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OSCILLATORY REACTIONS AND AERIAL OXIDATION OF ALDEHYDES

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ABSTRACT

General concepts of different types of oscillatory chemical reactions and aerial oxidation of aldehydes are given. Batch, semi-batch and continuously stirred tank reactors (CSTR) were designed and a comprehensive review on experimental and computer simulation results related to oscillatory aerial oxidation of benzaldehyde, acetaldehyde and propionaldehyde are also reported.

Keywords: aldehydes, OSCILLATORY & propionaldehyde

Oscillatory reactions and oscillatory phenomena are of considerable current interest. The study of oscillating chemical reactions is among the most fascinating chemical demonstrations [1]. It is an exciting area of research. A number of examples of oscillatory and related phenomena suggested that chemical oscillations and multistability [2-4]are a frequent form of behavior in far from equilibrium systems [5].The oscillatory behavior of reaction is indicated by the periodic variation of some property of the system with time or space. Accordingly, it is prefixed with the word temporal or spatial chemical oscillations are important from the point of view of understanding the biological control processes and might suggest useful models for interpreting some of the basic processes of life.

Among the dynamical phenomena, most commonly seen in chemical reactions are:

(i) Damped oscillations
(ii) Simple periodic or sustained oscillations
(iii) Complex periodic oscillations
(iv) Chemical chaos

These are represented in Fig. 1.

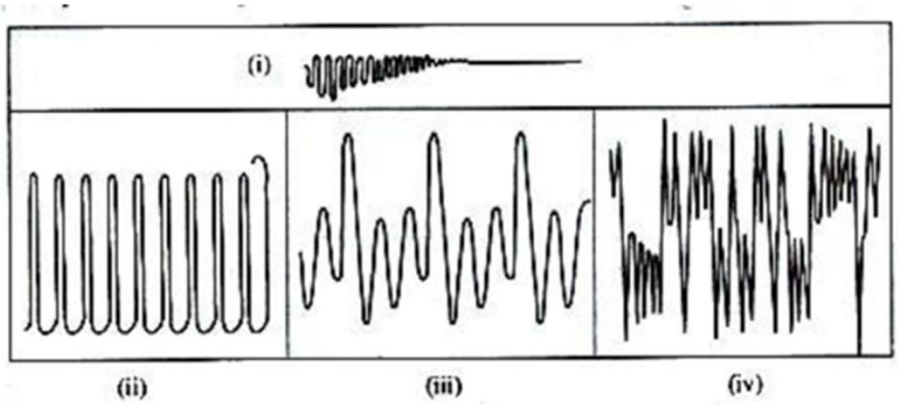

Fig. 1. Traces showing the various types of chemical oscillations (i) Dampedoscillation (ii) Simple periodic or sustained oscillation (iii) Complex periodicoscillation and (iv) Chemical chaos.

Work on oscillatory reactions has already made significant contributions to physical chemistry, especially chemical kinetics [4, 6-12].Mechanism of extremely complicated chemical reactions can be elucidated and put on firm ground by combining kinetic and constants deduced for a number of reactions. Rastogi *et al* [13] have described a low cost laboratory experiment for the demonstration of chemical oscillations using a locally fabricated colorimeter. The chemical oscillations are undoubtedly important to understand biological processes.

Conditions for oscillatory behavior:

Four conditions are required for oscillations to occur in a chemical system.

(i) The system must be maintained far from equilibrium.

(ii) The system must contain at least one autocatalytic reaction step of the type $A + X \rightarrow 2X$

(iii) There should be two steady states for the system at its initial conditions.

(iv) The values of the rate constants of component reactions must differ appreciably.

Closed systems show such behaviour for a limited time until thermodynamic equilibrium is achieved but oscillations are most readily apparent in open reactions such as Continuously Stirred Tank Reactor (CSTR).

Classification of Oscillatory Reactions:

Oscillatory reactions may be classified as:

(I). Oscillatory reactions in biological systems

(II). Oscillatory reactions in non biological systems.

(I). Oscillatory reactions in biological systems:

There is considerable interest in the study of oscillatory reactions in biological systems [6]. Many examples of biochemical and cellular oscillations are known and have been extensively studied. The glycolytic oscillations, oscillations in NADH and soluble enzyme systems are good examples of biochemical oscillations. Oscillatory phenomenon in muscles, in enzyme synthesis, in the rate of β-glycosidase synthesis, in asynchronously growing cultures of *E.coli*, *etc*. *A*ll these belong to this class of oscillatory reactions. Oscillations in biological and artificial membranes have attracted the attention of chemists in recent years. The first systematic study of sustained potential oscillations in an artificial membrane system was carried out. The system consisted of a porous plug or an ion exchange membrane separating two electrolyte solutions of different concentrations upon driving a constant electric current through the membrane. Periodic phenomena in biological systems may be classified as follows:

(a). Oscillations in enzymatic reactions.
(b). Oscillations in the synthesis of enzymes at the cellular level.
(c). Oscillations in the super cellular level.
(d). Rhythmic activity of the nervous system.
(e). Oscillations in Membranes.

Oscillatory reactions in non-biological systems:

In non biological systems, several reactions are known to exhibit oscillations. It may broadly be classified as:

(a). Homogeneous oscillations.
(b). Heterogeneous or non homogenous oscillations.
(c). Thermochemical oscillations.
(d). New chemical oscillatory reactions.
(e). Electrochemical oscillations.

(a). Homogeneous oscillations:

We can briefly describe homogenous oscillatory reactions in the following categories: (i). Iodate oscillators, (ii). Chlorite oscillators, (iii). Bromate oscillators and (iv). complex oscillators.

There are two peroxide iodate based oscillating systems (a) the acidic hydrogen peroxide and iodate in system (IO_3^- - H_2O_2), known as the Bray-Liebhafsky (BL) oscillator and (b) a system containing IO_3^-- H_2O_2 - Mn^{2+} - reductant, known as the Brigg's Rauscher (BR) type oscillator. These two systems show different oscillatory characteristics although the two systems have some components in common.

Chlorite driven oscillations in CSTR as well as in batch conditions have been reported.

The chlorite oscillators may be classified as follows: (i) Iodine containing chlorite oscillators eg. ClO_2^- - I^-, ClO_2^- - I^- -oxidant (*e.g.* IO_3^- - MnO_4^-) and ClO_2^- - IO_3^-/I_2 - Reductant (organic/Inorganic). (ii) Bromate containing clorite oscillators e.g. ClO_2^-- BrO_3^- -B_r^- and ClO_2^- - BrO_3^--reductant [e.g. SO_3^{-2}, Fe $(CN)_6^{-4}$] (iii)Thiosulphate containing chlorite oscillators (e.g.ClO_2^- - $S_2O_3^{-2}$, ClO_2^- - $S_2O_3^{-2}$ - oxidant e.g. IO_3^-).

Bromate ion driven chemical oscillators have played a critical role in the development of solution phase oscillating chemical reactions. Bromate oscillators may be classified as (i).uncatalyzed bromate oscillators, (ii). non-bromide ion controlled oscillators and (iii). catalyzed bromate oscillators. This class of oscillator may further be classified as(i) minimal oscillator (e.g. BrO_3^-- Br^- – Mn^+) where Mn^+ is the metal ion (ii)Oscillators having organic reductants (e.g. BrO_3^- - Mn+ - organic reductant), It is of two types:(i) classical B-Z reaction system having only one organic reactant(ii) B-Z reaction system having mixed organic substrate, (iii) B-Z system having inorganic reactant and (iv)The most prominent class of complex oscillators became known under the name of chaos. Chaotic oscillations are mainly characterised by the presence of an infinite number of periodic solutions plus an uncountable number of non periodic oscillating solutions. Chaos can also be obtained by periodically forcing an oscillatory system such as in cardiac cells and yeast glycolysis. Coupled oscillators are also receiving attention. It is possible to couple two bistable auto catalytic systems through a common intermediate. A system consisting of ClO_2^- - BrO^-_3& I^- ions in a CSTR exhibits a variety of dynamical phenomena which may be attributed to the coupling of the component ClO_2^-- I^- and BrO_3^-- I^- oscillatory subsystems. The discovery of birhythmicity in a coupled oscillator system is of special significance.

(b) Heterogeneous or Inhomogeneous oscillations:

Certain chemical systems do not oscillate, but when coupled to some physical processes such as diffusion, show the oscillatory behaviour. A well known example belonging to this class of reaction is the catalytic decomposition of hydrogen peroxide by mercury in slightly alkaline solution. It is periodic in nature due to the periodic breakdown and formation of a protective oxide film on the mercury surface.

(c) Thermochemical oscillations:

Periodicities originating in temperature changes have been reported in the combustion of hydrocarbon fuels vapour phase chlorination of methyl chloride[6]and oxidation of hydrogen sulphide.

(d) New chemical oscillatory reactions:

Oscillating chemical reactions are no more restricted to the reactions of oxyhalogen

ions but have extended to different oxidation reactions of sulphur compounds and to the aerial oxidation of some aromatic aldehydes. Some new chemical oscillatory reactions are

(i) Copper catalyzed oxidation of thiosulphate and thiocyanate by H_2O_2.e.g.
- (a) Cu^{2+} - $S_2O_3^{-2}$ - H_2O_2system and
- (b) $CuSO_4$ - KSCN- H_2O_2 - NaOH system.

(ii) Oxidation of S^{-2} by H_2O_2 and HS^- by bromate ion e.g.
- (a) S^{2-} - H_2O_2 system
- (b) HS^--BrO_3^- system

(iii) Silver ion catalyzed oxidation of sulphide by per sulphate e.g.
S^{2-} - $S_2O_8^{-2}$ - Ag^+ system

(iv) Silver ion catalyzed oxidation of oxalic acid by persulphate in aqueous solution of H_2SO_4e.g.
$S_2O_8^{-2}$ - $(COOH)_2$ - Ag^+ system.

(v) Oxidation of thiourea by iodate and bromated ions e.g.
- (a) IO_3^- - CS $(NH_2)_2$ system
- (b) BrO_3^--CS $(NH_2)_2$ system

(vi) Reaction between $KMnO_4$, H_2O_2 and H_3PO_4 ,$KMnO_4$ - H_2O_2 -H_3PO_4 system.

(vii) Iodate oxidation of sulphite in presence of ferrocyanide e.g.
KIO_3 - K_4[Fe $(CN)_6$] – Na_2SO_3 - H^+ system.

(viii) Air oxidation of sulphide ion to poly sulphide catalyzed by methylene blue.

(ix) Gas evolution oscillator (NH_4NO_2 oscillator).

(x) A new iodate driven non periodic oscillatory reaction in a Continuously Stirred Tank Reactor (CSTR) [4].The reaction between potassium iodate and H_3AsO_3 takes place as follows which auto catalytically produces I^- .

$$3\ H_3AsO_3 + IO_3^- \rightarrow 3H_3AsO_4 + I^-$$

Oscillations have been observed in this system using a CSTR as shown in Fig.2.

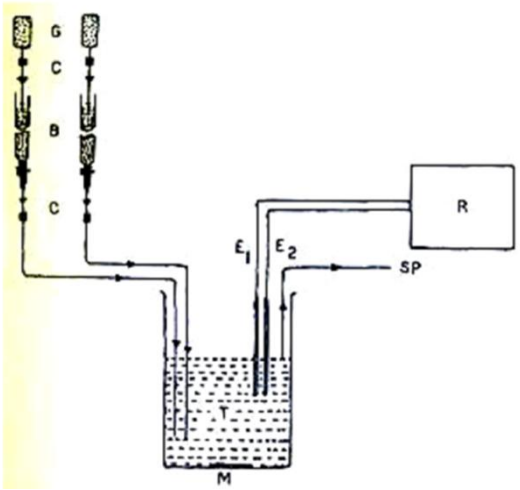

Fig.2. Experimental setup of the continuously stirred tank reactor. G, reactant reservoir ; C, control valves; E_1, silver-silver-iodide or platinum electrode; E_2, calomel electrode; R,reorder; SP, suction pump, T, reactor; M, magnetic stirrer [4].

Solution was prepared in a sulfate-bisulfate buffer of pH 1.5. The arsenous acid and iodate solutions were fed to the CSTR (40.0 ml. volume) at definite flow rates from glucose bottles through polyethylene tubes. The level of the solution in the CSTR was kept constant by a continuous outflow of solution using a suction pump. The solution in the CSTR was stirred with a magnetic stirrer at ~ 800 rpm. Visual oscillations in colour (yellow colourless) were immediately observed. Since in blank experiments the temperature rise in the oscillating reaction system was found to be insignificant (0.1 ^{0}C), experiments with a CSTR were performed at room temperature. The visual oscillation in colour was observed along with oscillations in redox potential and [I^-].The course of the reaction was monitored by noting the potential change of the platinum electrode with reference to the calomel electrode while[I^-] was monitored by Ag/AgI electrode coupled to a calomel electrode with an electronic recorder. The influence of ClO_3^-, CI^-, ClO_4^- and $NaHCO_3$ on the oscillations was studied. The occurrence of oscillations depends on the magnitude of k_0, the reciprocal of residence time (flow rate / reactor volume). Oscillations were found to occur when the value of $k_0$was between 0.0175 and 0.07 min^{-1}. Oscillations did not occur with k_0= 0.14 min^{-1}. Further, when k_0 was kept equal to 0.035 min^{-1}, the [Arsenite] was fixed and only the iodate concentration was varied, oscillations were found to occur in the range 0.1068- 0.1268 M for [IO_3^-] .Beyond this concentration, the system displayed bistability and switched to another state. Similarly, for the same k_0, when [IO_3^-] was kept equal to 0.1168 M and only [Arsenite] was varied, again oscillations were found to occur in the range 0.1539 - 0.3078 M. Oscillations cannot occur when [Arsenite] = 0.6156 M, while it switched to another steady state when [Arsenite] = 0.0769 M. Oscillations were also studied for the case when k_o was varied by varying the flow rate of iodate , keeping the arsenite flow rate fixed.

Salt water oscillator:

The salt-water oscillator was reported by the Japanese Scientists Yoshikawa *etal*[14] which may be useful for students of biology, chemistry and physics in understanding the non-equilibrium dynamics in a far from equilibrium conditions. Rhythmic oscillations of water flow were generated when vertically oriented syringe was filled with salt water and partially submerged in beaker. Experimental description is given in the paper by Yoshikawa *etal*[14].The oscillations appeared as a downward jet of salt water followed by an upward jet of pure water and so on. Later on, a simple explanation of this oscillator was given by Noyes [15]and new experimental results by Rastogi *etal*[16]. Periods up and down flow could be easily monitored from the measurement of electrical potential between the salt-water and pure water.

Electrochemical oscillations:

Electro chemical reactions with non-linear kinetics give rise to various dynamic self organization phenomena such as oscillations and spatio-temporal pattern formation [17-19]. Oscillatory electrodeposition and the formation of ordered dendrite structures provide a new possibility to prepare controlled 2D or 3D micro and nano structures on solid surfaces [20].Oscillatory electrodeposition results were also reported by Rastogi et al [9]. Nakanishi et al [20] have reported metal latticeworks formed by self- organization in oscillatory electrodeposition. Das and Ansari [21] have reported non-equilibrium growth patterns and oscillations during electrochemical deposition of Zn - Cu binarysystem in batch and flow reactors.This phenomenon has also been observed during electro polymerisation of pyrrole [11] and aniline [22]. A typical plot showing anode potential changes during electrochemical polymerization of nano structured aniline and corresponding morphologies are shown in Fig.3.

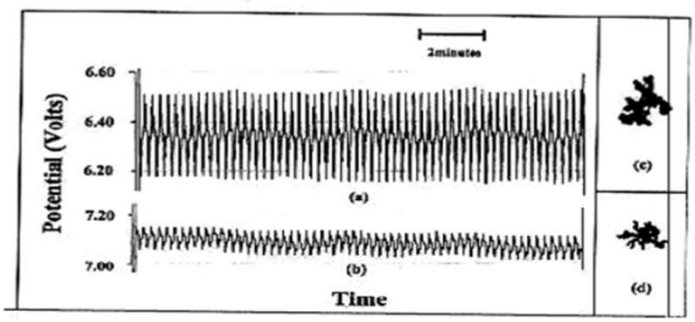

Fig.3. Anode potential changes with time (a, b) and corresponding morphologies of the polymer aggregates (c, d) obtained during electro polymerization of aniline [22].

Oscillations during aerial oxidation of aldehydes:

The term aerial oxidation is applied generally to the comparatively slow oxidation which can be affected by the free oxygen e.g. air. The aerial oxidation of organic compounds has long been the subject of great economic importance. The aerobic oxidation of aldehydes has recently been described by Vanoye *etal*[23] who emphasized that oxosynthesis was the most important process for producing higher aldehydes. In spite of the factthat aerial oxidation of aldehydes is an interesting class of oscillatory reaction, it hasnot been extensively studied as B- Z reaction. The technical literature concerning the subject on autoxidation of aldehydes is uncoordinated.

A new reaction was discovered by Jensen [24].He reported that during the aerial oxidationof benzaldehyde catalysed by cobalt and bromide ions, the solution oscillates between pink and brown. The colour change was accompanied by redox potential changes between 5 and 60 mV and can occur for several hours. Later on, experiments were performed at different conditions and results were reported.

Rastogi and Das [25]observed oscillations during the aerial oxidation of benzaldehyde and acetaldehyde in 90/10 acetic acid/water (w/w) solvent catalyzed by cobalt and bromide ion and observed for several hours.The colour change was accompanied by a change in the redox potential.The pink colour corresponds to a low Co (III) /Co (II) ratio while the brown/black colour corresponds to a high Co (III) /Co (II) ratio. A typical trace is shown in Fig.4 (a) which represents oscillations as a function of time during aerial oxidation of aldehydes.

During aerial oxidation of benzaldehyde , Rastogi and Das [25] concluded that:

1. All the reactions NaBr, Benzaldehyde or acelatdehyde and cabalt acetate areessential for producing oscillation.
2. Colour changes from pink to brown and redox potential during oscillations.
3. Hydroquinone stops the oscillations.
4. Autocatalytic reactions are the important steps in the oscillatory reaction mechanism.

The Pink colour and the brown colour correspond to reduced and oxidised states respectively. The cobalt (II) acetate exhibited absorption maximum at 510 mm. Autoxidation is a free radical chain process. Once free radicals are formed, they react in a chain to convert the material to a hydroperoxide. The chain is ended by termination reactions, in which free radicals enter to form a new bond. In general, there are following three stages:

(i). Chain initiation.
(ii). Chain propagation.
(iii). Chain termination.

Control conditions must be used to obtain reproducible results. The air must be added continuously and vigorous changing conditions often take a dramatic effect particularly on the frequency of oscillations. Experimental results also depend on temperature [Co (II) acetate], [PhCHO], [Br^-] and flow rate.

Based on the experimental observations, a tentative mechanism could be written as shown in scheme I

$$Ø\ CHO + O_2 \rightarrow Ø\ CO^{\bullet} + HO_2^{\bullet} \quad (1)$$

$$Ø\ CHO + HO_2^{\bullet} \rightarrow Ø\ C\ OOH + {}^{\bullet}OH \quad (2)$$

$$Ø\ CO^{\bullet} + HO_2^{\bullet} \rightarrow Ø\ COOOH \quad (3)$$

$$Co(II)_{aq} + Br^- \rightarrow [Co(II)Br_4]^{2-} \quad (4)$$

$[Co(II)Br_4]^{2-}$ + Ø COOOH $\rightarrow$ Co (II) complex (5)

Co(II) complex + $O_2 \rightarrow$ Co(III) complex (6)

Co(III) complex + Ø CHO $\rightarrow$ Co(II) complex + Ø COOH (7)

Scheme I

Steps similar to (5) and (6) have been postulated to explain the mechanism of oxidation of acetaldehyde. Aerial oxidation of acetaldehyde follows the mechanism as shown in scheme II

$CH_3 CHO + O_2 \rightarrow CH_3CO + HO_2$ (8)

$CH_3CO + O_2 \rightarrow CH_3 CO_3$ (9)

$CH_3 CO_3 + CH_3CHO \rightarrow CH3\ CO_3H + CH_3 CO$ (10)

$CH_3 CO_3H \rightarrow CH3COO + OH$ (branching reaction etc.) (11)

Scheme II

A comparison of the mechanisms of aerial oxidation of benzaldehyde and acetaldehyde revealed that there was a strong possibility of participation of free radicals in the oscillatory reaction. This is supported by the fact that the oscillations are quenched by hydroquinone as shown in Fig. 4 (b).

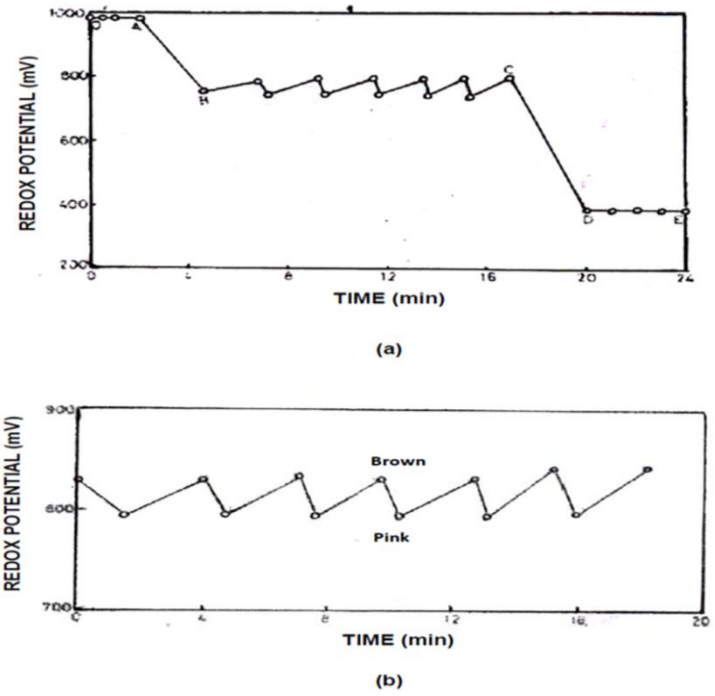

Fig.4. (a) Redox potential changes as a function of time during aerial oxidation ofBenzaldehyde catalysed by cobalt and bromide ions at 80° C . (b) Redox potentialchanges as a function of time when Na Br was added at stage A andhydroquinone at stage C in the reaction system containing cobalt acetate, benzaldehyde and acetic acid (90%) [25].

Further, it appeared that the free radical $C_6H_5CO^{\cdot}$was auto catalytically produced. This is in agreement with the investigations on the reaction by Jensen [24].One of the most convincing proof of the mechanism would be that aerial oxidation of acetaldehyde in presence of Co (II) was also oscillatory.

Roelofs *etal*[26]proposed a mechanism of an oscillatory oxidation of benzaldehyde with O_2 catalyzed by Co/Br. They described the time dependence of dissolved oxygen, $[Co^{3+}]$ and PhCHO concentrations and suggested a mechanism to account for the oscillation. They postulated that in one stage of oscillation, benzoyl radical reacts primarily with oxygen while in the second; benzoyl was oxidized by Co^{2+}. During Stage I, potential of the Pt electrode increased slowly with the time until it reached a maximum. At the maximum the colour of the solution was dark green, characteristic of Co^{3+} in acetic acid. In Stage II potential decreased to a minimum. At the minimum, the solution exhibited the pale pink colour of Co^{2+} in acetic acid. To account for these observations, Roelofs *etal* also proposed the following mechanism for the oxidation.

Roelofs *et*al [27] presented a substantially expanded experimental investigation and an elaborated mechanism. They proposed a mechanistic model in which the reaction proceeds alternately between two Stage I and II. The model gave a satisfactory agreement with a number of qualitative and quantitative features. Roelofs and Jensen[28] further studied the oxidation of benzaldehyde. EPR studies detected two free radically (g = 2.0033 and 2.0042) these experimental results were compared with the predictions of a mechanistic model for the oscillation.

Roelofs *et* al [28] subsequently proposed an eleven step mechanism for oxidation which stimulates oscillatory behavior, which was elaborated in a subsequent publication and given in scheme III

$(Co^{3+}{}_2 + Br^-(Co^{3+})_2\ Br^-$ (R1)

$(Co^{3+})_2Br^- + PhCHO \rightarrow PhCO^{\cdot} + Br^- + Co^{3+} + Co^{2+} + H^+$ (R2)

$PhCO^{\cdot} + O^2(l) \rightarrow PhCO_3^{\cdot}$ (R3)

$PhCO^{\cdot} + (Co^{3+})_2 + H_2O \rightarrow PhCO_2^{\cdot} + 2Co^{2+} + 2H^+$ (R4)

$PhCO^{\cdot} + (Co^{3+})_2 \rightarrow 2\ PhCO_2^{\cdot}$ (R5)

$PhCO_3^{\cdot} + PhCHO \rightarrow 2PhCO3H + PhCO^{\cdot}$ (R6)

$PhCO_3^{\cdot} + Co^{2+} + H^+ \rightarrow PhCO_3H + Co^{3+}$ (R7)

$PhCO_2^{\cdot} + PhCHO \rightarrow PhCO_2H + PhCO^{\cdot}$ (R8)

$PhCO_3H + 2\ Co^{2+} + 2\ H^+ \rightarrow PhCO_2H + (Co^{3+})_2 + H_2O$ (R9)

$Co^{3+} + Co^{3+} \rightarrow (Co^{3+})_2$ (R10)

$O_2(g) \rightarrow O_2(l)$ (R11)

Scheme III

Initiation steps R_1 and R_2 used a dimer ($Co^{3+})_2$, to produce a benzoyl radical at a rate proportional to the product of [PhCHO], [Br^-], and[($Co^{3+})_2$] .

Boga [29] described for first time a propagating reaction front in the dissolved oxygen- cobalt acetate – benzaldehyde closed system. The autocatalytic nature of the reaction raised the possibility of propagating reaction. They found that the velocity of the front increased with the concentration of the benzaldehyde and dissolved oxygen.The experimental findings were interpreted on the basis of a simplified version of the proposed mechanism of the reaction.

Colussi *etal* [30]have extended the experimental observations on oscillatory aerial oxidation of benzaldehyde in 90% aqueous acetic acid at 70^{o}C and found that the oxidation of the benzaldehyde to benzoic acid by air and catalyzed by Co(II) and bromide. Considering the observations of Jensen [26] they found that the rate of formation of Co (III) increased exponentially. They also found in their detailed investigation that free Br_2 was formed and could be entrained by gas flow; they proposed a detailed molecular mechanism for the oscillations and suggested additional experiments and computations.

Guslander *etal*[31]have simulated the oscillatory catalyzed oxidation of benzaldehyde by a skeleton model with only three independent composition variables and four chemical steps known as Cobaltator. The proposed model consisted of the following steps.

O_2 (g) $\rightleftharpoons$ O_2(solution) C1

O_2 (soln) + $R^{\bullet}$ $\longrightarrow$ g Co (III) C2

Co (III) $\longrightarrow$ $R^{\bullet}$ C3

Co (III) + $R^{\bullet}$ $\longrightarrow$ m $R^{\bullet}$ C4

This model involved only three variables O_2(soln), $R^{\bullet}$ and Co(III). O_2 (g) represents the constant supply of atmospheric oxygen available the system. The stoichiometric corfficients g and m must have values 3 and 1.1 respectively to exhibit oscillations.

Rastogi, Das*et* al [32]have also extended the work on oscillatory aerial oxidation of aldehydes in a semi-batch reactor as shown in Fig.5.

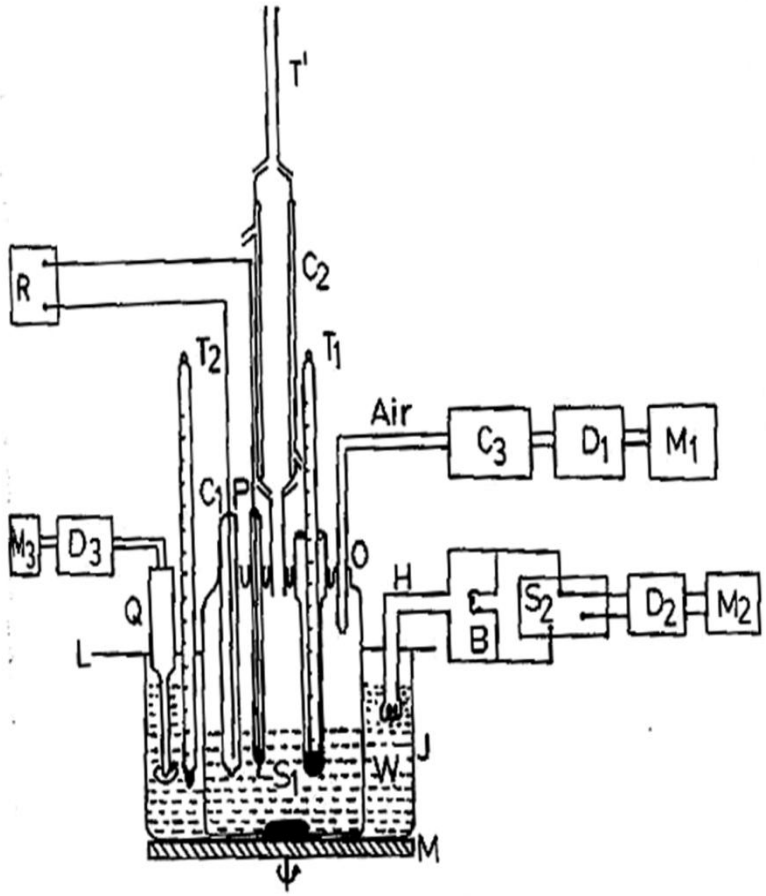

Fig.5. Experimental set-up of a semi-batch reactor [32].

Experimental set-up of a semi-batch reactor consisted of a Corning glass reaction cell fitted with a platinum electrode (P), a calomel electrode (C_1) and thermometer (T_1). In order to prevent changes in the concentrations of reactions due to evaporation, a water condenser (C_2) and a long tube (L) were attached. Air with controlled rate was passed through the reactor in a nozzle (O) and a compressor (C_1). The air flow rate was determined by water displacement method. The outlet of the nozzle (O) was kept above the surface of the oscillator solution to minimize disturbance at the surface. The solution was stirred with the help of a magnetic stirrer. The reaction was put in a water thermostat which could be maintained at the desired temperature with an accuracy of $\pm 0.5^0$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. Experiments were carried out under controlled conditions viz temperature, reactant concentration, oxygen flow rate in the semi-batch reator for the system containing acetaldehyde. Time period (tp) decreased with increase in [NaBr] and [CH_3 CHO] in a semi-batch reactor.

They reported that:

(i) Benzaldehyde could be replaced by acetaldehyde or propionaldehyde but not by formaldehyde in 90% acetic acid containing Co (II) acetate and sodium bromide.

(ii) Oscillations are not observed when cobalt (II) acetate is replaced by cobalt nitrate, cuprous chloride and manganese acetate.

(iii) Bromate ion or liquid Br_2, however, can replace NaBr.

(iv) Certain additives viz. CCl_4, Hg^{+2} ion, KI, I_2, phenol, aniline, 1, 10 - phenanthroline, ethylenediamine, acetylacetone and hydroquinone quenched the oscillations, Phenol and amines both act as antioxidants, may be due to hydrogen atom transfer.

(v) Addition of NaCl to the oscillatory system yielded different types of colour changes during oscillations (blue olive green instead of pink brown).

Following changes occur during oscillation when Cl^- is added to the reaction mixture.

(Pink) octahedral Co(II) □ (Brown) octahedral Co(III)

Cl^-

(Blue) tetrahedral Co(II) (olive green) octahedral Co(III)

They have performed experiments in a semi - batch reactor as shown it Fig.5. Later on, Rastogi,Das etal [33] also carried out oscillatory aerial oxidation of propioaldehyde in acetic acid / water medium in presence of Co^{2+} and Br^- ions under controlled conditions using a Continuously Stirred Tank Reactor as shown in Fig.6 (a) to maintain the system far from equilibrium for a longer duration. Results were compared with those obtained with a semi-batch reactor.CSTR is a modified version of a semi -batch reactor used earlier. In CSTR experiments thereactants NaBr, Co (II) acetate and C_2H_5CHO were taken in the reservoir G at room temperature and continuously led into the reactor at definite flow rate through polyethylene tubes. Volume of the reaction was kept constant by continuous out flow of solution using a suction pump (F). Initially a lowering of temperature (1^0C) was noticed due to influx of solution from the reservoir but after a few minutes, temperature attained a constant value. Principle utilized was that at lower temperature no reaction would occur. Visual oscillations in colour (Pink brown) were observed.

Experiments at various ko, values have been carried out and results are recorded in Fig.6 (b).

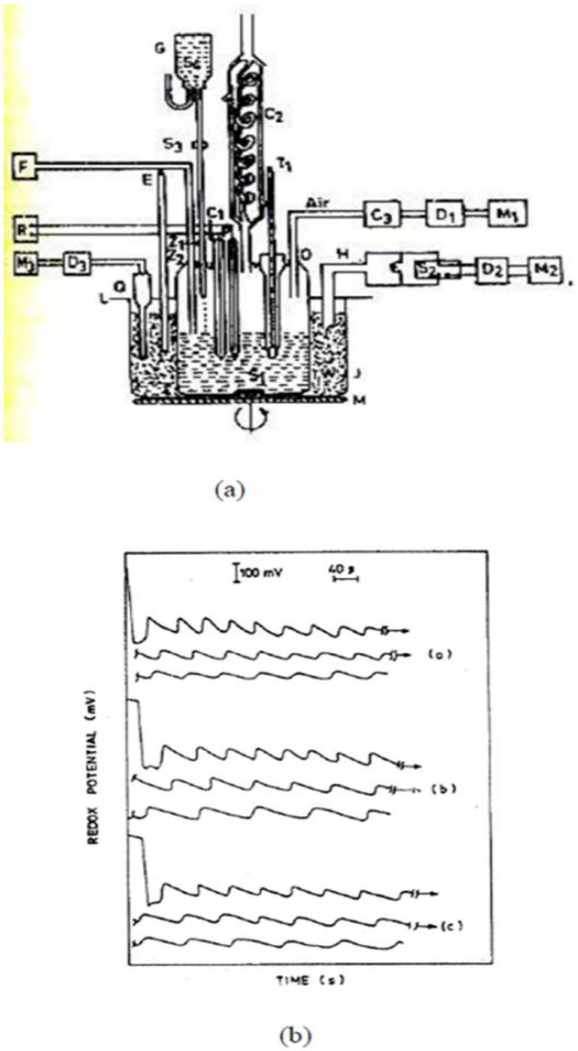

Fig.6. (a) Experimental set-up of continuous flow stirred tank reactor (CSTR), (b) Redoxpotential changes as a function of time for different values of ko in CSTR [33].

where k_0 is the inverse of residence time (flow rate/reactor volume). Frequency of oscillation increased with increase in flow rate. Rastogi,Das etal [34] have attempted to simulate the above experimental observations numerically by using eleven step reaction mechanism. Aerial oxidation of aldehydes is a free radical chain reaction. In the case of propionaldehyde, $C_2H_5CO^{\bullet}$ is the most important radical species corresponding to the $C_6H_5CO^{\bullet}$, postulated in the aerial oxidation of benzaldehyde. Further, due to electron donating nature of aliphatic groups and electron withdrawing nature of phenyl groups, the aromatic free radicals will be more stable than the corresponding aliphatic free radicals. Hence the rate constant for reaction steps where aliphatic free radicals are involved would be greater than the corresponding rate constant of aromatic free radicals.Computed results for time variation of $[Br^-]$, $[(Co^{3+})_2]$, $[(Co^{3+})_2\ Br]$, $[C_2H_5CHO]$, $[C_2H_5CO]$, $[C_2H_5CO_3]$,

$[C_2H_5CO_3H]$, $[Co^{3+}]$, $[Co^{2+}]$, and $[O_2(l)]$ gave evidence of oscillatory behavior.

CONCLUSION

In summary,a comprehensive review on the exciting area of oscillatory chemical reactions and aerial oxidation of aldehydes is reported. Batch, semi- batch and continuously stirred tank reactors (CSTR) were designed and experiments were performed at various experimental conditions. Results were critically analyzed and reported in this communication. In the case of aerial oxidation of propionaldehyde, computer simulation results were also reported.

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