Belousov-Zhabotinsky reaction

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Modeling and mathematical methods

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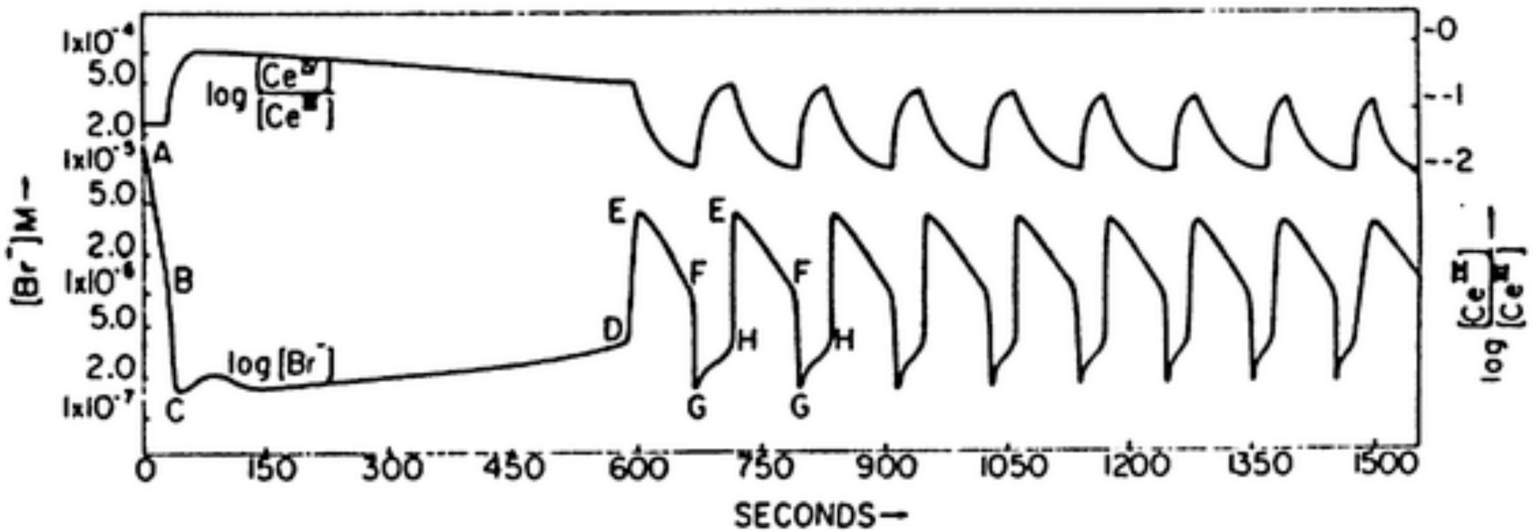
Experimental evidence (Cerium)

- Malonic acid oxidation by bromate in acidic solution, catalyzed by a metal ion (Ce^{4+})
- Long series of oscillations in the concentration of the intermediate species (with a chromatic effect)
- The main reactants are irreversibly consumed (but very slowly)
- Finally, the oscillations vanish and chemical equilibrium is monotonically approached



Initial concentrations were $[CH_2(COOH)_2]_0 = 0.032\ M$, $[KBrO_3]_0 = 0.063\ M$, $[KBr]_0 = 1.5 \times 10^{-5}\ M$, $[Ce(NH_4)_2(NO_3)_5]_0 = 0.001\ M$, $[H_2SO_4]_0 = 0.8\ M$.

Chemistry

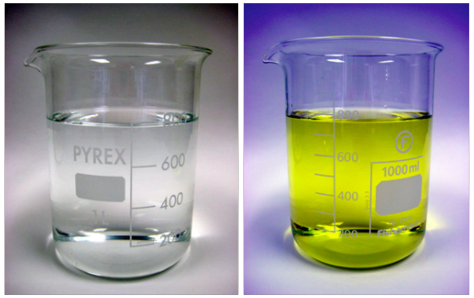
The main reaction driving the Belousov-Zhabotinsky system forward is given by the following equation:

$$2Br^- + BrO_3^- + 3CH_2(COOH)_2 + 3H^+ \rightarrow 3BrCH(COOH)_2 + 3H_2O$$

The cerium indicator

Ce^{3+}

Colourless



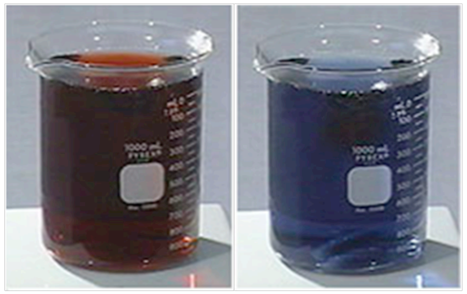
Ce^{4+}

Yellow

The ferroin-ferriin indicator

$Fe^{2+}(o\text{-}phen)_3$

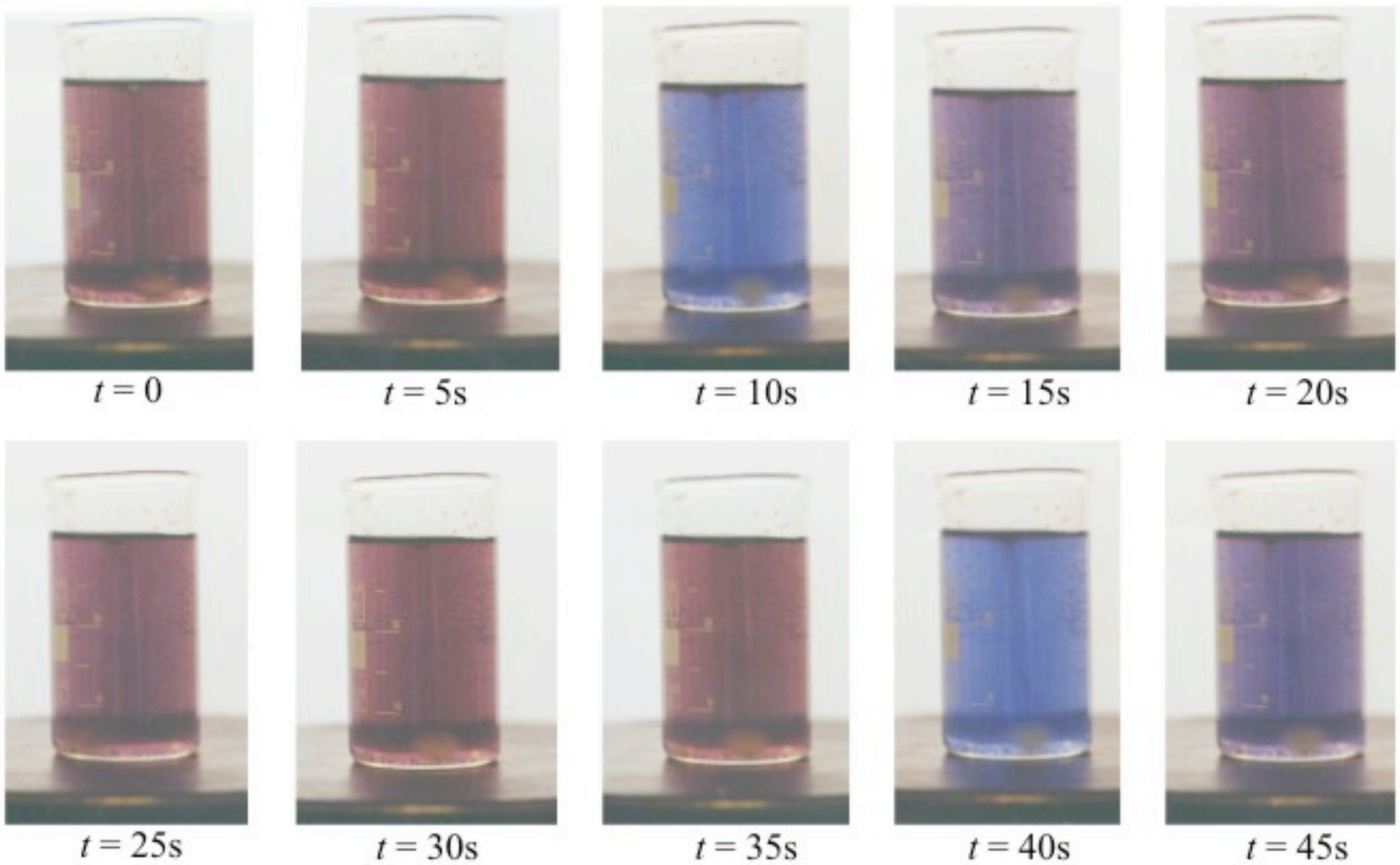
Purple-red predominant if system is in its reducing state.



$Fe^{3+}(o\text{-}phen)_3$

Blue predominant if system is in its oxidising state.

Experimental evidence (ferroin)



Detailed mechanism

TABLE I: Mechanistic Model of the Belousov–Zhabotinskii Reaction ([H_2O] = 55 M Included in the Rate Constants)[a]

		rate constant[b]	reference
	1. Inorganic Subset		
1	$\mathrm{HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O}$	2.3E+9 $M^{-2}\,s^{-1}$	23
2	$\mathrm{Br_2 + H_2O \rightarrow HOBr + Br^- + H^+}$	2.0 s^{-1}	23
3	$\mathrm{Br^- + HBrO_2 + H^+ \rightarrow 2HOBr}$	2.0E+6 $M^{-2}\,s^{-1}$	22[c]
4	$\mathrm{2HOBr \rightarrow Br^- + HBrO_2 + H^+}$	2.0E−5 $M^{-1}\,s^{-1}$	22, 23
5	$\mathrm{Br^- + BrO_3^- + 2H^+ \rightarrow HOBr + HBrO_2}$	2.0 $M^{-3}\,s^{-1}$	22[c]
6	$\mathrm{HOBr + HBrO_2 \rightarrow Br^- + BrO_3^- + 2H^+}$	3.3 $M^{-1}\,s^{-1}$	22[c]
7	$\mathrm{2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+}$	3.0E+3 $M^{-1}\,s^{-1}$	22
8	$\mathrm{BrO_3^- + HOBr + H^+ \rightarrow 2HBrO_2}$	7.5E−9 $M^{-2}\,s^{-1}$	22[c]
9	$\mathrm{BrO_3^- + HBrO_2 + H^+ \rightarrow Br_2O_4 + H_2O}$	33.0 $M^{-2}\,s^{-1}$	22[c]
10	$\mathrm{Br_2O_4 + H_2O \rightarrow BrO_3^- + HBrO_2 + H^+}$	2200 s^{-1}	22
11	$\mathrm{Br_2O_4 \rightarrow 2BrO_2^{\bullet}}$	7.4E+4 s^{-1}	22
12	$\mathrm{2BrO_2^{\bullet} \rightarrow Br_2O_4}$	1.4E+9 $M^{-1}\,s^{-1}$	22
13	$\mathrm{Ce^{3+} + BrO_2^{\bullet} + H^+ \rightarrow HBrO_2 + Ce^{4+}}$	6.2E+4 $M^{-2}\,s^{-1}$	22[c]
14	$\mathrm{HBrO_2 + Ce^{4+} \rightarrow Ce^{3+} + BrO_2^{\bullet} + H^+}$	7.0E+3 $M^{-1}\,s^{-1}$	22[c]
	2. Reactions Involving Organic Species		
	a. Reactions Not Consuming or Producing Radicals		
15	$\mathrm{MA \rightarrow ENOL}$	3.0E−3 s^{-1}	25, 38
16	$\mathrm{ENOL \rightarrow MA}$	200.0 s^{-1}	25, 38
17	$\mathrm{ENOL + Br_2 \rightarrow BrMA + Br^- + H^+}$	1.91E+6 $M^{-1}\,s^{-1}$	39[d]
18	$\mathrm{MA + HOBr \rightarrow BrMA + H_2O}$	8.2 $M^{-1}\,s^{-1}$	39
19	$\mathrm{BrMA + HOBr \rightarrow Br_2MA + H_2O}$	0.1 $M^{-1}\,s^{-1}$	f
20	$\mathrm{TTA + HOBr \rightarrow BrTTA + H_2O}$	5.0 $M^{-1}\,s^{-1}$	39[e]
21	$\mathrm{BrO_2MA + H_2O \rightarrow HBrO_2 + TTA}$	1.0 s^{-1}	47
22	$\mathrm{BrO_2MA \rightarrow HOBr + MOA}$	1.0 s^{-1}	47
23	$\mathrm{BrO_2TTA \rightarrow HBrO_2 + MOA}$	1.0 s^{-1}	47[e]
24	$\mathrm{BrTTA \rightarrow Br^- + MOA + H^+}$	1.0 s^{-1}	
	b. Reactions Producing Radicals		
25	$\mathrm{Ce^{4+} + BrMA \rightarrow Ce^{3+} + BrMA^{\bullet} + H^+}$	0.09 $M^{-1}\,s^{-1}$	39, 48
26	$\mathrm{Ce^{4+} + MA \rightarrow Ce^{3+} + MA^{\bullet} + H^+}$	0.23 $M^{-1}\,s^{-1}$	39, 57
27	$\mathrm{Ce^{4+} + TTA \rightarrow Ce^{3+} + TTA^{\bullet} + H^+}$	0.66 $M^{-1}\,s^{-1}$	39, 57
28	$\mathrm{HOBr + MOA \rightarrow Br^{\bullet} + OA + {}^{\bullet}COOH}$	140.0 $M^{-1}\,s^{-1}$	30[e,g]
29	$\mathrm{Ce^{4+} + MOA + H_2O \rightarrow Ce^{3+} + OA + {}^{\bullet}COOH + H^+}$	10.0 $M^{-1}\,s^{-1}$	30[e,g]
30	$\mathrm{HOBr + OA \rightarrow Br^{\bullet} + {}^{\bullet}COOH + CO_2 + H_2O}$	140.0 $M^{-1}\,s^{-1}$	30[g]
31	$\mathrm{Ce^{4+} + OA \rightarrow Ce^{3+} + {}^{\bullet}COOH + CO_2 + H^+}$	10.0 $M^{-1}\,s^{-1}$	30[g]
32	$\mathrm{BrO_3^- + OA + H^+ \rightarrow BrO_2^{\bullet} + {}^{\bullet}COOH + CO_2 + H_2O}$	1.6E−5 $M^{-2}\,s^{-1}$	30[g]
	c. Reactions Consuming Radicals		
33	$\mathrm{2Br^{\bullet} \rightarrow Br_2}$	1.0E+8 $M^{-1}\,s^{-1}$	30
34	$\mathrm{Br^{\bullet} + BrMA^{\bullet} \rightarrow Br_2MA}$	1.0E+9 $M^{-1}\,s^{-1}$	f
35	$\mathrm{2BrMA^{\bullet} + H_2O \rightarrow BrMA + BrTTA}$	1.0E+8 $M^{-1}\,s^{-1}$	
36	$\mathrm{BrMA^{\bullet} + MA^{\bullet} + H_2O \rightarrow MA + BrTTA}$	1.0E+9 $M^{-1}\,s^{-1}$	
37	$\mathrm{BrMA^{\bullet} + TTA^{\bullet} + H_2O \rightarrow TTA + BrTTA}$	1.0E+9 $M^{-1}\,s^{-1}$	
38	$\mathrm{BrMA^{\bullet} + Ce^{4+} + H_2O \rightarrow Ce^{3+} + BrTTA + H^+}$	1.0E+7 $M^{-1}\,s^{-1}$	30[e,g]
39	$\mathrm{BrMA^{\bullet} + BrO_2^{\bullet} + H_2O \rightarrow HBrO_2 + BrTTA}$	5.0E+9 $M^{-1}\,s^{-1}$	14[e]
40	$\mathrm{BrMA^{\bullet} + {}^{\bullet}COOH \rightarrow BrMA + CO_2}$	5.0E+8 $M^{-1}\,s^{-1}$	
41	$\mathrm{2MA^{\bullet} + H_2O \rightarrow MA + TTA}$	3.2E+9 $M^{-1}\,s^{-1}$	13
42	$\mathrm{MA^{\bullet} + TTA^{\bullet} + H_2O \rightarrow 2TTA}$	1.0E+9 $M^{-1}\,s^{-1}$	
43	$\mathrm{MA^{\bullet} + {}^{\bullet}COOH \rightarrow MA + CO_2}$	2.0E+9 $M^{-1}\,s^{-1}$	
44	$\mathrm{MA^{\bullet} + Br^{\bullet} \rightarrow BrMA}$	1.0E+9 $M^{-1}\,s^{-1}$	
45	$\mathrm{MA^{\bullet} + Ce^{3+} + H^+ \rightarrow MA + Ce^{4+}}$	1.7E+4 $M^{-2}\,s^{-1}$	57
46	$\mathrm{MA^{\bullet} + BrO_2^{\bullet} \rightarrow BrO_2MA}$	5.0E+9 $M^{-1}\,s^{-1}$	14
47	$\mathrm{2TTA^{\bullet} \rightarrow TTA + MOA}$	1.0E+9 $M^{-1}\,s^{-1}$	13[e]
48	$\mathrm{TTA^{\bullet} + {}^{\bullet}COOH \rightarrow TTA + CO_2}$	2.0E+9 $M^{-1}\,s^{-1}$	
49	$\mathrm{TTA^{\bullet} + Br^{\bullet} \rightarrow BrTTA}$	1.0E+9 $M^{-1}\,s^{-1}$	
50	$\mathrm{TTA^{\bullet} + Ce^{3+} + H^+ \rightarrow TTA + Ce^{4+}}$	1.7E+4 $M^{-2}\,s^{-1}$	57[e]
51	$\mathrm{TTA^{\bullet} + BrO_2^{\bullet} \rightarrow BrO_2TTA}$	5.0E+9 $M^{-1}\,s^{-1}$	14[e]
52	$\mathrm{2\,{}^{\bullet}COOH \rightarrow OA}$	1.2E+9 $M^{-1}\,s^{-1}$	30
53	$\mathrm{{}^{\bullet}COOH + Ce^{4+} \rightarrow Ce^{3+} + CO_2 + H^+}$	1.0E+7 $M^{-1}\,s^{-1}$	30[g]
54	$\mathrm{{}^{\bullet}COOH + Br^{\bullet} \rightarrow Br^- + CO_2 + H^+}$	1.0E+9 $M^{-1}\,s^{-1}$	
55	$\mathrm{{}^{\bullet}COOH + BrO_2^{\bullet} \rightarrow HBrO_2 + CO_2}$	5.0E+9 $M^{-1}\,s^{-1}$	14[e]
	d. Reactions Preserving Radicals		
56	$\mathrm{MA^{\bullet} + Br_2 \rightarrow BrMA + Br^{\bullet}}$	1.5E+8 $M^{-1}\,s^{-1}$	14[g]
57	$\mathrm{MA^{\bullet} + HOBr \rightarrow TTA + Br^{\bullet}}$	1.0E+7 $M^{-1}\,s^{-1}$	14[g]
58	$\mathrm{MA^{\bullet} + BrO_3^- + H^+ \rightarrow TTA + BrO_2^{\bullet}}$	40.0 $M^{-2}\,s^{-1}$	14[e]
59	$\mathrm{MA^{\bullet} + TTA \rightarrow MA + TTA^{\bullet}}$	1.0E+5 $M^{-1}\,s^{-1}$	
60	$\mathrm{TTA^{\bullet} + MA \rightarrow TTA + MA^{\bullet}}$	1.0E+5 $M^{-1}\,s^{-1}$	
61	$\mathrm{MA^{\bullet} + BrMA \rightarrow MA + BrMA^{\bullet}}$	1.0E+5 $M^{-1}\,s^{-1}$	h
62	$\mathrm{BrMA^{\bullet} + MA \rightarrow BrMA + MA^{\bullet}}$	5.0E+2 $M^{-1}\,s^{-1}$	
63	$\mathrm{TTA^{\bullet} + BrMA \rightarrow TTA + BrMA^{\bullet}}$	2.0E+5 $M^{-1}\,s^{-1}$	
64	$\mathrm{BrMA^{\bullet} + TTA \rightarrow BrMA + TTA^{\bullet}}$	5.0E+3 $M^{-1}\,s^{-1}$	
65	$\mathrm{TTA^{\bullet} + Br_2 \rightarrow BrTTA + Br^{\bullet}}$	1.0E+8 $M^{-1}\,s^{-1}$	14[e]
66	$\mathrm{TTA^{\bullet} + HOBr \rightarrow MOA + Br^{\bullet} + H_2O}$	1.0E+7 $M^{-1}\,s^{-1}$	14[e]
67	$\mathrm{TTA^{\bullet} + BrO_3^- + H^+ \rightarrow MOA + BrO_2^{\bullet} + H_2O}$	40.0 $M^{-2}\,s^{-1}$	14[e,i]
68	$\mathrm{BrMA^{\bullet} + Br_2 \rightarrow Br_2MA + Br^{\bullet}}$	1.0E+6 $M^{-1}\,s^{-1}$	14[e,f]
69	$\mathrm{BrMA^{\bullet} + HOBr \rightarrow BrTTA + Br^{\bullet}}$	1.0E+5 $M^{-1}\,s^{-1}$	14[e]
70	$\mathrm{BrMA^{\bullet} + BrO_3^- + H^+ \rightarrow BrO_2^{\bullet} + BrTTA}$	40.0 $M^{-2}\,s^{-1}$	14[e,i]
71	$\mathrm{{}^{\bullet}COOH + BrMA \rightarrow Br^- + MA^{\bullet} + CO_2 + H^+}$	1.0E+7 $M^{-1}\,s^{-1}$	
72	$\mathrm{{}^{\bullet}COOH + Br_2 \rightarrow Br^- + Br^{\bullet} + CO_2 + H^+}$	1.5E+8 $M^{-1}\,s^{-1}$	14[e]
73	$\mathrm{{}^{\bullet}COOH + HOBr \rightarrow Br^{\bullet} + CO_2 + H_2O}$	2.0E+7 $M^{-1}\,s^{-1}$	14[e]
74	$\mathrm{{}^{\bullet}COOH + BrO_3^- + H^+ \rightarrow BrO_2^{\bullet} + CO_2 + H_2O}$	2.1E+3 $M^{-2}\,s^{-1}$	30
75	$\mathrm{Br^{\bullet} + MA \rightarrow Br^- + MA^{\bullet} + H^+}$	1.0E+5 $M^{-1}\,s^{-1}$	
76	$\mathrm{Br^{\bullet} + TTA \rightarrow Br^- + TTA^{\bullet} + H^+}$	1.0E+6 $M^{-1}\,s^{-1}$	
77	$\mathrm{Br^{\bullet} + BrMA \rightarrow Br^- + BrMA^{\bullet} + H^+}$	5.0E+6 $M^{-1}\,s^{-1}$	
78	$\mathrm{Br^{\bullet} + MOA + H_2O \rightarrow Br^- + OA + {}^{\bullet}COOH + H^+}$	2.0E+3 $M^{-1}\,s^{-1}$	30[e]
79	$\mathrm{Br^{\bullet} + OA \rightarrow Br^- + {}^{\bullet}COOH + CO_2 + H^+}$	2.0E+3 $M^{-1}\,s^{-1}$	30
80	$\mathrm{BrO_2^{\bullet} + OA \rightarrow HBrO_2 + {}^{\bullet}COOH + CO_2}$	1.0E+2 $M^{-1}\,s^{-1}$	30[e]

Detailed mechanism – Inorganic subset

Mechanistic Model of the Belousov–Zhabotinskii Reaction ([H_2O] = 55 M Included in the Rate Constants)[a]

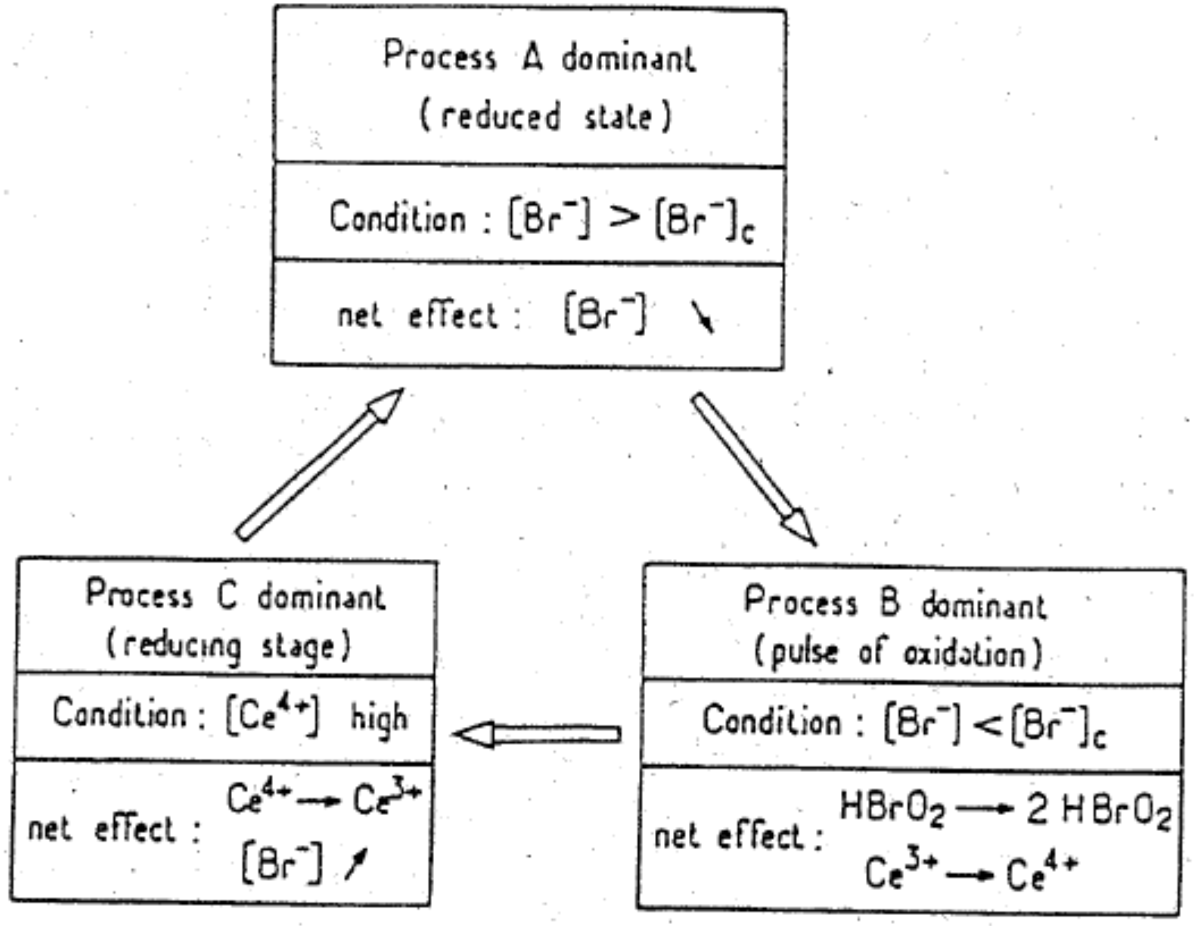
		rate constant[d]
	1. Inorganic Subset	
1	$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$	2.3E+9 $M^{-2}\ s^{-1}$
2	$Br_2 + H_2O \rightarrow HOBr + Br^- + H^+$	2.0 s^{-1}
3	$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr$	2.0E+6 $M^{-2}\ s^{-1}$
4	$2HOBr \rightarrow Br^- + HBrO_2 + H^+$	2.0E−5 $M^{-1}\ s^{-1}$
5	$Br^- + BrO_3^- + 2H^+ \rightarrow HOBr + HBrO_2$	2.0 $M^{-3}\ s^{-1}$
6	$HOBr + HBrO_2 \rightarrow Br^- + BrO_3^- + 2H^+$	3.3 $M^{-1}\ s^{-1}$
7	$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$	3.0E+3 $M^{-1}\ s^{-1}$
8	$BrO_3^- + HOBr + H^+ \rightarrow 2HBrO_2$	7.5E−9 $M^{-2}\ s^{-1}$
9	$BrO_3^- + HBrO_2 + H^+ \rightarrow Br_2O_4 + H_2O$	33.0 $M^{-2}\ s^{-1}$
10	$Br_2O_4 + H_2O \rightarrow BrO_3^- + HBrO_2 + H^+$	2200 s^{-1}
11	$Br_2O_4 \rightarrow 2BrO_2^\cdot$	7.4E+4 s^{-1}
12	$2BrO_2^\cdot \rightarrow Br_2O_4$	1.4E+9 $M^{-1}\ s^{-1}$
13	$Ce^{3+} + BrO_2^\cdot + H^+ \rightarrow HBrO_2 + Ce^{4+}$	6.2E+4 $M^{-2}\ s^{-1}$
14	$HBrO_2 + Ce^{4+} \rightarrow Ce^{3+} + BrO_2^\cdot + H^+$	7.0E+3 $M^{-1}\ s^{-1}$

Detailed mechanism – Radicals and organic species

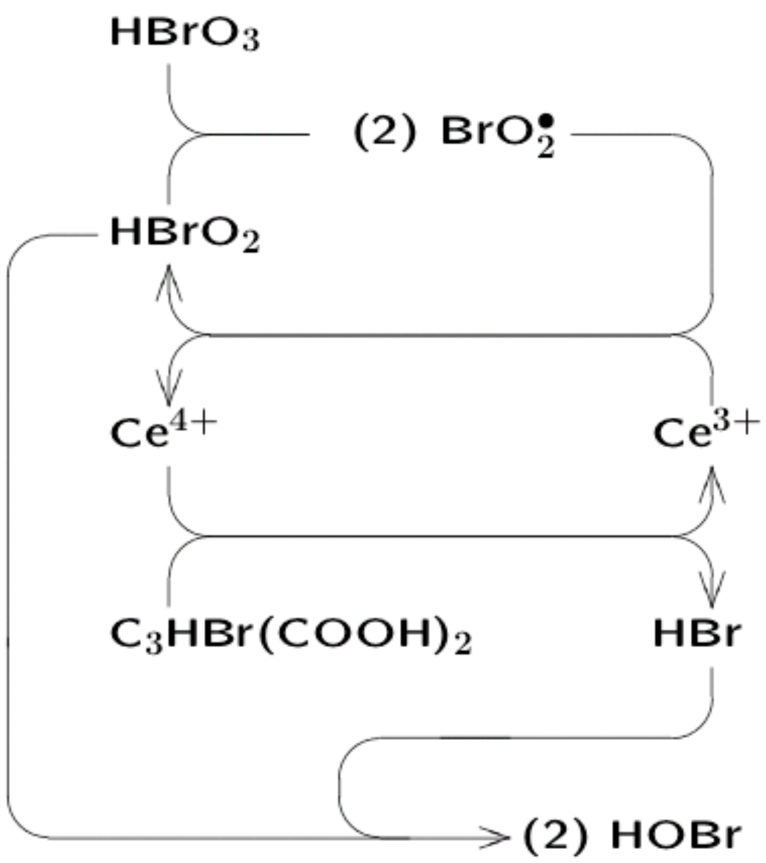
2. Reactions Involving Organic Species

No.	Reaction	Rate constant
	a. Reactions Not Consuming or Producing Radicals	
15	$MA \rightarrow ENOL$	$3.0E{-3}\ s^{-1}$
16	$ENOL \rightarrow MA$	$200.0\ s^{-1}$
17	$ENOL + Br_2 \rightarrow BrMA + Br^- + H^+$	$1.91E{+6}\ M^{-1}\ s^{-1}$
18	$MA + HOBr \rightarrow BrMA + H_2O$	$8.2\ M^{-1}\ s^{-1}$
19	$BrMA + HOBr \rightarrow Br_2MA + H_2O$	$0.1\ M^{-1}\ s^{-1}$
20	$TTA + HOBr \rightarrow BrTTA + H_2O$	$5.0\ M^{-1}\ s^{-1}$
21	$BrO_2MA + H_2O \rightarrow HBrO_2 + TTA$	$1.0\ s^{-1}$
22	$BrO_2MA \rightarrow HOBr + MOA$	$1.0\ s^{-1}$
23	$BrO_2TTA \rightarrow HBrO_2 + MOA$	$1.0\ s^{-1}$
24	$BrTTA \rightarrow Br^- + MOA + H^+$	$1.0\ s^{-1}$
	b. Reactions Producing Radicals	
25	$Ce^{4+} + BrMA \rightarrow Ce^{3+} + BrMA^{\bullet} + H^+$	$0.09\ M^{-1}\ s^{-1}$
26	$Ce^{4+} + MA \rightarrow Ce^{3+} + MA^{\bullet} + H^+$	$0.23\ M^{-1}\ s^{-1}$
27	$Ce^{4+} + TTA \rightarrow Ce^{3+} + TTA^{\bullet} + H^+$	$0.66\ M^{-1}\ s^{-1}$
28	$HOBr + MOA \rightarrow Br^{\bullet} + OA + {}^{\bullet}COOH$	$140.0\ M^{-1}\ s^{-1}$
29	$Ce^{4+} + MOA + H_2O \rightarrow Ce^{3+} + OA + {}^{\bullet}COOH + H^+$	$10.0\ M^{-1}\ s^{-1}$
30	$HOBr + OA \rightarrow Br^{\bullet} + {}^{\bullet}COOH + CO_2 + H_2O$	$140.0\ M^{-1}\ s^{-1}$
31	$Ce^{4+} + OA \rightarrow Ce^{3+} + {}^{\bullet}COOH + CO_2 + H^+$	$10.0\ M^{-1}\ s^{-1}$
32	$BrO_3^- + OA + H^+ \rightarrow BrO_2^{\bullet} + {}^{\bullet}COOH + CO_2 + H_2O$	$1.6E{-5}\ M^{-2}\ s^{-1}$
	c. Reactions Consuming Radicals	
33	$2Br^{\bullet} \rightarrow Br_2$	$1.0E{+8}\ M^{-1}\ s^{-1}$
34	$Br^{\bullet} + BrMA^{\bullet} \rightarrow Br_2MA$	$1.0E{+9}\ M^{-1}\ s^{-1}$
35	$2BrMA^{\bullet} + H_2O \rightarrow BrMA + BrTTA$	$1.0E{+8}\ M^{-1}\ s^{-1}$
36	$BrMA^{\bullet} + MA^{\bullet} + H_2O \rightarrow MA + BrTTA$	$1.0E{+9}\ M^{-1}\ s^{-1}$
37	$BrMA^{\bullet} + TTA^{\bullet} + H_2O \rightarrow TTA + BrTTA$	$1.0E{+9}\ M^{-1}\ s^{-1}$
38	$BrMA^{\bullet} + Ce^{4+} + H_2O \rightarrow Ce^{3+} + BrTTA + H^+$	$1.0E{+7}\ M^{-1}\ s^{-1}$
39	$BrMA^{\bullet} + BrO_2^{\bullet} + H_2O \rightarrow HBrO_2 + BrTTA$	$5.0E{+9}\ M^{-1}\ s^{-1}$
40	$BrMA^{\bullet} + {}^{\bullet}COOH \rightarrow BrMA + CO_2$	$5.0E{+8}\ M^{-1}\ s^{-1}$
41	$2MA^{\bullet} + H_2O \rightarrow MA + TTA$	$3.2E{+9}\ M^{-1}\ s^{-1}$
42	$MA^{\bullet} + TTA^{\bullet} + H_2O \rightarrow 2TTA$	$1.0E{+9}\ M^{-1}\ s^{-1}$
43	$MA^{\bullet} + {}^{\bullet}COOH \rightarrow MA + CO_2$	$2.0E{+9}\ M^{-1}\ s^{-1}$
44	$MA^{\bullet} + Br^{\bullet} \rightarrow BrMA$	$1.0E{+9}\ M^{-1}\ s^{-1}$
45	$MA^{\bullet} + Ce^{3+} + H^+ \rightarrow MA + Ce^{4+}$	$1.7E{+4}\ M^{-2}\ s^{-1}$
46	$MA^{\bullet} + BrO_2^{\bullet} \rightarrow BrO_2MA$	$5.0E{+9}\ M^{-1}\ s^{-1}$
47	$2TTA^{\bullet} \rightarrow TTA + MOA$	$1.0E{+9}\ M^{-1}\ s^{-1}$
48	$TTA^{\bullet} + {}^{\bullet}COOH \rightarrow TTA + CO_2$	$2.0E{+9}\ M^{-1}\ s^{-1}$
49	$TTA^{\bullet} + Br^{\bullet} \rightarrow BrTTA$	$1.0E{+9}\ M^{-1}\ s^{-1}$
50	$TTA^{\bullet} + Ce^{3+} + H^+ \rightarrow TTA + Ce^{4+}$	$1.7E{+4}\ M^{-2}\ s^{-1}$
51	$TTA^{\bullet} + BrO_2^{\bullet} \rightarrow BrO_2TTA$	$5.0E{+9}\ M^{-1}\ s^{-1}$
52	$2\,{}^{\bullet}COOH \rightarrow OA$	$1.2E{+9}\ M^{-1}\ s^{-1}$
53	${}^{\bullet}COOH + Ce^{4+} \rightarrow Ce^{3+} + CO_2 + H^+$	$1.0E{+7}\ M^{-1}\ s^{-1}$
54	${}^{\bullet}COOH + Br^{\bullet} \rightarrow Br^- + CO_2 + H^+$	$1.0E{+9}\ M^{-1}\ s^{-1}$
55	${}^{\bullet}COOH + BrO_2^{\bullet} \rightarrow HBrO_2 + CO_2$	$5.0E{+9}\ M^{-1}\ s^{-1}$
	d. Reactions Preserving Radicals	
56	$MA^{\bullet} + Br_2 \rightarrow BrMA + Br^{\bullet}$	$1.5E{+8}\ M^{-1}\ s^{-1}$
57	$MA^{\bullet} + HOBr \rightarrow TTA + Br^{\bullet}$	$1.0E{+7}\ M^{-1}\ s^{-1}$
58	$MA^{\bullet} + BrO_3^- + H^+ \rightarrow TTA + BrO_2^{\bullet}$	$40.0\ M^{-2}\ s^{-1}$
59	$MA^{\bullet} + TTA \rightarrow MA + TTA^{\bullet}$	$1.0E{+5}\ M^{-1}\ s^{-1}$
60	$TTA^{\bullet} + MA \rightarrow TTA + MA^{\bullet}$	$1.0E{+5}\ M^{-1}\ s^{-1}$
61	$MA^{\bullet} + BrMA \rightarrow MA + BrMA^{\bullet}$	$1.0E{+5}\ M^{-1}\ s^{-1}$
62	$BrMA^{\bullet} + MA \rightarrow BrMA + MA^{\bullet}$	$5.0E{+2}\ M^{-1}\ s^{-1}$
63	$TTA^{\bullet} + BrMA \rightarrow TTA + BrMA^{\bullet}$	$2.0E{+5}\ M^{-1}\ s^{-1}$
64	$BrMA^{\bullet} + TTA \rightarrow BrMA + TTA^{\bullet}$	$5.0E{+3}\ M^{-1}\ s^{-1}$
65	$TTA^{\bullet} + Br_2 \rightarrow BrTTA + Br^{\bullet}$	$1.0E{+8}\ M^{-1}\ s^{-1}$
66	$TTA^{\bullet} + HOBr \rightarrow MOA + Br^{\bullet} + H_2O$	$1.0E{+7}\ M^{-1}\ s^{-1}$
67	$TTA^{\bullet} + BrO_3^- + H^+ \rightarrow MOA + BrO_2^{\bullet} + H_2O$	$40.0\ M^{-2}\ s^{-1}$
68	$BrMA^{\bullet} + Br_2 \rightarrow Br_2MA + Br^{\bullet}$	$1.0E{+6}\ M^{-1}\ s^{-1}$
69	$BrMA^{\bullet} + HOBr \rightarrow BrTTA + Br^{\bullet}$	$1.0E{+5}\ M^{-1}\ s^{-1}$
70	$BrMA^{\bullet} + BrO_3^- + H^+ \rightarrow BrO_2^{\bullet} + BrTTA$	$40.0\ M^{-2}\ s^{-1}$
71	${}^{\bullet}COOH + BrMA \rightarrow Br^- + MA^{\bullet} + CO_2 + H^+$	$1.0E{+7}\ M^{-1}\ s^{-1}$
72	${}^{\bullet}COOH + Br_2 \rightarrow Br^- + Br^{\bullet} + CO_2 + H^+$	$1.5E{+8}\ M^{-1}\ s^{-1}$
73	${}^{\bullet}COOH + HOBr \rightarrow Br^{\bullet} + CO_2 + H_2O$	$2.0E{+7}\ M^{-1}\ s^{-1}$
74	${}^{\bullet}COOH + BrO_3^- + H^+ \rightarrow BrO_2^{\bullet} + CO_2 + H_2O$	$2.1E{+3}\ M^{-2}\ s^{-1}$
75	$Br^{\bullet} + MA \rightarrow Br^- + MA^{\bullet} + H^+$	$1.0E{+5}\ M^{-1}\ s^{-1}$
76	$Br^{\bullet} + TTA \rightarrow Br^- + TTA^{\bullet} + H^+$	$1.0E{+6}\ M^{-1}\ s^{-1}$
77	$Br^{\bullet} + BrMA \rightarrow Br^- + BrMA^{\bullet} + H^+$	$5.0E{+6}\ M^{-1}\ s^{-1}$
78	$Br^{\bullet} + MOA + H_2O \rightarrow Br^- + OA + {}^{\bullet}COOH + H^+$	$2.0E{+3}\ M^{-1}\ s^{-1}$
79	$Br^{\bullet} + OA \rightarrow Br^- + {}^{\bullet}COOH + CO_2 + H^+$	$2.0E{+3}\ M^{-1}\ s^{-1}$
80	$BrO_2^{\bullet} + OA \rightarrow HBrO_2 + {}^{\bullet}COOH + CO_2$	$1.0E{+2}\ M^{-1}\ s^{-1}$

Mechanism of the oscillations



Mechanism of the oscillations



$$BrO_3^- + Br^- \rightarrow HBrO_2 + HBrO$$

$$HBrO_2 + Br^- \rightarrow 2\ HBrO$$

$$BrO_3^- + HBrO_2 \rightarrow 2\ HBrO_2 + 2\ Ce^{4+}$$

$$2\ HBrO_2 \rightarrow BrO_3^- + HBrO$$

$$CH_2(COOH)_2 + Ce^{4+} \rightarrow f/2\ Br^- + \text{prodotti}$$

Mechanism of the oscillations

$$r_1 = k_1 [H^+]^2 [BrO_3^-][Br^-]$$

$$r_2 = k_2 [H^+][HBrO_2][Br^-]$$

$$r_3 = k_3 [H^+][HBrO_2][BrO_3^-]$$

$$r_4 = k_4 [HBrO_2]^2$$

$$r_5 = k_5 [Ce^{4+}][MA]$$

$$BrO_3^- + Br^- \rightarrow HBrO_2 + HBrO$$

$$HBrO_2 + Br^- \rightarrow 2\ HBrO$$

$$BrO_3^- + HBrO_2 \rightarrow 2\ HBrO_2 + 2\ Ce^{4+}$$

$$2\ HBrO_2 \rightarrow BrO_3^- + HBrO$$

$$CH_2(COOH)_2 + Ce^{4+} \rightarrow f/2\ Br^- + \text{prodotti}$$

Kinetic scheme: Oregonator

$$BrO_3^- + Br^- \rightarrow HBrO_2 + HBrO$$

$$HBrO_2 + Br^- \rightarrow 2\ HBrO$$

$$BrO_3^- + HBrO_2 \rightarrow 2\ HBrO_2 + 2\ Ce^{4+}$$

$$2\ HBrO_2 \rightarrow BrO_3^- + HBrO$$

$$CH_2(COOH)_2 + Ce^{4+} \rightarrow f/2\ Br^- + \text{prodotti}$$

$$\frac{d[HBrO_2]}{dt} = k_1[H^+]^2[BrO_3^-][Br^-] - k_2[H^+][HBrO_2][Br^-] + +k_3[H^+][BrO_3^-][HBrO_2] - 2k_4[HBrO_2]^2$$

$$\frac{d[Br^-]}{dt} = -k_1[H^+]^2[BrO_3^-][Br^-] - k_2[H^+][HBrO_2][Br^-] + +hk_5[CH_2(COOH)_2][Ce^{4+}]$$

$$\frac{d[Ce^{4+}]}{dt} = 2k_3[H^+][BrO_3^-][HBrO_2] - k_5[CH_2(COOH)_2][Ce^{4+}]$$

Kinetic scheme: Oregonator

$A = BrO_3^-$; $B = CH_2(COOH)_2$; $P = HBrO$; $X = HBrO_2$; $Y = Br^-$; $Z = Ce^{4+}$.

(O1) $\quad A + Y \rightarrow X + P$

(O2) $\quad X + Y \rightarrow 2\,P$

(O3) $\quad A + X \rightarrow 2\,X + 2\,Z$

(O4) $\quad 2\,X \rightarrow A + P$

(O5) $\quad B + Z \rightarrow h\,Y + \text{prodotti}$

Oregonator (dimensionless, pool chemical approximation)

$$\varepsilon \frac{dx}{d\tau} = qay - xy + ax - x^2$$

$$\delta \frac{dy}{d\tau} = -qay - xy + fbz$$

$$\frac{dz}{d\tau} = ax - bz$$

$\varepsilon = 0.12$ $\quad\delta = 0.0006$ $\quad q = 0.0008$

f = varying parameter ≈ 1 $\quad a, b$ = constant

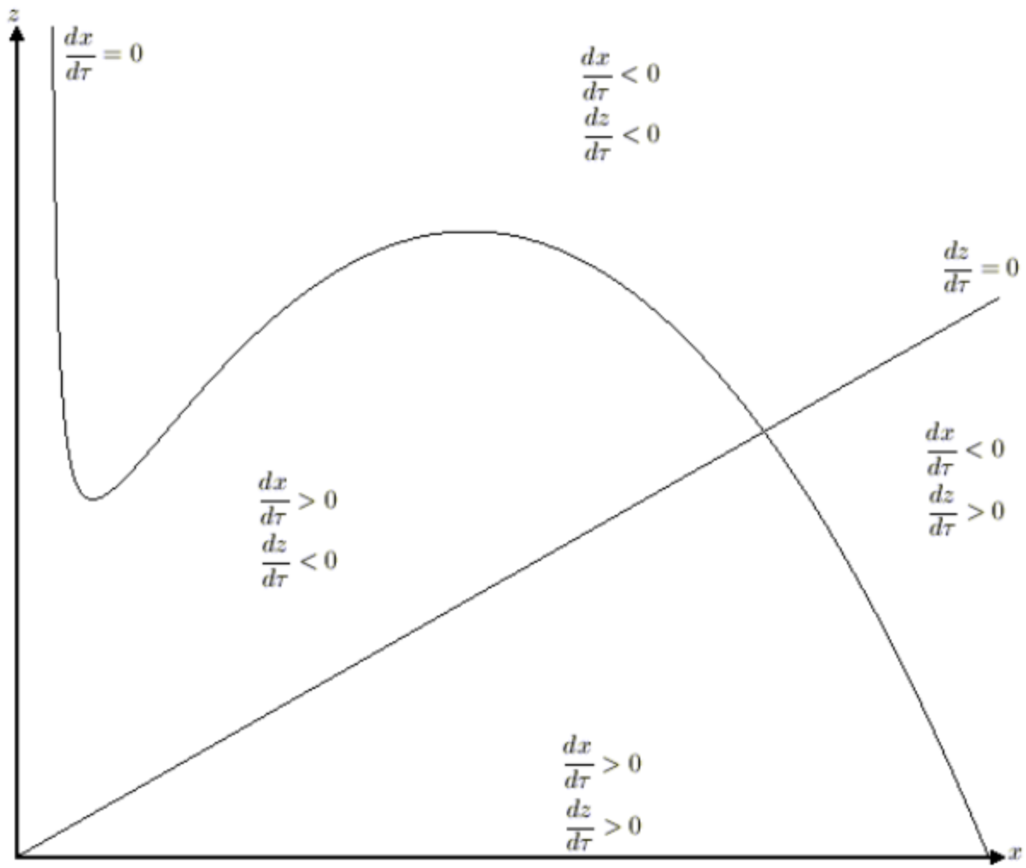
Reduced Oregonator

- Pseudo-steady-state approximation for y

$$y = y(x,z) = \frac{fbz}{x+qa}\,.$$

- Two-variable reduced Oregonator:

$$\varepsilon\frac{dx}{d\tau} = ax - x^2 - fbz\frac{x-qa}{x+qa}\,,$$
$$\frac{dz}{d\tau} = ax - bz\,.$$



Reduced Oregonator