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$_2$SO$_4$. mandelic acid KBrO$_3$/Ce$^{4+}$/H$_2$SO$_4$ or tartaric acid/KBrO$_3$/Ce$^{4+}$/H$_2$SO$_4$ systems, oscillations are observed when acetone-mandelic acid or acetone-tartaric acid are used as the organic substrates.

OSCILLATORY chemical reactions are of current research interest due to their occurrence in biological systems. Among the oscillatory chemical reactions occurring in non-biological systems, Belousov-Zhabotinskii reaction has been studied extensively. 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-pentanediol as organic substrates; Ce(III), Mn(II), Fr(Phen)$_2$, Fe(Dipy)$_2$ and Ru(Dipy)$_2$ (ref. 5-7) as catalysts and aqueous sulphuric, nitric and phosphoric acids 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. 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 (0.0025M) 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 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 (~30°C).

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

![Fig. 1 — Chemical oscillations with acetone-tartaric acid as the organic substrate in B-Z reaction](image)

![Fig. 2 — Chemical oscillations with acetone-mandelic acid as the organic substrate in B-Z reaction](image)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Time of initiation (minute)</th>
<th>Time period (minute)</th>
<th>Life time (minute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tartaric acid + acetone</td>
<td>125</td>
<td>1.0</td>
<td>54</td>
</tr>
<tr>
<td>Mandelic acid + acetone</td>
<td>225</td>
<td>2.4</td>
<td>80</td>
</tr>
</tbody>
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oxidation reaction and bromination reactions coupled with the autocatalytic fomation 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 oscillations. 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. Tartaric acid and mandelic acid are oxidized easily. It has been reported that acetone can also be oxidized by cerium but perhaps the rates of oxidation and bromination are faster and hence a combination of acetone and tartaric acid and acetone and mandelic acid should exhibit oscillations. Since most of the organic compounds which showed oscillations have a reactive methylene group or a β-keto group, it was thought for quite some time that such a group would be necessary for oscillations. It should be noted that β-keto group simply facilitates bromination.

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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References
18. STEWART, R., Oxidation mechanism (W. A. Benjamin, New York), 1964, 81.