New experimental results on oscillatory aerial oxidation of aldehydes

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Some new experimental results on the oscillatory aerial oxidation of acetaldehyde, propionaldehyde and benzaldehyde in 90% acetic acid containing cobalt (II) acetate and sodium bromide are reported. It has been observed that benzaldehyde can be replaced by acetaldehyde or propionaldehyde but not by formaldehyde. Oscillations are not observed when cobalt (II) acetate is replaced by cobalt nitrate, cuprous chloride, cupric acetate and manganese acetate. Bromate ion or liquid bromine, however, can replace sodium bromide. Certain additives, viz., CCl₄, Hg²⁺ ions, KI, I₂, phenol, aniline, 1,10-phenanthroline, ethylenediamine, acetylacetone and hydroquinone quench the oscillations. Addition of sodium chloride to the oscillatory system yields different types of colour oscillations (blue to olive green) instead of pink to brown. A semi-batch reactor has been used to study oscillatory system containing acetaldehyde under controlled conditions of temperature, oxygen flow-rate and the reactant concentrations.

Jensen and coworkers¹-² have recently reported a new type of oscillatory reaction in a system containing cobalt (II) acetate, benzaldehyde and sodium bromide in 90% acetic acid. Oscillations in redox potential and variations in O₂ concentration in the liquid phase were found to occur. Oscillations in [Br⁻] in this system were reported by Rastogi and Das³, who also observed oscillations when benzaldehyde was replaced by acetaldehyde. Roelofs et al.⁴ have postulated a mechanism accounting for many observations recorded in the above system. Recently, EPR studies of Roelofs et al.⁵ have shown that benzoyl radicals and benzaldehyde cation radicals are formed during the reaction. Hudson et al.⁶ have also investigated recently oxidation of benzaldehyde in a continuous gas-liquid stirred cell reactor.

We report herein some new observations and more detailed studies on the oscillatory aerial oxidation of aliphatic aldehydes. Thus, we find that benzaldehyde can be replaced by acetaldehyde and propionaldehyde but not by formaldehyde. When sodium chloride is added, the colour oscillations between blue and dark olive green are observed. Bromide ions can be substituted by bromate ions or liquid bromine but cobalt (II) acetate cannot be replaced by cuprous chloride, cupric acetate, manganese acetate and cobalt nitrate. Effects of temperature, oxygen and certain additives on the oscillatory characteristics have also been studied. The results on oscillatory aerial oxidation of acetaldehyde under controlled conditions in a semi-batch reactor have also been reported.

Materials and Methods

The following chemicals were used as received: cobalt acetate (Sarabhai Chemicals, LR), sodium bromide (BDH, LR), acetaldehyde (Ferakberlin), benzaldehyde (BDH, LR), propionaldehyde (E. Merck), glacial acetic acid (Sarabhai Chemicals, LR), liquid bromine (AR), potassium bromate (Baker, AR), mercuric acetate (Sarabhai Chemicals, LR), phenol (Sarabhai Chemicals, LR), aniline (Sarabhai Chemicals, LR), 1,10-phenanthroline (BDH, LR), ethylenediamine (SDS), acetylacetone (Baker, LR), carbon tetrachloride (Sarabhai Chemicals, LR), potassium iodide (E. Merck, LR), iodine (Glaxo, LR), sodium chloride (Glaxo, LR), hydroquinone (S. Merck, LR).

Procedure: Monitoring of oscillations in a batch reactor

Oscillations in redox potential were monitored in a batch reactor. For this purpose the reactants except aldehyde were taken in an appropriate ratio in a beaker (100 ml capacity), vigorously stirred and heated at the desired temperature and maintained with an accuracy of ±0.5°C. On the addition of calculated amount of an aldehyde, the colour of reaction mixture turned to dark brown and oscillations in colour between dark brown and pink were observed.

A bright platinum electrode and a reference calomel electrode were used to monitor redox potential changes. Dilute KCl (0.1 N) was filled in the calomel electrode to suppress inhibition of oscillations by Cl⁻ at higher concentrations. Potential changes were recorded using a x-y/t recorder (Encardio-rite, India). Redox potential changes in the oscillatory system CH₃CHO-Co(AcO)₂-NaBr were studied at varying [acetaldehyde] and [sodium bromide] while those in the system CH₃CHO-Co(AcO)₂-KBrO₃ at varying [BrO₃⁻].

Experiments were also carried out using liquid Br₂ in place of NaBr. Similar experiments were also carried out by taking cuprous chloride, cupric acetate, manganese acetate and cobalt nitrate in place of cobalt acetate in acetaldehyde and benzaldehyde systems.

Influence of various parameters on the nature of oscillations

The experiments to study the influence of temperature, O₂, Cl⁻ and additives on the nature of oscillations were carried out at 76 ± 1 and 81 ± 1°C for all the three systems.

In order to study the effect of atmospheric oxygen on oscillations in the system Co(AcO)₂-NaBr-CH₃CHO, the reaction cell was closed by an air tight stock cock. Visual observations showed that oscillations continued for sometime and finally stopped. The oscillations again started on opening the stop cock.

Addition of Cl⁻ on the oscillatory behaviour of system containing acetaldehyde/benzaldehyde was studied. The concentration of Cl⁻ ions in the system containing acetaldehyde was 2.7 x 10⁻² M while that in the system containing benzaldehyde it was 2.5 x 10⁻² M.

The influence of certain additives, viz. mercuric acetate, phenol, aniline, 1,10-phenanthroline, ethylenediamine, acetylacetone, hydroquinone, carbon tetrachloride, potassium iodide and iodine on the oscillatory characteristics in systems containing acetaldehyde and benzaldehyde was also studied.

Monitoring of oscillations in a semi-batch reactor

Experiments were carried out under controlled conditions in a semi-batch reactor. Experimental set-up consisted of a conning glass reaction cell fitted with a platinum electrode (P), a calomel electrode (C₁) and thermometer (T₁) (see Fig. 1). In order to prevent changes in the concentrations of reactants due to evaporation, a water condenser (C₁) and a long tube (LT) were attached. Air with controlled flow rate was passed through the reactor in a nozzle (O) and a compressor (C₃). The air flow rate was determined by water displacement method. The outlet of the nozzle (O) was kept above the surface of the oscillatory solution (S₁) to minimize disturbance at the surface. The solution was stirred with the help of a magnetic stirrer. The reactor was put in a water thermostat which could be maintained at the desired temperature with an accuracy of ±0.5°C.

The redox potential changes were monitored using a bright platinum electrode and a calomel reference electrode connected to the negative and positive terminals respectively of the recorder. Experiments were carried out at various reactant concentrations.

Spectrophotometric studies

Absorption spectra of various reaction systems were taken using Spectronic 100I and Bausch and Lomb spectronic 2000 spectrophotometers. Acetic acid/water mixture (90:10 w/w) was used as a reference solution.

Results and Discussion

Typical potentiometric traces depicting oscillations in the systems (i) cobalt (II) acetate-sodium bromide-acetaldehyde (ii) cobalt (II) acetate-sodium bromide-propionaldehyde and (iii) cobalt (II) acetate-sodium bromide-benzaldehyde systems in a batch reactor are shown in Fig. 2. Oscillations are not observed within the temperature range studied when formaldehyde was substituted for benzaldehyde. Oscillations in colour in the case of other aliphatic aldehydes are of the same-type
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Figure 2—Redox potential changes as a function of time for various oscillatory systems. Curve (a): [Co( AcO)₂] = 23 mM; [NaBr] = 4.7 mM; [CH₃CHO] = 200 mM; temp. = 81 ± 1°C. Curve (b): [Co( AcO)₂] = 18 mM; [NaBr] = 7.3 mM; [C₆H₅CHO] = 200 mM; temp. = 76 ± 1°C. Curve (c): [Co( AcO)₂] = 20 mM; [NaBr] = 4.0 mM; [C₆H₅CHO] = 800 mM; temp. = 81 ± 1°C. P and B denote pink (low potential) and brown (high potential) stages respectively. Origin for the two axes is arbitrary in this and subsequent figures.

Figure 3—Redox potential changes as a function of time for various oscillatory systems when Br₂ is used in place of NaBr. Curve (a): [Br₂] = 3.7 mM; [Co( AcO)₂] = 25 mM; [CH₃CHO] = 300 mM; temp. = 81 ± 1°C. Curve (b): [Br₂] = 3.7 mM; [Co( AcO)₂] = 25 mM; [C₆H₅CHO] = 200 mM; temp. = 76 ± 1°C. Curve (c): [Br₂] = 1.7 mM; [Co( AcO)₂] = 23 mM; [C₆H₅CHO] = 900 mM; temp. = 81 ± 1°C.

Figure 4—Potentiometric traces of oscillatory systems containing cobalt acetate + sodium bromide + acetaldehyde benzaldehyde before and after addition of sodium chloride at 82 ± 1°C. Curve (a): [Co( AcO)₂] = 21 mM; [NaBr] = 8.3 mM; [CH₃CHO] = 300 mM; [NaCl] = 27 mM. Curve (b): [Co( AcO)₂] = 19 mM; [NaBr] = 3.9 mM; [C₆H₅CHO] = 700 mM; [NaCl] = 25 mM. P, B, Bl and Dg denote pink, brown, blue and olive green states respectively. The arrows indicate the instant at which NaCl was added to the system.

The following changes occur during oscillations when Cl⁻ is added to the reaction mixture:

(pink) octahedral Co(II) ⇌ (Brown) octahedral Co(III)

(Blue) tetrahedral Co(II) ⇌ (Olive green) octahedral Co(III)

In order to have an insight into the nature of species, absorption maxima of different sub-systems were determined and the results are recorded in Table 1. Absorption spectra of both olive green and dark brown complexes exhibit λ_max at 607 and 646 nm
respectively. The maximum absorption ($\lambda_{\text{max}}$) for brown complex in solutions containing (i) cobalt (II) acetoacetdehyde (ii) cobalt (II) acetate-benzaldehyde was found to be 600 nm (Table I) whereas the value reported by Yuon and Noyes for the latter was 620 nm. It shows that the brown species produced in benzaldehyde and acetaldehyde systems contain Co(III).

Oscillations are stopped on the addition of Hg$^{2+}$, aniline, phenol, 1,10-phenanthroline, ethylenediamine, acetylacetone, hydroquinone, KI, I$_2$ and CCl$_4$. Addition of Hg(CH$_3$COOH) is found to stop the oscillations since Br$^-$ ions are removed due to formation of complex. Phenol and aromatic amines$^9$-$^{11}$ both act as antioxidants probably due to hydrogen atom transfer as follows:

$$\text{ROO}^- + \text{ArOH} \rightarrow \text{ROOH} + \text{ArO}$$
$$\text{ROO}^- + \text{ArNH}_2 \rightarrow \text{ROOH} + \text{ArNH}$$

Phenol and aniline may also act as scavengers for Br$_2$. 1,10-Phenanthroline, ethylenediamine and acetylacetone stop the oscillations since these form the corresponding cobalt complexes. Hydroquinone also stops the oscillations because it combines with free radicals$^{10}$. Carbon tetrachloride is miscible in the reaction mixture and the oscillations are stopped on addition of 1.45 and 1.38 mmoles of CCl$_4$ respectively in oscillatory systems containing acetaldehyde and benzaldehyde. Potassium iodide oscillations since Br$_2$ produced in the reaction generates I$_2$, on interaction with KI. The molecular iodine produced acts as a radical inhibitor$^9$.

No oscillations were observed when cobalt (II) acetate was replaced by manganese acetate, cuprous chloride, copper (II) acetate and cobalt (II) nitrate. Experiments were also carried out under controlled conditions, viz. temperature, reactant concentration, oxygen flow rate in a semi batch reactor shown in Fig. 1. Experimental results for the system containing acetaldehyde are shown in Figs 5-7.

It has been observed that oscillatory characteristics depend on the reactant concentration. Time period ($t_p$) decreases with increase in [Br$^-$] (Fig. 8) and [CH$_3$CHO] (Fig. 9). Roelofs et al.$^4$ also observed similar trend.

Our results are fitted by the Eqs (1) and (2):

$$t_p = \frac{3.4 \times 10^3}{[\text{Br}^-]} - 148 \quad \text{cor. coeff.} = 1$$

$$t_p = \frac{103}{[\text{CH}_3\text{CHO}]} - 74 \quad \text{cor. coeff.} = 0.99$$

Within the experimental range of parameters studied. However, no regular trend in oscillatory characteristics could be observed for the variation of [Co(AcO)$_2$].

Autoxidation of acetaldehyde and propionaldehyde is a free radical chain reaction. The free radicals CH$_3$CO and C$_2$H$_5$CO$^-$ in case of acetaldehyde and propionaldehyde respectively are the most important radical species and correspond to the C$_6$H$_5$CO$^-$ radical species postulated in the aerial oxidation of benzaldehyde. Hence we would expect that oscillatory features of the aerial oxidation of aliphatic aldehydes would be similar to those of

<p>| Table I - Absorption maxima obtained for various systems containing Co(II) and Co(III) |</p>
<table>
<thead>
<tr>
<th>System</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Cobalt (II) acetate solution</td>
<td>510</td>
</tr>
<tr>
<td>(ii) Cobalt (II) acetoacetdehyde</td>
<td>600</td>
</tr>
<tr>
<td>(iii) Cobalt (II) acetate-benzaldehyde</td>
<td>600</td>
</tr>
<tr>
<td>(iv) Cobalt (II) acetoacetdehyde treated with H$_2$O$_2$</td>
<td>530</td>
</tr>
<tr>
<td>(v) Cobalt (II) acetate-benzaldehyde treated with H$_2$O$_2$</td>
<td>530</td>
</tr>
<tr>
<td>(vi) Cobalt (II) acetoacetdehyde treated with liq. Br$_2$</td>
<td>540</td>
</tr>
<tr>
<td>(vii) Cobalt (II) acetate-benzaldehyde treated with liq. Br$_2$</td>
<td>490</td>
</tr>
<tr>
<td>(viii) Cobalt (II) acetoacetdehyde-Br</td>
<td>646</td>
</tr>
<tr>
<td>(ix) Cobalt (II) acetate-NaBr-benzaldehyde-Cl</td>
<td>607</td>
</tr>
</tbody>
</table>

*All solutions except aldehyde and H$_2$O$_2$ prepared in acetic acid-water (90:10, wt. wt) medium.

*Reported in ref. 8.
It may be noted that YN mechanism is simpler. The key steps of YN mechanism are shown in Scheme 1. It is easy to identify the autocatalytic step. When the ratio $[\text{Br}_2]/[\text{O}_2]$ becomes significant enough, net destruction of benzoyl radicals becomes faster than autocatalytic formation. The concentration of radicals then falls until the consumption of Co(III) and the transport of oxygen from the gas reduce $[\text{Br}_2]/[\text{O}_2]$ ratio to the point that autocatalysis again becomes dominant. Since Br₂ can scavenge these radicals, role of Br₂ can not be ignored in formulating a mechanism to account for all the experimental features. The experimental observations can be easily explained in terms of this picture in a qualitative fashion.

Scheme 1

Acknowledgement

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References


