Notes

Belousov-Zhabotinskii Reaction with Acetone-Tartaric Acid & Acetone-Mandelic Acid as Organic Substrates

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It has been reported that although no oscillations are produced in acetone/$KBrO_3$/$Ce^{4+}H_2SO_4$, mandelic acid $KBrO_3$/Ce^{4+}/H_2SO_4 or tartaric acid/$KBrO_3$/Ce^{4+}/H_2SO_4 systems, oscillations are observed when acetone-mandelic acid or acetone-tartartic acid are used as the organic substrates.

OSCILLATORY chemical reactions are of current research interest due to their occurrence in biological systems[1]. Among the oscillatory chemical reactions occurring in non-biological systems, Belousov-Zhabotinskii reaction has been studied extensively[2-4]. Chemical oscillations have been observed using citric acid, malonic acid, malic acid, acetone dicarboxylic acid, acetoacetic ester, barbituric acid, monobromomalonic acid, dibromomalonic acid, and 2,4-pentanedione as organic substrates; Ce(III), Mn(II), $Fr(Phen)_3^{2+}$, $Fe(Dipy)_3^{2+}$ and $Ru(Dipy)_3^{2+}$ (ref. 5-7) as catalysts and aqueous sulphuric, nitric[8] and phosphoric acids[9] as the reaction media. No substitute for potassium bromate has been reported so far. Detailed mechanism of this reaction has been proposed by Noyes and coworkers[10-14]. The purpose of this communication is to report that oscillations are observed when mixtures of acetone-tartaric acid and acetone-mandelic acid are used as organic substrates in Belousov-Zhabotinskii reaction.

Acetone (BDH), tartaric acid (BDH), mandelic acid (May & Baker), potassium bromate (Riedel), ceric sulphate (BDH), and sulphuric acid (Basynth) have been used without further purification.

Procedure — Chemical oscillations have been recorded by measuring e.m.f. across a bright platinum electrode and a calomel reference electrode dipped in the reaction mixture. The concentration of potassium chloride in calomel reference electrode was kept very low ($0{\cdot}0025M$) because chloride ions are known to inhibit chemical oscillations in Belousov-Zhabotinskii reaction. E.m.f. was recorded using an electronic recorder (Encardiorite Electronics Pvt. Ltd, Lucknow). The reaction was performed in a reaction cell[15] containing solutions of potassium bromate and ceric sulphate in $3N$ sulphuric acid. Solution of acetone and one of the organic acids ($3N$ sulphuric acid medium) was kept in the side limb of the cell which was fitted with a stopcock. The solution in the side limb was mixed with the main reactants in the cell by opening the stopcock. The solution was stirred electromagnetically. Experiments were performed at room temperature ($\approx 30°C$).

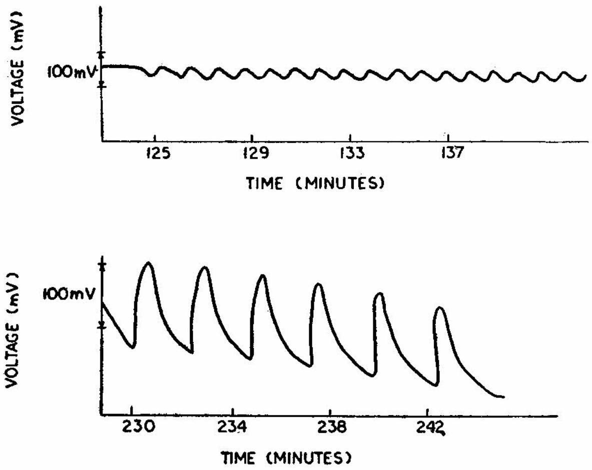

Fig. 1 — Chemical oscillations with acetone+tartaric acid as the organic substrate in B-Z reaction

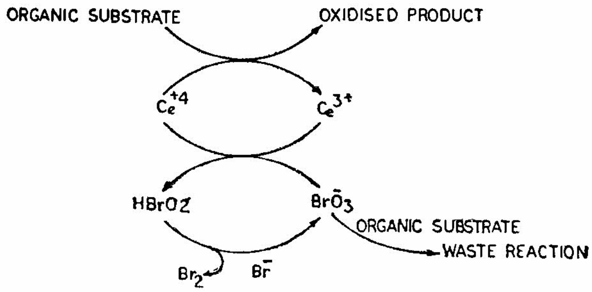

Fig. 2 — Chemical oscillations with acetone+mandelic acid as the organic substrate in B-Z reaction

Figs 1 and 2 show the type of oscillations which are observed in acetone-tartaric acid and acetone-mandelic acid systems. The characteristics of oscillations are recorded in Table 1.

It has been pointed out by Noyes and coworkers and Rastogi and coworkers that the primary reactions in Belousov-Zhabotinskii reagent are the

TABLE 1 — CHARACTERISTICS OF CHEMICAL OSCILLATIONS

[Potassium bromate = $0{\cdot}0404M$; ceric sulphate = $0{\cdot}0006M$; acetone = $0{\cdot}015M$; sulphuric acid = $1{\cdot}5M$; tartaric acid = $0{\cdot}0331M$; mandelic acid = $0{\cdot}0548M$]

Substrate	Time of initiation (minute)	Time period (minute)	Life time (minute)
Tartaric acid+acetone	125	1·0	54
Mandelic acid+acetone	225	2·4	80

oxidation reaction and bromination reactions coupled with the autocatalytic fromation of $HBrO_2$. The autocatalytic step would remain intact so long as cerous and bromate are in the mixture. The organic substrate in Belousov-Zhabotinskii reagent merely affects the rate of redox reaction and the bromination reaction. Since most of the organic compounds which showed oscillations have a reactive methylene group or a β-keto group, it was thought for quite sometime that such a group would be necessary for oscillation. It should be noted that β-keto group simply facilitates bromination.

It follows from the above arguments that a binary mixture of organic substrates one component of which undergoes bromination reaction and the other undergoes oxidation should also exhibit oscillations under suitable circumstances. Tartaric acid and mandelic acid do not undergo bromination whereas acetone can undergo bromination readily[16]. Tartaric acid and mandelic[17] acid are oxidized easily. It has been reported that acetone can also be oxidized by cerium[18] but perhaps the rates of oxidation of tartaric and mandelic are faster and hence a combination of acetone and tartaric acid and acetone and mandelic acid should exhibit oscillations. Since the expectation is experimentally satisfied, it follows that more organic substrates can be found which may have desired rates of oxidation and bromination to yield oscillations.

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Fourier Analysis of Chemical Oscillations

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Fourier analysis of oscillatory traces of e.m.f. versus time in Belousov-Zhabotinskii reaction having different organic substrates has been done. The number of significant harmonics have been ascertained.

SIGNIFICANT work on the mechanism of oscillations in Belousov-Zhabotinskii reaction has been reported recently[1,2]. Characteristics of oscillations have also been intensively studied[2-5]. Since typical oscillatory waves are obtained depending on the nature of reactants which are not periodic sine and cosine waves, it was thought of interest to perform Fourier analysis of the waves with the object of estimating the number of harmonics and characterization of oscillations.

Temporal oscillations in reaction systems (1) to (5) were experimentally studied.

Malonic acid + $KBrO_3$ + Mn^{2+} + H_2SO_4 ...(1)

Malonic acid + $KBrO_3$ + Ce^{4+} + H_2SO_4 ...(2)

Malic acid + $KBrO_3$ + Mn^{2+} + H_2SO_4 ...(3)

Citric acid + $KBrO_3$ + Mn^{2+} + H_2SO_4 ...(4)

Acetyl acetone + $KBrO_3$ + Mn^{2+} + H_2SO_4 ...(5)

The reaction was performed in a cell as was done by previous workers[4]. In all these systems the concentration of the organic substrate used was $0{\cdot}032M$, those of $KBrO_3$, Mn^{2+} (or Ce^{4+}, in system-2) and H_2SO_4 were $0{\cdot}044M$, $0{\cdot}008M$ $1{\cdot}5M$ respectively. The oscillations in e.m.f. denoting $[Ce^{4+}/Ce^{3+}]$ or $[Mn^{3+}/Mn^{2+}]$ were recorded by a potentiometric recorder (Encardiorite Electronics Pvt. Ltd, Lucknow) at 32°. The potentiometric traces are reproducible and characteristic of the system. These are represented in Fig. 1.

Any periodic function $f(t)$ of time t can be represented in general by Fourier series of the following type

$$f(t) = A_0 = A_1 \sin wt + A_2 \sin 2wt + A_3 \sin 3wt + \cdots + B_1 \cos wt + B_2 \cos 2wt + B_3 \cos 3wt + \ldots$$

where A_0, A_1, A_2, $\cdots$ and B_1, B_2, B_3, $\cdots$ are constants. w denotes the frequency. The number of sine and cosine terms in the series depends on the number of harmonics present in the system. The constant terms in the above equation can be evaluated by standard method described in the literature[6].

In case of system (3), a square wave is obtained and evaluation of constants is easy. For system (1), we observe that it is a combination of square wave and saw-tooth waves. In the case of (2), (4) and (5) the decay curves are parabolic curves. The equation for these cruves was fitted by the method of least squares and the Fourier constants evaluated. The results are recorded in Table 1 where y denotes the e.m.f. of the redox couple $[Ce^{4+}/Ce^{3+}]$ or $[Mn^{3+}/Mn^{2+}]$.

It should be noted that in the reaction where cerium ion is a reactant, noise in oscillations is