NOTES

Experimental studies on BZ reaction system containing oxalic acid and acetone as mixed organic substrate in a CSTR

C Basavaraja, V R Kulkarni*, S Mohan², Y M Iyer² & G V Subba Rao⁶
Department of Chemistry, Gulbarga University, 
Gulbarga 585 106, India
²Central Electrochemical Research Institute, Karaikudi 630 006, India
³Department of Physics, National University of Singapore, Singapore 119 260
E-mail: vijaykumar2@sancharnet.in

Received 4 March 2003; revised 10 December 2003

Belousov-Zhabotinsky reaction containing Bromate-CeIV-H₂SO₄-mixed organic substrate (oxalic acid and acetone) has been studied in a continuously stirred tank reactor. The behaviour with respect to flow rate and inflow concentrations has been investigated using platinum as the indicator electrode. Each of these variables show lower and upper limits for the appearance/disappearance of oscillating behaviour. These observations have been discussed with reference to model simulations. Necessity for modification of the model to account for discrepancies is indicated.

The study of chemical reactions far from equilibrium is a best source of experimental data on a variety of dynamical phenomena. It is now becoming accessible to explore systems consisting of complex mechanism for evidence of new dynamical behavior. The BZ reaction and other oscillating reactions are representative chemical systems with complex mechanism showing a variety of temporal behaviour and in some cases spatial pattern formation. Besides regular oscillations they may also show multistability, bursts of oscillations, quasiperiodicity and chaotic motions in open systems. In an experiment carried out in a continuously stirred tank reactor (CSTR), the concentrations of the reacting chemicals inside the reactor are maintained unchanged throughout the experiment by continuous feeding of the chemicals and the oscillations generated are sustained in character. Acidic bromate with metal catalyst constitutes the minimal bromate oscillator. This shows oscillations only in CSTR (not in batch) that too under very narrow range of constraints.

Addition of organic chemicals accentuate the oscillating behaviour profoundly. This addition can be a single substrate or a mixed organic substrate like oxalic acid and acetone. Gasper and Galambosi have studied the system in CSTR when oxalic acid alone is the additional organic species in the minimal bromate oscillator. This system shows oscillation in batch only when the accumulated bromine is removed either by bubbling inert gas or by addition of acetone. The presence of acetone without oxalic acid has also been reported to show oscillations in batch both at room temperature as well as at much higher temperatures. Recently Ruxin Cai et al. reported a study of bromate-manganese-diacetone system in a CSTR. Experimental as well as simulation studies of related oscillating systems is being taken up in our laboratory. Some of these experimental results of the system bromate-cerium-oxalic acid-acetone in CSTR is being reported here. Influences of the flow rate and the concentrations of the reactants on the system have been investigated. These observations are discussed with reference to model simulation performed on the basis of current mechanistic understanding of this system.

**Experimental**

All the chemicals are of AR grade and water used was doubly distilled. Study of oscillating chemical reactions in CSTR mode involves two or more inflows of reactants to a reactor vessel, which is continuously being stirred and the excess of the reaction mixture, is let out of the system. The pumping is done either by a peristaltic pump or by a syringe pump. Smaller the reactor volume lesser is the amount of flow necessary. However, the flow data can be scaled so that it can be universalized. The approach is to report the data in terms of inverse of residence time. Residence time is the ratio of the reactor volume to the total flow rate. Since there were two inputs in the CSTR, the components were premixed such that there were two feed solutions. The system consists of five chemicals namely, sulphuric acid, potassium bromate, ceric sulphate, oxalic acid and acetone. As all the solutions were prepared in sulphuric acid medium of the required concentration, there were only four chemicals to be explicitly considered. Thus one of the feed solutions was
Results and discussion

The inflow concentrations chosen as standard were $[\text{BrO}_3^-]_0 = 0.02 \, M$, $[\text{oxalic acid}]_0 = 0.05 \, M$, $[\text{acetone}]_0 = 1.5 \, M$, $[\text{Ce(IV)}]_0 = 0.001 \, M$. Fig. 1 indicates the platinum potential traces of standard composition when flow rate ($k_0$) is varied between $1.4 \times 10^{-3} \text{s}^{-1}$-$2.0 \times 10^{-2} \text{s}^{-1}$. It can be noted that the zero on the time scale is arbitrary. The portion showing constant sustained oscillations is presented in this figure except for the extreme flow rates, for which the measurements taken immediately after the flow mode is in operation namely after filling up of the reactor are presented.

At this composition we have observed no oscillations at both extremes of the flow rate. It can be noted that the nature of sustained oscillations obtained is a function of the flow rate. The oscillations appear as a compound one, wherein one type is entrained in another. They can also be looked at as involving a rapid increase in potential followed by a rapid decrease, a pseudo steady state and a slow decrease in potentials. At low $k_0$ they are nearly saw tooth with negligible duration of pseudo steady state. As the flow rate increases the duration of this pseudo steady state tends to increase. Hence during this range of flow rate they look like hump backed. The amplitude of oscillation decreases as $k_0$ is increased with the minimum potential of the oscillations showing a trend to increase. A look at the frequencies indicates it to be decreasing as the $k_0$ is increased. Thus the period of oscillations is $25 \, s$ when $k_0$ is $1.6 \times 10^{-3} \text{s}^{-1}$, $45 \, s$ when $k_0$ is $1.32 \times 10^{-3} \text{s}^{-1}$ and is $60 \, s$ when $k_0$ is $18.0 \times 10^{-3} \text{s}^{-1}$.

The available observations show that when $k_0$ is $1.4 \times 10^{-3} \text{s}^{-1}$ (low) there is a rapid increase of potential to about $840 \, \text{mV}$ within about $10 \, s$ after the flow mode is in operation, with the potential remaining nearly the same as time progresses, with no oscillations. While when $k_0$ is $2.0 \times 10^{-2} \text{s}^{-1}$ (high) no rapid increase of potential is observed; on the other hand the potential shows a slow increase followed by a slow decrease in the initial $20-30 \, s$ with the potential remaining in the neighborhood of about $790 \, \text{mV}$ as the time progresses, also with no oscillations. Thus one can infer that at low $k_0$ there exists a high steady state and at high $k_0$ there exists low steady state for the standard inflow compositions chosen.

The effect of $[\text{BrO}_3^-]_0$, $[\text{acetone}]_0$ and $[\text{oxalic acid}]_0$ have been studied. For this study a $k_0$ of $13.2 \times 10^{-3} \text{s}^{-1}$ was fixed as standard. During these studies one of the inflow concentrations was varied, while all others were kept constant as that of the standard.

$[\text{BrO}_3^-]_0$ was varied between $0.0075-0.06 \, M$. Oscillations were not observed at both the extremes of
The oscillations are nearly saw-tooth at low \([\text{BrO}_3^-]_0\) while they are hump-backed at high \([\text{BrO}_3^-]_0\). As the \([\text{BrO}_3^-]_0\) increases the amplitude and frequency decrease. While when \([\text{BrO}_3^-]_0\) is 0.0075 M (low), there is a slow decrease followed by a slow increase in the neighborhood of 910 mV as the time progresses with no oscillations. While when \([\text{BrO}_3^-]_0\) is 0.06 M (high), there is a slow increase in potential within 20-30 s of the flow mode with potential remaining in the neighborhood of 800 mV as the time progresses with no oscillations. This indicates that probably a low steady state exist at low \([\text{BrO}_3^-]_0\) and a high steady state at high \([\text{BrO}_3^-]_0\).

\(\text{[Acetone]}_0\) was varied between 0.25-1.3 M. Oscillations were not observed at both the extremes. The oscillations are nearly hump-backed, at lower \([\text{acetone]}_0\) while they are saw-tooth at high \([\text{acetone]}_0\). There is hardly any effect on the amplitude with increase in \([\text{acetone]}_0\). On the other hand frequency increases with the increase in \([\text{acetone]}_0\). When \([\text{acetone]}_0\) is 0.25 M (low), the platinum potential shows a relatively slow decrease followed by a rapid increase within about 10 s which asymptotically decreases to a value of about 880 mV. On the other hand, when \([\text{acetone]}_0\) is 1.3 M (high) initially a few sustained oscillations are observed followed by an abrupt cessation of oscillations when the system is in the high potential mode with the platinum potential remaining in the neighborhood of 880 mV. Thus there is difficulty here to ascertain the nature of steady state at the two extremes of \([\text{acetone]}_0\). However it appears that at low \([\text{acetone]}_0\) there probably may be low steady state while at high \([\text{acetone]}_0\) there is a high steady state.

The behaviour of the system was also studied by varying \([\text{oxalic acid}]/_0\) between 0.025-0.15 M. No oscillations are observed at both extremes. The oscillations are hump-backed at low \([\text{oxalic acid}]/_0\) while they are saw-tooth at high \([\text{oxalic acid}]/_0\). The oscillations at low \([\text{oxalic acid}]/_0\) are similar to that of observed at high \([\text{BrO}_3^-]_0\). As the \([\text{oxalic acid}]/_0\) increases the amplitude and frequency both increase. When \([\text{oxalic acid}]/_0\) is 0.025 M (low) an initial rapid increase in potential occurs within 10-15 s and potential remaining in the neighbourhood of 900 mV as the time progresses. While at 0.15 M (high) the platinum potential shows a relatively slow decrease followed by a rapid increase within about 10-20 s which asymptotically decreases to a value of about 860 mV. Thus one can possibly conclude that at low \([\text{oxalic acid}]/_0\) there exists a high steady state while at high \([\text{oxalic acid}]/_0\) there exists a low steady state.

A detailed mechanistic interpretation of the system Ce(IV)-BrO\(_3^-\)-oxalic acid-acetone in sulphuric acid media was proposed by Field and Boyed\(^8\), Rastogi and Misra\(^20\) utilized a simplified version to this interpretation to rationalize the experimental observations in batch of lower and upper critical concentration limits for the appearance and disappearance of oscillations. There have been some efforts at simulating the behaviour of the BZ reaction when oxalic acid alone in CSTR\(^7\) and also along with acetone in batch\(^18\-21\). In our recent effort at simulating the behaviour of this system\(^17\) we have utilized the simplified version of Rastogi and Misra\(^21\) by modifying it explicitly with simple non-radical reactions for the oxidation of oxalic acid as well as bromination of acetone. As presented therein, the results of this simulation are in contradiction with some of the experimental results presented here. Thus the experimental results here indicate decrease in the frequency as the flow rate is increased while simulation indicated increase in the frequency as the flow rate is increased. Though the steady state

![Fig. 1](image-url)
concentrations of the reactant chemicals remain constant and also they have enough time to react to oscillations appear/disappear and also with other observations in the critical ranges during which the reactor from zero time. However in practice these concentrations are attained exponentially depending on the flow rate. At the lower limit of the flow rate i.e., when the flow rate is minimal one can expect the behaviour of a batch system. When the residence time is of the order of the period of oscillations or few times higher we may expect sustained oscillations as concentrations of the reactant chemicals remain constant and also they have enough time to react to show the dynamics. But when the flow rate is much higher that is when the residence time is much smaller than the period of oscillation, possibility may exist wherein there may not be enough time for the reactants to react and to show any dynamics. Further the low/high state attained at the extremes of the flow rates and also the trends of the amplitude and frequency dependence may also be dependent on the inflow composition of the reacting system. Further there is necessity to make more number of observations in the critical ranges during which oscillations appear/disappear and also with other analytical tools. Experimental and modelling work on these lines is in progress.

Acknowledgement
The authors are thankful to DST, New Delhi for supporting this work. The authors thank Prof. B. K. Prabhakar, Chairman, Department of Chemistry, Gulbarga University, Gulbarga for facilities.

References