

# Influence of Heavy Water on the Bray–Liebhafsky Oscillating Reaction

Dragomir Stanisavljev,<sup>\*,†</sup> Nebojša Begović,<sup>‡</sup> and Vladana Vukojević<sup>†</sup>

Faculty of Physical Chemistry, University of Belgrade, P. O. Box 137, YU-11001 Belgrade, Yugoslavia, and  
Institute of General and Physical Chemistry, Belgrade, P. O. Box 551, YU-11001 Belgrade, Yugoslavia

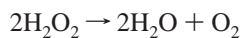
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The influence of heavy water on the Bray–Liebhafsky (BL) oscillating reaction was investigated for varying amounts of D<sub>2</sub>O, at three different temperatures. Evolution of the system was monitored potentiometrically. Simultaneous recordings of gaseous oxygen over the reaction solution were also performed. In separate experiments the iodine concentration was monitored spectrophotometrically. Replacement of H<sub>2</sub>O by D<sub>2</sub>O progressively intensifies the reactions of oxidation of the iodine species, compared to the reactions of their reduction. As a result there is a critical ratio of D<sub>2</sub>O/H<sub>2</sub>O, after which the dynamics of the system is considerably altered. The same effect is observed at all temperatures, but it is more pronounced at lower temperatures. Two possible explanations for the progressively intensified oxidation are discussed: the reverse isotope effect and the selective energy transfer. It is established that the oxidation and reduction of the iodine species in the BL reaction do not proceed through the same intermediates. The important role of bulk water in surmounting the high activation energy threshold of the oxidation branch is revealed in the experiments.

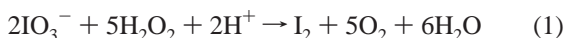
## 1. Introduction

Explorations of nonlinear systems led to recognition that nonlinear phenomena are widespread in the inanimate world and are essential for living systems—the metabolism of any living organism involves thousands of chemical reactions maintained in distinct stable states far from thermodynamic equilibrium. To understand such highly organized systems, it is beneficial to investigate properties of less complex systems exhibiting self-organization phenomena. The simplest examples of self-organization, comprising the same kinds of catalytic loops central to the metabolism, are the so-called “chemical clocks” or oscillating chemical reactions.<sup>1</sup>

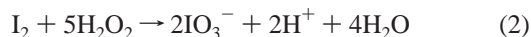
The aim of this study is to investigate the catalytic loops in the Bray–Liebhafsky (BL) oscillating reaction.<sup>2,3</sup> The BL reaction is the longest known inorganic reaction exhibiting a variety of dynamic structures under batch conditions<sup>4</sup> and in the CSTR.<sup>5</sup> The net reaction is the catalytic decomposition of hydrogen peroxide



proceeding through a number of elementary steps summarized as the overall reduction of the iodine species



and the overall oxidation of the iodine species



From a number of experimental results<sup>2–6</sup> it was derived that during the course of the reaction processes 1 and 2 periodically dominate over each other. On the basis of this notion, several models of the BL reaction were proposed.<sup>7</sup> Though it is possible to obtain an agreement between some experimental observations

and some of the model's predictions, the postulated models do not consider the energetic requirements for the assumed reactions.<sup>8</sup> Further investigations of the actual reaction mechanism are therefore necessary.

Replacement of ordinary water by heavy water is a simple experimental procedure by which new information about catalytic loops in the BL reaction can be obtained.

## 2. Experimental Section

The BL reaction is conducted under batch conditions and without stirring. The reaction vessel is a cylindrical glass tube of an inner diameter  $d = 10$  mm. Volume of the reaction mixture is 2.55 mL. Experiments are performed in an open vessel, at atmospheric pressure.

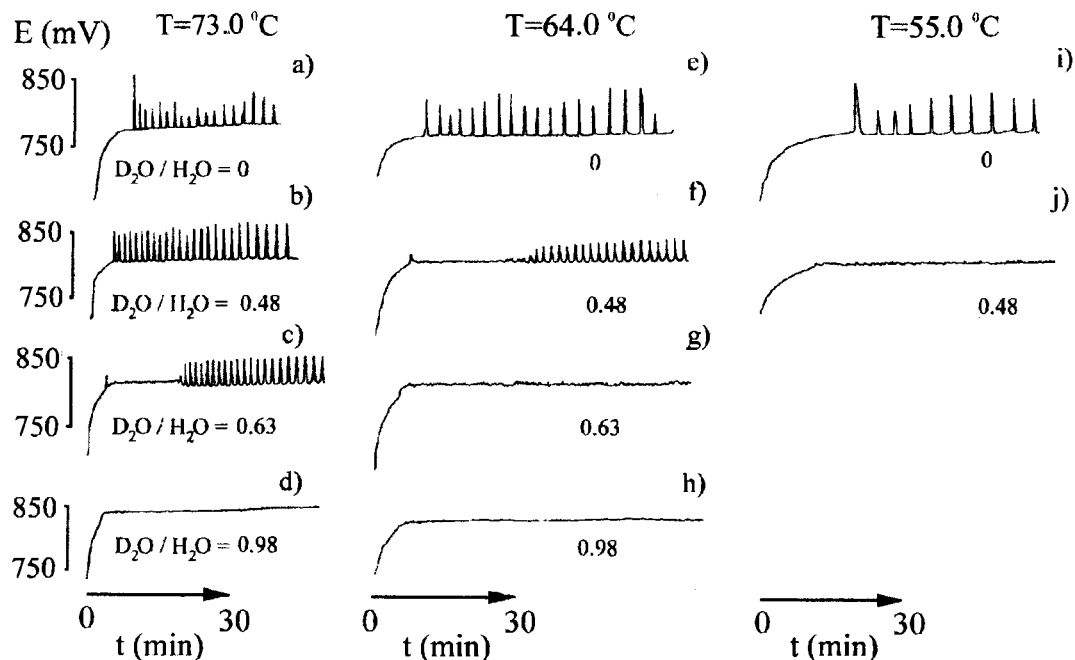
Stock solutions are 0.15 mol dm<sup>-3</sup> potassium iodate, prepared by dissolving the crystals in either H<sub>2</sub>O or D<sub>2</sub>O; 1.00 mol dm<sup>-3</sup> sulfuric acid, prepared by dissolving 18.11 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> in either H<sub>2</sub>O or D<sub>2</sub>O; 10.31 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>. Appropriate volumes of the stock solutions are mixed at room temperature (at which the reaction is very slow), to obtain a reaction mixture with the following initial concentrations of the reactants: [KIO<sub>3</sub>]<sub>0</sub> = 7.34 × 10<sup>-2</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>0</sub> = 4.89 × 10<sup>-2</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 2.22 × 10<sup>-1</sup> mol dm<sup>-3</sup>, and with required ratios D<sub>2</sub>O/H<sub>2</sub>O. The reaction commences by placing the reaction vessel into a thermostating bath, at working temperature.

Experiments are performed at three different temperatures: 55.0 °C, 64.0 °C, and 73.0 °C. The temperature is controlled within ±0.1 °C.

The oscillations are monitored potentiometrically by microelectrodes. The monitoring set consists of a platinum microelectrode (platinum wire of 0.5 mm diameter and 5 mm length, sealed in a glass body of outer diameter 2.5 mm) and a double-junction Ag/AgCl microreference electrode with a ceramic diaphragm tip (a ceramic diaphragm of 0.5 mm in diameter is sealed in a glass body of outer diameter 2.5 mm). The inner electrolyte is a 3 mol dm<sup>-3</sup> solution of KCl, and the outer electrolyte is a saturated solution of K<sub>2</sub>SO<sub>4</sub>.

<sup>†</sup> University of Belgrade.

<sup>‡</sup> Institute of General and Physical Chemistry.



**Figure 1.** Time series showing potentiometrically recorded evolution of the Bray–Liebhaftsky (BL) oscillating reaction for varying amounts of heavy water, at three different temperatures. The initial concentrations of the reactants in all experiments are  $[\text{KIO}_3]_0 = 7.34 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4]_0 = 4.89 \times 10^{-2} \text{ mol dm}^{-3}$ , and  $[\text{H}_2\text{O}_2]_0 = 2.22 \times 10^{-1} \text{ mol dm}^{-3}$ . The experiments are performed in a batch reactor with a volume of the reaction mixture  $V = 2.55 \text{ mL}$ , without stirring. The amount of  $\text{D}_2\text{O}$  is given as the volume's ratio,  $\text{D}_2\text{O}/\text{H}_2\text{O} = V_{\text{D}_2\text{O}}/(V_{\text{D}_2\text{O}} + V_{\text{H}_2\text{O}})$ . In experiments a, e, and i there is no heavy water present in the system, in b, f, and j the amount of heavy water is  $\text{D}_2\text{O}/\text{H}_2\text{O} = 0.48$ , in c and g  $\text{D}_2\text{O}/\text{H}_2\text{O} = 0.63$ , and in d and h  $\text{D}_2\text{O}/\text{H}_2\text{O} = 0.98$ . In experiments a–d the temperature is  $T = 73 \text{ }^\circ\text{C}$ , in e–h  $T = 64 \text{ }^\circ\text{C}$ , and in i and j  $T = 55 \text{ }^\circ\text{C}$ .

Simultaneously with the potentiometric oscillations, evolution of gaseous oxygen over the reaction solution is monitored by an oxygen electrode (Jenway, model 9015).

In separate experiments the iodine concentration is monitored spectrophotometrically, at  $\lambda = 460 \text{ nm}$ . In these experiments the reaction is conducted in a rectangular glass cuvette. The different geometry has no observable effect on the reaction's progression.

All chemicals are used without further purification:  $\text{KIO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{O}_2$  from Merck;  $\text{D}_2\text{O}$  from Fluka (99.8% D) and Cambridge Isotope Laboratories (99.96% D).

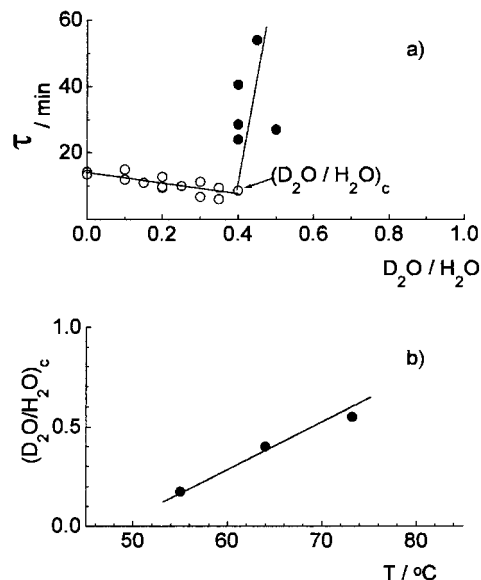
Deionized ordinary water of specific resistance  $\rho = 18 \text{ M}\Omega \text{ cm}^{-1}$  is used throughout.

### 3. Results

Figure 1 presents the influence of the amount of heavy water on the reaction course at three different temperatures. The amount of  $\text{D}_2\text{O}$  is given as the volume's ratio,  $\text{D}_2\text{O}/\text{H}_2\text{O} = V_{\text{D}_2\text{O}}/(V_{\text{D}_2\text{O}} + V_{\text{H}_2\text{O}})$ .

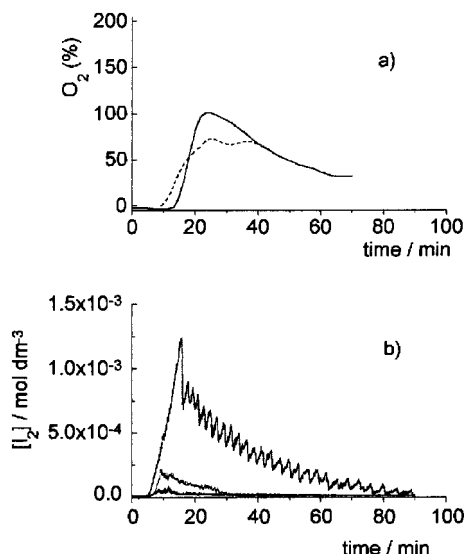
At each temperature there is a threshold ratio designated as the critical ratio  $(\text{D}_2\text{O}/\text{H}_2\text{O})_c$ , see Figure 2a, after which the dynamic of the reaction is appreciably altered. For amounts of heavy water smaller than the critical ratio, the oscillatory pattern is only slightly changed—the preoscillatory period is somewhat decreased, and typical relaxation oscillations arise. For amounts of heavy water larger than the critical ratio the dynamics of the system undergoes a considerable modification: prior to the oscillations there is a steady state, after which the oscillations appear through an unstable focus. For large enough ratios of  $\text{D}_2\text{O}/\text{H}_2\text{O}$ , the oscillations are dismissed during the observation time (see Figure 1).

As can be seen from Figure 2b, the effect of heavy water is more pronounced at lower temperatures; i.e., at lower temperatures the oscillatory evolution is hampered at lower values of  $(\text{D}_2\text{O}/\text{H}_2\text{O})_c$ .



**Figure 2.** (a) Dependence of the preoscillatory period  $\tau$  on the amount of heavy water present in the reaction system. Concentrations of the reactants are given in the caption to Figure 1,  $T = 64 \text{ }^\circ\text{C}$ . The preoscillatory period is measured from the beginning of the reaction ( $t = 0 \text{ min}$ ) to the appearance of the first oscillation. Open circles indicate the elapsed time prior to the appearance of the relaxation oscillations. Solid circles indicate the preoscillatory period in experiments in which oscillations emerge through an unstable focus. The threshold ratio of  $\text{D}_2\text{O}/\text{H}_2\text{O}$  at which this change in the systems dynamic appears is designated as the critical ratio  $(\text{D}_2\text{O}/\text{H}_2\text{O})_c$ . (b) Temperature dependence of the critical ratio  $(\text{D}_2\text{O}/\text{H}_2\text{O})_c$ .

Simultaneously with the potentiometric oscillations gaseous oxygen emerging over the liquid surface was monitored. Recordings obtained for the two endmost experiments performed in ordinary water and in heavy water ( $\text{D}_2\text{O}/\text{H}_2\text{O} = 0.98$ ) at  $T = 64 \text{ }^\circ\text{C}$  are presented in Figure 3a. The amount of evolved gaseous oxygen is proportional to the area under the corre-



**Figure 3.** (a) Time series showing the evolution of gaseous oxygen over the reaction mixture. Reactant concentrations are as given in caption to Figure 1,  $T = 64$  °C. The solid curve corresponds to the experiment in Figure 1e. The dashed curve corresponds to the experiment in Figure 1h. (b) Time series showing the gradually diminishing iodine concentration for increasing amounts of heavy water. Reactant concentrations are as given in caption to Figure 1,  $T = 64$  °C. The upper curve corresponds to the experiment in Figure 1e; the lower curve corresponds to the experiment in Figure 1h. The middle curve corresponds to  $D_2O/H_2O = 0.61$ .

sponding curve. In all experiments the areas under the corresponding curves agree within an experimental error of  $\pm 5\%$ . Hence, we conclude that the overall amounts of evolved oxygen are not affected appreciably by the presence of heavy water.

On the contrary, iodine concentrations are changed significantly by the presence of D<sub>2</sub>O. In Figure 3b the saw-tooth curve reflects the change in iodine concentration in ordinary water,  $D_2O/H_2O = 0.61$  and  $D_2O/H_2O = 0.98$ . Thus, the steady-state typical for experiments in which  $(D_2O/H_2O) > (D_2O/H_2O)_c$  is characterized by an alike oxygen production and a lowered iodine concentration, compared to the corresponding experiments in ordinary water. This steady state with extended and intensified oxidation of iodine species should not be confused with the induction period preceding the oscillatory evolution during which reduction of iodine species is dominant.<sup>4,7</sup>

#### 4. Discussion

Comparison of experiments with stirring at a stirring rate of 1100 rpm and without stirring show that, under investigated conditions, all essential properties of the dynamic pattern are retained. The only difference in the absence of stirring is that the period between the oscillations is somewhat shorter and the amplitudes of the potentiometrically recorded oscillations are smaller. In addition, the experiments without stirring are well-reproducible, ascertaining that stirring is not an essential reaction parameter at this operating point. Therefore, all experiments are performed in the absence of stirring, without losing any generality in the discussion.

In the presence of both hydrogen and deuterium in the BL reaction a number of new species, HDO, HDO<sub>2</sub>, D<sub>2</sub>O<sub>2</sub>, DSO<sub>4</sub><sup>+</sup>, D<sub>2</sub>SO<sub>4</sub>, etc., are produced as a result of the fast isotope exchange. There are no changes in the molecular potential-energy surface when an atom is replaced by its isotope, but only small changes in its zero-point energies.<sup>9,10</sup> Therefore

chemical properties of isotopically substituted molecules do not differ appreciably from the corresponding counterparts with hydrogen. So, the general chemistry of the BL reaction is preserved in the sense that no new chemical reactions are created. Thus, the overall reduction of iodine species by hydrogen/deuterium peroxide will be accompanied by the peroxide's oxidation to oxygen, while the oxidation of the iodine species by peroxide will be accompanied by the peroxide's reduction to water.

As can be seen from Figures 1–3 the replacement of ordinary water by heavy water has a considerable effect on the reaction dynamics at all investigated temperatures. Since the general influence of D<sub>2</sub>O on the BL reaction is similar at all temperatures, we will discuss further on only the changes observed at  $T = 64$  °C.

Replacement of ordinary water by heavy water resulted in an unperturbed oxygen production within an experimental uncertainty of  $\pm 5\%$  (Figure 3a). Because oxygen is produced only in reactions of reduction of iodine species by peroxide, the amount of evolved oxygen reflects the extent of reduction of iodine species. Accordingly, the extent of reduction of iodine species is nearly unaffected by heavy water.

However, the iodine concentration in heavy water is drastically lower (Figure 3b). It is well-accepted<sup>11</sup> that the reduction of IO<sub>3</sub><sup>-</sup> to I<sub>2</sub> in ordinary water can be presented schematically by a skeleton sequence of intermediates common to all postulated models<sup>7</sup> (though other intermediates are also involved):

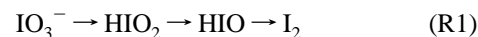


Figure 3b shows that the reduction of IO<sub>3</sub><sup>-</sup> in the presence of heavy water also proceeds to I<sub>2</sub>. However, the maximum concentration of I<sub>2</sub> gradually diminishes for increasing amounts of D<sub>2</sub>O.

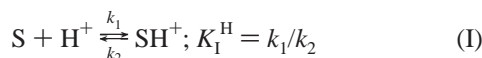
Decreasing of the rate constant in the reduction scheme (R1) as a result of the primary kinetic isotope effect may cause the lowering of iodine concentration for increasing D<sub>2</sub>O/H<sub>2</sub>O ratios. However, according to the general stoichiometry of the summarized reduction reaction 1, lower reduction rates will result in a simultaneous decrease of both I<sub>2</sub> and O<sub>2</sub> concentrations. Since the amount of evolved oxygen is nearly unaffected by D<sub>2</sub>O, we conclude that the primary kinetic isotope effect is not dominant. Taking into account that the extent of the reduction reactions is not significantly altered, the lower [I<sub>2</sub>] may be explained by its intensified oxidation together with an intensified oxidation of HIO. (Intensified oxidation of HIO will enhance the hydrolysis of I<sub>2</sub>).<sup>7,11</sup> This is an important result of the simple replacement of ordinary water by D<sub>2</sub>O because of the uncertainties associated with the oxidation of iodine species in the BL reaction. Namely, the oxidation of iodine has a large activation energy,<sup>6,8</sup> and none of the existing models can explain satisfactorily how this energetic barrier may be surmounted.<sup>8</sup>

Since the oxidation is speeded up compared to the reduction, which is nearly unaffected in the presence of heavy water, it is possible to derive another important conclusion. The intermediate iodine species involved in the oxidation reactions should be different from the intermediates in the reduction; i.e., they should be rather oxidized by hydrogen peroxide than reduced. If the oxidation of the iodine species would proceed through the same intermediates as the reduction of iodate, the speeded up oxidation of iodine species by peroxide would be accompanied by a proportionally higher oxygen production owing to their simultaneously intensified parallel reduction by hydrogen peroxide. Since this is not observed in the experiments, we

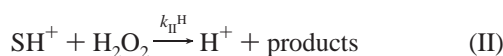
conclude that the oxidation and the reduction reactions proceed through different intermediates. The reduction reactions constitute the reduction branch (1) and the oxidation reactions the oxidation branch (2).

We will consider two possible ways in which heavy water can influence the oxidation branch: the reverse isotope effect<sup>9</sup> and the selective energy transfer.

The reverse isotope effect is associated with specific acid-catalyzed reactions, in which a preequilibrium is established. In such reactions the first step involves a proton transfer to the substrate molecule S:



In the BL system the substrate molecule may be I<sub>2</sub> itself or HIO. Since SH<sup>+</sup> is a stronger acid than SD<sup>+</sup>, the substitution of hydrogen by deuterium causes the preequilibrium to lie more over to the right, that is, K<sub>1</sub><sup>D</sup> > K<sub>1</sub><sup>H</sup>. If the subsequent step



is rate-determining, the overall rate is proportional to K<sub>1</sub><sup>H</sup>k<sub>II</sub><sup>H</sup>. Though the rates of processes involving H<sup>+</sup> transfer are usually greater than those in which there is a D<sup>+</sup> transfer (k<sub>II</sub><sup>H</sup> > k<sub>II</sub><sup>D</sup>), the effect of preequilibrium can predominate K<sub>1</sub><sup>D</sup>k<sub>II</sub><sup>D</sup> > K<sub>1</sub><sup>H</sup>k<sub>II</sub><sup>H</sup>, resulting in a reverse isotope effect—the overall reaction rate in D<sub>2</sub>O catalyzed by D<sup>+</sup> is greater than the reaction rate in H<sub>2</sub>O catalyzed by H<sup>+</sup>.

Thus, if there exist specific acid-catalyzed feedback loops governing the oxidation of I<sub>2</sub> or HIO they can be speeded up by the reverse isotope effect. However, the maximized contribution of the reverse isotope effect, estimated in accordance with the equilibrium isotope effect,<sup>9,10</sup> is

$$\Delta G_D^\circ - \Delta G_H^\circ = -RT \ln(K_D/K_H) = -RT \ln 14.9$$

At *T* = 25 °C this contribution is −6.7 kJ mol<sup>−1</sup>, which alone is too small to initiate the oxidation branch through I<sub>2</sub> and HIO because of the thermodynamically unfavorable step of the oxidation of HIO to IO• requiring Δ*G*<sup>°</sup> = 220 kJ mol<sup>−1</sup>.<sup>8</sup> Therefore, the acid catalysis can only be superimposed on another effect responsible for the initiation of the oxidation branch.

Recently obtained NMR experimental results indicate that in the BL system structural rearrangements of the bulk water may arise on a longer time scale,<sup>12</sup> despite a small change in the concentrations of the reactants. Furthermore, from Figures 2a and 3, it is apparent that oxidation is sustained for an extended time only when the concentration of heavy water is much higher (≈22 mol dm<sup>−3</sup>) compared to the concentration of the reactants. Thus, they are experimental indications of the importance of bulk water in the reaction mechanism.

To consider the influence of bulk water on the initiation of the oxidation branch in the BL reaction, we invoke the selective energy-transfer mechanism. On the basis of the solvent response to chemical dynamics,<sup>13,14</sup> in liquid water the energy released in chemical reactions is dissipated mainly into the mutual bonds between the water molecules.<sup>13–15</sup> Water has a wide frequency distribution of the intermolecular vibrations and can yield a response even to the very fast reactions.<sup>13</sup> Because most of the energy released in chemical reactions is dissipated into the bulk water, activation of chemical reactions must depend on some reversed mechanism of energy transfer to the reacting molecules.<sup>13–15</sup> We regard this energy transfer to be essential

for periodic overcoming of the high activation energy and the selective initiation of the oxidation branch in the BL system in both H<sub>2</sub>O and D<sub>2</sub>O. It is well-known that accumulation of energy above a certain threshold value leads to creation of dissipative structures,<sup>16,17</sup> i.e., highly organized flow of energy through the system. Creation of a dissipative structure, in turn, may explain how the energy can be transferred selectively into the oxidation branch. In that case, one would expect that replacement of H<sub>2</sub>O by D<sub>2</sub>O will result in a more efficient energy transfer because of a greater structural nature of the solvent due to stronger intermolecular forces.<sup>18,19</sup> Thus, the solvent structure must be invoked as an important reaction parameter in describing dissipative systems such as the oscillatory chemical reactions.

For concentrations of heavy water smaller than the critical value the small decrease in the preoscillatory period, as can be seen from Figure 2a, appears mainly through the reverse isotope effect superimposed on the already existing selective transfer of energy in H<sub>2</sub>O, for the properties of bulk water are not affected sufficiently. After the critical ratio (D<sub>2</sub>O/H<sub>2</sub>O)<sub>c</sub>, the properties of bulk water are significantly modified and invigorated energy transfer allows a sustained oxidation of iodine species.

For the same amounts of D<sub>2</sub>O/H<sub>2</sub>O, the steady state with a low iodine concentration is stabilized at lower temperatures; i.e., the system remains in this state for a longer time (Figure 1). Such temperature dependence is in accordance with either of the discussed ways of the influence of heavy water on the BL reaction. In the case of selective energy transfer, lowering the temperature will strengthen the solvent structure, resulting in a more efficient transfer of energy to the oxidation branch. Therefore the oxidation will be predominant, retaining the system in this steady state for lower concentrations of hydrogen peroxide, compared to experiments at higher temperatures. This effect may be further enhanced at lower temperatures by acid catalysis, through the influence of temperature on the preequilibrium dissociation constant K<sub>1</sub> of the SH<sup>+</sup> complex. At lower temperatures, the acid-catalyzed oxidation rate expressed as *v* = K<sub>1</sub>k<sub>II</sub>[S][H<sup>+</sup>][H<sub>2</sub>O<sub>2</sub>] is increased because of the increased value of K<sub>1</sub> (the dissociation of the SH<sup>+</sup> complex is reduced).

## 5. Conclusion

Replacement of ordinary water by heavy water modifies the overall dynamics of the Bray–Liebhafsky (BL) reaction.

The oxidation and reduction branches are affected differently by the presence of heavy water, indicating that these processes do not proceed through the same intermediates.

There is a threshold ratio of (D<sub>2</sub>O/H<sub>2</sub>O)<sub>c</sub> after which the oxidation of iodine species is considerably intensified compared to their reduction. Consequently, the dynamics of the BL reaction is modified. The relaxation oscillations typical for ordinary water and mixtures with smaller amounts of D<sub>2</sub>O are replaced by a preoscillatory steady state characterized by an enhanced oxidation of iodine species, after which the oscillations emerge through an unstable focus.

Intensified oxidation of iodine species is effectuated through two superimposed mechanisms: the selective energy transfer and the specific acid catalysis.

Experiments revealed the important role of bulk water in surmounting the high activation energy threshold of the oxidation branch.

The threshold ratio (D<sub>2</sub>O/H<sub>2</sub>O)<sub>c</sub> decreases with decreasing the temperature, indicating that the effect of heavy water on the BL reaction is more pronounced at lower temperatures.



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