ_1, ends (Figure 1, first three rows). For higher contents of D_2O, the oscillatory evolution is postponed (Figure 1, fourth row), and a second preoscillatory period, τ_2, appears. It lasts $\tau_2 = \tau - \tau_1$, where τ denotes the time when the first oscillation appears in the system. For the highest volume fractions of D_2O, oscillations are not observed (Figure 1, last row).

During the first preoscillatory period, τ_1, a maximum concentration of iodine in the system is achieved (Figure 1, second column), through a domination of the reduction pathway (A). As well, during this period the rate of oxygen production increases monotonically (Figure 1, third column).

During the second pre-oscillatory period, τ_2, a pseudostationary state accompanied by intensive O_2 production, i.e., intensive hydrogen peroxide decomposition, is established. Duration of this period of monotonic decomposition of hydrogen peroxide is proportional to the amount of D_2O. For the highest volume fractions of D_2O, oscillations (if any) were not observed. The oscillations are either "infinitely" postponed, or absent, since the concentration of hydrogen peroxide may fall below the amount required for the onset of the oscillations (as a result of its intensive decomposition during prolonged τ_2).

The effect of D_2O on the first and second pre-oscillatory periods at all investigated temperatures is shown in Figure 2. Duration of the first pre-oscillatory period, τ_1, for different volume fractions of heavy water, V_{D_2O}/V, is represented by the solid symbols. The time of appearance of the first oscillation, τ, is given by the open symbols. For small contents of D_2O these two characteristic times coincide, $\tau_1 = \tau$. For higher amounts of D_2O the oscillatory evolution is postponed, and the

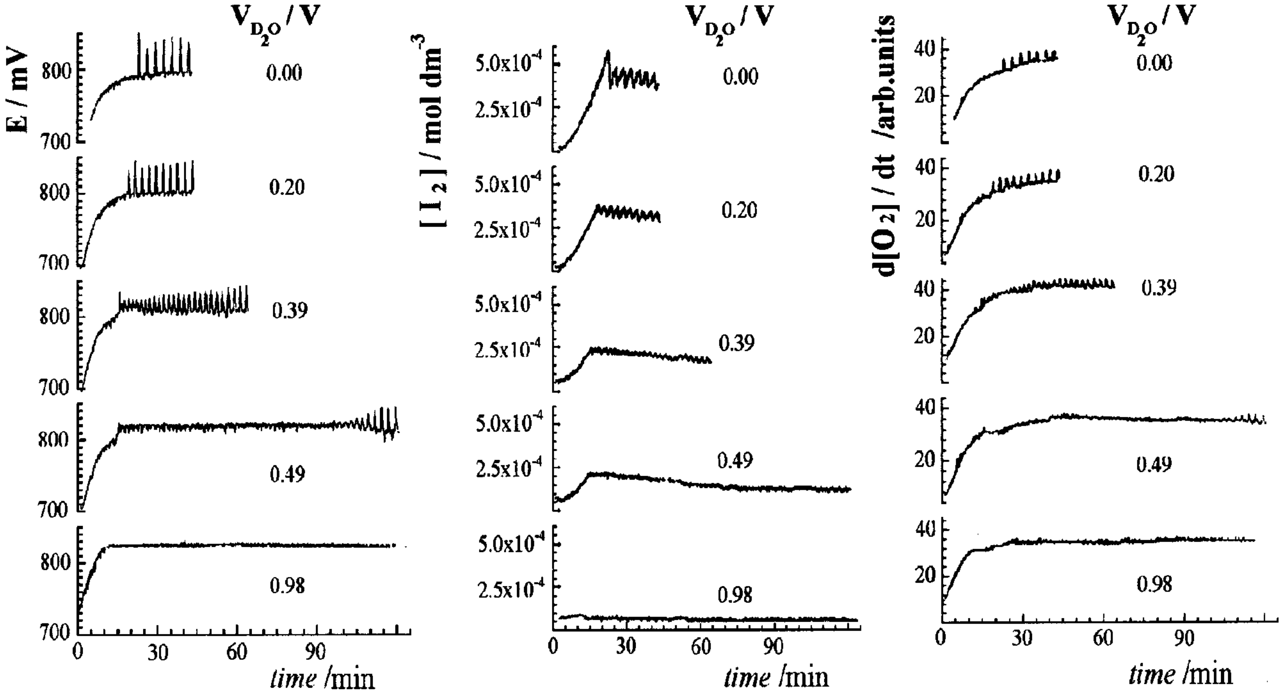

Figure 1. Time series showing the dynamics of the BL reaction for different volume fractions of heavy water, V_{D_2O}/V, under the following conditions: $[KIO_3]_0 = 7.34 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4]_0 = 4.89 \times 10^{-2}$ mol dm^{-3}, $[H_2O_2]_0 = 2.22 \times 10^{-1}$ mol dm^{-3}, and $T = 55.0$ °C. The dynamics is monitored by simultaneously measuring the platinum electrode potential (first column), the I_2 concentration (second column), and the oxygen production rate (third column).

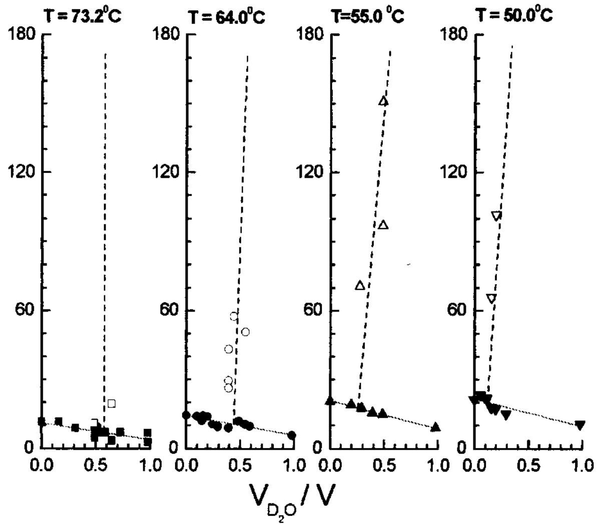

Figure 2. Dependence of the characteristic times τ_1 (solid line) and τ (dashed line) on the amount of heavy water present in the reaction mixture, at different temperatures. The crossing of the dotted and dashed lines determines the critical amount of heavy water $(V_{D_2O}/V)_c$ at which the evolution of the BL reaction is substantially changed. For contents of heavy water $(V_{D_2O}/V) < (V_{D_2O}/V)_c$ the two characteristic times coincide. For $(V_{D_2O}/V) > (V_{D_2O}/V)_c$ the oscillatory evolution is postponed, and the characteristic times corresponding to the same V_{D_2O}/V begin to differ. Eventually, only τ_1 can be identified. At lower temperatures, the influence of heavy water is more pronounced since substantial changes of the reaction evolution are brought about by smaller amounts of D_2O.

characteristic times corresponding to the same V_{D_2O}/V begin to differ. For the highest V_{D_2O}/V, only τ_1 is identified.

The transition from the usual oscillatory evolution (with only one induction period, τ_1) to the postponed oscillations (with two induction periods, τ_1 and τ_2) at 73.2 °C is rather sharp. Therefore, for the time of monitoring, only "ordinary" oscillograms were observed.

The crossing of the solid and dashed lines representing changes of the two characteristic times, determines the critical amount of heavy water $(V_{D_2O}/V)_c$ at which the dynamics of the BL reaction is substantially changed, at all investigated temperatures. It ranges from $(V_{D_2O}/V)_c \approx 10\%$ at 50.0 °C to $(V_{D_2O}/V)_c \approx 55\%$ at 73.2 °C, which corresponds approximately to 7−27 mol dm^{-3} of D_2O in the reaction mixture. At lower temperatures, the influence of heavy water is more pronounced since substantial changes of the reaction evolution are brought about by smaller amounts of D_2O.

For $V_{D_2O}/V < (V_{D_2O}/V)_c$ a small decrease in τ_1, i.e., an earlier appearance of the oscillations, is observed at all investigated temperatures (Figure 2). This can be related to an earlier prevalence of the oxidation pathway (B) over the reduction pathway (A).

Although a qualitative influence of D_2O on the oscillatory evolution of the BL reaction is evident, its influence on the kinetic pathways (A) and (B) can be analyzed more thoroughly by correlating the concentration of iodine in the reaction mixture with the rate of the O_2 production over the reaction mixture. In Figure 3, the maximum concentration of iodine, $[I_2]_{max}$, and the corresponding rate of oxygen production, $(dO_2/dt)_{[I_2]_{max}}$, established at the end of the first pre-oscillatory period, τ_1, are shown as a function of the volume fraction of D_2O. We have chosen to compare these quantities at the characteristic time τ_1 because at this instant the BL reaction is found in kinetically equivalent states, in all experiments. As can be seen from Figure 3, it is evident that $[I_2]_{max}$ decreases significantly with the increasing amount of D_2O, whereas the production of oxygen remains virtually independent of the content of D_2O.

3.2. pH and pD Measurements. Simultaneous recordings of the outputs of the platinum and glass electrodes, when the BL reaction is conducted in H_2O and D_2O, are shown in Figure 4. The pD values are determined as pD = meter reading + 0.4.[13]

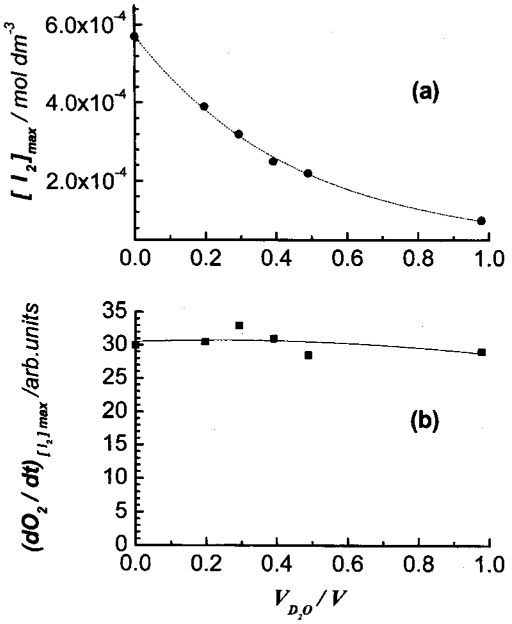

Figure 3. Dependence of the (a) maximum I_2 concentration and (b) the oxygen production rate achieved at the end of the first pre-oscillatory period, $t = \tau_1$, as a function of the volume fraction of D_2O. The experimental conditions are given in the caption to Figure 1.

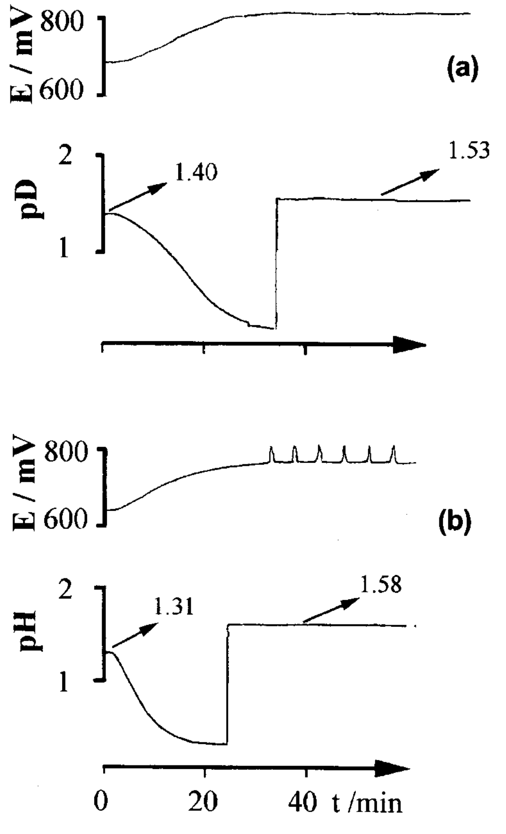

Figure 4. Simultaneous recordings of the potential of the platinum electrode and (a) pD and (b) pH values. The volume of the reaction mixture was 10.1 mL. The initial concentrations are $[KIO_3]_0 = 7.42 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4]_0 = 4.95 \times 10^{-2}$ mol dm^{-3}, and $[H_2O_2]_0 = 8.80 \times 10^{-2}$ mol dm^{-3}. The volume fraction of D_2O in the experiment was 0.99. The initial values of pH and pD are measured at $T = 19.8$ °C, whereas the other ones are measured at $T = 58.0$ °C.

pH and pD values are measured right after mixing the reactants, at the room-temperature $T = 19.8$ °C, as well as after thermostating the reaction mixture at $T = 58.0$ °C. At $T = 19.8$ °C, where the reaction is slow enough so that it can be assumed that the initial concentrations of the reactants are unchanged, the following values are obtained: $pH_{20} = 1.31$ and $pD_{20} = 1.40$, corresponding to $a_{H^+}{}^{20} = 0.049$ and $a_{D^+}{}^{20} = 0.040$, respectively. To obtain the corresponding values at $T = 58.0$ °C, temperature compensation of the pH-meter readings is performed when the required temperature is reached. The pH and pD values were subsequently monitored. Although an oscillatory evolution is observed in light water, no oscillations in the pH nor in the pD were observed at $T = 58.0$ °C, and the following values are obtained: $pH_{58} = 1.58$ and $pD_{58} = 1.53$, corresponding to $a_{H^+}{}^{58} = 0.026$ and $a_{D^+}{}^{58} = 0.029$, respectively.

The pH and pD values measured in the BL reaction mixture at $T = 19.8$ °C, are compared to corresponding values calculated from the acid dissociation constants. In "light" water, the first dissociation constant for sulfuric acid is $K_{1H} = 1.0 \times 10^2$, the second dissociation constant for sulfuric acid is $K_{2H} = 1.2 \times 10^{-2}$, and the dissociation constant for iodic acid is $K_{3H} = 1.6 \times 10^{-1}$.[14] In the calculations, it is assumed that KIO_3 is completely dissociated in the BL reaction mixture, and the Davies approximation[13] for the activity coefficients for ionic species in aqueous solution is applied.

To calculate the pD values, the corresponding dissociation constants in heavy water are determined from $pK_D = 1.02pK_H + 0.42$,[15] where the subscript D denotes the pK value in heavy water, and the subscript H that in light water. Thus, the acid dissociation constants in heavy water are the first dissociation constant for sulfuric acid, $K_{1D} = 4.2 \times 10^1$, the second dissociation constant for sulfuric acid, $K_{2D} = 4.2 \times 10^{-3}$, and the dissociation constant for iodic acid, $K_{3D} = 5.9 \times 10^{-2}$.

The calculated pH value at the beginning of the reaction is $pH_{calc} = 1.25$, which is in agreement with the experimentally determined value $pH_{exp} = 1.31 \pm 0.05$ (Figure 4) within the limits of the experimental error. Also, the calculated pD value at the beginning of the reaction $pD_{calc} = 1.45$ is in agreement with the experimentally determined value $pD_{exp} = 1.40 \pm 0.05$ (Figure 4). As can be seen, at $T = 19.8$ °C, the measured pH and pD values agree with the calculated ones within experimental error. Besides, lower acidity in the presence of D_2O is also expected from theoretical predictions, since deuterium forms slightly stronger bonds than hydrogen and therefore deuterated acids have a lower tendency to dissociate. We regard this agreement to be a substantial confirmation of consistency between the measured results and the theoretical predictions.

pH and pD values measured at $T = 58.0$ °C agree with each other within the experimental uncertainties. Since dynamics of the BL reaction conducted in D_2O and H_2O are different (Figure 4), the pH and pD cannot be directly related with the initial values measured at $T = 19.8$ °C (Figure 4). Also, a comparison with the calculated pH and pD values at this temperature is not performed, due to lack of experimental values for the dissociation constants.

3.3. Spectrophotometric Measurements. When the BL reaction dynamics is followed spectrophotometrically at $\lambda = 460$ nm, where iodine has an absorption maximum, lower absorbancies are observed for increasing volume fractions of D_2O (Figures 1 and 3). To check whether the observed decrease in absorbency can be simply explained as a consequence of grossly enhanced iodine hydrolysis in heavy water, we compared the VIS spectra of saturated iodine solutions in both solvents. We have determined that the VIS spectra of saturated iodine solutions in the two solvents are identical, within experimental errors. To investigate possible effects of deuterated D_2SO_4, we diluted equal aliquots of the saturated solutions with (a) H_2O,

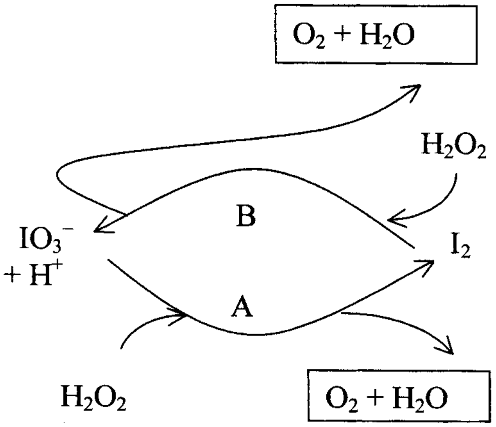

Figure 5. Schematic presentation of the reduction pathway (A) and the oxidation pathway (B), which is accompanied by the catalytic decomposition of hydrogen peroxide (C).

(b) a solution of 0.1 mol dm^{-3} H_2SO_4 in H_2O, and (c) a solution of 0.1 mol dm^{-3} H_2SO_4 in D_2O, and followed the changes spectrophotometrically. Again, no other differences in the VIS spectra, except the one appearing as a result of dilution, were observed. Therefore, we conclude that the observed lowering in absorbency at $\lambda = 460$ nm cannot be explained simply as a consequence of significantly enhanced iodine hydrolysis neither in D_2O nor in the presence of D_2SO_4.

Lower absorbancies at $\lambda = 460$ nm could be also observed in the BL-D_2O system if the products of iodine hydrolysis are more efficiently oxidized by D_2O_2 than by H_2O_2. This would shift the equilibrium process toward the products, decreasing the iodine concentration. To examine this possibility, iodine and D_2O_2 (in the presence of D^+) are kept in contact at 67.0 °C for 6 h. By spectrophotometric measurements, it is established that oxidation of iodine remains a slow process. In this way, we confirmed that a direct oxidation of iodine by the deuterated peroxide does not proceed very efficiently. Hence, it may not be regarded as a simple explanation for the observed decrease in absorbency.

Let us note that when even small amounts of KIO_3 are added into the acidified mixture of iodine and peroxide an instantaneous discoloration is observed in both H_2O and D_2O.

4. Discussion

4.1. Influence of D_2O Derived from the Dynamics of the BL Reaction. In general, the influence of heavy water on the reaction pathways, (A) and (B), can be discussed by analyzing the phase correlation between the concentration of iodine in the reaction mixture and the production of oxygen over the reaction mixture. However, this is not a simple task because during the course of the BL reaction both pathways (A) and (B) proceed simultaneously, but to different extents. Therefore, it is possible to measure experimentally only the total amount of oxygen produced in both pathways, but not their individual contributions.

To discuss the effects of D_2O on the main reaction pathways (A) and (B), a schematic presentation of (A), (B), and (C) given in Figure 5 can be helpful. Oxygen is produced during the reduction pathway (A), as well as during the oxidation pathway (B). According to this scheme, the amount of oxygen produced should be directly proportional to the amount of iodine formed in (A). The more iodine is formed, the more oxygen is produced as a result of the reduction pathway (A). Also, the more iodine is oxidized, the more oxygen is produced during the oxidation pathway (B). As a consequence, a smaller amount of iodine formed in (A) will necessary produce lower amount of oxygen.

It is established that the oxygen production rate at τ_1, $(dO_2/dt)_{[I_2]_{max}}$, is almost constant (Figure 3) and independent of the content of D_2O. On the other side, maximal iodine concentration $[I_2]_{max}$ significantly decreases with the increasing content of D_2O. The first preoscillatory period τ_1 (time for the achieving $[I_2]_{max}$) is not independent of the amount of D_2O; i.e., a small decrease of τ_1 for higher contents of D_2O (Figure 2) is observed. This indicates that the same rate of oxygen production is achieved for shorter times. Further, since the production of oxygen must be proportional to the amount of the produced iodine, it means that about the same amount of iodine must be produced for shorter times; i.e., the reduction pathway (A) is slightly accelerated in the presence of D_2O. Although the reduction pathway is slightly accelerated, a significant decrease of the observed maximal concentration of iodine (Figure 3a) clearly shows that the oxidation pathway (B) is far more accelerated in the presence of D_2O. It means that the formed iodine in the reduction pathway (A) is more efficiently oxidized in the presence of increasing amount of D_2O so that progressively lower $[I_2]_{max}$ can be observed.

This is consistent with the results given in Figure 1, as well as with results given in Figure 2, showing that for $V_{D_2O}/V < (V_{D_2O}/V)_c$ the oscillatory evolution, i.e., oxidation pathway (B), commences earlier than in ordinary water. Following this argument, we may deduce that for $V_{D_2O}/V > (V_{D_2O}/V)_c$ the oxidation pathway (B) is so facilitated that almost all of the produced iodine is efficiently oxidized, resulting in a monotonic decomposition of hydrogen peroxide.

4.2. Influence of D_2O on the BL Reaction Dynamics through Changed Acidity. One obvious change in properties of the BL system, occurring as a result of the primary isotopic effect, is the change of acidity. All deuterated species having stronger bonds with D than with H due to lowering the zero point energies in the corresponding molecules, will change their acidic dissociation constants.[16] This will result in a changed concentration of D^+, followed by an “adjustment” of the concentration of the corresponding anions and undissociated components to the new values of the dissociation constants. Since most of the primary isotopic effect in the BL system conducted in D_2O arises from the lower dissociation of the $-O-D$ bond relative to the $-O-H$ bond, its influence on the BL reaction can be formally analyzed by comparing the influence of lowered initial acidity in an isotopically unchanged system. For the procedure to be valid, it is necessary to keep the initial concentration of KIO_3 constant.

It is known from other experiments[17] that, for values of $[KIO_3]_0$ similar to those in our experiments, the reaction dynamics changes considerably with acidity and the $[H_2O_2]_0$. In the mentioned work, the authors have established that either when $[H_2SO_4]_0 \leq 3.2 \times 10^{-2}$ mol dm^{-3}, or when $[H_2SO_4]_0 \geq 5.4 \times 10^{-2}$ mol dm^{-3}, the oscillatory evolution characterized with two induction periods may appear depending on the $[H_2O_2]_0$. For lower $[H_2O_2]_0$, oscillations preceded by only one induction period are observed, whereas for higher $[H_2O_2]_0$, two induction periods may appear. At the same time, for concentrations of sulfuric acid in the range 3.2×10^{-2} mol dm^{-3} $\leq [H_2SO_4]_0 \leq 5.4 \times 10^{-2}$ mol dm^{-3}, only oscillations with one induction period were observed. This is consistent with the present experiments in H_2O, where we have observed oscillatory evolution with a single induction period (Figure 1) for the initial value of $[H_2SO_4]_0 = 4.89 \times 10^{-2}$ mol dm^{-3} and for a rather large $[H_2O_2]_0$ of 2.20×10^{-1} mol dm^{-3}. This suggests that our system can be described with the "one induction period dynamics". When ordinary water is replaced by heavy water, the measured change in acidity is equivalent to a decrease in the initial concentration of sulfuric acid of approximately 11%. This is well within the region of the concentration phase space where oscillations with only one induction period are observed. So, the postponement of the oscillations in the presence of D_2O cannot be formally explained by the appearance of a second induction period at the lower acidity of the system.

Furthermore, it is well-known from experiments[7,18] that lowering the acidity causes an increase in the iodine concentration, i.e., facilitates the reduction pathway. Contrary to this, the results presented in Figures 2 and 3 show that when the amount of D_2O is increased (lowering acidity), the concentration of iodine decreases, so that the oxidation pathway is facilitated. Thus, we may conclude that the effect of D_2O on the reaction dynamics cannot be trivially explained by the changed acidity of the system.

4.3. Influence of D_2O on the BL Reaction Dynamics through Iodine Hydrolysis. Another possible cause of the observed change in the dynamic behavior may be due to differences in iodine hydrolysis in H_2O and D_2O:

$$I_2 + H_2O = HIO + I^- + H^+$$

As it is known, the BL reaction commences by a buildup of iodine through the domination of the reduction pathway (A). Prevalence of the oxidation pathway (B) over the reduction (A) causes the subsequent fast decrease of iodine concentration. The actual mechanism through which this is achieved is not yet well understood, since it is known that oxidation of iodine by hydrogen peroxide is a rather slow process. In theoretical investigations of the BL reaction mechanism it is generally assumed that the first step in process B is hydrolysis of iodine.[19-27] This complex process[8,9,11] involves a number of proton-containing intermediates and may be influenced in the presence of D_2O as a result of the primary isotope effect. For that reason, it is important to establish how is iodine hydrolysis affected by D_2O. Unfortunately, the equilibrium constant of this reaction is very low ($K = 5.4 \times 10^{-13}$),[27] and the amount of hydrolyzed iodine cannot be determined with standard spectrophotometric techniques since it is very small. From our own measurements in the VIS region, we may only conclude that iodine hydrolysis (without initially present iodate) is not grossly enhanced in D_2O. However, even small changes in iodine hydrolysis, which may occur as a consequence of the isotopic substitution, may be "amplified" in the nonlinear BL system through reactions taking place in the presence of iodate. This is not yet fully understood; however, it seems from our experiments that this part of the BL reaction is mostly affected in the presence of D_2O.

Yet another possibility, which should be also discussed, is the possibility of a more efficient oxidation of the products of hydrolysis, by the deuterated H_2O_2 in the presence of D^+. Namely, an efficient removing of the hydrolysis products I^- or HIO (or I_2O, which is proposed to be in a fast equilibrium with HIO)[19] would shift the equilibrium to the "right", resulting in a considerable decrease in the iodine concentration. As was shown in subsection 3.3, this is not observed experimentally. Therefore, a significantly enhanced direct oxidation of iodine or its hydrolysis products by the deuterated peroxide cannot be regarded as a simple explanation for the observed lowering in absorbency. Again, the effect of the possible small differences may reveal themselves as measurable diminution of $[I_2]$ in the BL-D_2O system, but only through reactions occurring in the presence of iodate.

Since even small amounts of added KIO_3 cause a fast discoloration of the mixture of I_2, H_2O_2, and H_2SO_4 in D_2O, and since deuterated H_2O_2 cannot oxidize iodine in a direct reaction, the only possibility is that iodate and peroxide create the necessary reaction intermediates enabling an efficient initiation of the oxidation process. The oxidation of iodine by hydrogen peroxide in the presence of iodate is investigated by many authors.[7,10,28,29] It is generally accepted that iodine oxidation (pathway B) coincides with low iodide concentration in the BL system, whereas high iodide concentration can be related with the prevalence of the reduction pathway (A). Since iodate alone (in an acidic medium, but in absence of H_2O_2) cannot oxidize iodine, the necessary intermediates for a fast oxidation of iodine (or its hydrolysis products, I^- and HIO) should be formed in the reaction between iodate and hydrogen peroxide. So far, the best formal modeling of this process is given by Schmitz,[29] who introduced I_2O (an experimentally unidentified reactive intermediate, until now) to account for known experimental data. Since our experiments with D_2O revealed that heavy water selectively influences just the oxidation reaction pathway, they may be helpful in better understanding this process.

In that sense, we shall further discuss a possible effect of bulk D_2O on the BL reaction dynamics, connecting our results with obvious facts accumulated in the literature over many years.

4.4. Possible Role of Bulk Water and the Influence of D_2O. In our opinion, it is very important to consider other plausible explanations to understand why the oxidation pathway is enhanced relative to the reduction pathway in the presence of D_2O. As already mentioned in subsection 3.1, a qualitative change in the reaction dynamics is observed in the presence of large amounts of heavy water, corresponding to concentrations ranging from 7 to 27 mol dm^{-3} of D_2O. We therefore think that a cooperative effect of a large number of water molecules ought to be considered as a plausible explanation of the experimentally observed effects. Hence, the role of bulk water in the process of facilitating the shifting of the whole reaction mechanism toward the oxidation pathway has to be taken into account as well.

Before proceeding in this way, we would like to summarize shortly what is already known about the oxidation pathway in the BL reaction, and try to discuss it in the light of the new results obtained in the presence of D_2O.

It is experimentally established that the oxidation of iodine by hydrogen peroxide is a kinetically unfavorable process, and that these two components can stay together for days without an appreciable change in the iodine concentration.[6] From our experiments (subsection 3.3) the same is true for the deuterated H_2O_2. Also, iodate alone cannot oxidize I_2 to iodate. (The oxidation of iodine by iodate would be accompanied by the corresponding reduction of iodate back to iodine. Also, the "accumulation" of large amounts of iodine in components with higher oxidation numbers of iodine during this process is prevented because of their high instability.) Though neither iodate alone, nor peroxide, can oxidize iodine, it is efficiently oxidized when they are both present in an acidic media. It means that during the reduction of iodate by peroxide, a sufficient amount of reactive intermediate that is necessary for the onset of the oxidation pathway may be created. Under the conditions of the BL reaction, formation of this reactive intermediate takes over the otherwise favored reduction periodically, leading to oscillatory behavior.

The actual mechanism, through which the switching from the reduction to the oxidation pathway occurs in the BL system, is not yet fully understood. As the direct oxidation of iodine by hydrogen peroxide, given by reaction B, is not possible, it is usually accepted that the oxidation pathway in the BL system commences through certain reactive intermediate(s). As is shown, necessary reactive intermediate(s) must be created in a process parallel to the reduction of IO_3^- by H_2O_2, i.e., during process A. Under the BL reaction conditions, accumulation of the iodine through process A proceeds first, showing that the free energy barrier for the creation of those reactive intermediate(s) must be higher than the energy barrier of the reduction pathway (A). Yet, during some intervals of the BL reaction, the production of these reactive intermediates is so facilitated (the free energy barrier for their formation is lowered) that oxidation of iodine (B) becomes a predominant process. The thermodynamic investigations of the relative stability of known iodine species[30,31] indicates that the highest thermodynamic barrier should be related with the oxidation of $I^{(1+)}$ component(s) (either HIO or I_2O)[19] to components with higher oxidation numbers. This can possibly explain also why the concentration of iodine in the mixture with H_2O_2 remains unchanged for extended periods of time, i.e., why it is not easily oxidized with H_2O_2 directly.

The experiments with D_2O showed that the oxidation pathway is by far more influenced by D_2O than the reduction pathway. This fact enables us to discuss closer the mechanism that facilitates the oxidation path with a higher energy barrier.

Looking from the microscopic point of view (in the ordinary, isotopically unchanged BL system), the switching from the favorable reduction pathway to the unfavorable oxidation pathway may take place when the quantum energy states of the oxidation branch become more accessible than the states of the reduction branch.[14] This may be established by lowering the energy barrier between the zero point energies of the two pathways (the enthalpy contribution) or/and by increasing the density of energy states of the oxidation branch (the entropy contribution). For example, it is possible to decrease the energy barrier between the two pathways if a more "energetic" intermediate, which can initiate the oxidation pathway, is formed. Or/and, it is possible to increase the density of states of the oxidation branch by efficiently including this intermediate in the water network so that a number of new normal modes can be created.

In that sense, the effect of D_2O on the reaction mechanism could be also considered. The isotope exchange cannot create intermediates that are chemically different from the ones that are being created in ordinary water. But, it can decrease the zero point energy of the two pathways. If only the zero point energy state of the oxidation branch is lowered, related with molecules containing an exchangeable hydrogen atom, the isotopic exchange with deuterium can produce a maximal enthalpy contribution $E_H - E_D = -5.1$ kJ mol^{-1}.[16] If both zero point energies are lowered simultaneously due to the isotope exchange, the enthalpy contribution should be <-5.1 kJ mol^{-1}. Since the maximal semiempirically estimated enthalpy contribution due to the primary isotope effect is rather small, we believe that it cannot entirely explain the efficient facilitation of the oxidation pathway in the presence of D_2O.

Even if the enthalpy contribution exists, the accessibility of the states of the oxidation pathway cannot be increased if the density of the states of the oxidation pathway is not increased in relation to the density of the states of the reduction pathway (the entropy contribution). This can be achieved by an efficient incorporation of reactive intermediate(s) in the hydrogen-bonded network of the water molecules. In this case, the changed structurality of the water network may have a considerable influence on the density of states. In the presence of heavy water, the structurality of the water network is somewhat changed due to stronger hydrogen bonding between the molecules. Although deuterium bonds are stronger, large changes of the reduced mass μ in isotopically substituted H_2O molecules causes a smaller "distance" between the vibrational modes of D_2O, relative to H_2O ($\sqrt{k_D/\mu_D} < \sqrt{k_H/\mu_H}$). This is confirmed by a considerable shift of the infrared bands toward lower frequencies that is observed in the IR absorption spectra of D_2O, compared to the spectra of H_2O.[32,33] In accordance with this, the normal modes of D_2O that are disposed toward lower frequencies should be more accessible than the modes of H_2O. Thus, in the presence of D_2O, the entropy contribution due to changed density of states seems to be crucial for the observed facilitation of the oxidation reaction pathway.

The same mechanism of initiation of the oxidation pathway should be involved in the BL reaction conducted in ordinary water. Since there is no isotopic substitution, there is no enthalpy contribution. Hence, the switching mechanism from the reduction to the oxidation pathway should be governed by the entropy contribution alone. The changed structurality of water may alter the distribution of energy in the system, having a direct impact on the rate constants and reaction dynamics.

This concept is further supported with ^{1}H NMR results.[12] In these experiments, a periodic splitting of the water line during the domination of the exothermal oxidation pathway[5,34] is observed. It may be regarded as an indication that the water network may change during the course of the BL reaction.

That structurality of bulk water plays an important role in the BL reaction mechanism can also be inferred from results obtained at high pressure, $p = 2000$ bar.[35] Here, it is shown that the reaction dynamics changes dramatically, the "frequency" of oscillations decreases, and the rate of the oxidation process increases. Similar effects are obtained when the reaction mixture was pressurized with N_2 and O_2 at $p = 100$ bar. In this way it was excluded that the observed effects can be completely ascribed by the increased concentration of dissolved oxygen, leaving the possibility of introducing the change in water structurality as an important parameter in the reaction mechanism.

By the given conception, i.e., by introducing bulk water as an important reactant in the BL reaction system, it is also possible to discuss the experimentally observed influence of gaseous I_2 and O_2 on the reaction dynamics.[36−38] Namely, by changing its structurality, water can influence the level of oxygen supersaturation in the reaction mixture. This, in turn, influences the rate of oxygen and iodine interface transport,[36,37;38]controlling in this way the amount of energy in the system. Since the dissolved oxygen can also influence the structurality of water,[12] a necessary regulatory feedback in the reaction mechanism could be achieved.

5. Conclusion

The influence of heavy water on the two major reaction pathways in the BL reaction is examined at four temperatures, by simultaneously monitoring the potential of the platinum electrode, the concentration of iodine and the oxygen production rate.

It is established that by introducing heavy water the maximal concentration of iodine decreases whereas the corresponding production of oxygen stays virtually constant. This is regarded to be a consequence of an enhancement of the oxidation pathway in the presence of heavy water, so that the formed iodine is more efficiently oxidized. The critical concentrations of heavy water, which causes a considerable enhancement of the oxidation pathway, are determined at four different temperatures. It is confirmed that the influence of D_2O is more pronounced at lower temperatures.

The influence of decreased acidity in the presence of heavy water on the BL reaction dynamics is considered. From the experimental results, it is established that it is not possible to explain the observed effects solely as a result of changed acidity, occurring from the isotopic effect. The importance of iodine hydrolysis itself, and how it is influenced in the presence of D_2O, are also considered as plausible explanations for the experimental observations. We conclude that further investigations are required to establish to what degree iodine hydrolysis is affected by the isotopic substitution, and how these changes influence the BL reactions dynamics.

The obtained results are discussed from a microscopic point of view, suggesting that change in the structurality of the water network may influence the reaction's dynamics. In this way, we considered bulk water as a possibly important species in the controlling processes of the BL reaction mechanism.

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