kth volume. The homogeneous kinetics was calculated by applying the law of mass action to the mechanism in Table I. k = 1, ..., NI or b

$$MIX_{ij} = V_j c_{ij} / t_M + (c_{ij} - c_{ib}) V_j / t_j \quad i = 1, ..., NC; j = 1, ..., NI (S5)$$

is the influx from the segregated regions into the bulk by mass transfer (first term) and by diffusive micromixing (second term)

$$\alpha' = \alpha Q / V_{\text{tot}} \tag{S6}$$

is the fraction of the segregated volumes leaving the reactor without mixing into the bulk (escape fraction). If  $\alpha = 1$  (dimensionless escape fraction) then the residence time distribution of the reactor is the same as that of an ideal CSTR.

# Notation

- NI = number of inlets
- NC = number of components of varying concentration
- $V_{\rm tot}$  = volume of the reactor (dm<sup>3</sup>)
- $t_{\rm M}$  = characteristic time of mass transfer from the segregated zones into the bulk of the reactor (s)
- $t_{ii}$  = characteristic time of exchange between two segregated regions (s)  $t_j$  = characteristic time of exchange between a segregated region and the bulk (s)
- $Q_i$  = volumetric flow rate through the *j*th inlet (dm<sup>3</sup> s<sup>-1</sup>)
- $\tilde{Q}$  = total volumetric flow rate  $(\sum_{i=1}^{NI} Q_i)$  (dm<sup>3</sup> s<sup>-1</sup>)
- $\underline{c}_i$  = concentration array of components of varying concentration in the ith volume (segregated region or bulk)
- $c_{ij,0}$  = concentration of the *i*th component in the *j*th feed stream (M) Registry No. BrO<sub>3</sub><sup>-</sup>, 15541-45-4; Ce<sup>3+</sup>, 18923-26-7; Br<sup>-</sup>, 24959-67-9.

# Kinetics and Mechanism of the BrO<sub>3</sub><sup>--</sup>SCN<sup>--</sup>H<sup>+</sup> Reaction

## Yi-Xue Zhang and Richard J. Field\*

Department of Chemistry, University of Montana, Missoula, Montana 59812 (Received: July 19, 1991; In Final Form: September 20, 1991)

The reaction of BrO<sub>3</sub><sup>-</sup> with SCN<sup>-</sup> in dilute HClO<sub>4</sub> is investigated in both batch and flow reactor modes. The stoichiometry of the reaction is  $BrO_3^- + SCN^- + H_2O \rightarrow HSO_4^- + HCN + Br^-$  when  $SCN^-$  is in excess and  $7BrO_3^- + 5SCN^- + 2H^+$  $\rightarrow$  5BrCN + Br<sub>2</sub> + 5SO<sub>4</sub><sup>2-</sup> + H<sub>2</sub>O when BrO<sub>3</sub><sup>-</sup> is in excess. There is a two-stage induction period in the batch mode when  $BrO_3^-$  is in excess before the occurrence of a third stage in which  $Br_2$  finally accumulates. The end of the first stage corresponds to the consumption of SCN<sup>-</sup>, and the end of the second corresponds to the consumption of CN<sup>-</sup>. Both of these species react rapidly with Br<sub>2</sub>. Bromine accumulates during the third stage as a result of the reaction of Br<sup>-</sup> with BrO<sub>3</sub><sup>-</sup>. A large range of feed-stream concentrations and flow rates was investigated in CSTR mode. No periodic or quasiperiodic oscillations were found that could not be eliminated by substituting gravity feeding for a peristaltic pump. However, the system is very sensitive to environmental perturbation and thus very noisy at low flow rates. The reaction is simulated on the basis of a mechanism proposed here. The agreement between experiments and simulations is very good. Simulations at low flow rates show a very rapid change with flow rate of steady-state  $[Br_2]$  along a line connecting the three stages mentioned above with  $BrO_3^$ in excess. This is likely the source of the experimental sensitivity to perturbation.

## Introduction

The study of various nonlinear dynamic behaviors of oscillatory chemical reactions has become a very active field of research<sup>1</sup> since the work<sup>2</sup> of Field, Körös, and Noves in 1972 on the mechanism of the Belousov-Zhabotinsky reaction. The number of known chemical oscillators has grown considerably since then due largely to their systematic design<sup>3</sup> on the basis of a simple mathematical model<sup>4</sup> and to better understanding of the requirements for chemical oscillations to occur.<sup>4</sup> The range of chemistry involved has been extended from oxyhalogens to reactions involving sulfur-containing species, 5-10 organic autoxidations, 11 nitrogen-containing species,<sup>12</sup> and transition-metal compounds.<sup>13</sup> Various pH-regulated oscillators<sup>14</sup> also have been discovered.

Sulfur-containing oscillators have been of considerable interest recently. The mechanism of the methylene blue-HS<sup>--</sup>O<sub>2</sub> oscillator has been elucidated by Resch et al.<sup>5</sup> A simplified skeleton of this mechanism has been obtained by Zhang et al.<sup>6</sup> The work of Epstein et al.<sup>7-10</sup> has led to the understanding of the mechanisms of the  $H_2O_2$ -SCN<sup>-</sup>-Cu<sup>2+</sup> and several SO<sub>3</sub><sup>2-</sup> containing chemical oscillators.

The BrO<sub>3</sub>-SCN-H<sup>+</sup> reaction was reported to be oscillatory by Simoyi<sup>15</sup> in 1987. Simple periodic and chaotic behaviors were observed in a continuous-flow stirred tank reactor (CSTR). However, little was known about the mechanism of this reaction as SCN<sup>-</sup> chemistry was not well understood. We report here a kinetic and mechanistic study of this reaction in a batch reactor and in a CSTR.

#### **Experimental Section**

The following chemicals were used: Fisher sodium thiocyanate and Baker Analyzed Reagent Grade 70% perchloric acid, KBr, FeNH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, KCN, and KBrO<sub>3</sub> (which was slurried several times with methyl alcohol to remove KBr). All solutions were made up by weight using singly distilled deionized water. Kinetic experiments were carried out in a stirred, 1-cm spectro-

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Figure 1. Absorbance at 310 and 396 nm vs time during the reaction of  $BrO_3^-$  and  $SCN^-$  in 0.08 M HClO<sub>4</sub> at 25 °C in a batch reactor. The solid lines are experimental, and the dashed lines are simulations based on the reactions and rate constants in Table I. The absorbance at 310 nm is mainly due to Br<sub>3</sub><sup>-</sup>. The absorbance at 396 nm is due mainly to Br<sub>2</sub>. Initial concentrations:  $[BrO_3^-] = 0.06 \text{ M}; [SCN^-] = 0.004 \text{ M};$  $[HClO_4] = 0.08 M.$ 

photometer cell in a HP 8452A diode-array spectrophotometer. Reactions were initiated by injecting the final reagent into the cell from a syringe. The absorption coefficients for  $Br_2$  and  $Br_3^$ reported by Zhang and Field<sup>16</sup> were used. Flow experiments were carried out in a thermostated 27.6 cm<sup>3</sup> CSTR with three inlets fed by a Buchler peristaltic pump. A platinum electrode and a double-junction Ag-AgCl reference electrode were used to monitor redox potential. Stopped-flow experiments were carried out using an Aminco-Morrow instrument modified by On-Line Systems.<sup>17</sup> Simulations were carried out on a VAX 8600 computer using the program SIMULATE<sup>18</sup> based on the numerical integrator ROW4S.<sup>19</sup> A relative error tolerance of  $1 \times 10^{-3}$  was used in the numerical integrations.

## **Results and Discussion**

Stoichiometry. The reaction between  $BrO_3^-$  and  $SCN^-$  was studied in 0.08 M HClO<sub>4</sub>. It is known<sup>20</sup> that the overall limiting stoichiometry is (1) when SCN<sup>-</sup> is in excess. However, there is

$$BrO_3^- + SCN^- + H_2O \rightarrow HSO_4^- + HCN + Br^-$$
(1)

some disagreement on the limiting stoichiometry when  $BrO_3^{-1}$  is in excess. While Simoyi<sup>15</sup> suggested that stoichiometry 2 is

$$6BrO_3^- + 5SCN^- + 2H_2O \rightarrow 3Br_2 + 5SO_4^{2-} + 5CN^- + 4H^+$$
(2)

$$7BrO_3^- + 5SCN^- + 2H^+ \rightarrow 5BrCN + Br_2 + 5SO_4^{2-} + H_2O$$
(3)

dominant under this condition, thermodynamic data and our results suggest that the overall reaction actually is stoichiometry 3, because reaction 4 between  $Br_2$  and  $CN^-$  is very fast and

$$Br_2 + HCN \rightarrow BrCN + Br^- + H^+$$
(4)

irreversible with a  $\Delta G^{\circ} \approx -70 \text{ kJ/mol}$ . This is in contrast to the  $IO_3^-SCN^-$  system where the  $I_2$ -HCN reaction has  $\Delta G^\circ = 0.42$ kJ/mol, suggesting that HCN could be a final product in strongly acidic media.

Reaction 3 can be thought of as the sum of reactions 1, 4, and Reactions 4 and 6 are so favorable that they are used in

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$
 (5)



Figure 2. Enlarged view of the induction period in Figure 1. The solid line is experimental and the dashed line is a simulation.



Figure 3. Repeat of the experiment in Figure 1 with Fe<sup>3+</sup> initially present in the reaction mixture. The nearly vertical line at the end of the first stage of the induction period corresponds to the rapid disappearance of the red color due to  $Fe(SCN)^{2+}$ .

standard analytical methods for CN<sup>-</sup> and SCN<sup>-</sup> in acidic solution.<sup>21</sup> The stoichiometry of reaction 3 is confirmed by the

$$4Br_2 + SCN^- + 4H_2O \rightarrow BrCN + SO_4^2 + 7Br^- + 8H^+$$
 (6)

spectrophotometric measurement of [Br<sub>2</sub>] shown in Figure 1. The  $[Br_2]$  and  $[Br_3^-]$  were monitored at 396 nm  $[\epsilon(Br_2) = 172 \text{ M}^{-1}]$  $cm^{-1}$  and  $\epsilon(Br_3^{-}) = 533 M^{-1} cm^{-1}$ ) and at 310 nm { $\epsilon(Br_2) = 9 M^{-1}$  $cm^{-1}$  and  $\epsilon(Br_3) = 7400 M^{-1} cm^{-1}$ , respectively. Simoyi<sup>15</sup> reported finding nearly twice as much Br<sub>2</sub> as in Figure 1 under the same conditions, presumably because the HCN evaporated from his open vessel rather than reacting with  $Br_2$  as in our closed vessel.

**Batch Experiments.** A typical kinetic curve is shown in Figure 1. There is a long induction period before  $Br_2$  begins to accumulate. The length of the induction period increases with decreasing initial concentrations of BrO<sub>3</sub><sup>-</sup> and H<sup>+</sup> or increasing initial concentration of SCN<sup>-</sup>. Furthermore, it is apparent in Figure 2 that there are two stages within the induction period. The  $Br_2$ and  $Br_3^-$  concentrations are much higher in the second than the first stage, and the switch from the first to second stage is very sharp.

We suggest that the three stages of reaction correspond to the following steps. Initially SCN<sup>-</sup> reacts with BrO<sub>3</sub><sup>-</sup> in reaction 1 to yield Br<sup>-</sup> and CN<sup>-</sup>. Very little Br<sub>2</sub> accumulates during this stage because HOBr, HBrO<sub>2</sub>, and Br<sub>2</sub>, which result from the reaction of Br<sup>-</sup> with BrO<sub>3</sub><sup>-</sup>, all react rapidly with SCN<sup>-</sup>. The first stage of the induction period ends with the consumption of SCN<sup>-</sup>. The second stage of the induction period corresponds to the reaction of  $Br_2$  produced in reaction 5 with  $CN^-$  in reaction 4. The accumulation of  $Br_2$ , the third stage, begins when  $CN^-$  is consumed. The presence of SCN<sup>-</sup> may be monitored by addition of Fe(III) to form the highly colored, but fairly weak (K = 139 M), Fe-(SCN)<sup>2+</sup> complex. Figure 3 shows that the absorbance due to

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Figure 4. Test of the effect of added  $CN^-$  during the second stage of the induction period in a repeat of the experiment in Figure 1 but with the injection of 0.10 mL of 0.014 M KCN at the indicated time. The initial volume of the reaction mixture was 3 mL.



Figure 5. Test of the effect of added  $CN^-$  during the third stage of reaction in a repeat of the experiment in Figure 1 but with injection of 0.10 mL of 0.014 M KCN at the indicated time.

Fe(SCN)<sup>2+</sup> is gone at the end of the first stage of the induction period. Further experiments indicate that the addition of Fe<sup>3+</sup> has little effect on either the length of the induction period or the final concentration of Br<sub>2</sub>. The importance of CN<sup>-</sup> and BrCN during the second stage of the induction period was tested by injecting CN<sup>-</sup> into the reaction mixture. Figure 4 shows that the length of the second stage of the induction period increases and the final [Br<sub>2</sub>] decreases considerably when CN<sup>-</sup> is injected during it. The final [Br<sub>2</sub>] decreases because bromine atoms are tied up as BrCN. Figure 5 shows a second experiment in which the same amount of CN<sup>-</sup> was injected during the Br<sub>2</sub> accumulation in the third stage of the reaction. These experiments demonstrate that Br<sub>2</sub> reacts rapidly with CN<sup>-</sup> and that BrCN rather than CN<sup>-</sup> is the final product.

Flow Experiments. The CSTR behavior of the BrO<sub>3</sub><sup>--</sup>SCN<sup>-</sup> reaction was investigated in order to supplement the results of Simoyi et al.<sup>15</sup> A wide range of reactant feed-stream concentrations and flow rates were searched, but no oscillations were found. There are some experimental problems, however. The oscillations reported by Simoyi et al.<sup>15</sup> occurred at very low flow rates (residence times of about 40 min) where there are very serious problems with pulsing from the peristaltic pump. We did indeed observe periodic and more frequently quasiperiodic or noisy oscillations of redox potential at low flow rates. However, it turned out that these phenomena are closely related to the pulsing of the peristaltic pump. Gravity feeding eliminates the periodic and quasiperiodic oscillations, but the noisy oscillations with random period and amplitude remain. We attribute this to an extreme sensitivity of the system to environmental perturbation in the low-flow-rate region. The periodic and quasiperiodic oscillations are probably the result of periodic forcing phenomena such as those studied in detail by Marek et al.<sup>22</sup> It is also apparent that the behavior of the reaction is very sensitive to inflow of the reactants,

(22) Marek, M. Private communication.

especially  $SCN^-$  ion, as small disturbances of the feed lines have a significant effect on behavior in the CSTR.

**Mechanism.** A mechanism is proposed and simulations carried out on the basis of it. The pertinent oxybromine chemistry is well known. Reactions 7-11 are expected to be important.<sup>23</sup> The

$$BrO_3^- + Br^- + 2H^+ \rightleftharpoons HBrO_2 + HOBr$$
 (7)

$$HBrO_2 + Br^- + H^+ \rightleftharpoons HOBr + HOBr \qquad (8)$$

$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \tag{9}$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2^* + H_2O \qquad (10)$$

$$HBrO_2 + HBrO_2 \rightleftharpoons HOBr + BrO_3^- + H^+$$
(11)

$$Br^- + Br_2 \rightleftharpoons Br_3^- \tag{12}$$

values of  $k_{12}$  and  $k_{-12}$  used here are large enough to assure that reaction 12 is always at equilibrium but are about 1 order of magnitude smaller than values recently reported by Ruasse et al.<sup>24</sup> The chemistry of SCN<sup>-</sup> is not as well understood. There have been a number of studies<sup>25-27</sup> of oxidations of SCN<sup>-</sup> by various oxidants, and reactions 13-15 have been proposed. It is reported

$$HOSCN + SCN^- + H^+ \rightleftharpoons (SCN)_2 + H_2O \qquad (13)$$

$$HOSCN + HOSCN \rightarrow SCN^- + HO_2SCN$$
 (14)

$$HO_2SCN + H_2O \rightarrow H_2SO_3 + HCN$$
(15)

that  $K_{13} = 1.7 \times 10^{12} \text{ M}^{-1}$  and  $k_{-13} = 2 \times 10^4 \text{ s}^{-1}$ .<sup>28</sup> However, there is some uncertainty in the application of these data here because of differences in pH. Reactions 14 and 15 were reported<sup>28</sup> to be fast, but no experimental data are available. Other possible reactions are (16)–(23). It turns out that reaction 18 cannot

$$Br_2 + SCN^- \rightarrow BrSCN + Br^-$$
 (16)

$$BrSCN + H_2O \rightarrow HOSCN + Br^- + H^+$$
(17)

 $HOBr + SCN^- \rightarrow HOSCN + Br^-$  (18)

$$HBrO_2 + SCN^- + H^+ \rightarrow HOBr + HOSCN$$
(19)

$$BrO_3^- + SCN^- + 2H^+ \rightarrow HBrO_2 + HOSCN \qquad (20)$$

$$HOBr + HOSCN \rightarrow HO_2SCN + Br^- + H^+$$
 (21)

 $HBrO_2 + HOSCN \rightarrow HO_2SCN + HOBr$  (22)

$$HOBr + (SCN)_2 \rightarrow BrSCN + HOSCN$$
 (23)

compete with reaction 9 and could be deleted. The combination of  $K_{13}^{28}$  and  $E^{\circ}\{(SCN)_2/SCN^{-}\}$  yields  $E^{\circ}\{HOSCN/(SCN)_2\} =$ 1.49 V. Two rules then can be obtained from tables of standard potentials, which may be useful in deciding the importance of various reactions: (1) For X<sup>-</sup> (halide and pseudohalide, e.g. SCN<sup>-</sup>, ions), the order of reducing strength is F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > SCN<sup>-</sup> > l<sup>-</sup> > CN<sup>-</sup>. (2) The orders of oxidation strength for X<sub>2</sub> and HOX are F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > (SCN)<sub>2</sub> > I<sub>2</sub> > (CN)<sub>2</sub> and HOF > HOCl

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TABLE I: Mechanism of the Reaction of BrO<sub>3</sub><sup>-</sup> and SCN<sup>-</sup> in Acidic Solution

reaction	
$BrO_3^- + Br^- + 2H^+ \rightleftharpoons HBrO_2 + HOBr$	
$HBrO_2 + Br^- + H^+ \rightleftharpoons HOBr + HOBr$	
$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O$	
$HBrO_2 + HBrO_2 \rightleftharpoons BrO_3^- + HOBr + H^+$	
$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2^+ + H_2O$	
$\begin{array}{l} BrO_3^- + SCN^- + 2H^+ \rightarrow HBrO_2 + HOSCN \\ HOSCN + HOSCN \rightarrow HOS(O)CN + SCN^- + H \\ HOS(O)CN + H_2O \rightarrow H_2SO_3 + HCN \\ BrO_3^- + H_2SO_3 \rightarrow HBrO_2 + HSO_4^- \\ HBrO_2 + SCN^- + H^+ \rightarrow HOBr + HOSCN \\ HOBr + SCN^- + H^+ \rightarrow HOSCN + Br^- + H^+ \\ HOBr + H_2SO_3 \rightarrow H_2SO_4 + Br^- + H^+ \\ Br_2 + SCN^- \rightarrow BrSCN + Br^- \\ BrSCN + H_2O \rightarrow HOSCN + Br^- + H^+ \\ Br_2 + H_2SO_3 \rightarrow HBrSO_3 + Br^- + H^+ \\ HBrSO_3 + H_2O \rightarrow H_2SO_4 + Br^- + H^+ \\ HBrSO_3 + H_2O \rightarrow H_2SO_4 + Br^- + H^+ \\ HOBr + HCN \rightarrow BrCN + Br^- + H^+ \\ HOBr + HCN \rightarrow BrCN + H^- + H^- \\ HOSCN + SCN^- + H^+ \rightleftharpoons (SCN)_2 + H_2O \end{array}$	<b>1</b> +

 $Br_2 + Br^- \rightleftharpoons Br_3^-$ 

> HOBr > HOSCN > HOI > HOCN.

The kinetics of the reaction of  $BrO_3^-$  with  $SCN^-$  was studied by Treindl and Kostrová<sup>30</sup> at 20 °C by measurement of the limiting polarographic current of  $SCN^-$  in the presence of hydrochloric acid. The following rate expression was obtained

rate = 
$$k'[BrO_3^-][SCN^-][H^+]^2$$
 (24)

with  $k' \approx 20 \text{ M}^{-3} \text{ s}^{-1}$ . This suggests that reaction 20 is the rate-determining step in the reaction of  $\text{BrO}_3^-$  and  $\text{SCN}^-$ . The value  $k_{20} = 55 \text{ M}^{-1} \text{ s}^{-1}$  is used in this study to account for the temperature difference and to fit the experimental data.

Reaction 16 was investigated by stopped-flow methods at room temperature and found to be very rapid with  $k_{16} > 10^5$  M<sup>-1</sup> s<sup>-1</sup>. Comparison of reaction 18 with the analogous reaction between HOBr and I<sup>-</sup> suggests that reaction 18 also is very fast. Reactions 17, 19, 21–23 are all fast reactions whose rate constants were estimated here to fit experiment. The values chosen for these rate constants do not strongly affect the results of simulations because these reactions are not rate determining.

The rate constant of reaction 4 can be estimated by assuming that the Br<sub>2</sub> concentration in the second part of the induction period is in a pseudosteady state with Br<sub>2</sub> consumption by reaction 4 and production via reactions 7–9 (overall reaction 5) with reaction 7 as the rate-determining step. The value  $k_4 \approx 800 \text{ M}^{-1} \text{ s}^{-1}$  is obtained from equation 25. This value of  $k_4$  is approximate

$$k_{4} = \frac{3k_{7}[\text{BrO}_{3}^{-}]_{ss}[\text{Br}^{-}]_{ss}[\text{H}^{+}]_{ss}^{2}}{[\text{Br}_{2}]_{ss}[\text{HCN}]_{ss}}$$
(25)

due to uncertainties in ascertaining the steady-state concentrations in equation 25. We estimate that the value of  $k_4$  lies in the range 10-1000 M<sup>-1</sup> s<sup>-1</sup> and choose the value 800 M<sup>-1</sup> s<sup>-1</sup> as being most consistent with our experimental results. Table I summarizes the mechanism used in our simulations.

**Simulations.** The differential equations resulting from the mechanism in Table I in a batch reactor were integrated numerically, and the absorbances at 396 (mainly due to  $Br_2$ ) and at 310 nm (mainly due to  $Br_3^-$ ) were calculated. Figures 1 and 2 show the excellent agreement obtained between experiment and simulation.

The experimental data in Figure 6 are  $[Br^-]$  during the  $BrO_3^-$ -SCN<sup>-</sup> reaction derived from the absorbances of  $Br_3^-$  and





Figure 6. Experimental and simulated  $[Br^-]$  vs time during the  $BrO_3^-$ -SCN<sup>-</sup> batch reaction. The experimental data were derived from the absorbances at 310 and 396 nm shown in Figure 1.



Figure 7. Calculated CSTR steady-state  $[Br_2]$  vs flow rate. Initial concentrations:  $[BrO_3^-]_0 = 0.0167$  M;  $[SCN^-]_0 = 0.0067$  M;  $[H^+]_0 = 0.133$  M.

Br<sub>2</sub> by use of reaction 12 with  $K_{12} = 18 \text{ M}^{-1}$ . The agreement between experiment and simulation again is quite good. The data in this figure also show that the amount of Br<sup>-</sup> produced after the first part of the induction period is in agreement with the stoichiometry of equation 1.

The mechanism failed to show oscillations in a CSTR over a very wide range of feedstream concentrations and flow rates, as found experimentally. However, the steady state  $[Br_2]$  changes

<sup>(30)</sup> Treindl, L.; Kostrová, L. Chem. Zvesti 1965, 19, 34.

very rapidly at low flow rates. Values corresponding to the three stages of the batch reaction appear over a very narrow flow rate range as is shown in Figure 7. The simulations are very sensitive in this region, and it may be that the observed noisy oscillations in our and Simoyi's<sup>15</sup> CSTR experiments result from an extreme sensitivity of the experimental system to environmental perturbation. The effect of mixing<sup>31</sup> experimentally and in this model

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should be carefully investigated. The CSTR experiments also need to be repeated with more precisely controlled pumps.

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# Confirmation of High Flow Rate Chaos in the Belousov-Zhabotinsky Reaction

# Laszlo Györgyi,<sup>†,‡</sup> Richard J. Field,<sup>\*,†</sup> Zoltan Noszticzius,<sup>§,||</sup> William D. McCormick,<sup>§</sup> and Harry L. Swinney<sup>\*,§</sup>

Department of Chemistry, University of Montana, Missoula, Montana 59812, Center for Nonlinear Dynamics and Department of Physics, University of Texas at Austin, Austin, Texas 78712, Institute for Inorganic and Analytical Chemistry, Lorand Eotvos University, Budapest H-1528, Hungary, and Department of Chemical Physics, Technical University of Budapest, Budapest H-1521, Hungary (Received: July 23, 1991)

Past experiments and simulations on the Belousov-Zhabotinsky (BZ) reaction clearly demonstrated the existence of chaos in stirred flow reactors at low flow rates. However, the existence of chaos at high flow rates has remained the subject of controversy. The controversy is resolved by the present experiments at high flow rates, which accurately reproduce the complex sequence of periodic, complex periodic, and chaotic states observed by Hudson and co-workers (Hudson et al., 1979; Hudson and Mankin, 1981); the flow rates observed here for the different dynamical regimes agree with those of Hudson et al. within a few percent. This striking reproducibility of the complex periodic and chaotic dynamics is found to be insensitive to stirring rate, size of the reactor, purity of the reagents, temperature, and type of pumping (peristaltic or piston pumps, premixed or nonpremixed feeds). Moreover, the observed sequence is reproduced qualitatively by a four-variable model of the BZ reaction. Thus, this work provides definitive evidence for the existence of deterministic chaos in the BZ reaction at high flow rates. We conclude that past descriptions of aperiodic behavior at high flow rates in terms of various stochastic mechanisms, including incomplete mixing or switching between adjacent periodic states, are inappropriate for the conditions of the Hudson's experiments.

# I. Introduction

The most striking examples of the occurrence of nonlinear dynamical phenomena<sup>1</sup> in chemical systems maintained far from equilibrium have been provided by the oscillatory Belousov– Zhabotinsky<sup>2</sup> (BZ) reaction. Periodic, quasiperiodic, and aperiodic oscillations, intermittency, phase-locking, bistability, hysteresis, excitability, and spatial pattern formation have all been observed under appropriate conditions. We are concerned here with the question of the existence of deterministic chaos when the BZ reaction is run in a continuous-flow, stirred tank reactor (CSTR).

The CSTR is a convenient and versatile tool<sup>3</sup> for studying the dynamical behavior of chemical systems. The major reactants are pumped into a vigorously stirred reactor at a particular flow rate while the reaction mixture flows out at the same rate. The system is thus maintained away from equilibrium, and the dynamics of the flow may couple with the chemical dynamics. A further advantage of CSTR experiments is that true stationary states can be obtained and their characteristics, as well as the bifurcations separating them, can be explored in detail. The dynamical behavior of the system can thus be determined by searching the space of the main control parameters: flow rate, temperature, and reagent concentrations in the feed streams. The flow rate is usually used as the bifurcation parameter at a particular temperature and set of feed stream concentrations because it is easy to control.

Under typical experimental circumstances the BZ reaction shows an oxidized steady state at high flow rates, a reduced steady state at low flow rates, and, often, periodic oscillations at intermediate flow rates. Residence times range from minutes to hours. Aperiodic oscillations are also possible and were first found at high CSTR flow rates by Schmitz et al.<sup>4</sup> and further studied by Hudson and co-workers.<sup>5,6</sup> Many more aperiodic regions have been discovered since then near the bifurcations between steady state and oscillatory behavior at both high and low flow rates. The aperiodicity was shown to be deterministic chaos by examination of the attractor in the reconstructed phase space of the system, by return maps taken from Poincaré sections of that

<sup>\*</sup>Authors to whom correspondence should be addressed.

<sup>&</sup>lt;sup>†</sup>University of Montana.

<sup>&</sup>lt;sup>‡</sup>Lorand Eotvos University.

<sup>&</sup>lt;sup>5</sup>University of Texas.

<sup>&</sup>lt;sup>1</sup>Technical University of Budapest.

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