

# Microwaves and coherence in the Bray–Liebhafsky oscillatory reaction

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## Abstract

Simultaneous application of microwave (MW) heating and mechanical stirring to the Bray–Liebhafsky reaction supports the ‘nucleation’ theory of nonequilibrium transitions. The opposite effects of microwaves and stirring on the oscillatory reaction dynamics stress the predominant effect of microwaves on the coherence mechanism, preventing in-phase macroscopic oscillations. The obtained results can contribute to the understanding of the mechanism of nonequilibrium transitions on a more general level.

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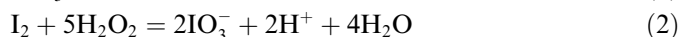
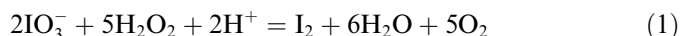
## 1. Introduction

Oscillatory reactions belong to the class of non-equilibrium chemical processes characterized by spontaneous periodic transitions between oxidized and reduced forms of intermediates. Such processes are common in nature, having particularly important role in living organisms [1]. Despite of their importance and universality, understanding of their mechanism is still controversial. The investigations of general features of the oscillatory reactions are mostly related with the study of inorganic oscillators [2], which are chemically simpler and easier to handle. The subtle connection between the inorganic and biochemical oscillators may be due to the participation of liquid water, whose hydrogen bonds undergo considerable changes during oscillations [3,4].

One of the first discovered oscillatory reactions, taking place in water solution, is the Bray–Liebhafsky (BL) oscillatory reaction [5,6]. This reaction, composed of only several components dissolved in water (potassium iodate, sulfuric acid, and hydrogen peroxide), is often used as a model system for investigating chemical oscillators.

The reaction can be formally described as periodic domination of two complex processes: reduction of iodate (rep-

resenting the iodine component in the high oxidation state) and backward oxidation of the formed elementary iodine (low oxidation state of the iodine).



Although the reaction has been known for almost a century and its chemical initial composition is simple, there exists a controversy in modeling the reaction mechanism.

According to formal kinetic approach [2] complex processes (1) and (2) are split into a number of steps whose kinetics is described by a ‘law of mass action’ [7]. They contain several extremely reactive intermediates and in some cases, their kinetic parameters are known with huge uncertainty or are only assumed. The formal kinetic approach consists in fitting those parameters so that the numerical solutions of the kinetic differential equations describe the experiments as close as possible. Although this procedure is not unique (introducing new intermediates requires modification of the parameter sets), it is the only one that gives the possibility to treat the problem numerically [2] and obtain an oscillatory output. However, such treatment may obscure important phenomena, preventing deeper understanding of the reaction mechanisms and predicting the reaction behavior.

One of the first phenomena indicating more subtle nature of the BL reaction is the effect of mechanical mixing.

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By turning on vigorous stirring during the oscillatory regime, the oscillatory evolution may be stopped [8–11]. Convective loss of iodine was investigated as a possible explanation, but it was found that even the very high stirring rate of 1000 rpm (which is much above the critical rate for oscillations) produces slow escape of iodine with  $t_{1/2} = 30$  min [11]. The period between oscillations is about a few minutes, which is much shorter than  $t_{1/2}$ . Hence, the convective loss of iodine during this period is too small to affect considerably the next regular oscillation. Therefore, another phenomenon should be identified that can explain the interruption of the oscillatory evolution.

The mixing effect in nonequilibrium transitions (to which oscillatory processes belong) can be considered from a more general point of view. It was found experimentally [12] that nonequilibrium transitions have properties of the nucleation process. Transitions to another nonequilibrium state are initiated in small volumes ('nucleuses') of the reaction solution, where large fluctuations may initiate processes that are characteristic for the kinetically unfavorable dynamic state described by Eq. (2). Vigorous mixing homogenizes the solution and decreases fluctuations. In this way, the initiation of the transition may be stopped. The importance of inhomogeneities is additionally stressed experimentally as the 'myth of the well-stirred CSTR' [13].

Besides the ability to explain the mixing experiments, this approach indicates general explanation for all non-equilibrium transitions. Unfortunately, an experimental investigation of the role the inhomogeneities is a very difficult task, which prevents their broader incorporation into the modeling process.

We believe that our experiments with microwaves (MW) strongly indicate the existence of the nucleation-like processes and enable its elaboration with more details.

The MW heating is widely used in chemistry due its efficiency. Despite the low energy of MW quanta, the efficient heating of water solutions is explained by the dipolar and conduction processes [14,15] associated with breaking and reforming hydrogen bonds of water molecules [16]. Regardless of the wide applications of microwaves, experimental investigation of the processes during irradiation is not easy. Any metal wires that are parts of sensors, act as antennas transmitting high voltages to the measuring apparatus. Careful construction enabled electrochemical measurements during irradiation [17,18]. It is found that only for very thin platinum electrodes and high MW fields, the electrode currents are modified due to the convection produced by overheating near electrode surface.

The potential of the nonpolarized electrode, in our experiments, depends mainly on the ratio of concentrations of the oxidized and reduced components at the electrode surface and temperature. As a result, the electrode reading should be unchanged by the MW field if large overheating in the electrode vicinity is prevented. Due to the convection effects, electrode ought to reflect concentration changes in the bulk solution and enable monitoring reaction dynam-

ics. This fact is confirmed by the standard addition method [19] and by the close values of the basic electrode potentials during the BL reaction [19,20] in the presence and absence of microwaves.

Since mechanical mixing may stop the oscillatory dynamics, special attention was paid to investigation of thermally induced convection flows during MW irradiation. Using a thick and well-shielded platinum wire, thermally induced convection is minimized [19,20]. The small effects of convection (macromixing) induced by the MW field are confirmed [20] by comparison with the convection caused by thermal gradients in conventional experiments and with convection induced by intensive stirring (at the same temperature). In addition, micromixing effects [2] are excluded from consideration [20] by showing only negligible displacements of ions in the MW field. As previously discussed [20], microwave heating suppresses oxidation branch, which results in smaller production of oxygen and corresponding iodine removal. Since the iodine and oxygen are not polar molecules, microwaves do not additionally influence their movement throughout solution. Although all classical effects that can be related to the MW irradiation (which can considerably modify the reaction mechanism) are insignificant, relatively low absorbed microwave powers (<4 W) annihilate the oscillatory dynamics.

## 2. Experimental

As a source of microwave radiation (2.45 GHz), the focused CEM reactor with adjustable output power DISCOVER is used throughout. A standard fiber optic sensor measures the temperature at the reference point in the reaction mixture. External thermostating of the reaction mixture ( $V = 6.05$  ml in a cylindrical glass vessel of diameter  $D \approx 21$  mm) is applied to provide constant MW irradiation and constant temperature at the reference point inside the mixture. The thick sensor platinum electrode (0.5 mm diameter) and electrolytic bridge of the reference electrode are shielded from microwaves by a well-grounded brass tube. The incorporated magnetic stirrer, operating at 400 rpm, enabled various stirring intensities using magnetic bars of different sizes whose dimensions (diameter  $\times$  height) are  $2.5 \text{ mm} \times 5.5 \text{ mm}$  and  $3 \text{ mm} \times 10 \text{ mm}$ . Experiments are performed at the temperature of  $62^\circ\text{C}$ . The absorbed MW power is calculated calorimetrically by measuring the temperature increase of the mixture at the beginning of MW heating. The initial composition of the mixture, in all experiments, is  $[\text{KIO}_3]_0 = 0.074 \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4]_0 = 0.049 \text{ mol dm}^{-3}$ , and  $[\text{H}_2\text{O}_2]_0 = 0.12 \text{ mol dm}^{-3}$ . All chemicals are p.a. grade:  $\text{KIO}_3$  and  $\text{H}_2\text{SO}_4$  from Merck and  $\text{H}_2\text{O}_2$  from Fluka.

## 3. Results

The results of the experiments are shown in Figs. 1–3 and summarized in Table 1. The experiments without

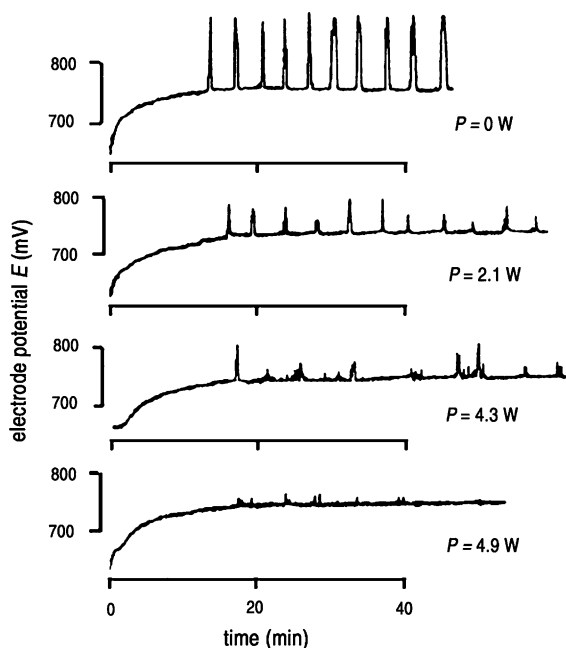


Fig. 1. Oscillograms obtained without mixing at temperature 62 °C, for various absorbed microwave power  $P$ . The initial chemical composition is the same in all experiments.

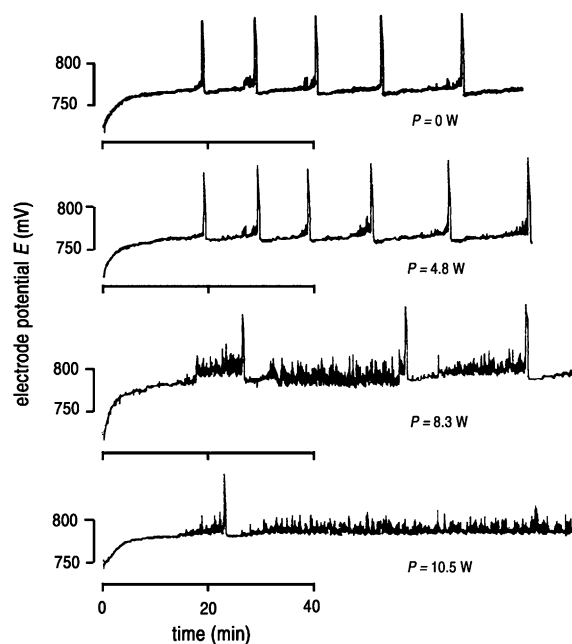


Fig. 3. Oscillograms at temperature 62 °C obtained with 3 mm  $\times$  10 mm stirrer at 400 rpm, for various absorbed microwave power  $P$ .

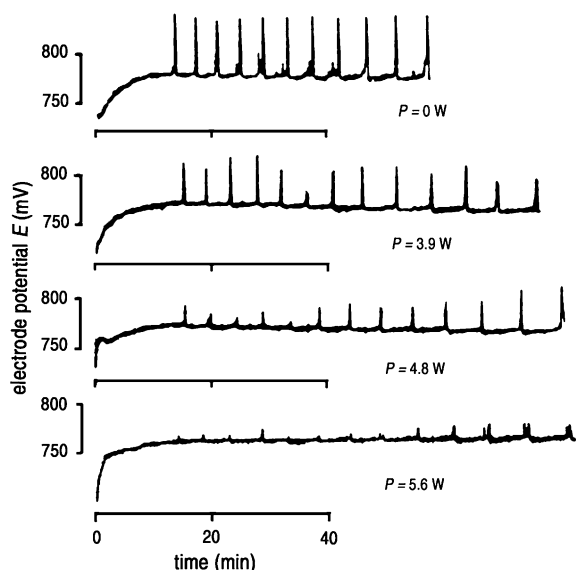


Fig. 2. Oscillograms at temperature 62 °C obtained with 2.5 mm  $\times$  5.5 mm stirrer at 400 rpm, for various absorbed microwave power  $P$ .

microwaves show that even at high stirring intensities, the oscillatory evolution is preserved. Since the MW induced convection is much smaller [20], this is, again, a strong confirmation that the microwave effects cannot be ascribed to simple mixing.

Additional evidence is that the higher stirring intensity requires higher absorbed MW power to annihilate oscillations. It is an indication that the mixing and MW have different effects on the reaction dynamics. If they had the same effect, then a superposition would occur and the

Table 1

Effects of stirring intensity and absorbed MW power on reaction dynamics

Stirrer dimensions $d$ mm $\times$ $h$ mm	Absorbed MW power (W)	MW effect
Without stirring	0	
	2.1	Yes
	4.3	Yes
	4.9	Yes
2.5 $\times$ 5.5	0	
	3.9	Slight
	4.8	Yes
	5.6	Yes
3 $\times$ 10	0	
	4.8	No
	8.3	Yes
	10.5	Yes

higher mixing rate would inevitably require smaller microwave irradiation to stop oscillations. Because a contrary relationship is observed, it can be concluded that the mixing and MW irradiation modify reaction dynamics in opposite directions. The mixing ‘stabilizes’ oscillations in the sense that higher MW perturbation is needed to annihilate the oscillations.

#### 4. Discussion

Such a relation between the mixing and the MW irradiation can be understood by invoking the ‘nucleation’ description of nonequilibrium transitions developed theoretically in [21]. In small volumes (‘nucleation centers’), large fluctuations may start chemical processes that are characteristic for the nonequilibrium state (2). This process alone is insufficient to create macroscopic oscillations. To

obtain transitions that are simultaneously spread throughout the whole system, an additional mechanism must exist that provides communication (coherence) among the nucleation centers. Otherwise, the processes initiated in the nucleation centers will not have the same phase, which will result only in intensive noise.

Following this reasoning, the mechanical mixing alone, without the microwave heating (the first oscillograms in Figs. 1–3), has a twofold effect. The stronger convection increases the communication between the nucleation centers, which is manifested by oscillations that have more regular amplitude and shape. On the other hand, homogenizing the mixture decreases formation of ‘nucleation’ centers, thus decreasing the number of macroscopic oscillations. Based on this approach, the increase of stirring intensity beyond a critical value will result in stopping the oscillatory dynamics, as has been established experimentally [8–11]. In general, oscillations are observed only if both processes are properly balanced.

The opposite effects of the stirring and the microwaves can be explained by the predominant influence of the microwaves on the mechanism that provides the coherence. Relatively small contribution of microwaves on destroying the ‘nucleation’ centers may be anticipated due to two reasons. First, micromixing (mixing on molecular scale) may be neglected due to the small displacements of ions [20]. The second reason is related to the opposite effects of the mechanical mixing and the microwaves: if both destroy the ‘nucleation’ centers, the effects should superimpose (contrary to the experimental results). Thus, the effects of microwaves can be ascribed mainly to destroying the coherence mechanism. The system behaves as if its ability to oscillate is preserved, but the macroscopic oscillations are greatly modified by the out-of-phase microscopic processes in the ‘nucleation’ centers. This is confirmed by the decreasing amplitude of oscillations and the appearance of high-intensity noise (Figs. 1–3).

At the same time, due to the microscopic aspect of the microwave heating [16], its influence on the coherence mechanism is achieved by permanent breaking and reforming the hydrogen bonds of water network. Hence, an important conclusion can be given regarding the reaction mechanism, i.e., the coherence between nucleation centers is achieved through intermolecular water hydrogen bonds. It ascribes the important role to bulk water in the theory of nonequilibrium transitions and opens possibility of controlling reactions with peculiar evolution, by modifying the dynamics of hydrogen-bonded water network. These suggestions are indicated by other experiments too [3,4,22,23], and deserve further investigations.

## 5. Conclusion

The modeling of the BL oscillator (and other chemical oscillators) is predominantly based on mathematical-chemical approach. Our experiments showed that for deeper understanding and predicting the reaction behavior, inclu-

sion of a more physically oriented approach is necessary. The physical side of the problem is related with existence of nucleation-like processes. Relaying on them, consistent explanation can be given for both conventional and microwave experiments. The opposite effects of mechanical stirring and microwave heating (at constant temperature) show that microwaves predominantly affect the coherence between nucleation centers, which is responsible for the in-phase oscillations and spreading the nonequilibrium transitions through the entire system. Due to the microscopic aspect of the microwave heating, coherence between nucleation centers is achieved through intermolecular water hydrogen bonds. This approach can be of special significance for understanding the coherent functioning in living organisms where water is the most abundant component and chemical oscillations may trigger important biological processes.

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