

# Simulation of the effect of oxalic acid and acetone on the bistable behaviour of the minimal bromate oscillator in a CSTR

C Basavaraja<sup>a</sup>, V R Kulkarni<sup>a,\*</sup>, T K Vishnuvardhan<sup>a</sup>, S Mohan<sup>b</sup>, Y M Iyer<sup>b</sup> & G V Subba Rao<sup>c</sup>

<sup>a</sup>Department of Chemistry, Gulbarga University, Gulbarga 585 106, India

<sup>b</sup>Central Electrochemical Research Institute, Karaikudi 630 006, India

<sup>c</sup>Department of Physics, National University of Singapore, Singapore 119 260

Email: vijaykumar2@sancharnet.in

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Simulation of the effect of oxalic acid as well as acetone on the bistable behaviour of the minimal bromate oscillator in a CSTR is reported. In these simulations, flow mode is set in with a minimum value of  $[\text{Br}]_0$ , the observation is done for a certain period of time and the resulting steady state value of bromide in the system  $[\text{Br}]_{ss}$  is noted. After this duration is over, the  $[\text{Br}]_0$  is increased steadily with the indicated values and  $[\text{Br}]_{ss}$  is recorded as earlier. After reaching a certain high value of  $[\text{Br}]_0$ , the same observations are repeated by decreasing  $[\text{Br}]_0$ . The system is found to be bistable between certain ranges of  $[\text{Br}]_0$ . It has been found that this range of values of  $[\text{Br}]_0$  is broadened when oxalic acid and/or acetone are additionally present in the minimal bromate oscillator.

The BZ reaction system exhibits a variety of non-linear dynamical phenomena, which depends a lot on the inflow concentrations, flow rate of the feed chemicals and other external parameters such as temperature, stirring and mixing<sup>1,4</sup>. Bistability is an inherent property of a chemical oscillator that gets exhibited in a flow reactor. Several authors have indicated that the addition of some organic substrates may accentuate the oscillating behaviour profoundly<sup>5-8</sup>. This addition can be a single substrate or mixed organic substrate like oxalic acid and acetone. Rastogi and Yadava<sup>7</sup> have reported in their experimental results of the mixed organic substrate on the BZ systems the effect of the bromate and acetone on the bistable behaviour by considering the flow rate as the bifurcation parameter. Recently, we have undertaken studies on these systems in a Continuously Stirred Tank Reactor (CSTR)<sup>10-14</sup>. It is in this context that an effort has been made to simulate the effect of oxalic acid and acetone on the bistable behaviour of the minimal bromate oscillator.

## Theoretical

### Reaction mechanism and computation method

The simulation was carried out with the software "Simulate" which incorporates the powerful Rosenbrock's integrator of Stiff differential systems. The

Simulate software sets-up its own differential equations and the result is computed as integrated values. However, appropriate mechanism, initial and inflow concentrations and the flow rates have to be given. For the present studies, the error tolerance of integrator is  $10^{-7}$ , initial step size is  $10^{-8}$  and maximum step size is 2.0. Table 1 describes the mechanism along with the rate constants utilized for the simulation study. The reactions 1-7 form the NFT mechanism considered by Bar-Eli and Geiseler<sup>9</sup> in their study of the bistability of the minimal bromate oscillator. The reactions 8-10 are taken from the Field and Boyd<sup>9</sup> mechanism reported for the batch behaviour of the mixed organic substrate system. Reactions 11 and 12 consist of the established pathway for the bromination of acetone<sup>9</sup>. The constraints of concentration and flow rate chosen during these simulations correspond to that reported earlier<sup>9</sup> and the parameter at the indicated constraints: the initial and inflow concentrations being same except for  $[\text{Br}]_0$ . These constants are identical to that used by Bar Eli and Geiseler<sup>9</sup>. During the simulations, it was found that the region of bistability is a function of the increments considered in the sense that for sufficiently small increments the region approaches the values indicated by Bar-Eli and Geiseler<sup>9</sup>. Larger increments eventually lead to the disappearance of the region of bistability with a smooth curve joining both high and low values.

Table 1 — Set of reactions and rate constants

No.	Reaction	Rate constants
1.	$\text{Br}^- + \text{BrO}_3^- + 2\text{H}^+ = \text{HOBr} + \text{HBrO}_2$	$k_1 = 2.1M^{-3}s^{-1}$ , $k_{-1} = 1 \times 10^4 M^1 s^{-1}$
2.	$\text{Br}^- + \text{HBrO}_2 + \text{H}^+ = 2\text{HOBr}$	$k_2 = 2.0 \times 10^9 M^2 s^{-1}$ , $k_{-2} = 5.0 \times 10^5 M^1 s^{-1}$
3.	$\text{Br}^- + \text{HOBr} + \text{H}^+ = \text{Br}_2 + \text{H}_2\text{O}$	$k_3 = 8.0 \times 10^9 M^2 s^{-1}$ , $k_{-3} = 110 s^{-1}$
4.	$\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ = \text{H}_2\text{O} + \text{BrO}_2$	$k_4 = 1.0 \times 10^4 M^2 s^{-1}$ , $k_{-4} = 2.0 \times 10^7 M^1 s^{-1}$
5.	$\text{BrO}_2 + \text{Ce}^{+3} + \text{H}^+ = \text{Ce}^{+4} + \text{HBrO}_2$	$k_5 = 6.5 \times 10^5 M^2 s^{-1}$ , $k_{-5} = 2.4 \times 10^7 M^1 s^{-1}$
6.	$\text{Ce}^{+4} + \text{BrO}_2 + \text{H}_2\text{O} = \text{Ce}^{+3} + \text{BrO}_3^- + 2\text{H}^+$	$k_6 = 9.6 M^1 s^{-1}$ , $k_{-6} = 1.3 \times 10^{-4} M^3 s^{-1}$
7.	$\text{HBrO}_2 + \text{HBrO}_2 = \text{BrO}_3^- + \text{HOBr} + 2\text{H}^+$	$k_7 = 4 \times 10^7 M^1 s^{-1}$ , $k_{-7} = 2.1 \times 10^{10} M^2 s^{-1}$
8.	$\text{Ce}^{+4} + (\text{COOH})_2 \rightarrow (\text{Ce}^{+3} + \text{H}^+ + \text{CO}_2 + \text{HCO}_2^-)$	$k_8 = 27.5 M^1 s^{-1}$
9.	$\text{Ce}^{+4} + \text{HCO}_2^- \rightarrow (\text{Ce}^{+3} + \text{OP}^1)$	$k_9 = 1 \times 10^6 M^1 s^{-1}$
10.	$\text{HOBr} + (\text{COOH})_2 \rightarrow (\text{H}_2\text{O} + \text{HCO}_2^0 + \text{CO}_2 + \text{Br}^-)$	$k_{10} = 25 M^1 s^{-1}$ , $k_{11} = 8.3 \times 10^5 M^1 s^{-1}$
11.	$\text{CH}_3\text{COCH}_3 + \text{H}^+ = \text{CH}_2 = \text{CHOHCH}_3 + \text{H}^+$	$k_{-11} = 21.3 M^1 s^{-1}$
12.	$\text{CH}_2 = \text{CHOHCH}_3 + \text{Br}_2 \rightarrow (\text{BrCH}_2\text{COCH}_3 + \text{Br}^- + \text{H}^+)$	$k_{12} = 1.03 \times 10^7 M^1 s^{-1}$

## Results and Discussion

### Behaviour of minimal oscillator

Figure 1 indicates the nature of bistability when  $[\text{Br}^-]_0$  is the bifurcation/hysteresis parameter at the indicated initial and inflow concentrations. During the simulations, it was found that the region of bistability is a function of the increments considered in the sense that larger increments eventually lead to disappearance of the region of bistability. In these simulations, flow mode is set in with the minimum of the  $[\text{Br}^-]_0$  indicated and the observation is done for about 20,000 seconds and the resulting steady value of bromide in the system namely,  $[\text{Br}^-]_{ss}$  is noted. After this duration is over, the  $[\text{Br}^-]_0$  is increased steadily with the indicated values and  $[\text{Br}^-]_{ss}$  is recorded as earlier.  $[\text{Br}^-]_{ss}$  varies gradually as  $[\text{Br}^-]_0$  increases along ABC during the rising part till point C. This steady state may be called as SSI. At C where  $[\text{Br}^-]_0 = 8.21 \times 10^{-7} M$ , there is a sudden jump of  $[\text{Br}^-]_{ss}$  from  $3.29 \times 10^{-10}$  (C) to  $1.19 \times 10^{-8}$  (D). Further increase in  $[\text{Br}^-]_0$  increases  $[\text{Br}^-]_{ss}$  steadily along DE. However, when  $[\text{Br}^-]_0$  is gradually decreased starting from point E the value of  $[\text{Br}^-]_{ss}$  during the return path traverses along EDC<sup>1</sup> instead of EDC. The steady state along EDC<sup>1</sup> may be called as SSII. After reaching C<sup>1</sup> where  $[\text{Br}^-]_0 =$

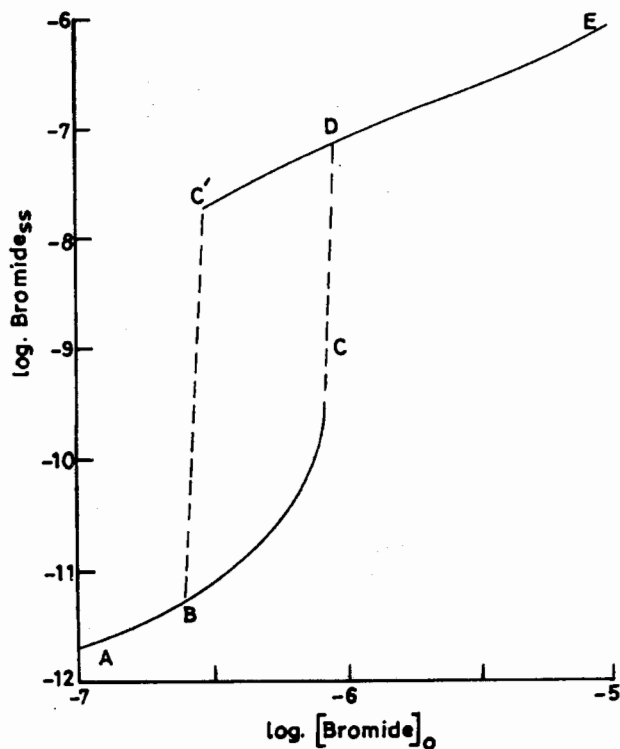


Fig. 1 — Change of  $[\text{Br}^-]_{ss}$  with  $[\text{Br}^-]_0$  in the case of the minimal oscillator with other constraints.  $\{[\text{Ce}^{+3}]_0 = 1.5 \times 10^{-4} M$ ,  $[\text{BrO}_3^-]_0 = 0.002 M$ ,  $[\text{H}^+]_0 = 1.5 M$  and  $k_0 = 4.0 \times 10^3 s^{-1}\}$ .

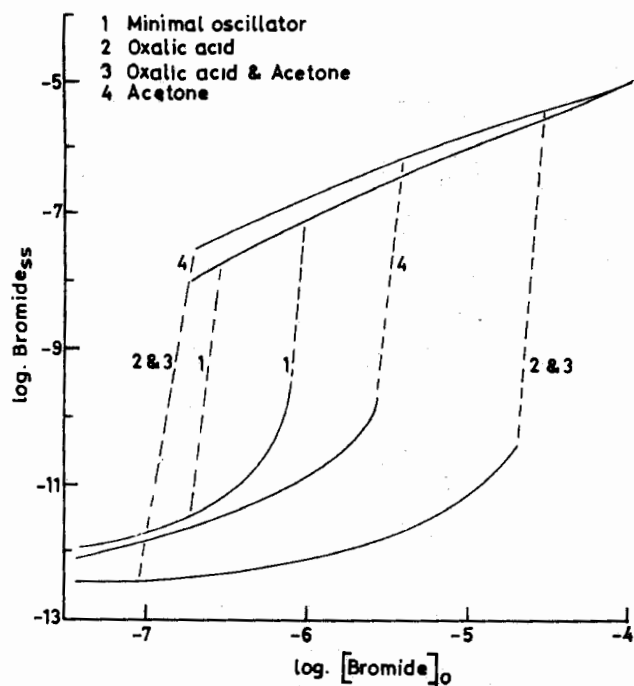


Fig. 2 — Change of  $[\text{Br}^-]_{\text{ss}}$  with  $[\text{Br}^-]_0$  in case of oxalic acid and/or acetone with other constraints as in Fig. 1.  $\{[\text{oxalic acid}]_0 = 0.005 \text{ M}$  and/or,  $[\text{acetone}]_0 = 0.05 \text{ M}\}$ .

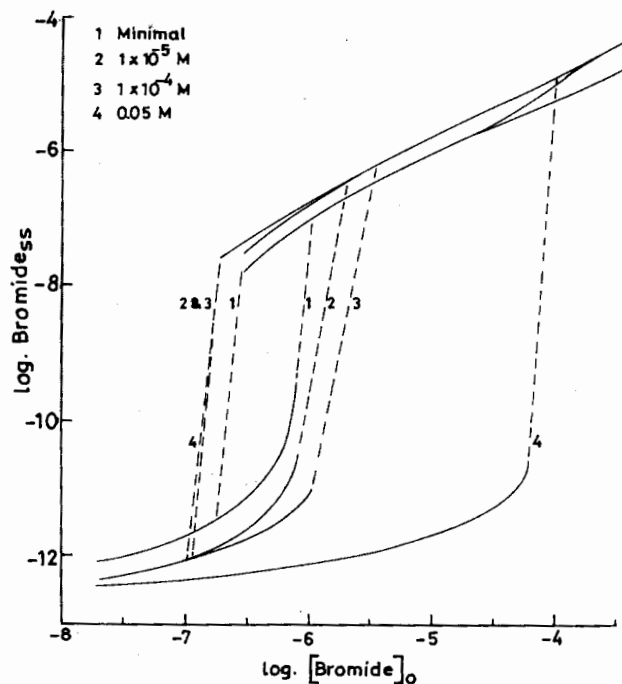


Fig. 3 — Change of  $[\text{Br}^-]_{\text{ss}}$  with  $[\text{Br}^-]_0$  at different  $[\text{oxalic acid}]_0$  with other constraints as in Fig. 1.

Table 2 — Values of  $[\text{Br}^-]_0$  at the transition points when  $[\text{oxalic acid}]_0 = 0.005 \text{ M}$  and  $[\text{acetone}]_0 = 0.05 \text{ M}$  are present in the minimal bromate oscillator (separate as well as in combination) (Constant constraints:  $[\text{Ce}^{+3}]_0 = 1.5 \times 10^{-4} \text{ M}$ ,  $[\text{BrO}_3^-]_0 = 0.002 \text{ M}$ ,  $[\text{H}^+]_0 = 1.5 \text{ M}$ , and  $k_0 = 4.0 \times 10^{-3} \text{ s}^{-1}$ )

	SSI → SSII	SSII → SSI
Minimal	$8.21 \times 10^{-7}$	$3.12 \times 10^{-7}$
Minimal + acetone	$2.51 \times 10^{-6}$	$2.22 \times 10^{-7}$
Minimal + oxalic acid	$2.15 \times 10^{-5}$	$2.21 \times 10^{-7}$
Minimal + oxalic acid + acetone	$2.15 \times 10^{-5}$	$2.21 \times 10^{-7}$

$3.12 \times 10^{-7} \text{ M}$ , further decrease in  $[\text{Br}^-]_0$  leads to the reverse jump  $\text{C}^1\text{B}$  after which the path  $\text{BA}$  is retraced. Bistability exists in the region  $\text{BCDC}^1$ . Thus, the forward jump of  $[\text{Br}^-]_{\text{ss}}$  from  $\text{C}$  to  $\text{D}$  is the transition from SSI to SSII while the reverse jump of  $[\text{Br}^-]_{\text{ss}}$  from  $\text{C}^1$  to  $\text{B}$  is the transition from SSII to SSI. Thus, the steady state value of bromide,  $[\text{Br}^-]_{\text{ss}}$  would be lower for SSI, while it would be much higher for SSII. On the other hand,  $[\text{Br}^-]_0$  for the transition SSI-SSII would be higher while it would be much lower for the transition SSII to SSI.

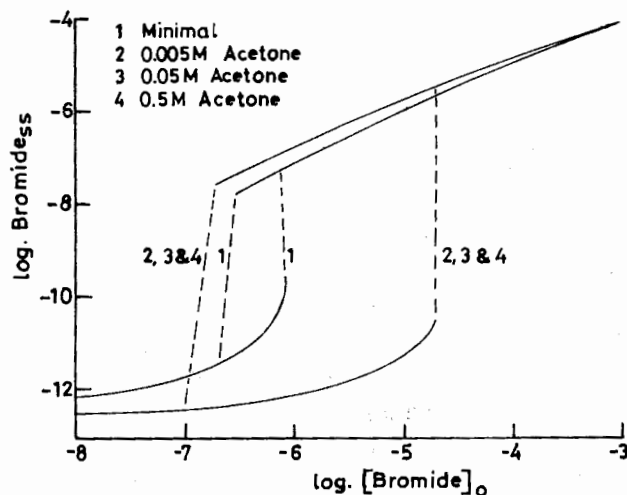


Fig. 4 — Change of  $[\text{Br}^-]_{\text{ss}}$  at  $[\text{Br}^-]_0$  at different  $[\text{acetone}]_0$  with other constraints as in Fig. 1.

#### Effect of oxalic acid and acetone

Figure 2 indicates the effect of presence of oxalic acid and acetone when present separately as well as in combination in the minimal bromate oscillator at the indicated constraints. Table 2 presents the  $[\text{Br}^-]_0$  values at the transition points from SSI to SSII and SSII to SSI for all the systems. It can be noted that the presence of acetone and/or oxalic acid broadens the

Table 3 — Values of  $[\text{Br}^-]_0$  at the transition points when  $[\text{acetone}]_0 = 0.05 \text{ M}$  is present in the minimal bromate oscillator with different  $[\text{oxalic acid}]_0$  (Constant constraints:  $[\text{BrO}_3^-]_0 = 0.002 \text{ M}$ ,  $[\text{Ce}^{+3}]_0 = 1.5 \times 10^{-4} \text{ M}$ ,  $[\text{H}^+]_0 = 1.5 \text{ M}$ ,  $k_0 = 4.0 \times 10^{-3} \text{ s}$  and  $[\text{acetone}]_0 = 0.05 \text{ M}$ )

$[\text{oxalic acid}]_0 (M)$	SSI $\rightarrow$ SSII	SSII $\rightarrow$ SSI
$1 \times 10^{-5}$	$1.77 \times 10^{-7}$	$1.12 \times 10^{-7}$
$5 \times 10^{-5}$	$1.78 \times 10^{-7}$	$1.24 \times 10^{-7}$
$1 \times 10^{-4}$	$1.65 \times 10^{-6}$	$1.54 \times 10^{-7}$
$1 \times 10^{-3}$	$2.13 \times 10^{-5}$	$9.33 \times 10^{-7}$
$5 \times 10^{-3}$	$2.15 \times 10^{-5}$	$2.21 \times 10^{-6}$
$2 \times 10^{-2}$	$1.0 \times 10^{-4}$	$1.48 \times 10^{-5}$
$1 \times 10^{-1}$	$5.0 \times 10^{-4}$	$7.07 \times 10^{-5}$

region of bistability by allowing the transition from SSI to SSII at higher  $[\text{Br}^-]_0$  values. The transition from SSII to SSI is not much affected. However, there is a tendency for this transition to occur at lower  $[\text{Br}^-]_0$  values in presence of acetone and/or oxalic acid. When acetone alone is present  $[\text{Br}^-]_0$  value for transition from SSI to SSII is at  $2.51 \times 10^{-6} \text{ M}$  for indicated inflow concentration of acetone, namely  $0.05 \text{ M}$ . When oxalic acid alone is present,  $[\text{Br}^-]_0$  value for transition from SSI to SSII is at  $2.15 \times 10^{-5} \text{ M}$  for indicated inflow concentration of oxalic acid, namely at  $0.005 \text{ M}$ . Thus, the effect of oxalic acid is much pronounced and as such when both acetone and oxalic acid are simultaneously present, the acetone effect gets masked by the predominant effect of oxalic acid.

Figures 3 and 4 and Tables 3 and 4 give the effect of increasing oxalic acid and that of acetone when both are simultaneously present in the minimal bromate oscillator. It can be noted that  $[\text{Br}^-]_0$  for the transition from SSI to SSII and SSII to SSI change to higher values as  $[\text{oxalic acid}]_0$  and  $[\text{acetone}]_0$  increase.

Gasper and Galambosi<sup>8</sup> have experimentally observed bistability in a BZ system with oxalic acid alone in CSTR in a narrow region of the bifurcation phase space (bromate vs oxalic acid). Rastogi and Yadava<sup>7</sup> have experimentally indicated bistability in

Table 4 — Values of  $[\text{Br}^-]_0$  at the transition points when  $[\text{oxalic acid}]_0 = 0.005 \text{ M}$  is present in the minimal bromate oscillator with different  $[\text{acetone}]_0$  (Constant constraints:  $[\text{BrO}_3^-]_0 = 0.002 \text{ M}$ ,  $[\text{Ce}^{+3}]_0 = 1.5 \times 10^{-4} \text{ M}$ ,  $[\text{H}^+]_0 = 1.5 \text{ M}$ ;  $[\text{oxalic acid}]_0 = 0.005 \text{ M}$  and  $k_0 = 4.0 \times 10^{-3} \text{ s}^{-1}$ )

$[\text{acetone}]_0 (M)$	SSI $\rightarrow$ SSII	SSII $\rightarrow$ SSI
0.005	$2.24 \times 10^{-5}$	$1.62 \times 10^{-7}$
0.025	$2.42 \times 10^{-5}$	$1.65 \times 10^{-7}$
0.05	$2.51 \times 10^{-5}$	$2.21 \times 10^{-7}$
0.1	$2.86 \times 10^{-5}$	$2.64 \times 10^{-7}$
0.2	$2.85 \times 10^{-5}$	$2.64 \times 10^{-7}$
0.5	$2.86 \times 10^{-5}$	$2.64 \times 10^{-7}$

mixed organic substrate systems with flow rates as the bifurcation parameter. Their studies when compared to the work of Bar-Eli and Geiseler<sup>9</sup> for the case of minimal bromate oscillator are introductory in nature. The simulations done in the present work, as enumerated above, suggest a detailed experimental as well as simulation analysis of bistability of these systems by considering many other constraints as bifurcation parameters, as such, these studies are under progress.

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