

Investigation of microwave effects on the oscillatory Bray–Liebhafsky reaction

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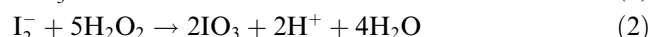
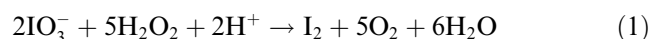
Abstract

A specific control of the Bray–Liebhafsky oscillatory reaction is achieved by changing the microwave (MW) participation in heating the reaction mixture. Experiments are performed at temperatures $T_{\text{rm}} = 62, 65, 68\text{ }^{\circ}\text{C}$. Before the bifurcation point, increased MW participation has no effect on the reaction mechanism. In the sensitive state close to the bifurcation point, increased MW participation stops the oscillatory evolution. To explain the reaction dynamics in the MW field, we consider classical causes (overheating and convection effects) in contrast to some specific effects of the MW heating.

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1. Introduction

Although microwaves (MW) are widely used in chemical synthesis [1–3], investigations of reaction dynamics during irradiation are rarely performed. Microwave heating effects are usually interpreted as thermal effects [1,3], although specific MW effects are also reported [1,2]. Having very low energy, quanta of MW radiation cannot affect chemical bonds. Efficient heating is attributed to dipolar and conduction effects related with the destruction and reformation of hydrogen bonds [4]. The aim of the present experiments is to expand our preliminary investigations [5] to identify possible causes of the observed MW effects. The Bray–Liebhafsky (BL) oscillatory reaction [6] is chosen as a model system for two reasons. First, it is one of the ‘simplest’ liquid oscillatory systems represented with two alternating reaction pathways (branches):



Second, periodical processes are frequent in nature. The ability to control them without introducing additional chemicals may be of great importance.

2. Experimental

The single-mode 2.45 GHz microwave CEM reactor (Discovery) is used. The temperature inside the reaction mixture is measured with a CEM-designed fiber sensor, enabling accuracy of the temperature reading within $1\text{ }^{\circ}\text{C}$. To minimize the ambiguity in interpreting the MW experiments, the reaction is followed by using the simplest, and already exploited potentiometric method, i.e., by recording the platinum electrode ($5 \times 0.5\text{ mm}$ glass-sealed platinum wire) potential versus a double-junction Ag/AgCl reference electrode (with a saturated K_2SO_4 electrolyte bridge, Fig. 1). All sensors are protected from microwaves by a copper tube. The electrical signal from the electrodes is filtered to remove the MW interference [5].

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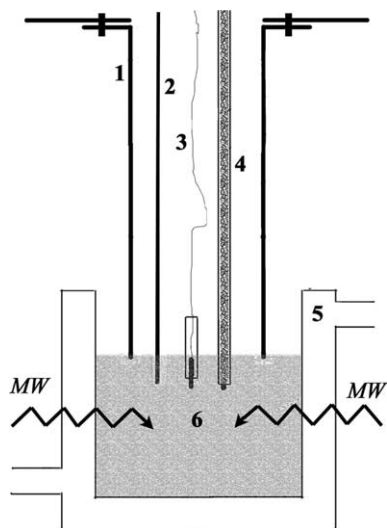


Fig. 1. Experimental setup: 1, shielding copper tube; 2, temperature sensor; 3, Pt-electrode; 4, reference electrode; 5, reaction vessel; 6, reaction mixture.

To provide constant microwave irradiation and a constant temperature (measured in the vessel centre), the excessive heat during MW heating is removed by conventional thermostating.

The volume of the BL reaction mixture in the cylindrical glass vessel (inner diameter $d \approx 21$ mm) was $V = 6.05$ ml. The initial composition in all experiments was $[\text{KIO}_3]_0 = 8.1 \times 10^{-2} \text{ mol/dm}^3$, $[\text{H}_2\text{SO}_4]_0 = 5.0 \times 10^{-2} \text{ mol/dm}^3$, and $[\text{H}_2\text{O}_2]_0 = 1.6 \times 10^{-2} \text{ mol/dm}^3$. To be able to compare temperature gradients, the reaction is conducted without mechanical mixing. The experiments are performed at the reaction mixture temperatures $T_{\text{rm}} = 62, 65, 68^\circ\text{C}$.

All chemicals were p.a. grade: KIO_3 and H_2SO_4 from Merck, and H_2O_2 from Fluka. Deionised water of resistivity $\rho = 18 \text{ M } \Omega \text{ cm}$ was used.

3. Results

3.1. Microwave experiments

To describe our experiments, we define the following parameters: the temperature of the vessel walls (T_{wall} , i.e., the temperature of the thermostating fluid), the temperature of the conventionally heated reaction mixture without microwaves (T_{conv}), the temperature increase achieved by the MW heating (ΔT_{MW}), and the relative fraction of the MW heating,

$$F_{\text{MW}} = \frac{\Delta T_{\text{MW}}}{T_{\text{rm}}} = \frac{T_{\text{rm}} - T_{\text{conv}}}{T_{\text{rm}}}, \quad (3)$$

where F_{MW} is directly proportional to the MW energy absorbed by the reaction mixture. Hence, it character-

izes the experiments better than the power emitted by the CEM reactor.

The temperature of the circulating water is measured at the exit from microwave cavity with and without the MW field. Only a negligible difference of 0.1°C is observed, showing that the speed of the thermostating fluid is high enough to prevent its considerable MW heating and large deviations in T_{conv} and T_{wall} .

The main temperature gradient ($\approx 40^\circ\text{C}$ directed towards the upper surface, which is at room temperature) was the same in the MW and conventional experiments at the same T_{rm} . Hence, only the gradients from/to the vessel walls (proportional to $T_{\text{rm}} - T_{\text{wall}}$) are determined. All experiments are conducted similarly, keeping the assembly inside the MW cavity, thus preserving the same heat losses. The accuracy of all gradients is within 1°C .

Oscillograms obtained with different F_{MW} at $T_{\text{rm}} = 68, 65, 62^\circ\text{C}$ are presented in Figs. 2–4, respectively. All characteristic parameters are given in Table 1.

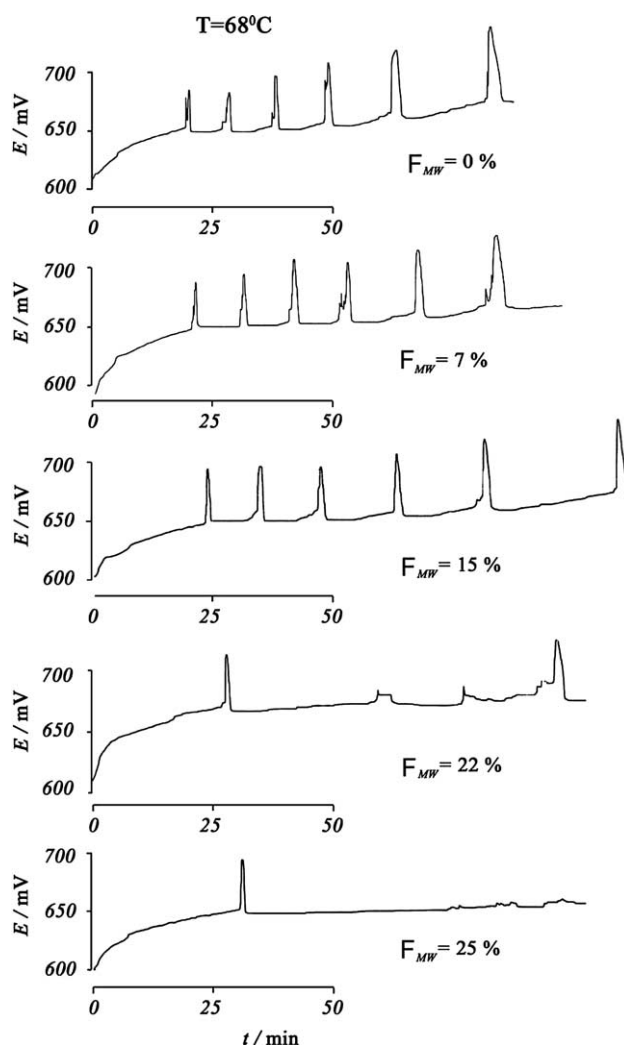


Fig. 2. Dynamics at $T_{\text{rm}} = 68^\circ\text{C}$.

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