*Communication*

# Isotopic Effect on the Kinetics of the Belousov-Zhabotinsky Reaction

**Federico Rossi [1],\*, Mauro Rustici [2], Claudio Rossi [3] and Enzo Tiezzi [4]**

1 Department of Physical Chemistry "F. Accascina", University of Palermo, Viale delle Scienze Pad. 17, Palermo, Italy; E-mail: f.rossi@unipa.it
2 Department of Chemistry, University of Sassari, Via Vienna 2, Sassari, Italy; E-mail: rustici@uniss.it
3 Department of Chemical and Biosystems Science, University of Siena, Via Aldo Moro 3, Siena, Italy; E-mail: rossi@unisi.it
4 Department of Chemical and Biosystems Science, University of Siena, Via della Diana 2/a, Siena, Italy; E-mail: tiezzienzo@unisi.it

\* Author to whom correspondence should be addressed; Fax: +39-091590015; E-mail: f.rossi@unipa.it

**Abstract:** In this work we present results about the deuterium isotope effect on the global kinetics of a Belousov-Zhabotinsky reaction in batch conditions. A nonlinear dependence of the Induction Period upon the percentage of deuterated reactants was found. The isotopic effect on the bromination reaction of malonic acid was evaluated.

**Keywords:** Belousov-Zhabotinsky reaction, Isotopic effect, Induction Period, Enolization, Bromination reaction.

## 1. Introduction

The Belousov-Zhabotinsky (BZ) reaction represents the most famous example of chemical oscillator [1]. Briefly it consists of a catalytic oxidation of an organic substrate with active methylenic groups, by bromate ions in acidic aqueous solution. The most used substrate is malonic acid (MA), catalysts are generally metal redox couples (Ce(IV)/Ce(III), Mn(III)/Mn(II)) or metallo-complexes (ferroin, $Ru(bpy)_3^{2+}$).

From 1972 various detailed kinetic models have been proposed to explain the oscillatory behavior of the BZ reaction. The first and simplest is known as the FKN [2], which involves 18 elementary steps

and 21 chemical species but can be simplified considering the role of three key species: $HBrO_2$ as exchange intermediate, $Br^-$ as control intermediate and $M^{ox}$, i.e. the oxidized form of the catalyst, as regeneration intermediate. Successively other models have been proposed to improve or fix some aspects of the FKN mechanism: the radicalator model [3], the GTF model [4] and the MBM model [5].

Isotopic effect due to the Hydrogen substitution by Deuterium is a subject of widespread interest among the chemical kinetics discipline. Several organic and inorganic reactions (enolization, substitution, exchange) have been studied in the past for a large class of compounds. The implications of the H-D substitution are also important for the kinetics and the rate of more complex reaction mechanisms. As an example, in the past, the kinetics of the isotope exchange reactions of $RCH(COOH)_2$ (R=H, D, Me, Et, Bu, and Ph) in $D_2O$ solutions were studied by using ^{1}H NMR spectroscopy, and the implications for the BZ reaction have been discussed [6].

The influence of deuterated compounds on the global kinetics of BZ reaction was discussed by Karavaev et al. for Ru-catalyzed systems [7]. It was found that the substitution of $H_2O$ by $D_2O$ as solvent caused a complete suppression of the oscillating regime.

In our study we found a nonlinear increment of the Induction Period (IP) upon the addiction of deuterium substituted reactants for a Ce-catalyzed BZ system.

The Induction Period is the preoscillatory stage in which $[Br^-]$ is increased and brominated organic species are accumulated. According to the GTF model [4] the length of IP is determined by the concentration of bromomalonic acid (BrMA). The crucial amount of BrMA necessary for the onset of oscillations is produced through two main pathways: (a) the bromination of the enol form of malonic acid by $Br_2$ and (b) the reaction between $Br_2$ and the malonyl radical formed in the Ce-MA subsystem [8]. Previous works showed a direct relationship between the enolization constant of different organic substrates in BZ-like oscillating systems and the length of the IP [9-11].

In this paper we evaluate the effect of hydrogen-deuterium substitution for reaction pathway (a).

## 2. Experimental Section

Isotopic effect on bromination reaction was evaluated following changes in the bromine concentration with a double beam spectrophotometer (ULTROSPEC 2000 UV-VIS, Pharmacia Biotech) at $\lambda = 500$ nm, where $Br_2$ has an absorption shoulder and its molar extinction coefficient $\varepsilon$ is $37.5$ $M^{-1}$ $cm^{-1}$. Measures were performed in thermostated quartz cuvettes (1 x 1 x 4.5 cm) at 20 °C. The spectrophotometer was connected to a PC for data storage and treatment. All reagents were of analytical grade (SIGMA) and they were used without further purifications. The following stock solutions were prepared: $BrO_3^-$ / $H_2(D_2)SO_4$ 0.5 M, $Br^-$ 0.97 M and malonic acid (MA) 0.5 M, reagents were dissolved in double distilled water and/or 99.98% $D_2O$ (SIGMA). Effective deuteration of the methylenic group of MA was checked by ^{1}H NMR measurements, which showed a signal at $\delta = 3.388$ ppm corresponding to the $CH_2$ and a signal at $\delta = 3.247$ ppm corresponding to CHD for deuterated solutions. The intensity of the signal was proportional to the percentage of $D_2O$ used to dissolve MA.

Solutions at known bromine concentrations were prepared according to the following reaction:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \tag{1}$$

All solutions were prepared in stoichiometric proportions immediately before each spectrophotometric run. Solutions at different known $[Br_2]$ were used to calibrate the instrument both in $H_2O$ and $D_2O$.

Measurements of BZ Induction Period were performed with a double beam spectrophotometer (Varian, 634 series), in thermostated quartz cuvettes (1 x 1 x 4 cm) at 20 °C following the behavior of Ce(IV) at $\lambda = 320$ nm. BZ oscillators in $H_2O$ and $D_2O$ were prepared using following stock solutions: $CeSO_4 \cdot 2H_2O$ 8 x $10^{-3}$ M, MA 0.6 M, $NaBrO_3$ 0.18 M; each stock solution was 1 M $H_2SO_4$ or $D_2SO_4$. Reagents were prepared both in double distilled water and 99.98% $D_2O$ (SIGMA). BZ systems were prepared mixing normal and deuterated reagents in different proportions, in order to get a final composition of $[MA]_t = 0.1$ M, $[BrO_3^-]_t = 3$ x $10^{-2}$ M, $[Ce]_t = 1.3$ x $10^{-3}$ M and 1 M $H_2$ $(D_2)SO_4$, where $[X]_t$ indicates the sum of deuterated and normal reagents.

## 3. Results and Discussion

Figure 1 shows the comparison between a BZ reaction with fully deuterated reagents (Figure 1a) and a BZ reaction in $H_2O$ (Figure 1b). The effect of deuterium substitution is not as dramatic as in the Ruthenium catalyzed BZ systems, where oscillations are completely damped [7], nevertheless the global kinetics of the reaction results slower. Addition of deuterated reactants does not alter the qualitative profile of the absorbance as a function of time but influences the oscillatory parameters. This fact is particularly evident from a markedly longer Induction Period, from 150 seconds in $H_2O$ to 390 seconds in $D_2O$.
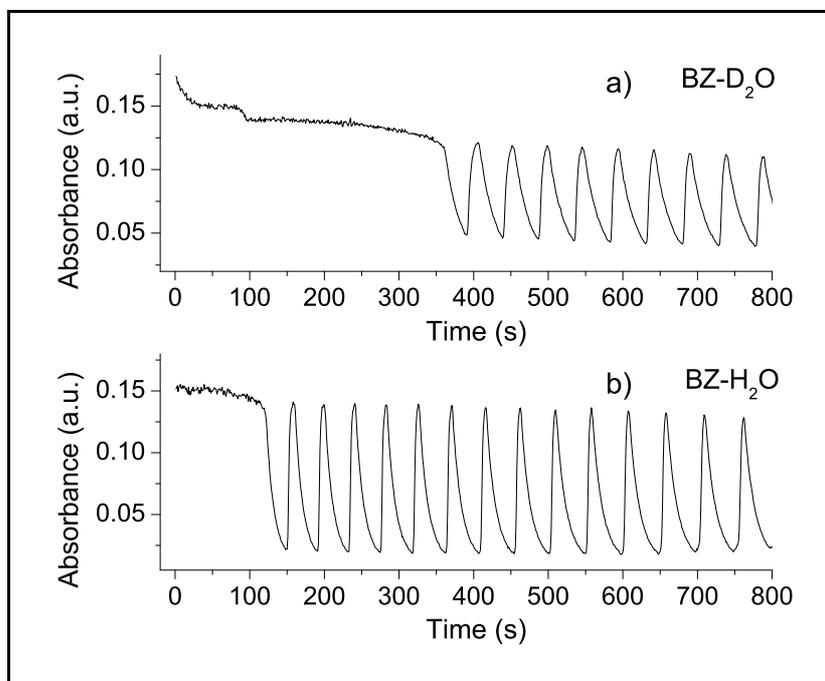


**Figure 1.** Comparison between a BZ reaction in $D_2O$ (a) and in $H_2O$ (b) at 20 °C. Temporal series were recorded at $\lambda = 320$ nm where Ce(IV) has an absorption maximum. For both systems the following reactants concentrations were used: $[MA] = 0.1$ M, $[BrO_3^-] = 3$ x $10^{-2}$ M, $[H_2SO_4] = 1$ M and $[Ce] = 1.3$ x $10^{-3}$ M.
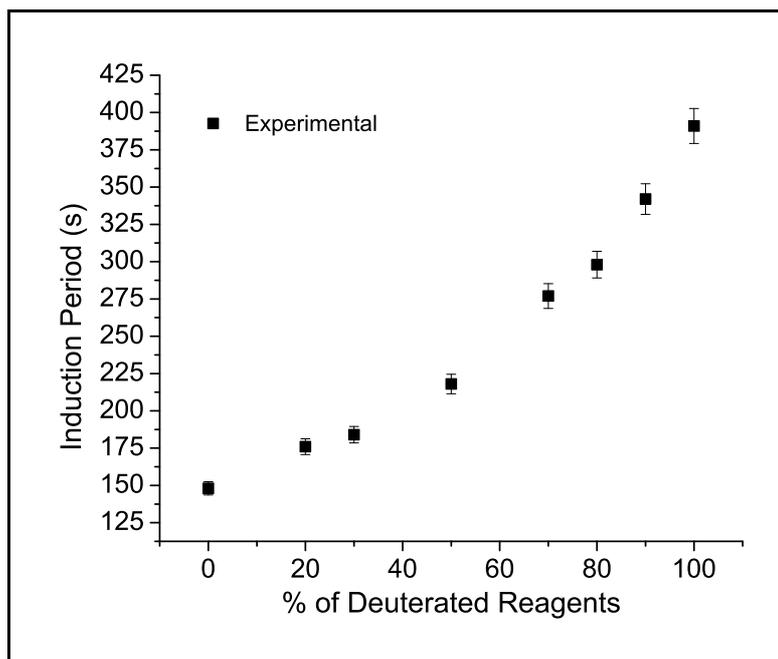
**Figure 2.** Dependence of Induction Period upon percentage of deuterated reactants at 20 °C for BZ reactions with the following composition [MA] = 0.1 M, [BrO$_3^-$] = 3 x 10$^{-2}$ M, [H$_2$SO$_4$] = 1 M and [Ce] = 1.3 x 10$^{-3}$ M.

Kreuels et al. [12] found a linear D$_2$O dosage dependence of the oscillation frequency (OF) both at low (increased OF) and high (decreased OF) catalyst concentration. In our experimental condition the oscillation frequency was found substantially independent from D$_2$O dosage, in fact it changes from 0.023 Hz in H$_2$O to 0.021 Hz for fully deuterated reagents.

On the contrary, respect to data on the oscillation frequency, a nonlinear response of IP to D$_2$O content was found. The dependence of IP upon the percentage of deuterated reactants present in solution is shown in Figure 2. The monotonic increase of IP is in line with an expected isotopic effect, which generally slows down rates of elementary reactions with proton involvement [13].

As stated before, to understand the IP behavior we investigated the bromination reaction of malonic acid through its enolic form. For practical purposes this study reduces to the investigation of the keto-enolic equilibrium, which is the rate determinant step [14,15]. According to the GTF model, the bromination proceeds as follows:

$$CH_2(COOH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (COOH)CHC(OH)_2 \tag{2}$$

$$(COOH)CHC(OH)_2 + Br_2 \overset{k_2}{\longrightarrow} BrCH(COOH)_2 + H^+ + Br^- \tag{3}$$

$$CH_2(COOH)_2 + HOBr \overset{k_3}{\longrightarrow} BrCH(COOH)_2 + H_2O \tag{4}$$

$$HOBr + Br^- + H^+ \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} Br_2 + H_2O \tag{5}$$

Where CH$_2$(COOH)$_2$ is the keto form (MA) and (COOH)CHC(OH)$_2$ is the enolic form (ENOL).

It has been shown [15] that HOBr in reaction (4) does not compete with $Br_2$, hence the kinetics of bromination is well described by steps (2), (3) and (5). In particular we were interested in the first two steps. The global reaction rate can be written in terms of $Br_2$ disappearance [14]:

$$\frac{d[Br_2]}{dt} = -k_2[ENOL][Br_2] \tag{6}$$

From equations (2) and (3) we know that:

$$\frac{d[ENOL]}{dt} = k_1[MA] - k_{-1}[ENOL] - k_2[ENOL][Br_2] \tag{7}$$

We can consider some approximations: in strong acidic medium (0.05 M < $[H_2SO_4]$ <1 M) [MA] is approximatively equal to the analytic concentration $[MA]_0$ and being $k_2 \gg k_1$ [16], the variation of enol concentration with time is close to 0 (steady state approximation) [14]:

$$\frac{d[ENOL]}{dt} \cong 0 \tag{8}$$

It follows that:

$$[ENOL] = \frac{k_1[MA]_0}{k_{-1} + k_2[Br_2]} \tag{9}$$

Substituting in (6):

$$\frac{d[Br_2]}{dt} = -\frac{k_1 k_2[Br_2][MA]_0}{k_{-1} + k_2[Br_2]} \tag{10}$$

Finally, in our experimental condition we know that $k_2[Br_2] \gg k_{-1}$, so at the end we get the operative equation to calculate enolization rate constant:

$$\frac{d[Br_2]}{dt} = -k_1[MA]_0 \tag{11}$$

Equation (11) describes a *pseudo* zero order kinetics.

Figure 3 shows the absorbance plots of $Br_2$ against time during the halogenation of malonic acid in $D_2O$ (Figure 3a) and $H_2O$ (Figure 3b). The linear trend of $Br_2$ disappearance confirmed an effective zero order reaction both in $H_2O$ and $D_2O$ solutions. In our experiments we used [MA] = 0.25 M for all spectrophotometric runs and we varied $[Br_2]$ between 7.5 x $10^{-3}$ M and 5.2 x $10^{-2}$ M, $Br_2$ was produced *in situ* according to reaction (1).

Using calibration curves and equation (11) we finally could calculate enolization constants from spectrophotometric data for $H_2O$ system ($k_1^h$ = 2.025 x $10^{-3}$ $s^{-1}$, slightly lower than that reported in literature at 25 °C, 3 x $10^{-3}$ $s^{-1}$) and $D_2O$ system ($k_1^d$ = 2.666 x $10^{-4}$ $s^{-1}$). The value of the ratio $k_1^h/k_1^d$ = 7.6 suggests a primary isotopic effect [13] due to the D-H substitution of the methylenic hydrogens of malonic acid.
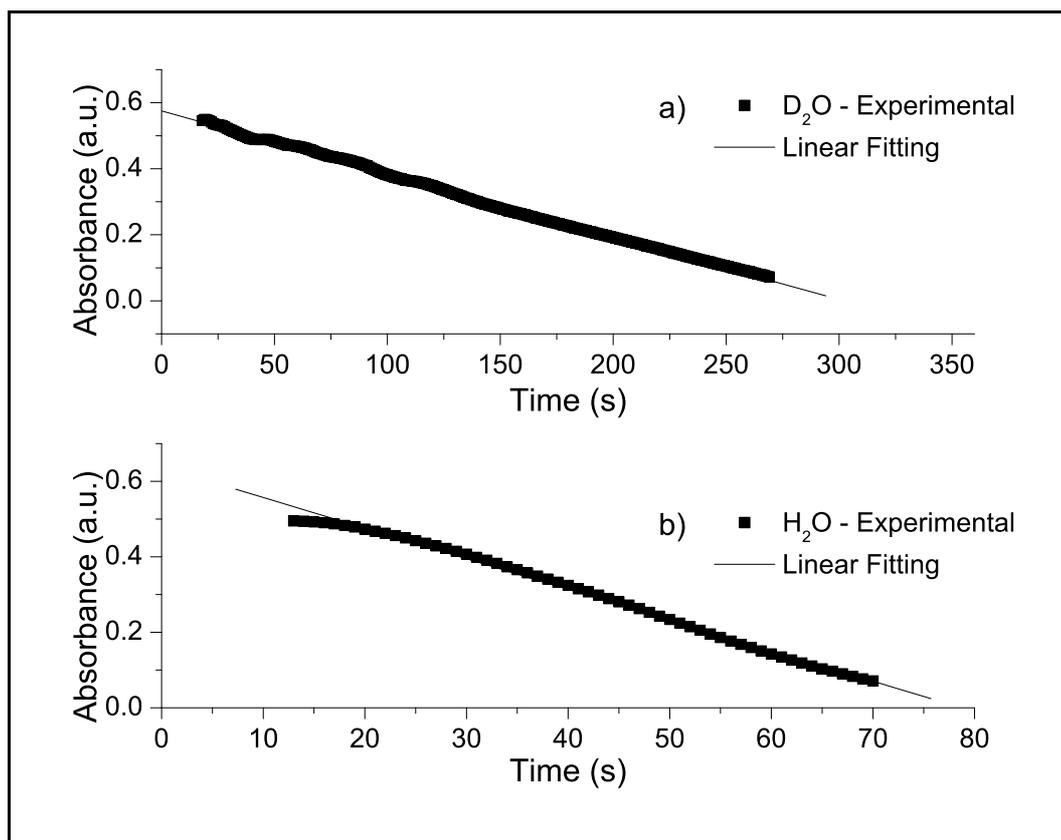
**Figure 3.** Disappearance of $Br_2$ followed spectrophotometrically at 500 nm in $H_2O$ syatem (a) and $D_2O$ system (b). Solution composition was [MA] = 0.25 M, [$Br_2$] = 7.5 x $10^{-3}$ M.

In conclusion, we showed how the progressive substitution of deuterated reactants in a Cerium catalyzed BZ reaction caused an increase in the Induction Period length. Data on the bromination reaction revealed a primary isotopic effect on the enolization kinetic constant of malonic acid, which in turn determined a slower production of bromomalonic acid contributing to a delayed onset of oscillations. In order to fully understand modifications induced by deuterated reagents to the BZ system, also the BrMA production occurring through the reaction between $Br_2$ and the malonyl radical should be investigated. A deeper investigation can result in a better understanding of experimental data reported in Figure 2.

## Acknowledgements

## References and Notes

1.  Taylor, A.F. Mechanism and Phenomenology of an Oscillating Chemical Reaction. *Prog. Reac. Kin. Mech.* **2002**, *27*, 247-325.
2.  Field, R.J.; Korös, E.; Noyes, R.M. Oscillations in chemical systems. II. Thorough analysis of temporal oscillation in the bromate-cerium-malonic acid system. *J. Am. Chem. Soc.* **1972**, *94*, 8649-8664.

3. Försterling, H.D.; Muranyi, S.; Noszticzius, Z. Evidence of malonyl radical controlled oscillations in the Belousov-Zhabotinskii reaction (malonic acid-bromate-cerium system). *J. Phys. Chem.* **1990**, *94*, 2915-2921.

4. Gyorgyi, L.; Turanyi, T.; Field, R.J. Mechanistic details of the oscillatory Belousov-Zhabotinskii reaction *J. Phys. Chem.* **1990**, *94*, 7162-7170.

5. Hegedus, L.; Wittman, M.; Noszticzius, Z.; Yan, S.H.; Sirimungkala, A.; Försterling, H.D.; Field, R.J. HPLC analysis of complete BZ systems. Evolution of the chemical composition in cerium and ferroin catalysed batch oscillators: experiments and model calculations. *Faraday Discuss.* **2001**, *120*, 21-38.

6. Hsu, M.C.; Jwo, J.J. Kinetic study of the isotope exchange reactions of malonic acid and its derivatives in various acidic D2O media using 1H NMR spectroscopy. Implication in the Belousov-Zhabotinsky reaction. *Int. J. Chem. Kin.* **1999**, *31*, 455-461.

7. Karavaev, A.D.; Kazakov, V.P.; Tolstikov, G.A. Deuteration Effect in Auto-Oscillation Chemiluminescence of the Belousov-Zhabotinskii Reaction. *React. Kinet. Catal. Lett.* **1986**, *32*, 21-26.

8. Cadena, A.; Pérez, N.; Ágreda, J.A.; Barragán, D. Understanding the Induction Period of the Belousov-Zhabotinsky Reaction. *J. Braz. Chem. Soc.* **2005**, *16*, 214-219.

9. Berenstein, I.; Agreda J.; Barragán, D. Induction Period in the $BrO_3^-$, Ce(III), $H_2SO_4$, oxalic acid and ketone oscillating reaction. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4601-4603.

10. Berenstein, I.; Agreda, J.; Barragán, D. Effect of Methyl Ketones in the Belousov-Zhabotinskii Reaction. *J. Phys. Chem. A.* **1999**, *103*, 9780-9782.

11. Berenstein, I.; Barragán, D. Additive Effects of Methyl Ketones in the Belousov-Zhabotinsky Reactions. *J. Braz. Chem. Soc.* **2004**, *15*, 844-848.

12. Kreuels, T.; Martin, W.; Brinkmann, K. Influence of $D_2O$ on the Belousov-Zhabotinsky Reaction. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 411-412.

13. Collins, C.J.; Bowman, N.S. Eds.; *Isotope Effects in Chemical Reactions*; ACS Monograph No. 167; Van Nostrand Reinhold: New York, 1970.

14. Sirimungkala, A.; Försterling, H.D.; Dlask, V.; Field, R.J. Bromination Reactions Important in the Mechanism of the Belousov-Zhabotinsky System. *J. Phys. Chem. A* **1999**, *103*, 1038-1043.

15. Sevcík, P.; Snirková, M.; Hlavácová, J. Kinetics and Simulations of the Malonic Acid-Bromine Reaction. *React. Kinet. Catal. Lett.* **1994**, *52*, 161-168.

16. Edelson, D; Noyes, R.M.; Field, R.J. Mechanistic Details of the Belousov-Zhabotinsky Oscillations. II. The Organic Reaction Subset. *Int. J. Chem. Kin.* **1979**, *11*, 155-164.