

Iron Catalyst Local Concentration Fluctuations Found in Dissipative Reactions by X-Ray Microanalysis

Csaba P. KESZTHELYI,^{*,††} József SOÓS, András G. S. JANOSSY, and Kristóf VOVÁCS[†]

Institute of Biophysics, Biological Research Centre, Hungarian Academy of Sciences, H-6701 Szeged, Hungary

[†]Department of Silicate Chemistry, Technical University for Chemistry, H-8200 Veszprém, Hungary

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Synopsis. The present work provides the first application of the powerful X-ray microanalysis technique in the study of “Zhabotinskii-type” oscillatory reactions. The modified HNO_3 : KBrO_3 : $[\text{Fe}(\text{phen})_3]^{2+}$: malonic acid system is quantitatively described. Systematic variation, spatially correlated with the dissipative structures, was found in the Fe concentration.

The very occurrence of concentration oscillations and temporal periodicity in initially homogeneous chemical systems was a matter of scientific controversy until recent years. His unusual insight into biological morphogenesis led Turing¹⁾ to propose the feasibility of the formation of spatial concentration patterns in an initially uniform chemical medium as early as 1952. Such were the ramifications of the ideas raised by Turing’s paper that a new area of thermodynamics, the “far from equilibrium” or “dissipative” branch was born.^{2,3)} Related research stands out in a unique way: while science is experiencing day to day fragmentation due to the sheer bulk of new results and new techniques, while researchers often fit into the order of things by adopting a mosaic vision, the theories on dissipative structures cut across diverse fields such as biology, chemistry, ecology, mathematics, physics, population dynamics and sociology, once again giving impetus to the quest for fundamental principles and inter-relationships.³⁾ The topic has claimed the interest of several major research groups, as can be gauged from some excellent review articles.⁴⁾ Particularly relevant is the conclusion of Procaccia and Ross,⁵⁾ that experimental efforts lag behind theoretical advances in this area.

The present work provides the first application of the powerful X-ray microanalysis technique in the study of “Zhabotinskii-type,” dissipative oscillatory chemical reactions. Upon cursory examination, the match between the system of interest and the chosen instrumental technique appears distressing: the oscillatory reactions commonly occur in aqueous solution, whereas no water is admissible to the analytical electron microscope. In devising a suitable procedure, as a first step we found in agreement with Winfree⁶⁾ that the oscillatory reactions proceed quite well in membrane filters also. Next it is an easy matter to quench the reaction by immersing the filter bearing the characteristic bands of spatial periodicity into liquid N_2 . Subsequent drying of the fixed reaction by vacuum under a temperature gradient is not feasible with the typical mixtures containing H_2SO_4 or HClO_4 , due to non-volatility of these acids. Nitric acid was found to be an acceptable

substituent for H_2SO_4 as reported by Winfree;⁶⁾ the modified system is described in conjunction with Fig. 1 as follows. The solutions used to prepare the reaction mixture: **A.** 5 g KBrO_3 +67 ml H_2O +3 ml concd HNO_3 ; **B.** 10% aq KBr ; **C.** 10% aq malonic acid; **D.** 25 mM aq $[\text{Fe}(\text{phen})_3]^{2+}$. Reagent **D** needs to be prepared under rigorously chloride free conditions, in agreement with Winfree’s comment. The reagents were mixed in the sequence: 3 ml **A**+0.5 ml **B**, followed by the addition of 0.5 ml **C**. At this stage bromination of the malonic acid occurs within 3–4 min at room temperature. Addition of 0.3–0.5 ml **D** initiates the characteristic temporal oscillations which can be visually followed by observing the red-blue color change of the catalyst. Spatial patterns emerge subsequently, either spontaneously or facilitated.⁶⁾

We measured oscillation period parameters at 27 °C in the standard manner at 550 nm, using a UNICAM SP 1800 spectrophotometer with 5 mm cuvettes. Determined from the data depicted in Fig. 1 by the method of least squares, we obtained with better than 0.99 correlation coefficient:

$$\text{induction period(s)} = 394 \times 0.0227C, \quad (1)$$

$$\text{first oscillation period(s)} = 181.7 \times 2.90C, \quad (2)$$

where C is the concentration (mol/dm^3) of HNO_3 .

With the modified system it was possible to produce membrane filters (Sartorius SM 11306) on which the original dissipative structures were preserved intact after drying. Working with ferroin as catalyst had the great advantage of constantly being able to see the status and quality of the samples, and correlate

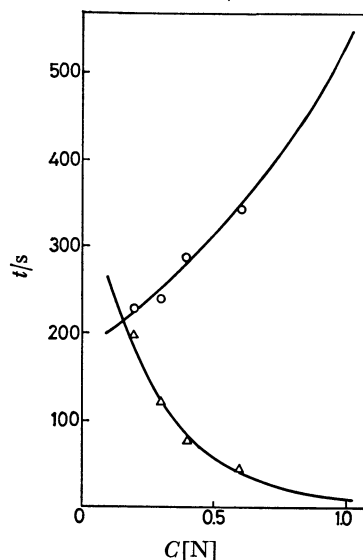


Fig. 1. Temporal oscillatory characteristics of the HNO_3 : $[\text{Fe}(\text{phen})_3]^{2+}$: KBrO_3 : malonic acid system.

^{††} U. S. National Academy of Sciences–Hungarian Academy of Sciences exchange professor; permanent address: Louisiana Academy of Science, University Station # 22315, Baton Rouge, Louisiana 70893, U. S. A.

instrumental readings with visual observations.

From properly prepared filters selected portions *ca.* 3 mm wide and over 1 cm long were introduced to the analytical electron microscope, JEOL JEM 100B. Analysis was performed in the SEI mode, using 20, 40, and 80 kV nominal excitation voltage. Areas of 0.1×0.1 mm² were subjected to X-ray microanalysis in steps of 0.25 mm. Utilizing an EDAX 707B X-ray analyser, a typical result is shown in Fig. 2. In the energy dispersive X-ray spectrum covering the 0–10 keV range, Br L_{α} , K K_{α} , and Fe K_{α} peaks are readily identifiable (Cu lines are indigenous to the measuring technique). Over 100 linearly correlated points were individually subjected to microanalysis, and weight ratios were calculated with the 7. EP program of EDAX, Inc. Major fluctuations spatially correlated with the dissipative structures were

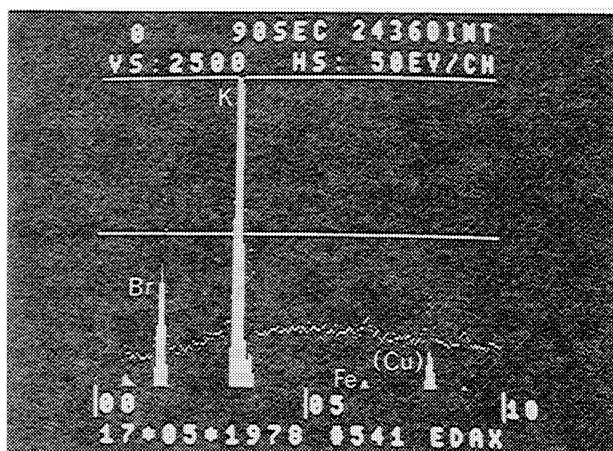


Fig. 2. Typical energy dispersive X-ray spectrum of the Zhabotinskii-type reaction described in Fig. 1. The spectrum shows Br L_{α} line at 1.48 keV, K K_{α} line at 3.30 keV, and Fe K_{α} line at 6.40 keV. Additional peaks at 8.04 and 8.90 keV represent the Cu K_{α} and K_{β} lines, and stem from microscope hardware outside the analyzed area excited by scattered electrons and X-rays.

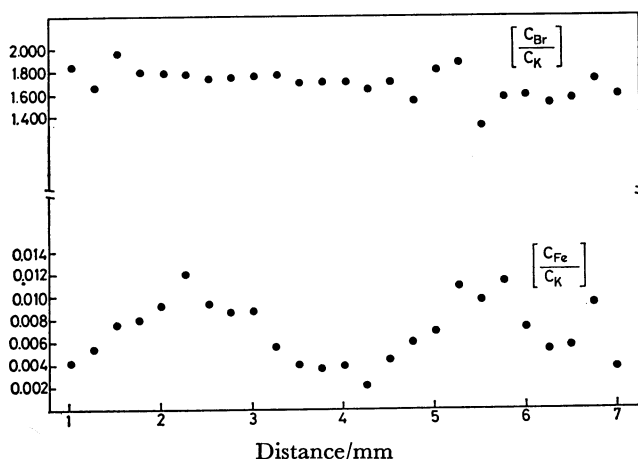


Fig. 3. Weight ratios of Fe/K show fluctuation pattern characteristic of dissipative structures if displayed as a function of distance (here in steps of 0.25 mm). For comparison, Br/K weight ratios show only random variation within limits of accuracy.

found in the Fe/K and Fe/Br, but not in the Br/K ratios (Fig. 3). The fact that we did not pick up the small changes in bromide concentration superimposed on a high bromine background was anticipated. The unmistakable correlation between the dissipative structures and total Fe(ferroin+ferriin) based on Fe/K and Fe/Br, on the other hand, indicates that the catalyst participates in the oscillatory reaction dynamics in a more profound manner than commonly envisaged. Although direct measurements of this kind have not been reported, nor are there model calculations which could be called closely relevant, the results on secondary participation in dissipative processes are in qualitative agreement with some recent theoretical advances.^{7,8)}

In closing we should like to make a few brief remarks about the experimental aspects, deemed so essential by Procaccia and Ross.⁵⁾ We have invariably noted, even on the satisfactory samples, a slight broadening of the dissipative structures during the drying process. Such limitation of spatio-features resolution could be circumvented by using an electron microscope equipped with a cryogenic stage. Additional advantages to consider in this respect are: (1) the cumbersome drying procedure would be bypassed; (2) the frozen samples would be completely free of possible complications arising from different solubility of the oxidized and reduced form of the catalyst. With experimental methodology that does not depend on visual confirmation to the extent afforded by the ferroin-ferriin pair, the investigation of secondary participation effect could be extended to cerium and manganese catalysed reactions, for example, thereby allowing comparison, and promoting fuller theoretical explanation.

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