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Effect of Manganese Salts on an Oscillatory Chemical Reaction in Different Acid Media

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***Abstract*—Studies on the oscillatory behavior of resorcinol with different catalysts, different co-ions for the same catalyst (acetate, carbonate, sulphate) and different media give different trends. The use of different catalysts shows that Mn(II) is most reactive and Ferroin is least reactive with respect to resorcinol with respect to different oscillatory parameters like time period and induction period. The use of different acidic media clearly shows the ease with which protonated species is formed in sulfuric acid and hence maximum number of oscillations is seen in this medium as compared to orthophosphoric acid where no oscillations are seen. Study on the different co-ions is carried out for the first time and it is observed that co-ions also have a good impact on nature of oscillations. Such ions can be treated as co-substrates although oscillations are not observed while using such compound separately with the bromate (i.e. in absence of resorcinol).**

***Index Terms*—BZ Reaction, catalyst, auto catalytic oxidation, mixed mode oscillations.**

I. INTRODUCTION

The non-linear chemical phenomena known as ‘oscillating chemical reactions’ are complex dynamic systems that have so far been examined mainly in physico-chemical terms in order to elucidate their intricate underlying mechanisms. Thus, various dynamic regimes including regular oscillations, periodic doubling, quasi-periodicity and deterministic chaos, among others, have been explored. Applications of oscillating chemical reactions in analytical chemistry have grown substantially in the last few years, especially since the introduction of the continuous-flow stirred-tank reactor (CSTR) which allows one to design and implement new chemical oscillators. In such systems, the relationship of the oscillation attributes (period, amplitude, Lyapunov exponent, *etc.*) to the perturbation concentration can be used to construct calibration graphs. In order to improve the analytical figures of merit of these determinations, a sound physico-chemical knowledge of the oscillating chemical reactions involved is advisable. Oscillations can arise in a macroscopic medium if the system is sufficiently far from the state of thermodynamic equilibrium [1]. These reactions have been known for about three hundred years, but were mainly heterogeneous reactions. By the beginning of the 20th century, two excellent examples of heterogeneous oscillating reactions had been discovered: the so-called "iron nerve"- the periodic dissolution of an iron wire in nitric acid, and the "mercury heart" - the oscillatory decomposition of hydrogen peroxide on the surface of metallic mercury [2, 3]. The Belousov-Zhabotinsky (BZ) reaction is a family of oscillating chemical reactions [4]. During these reactions, transition-metal ions catalyze oxidation of various, usually organic, reductants by bromic acid in aqueous acid solution. Most BZ reactions are homogeneous. The BZ reaction makes it possible to observe development of complex patterns in time and space by naked eye on a very convenient human time scale of dozens of seconds and space scale of several millimeters. The BZ reaction can generate up to several thousand oscillatory cycles in a closed system, which permits studying chemical waves and patterns without constant replenishment of reactants [5-8]. An oscillatory cycle can be qualitatively described in the following way. Suppose that a sufficiently high Ce^{4+} concentration is present in the system. Then, Br^- will be produced rapidly, and its concentration will also be high. As a result, autocatalytic oxidation of Ce^{3+} is completely inhibited, and the $[Ce^{4+}]$ decreases due to its reduction by organic substrate and its bromoderivative. The $[Br^-]$ decreases along with that of $[Ce^{4+}]$. When $[Ce^{4+}]$ reaches its lower threshold, the bromide ion concentration drops abruptly. The rapid autocatalytic oxidation starts and raises $[Ce^{4+}]$. When $[Ce^{4+}]$ reaches its higher threshold $[Br^-]$ increases sharply and inhibits the autocatalytic oxidation of Ce^{3+}. The cycle then repeats. The reader can check this description by tracing a limit cycle generated by the Oregonator model [9] which shows that HOBr was the final product of the oxidation of Ce^{3+} to Ce^{4+} by $HBrO_3$. Vavilin put forward the simplest mechanism of the autocatalytic oxidation of Ce^{3+} or ferroin by bromate and its inhibition by bromide ion [10].

$$HBrO_3 + HBrO_2 \rightarrow 2BrO_2^{\bullet} + H_2O \tag{1}$$

$$H^+ + BrO_2^{\bullet} + Fe(phen)_3^{2+} \rightarrow Fe(phen)_3^{3+} + HBrO_2 \tag{2}$$

$$HBrO_2 + H^+ + Br^- \rightarrow 2HOBr \tag{3}$$

In a similar manner, uncatalysed oscillatory reactions, initially started by Orban, Koros and Noyes, developed a keen interest. Orban and Koros [11], in 1978 discovered oscillations in redox potential ,bromide ion concentration and color in a system containing only sulphuric acid, bromate and organic species such as gallic acid (3,4,5 trihydroxybenzoic acid). This was the first class known as uncatalyzed B-Z oscillators [12] which now includes 23 other organic substrates [13-14]. The oscillatory behaviour of uncatalyzed

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bromate oscillators have been explained in terms of OKN mechanism (a modification of FKN mechanism) Numerical simulations based on this mechanism by Herbine and Field [15] reproduced the main features of uncatalyzed oscillations. Extended models were suggested by Liu and Scott [16, 17] and by Gyori et al [18]. A quinone derivative of the original organic reactant like gallic acid plays the role of metal ion catalyst. The mechanism of uncatalysed systems is similar to FKN mechanism. Field, Koros and Noyes (FKN) [19] presented a detailed and systematic mechanism for the BZ oscillations including the reactions discussed above as well as the additional reactions given below that are necessary for oscillations to occur.

$$2H^+ + BrO_3^- + Br^- \rightarrow HBrO_2 + HOBr \qquad (4)$$

$$HBrO_2 + HBrO_2 \rightarrow HOBr + BrO_3^- + H^+ \qquad (5)$$

They performed systematic and detailed thermodynamic and kinetic analysis of the basic quasi-elementary reactions involved in the BZ reaction and suggested a detailed mechanism of the reaction responsible for oscillations. To overcome some problems associated with the above mechanism Gyorgyi, Turanyi and Field [20, 21] proposed a GTF mechanism. The GTF mechanism aimed to incorporate all the experimental information available at that time. Free radicals also play an important role in this mechanism but GTF assumed that organic free radicals, when they react with each other, disproportionate rather than recombine. The Marburg-Budapest-Missoula (MBM) [22] model includes both negative feedback loops (bromous acid-bromide ion Oregonator type and bromine dioxide-organic free radicals type feedback) deals only with cerium catalyzed system. A detailed study of the BZ reaction with aliphatic compounds like oxalic acid [23], malonic acid [24-26], citric acid [4], glucose [27], pyrocatechol [28] and ketones viz. cyclohexanone [29] and acetone [30] in wide range of concentrations of the substrates have been reported. Although it is reported that oscillations exhibit remarkable change with increasing or decreasing concentrations of reaction medium, e.g. increasing or decreasing the concentration of sulfuric acid results in increase or decrease in the formation of the protonated substrate. The varying concentration of reaction medium affects the induction period (t_{in}), time period (t_p) as well as the rate of reaction. Surely temperature is one of the environmental factors that have a pronounced effect on bromate driven oscillators. Temperature dependence for a variety of catalyzed and uncatalyzed bromate driven oscillators have been characterized [31-36].

In the present communication, we have studied the effect of the following factors on the oscillatory behavior of the system containing Resorcinol ($C_6H_4(OH)_2$) [37] as the organic substrate, inorganic bromate as the oxidant and various metal ions as catalysts in different aqueous acid media.

- Catalysts like Mn(II), Ce(III), Ce(IV), Fe(II)
- Media like sulfuric acid, nitric acid, orthophosphoric acid and perchloric acid
- Co-ions like sulfate, acetate, carbonate of the catalyst i.e. Mn(II)

However Manganese (II) ion in 1.3*M* sulfuric acid is used for all other reactions because of the fact that this system gives better oscillations amongst the used catalysts.

II. EXPERIMENTAL

All reagents used were either analytical grade chemicals or else of high purity. The reagents used were Resorcinol 99% (Himedia, AR), Potassium bromate 99% (Merck), Manganese(II) sulfate monohydrate (s.d.fine), Nitric acid, Orthophosphoric acid, Perchloric acid, Sulphuric acid (Merck, LR), Manganese(II) acetate, Manganese(II) carbonate, Ferroin, Cerium(III) nitrate tetrahydrate (s.d.fine), Cerium(IV)sulphate,

The ion analyzer (ELICO LI-126) having pH as well as mV option was calibrated in ORP mode with the standard solutions, using Platinum electrode as the indicator and Calomel (SCE) as the reference electrodes. Then the equipment was hooked to two half cells, one containing any of the reaction systems under investigation into which Platinum electrode was dipped as indicator electrode. The another half cell was filled with 2.5×10^{-4} mol L^{-1} solution of Potassium chloride and the calomel electrode was dipped into it as reference electrode. The two half cells were connected through salt bridge filled with potassium nitrate and thermostated at a temperature of $30^o \pm 0.1^oC$ in a Siskin Julabo water bath. All the solutions used in the reaction systems were first kept under thermostatic conditions at desired temperatures for about ten minutes in order to attain the temperature of the bath.

III. RESULTS AND DISCUSSION

The BZ reaction involving different metal ions as catalysts for the resorcinol as substrate is studied for the first time. From Figure 1 and Table 1, the t_{in} and t_p values clearly depicts that Mn(II) ion reacts faster and Fe(II) ions reacts slower to form $HBrO_2$ and the oxidized species like Mn(III) and Fe(III) respectively. This can be further explained from Figure 2, wherein the slow increase (process A) involves reaction of metal ion and the substrate to oxidize the metal ion, the sharp increase (Process B) is because of the reaction of the catalyst and the bromoderivatives of the substrate. From these two steps the oxidation of catalyst takes place which causes a negative feedback in the reaction and sharp decrease (Process C) takes place involving the formation of the Mn(II) from the reaction of Mn(III) and the bromoderivatives of the substrate(resorcinol). On the basis of the FKN mechanism, Field and Noyes [38] have developed a mathematical model of the BZ reaction named Oregonator. It includes additionally reaction of $HBrO_3$ with Br^- that produces $HBrO_2$, and disproportionation of $HBrO_2$. Tyson [39, 40] reduced Oregonator to two two-variable versions with the fast variable being $[Br^-]$ or $[HBrO_2]$, and the slow variable $[Ce^{4+}]$. The only irreplaceable initial reagent is the oxidant bromate. The Tyson [41] expression for velocity of the wave is

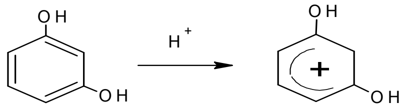
$$\text{Velocity} = 2(kD[H^+][BrO_3^-])^{1/2}$$

Where k is the rate constant for the formation of $HBrO_2$ and $D = 2 \times 10^{-5}$ $cm^2 s^{-1}$ is the diffusion coefficient for $HBrO_2$. From above expression velocity is directly proportional to the concentration of bromate and from reactions (1) and (2) the formation of $HBrO_2$ directly depends on the $[BrO_3^-]$. So the $[BrO_3^-]$ is directly related to the velocity which in turn is used to calculate the rate of reaction. The order of the reactivity of different metal ions is

Mn(II) > Ce(IV) > Ce(III) > Fe(II)

From this trend it is also observed that use of the oxidized form of the catalyst like Ce(IV) in place of Ce(III) enhances its reactivity.

The acidic medium in BZ reaction gives rise to protonation of the substrate like



Resorcinol Protonated Resorcinol

The reactive protonated intermediate acts as a good nucleophile for bromide ion to form bromoderivatives. Table 2 gives a comparative trend for the use of different media like sulfuric acid, nitric acid, orthophosphoric acid and perchloric acid. In perchloric acid protonation occurs at higher concentration of acid, whereas in nitric acid, oscillations are seen with larger values of t_{in} and t_p. On the other hand sulfuric acid gives a good number of oscillations at lower as well as higher concentrations and the system is not reactive at all in orthophosphoric acid. Complex (mixed mode) type of oscillations is observed for 1.0*M* sulfuric acid medium (figure 3), having a combination of large and small amplitude peaks. Mixed mode [42, 43] type of oscillations is perhaps the most commonly occurring form of complex oscillations in chemical systems. The discovery of complex periodic behavior in such system provides important support for notion that chemical chaos is a phenomenon of some generality. At present there is little or no mechanistic insight into the workings of this oscillator. Further the effect of concentration of different reagents like $[Mn^{2+}]$, $[BrO_3^-]$ is also studied at 30ºC (table 3). From this trend the effective concentration range where oscillations are seen is 0.05*M* to 0.2*M* for $[BrO_3^-]$, $4 \times 10^{-3}M$ to $8 \times 10^{-3}M$ for $[Mn^{2+}]$. Here we have seen that increase in concentration of bromate causes an increase in the reaction between resorcinol and bromate and there are lesser chances of negative feedback caused by the critical bromide ion concentration, therefore lesser number or no oscillations are seen. Same is the case with metal ion concentration.

The effect of co-ions of the catalyst in BZ reaction is also studied in the present work. Here we have used acetate, carbonate, sulfate of the Mn(II) ion and results are quite fascinating (table 4). Although we have used same catalyst i.e. Mn(II) ion in all three salts but the oscillatory parameters for all three reaction systems are quite different. Kinetically the rate of reaction with respect to Mn(II) acetate is faster than the Mn(II) carbonate which in turn is faster than Mn(II) sulfate. This can be due to the difference in the release of metal ions by these anions or the other reason can be that anions can act as the co-substrates in these reactions. The later cause seems to be more promising. The trend with respect to t_p is

Mn(II) acetate < Mn(II) carbonate < Mn(II) sulfate

and with respect to t_{in} trend is

Mn(II) carbonate < Mn(II) acetate < Mn(II) sulfate

The anions acting as co-substrates seem to be in agreement with the other co-substrates used separately in BZ reactions. So we could study their effect as co-substrates without using them externally, but to have the salt of such an organic substrate and metal ion as the catalyst. However the only use of such salts with bromate did not show oscillations defying the use of organic substrate (resorcinol in this case). Hence we can say that such salts have made it easy to study the co-substrate effect of such systems. Work with respect to some other salts having same metal ion but different co-ions (anions) is going on with this system as well as with some other systems, which may be communicated in near future.

IV. SUMMARY

Resorcinol responded very well as the BZ oscillator in aqueous acid media. Amongst different metal ions, the oscillatory characteristics are much more pronounced with Mn(II) ion and least pronounced with Fe (II) ion as catalyst. However, the use of oxidizable form of catalyst like Ce(IV) have a forthcoming effect on induction period. The reaction system showed good oscillatory parameters both at lower and higher concentrations of aqueous sulfuric acid, while as for orthophosphoric acid as medium, it shows no such behavior over a wide concentration range. Moreover, the co-ions of the same metal like Mn^{2+} (studied for the first time) influences the oscillatory characteristics, which adds new scope in studying BZ reaction with respect to mechanism and kinetics of such reactions.

V. DATA

A. Figures and Tables

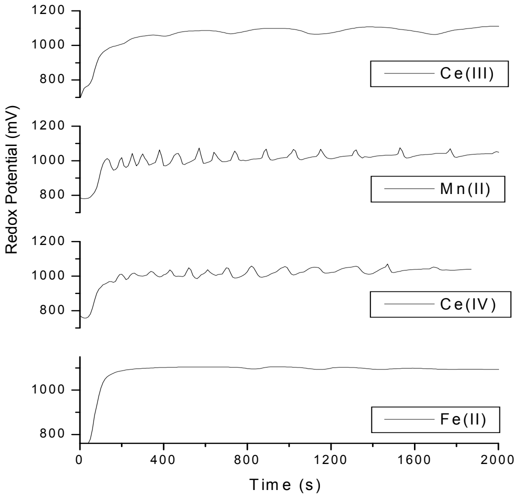


Figure 1: Potential (*m*V) versus time (*s*) plots for the systems containing [Ce(III)] = [Ce(IV)] = [Mn(II)] = [Fe(II)] = $4 \times 10^{-3}M$, $[BrO_3^-] = 0.1M$, [Resorcinol] = 0.0225*M* at 30 ± 0.1ºC

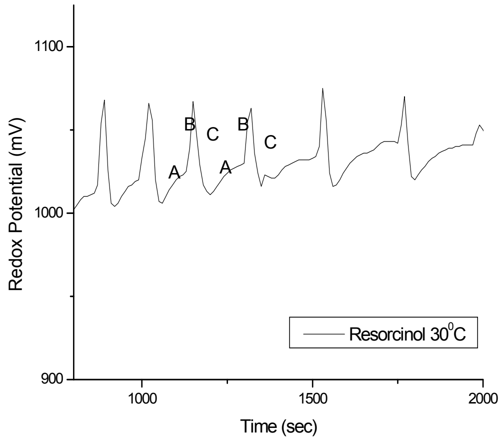


Figure 2: Potential versus time plot of the system [Mn(II)] = 4 × $10^{-3}M$, $[BrO_3^-]$ = 0.1M, [Resorcinol] = 0.0225M at 30 ± 0.1ºC (explaining mechanism).

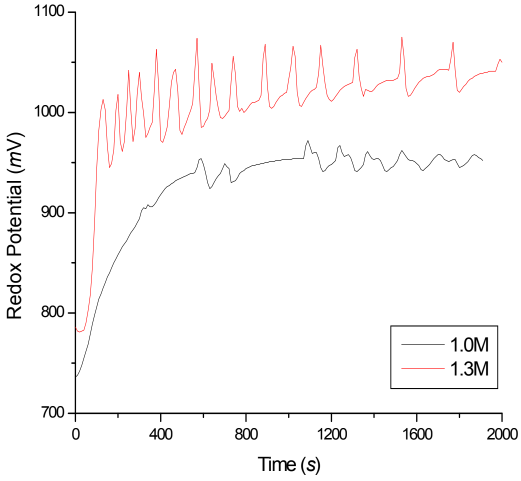


Figure 3: Comparative potential (mV) verses time (s) plots showing mixed mode oscillations for 1.0*M* H_2SO_4 (lower plot) and 1.3*M* H_2SO_4 (Normal, upper plot), [Resorcinol] = 0.0225 *M*, $[BrO_3^-]$ = 0.1 *M*, $[Mn^{2+}]$ = 4 × $10^{-3}M$.

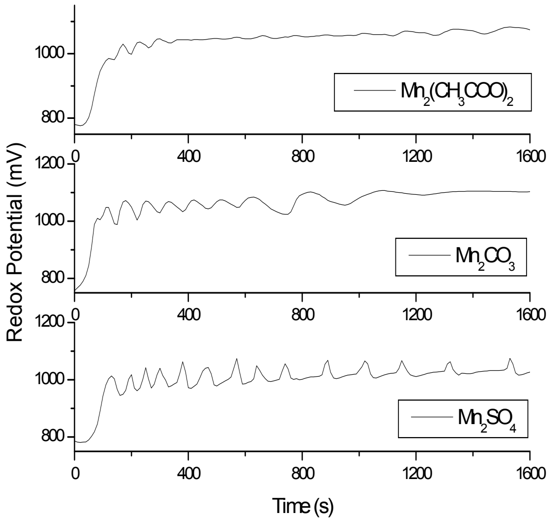


Figure 4: Potential (*m*V) versus time (*s*) plots for the systems containing different salts of same metal ion with [Mn(II)] = 4 × $10^{-3}M$, $[BrO^{3-}]$ = 0.1*M*, [Resorcinol] = 0.0225*M* at 30 ± 0.1ºC

Table 1: Time Period and Induction Period of the Systems Containing $[Mn^{2+}] = [Ce^{3+}] = [Ce^{4+}] = [Fe^{2+}] = 4 \times 10^{-3}M$, [Resorcinol] = 0.0225*M*, $[BrO_3^-]$ = 0.1*M*, Temperature = 30 ± 0.1ºC.

Metal ions	Induction period, t_{in} (*s*)	Time period, t_p (*s*)
Mn^{2+}	130	67.5
Ce^{3+}	350	460
Ce^{4+}	470	310
Fe^{2+}	140	100

Table 2: Change in the Oscillatory Parameters for Different Acids with a Range of Concentrations.

Acid	Conc.of acid, M	No. of oscillations	Time period (*s*)	Induction period,(*s*)
H_2SO_4	0.5	**	**	**
	0.8	**	**	**
	1.0	>10	300	330
	1.3	>40	67.5	130
	1.8	**	**	**
HNO_3	0.5	**	**	**
	0.8	**	**	**
	1.3	**	**	**
	1.8	>10	170	420
H_3PO_4	0.8	**	**	**
	1.3	**	**	**
	1.8	**	**	**
$HClO_4$	0.8	**	**	**
	1.8	>5	480	1170
	2.5	>20	115	340

** No oscillations are seen

Table 3: Effect of $[Mn^{2+}]$ and $[BrO_3^-]$ on the Oscillatory Parameters of the Systems Containing [Resorcinol] = 0.0225*M* at 30 ± 0.1ºC

$[BrO_3^-]$, *M*	$[Mn^{2+}]$, *M*	Time period (*s*)	No. of Oscillations
0.05	0.004	110	11
0.1	0.008	80	>1
0.2	0.008	**	**
0.2	0.004	77	5
0.1	0.005	80	9

** No oscillation is seen

Table 4: Time Periods and Induction Periods of the Systems Containing the [Salt] = 4 × $10^{-3}M$, $[BrO_3^-]$ = 0.1*M*, [Resorcinol] = 0.0225*M* at 30 ± 0.1ºC

Salt	Induction period, t_{in} (*s*)	Time period, t_p (*s*)
Mn(II) acetate	110	87.5
Mn(II) sulfate	120	153.3
Mn(II) carbonate	80	95.0

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