Microwave effect on the dynamics of oscillatory Bray–Liebhafsky Reaction

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The well known oscillatory Bray–liebhafsky reaction (which can be considered as the decomposition of \( H_2O_2 \) in presence of \( IO_3^- \) into \( O_2 \) and \( H_2O \)) is one of the simplest liquid oscillatory systems represented with two alternating reaction pathways (branches):

Reduction pathway: \( 2IO_3^- + 5H_2O_2 + 2H^+ \rightarrow I_2 + 5O_2 + 6H_2O \)

Oxidation pathway: \( I_2 + 5H_2O \rightarrow 2IO_3^- + 4H_2O + 2H^+ \)

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 \( T_{rm} = 62, 65, 68^\circ C \). 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.

The regularity of oscillations can be attributed to the batch oscillations. With the used volume of the reaction mixture and the irksome effects of the convection (caused by the temperature gradients and initiation of \( O_2 \) bubbles), regular spreading of travelling waves [3] is not possible.

The oscillatory evolution is characteristic in the whole temperature range considered, so that temperature itself is not a bifurcation parameter.

Due to the theory of hot spots[1], the bulk solution, during MW heating could be regarded as overheated with respect to the measured temperature. Conventional experiment show that the increased temperature favors the participation of oxidation branch (more frequent oscillations), whereas increased MW heating suppresses the oscillations. The same contradiction arises from formal kinetic consideration. The well known Arrhenius Equation, \( k = Aexp(\frac{E_a}{RT}) \) predicts with increased temperature the reactions with higher \( E_a \) (activation energy) are favored[4].

Again vigorous mechanical stirring (mixing) is able to suppress the oscillation[5]–[8].

Bubbling the reaction mixture with \( O_2 \) [10] and [11] and pressurising the reaction mixture (with inert \( N_2 \)) revealed quite similar effects, i.e. non chemical coupling of the \( O_2 \) with the BL mechanism. This coupling is attributed to removal of iodine by \( O_2 \) bubbles from the reaction mixture – accompany the oxidation branch. Since in the MW experiments the oxidation branch is suppressed, the production of oxygen should be much smaller than in the conventional experiments. Hence the removal of iodine by oxygen bubbles should be smaller than in the conventional experiments and it is not the main reason of destroying the oscillatory dynamics.

As classical effects cannot explain this MW experiment we find resort to the peculiar characteristic of the MW heating[9] (destruction and reformation of H-bonds). The very essence of MW heating is the time lag of the polarisation in the sample behind the applied electric field. This is the indication that the connectivity[12] of the H-bonded network is different in MW and conventional experiments (at the same temperature). As a result the matrix in which reactions take place is changed. Being in a sensitive state close to the bifurcation point, such a changed matrix may influence the critical processes by different solvation of reacting molecules and active complexes[2] as well as the energy transfer between molecules. The importance of the structure of the hydrogen bonded network and indicated with other experiments too. Periodic strengthening and loosening of the large number of H-bonds is recorded[13]. The same is also observed in the Belousov-Zhabotinsky reaction[14].

All these experiments mentioned in the reference section showed that for deeper understanding and predicting the reaction behaviour, the physical side of the problem should also be considered – i.e. the related existence of nucleation-like process. We are trying to get the full picture of this phenomenon. We also intend to study the coherence between nucleation centres, achieved through the intermolecular water hydrogen bonds.

References