

## Oscillatory Chemical Reactions — Mechanism of Belousov-Zhabotinskii Reaction

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Complexity of the oscillating reaction in Belousov-Zhabotinskii reaction has been discussed in detail. The data on time of initiation, time-period and lifetime of oscillations for (i) malonic acid/ $\text{KBrO}_3/\text{Mn}^{2+}/\text{H}_2\text{SO}_4$ , (ii) malonic acid/ $\text{KBrO}_3/\text{Ce}^{4+}/\text{H}_2\text{SO}_4$ , (iii) malic acid/ $\text{KBrO}_3/\text{Ce}^{4+}/\text{H}_2\text{SO}_4$ , (iv) acetylacetone/ $\text{KBrO}_3/\text{Mn}^{2+}/\text{H}_2\text{SO}_4$  and (v) citric acid/ $\text{KBrO}_3/\text{Mn}^{2+}/\text{H}_2\text{SO}_4$  systems have been examined in detail to elucidate the mechanism of oscillations. The results show that key role in the reaction is played by  $\text{Br}^-$  and further the oscillations are produced on account of delayed activation of (a) reactions leading to the production of  $\text{Br}^-$  and (b) the reactions leading to the consumption of  $\text{Br}^-$ .

**B**ELOUSOV-ZHABOTINSKII reaction<sup>1,2</sup> involving an organic substrate (containing a reactive methylene group or a  $\beta$ -keto group), potassium bromate and a redox couple ( $\text{Ce}^{4+}/\text{Ce}^{3+}$ ,  $\text{Mn}^{3+}/\text{Mn}^{2+}$  or  $[\text{Ru}(\text{bipy})_3]^{3+}/[\text{Ru}(\text{bipy})_3]^{2+}$  in sulphuric acid has been investigated by several group of workers in view of considerable current interest. Efforts have been made by one group of workers to elucidate the mechanism on the basis of kinetic evidence<sup>3-9</sup> and redox potentials of the couples, while the other group has investigated the oscillatory features of several reactions in great detail<sup>10-15</sup>. Both the approaches are complementary as far as elucidation of the mechanism is concerned. In spite of the unusually complicated nature of the reactions, the broad features of the mechanism are clearer<sup>7,8</sup>. In this paper we shall review and analyse the oscillatory characteristics of the reactions in order to understand the mechanism of oscillations.

### Salient Features of the Reactions

(1) *Products of the reaction* — For each organic substrate, a number of organic products are formed. In no case these have been completely characterized. Some of the products are given in Table 1.

(2) *Stoichiometry of the reaction* — Stoichiometry of the reaction is not known. Stoichiometry of  $\text{Ce}^{4+}$  oxidation of malonic acid has been investigated by Noyes and coworkers<sup>7</sup> but an unambiguous picture has not emerged.

(3) *Possible intermediate species* — A number of organic and inorganic intermediates are expected to be present in the system. These are summarized in Table 2.

(4) *Types of reaction* — Belousov-Zhabotinskii reaction is essentially an oxidation-reduction reaction involving electron transfer. However, it is complicated by free radical reactions and bromination reaction which proceeds by enolization mechanism which is facilitated by  $\beta$ -keto group in the organic substrate.

(5) *Inhibitors* — Oscillations are inhibited<sup>7</sup> by alcohol,  $\text{Cl}^-$  and excess of  $\text{Br}^-$ .

(6) *Influence of light* — Oscillatory reaction is sensitive to UV<sup>16</sup> variations particularly with light at a wavelength of  $<3000 \text{ \AA}$ . By increasing the intensity of irradiation, it is possible to modify and finally to suppress completely the oscillations. It has been postulated that this is due to photo-decomposition of bromo-derivatives to produce  $\text{Br}^-$ . However, this is still open to question although it has been found that a solution of bromomalonic acid produces  $\text{Br}^-$  when exposed to UV light of wavelength  $<3000 \text{ \AA}$ . There is a further possibility of photo-reaction with inorganic ions. Quite recently the photo-redox chemistry of iron(III) chloride and iron(III) perchlorate in aqueous media has been investigated<sup>17</sup>. The primary photo-reaction is postulated to be  $\text{Fe}^{3+} \cdot \text{OH}^- \rightarrow \text{Fe}^{2+} + \text{OH}^\cdot$ . Further, the flash photolysis of aqueous ceric

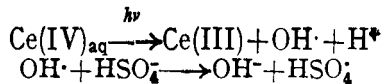
TABLE 1 — PRODUCTS OF OSCILLATORY REACTIONS

Organic substrate	Products detected
Malonic acid <sup>7</sup>	$\text{CO}_2$ , monobromoacetic acid, monobromo malonic acid, acetic acid, formic acid
Malic acid <sup>18</sup>	$\text{CO}_2$ , bromooxalacetic acid
Citric acid <sup>15</sup>	$\text{CO}_2$ , some organic bromo-derivatives
Acetylacetone <sup>14</sup>	bromo-derivatives, no $\text{CO}_2$ , acetic acid

TABLE 2 — INTERMEDIATES OF OSCILLATORY REACTIONS

Organic substrate	Inorganic intermediates	Organic intermediates
Malonic acid	$\text{BrO}_2$ , $\text{HBrO}^\cdot$ , $\text{HBrO}_2$ , $\text{Br}^\cdot$ , $\text{BrO}^\cdot$ , $\text{OBrO}^\cdot$ , $\text{BrOO}^\cdot$ , and $\text{BrO}_3^\cdot$	$\text{CH}_2\text{COOH}$ $\text{CH}_2$ $\begin{matrix} \diagup \text{COOH} \\ \diagdown \text{COO}^\cdot \end{matrix}$
Malic acid	do	$\text{CH}_2(\text{COOH})$ $\text{CH}_2\text{COO}^\cdot$ $\begin{matrix}   \\ \text{CO-COOH} \end{matrix}$ $\begin{matrix}   \\ \text{CO-COOH} \end{matrix}$
Citric acid	do	—
Acetylacetone	do	—

sulphate suggests the following processes<sup>18</sup>:



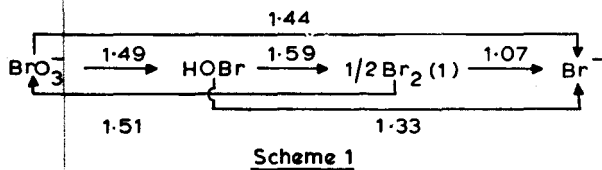
Suppression of oscillations on exposure of reaction medium to UV light can be understood as follows. Photochemical decarboxylation of malonic acid is known to occur at a wavelength <2500 Å to give acetic acid and CO<sub>2</sub>; acetic acid produced can reduce the bromide ion concentration by subsequent bromination.

Another possibility which needs to be examined is that effective *E*<sup>o</sup> for RCOO<sup>-</sup>/ROO<sup>•</sup> system or RCOO<sup>-</sup>/R<sup>•</sup> system may change since on exposure to UV light, the excited states may have a different *E*<sup>o</sup>.

(7) *Complexity of the reactions* — Taking the case of acetylacetone, it turns out that during oscillations 24 species may be present in the reaction mixture amongst which 15 reactions may be possible. These are well illustrated by a graph in Fig. 1. Similarly in the case of malonic acid 15 species can exist in the system. It can be seen that graph in Fig. 1 is disconnected and that it can be factorized<sup>19</sup>. The factors relating to electron-transfer reactions and bromination reactions are indicated in Figs. 2a and 2b.

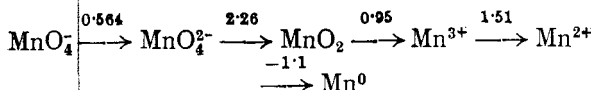
The reaction involves a delicate balance of (i) series of electron-transfer reactions, (ii) free-radical reactions and (iii) bromination reactions. We shall comment on these one by one.

(i) *Electron-transfer reactions* — There are two strong oxidizing agents BrO<sub>3</sub><sup>-</sup> and Ce<sup>4+</sup> (or Mn<sup>3+</sup>) in the system. The course of reaction would be governed by their potential diagrams. BrO<sub>3</sub><sup>-</sup> undergoes reduction in the manner<sup>7</sup> shown in Scheme 1

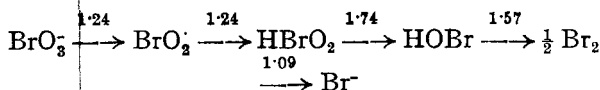


(the values of *E<sub>A</sub>* are given). *E<sub>A</sub>* values of one-electron reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> in 1M HCl, 1M H<sub>2</sub>SO<sub>4</sub>, 1M HNO<sub>3</sub> and 1M HClO<sub>4</sub> are 1.28, 1.44, 1.61 and 1.70 respectively.

Permanganate ion is reduced in the following manner:



Bromate can follow another path for its reduction as well.



It is obvious from the above data that the redox potentials of the couples BrO<sub>3</sub><sup>-</sup>/Br<sup>-</sup>, Ce<sup>4+</sup>/Ce<sup>3+</sup> and Mn<sup>3+</sup>/Mn<sup>2+</sup> are similar and differ by small amounts. The values of potentials quoted correspond to standard state. The actual values of electrode

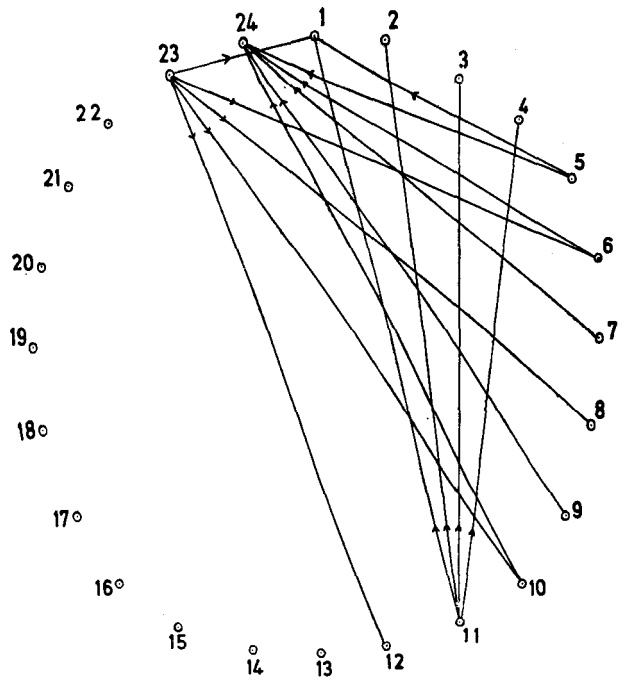


Fig. 1 — Graph of the possible reaction pathways in the reaction system consisting of acetylacetone, potassium bromate, and manganous sulphate in dilute sulphuric acid medium. The direction of the arrow A → B indicates that A oxidizes B. In case of arrows emanating from centre 11, the direction of bromination reaction is indicated [1, CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>; 2, CH<sub>3</sub>COCH<sub>2</sub>COOH; 3, CH<sub>3</sub>COOH; 4, CH<sub>2</sub>COCOOH; 5, BrO<sub>3</sub><sup>-</sup>; 6, HBrO<sub>2</sub>; 7, HOBr; 8, BrO<sub>2</sub><sup>-</sup>; 9, BrO<sup>-</sup>; 10, Br<sup>-</sup>; 11, Br<sup>-</sup>; 12, Br<sup>-</sup>; 13, CHBr<sub>2</sub>COCH<sub>3</sub>; 14, CH<sub>2</sub>BrCOCH<sub>3</sub>; 15, CHBr<sub>2</sub>COOH; 16, CH<sub>2</sub>BrCOOH; 17, CH<sub>3</sub>COCHBrCOOH; 18, CH<sub>2</sub>COCHBrCOOH; 19, BrCH<sub>2</sub>COCH<sub>2</sub>COCH<sub>2</sub>Br; 20, BrCH<sub>2</sub>COCH<sub>2</sub>COCH<sub>3</sub>; 21, CH<sub>3</sub>COCHBr<sub>2</sub>COCH<sub>3</sub>; 22, CH<sub>3</sub>COCHBrCOCH<sub>3</sub>; 23, Mn<sup>3+</sup>; 24, Mn<sup>2+</sup>]

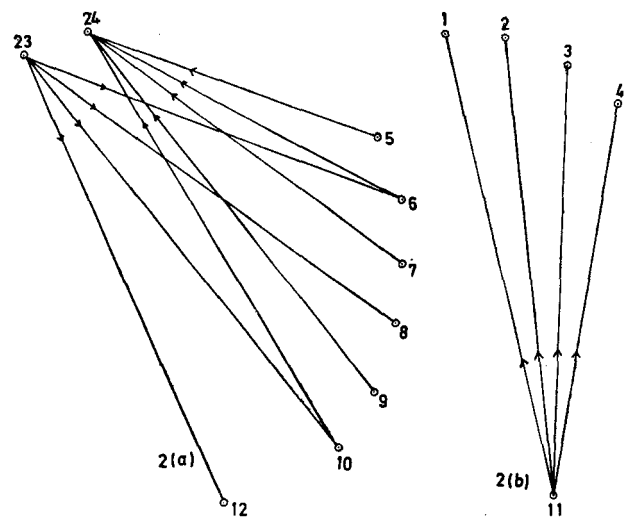


Fig. 2(a) — Graph of the possible bromination reactions in the reaction system containing acetylacetone, potassium bromate and manganous sulphate in sulphuric acid medium

Fig. 2(b) — Graph of the possible electron transfer reactions in the reaction system containing acetylacetone, potassium bromate and manganous sulphate in sulphuric acid medium

TABLE 3 — FREE RADICAL PARTICIPATION IN REACTION SYSTEMS

Reaction	Time taken for the formation of free radicals
1. Malic acid + BrO <sub>3</sub> <sup>-</sup>	2 hr
2. Malic acid + Ce <sup>4+</sup>	Instantaneous
3. BrO <sub>3</sub> <sup>-</sup> + Ce <sup>3+</sup>	Slow
4. Ce <sup>4+</sup> + BrO <sub>3</sub> <sup>-</sup> + malic acid	Instantaneous
5. Citric acid + BrO <sub>3</sub> <sup>-</sup>	Slow
6. Citric acid + Ce <sup>4+</sup>	Instantaneous
7. Ce <sup>3+</sup> + BrO <sub>3</sub> <sup>-</sup> + citric acid	do
8. Malonic acid + Ce <sup>4+</sup>	do
9. Malonic acid + Ce <sup>3+</sup> + BrO <sub>3</sub> <sup>-</sup>	do
10. Ce <sup>4+</sup> + BrO <sub>3</sub> <sup>-</sup>	Slow
11. Mn <sup>3+</sup> + acetylacetone	No free radicals formed
12. KBrO <sub>3</sub> + acetylacetone	1/2 hr
13. KBrO <sub>3</sub> + Mn <sup>2+</sup>	1 hr
14. KBrO <sub>3</sub> + Mn <sup>2+</sup> + acetylacetone	Instantaneous

potentials pertinent for the present studies are given by

$$E = E^{\circ} + \frac{RT}{nF} \log \frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

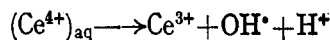
where  $n$  is the number of electrons transferred and  $F$  is the faraday.

It is observed in oscillating chemical reaction that in one part of the cycle a particular reaction is favoured while in other part of the cycle the reaction stops and other reaction starts. It seems that the free energy of such reactions oscillates around zero so that a particular reaction occurs in that part of the cycle when free energy change is negative. In switching on and switching off, thermodynamic considerations are still important. If  $E_1$  and  $E_2$  are the effective electrode potentials of BrO<sub>3</sub><sup>-</sup>/Br<sup>-</sup> and Ce<sup>4+</sup>/Ce<sup>3+</sup> couples, then if  $E_1 > E_2$ , BrO<sub>3</sub><sup>-</sup> will oxidize Ce<sup>3+</sup> but when  $E_1 < E_2$ , this will not happen. This is likely when Br<sup>-</sup> concentration is in excess since [BrO<sub>3</sub><sup>-</sup>]/[Br<sup>-</sup>] will have a lower value and effective  $E_1$  in some stage of the cycle may be less than  $E_2$ . The concentrations of Br<sup>-</sup> and Ce<sup>4+</sup> ion are controlled by organic substrate through bromination reaction and oxidation reaction so that a delay in switching the different reactions is introduced.

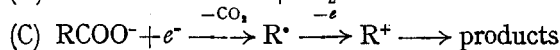
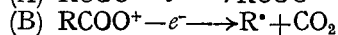
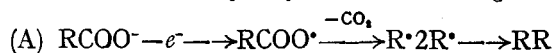
It further follows that Ce<sup>4+</sup>/Ce<sup>3+</sup> potential is so low in HCl medium and so high in HNO<sub>3</sub> and HClO<sub>4</sub>, that the reactions would proceed in only one direction with no possibility of oscillations as is experimentally found to be the case. Recently oscillations have been observed<sup>20</sup> in HNO<sub>3</sub> with malonic acid and citric acid systems with Mn<sup>3+</sup>/Mn<sup>2+</sup> couple. Oscillations are also reported<sup>21</sup> in the system malonic acid/KBrO<sub>3</sub>/Mn<sup>2+</sup>/H<sub>3</sub>PO<sub>4</sub>. Further it has been observed<sup>20</sup> that malic acid, acetylacetone and citric acid give oscillations in Mn<sup>3+</sup>/Mn<sup>2+</sup> and Ce<sup>4+</sup>/Ce<sup>3+</sup> in H<sub>3</sub>PO<sub>4</sub> medium.

(ii) *Free radical reactions* — In order to test whether free radicals are formed in the reaction system, acrylonitrile was added. Polymerization indicated the presence of free radicals. The results of such experiments<sup>13-15</sup> are given in Table 3.

Ceric ions can generate free radicals<sup>18</sup> if exposed to light as follows:



However, this does not appear to be true in our case since reaction (10 in Table 3) generates free radicals only after a long time. Presumably, decarboxylation of organic acids occurs via free radical mechanism by any of the following routes:



(iii) *Bromination reaction* — The enolization of keto group in an acid medium involves first oxonium-salt formation and second removal of an  $\alpha$ -proton with water or other proton acceptors. Subsequently, the enol or the enolate ion can combine rapidly with bromine to give bromo-derivatives. Thus for bromination it is essential that Br<sub>2</sub> should be available. This is easily generated in the system by the oxidation of Br<sup>-</sup> by BrO<sub>3</sub><sup>-</sup> in the system.

The key role is played by electron-transfer reactions in oscillations. Free-radical reactions and bromination reactions merely play a secondary role.

(8) *Oscillatory character of the reactions* — Following quantities oscillate with time in course of oscillatory reaction: (i) concentration of Br<sup>-</sup>; (ii) instantaneous redox potential of the system; (iii) rate of production of bromomalonic acid with time; (iv) rate of increase of partial pressure of carbon dioxide with time; and (v) rate of temperature rise with time.

In order to have a composite picture, time variation of all the above quantities have been plotted in Fig. 3. We shall now discuss some of the oscillatory characteristics of the system.

(i) *Time of initiation* — If the rate of variation of the concentration of particular species depends on the concentration of  $n$  the other species such that

$$\frac{dc_1}{dt} = F(c_1, c_2, \dots, c_n)$$

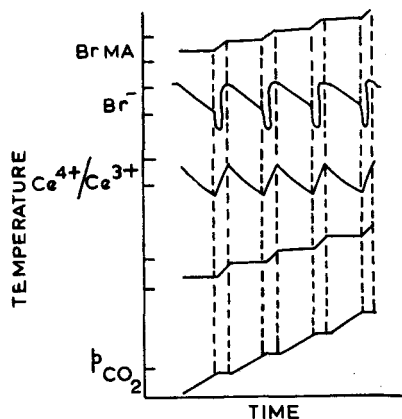


Fig. 3 — Simultaneous change in the concentration of bromide ion<sup>7,26</sup>, bromomalonic acid<sup>26</sup>, cerous/ceric ratio<sup>6,7</sup>, pressure of carbon dioxide<sup>6</sup> and temperature<sup>13</sup> in Belousov-Zhabotinskii reaction with time

TABLE 4 — CHARACTERISTIC PARAMETERS OF THE REACTION SYSTEM

 {[C=catalyst; (Ce<sup>3+</sup>); O=organic substrate]}

System	Time of initiation of			Lifetime*
	[O+BrO <sub>3</sub> ]+C	(O+C)+BrO <sub>3</sub>	[C+BrO <sub>3</sub> ]+O	
Malonic acid/Ce <sup>4+</sup>	9 min	9½ min	10 min	3-7 hr
Malonic acid/Mn <sup>2+</sup>	>1 min	>1 min	—	1-3 hr
Malic acid/Ce <sup>4+</sup>	~0 min	~1-2 min	~30 sec	40 min
Citric acid/Ce <sup>4+</sup>	7 min	7½ min	6 min	5 hr
Acetylacetone/Mn <sup>2+</sup>	No oscillations	~10-40 sec	~100 sec	15 min

\*Lifetime of oscillations does not depend on the order of addition of reagents.

TABLE 5 — DEPENDENCE OF TIME OF INITIATION ON CONCENTRATION OF COMPONENTS

Component	System				
	A	B	C	D	E
Potassium bromate	$t_{in}=8.08 \times [\text{KBrO}_3]^{1/2}$	Decreases with increasing [KBrO <sub>3</sub> ]	$t_{in}=0.47 \times [\text{KBrO}_3]^{-0.296}$	Increases with decreasing [KBrO <sub>3</sub> ]	$t_{in}=27.61[\text{KBrO}_3]^{-0.427}$
Organic substrate	$t_{in}^{\infty}=0.37 \times [\text{MA}]^{-1/2}$	Minima in $t_{in}$ vs [MA] curve	$t_{in}=0.18 \times [\text{MA}]^{-0.35}$	Increases with increasing [acetylacetone]	$t_{in}=0.92[\text{citric acid}]^{-1.815}$
Redox couple	$t_{in}^{\infty}=2.07 \times e^{-0.011[\text{MnSO}_4]^{1/2}}$	Decreases with increasing Ce <sup>3+</sup>	$t_{in}=512.5 \times [\text{Ce}^{4+}] + 0.66$	Increases with decreasing (Mn <sup>2+</sup> )	$t_{in}=0.53[\text{Mn}^{2+}]^{-1.316}$
H <sub>2</sub> SO <sub>4</sub>	Independent	Independent	$t_{in}=2.22 \times [\text{H}_2\text{SO}_4]^{-0.7653}$	$t_{in}=-7.08[\text{H}_2\text{SO}_4] + 44$	—
Temperature	Decreases with increase in T	Decreases with increase in T	$t_{in}=-0.057 T + 18.8$	Increases with decreasing T	$t_{in}=1.213 \times 10^{82}[\text{T}]^{-32.2}$

 (A) Malonic acid/MnSO<sub>4</sub>/KBrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (ref. 11, 23).

 (B) Malonic acid/Ce<sup>3+</sup>/KBrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (ref. 10, 24).

 (C) Malic acid/Ce<sup>4+</sup>/KBrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (ref. 13, 25).

 (D) Acetylacetone/Mn<sup>2+</sup>/KBrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (ref. 14).

 (E) Citric acid/Mn<sup>2+</sup>/KBrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (ref. 15).

The steady state would then be defined by  $dc_1/dt=0$  when  $c_1=c_1^0$ , the steady state concentration and so on. The time of initiation is the time which the system takes to reach the neighbourhood of the steady state. If this interpretation is correct, the time of initiation should not depend on the nature of pace-makers as has been confirmed experimentally<sup>22</sup>.

The time of initiation depends on the order of addition of reagents as shown in Table 4. Column 2 shows how the reagents were added. The species in the first bracket were taken first and the third species was added afterwards.

Following conclusions can be drawn on the basis of the above results:

(a) When [O+BrO<sub>3</sub>] and [C+BrO<sub>3</sub>] are the starting mixtures, the time of initiation is always shorter. These mixtures would generate Br<sup>-</sup> or Br<sub>2</sub>. From this it follows that it is necessary to build up the requisite concentration of Br<sup>-</sup> or Br<sub>2</sub> before oscillations can start.

(b) Acetylacetone is an exception since it is rapidly oxidized by BrO<sub>3</sub> and bromination of the decomposition products also occurs quickly so that addition of catalyst to the mixture of [O+BrO<sub>3</sub>] the requisite concentration of Br<sup>-</sup> is rapidly built up, but acetylacetone remains no more in the system and hence no oscillations are expected,

as experimentally found to be the case. The lifetime is also shortest on account of rapid consumption of Br<sup>-</sup> or Br<sub>2</sub> during the bromination of acetylacetone and its decomposition products.

Time of initiation depends on the concentration of reactants. The results are summarized in Table 5.

The analysis of the above results shows that the reaction sequence up to the start of oscillation is similar in case of Mn<sup>2+</sup> ion and Ce<sup>3+</sup> catalysed reaction. It is perhaps little different when malic acid is used instead of malonic acid. In all the cases, time of initiation decreases with increase in temperature.

The time of initiation is independent of the concentration of H<sub>2</sub>SO<sub>4</sub> in case of malonic acid showing thereby that the reactions are independent of H<sup>+</sup> whereas perhaps this is not so in the case of malic acid and acetylacetone. In the case of malonic acid, citric acid and acetylacetone time of initiation decreases with increase in the concentration of redox couple. With acetylacetone time of initiation increases with increase in acetylacetone concentration while in other cases time of initiation decreases with increase in organic substrate concentration.

(ii) *Time period of oscillations* — Different organic substrates give different potentiometric traces. The time period depends on the concentration of the

TABLE 6 — DEPENDENCE OF TIME PERIOD OF OSCILLATIONS ON COMPONENTS

Component	System				
	A	B	C	D	E
Potassium bromate	$t = A_{ce}/T[MA]^{-1/2} \times [KBrO_3]^{-1/2}[H_2SO_4]^{-1}$	$t = K_1[MA]^{-0.6} \times [KBrO_3]^{-0.94} \times [H_2SO_4]^{-1.28}$	$t = K_2[KBrO_3]^{-0.95} [MA]^{-0.3} \times [H_2SO_4]^{-1.12}$	$t = 0.6[KBrO_3]^{-0.98}$	$t = 2.5[KBrO_3]^{-0.885}$
Organic substrate				Decreases with decrease in [acetylacetone]	$t = 10.64 \times [\text{citric acid}]^{-0.34}$
H <sub>2</sub> SO <sub>4</sub>				$t = 60.26 \times [H_2SO_4]^{-1.33}$	$t = 55.68 \times [H_2SO_4]^{-1.28}$
Redox couple	Independent	Independent	$t = 3.5 \times [Ce^{4+}]^2 \times 10^5 + 0.2$	Decrease with decrease in [Mn <sup>2+</sup> ]	$t = 6.34[Mn^{2+}]^{-0.28}$
Temperature	Increase with decreases in temperature	Decreases with increase in temperature	$t = 1.22 \times 10^{61} \times T^{-24.66}$	$t = 1.23 \times 10^7 \times T^{-3.77}$	$t = 1.36 \times 10^{85} \times T^{-33.88}$

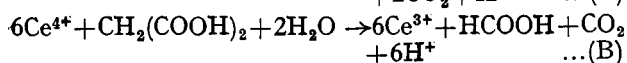
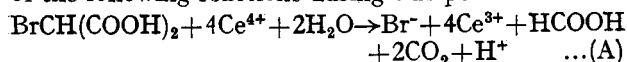
reactants and the temperature. The analytical equations which fit the data are given in Table 6.

Thus, time period =  $f(T, \text{concentration of reactants})$ .

From the potentiometric traces (Fig. 3) following conclusions can be drawn.

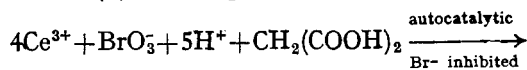
(a) In a cycle, there is a period of Ce<sup>4+</sup> (or Mn<sup>3+</sup>) consumption followed by a period of rapid production of Ce<sup>4+</sup> (or Mn<sup>3+</sup>). During the former Br<sup>-</sup> is consumed while it is produced in the latter. It is understandable that when Ce<sup>3+</sup> and BrO<sub>3</sub><sup>-</sup> are present simultaneously, both ceric ion and bromide ion would be produced.

(b) Rapid production of CO<sub>2</sub> occurs during the consumption of Ce<sup>4+</sup> ion indicating the occurrence of the following reactions during this period:



These reactions have been postulated by Noyes *et al.* but the stoichiometry is not unambiguous.

(c) The rapid temperature rise occurs in the period when Ce<sup>4+</sup> is being produced showing thereby that in the particular part of the cycle, the following reaction (C) takes place:



This is substantiated by the thermochemical studies of the reaction by Rastogi and coworkers<sup>12</sup>, the results of which are reproduced below:

Reactant	Temp. rise in first 15 min (°C)	(dT/dt) <sub>t=0</sub>
Bromide/bromate	0.60	0.550
Bromide/bromate/malonic acid	2.20	0.275
Cerous/bromate/malonic acid	0.98	0.085

Out of a number of component reactions of the overall oscillatory reaction, only the above three are highly exothermic.

TABLE 7 — FOURIER ANALYSIS OF CHEMICAL OSCILLATIONS

Reaction system	Fourier series	No. of significant harmonics	Frequencies present
Malonic acid + Mn <sup>2+</sup> + KBrO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	$y = 4.8 + 1.16 \sin wt - 5.6 \sin 2wt + 3.7 \sin 3wt + \dots + 4.2 \cos wt - 0.5 \cos 2wt - 1.04 \cos 3wt + \dots$	3	w, 2w, 3w
Malonic acid + Ce <sup>4+</sup> + KBrO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	$y = 6.09 - 2.1 \sin wt - 5.5 \sin 2wt + 0.2 \sin 3wt + 0.7 \sin 4wt + \dots + 6.14 \cos wt - 0.5 \cos 2wt + 0.2 \cos 3wt - 0.3 \cos 4wt + 1.0 \cos 5wt + \dots$	4	w, 2w, 4w, 5w
Malic acid + KBrO <sub>3</sub> + Mn <sup>2+</sup> + H <sub>2</sub> SO <sub>4</sub>	$y = 6.5 - 8.3 \sin wt - 2.76 \sin 2wt - 1.65 \sin 5wt - 1.2 \sin 7wt + \dots$	4	w, 3w, 5w, 7w
Citric acid + Mn <sup>2+</sup> + KBrO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	$y = 6.5 + 7.6 \sin wt + 3.8 \sin 2wt + 2.5 \sin 3wt + 1.9 \sin 4wt + 1.5 \sin 5wt + 7.0 \cos wt + 1.76 \cos 2wt + 0.78 \cos 3wt + 0.44 \cos 4wt + 0.28 \cos 5wt$	5	w, 2w, 3w, 4w, 5w
Acetylacetone + Mn <sup>2+</sup> + KBrO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	$y = 5.7 + 2.4 \sin wt + 0.14 \sin 2wt + 1.5 \sin 5wt - 1.8 \sin 3wt - 0.6 \sin 4wt + 3.7 \sin 6wt - 0.6 \sin 7wt + \dots - 0.5 \cos wt - 9.9 \cos 2wt - 2.6 \cos 3wt + 2.5 \cos 4wt - 4.3 \cos 5wt + \dots$	5	w, 2w, 3w, 4w, 5w

(d) Results obtained by Körös<sup>26</sup> show that BrMA accumulates in the system and that its production is more rapid when Br<sup>-</sup> concentration increases more rapidly which further confirms the occurrence of reaction (C) in this period. What happens in the system is that more BrMA is produced by

TABLE 8 — DEPENDENCE OF LIFE-TIME ON THE CONCENTRATION OF THE REACTANTS AND TEMPERATURE

Component	System				
	A	B	C	D	E
Potassium bromate	Maxima is obtained when the ratio $[\text{KBrO}_3]:[\text{MA}]$ is 1:1	Maxima is obtained when the ratio of $[\text{KBrO}_3]:[\text{MA}]$ is 1:1	Maxima is obtained when the ratio of $[\text{KBrO}_3]:[\text{MA}]$ is 1:2:1	$t_1 = 1.67[\text{KBrO}_3]^{-1.76}$	—
Organic substrate	Maxima is obtained	Independent	$t_1 = 80.18[\text{MA}] + 52.91$	Maxima is obtained	Independent
Redox couple	Maxima at 0.0004M	Decreases with increase in $[\text{Ce}^{3+}]$	$t_1 = 0.9[\text{Ce}^{3+}]^{-0.54}$	Maxima is obtained	$t_1 = 75.61[\text{Mn}^{2+}]^{0.55}$
$\text{H}_2\text{SO}_4$	Maxima at 1M	Maxima at 1M	Maxima at 1.25M	$t_1 = 4093 \times [\text{H}_2\text{SO}_4]^{-2.1}$	$t_1 = 2580[\text{H}_2\text{SO}_4]^{-1.1}$
Temperature	$t_1 = 1.45 \times 10^8 e^{-0.0259T}$	Decreases with increase in temperature	$t_1 = 7.6 \times 10^9 e^{-0.0028T}$	$t_1 = 1.24 \times 10^7 T^{-2.9}$	$t_1 = 8.82 \times 10^4 \times T^{-24.79}$

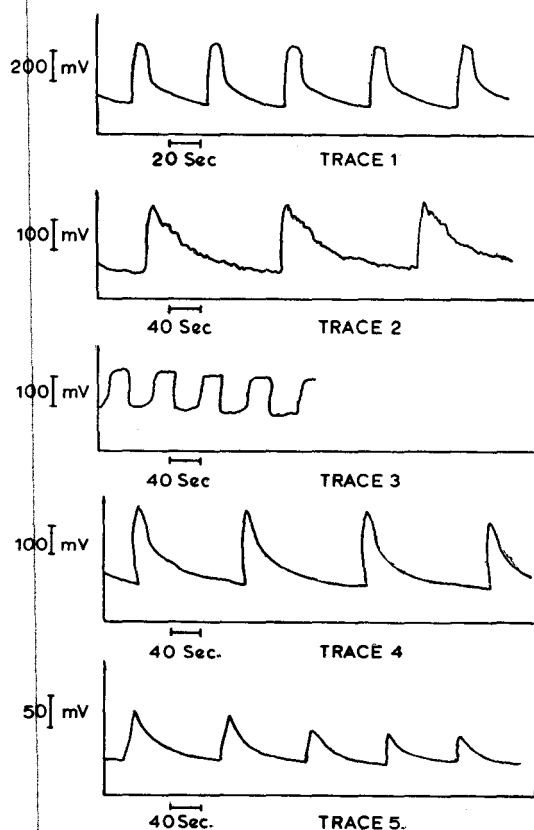


Fig. 4 — e.m.f. vs time trace for reaction mixture containing malonic acid/ $\text{KBrO}_3/\text{Mn}^{2+}/\text{H}_2\text{SO}_4$  (Trace 1); malonic acid/ $\text{KBrO}_3/\text{Ce}^{4+}/\text{H}_2\text{SO}_4$  (Trace 2); malonic acid/ $\text{KBrO}_3/\text{Mn}^{2+}/\text{H}_2\text{SO}_4$  (Trace 3); citric acid/ $\text{KBrO}_3/\text{Mn}^{2+}/\text{H}_2\text{SO}_4$  (Trace 4); and acetylacetone/ $\text{KBrO}_3/\text{Mn}^{2+}/\text{H}_2\text{SO}_4$  (Trace 5)

reaction (C) than is consumed by reaction (A) so that net accumulation of BrMA takes place and  $d(\text{BrMA})/dt$  oscillates.

(e) The oscillations are represented by a Fourier series<sup>27</sup> given by

$$F_{\text{redox}} = A_0 + A_1 \sin wt + A_2 \sin 2wt + \dots + B_1 \cos wt + B_2 \cos 2wt + \dots$$

The number of harmonics obtained in the case of different organic substrates are recorded in

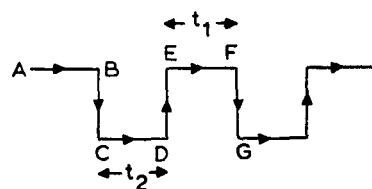


Fig. 5 — Square waves obtained in the case of malic acid

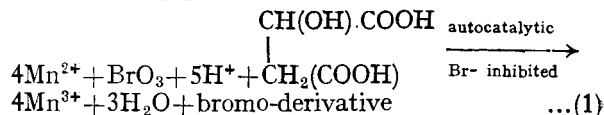
Table 7 and the potentiometric traces are recorded in Fig. 4.

(f) Oscillations in the system do not belong to the class of limit cycle type of oscillations since damped oscillations are observed.

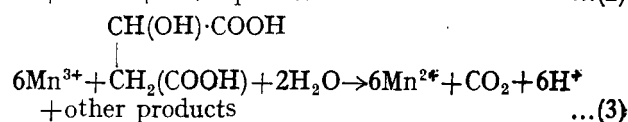
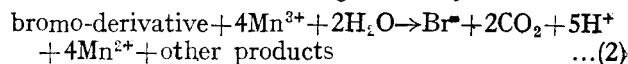
(iii) *Lifetime of oscillations* — The time after which the oscillations die out depends on the concentration of the reactants as well as the temperature. The results are summarized in Table 8.

*Mechanism of the reaction* — We recall the square waves (Fig. 5) which are obtained in the case of malic acid and we shall use it for illustrating the mechanism.

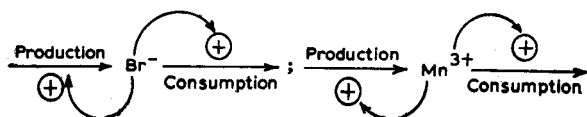
Let us consider one cycle CDEFG of the oscillation. There is an induction period  $t_2$  thereafter there is rapid increase in  $[\text{Mn}^{3+}]$ , which is obviously catalytic in nature. Again after an induction period equal to  $t_1$  there is a rapid fall in  $[\text{Mn}^{3+}]$  ion which also is obviously catalytic. We can identify the two reactions on the basis of data presented in the paper. Thus, in the sub-cycle DE, reaction (1) must be taking place,



Similarly, reactions (2) and (3) which consume  $\text{Mn}^{2+}$  ions must be occurring in sub-cycle FG.



Following the concepts suggested by Franck<sup>28</sup>, it seems that the key reactions are:



Both the consumption reaction and the production reaction of  $\text{Br}^-$  and  $\text{Mn}^{3+}$  are autocatalysed. The oscillations arise on account of delayed activation of both the processes<sup>28</sup>.

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