

RATE SENSITIVITY ANALYSIS OF A MODEL OF THE  
BRIGGS-RAUSCHER REACTION

T. Turányi

Central Research Institute for Chemistry of the Hungarian  
Academy of Sciences, H-1525 Budapest, P.O.Box 17, Hungary

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An updated mechanism for the Briggs-Rauscher reaction (also known as "Iodine Clock" reaction) has been investigated by the principal component analysis of the rate sensitivity matrix. The analysis revealed that five reactions of the 15-step model were redundant. The results of principal component and of rate-of-production analyses together gave an insight into the basic processes of the "Iodine Clock" reaction.

Современный механизм реакции Бригса-Раушера (известной также как реакция "иодных часов") был исследован с помощью принципиального компонентного анализа матрицы чувствительности реакции. Анализ подтверждает, что 5 реакций из 15и-ступенчатой модели можно считать излишними. Результаты анализа принципиального компонента и скорости получения вместе дают более глубокие представления о механизме реакции "иодных часов".

INTRODUCTION

The Briggs-Rauscher reaction [1] (oxidation of malonic acid by  $\text{IO}_3^-$  ions in acidic solution in the presence of  $\text{Mn}^{2+}$  and  $\text{H}_2\text{O}_2$ ) is often used in school demonstrations of oscillating reactions. This is the famous "Iodine Clock" reaction. Knowledge of the Briggs-Rauscher reaction was summarized in the review of Furrow

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[2]. Two, almost identical mechanisms were proposed by Noyes and Furrow [3] and by De Kepper and Epstein [4]. Later Furrow developed further this mechanism [5] on the basis of new experimental results. Recently he proposed [6] a new rate coefficient for reaction  $I_5$  to achieve a better agreement with the experimental observations.

This updated mechanism of the BR reaction was now investigated by new computational methods for the analysis of complex reaction mechanisms. These methods allowed the identification of redundant species [7] and the investigation of the importance and interaction of reactions by the principal component analysis [8] of the rate sensitivity matrix [9]. The application of sensitivity methods for the analysis of reaction mechanisms was reviewed recently [10]. The calculations were carried out by program package KINAL [11].

### REDUCTION OF THE MECHANISM

The mechanism investigated here is given in Table 1. The values of rate coefficients and their references are:

$$\begin{aligned}k_1 &= 3.6 \times 10^9 \text{ [5]}, & k_2 &= 0.0018/[\text{H}^+] \text{ [3]}, & k_3 &= 5 \times 10^9 \text{ [5]}, \\k_4 &= 1430 \times [\text{IO}_3^-][\text{H}^+] \text{ [3]}, & k_5 &= 240 \text{ [5]}, & k_6 &= 0.3/[\text{H}^+] \text{ [5]}, \\k_7 &= 4.2 \times 10^5 \times [\text{IO}_3^-][\text{H}^+]^2 \text{ [6]}, & k_8 &= 1.607 \times 10^9 \text{ [3]}, \\k_9 &= 7.5 \times 10^5 \text{ [3]}, & k_{10} &= 5 \times [\text{H}_2\text{O}_2] \text{ [5]}, & k_{11} &= 1.0 \times 10^4 \times [\text{Mn}^{++}] \\& & & & & \text{[3]}, \\k_{12} &= 3.2 \times 10^4 \times [\text{H}_2\text{O}_2] \text{ [3]}, & k_{13} &= 3.9 \times 10^{-3} \times [\text{RH}] \text{ [3]}, \\k_{14} &= 91 \text{ [3]}, & k_{15} &= 9.1 \times 10^5 \text{ [3]}.\end{aligned}$$

The second column of Table 1 contains the traditional notation of reaction steps which has been used in the literature of the Briggs-Rauscher [2] reaction. The mechanism was investigated in an open system, that is the concentrations of  $\text{H}_2\text{O}_2$ ,  $\text{IO}_3^-$ ,  $\text{H}^+$ ,  $\text{H}_2\text{O}$ ,  $\text{Mn}^{2+}$ , and malonic acid (RH) were fixed. A previously used [3,12] concentration set for the investigation of the mechanisms of the Briggs-Rauscher reaction was applied:

Table 1

Mechanism of the Briggs-Rauscher reaction. Reactions marked by sign "o" are those which are important at reaction times indicated (see text)

		No. of reaction times										
		1	2	3	4	5	6	7	8	9	0	1
1.	$I_1$ $\text{HOI} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}$	o	o	o	o	o	o	o	o	o	o	o
2.	$I_{-1}$ $\text{I}_2 + \text{H}_2\text{O} \rightarrow \text{HOI} + \text{I}^- + \text{H}^+$									o		
3.	$I_2$ $\text{HIO}_2 + \text{I}^- + \text{H}^+ \rightarrow 2 \text{HOI}$	o	o	o	o	o	o	o	o	o	o	o
4.	$I_3$ $\text{I}^- + \text{IO}_3^- + 2 \text{H}^+ \rightarrow \text{HIO}_2 + \text{HOI}$	o	o	o					o	o	o	o
5.	$I_{-3}$ $\text{HIO}_2 + \text{HOI} \rightarrow \text{I}^- + \text{IO}_3^- + 2 \text{H}^+$											
6.	$I_4$ $2 \text{HIO}_2 \rightarrow \text{HOI} + \text{IO}_3^- + \text{H}^+$											
7.	$I_5$ $\text{HIO}_2 + \text{IO}_3^- + \text{H}^+ \rightarrow 2 \text{.IO}_2 + \text{H}_2\text{O}$	o	o	o	o	o	o	o	o	o	o	o
8.	$I_{-5}$ $2 \text{.IO}_2 + \text{H}_2\text{O} \rightarrow \text{HIO}_2 + \text{IO}_3^- + \text{H}^+$				o	o	o	o				
9.	$O_2$ $2 \text{.HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$											
10.	$D_1$ $\text{HOI} + \text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{O}_2 + \text{H}^+ + \text{H}_2\text{O}$				o	o	o	o				
11.	$M_1$ $\text{.IO}_2 + \text{Mn}^{2+} + \text{H}_2\text{O} \rightarrow \text{HIO}_2 + \text{Mn}(\text{OH})^{2+}$	o	o	o	o	o	o	o	o	o	o	o
12.	$M_2$ $\text{Mn}(\text{OH})^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{.HO}_2 + \text{Mn}^{2+} + \text{H}_2\text{O}$											
13.	$C_3$ $\text{RH} \rightarrow \text{enol}$	o	o	o	o	o	o	o	o	o	o	o
14.	$C_{-3}$ $\text{enol} \rightarrow \text{RH}$	o	o	o	o	o	o	o	o	o	o	o
15.	$C_4$ $\text{I}_2 + \text{enol} \rightarrow \text{I}^- + \text{RI} + \text{H}^+$	o	o	o	o	o	o	o	o	o	o	o

$[\text{H}_2\text{O}_2] = 1.1 \text{ M}$ ,  $[\text{IO}_3^-] = 0.019 \text{ M}$ ,  $[\text{H}^+] = 0.057 \text{ M}$ ,  $[\text{Mn}^{2+}] = 0.004 \text{ M}$ , and  $[\text{RH}] = 0.013 \text{ M}$ ,  $[\text{I}^-] = 10^{-10} \text{ M}$ .

After 100 s the solution of the system was very close to the limit cycle. Therefore, 100 s of the simulation was chosen to be the zero time of the investigation and the analysis was made at the following times: 0.0 s, 10.0 s, 21.2 s (this was the time when there was a minimum of  $[\text{I}_2]$  and maximum of  $[\text{enol}]$ ), 22.3 s (minimum of  $[\text{I}^-]$ ), 23.5 s (maximum of  $[\text{HIO}_2]$ ,  $[\text{.IO}_2]$ ,  $[\text{.HO}_2]$ , and  $[\text{Mn}(\text{OH})^{2+}]$ ), 24.0 s (maximum of  $[\text{HOI}]$ ),

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27.1 s (minimum of [enol], maximum of  $[I_2]$ ), 28.7 s (here  $[I^-] = [I^-]_{\max}/2$ ), 31.7 s (minimum of  $[HIO_2]$ ,  $[.IO_2]$ , and  $[Mn(OH)^{2+}]$  maximum of  $[I^-]$ ), 48.3 s (minimum of  $[HOI]$ ), 56.3 s (minimum of  $[.HO_2]$ ). The aim of the selection of reaction times was that they had to include all characteristic times and they had to cover a whole period.

Redundancy of species was investigated by the first method described in [7], i.e. a species was considered redundant if the omission of all of its consuming reactions had no significant effect on the calculated concentrations of important species. Our investigations revealed that the calculation of the concentrations of  $Mn(OH)^{2+}$  and  $.HO_2$  are not necessary for the reproduction of  $I_2$  and  $I^-$  oscillations. All species except these two redundant ones were considered in the objective function of the principal component analysis. Threshold values were  $10^{-4}$  for eigenvalues and 0.1 for eigenvectors. The results, summarized in Table 1, indicated that step 4 was important only in the low  $[HIO_2]$  stage, while reaction steps 8 and 10 were important in the high  $[HIO_2]$  stage. Reactions 5, 6, 9 and 12 were

Table 2

Comparison of solutions of the original and reduced models.  
Concentrations are in M

	Original	RED1	RED2	RED3
Number of species	8	6	6	5
Number of reactions	15	11	10	8
$t_{\text{period}}$	57.4 s	57.4 s	58.5 s	53.3 s
$[I^-]$ min.	9.16E-11	9.16E-11	8.69E-11	8.68E-11
$[I^-]$ max.	2.03E-05	2.03E-05	2.08E-05	1.96E-05
$[I_2]$ min.	1.58E-07	1.77E-07	1.77E-07	1.77E-07
$[I_2]$ max.	5.30E-05	5.32E-05	5.54E-05	4.58E-05

species	point of time										
	1	2	3	4	5	6	7	8	9	10	11
$I^-$	15/1(3.4)			10/3		10/3.1	15.10 /1.3	15/1	15/1(3.4)		
$I_2$	1/15										
HOI	3(4)/1			3/10.1				3.2/1	3(4)/1		
$HIO_2$	4/3	4(11)13	11/37	8/7				4/3			
$\cdot IO_2$	7/11			7/8				7/11			

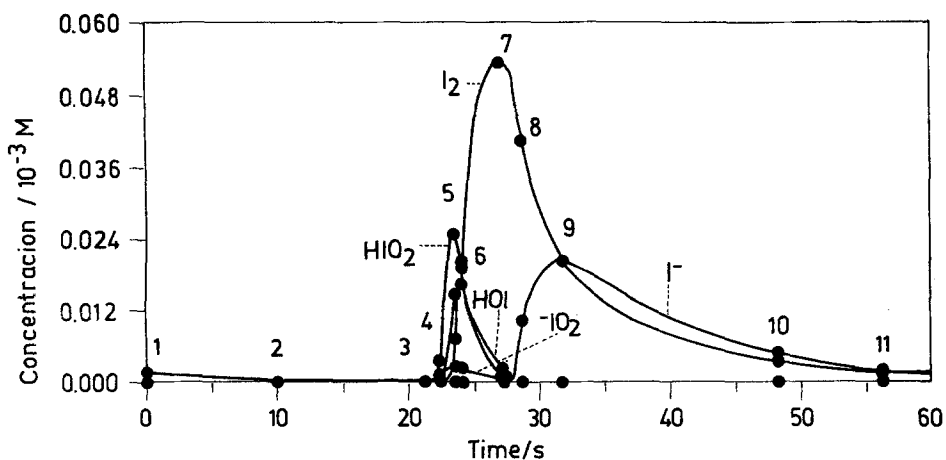


Fig. 1. The most significant producing and consuming reactions (before and after the slash, respectively) at different reaction times and the concentration-time profiles of five iodine containing species

redundant and their elimination yielded a reduced model (RED1) which gave almost identical solutions to that of the original model. Step 2 was important only near the 8th reaction time (28.7 s) and its further elimination (RED2) increase slightly the period time. This model can be reduced further by assuming an equilibrium concentration for the enol form (RED3). A comparison of the solutions of the original and the reduced models

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is seen in Table 2.

INSIGHT INTO OPERATION OF THE MODEL

A parallel study of the most important producing and consuming reactions of the species (see Fig. 1) and of the importance of reactions at different reaction times (given in Table 1) offered an insight into the operation of the model.

The operation of the Briggs-Rauscher reaction consists of the cyclic repetition of two stages, characterized by low and high  $\text{HIO}_2$  concentrations, respectively.

Stage 1:  $\text{I}_2$  is converted into  $\text{I}^-$  by reaction 15 and  $\text{I}^-$  is converted into  $\text{HIO}_2$  by reaction 4 (28.7 s - 57.4 s; 0 s - 22.3 s, points 8-11 and 1-3).

Stage 2: The concentration of  $\text{HIO}_2$  is high and even more  $\text{HIO}_2$  is produced by reactions 7 and 11:  $\text{HIO}_2 \rightarrow 2 \text{HIO}_2$ .  $\text{HIO}_2$  produces  $\text{HOI}$  in an autocatalytic way by reactions 3 and 10.  $\text{HOI}$  is converted into  $\text{I}_2$  by step 1. (22.3 s  $\approx$  28.7 s, points 4-7).

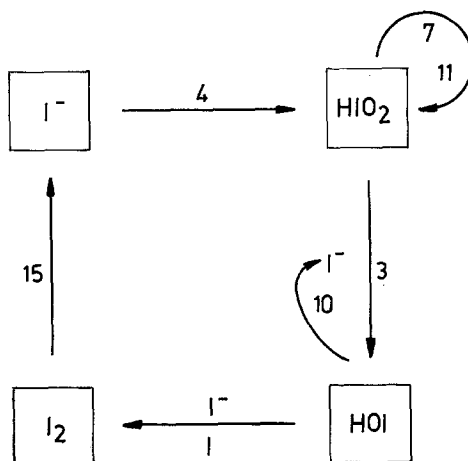


Fig. 2. A summary of the basic processes of the Briggs-Rauscher reaction

These reactions, summarized in Fig. 2, can be interpreted as the cyclic transformations of four iodine-containing molecules. These processes result in a sequence of peaks of the concentrations of  $\text{HIO}_2$ ,  $\text{HOI}$ ,  $\text{I}_2$  and  $\text{I}^-$  in each period, respectively. The peak concentrations of these species are not equal, because the iodine content inherent in these compounds is increased by reactions 4 and 7 and decreased by step 15.

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