React. Kinet. Catal. Lett., Vol. 33, No. 1, 81-86 (1987)

NUMERICAL SIMULATION OF THE BZ REACTION OF OXALIC ACID WITH A SIMPLE FOUR-VARIABLE MODEL

V. Gáspár, Z. Noszticzius* and H. Farkas*

Department of Physical Chemistry, Institute of Chemistry, Kossuth Lajos University, H-4010 Debrecen, P.O. Box 7, Hungary

* Department of Chemical Engineering, Institute of Physics, Technical University of Budapest, H-1521 Budapest, Hungary

Received December 18, 1985
Accepted May 13, 1986

A simple model of the bromate-cerium-oxalic acid batch oscillatory system has been constructed and examined by calculations. The model predicts a parameter range and a frequency which agree rather well with the observed values, but it does not describe the peculiar saddle-node infinite period bifurcations found experimentally in the system.

Сконструирована и проверена на расчетах простая модель осциллирующей системы бромат - церий - щавелевая кислота. На основе модели предсказан предел параметров и частота колебаний, которые хорошо согласуются с наблюдаемыми величинами, но не описывают экспериментально найденные седло-узловые бифуркации с бесконечным периодом.

INTRODUCTION

In a recently published paper Noszticzius et al. [1] have reported on investigation of the bromate-cerium-oxalic acid batch oscillatory system. To sustain the oscillation, the bromine produced has to be removed, e.g. by an inert gas stream. The loss of bromine was described by the rate equation:

$$-\frac{d[Br_2(sol)]}{dt} = k[Br_2(sol)]$$

The value of k is proportional to the flow rate of the gas stream. The results can be summarized as follows:

(a) Oscillations are observed in a certain region of k values ($0.0078 - 0.021\ s^{-1}$).

(b) Below and above this region the so-called "LO" and "HI" steady states are reached. They correspond to the two well-distinguishable branches of potential values measured by a bright platinum electrode.

(c) The amplitude of oscillation is almost constant, while the period goes through a flat minimum of about 40 s,and tends to infinity in the vicinity of the lower and upper limits of k.

(d) Both steady states are excitable near the bifurcation points.

These observations can be explained by the so-called saddle-node infinite period bifurcation [1] from an oscillatory state to an excitable steady state. Similar results have been obtained in CSTR by Gáspár and Galambosi [2].

Now we report a numerical simulation of the above system based on the available experimental data. As a first approximation, our simple model is based entirely on the chemistry of bromine, because the common component in all BZ systems is the acidic bromate.

A SIMPLE MODEL OF THE SYSTEM

The detailed mechanism of the BZ reaction is still a subject of controversy in the literature. Two new models were proposed recently: the Explodator [3] and the Revised Oregonator [4]. Both contain two autocatalytic processes and different oxidation levels of bromine as intermediates. However, the as-

signments of the intermediates are somewhat different: $HBrO_2$, HOBr and Br_2 in the Explodator and $HBrO_2$, HOBr and Br^- in the Revised Oregonator. Both the neglect of Br^- in the Explodator [5] and the neglect of Br_2 in the Revised Oregonator may cause some problems (e.g. in the oxalic acid BZ system [6]). Thus, it is a next logical step to study a model including all the four bromine species as intermediates. We regarded the following skeleton mechanism:

$$A + X \longrightarrow 2\,X \qquad (1)$$

$$X + Y \longrightarrow 2\,Z \qquad (2)$$

$$B + Z \longrightarrow Y + \text{inert products} \qquad (3)$$

$$Z + Y \Longrightarrow W \qquad (4)$$

$$W \longrightarrow \text{inert bromine} \qquad (5)$$

$$A + Y \longrightarrow X + Z \qquad (6)$$

$$2\,X \longrightarrow Z + A \qquad (7)$$

$$A + B \longrightarrow X + \text{inert products} \qquad (8)$$

where $A \equiv BrO_3^-$, $B \equiv (COOH)_2$, $X \equiv HBrO_2$, $Y \equiv Br^-$, $Z \equiv HOBr$, and $W \equiv Br_2(sol)$. The concentrations of A and B are supposed to be constant.

The reactions (3) and (8) are well-known [7,8]. Reaction (5) is the first-order removal of bromine by the gas stream. Notably a very similar model has been developed by Bódiss and Field [9], but reactions of $BrO_2^{\bullet}$, cerium(III) and (IV) were also included, in addition. They succeeded in computer simulation of one of the original experiments of Noszticzius and Bódiss [10]. Recently, Field and Boyd [15] developed a five-variable modified Oregonator model which is also similar to the above model.

The four-variable system of ordinary differential equations [14] constructed by the mass action rates form the skeleton (1-8) was solved by Gear's method [11].

The applied rate constants are listed in Table 1. We have chosen the so-called "LO"-set values [12], because they are more realistic according to the latest experimental data [13].

Table 1

Rate constants for calculations. The values were calculated according to the experimental conditions:
$[BrO_3^-] = [(COOH)_2] = 4.0 \times 10^{-2}$ M: $[H^+] = 1.5$ M (H_2SO_4). (Ref. :[1])

Step	Value	Definition	References
1	6.0×10^{-1} s^{-1}	$10[H^+][BrO_3^-]$	12
2	1.5×10^{6} $M^{-1}s^{-1}$	$10^6[H^+]$	12
3	8.8 s	$220[(COOH)_2]$	8
4	1.2×10^{10} $M^{-1}s$	$8 \times 10^9[H^+]$	12
-4	100 s^{-1}	------	12
5	varied		
6	1.8×10^{-1} s^{-1}	$2[H^+]^2[BrO_3^-]$	12
7	4×10^{3} $M^{-1}s^{-1}$		13
8	1.44×10^{-6} M s^{-1}	$6 \times 10^{-4}[H^+][BrO_3^-][(COOH)_2]$	7

RESULTS AND DISCUSSION

The calculated time period and amplitude of the oscillations as functions of the bifurcation parameter k are shown in Fig. 1.

In accordance with the experiments, there is a certain region of k values (0.035 - 0.1 s^{-1}) in which oscillation was found by calculations. Noteworthy, both lower and upper values are higher than the experimental ones by nearly the same factor (4.48 and 4.76, respectively). The calculated time periods are also not too far from the observed 40S. The simulations show two different steady states outside the oscillatory region with high Br^- concentration at low k values and with low Br^- concentration when k is relatively high. This is also in accordance with the experimental results.

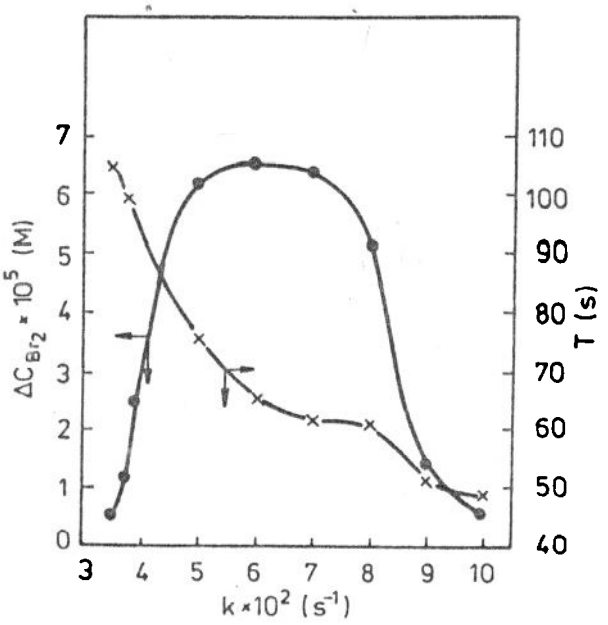

Fig. 1. The calculated dependence of time period (x) and amplitude (●) of oscillations ($\Delta c_{Br_2} = c_{Br_2 max} - c_{Br_2 min}$) on the bifurcation parameter k

Figure 1 shows, however, that the changes of amplitude and time period are completely different from the ones observed in the experiments. The data suggest that bifurcations from steady states to periodic orbits and vice versa proceed by supercritical Hopf bifurcation. As a consequence, it is not surprising that the experimentally observed excitability of the steady states were not detectable in our calculations.

An analytical proof that only Hopf bifurcation can occur in the above model independently of the numerical values of the rate constants will be given in a forthcoming paper [14].

REFERENCES

1. Z. Noszticzius, P. Stirling, M. Wittmann: J. Phys. Chem. 89, 4914 (1985).
2. V. Gáspár, P. Galambosi: J. Phys. (submitted)

3. Z. Noszticzius, H. Farkas, Z.A. Schelly: Chem. Phys., 80, 6062 (1984).
4. R.M. Noyes: J. Chem. Phys., 80, 6071 (1984).
5. Z. Noszticzius, V. Gáspár, H.D. Försterling: J. Am. Chem. Soc., 107, 2314 (1985).
6. R.J. Field: in "Oscillations and Traveling Waves in Chemical Systems"; R.J. Field, M. Burger, Eds., Chapter 2, Wiley, New York 1985.
7. P. Ševčik, L. Adamčikova, D. Gunarova, Kovačikova: Acta F.R.N. Univ. Comen. - Chimia, 31, (1983).
8. a) Y. Knoller, B. Perlmutter-Hayman: J. . Chem. Soc., 77, 3212 (1955).
   b) R.H. Smith: Aust. J. Chem., 25, 2503 (1972).
9. J. Bódiss, R.J. Field: in ref. 6, Chapter 2, p. 70.
10. Z. Noszticzius, J. Bódiss: J. Am. Chem. Soc., 101, 3177 (1979).
11. C.W. Gear: "Numerical Initial Value Problems in Ordinary Differential Equations" pp. 209-229 Prentice-Hall Englewood Cliffs, N.J. 1971.
12. J.J. Tyson: in ref. 6, Chapter 3.
13. a) Z. Noszticzius, E. Noszticzius, Z.A. Schelly: J. Phys. Chem., 87, 510 (1983).
   b) F. Ariese, Zs. Ungvári-Nagy: J.Phys. Chem., 90, 1 (1986).
   c) H.D. Försterling: private communication.
   d) R.J. Field: private communication.
14. H. Farkas, Z. Noszticzius: React. Kinet. Catal. Lett., 33, 93 (1987).
15. R.J. Field, P.M. Boyd: J. Phys. Chem., 89, 3707 (1985).