

Zhabotinskii A M. Periodicheskie oksilnitelnye reaktsii v zhidkoi faze (Periodic oxidizing reactions in liquid phase). *Dokl. Akad. Nauk SSSR* 157:392-5, 1964.

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The mechanism of the oscillating chemical reaction in liquid phase is formulated, where the autocatalytic step, which is the oxidation of metal ion by bromate, is strongly inhibited by its remote product—bromide ion. Br^- is produced as a result of the reduction of the oxidized metal ion by brominated organic compounds. The active species in the autocatalytic step is bromous acid or some oxobromine free radical. [The SC7® indicates that this paper has been cited in over 205 publications.]

Bromide as Inhibitor in an Oscillating Reaction

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June 6, 1988

In 1961, after graduating from the Biophysical Department of Moscow State University, I intended to study intracellular biochemical oscillations. It seemed that the most suitable topic was glycolytic oscillations. However, Professor S.E. Shnoll advised me to start with the Belousov reaction mainly because of the limited experimental supply. He had provided me with Belousov's recipe, which contained bromate, cerium, and citric acid. I had not been familiar with Belousov's only published paper.¹ At that time oscillations during homogeneous chemical reaction were considered as quite unusual or even impossible phenomena. The chemical mechanisms of oscillating reactions were totally unknown. Only a few papers on the subject had been published.

Belousov's original prescription produced clear oscillations of the solution color, but it was not convenient for optical measurements due to the intensive evolution of gas and precipitate formation. I made some empirical replacements of the reaction components. As a

result, a more convenient reductant, malonic acid, was chosen to replace citric acid. The oscillations in color result from oscillations of ceric ion concentration. Further, free bromine did not accumulate in detectable amounts. Bromate oxidizes cerous ion autocatalytically. An inhibitor of this step is produced during that part of the oscillatory cycle where ceric ions are reduced.²

The central finding of the paper under discussion was the identification of the inhibitor. Bromide ion, being the well-known inhibitor of free radical reactions, seems to be the most likely candidate. I showed that introduction of bromide ions into the system at a constant rate cancels the oscillations, whereas cerium is maintained in the reduced state. Later the inhibitory role of the bromide ions was confirmed by several different methods. Bromide ions were produced during the reduction of ceric ions by brominated derivatives of malonic acid. Because of that, the constant infusion of ceric ions retained cerium in the reduced state. These findings resulted in the formulation of the mechanism of the oscillations. Modifications of the reaction were also described in the paper to demonstrate that the oscillating chemical reaction is not an exceptional phenomenon. Two points were stressed—the possibility of chemical oscillations in a closed homogeneous system and the advantage of catalytic systems for providing a natural concentration and temporal scale separation. Many topics just briefly described in the paper were later developed in numerous publications from other laboratories.

The BZ reactions are the most intensively studied among the oscillating reactions.³ The *Citation Classic* was the first publication giving the qualitative description of the mechanism of oscillations with all significant intermediate compounds. This is probably the main reason for its frequent citation. The paper was one of the most important factors in being awarded the Lenin Prize in 1980.

1. Belousov B P. A periodic reaction and its mechanism. *Collect. Commun. Radiat. Med.* 1959:145-7. (Cited 155 times.)

2. Zhabotinskii A M. Periodic reaction of malonic acid oxidation in solution (Study of the Belousov reaction kinetics). *Biofizika* 9:306-11, 1964. (Cited 145 times.)

3. Field R J & Burger M, eds. *Oscillations and traveling waves in chemical systems*. New York: Wiley, 1985. 681 p.