

# Onset of B-Z Oscillations in Mixed Substrate : Lactic Acid-Acetone-KBrO<sub>3</sub>-Mn<sup>II</sup>-H<sub>2</sub>SO<sub>4</sub>

R. L. PITLIYA\*

Department of Chemistry, MLV Government College, Bhilwara-311 001

and

G. V. BAKORE

Department of Chemistry, Sukhadia University, Udaipur-313 001

Manuscript received 11 March 1986, revised 7 April 1987, accepted 6 July 1987

Oscillations with lactic acid-acetone as mixed substrate at different concentrations of reactants and temperature have been observed and the effect of these on induction period has been studied. It has been observed that the onset time can be reduced by proper choice of the concentration.

A large number of organic substrates gives oscillations with acidic bromate with appropriate catalysts, like Ce<sup>III</sup>, Mn<sup>II</sup> or Fe<sup>II</sup> *etc.*<sup>1-6</sup>. In malonic acid system, when Ce<sup>III</sup> or Mn<sup>II</sup> catalyst are used, induction period has been observed, and the critical concentration of bromomalonic acid is responsible for the oscillatory behaviour. Edelson<sup>7</sup> made some studies on induction period in B-Z oscillations. Burger and Körös<sup>8</sup> studied B-Z systems and observed that chemical oscillations start only after the concentrations of BrMA reaches a critical value. Rastogi and Prasad<sup>9</sup> studied the onset of chemical oscillations in malonic acid system catalysed by Mn<sup>II</sup> and the mechanism of this reaction has been proposed by Noyes *et al.*<sup>10</sup>. The B-Z reactions with mixed substrate tartaric acid-acetone were first reported by Rastogi *et al.*<sup>11</sup>. Much attention, however, has not been paid to the studies on induction period using other organic compounds as mixed substrates. In this paper, we report data on initiation time of lactic acid-acetone mixed substrate system and its dependence on different concentration parameters.

## Experimental

The reaction was started by adding KBrO<sub>3</sub> solution to the mixture of the other components and the experimental temperature was 35°. The potential of platinum electrode coupled to a calomel electrode (concentration of KCl solution, 2.5 × 10<sup>-4</sup> M) through KNO<sub>3</sub> salt-bridge was measured on a Systronics 335 digital pH meter followed by continuous recording on x-t recorder (omniscrite). The experiment was repeated at several temperatures.

Initially the e.m.f. was found to be decreased with time. A sudden rise of e.m.f. signalled the onset of oscillations. The time elapsed between the starting of the reaction and the first occurrence

of rise in e.m.f. was taken as time of initiation (also called induction period),  $T_{in}$ .

## Results and Discussion

The values of induction period at different concentrations of the various components have been shown in Table 1. The concentrations of the components, when not varied, were as follows: [Lactic acid] = 6.0 × 10<sup>-2</sup> M, [Acetone] = 1.36 M, [H<sub>2</sub>SO<sub>4</sub>] = 1.5 M, [Mn<sup>II</sup>] = 1.5 × 10<sup>-3</sup> M, [Pyrothosphate] = 2.0 × 10<sup>-2</sup> M, [KBrO<sub>3</sub>] = 6.0 × 10<sup>-3</sup> M. The dependence of  $T_{in}$  on temperature is given in Table 2.

TABLE 1—DEPENDENCE OF  $T_{in}$  AT DIFFERENT CONCENTRATIONS OF VARIOUS COMPONENTS

Component	Concn. mol dm <sup>-3</sup>	$T_{in}$ in min
KBrO <sub>3</sub>	2.0 × 10 <sup>-3</sup>	30.0
	4.0 × 10 <sup>-3</sup>	44.0
	6.0 × 10 <sup>-3</sup>	50.0
	8.0 × 10 <sup>-3</sup>	57.0
	10.0 × 10 <sup>-3</sup>	60.0
	16.0 × 10 <sup>-3</sup>	68.0
Lactic acid	1.0 × 10 <sup>-2</sup>	92.0
	2.0 × 10 <sup>-2</sup>	80.0
	4.0 × 10 <sup>-2</sup>	62.0
	5.0 × 10 <sup>-2</sup>	55.0
	7.0 × 10 <sup>-2</sup>	44.0
	10.0 × 10 <sup>-2</sup>	35.0
	12.0 × 10 <sup>-2</sup>	30.0
15.0 × 10 <sup>-2</sup>	26.0	
MnSO <sub>4</sub>	0.25 × 10 <sup>-3</sup>	72.0
	0.50 × 10 <sup>-3</sup>	60.0
	1.0 × 10 <sup>-3</sup>	58.0
	1.5 × 10 <sup>-3</sup>	49.0
	2.5 × 10 <sup>-3</sup>	42.0
	4.0 × 10 <sup>-3</sup>	28.0
	5.0 × 10 <sup>-3</sup>	22.0
	8.0 × 10 <sup>-3</sup>	20.0
10.0 × 10 <sup>-3</sup>	18.0	

(Table 1 contd.)

H <sub>2</sub> SO <sub>4</sub>	1.5	48.0
	2.0	29.0
	2.5	17.0
	3.0	10.0
	3.5	6.0
	4.0	4.0
Acetone	0.34 M	78.0
	0.68 M	68.0
	1.36 M	48.0
	2.04 M	37.0
	2.72 M	31.0
	3.40 M	25.0
Pyrophosphate	4.08 M	20.0
	5.44 M	12.0
	0.5 × 10 <sup>-3</sup>	48.0
	2.0 × 10 <sup>-3</sup>	48.0
	3.0 × 10 <sup>-3</sup>	52.0
	4.0 × 10 <sup>-3</sup>	55.0
	6.0 × 10 <sup>-3</sup>	65.0
	8.0 × 10 <sup>-3</sup>	75.0

TABLE 2—DEPENDENCE OF T<sub>10</sub> ON TEMPERATURE

Temp. K	T <sub>10</sub> min
303	70
308	49
313	28
318	19

The onset time(s) depends on the concentration of the reactants in a systematic manner. From the appropriate plots, the following expressions were obtained,

$$\frac{1}{T_{10}} = \frac{1}{15.0 \times 10^4} \frac{1}{[\text{KBrO}_3]} + \frac{2.2}{10^4} \quad (1)$$

$$T_{10} = \frac{456.7}{[\text{LA}]^{0.65}} \quad (2)$$

$$T_{10} = \frac{61.0 \times 10^3}{[\text{H}_2\text{SO}_4]} - 14.0 \times 10^3 \quad (3)$$

$$T_{10} = \frac{100.0}{[\text{Mn}^{II}]^{0.52}} \quad (4)$$

$$\frac{1}{T_{10}} = 1.46 \times 10^{-4} [\text{Acetone}] + 1.7 \times 10^{-4} \quad (5)$$

$$T_{10} = 2.6 \times 10^4 [\text{Pyrophosphate}] + 23.5 \times 10^3 \quad (6)$$

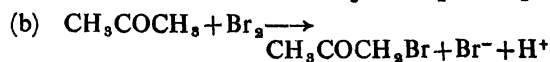
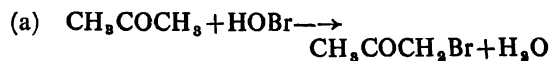
The pyrophosphate is used to alter the reduction potential of Mn<sup>III</sup>-Mn<sup>II</sup> couple. The onset time also depends on temperature according to equation,

$$\log \frac{1}{T_{10}} = A - \frac{E}{2.303 RT}$$

where, *E* is the energy of activation for the reaction, the value of which works out to be 16.5 kcal mol<sup>-1</sup> (69.0 kJ mol<sup>-1</sup>).

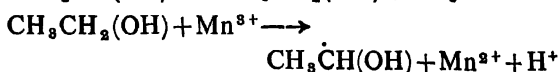
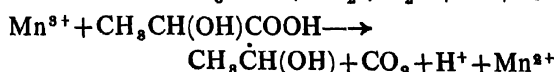
The results show that the induction period can be decreased by appropriate control of the reactant concentration and the oscillations can be produced almost instantaneously.

The importance of the presence of acetone in causing and controlling these reactions must be emphasised. Acetone can react in the following ways,



The 'inert Br' in these reactions is CH<sub>3</sub>COCH<sub>2</sub>Br in which the oxidation number of bromine is formally +1.

The proposed mechanism for the lactic acid is as follows,



and the overall reaction is



#### Acknowledgement

One of the authors (R.L.P.) thanks U.G.C., New Delhi, for the award of a Teacher Fellowship.

#### References

1. R. J. FIELD and R. M. NOYES, *Acc. Chem. Res.*, 1977, **10**, 214.
2. R. M. NOYES and R. J. FIELD, *Acc. Chem. Res.*, 1977, **10**, 273.
3. P. G. BOWERS, CALDWELL, and P. DERGAST, *J. Phys. Chem.*, 1972, **76**, 2186.
4. R. P. RASTOGI, K. D. S. YADAVA and P. RASTOGI, *Indian J. Chem., Sect. A*, 1977, **15**, 838.
5. M. ORBAN and E. KOROS, *J. Phys. Chem.*, 1978, **82**, 1672.
6. R. L. PITLIYA and G. V. BAKORE, *Z. Phys. Chem., (Leipzig)*, 1986, **267**, 1029.
7. D. EDELSON, *Int. J. Chem. Kinet.*, 1979, **11**, 1281.
8. M. BURGER and E. KOROS, *J. Phys. Chem.*, 1980, **84**, 496.
9. R. P. RASTOGI and K. PRASAD, *Indian J. Chem., Sect. A*, 1982, **21**, 1011.
10. R. M. NOYES, *J. Am. Chem. Soc.*, 1980, **102**, 4644.
11. RASTOGI R. P. SINGH, Kinetics of Physicochemical Oscillations Aachen Discussion of Deutsche Bunsengesellschaft fur Physikalische Chemie, Preprints of Submitted Papers, 1979 p. 98.