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

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Belousov-Zhabotinskii reaction containing Bromate-Ce^{IV}-H_2SO_4-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 multi-stability, bursts of oscillations, quasiperiodicity and chaotic motions in open systems[1-6]. 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[7] 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[8-11]. 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[12-14]. Recently Ruxin Cai *et al.*[15] 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[16,17]. 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 potassium bromate of the required concentration in sulphuric acid medium. In the other feed solution, remaining three chemicals namely cericsulphate, oxalic acid and acetone were mixed with appropriate concentrations in the same sulphuric acid medium as the first feed solution. Since the stoichiometry of the oxalic acid was always much higher than that of the ceric sulphate, it was thus reduced completely in this feed solution. This does not affect the measurements as results obtained were reproducible. The flow was checked before and after each experiment and flow rate was taken as the average of the two. Thus the inflow concentration of each component would be half that present in each of the feed solutions, except sulphuric acid which was of the same concentration in both the feed solutions. Study of the dynamics in CSTR could be made either by initially having a batch system in the reactor and this batch system is then converted to the flow system by starting the flows. Another way of studying the dynamics is starting with an empty reactor vessel and studying the dynamics after the CSTR is operating in the flow mode namely after filling of the reactor volume; the system will be in the pseudo batch mode till the reactor is filled with the reactants. The latter method is used in the present study. The pumps used to feed the solutions into the reactor cell are PP20-4C (Miclins India, Chennai). There were difficulties in adjusting equal flows using one peristaltic pump, therefore, two peristaltic pumps were used which had been calibrated so that two flows are equal. Thus the total flow rate (k_0) is the ratio of sum of the two identical input flow rates to that of the reactor volume.

Smooth bright platinum foil was employed as an indicator electrode which is inside the CSTR cell and saturated calomel was used as the reference electrode together with 10% KNO_3 (along with agar-agar) as salt-bridge having a sintered disc at the end dipping in the reactor mixture. Thus the potentials indicated here are with respect to SCE. The whole experiment was carried out at room temperature (≈ 30 ± 0.5°C). The signal from the indicator electrode and the reference electrode was fed to Elico-strip chart recorder (model LR-103) and also parallelly to a multimeter. A data acquisition card was also utilized intermittently for recording the traces. The reaction mixture was stirred with a magnetic stirrer at a speed of 600 rpm, active volume of the reactor being 30 ml.

Results and discussion

The inflow concentrations chosen as standard were $[BrO_3^-]_0 = 0.02\ M$, $[\text{oxalic acid}]_0 = 0.05\ M$, $[H^+]_0 = 1.5\ M$, $[\text{acetone}]_0 = 0.5\ M$, $[\text{Ce(IV)}]_0 = 0.001\ M$. Fig. 1 indicates the platinum potential traces of standard composition when flow rate (k_0) is varied between $1.4\times10^{-3}s^{-1}$-$2.0\times10^{-2}\ s^{-1}$. 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 tendency 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 $1.6\times10^{-3}\ s^{-1}$, 45 s when k_0 is $13.2\times10^{-3}\ s^{-1}$ and is 60 s when k_0 is $18.0\times10^{-3}\ s^{-1}$.

The available observations show that when k_0 is $1.4\times10^{-3}\ s^{-1}$ (low) there is a rapid increase of potential to about 840 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 $2.0\times10^{-2}\ s^{-1}$ (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 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 $[BrO_3^-]_0$, $[\text{acetone}]_0$ and $[\text{oxalic acid}]_0$ have been studied. For this study a k_0 of $13.2\times10^{-3}\ s^{-1}$ 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.

$[BrO_3^-]_0$ was varied between 0.0075-0.06 M. Oscillations were not observed at both the extremes of

$[BrO_3^-]_0$. The oscillations are nearly saw-tooth at low $[BrO_3^-]_0$ while they are humpbacked at high $[BrO_3^-]_0$. As the $[BrO_3^-]_0$ increases the amplitude and frequency decrease. While when $[BrO_3^-]_0$ is 0.0075 *M* (low), there is a slow decrease followed by a slow increase a relatively rapid increase in potentials within about 20-30 s of the flow mode with potential remaining in the neighborhood of 810mV as the time progresses with no oscillations. While when $[BrO_3^-]_0$ 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 935 mV as the time progresses also with no oscillations. This indicates that probably a low steady state exist at low $[BrO_3^-]_0$ and a high steady state at high $[BrO_3^-]_0$.

[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 [acetone]$_0$ while they are saw-tooth at high [acetone]$_0$. There is hardly any effect on the amplitude with increase in [acetone]$_0$. On the other hand frequency increases with the increase in [acetone]$_0$. When [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 870 mV. On the other hand, when [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 neighbourhood of 880 mV. Thus there is difficulty here to ascertain the nature of steady state at the two extremes of [acetone]$_0$. However it appears that at low [acetone]$_0$ there probably may be low steady state while at high [acetone]$_0$ there is a high steady state.

The behaviour of the system was also studied by varying [oxalic acid]$_0$ between 0.025-0.15 *M*. No oscillations are observed at both extremes. The oscillations are hump-backed at low [oxalic acid]$_0$ while they are saw-tooth at high [oxalic acid]$_0$. The oscillations at low [oxalic acid]$_0$ are similar to that of observed at high $[BrO_3^-]_0$. As the [oxalic acid]$_0$ increases the amplitude and frequency both increase. When [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 [oxalic acid]$_0$ there exists a high steady state while at high [oxalic acid]$_0$ there exists a low steady state.

A detailed mechanistic interpretation of the system Ce(IV)-BrO_3^--oxalic acid-acetone in sulphurinc acid media in batch 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

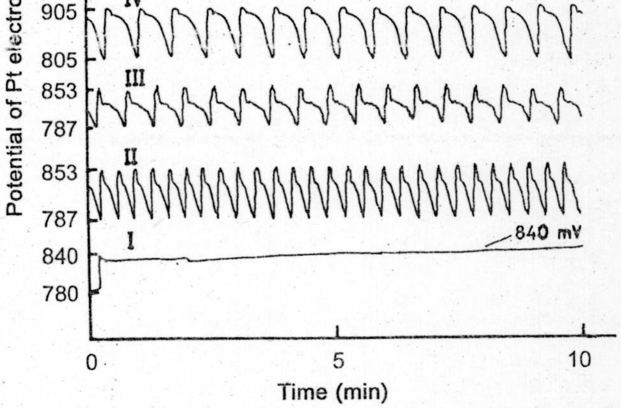

Fig. 1—Platinum electrode traces for different flow rate with the inflow concentrations as $[BrO_3^-]_0 = 0.02$ *M*, [oxalic acid]$_0$ = 0.05 *M*, $[H^+]_0 = 1.5$ *M*, [acetone]$_0$ = 0.5 *M*, [Ce(IV)]$_0$ = 0.001 *M*. k_0 : I = 1.4×10^{-3} s^{-1}, II = 1.6×10^{-3} s^{-1}, III = 8.0×10^{-3} s^{-1}, IV = 1.32×10^{-2} s^{-1}, V = 1.6×10^{-2} s^{-1}, VI = 1.8×10^{-2} s^{-1}, VII = 2.0×10^{-2} s^{-1}

behaviour of simulation at extremes of $[BrO_3^-]_0$ and $[\text{oxalic acid}]_0$ agree with experiment, the situation with regard to extremes of $[\text{acetone}]_0$ and k_0 is not. Further the model does not show oscillations for the experimental standard composition indicated in Fig. 1. Hence there is necessity to further modify the model such that at least it agrees with the experimental trends if not finer details.

The dynamics of non-linear oscillating chemical systems in a CSTR depend lot on the flow rate of the feed chemicals. It is desirable that the concentration of the reactant chemicals is constant in nature in side 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.

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