

Effective rate constant of ferriin reduction in the Belousov–Zhabotinsky reaction

J. Ungvarai,^a Zs. Nagy-Ungvarai,^{b*} J. Enderlein^c and S. C. Müller^{c†}

^a University L. Eötvös, Institute of Low Temperature Physics, Puskin u. 5-7, H-1088 Budapest, Hungary

^b University L. Eötvös, Institute of Analytical and Inorganic Chemistry, PO-Box 32, H-1518 Budapest, Hungary

^c MPI für molekulare Physiologie, Rheinlanddamm 201, D-44139 Dortmund, Germany

The relaxation tail of wave profiles in the ferroin-catalysed Belousov–Zhabotinsky reaction was analysed combined with calculations on the basis of a slightly modified Oregonator model. The frequently used rate constant for the reaction between ferriin and the organic substrates malonic acid and bromomalonic acid was determined at 25 °C as $k_j = (3.1 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$.

The mechanism of the Belousov–Zhabotinsky (BZ) reaction, including a thermodynamically consistent set of rate constants, was developed by Field, Körös and Noyes.¹ It consists of seven elementary inorganic and three complex organic reaction steps. A revised set of rate constants of the inorganic component reactions, based on later theoretical² and experimental³ findings, was presented by Field and Försterling. However, the organic reactions which are responsible for the recovery of the reduced catalyst and to some extent the control intermediate Br^- are not yet fully understood, being experimentally also less accessible. Efforts in this direction using cerium^{4,5} and ruthenium bipyridyl^{6,7} as catalysts are presently of interest.

Regarding the ferroin-catalysed case, still less is known about the organic steps^{8–11} and the published kinetic results for the reaction between ferriin and malonic acid are contradictory.^{8,9,11} While some kinetic details of the ferriin + bromomalonic acid reaction were studied very carefully,¹¹ the net rate constant of the reaction was measured only at 40 °C¹⁰ and as the activation energy is not known no satisfactory data are available at 25 °C.

Analysis of the trigger waves in thin layers of the BZ reaction offers a further possibility to quantify the rate constants of the reaction, because the concentration distribution of the components in the BZ waves is determined by the respective chemical reactions influenced by diffusion.² Some of the rate constants of the inorganic reactions were evaluated from such experiments on the basis of the velocities of chemical waves.³ Analysis of the wave profiles also offers an independent way to determine the rate constants of the organic reactions. In this work we present an experimental analysis of the relaxation tail of wave profiles in the ferroin-catalysed BZ reaction and combine the results with calculations on the basis of a slightly modified Oregonator model.¹² Thus we determine the net rate constant of the reaction between ferriin and the organic substances malonic acid and bromomalonic acid.

Experimental

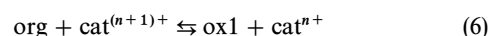
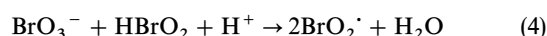
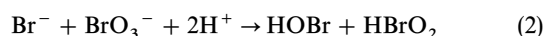
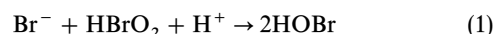
The experiments were carried out at 25.0 ± 0.1 °C in thin layers of ferroin-catalysed BZ solutions at initial concentrations of 0.3 M NaBrO_3 , 0.03–0.15 M malonic acid (MA), 0.03–

0.15 M bromomalonic acid (BrMA), 0.28 M H_2SO_4 and 0.002–0.004 M ferroin (cat). Malonic acid, NaBrO_3 , NaBr (Riedel de Haën), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, *o*-phenanthroline and sulfuric acid (Merck) were of analytical reagent grade. A volume of 3.63 ml of the BZ solutions was placed in an optically flat Petri dish leading to a layer depth of 0.56 ± 0.03 mm. The dish was covered by a glass plate leaving a thin air gap above the solution layer.

The spatial distribution of the catalyst was measured by a two-dimensional spectrophotometer as described earlier.¹³ The two-dimensional transmission of light through the reaction layer was detected by a CCD camera (Hamamatsu C3077) and stored on a video recorder. Single pictures were selected and digitized by an image acquisition card (Data Translation DT-2851) and stored on a PC for further analysis. Spatial concentration profiles of ferroin ($[\text{cat}]$ vs. x curves) were derived along a line perpendicular to the wavefronts¹³ in experiments without any dispersion effect, *i.e.* at sufficiently large distances between the wavefronts. In such a case, the concentration profile of a wavefront remains unchanged, while it is moving with constant velocity, v .^{14,15} Therefore, the time (t) and space (x) coordinates of a wave profile are simply linearly related to each other ($x = vt$). The velocity of wavefronts was determined from time series of $[\text{cat}]$ vs. x curves. The spatial concentration profiles were converted to time functions ($[\text{cat}]$ vs. t curves), neglecting ferriin diffusion because of the small concentration gradient in the relaxation tail.

Modelling

The model equations are deduced from the irreversible Oregonator model of Field and Noyes¹⁶ taking into account some modifications proposed by Rovinsky and Zhabotinsky.^{10,12} The main properties of the ferroin-catalysed BZ reaction can be explained by the following subset of the FKN mechanism:



† Permanent address: Institut für Experimentelle Physik, Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany.

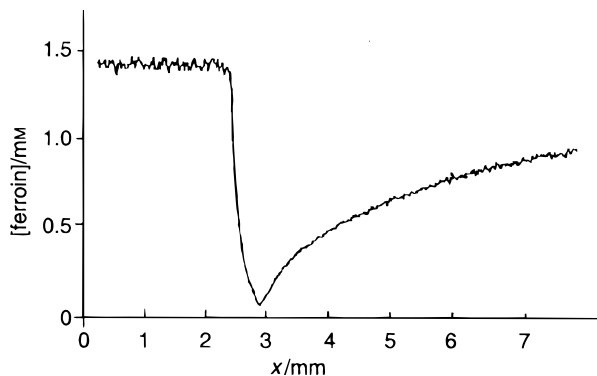
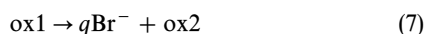


Fig. 1 Spatial concentration profile of ferroin across a single trigger wave determined experimentally by two-dimensional spectrophotometry at initial concentrations of 0.3 M NaBrO₃, 0.03 M MA, 0.09 M BrMA, 0.28 M H₂SO₄ and 0.003 M ferroin (no. 7. in Table 1)



where org represents the organic substances MA + BrMA, ox1 and ox2 oxidation products, and cat the catalyst. The principal feature of the modification¹² is pointing out the reversibility of the non-elementary process in eqn. (6). Because of the low redox potential of the ferroin-ferroin couple, as compared to Ce^{IV}-Ce^{III}, eqn. (4) and (5) are irreversible and can be condensed into one step,¹⁶ however, the equilibrium of eqn. (6) is shifted to the left-hand side ($k_{-6} \gg k_6$). The reversibility suggested by Rovinsky and Zhabotinsky was used also in computations by other authors,^{17,18} and was also experimentally confirmed by Försterling using a simple chemical method for shifting equilibria.¹⁹

In the relaxation tail of the BZ waves the concentration of HBrO₂ becomes negligibly small and the kinetic equation of

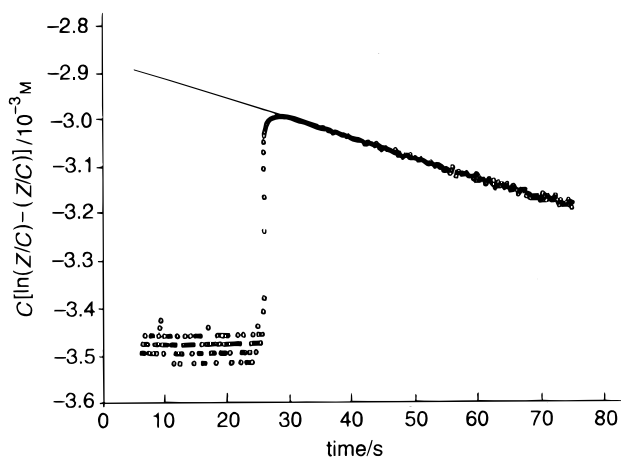


Fig. 2 Experimental data shown in Fig. 1 are plotted in terms of the expression $C[\ln(Z/C) - (Z/C)]$ as a function of time. A straight line is fitted to the relaxation tail.

Table 1 Wave velocity v and kinetic constant k_j of the different BZ systems. The concentrations of NaBrO₃ and H₂SO₄ were kept constant at 0.3 M and 0.28 M, respectively

no.	[MA]	[BrMA]	[ferroin]	$v/\mu\text{m s}^{-1}$	$k_j/10^5 \text{ s}^{-1}$
1	0.09	0.09	0.003	114.3	3.22
2	0.15	0.09	0.003	115.1	2.93
3	0.09	0.03	0.003	115.0	2.97
4	0.03	0.15	0.003	116.9	3.12
5	0.03	0.09	0.002	115.5	3.14
6	0.03	0.09	0.004	115.0	3.19
7	0.03	0.09	0.003	113.7	3.25

ferriin is determined practically only by processes (7) and (8):

$$\frac{dZ}{dt} = -k_6 BZ + k_{-6} B^*(C - Z) \quad (I)$$

$$\frac{dB^*}{dt} = k_6 BZ - k_{-6} B^*(C - Z) - k_7 B^* \quad (II)$$

where $Z = [\text{Fe}(\text{phen})_3^{3+}]$, $C = [\text{Fe}(\text{phen})_3^{3+}] + [\text{Fe}(\text{phen})_3^{2+}]$, $B = [\text{org}]$, $B^* = [\text{ox1}]$.

As the concentration of B^* evolves much faster than that of ferroin,^{9,10} B^* can be excluded from eqn. (I) which, after some transformations, can be written in the form:

$$\frac{dZ}{dt} = -\frac{k_6 k_7 BZ}{k_7 + k_{-6}(C - Z)} \quad (III)$$

Rovinsky and Zhabotinsky provide arguments^{10,12} that for the rate constants of the organic processes the relation $k_{-6} \gg k_7 \gg k_6$ is valid. Therefore, the temporal change of ferroin in the relaxation tail of the BZ waves can finally be expressed as

$$\frac{dZ}{dt} = -\frac{k_6 k_7 BZ}{k_{-6}(C - Z)} \quad (IV)$$

Integrating eqn. (IV) from 0 to t and assuming $Z(t=0) = C$ one obtains the explicit relation

$$C[\ln(Z/C) - (Z/C) + 1] = -\frac{k_6 k_7}{k_{-6}} Bt \quad (V)$$

between ferroin concentration Z , total catalyst concentration C and time t .

Results

In our experiments the spatial concentration profile of ferroin was determined in single trigger waves. One example is shown in Fig. 1. During the movement of the waves it was verified that the concentration profiles did not change their shape in time. From time series in five independent experiments, the velocity of the waves was determined and for the example in Fig. 1 this value was $(113.7 \pm 6.6) \mu\text{m s}^{-1}$. Using the velocity values, the spatial concentration profiles were converted to $Z = f(t)$ data. According to eqn. (V), the expression $C[\ln(Z/C) - (Z/C)]$ was calculated as a function of time. The results give an excellent linear time dependence in the relaxation part of the waves. One case is plotted in Fig. 2 derived from the example shown in Fig. 1. The slope of the straight line corresponds to $-k_j B$, where

$$k_j = \frac{k_6 k_7}{k_{-6}}$$

We carried out a similar analysis for the data of independent series of experiments at different concentrations of MA, BrMA and ferroin. The respective velocity and k_j values are collected in Table 1. The mean value of the kinetic constant k_j was determined as $(3.1 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$

Discussion

A comparison between our analysis and that of the classical Oregonator model¹⁶ is made in Fig. 3. In the Oregonator the reverse reaction (-6) is neglected and eqn. (V) would read

$$\ln(Z/C) = -k_6 Bt \quad (VI)$$

According to this equation, the expression C in $\ln(Z/C)$ should be a linear function of time which can be comfortably compared with the $C[\ln(Z/C) - (Z/C)]$ vs. time relationship (Fig. 3). The upper curve of Fig. 3 shows a significant deviation of the $C \ln(Z/C)$ plot from a straight line, while the linearity of the $C[\ln(Z/C) - (Z/C)]$ curve is obvious.

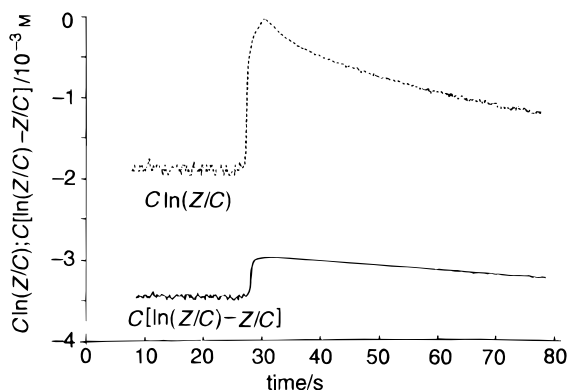


Fig. 3 Comparison of the data fit using the classical Oregonator (dashed curve), to the fit $C[\ln(Z/C) - (Z/C)]$ for the example shown in Fig. 2 (—)

Wood and Ross carried out calculations of the relaxation of the wave profiles and observed a nonlinearity of the $\ln(Z/C) = f(t)$ curves similar to that shown in Fig. 3. Furthermore, their simulations of the wave profile, using the Oregonator model involving diffusion terms, predict a relaxation from the peak amplitude to the steady state 2.5–10 times faster than the experimental observation.¹⁴ This discrepancy is also most likely caused by the missing reverse reaction (–6).

Similarly as the reversibility of reactions (4) and (5) is essential in modelling the Ce-catalysed BZ systems,^{3,20} the reversibility of the organic processes is crucial in the correct description of the ferriin-catalysed BZ oscillations and waves. Certainly, the rate constant $k_j = 0.4 \text{ M}^{-1} \text{ s}^{-1}$, valid for the Ce catalyst,²⁰ should not be used for the ferriin case.^{21,22}

On the other hand, the k_j value of $2 \times 10^{-6} \text{ s}^{-1}$ used by Aliev and Agladze²³ takes into account the reversibility of the organic steps correctly, but it was calculated from an experimental value measured at 40 °C.¹⁰ Since the activation energy of the reaction is not known, it can not be considered as a reliable estimate of k_j at 25 °C.

Jwo and co-workers also confirmed the reversibility of the reaction of ferriin with malonic acid and bromomalonic acid.¹¹ They determined the rate constant k_6 experimentally, but for the backward reaction (–6) they used a thermodynamically estimated value.

The k_j values determined in our work and used in the reversible descriptions of the organic reactions^{11,18,23} certainly have a low value but in the corresponding rate equations the term $[Z/(C - Z)]$ appears instead of Z which compensates for the small value of k_j . This combination can correctly describe the behaviour of the ferriin-catalysed BZ reaction^{18,23} even with respect to features (such as change of ferriin concentration in the wavefronts) that the previously used kinetic models were unable to reconstruct.²⁰

The k_j value determined in our work may be influenced by the oxygen content of the solutions which can lead to reac-

tions increasing the concentration of the oxidized catalyst. Therefore its value may be somewhat higher than in the absence of O_2 . Measurements are in progress to determine the value of k_j in an inert atmosphere. However, most of the experiments, like our own, on spatial patterns were performed under atmospheric conditions which underlines the importance and justifies the use of the determined k_j value.

Conclusion

This work adds direct information at 25 °C about the frequently used rate constant k_j of the Oregonator model of the BZ reaction. The use of two-dimensional spectrophotometry for the investigation of chemical waves shows an independent approach for such a kinetic analysis.

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