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The Influence of Visible Light on the Belousov-Zhabotinskii Oscillating Reactions applying Different Catalysts

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With 3 Figures

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Abstract

The influence of visible light on the BELOUISOV-ZHABOTINSKII [1, 2] (BZ) oscillating systems using different catalysts (Ce^{4+} , $\text{Fe}(\text{phen})_2^{2+}$ and $\text{Ru}(\text{dipy})_2^{2+}$) were investigated. Light has no effect on the BrO_3^- -malonic acid- H_2SO_4 - Ce^{4+} system. However, using the complexes as catalysts the amplitude and frequency changed and even initiation and inhibition of oscillation was observed by the effect of illumination. In a modified (viz. containing an excess of Fe^{2+} , oxalic acid and that of phenantroline) BZ system applying ferriin catalyst, at a certain composition, oscillation occurred only on illumination.

Introduction

In 1973 NITZAN and ROSS [3] from thermodynamic and kinetic considerations predicted that oscillations might be generated in a simple system pumped by energy flux such as continuous illumination.

Oscillation of the fluorescence intensity was detected on the effect of UV-irradiation in photochemical reactions of 1,5naphthyridine [4] acetone [5] and 9,10-dimethyl-antracene [6].

It is expected that illumination can modify the character of an oscillating system, too. There are a few examples in the literature on the light sensitivity of homogeneous oscillating reactions.

ZHABOTINSKII et al. [7, 8] found that oscillation was modified or even ceased in the BrO_3^- -malonic acid (MA)- H_2SO_4 - Ce^{4+} system on illumination ($\lambda < 300$ nm). They proposed that oscillation was stopped by the effect of light due to the formation of Br^- in the photochemical reactions of bromomalonic and bromoacetic acids.

KUHNERT and LINDE [9] detected a potential oscillation in the BrO_3^- -MA-dipy-trisoxalatoferriate[III]- H_2SO_4 system after interrupting the illumination with UV-light.

According to SHARMA and NOYES [10] the visible light can cause or stop oscillation in the BRAY-LIEBHAFSKY [11, 12] (H_2O_2 - IO_3^-) system.

Although iron-phenantroline and ruthenium-dipyridile complexes absorb in the visible region, the influence of *visible light* on the BZ systems with these catalysts has not been studied before.

The reduction of ferriin to ferriin by solvent molecules is accelerated by light of 580-700 nm [13]. The photochemical reaction produces $\text{OH}\cdot$ radicals and the formation of complex radicals was also observed [14].

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There have been several studies of the photochemistry of ruthenium-dipyridile complexes. $\text{Ru}(\text{dipy})_3^{2+}$ can be oxidized and $\text{Ru}(\text{dipy})_3^{3+}$ can be reduced in solution on the effect of the visible light [15–17].

Experimental

Stock solutions were prepared from analytical grade chemicals (Reanal products) and kept under argon atmosphere. $\text{Ru}(\text{dipy})_3^{2+}$ was prepared according to the method of JONES and COLE-HAMILTON [18].

The initial concentrations of the reactants were: $[\text{BrO}_3^-]_0$: 0.05 mol dm^{-3} (except in case of the BZ system with ferroin catalyst, where $[\text{BrO}_3^-]_0$ was 0.06 mol dm^{-3} , since this was used most frequently in the literature); $[\text{MA}]_0$: 0.02 mol dm^{-3} [except in case of the BZ system with ruthenium-complex catalyst, where $[\text{MA}]_0$ was 0.2 mol dm^{-3}]; $[\text{Ce}^{4+}]_0$: $0.002 \text{ mol dm}^{-3}$; $[\text{ferroin}]_0$: $0.001 \text{ mol dm}^{-3}$; $[\text{Ru}(\text{dipy})_3^{2+}]_0$: $1 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4]_0$: 0.5 mol dm^{-3} .

85 cm^3 of reaction mixture was put into a thermostated (298 K) cylindrical glass vessel containing a magnetic stirrer. The vessel was positioned on the axis of an optical bench. A continuous flow of argon was passed over solution.

The light source was a TUNGSRAM R-7, s-15 type halogen lamp (1000 W). The length of the filament was similar to the height of the reaction vessel; thus the illumination was nearly equal in every part of the system. The illumination was measured with a lux-meter. The following table shows the different values of the illumination at different distances:

Distance (cm)	Illumination (lx)
13	225000
16	150000
25	65000
41	28000

The value of the diffuse illumination was never higher than 200 lx.

No differences were found between using diffuse illumination and total darkness.

Potentials between a bright platinum electrode and a Radiometer type K 401 SCE electrode connected by a saturated KNO_3 salt bridge were measured with a Radiometer PHM-51 mV-meter fitted with a Radelkis type OH-814/1 recorder.

Results

BZ systems with different catalysts

With *cerium as the catalyst* there were no detectable effects with either diffuse light or intensive illumination.

In the *ferroin catalyzed* system the amplitude and the period of the oscillation continuously increased on continuous increasing the illumination. At a critical illumination (the distance of the lamp was 16 cm) the oscillation ceased. It can be seen on Fig. 1

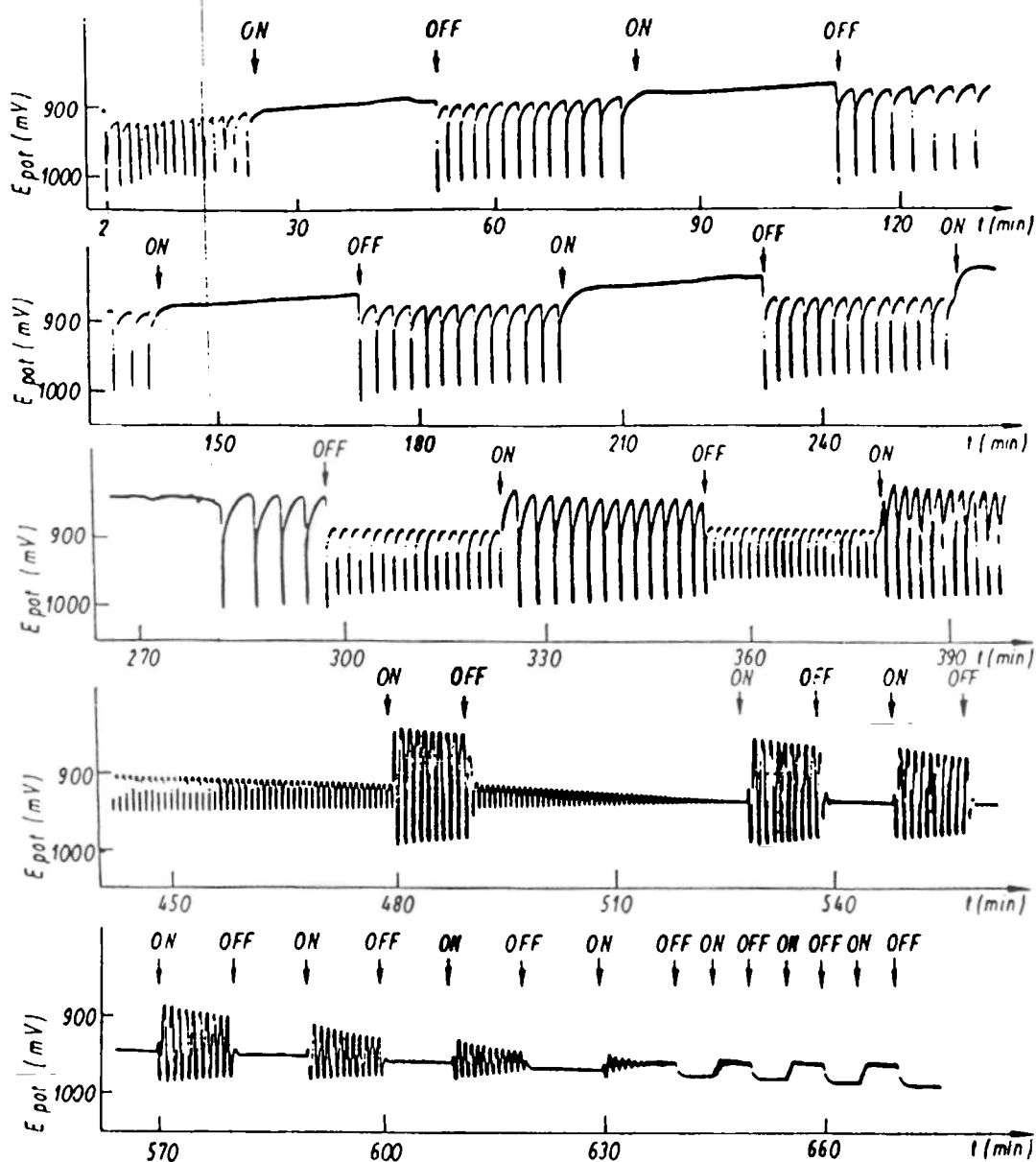


Fig. 1. The ferroin catalyzed oscillating system.

Composition: $[\text{BrO}_3^-]_0: 0.06 \text{ mol dm}^{-3}$, $[\text{MA}]_0: 0.02 \text{ mol dm}^{-3}$

$[\text{ferroin}]_0: 0.001 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4]_0: 0.5 \text{ mol dm}^{-3}$.

The distance of the lamp: 16 cm

that at this illumination the light inhibited the oscillation for a few hours. On the other hand at the fifth hour the system started to oscillate during illumination. The amplitude and period were higher than with diffuse light. This type of oscillation *initiated and sustained* by light was capable of repetition.

With $\text{Ru}(\text{dipy})_3^{2+}$ as the catalyst the amplitude and the period continuously decreased on increasing the illumination (Fig. 2). At a critical illumination (the distance of the lamp was 13 cm) the oscillation was also inhibited. This cessation of oscillation is not the same as that in the BZ system with ferroin catalyst. During illumination a new

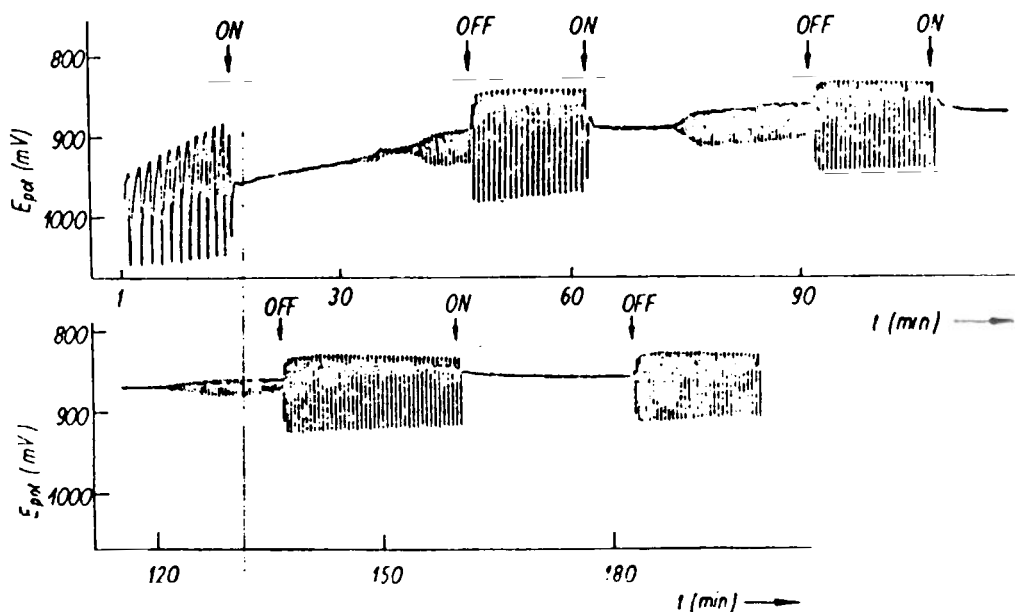


Fig. 2. The ruthenium-dipyridile catalyzed oscillating system.

Composition: $[\text{BrO}_3^-]_0$: 0.05 mol dm^{-3} , $[\text{MA}]_0$: 0.2 mol dm^{-3} ,
 $[\text{Ru}(\text{dipy})_3^{2+}]_0$: $1 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4]_0$: 0.5 mol dm^{-3} .
 The distance of the lamp: 13 cm

oscillation developed without a preoscillation period. The amplitude of this oscillation increased with time. After a few illuminations the system did not oscillate in the presence of light, but in darkness the oscillation appeared again.

A modified BZ system with ferroin catalyst

An interesting phenomenon was found in the following experiments (Fig. 3):

Initial concentrations were chosen so that oscillation would not take place in diffuse light during three hours:

$[\text{BrO}_3^-]_0$: $0.0375 \text{ mol dm}^{-3}$; $[\text{MA}]_0$: $0.003 \text{ mol dm}^{-3}$;

$[\text{ferroin}]_0$: $2.5 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4]_0$: 0.5 mol dm^{-3}

Beside these species the modified BZ system contained also $5 \times 10^{-4} \text{ mol dm}^{-3}$ iron(II)-ion, $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ oxalic acid (OX) and the same concentration of phenantroline. The order of the mixing was: H_2SO_4 - BrO_3^- - Fe^{2+} - MA - OX -phen-ferroin-water. In this modified BZ system oscillation occurred in darkness without a preoscillation period. However, this oscillation shortly ceased.

When the distance of the lamp was 25 cm (point a. on Fig. 3) a jump and then a slow decrease of potential were observed on illumination.

Sitting the lamp at 41 cm from the reaction vessel (point b. on Fig. 3) oscillation developed. This continued at a different frequency and amplitude on switching off. The influence of the light to initiate and to preserve oscillation was detectable also at repeated illuminations.

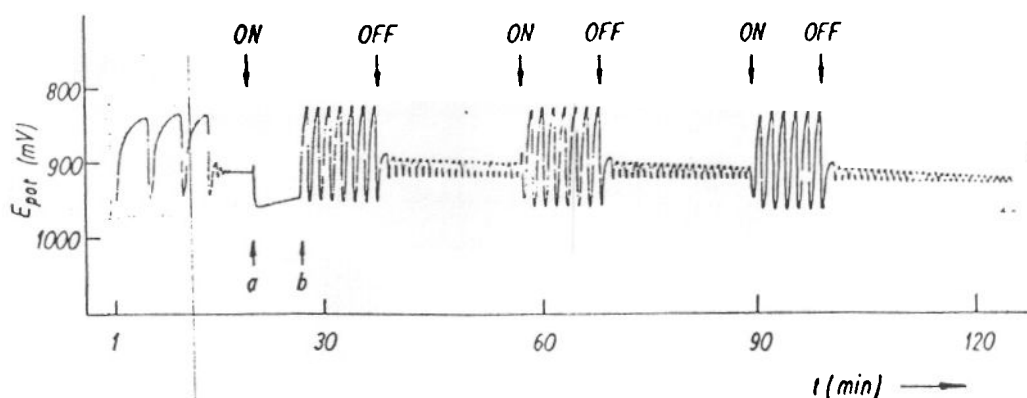


Fig. 3. The modified BZ system with ferroin catalyst.

The composition in order of the mixing:

$[\text{H}_2\text{SO}_4]_0$: 0.5 mol dm^{-3} , $[\text{BrO}_3^-]_0$: $0.0375 \text{ mol dm}^{-3}$,

$[\text{Fe}(2^+)]_0$: $5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{MA}]_0$: $0.003 \text{ mol dm}^{-3}$, $[\text{OX}]_0$: $0.0015 \text{ mol dm}^{-3}$,

$[\text{phen}]_0$: $0.0015 \text{ mol dm}^{-3}$, $[\text{ferroin}]_0$: $2.5 \times 10^{-3} \text{ mol dm}^{-3}$.

a) The distance of the lamp: 25 cm,

b) The distance of the lamp: 41 cm

When the composition was the following:

$[\text{H}_2\text{SO}_4]_0$: 0.5 mol dm^{-3} ; $[\text{Fe}^{2+}]_0$: $4.16 \times 10^{-4} \text{ mol dm}^{-3}$;

$[\text{BrO}_3^-]_0$: $0.0375 \text{ mol dm}^{-3}$; $[\text{OX}]_0$: $7.5 \times 10^{-4} \text{ mol dm}^{-3}$;

$[\text{MA}]_0$: $0.003 \text{ mol dm}^{-3}$; $[\text{phen}]_0$: $7.5 \times 10^{-4} \text{ mol dm}^{-3}$;

$[\text{ferroin}]_0$: $8.33 \times 10^{-5} \text{ mol dm}^{-3}$ and the distance of the lamp was 16 cm, oscillation occurred only on illumination.

Discussion

In explaining the dramatic effects of visible light on complex catalyzed BZ reactions a number of reasons should be considered. On illumination the rate of both oxidation and reduction of the catalyst may be increased. This may result in a change in the concentration of different species including radicals which play a crucial role in the oscillatory kinetics [19, 20].

Under our experimental conditions the reduction of ferroin, as well as both the reduction of $\text{Ru}(\text{dipy})_3^{3+}$ and oxidation of $\text{Ru}(\text{dipy})_3^{2+}$ is accelerated by illumination and the rates of these reactions are comparable to the rates of changes in the oscillating systems. To make any quantitative assessment of the mechanism it would be necessary to get information on the relation between the intensity of illumination and the concentration of radicals. Unfortunately no clear-cut method for the determination of concentration of radicals is available. It is intended to see if ESR studies can be helpful in this respect.

Clearly effects of illumination on modified BZ systems are complex. One must consider the photolysis of trisoxalatoferriate(III) complex, the effect of radicals formed in this reaction on the oscillatory system and a competition between oxalate ion and

phenantroline for iron(II) ion. Beside the study of the composite system we are studying reactions in subsystems where the relations are simpler and more available for a quantitative study.

This investigation strongly indicates that in the mechanism of catalyzed oscillating reactions the role of the steps in which the oxidized and reduced forms of the catalysts are involved is much greater than assumed by the previously proposed mechanisms.

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