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## KINETIC STUDIES ON METAL-ION CATALYSED OSCILLATORY CHEMICAL REACTION WITH GALLIC ACID IN PRESENCE OF ADDITIVES

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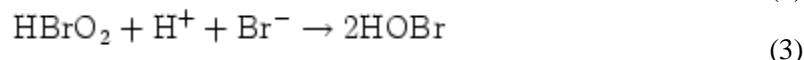
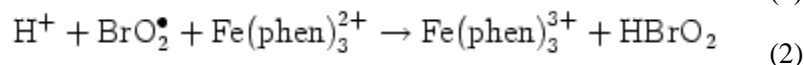
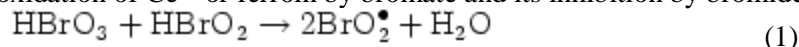
### ABSTRACT

The Ce(III)-, Ce(IV)-, Mn(II)- and Ferroin (Fe(phen)<sub>3</sub><sup>2+</sup>) catalyzed reaction of bromate ion and gallic acid (GA) exhibit oscillatory behavior. Ferroin acts as a good catalyst than Ce or Mn ions in catalyzing the aforesaid oscillating reaction systems. The kinetics of reactions of GA, bromate and H<sup>+</sup> with Ce(III), Ce(IV), Mn(II) and Fe(phen)<sub>3</sub><sup>2+</sup> were investigated. The order of relative reactivity of gallic acid (GA) and bromate towards reaction with acetone (GAA), butanone (GAB), pentanone (GAP) with Ce(III), Ce(IV), Mn(II), or Fe(phen)<sub>3</sub><sup>2+</sup> is GA>GAA>GAB>GAP and that of metal ions towards the reaction with gallic acid in presence of ketones is Fe(phen)<sub>3</sub><sup>2+</sup> > Ce(IV) > Ce(III) > Mn(II). The rates of protonation reaction of gallic acid in different acids like H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> depends on the strength of the acid.

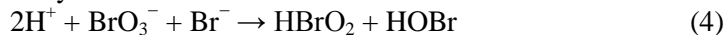
**Key Words:** BZ Reaction, Gallic Acid, Methyl Ketones, Arrhenius Equation

### INTRODUCTION

Over the past two decades, the study of oscillatory chemical reactions has grown to become a major area of chemical research. The Belousov-Zhabotinsky (BZ) (Belousov, 1958; Zhabotinsky, 1964) reaction has attracted much attention and has been studied most thoroughly. Basically, the classical BZ reaction is a metal-ion catalyzed oxidation and bromination of an organic substrate by bromate ions in aqueous acid media (Noyes *et al* 1980). Field, Koros, and Noyes (FKN) (1972) proposed a detailed mechanism for the BZ reaction with malonic acid (MA). An oscillatory cycle can be qualitatively described in the following way: Suppose a sufficiently high Ce<sup>4+</sup> concentration is present in the system, then, Br<sup>-</sup> will be produced rapidly, and its concentration will also be high. As a result, autocatalytic oxidation of Ce<sup>3+</sup> is completely inhibited, and [Ce<sup>4+</sup>] decreases due to its reduction by organic substrate and its bromoderivative. The [Br<sup>-</sup>] decreases along with that of [Ce<sup>4+</sup>]. When [Ce<sup>4+</sup>] reaches its lower threshold, the bromide ion concentration drops abruptly. The rapid autocatalytic oxidation starts and raises [Ce<sup>4+</sup>]. When [Ce<sup>4+</sup>] reaches its higher threshold, [Br<sup>-</sup>] increases sharply and inhibits the autocatalytic oxidation of Ce<sup>3+</sup> and then the cycle repeats. The aforesaid description is also justified by a limit cycle generated by the Oregonator model (Field *et al* 1974; Vavilin *et al* 1968) which shows that HOBr was the final product of the oxidation of Ce<sup>3+</sup> to Ce<sup>4+</sup> by HBrO<sub>3</sub>. Vavilin put forward the simplest mechanism of the autocatalytic oxidation of Ce<sup>3+</sup> or ferroin by bromate and its inhibition by bromide ion (Vavilin *et al* 1971).



Field, Koros and Noyes (FKN) (1972) 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.



They performed systematic and detailed thermodynamic and kinetic analyses of the basic quasi-elementary reactions involved in the BZ reaction and suggested a detailed mechanism of the reaction

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responsible for oscillations. To overcome some problems associated with the above mechanism, Gyorgyi, Turanyi and Field (1993, 1990) proposed a GTF mechanism in which the latest experimental information available till then was incorporated. Although free radicals 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) (Hegedius *et al* 2001) model includes both the negative feedback loops (bromous acid-bromide ion Oregonator type and bromine dioxide-organic free radicals type) deals only with cerium catalyzed system. Studies on BZ reaction with aliphatic compounds like oxalic acid (Field *et al* 1985; Basavaraja *et al* 2004), malonic acid (Blagogevic *et al* 2000; Burger *et al* 1985), citric acid (Belousov, 1958), glucose (Rastogi *et al* 2005), pyrocatechol (Harati *et al* 2008), ketones viz. cyclohexanone (Shin *et al* 2000) and acetone (Pojman *et al* 1992) and resorcinol (Ganaie *et al* 2009; 2010), etc. 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. The FKN mechanism and its skeletonized version, called the Oregonator,<sup>5</sup> have been successful in interpreting essentially all observed behaviors of the BZ reaction and various bromate oscillators derived from it. The modeling computations of Edelson *et al* (1975; 1979) and of Field *et al* (1974; 1985) strongly supported the FKN mechanism. Ruoff *et al* (1983; 1985; 1989) and Jwo *et al* (1993) studied the BZ reaction with methylmalonic acid (MeMA). Koros (Koros *et al* 1974) identified two different kinds of metal-ion catalysts for the BZ reaction, namely, the labile Ce(III)/Ce(IV) and Mn(II)/Mn(III) complexes with reduction potentials of about 1.5 V and the inert Fe(phen)<sub>3</sub><sup>2+</sup>/Fe(phen)<sub>3</sub><sup>3+</sup> and Ru(bpy)<sub>3</sub><sup>2+</sup>/Ru(bpy)<sub>3</sub><sup>3+</sup> complexes with reduction potentials of about 1.0-1.3 V. Noyes<sup>3</sup> pointed out that both kinetic and thermodynamic arguments indicate that ferriin (Fe(phen)<sub>3</sub><sup>3+</sup>) should not oxidize MA by the same mechanism as does Ce(IV) ion. This argument is further supported by the kinetic study of the ferriin oxidation of MA and its derivatives reported by Jwo *et al* (1993). Both Koros *et al* (1974) and Smoes *et al* (1979) have noted that the BZ reaction with MA catalyzed by ferroin (Fe(phen)<sub>3</sub><sup>2+</sup>) oscillates without an induction period, whereas the reaction catalyzed by Ce(III) ion does not. In contrast, the ferroin-catalyzed BZ reaction with MeMA has a considerably longer induction period than the cerous-catalyzed system (Jwo *et al* 1993; Koros *et al* 1974; Smoes *et al* 1979; Babu *et al* (1976) studied a modified BZ reaction by replacing malonic acid with gallic acid (GA) and claimed that the observed oscillating reaction was catalyzed by cobalt and cerium ions. However, Koros and Orban (1978) reported that this oscillating reaction was not catalyzed by Co(III) ion.

These observations led to the discovery of the uncatalyzed class of bromate oscillators, which do not require any metal-ion catalyst, and the organic substrate performs some of the functions of the metal ion as well. All of the organic substrates that give oscillations are phenol and aniline derivatives with at least one unblocked ortho or para position. Jwo *et al* (1989) studied the behavior of oscillatory parameters with gallic acid as a substrate, first using the Ce(III) and ferroin and latter without these (Misra *et al* 1998), wherein he observed that Ce(III) is not a good catalyst as compared to ferroin.

Our recent observations show that even though the main features of the catalyzed BrO<sub>3</sub><sup>-</sup>-GA oscillating reaction are reasonably well understood, its kinetics still needs further investigation. In the present study, a comparative trend of the BZ reaction with galic acid (GA) catalyzed by Ce(III), Ce(IV), Mn(II), or ferroin ion is evolved and it is observed that the ferroin-catalyzed reaction of bromate ion and galic acid (GA) exhibits good oscillatory behavior in contrast to the Ce (IV), Ce(III) or Mn(II)-catalyzed systems. Further, the oscillatory parameters were studied in different acid media in order to have a comparable trend in these aqueous acid media. Besides, a detailed kinetic study has been performed with and without methyl ketones as additives to the systems under investigation.

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### MATERIALS AND METHODS

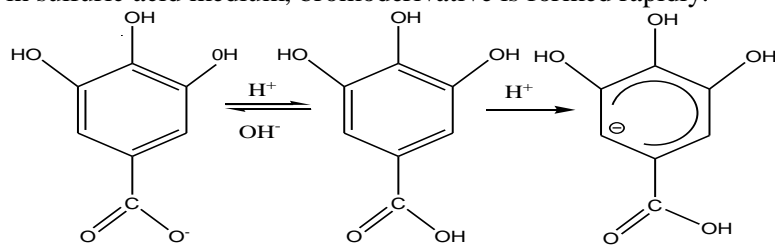
All reagents used were of analytical grade chemicals and these include gallic acid 99% (Himedia, AR), potassium bromate 99% (Merck), manganese(II)sulfate monohydrate (s.d.fine), nitric acid (Merck), orthophosphoric acid (Qualigens), perchloric acid (Merck), sulphuric acid (Merck, AR), acetone (Himedia), butanone (Himedia), pentanone (Himedia), ferroin (s.d.fine), cerium(III) nitrate tetrahydrate (s.d.fine), cerium(IV)sulphate (S.D.fine).

The ion analyzer (ELICO LI-126) was calibrated in ORP mode with the standard solutions, using Platinum and Calomel (SCE) as indicator and reference electrodes respectively. The equipment was hooked to two half cells, one containing the reaction system under investigation with Platinum electrode and another containing solution of potassium chloride ( $2.5 \times 10^{-4} \text{ mol L}^{-1}$ ) with calomel electrode dipped into it. The two half cells were connected through salt bridge filled with potassium nitrate and thermostated to different temperatures in a Siskin Julabo high precision water bath ( $\pm 0.1^\circ\text{C}$ ). The reaction started by injecting 2mL of potassium bromate to the mixture containing 2mL each of gallic acid and metal ion solutions. No stirring was done to the reaction mixture and after each trial the electrodes and salt bridge were washed thoroughly with double distilled water. The change in potential (mV) with time (s) was recorded at the intervals of ten seconds. A typical plot of redox potential (mV) versus time (s) of the system under investigation is depicted as Figure 1. The oscillatory parameters like induction period ( $t_{in}$ ), time period ( $t_p$ ), life time ( $t_l$ ) were derived from the similar potential versus time plots and these parameters were explored to derive the kinetic parameters of the system.

### RESULTS AND DISCUSSIONS

#### Effect of media

Acidic medium in BZ reaction is equally important as the other reacting species. The  $\text{H}^+$  ion gives the protonation of the substrate molecule and the protonated intermediate form acts as a good nucleophile for  $\text{Br}^-$  ion to form the bromoderivative. As such the first emphasis in the present investigation was laid on the selection of a proper acidic medium for monitoring the oscillatory behavior of the system without additives and with additives like acetone (GAA), butanone (GAB) and pentanone (GAP). The data pertaining to this effect in different aqueous acid media like sulfuric acid, nitric acid, orthophosphoric acid and perchloric acid is reported in Table 1. In each acid medium, the oscillatory parameters of the reaction system were monitored with and without additives. Sulfuric acid has been found to be most suitable for the observation of oscillations in the system. That is why the system shows oscillations in 1.1 mol L<sup>-1</sup> sulfuric acid, a much lower concentration than nitric acid (2.0 mol L<sup>-1</sup>), orthophosphoric acid (3.0 mol L<sup>-1</sup>) and even perchloric acid (1.5 mol L<sup>-1</sup>). This is justified on the basis of rate of protonation of the gallic acid which seems to be very quick in sulfuric acid as compared to other inorganic acids. That is why, though oscillations occur in all the given media, but the induction period is comparatively low in sulfuric acid than in other acids. It stands a testimony to our assumption that owing to quick protonation in sulfuric acid medium, bromoderivative is formed rapidly.



It is also observed that the oscillatory behavior is not well prominent in presence of methyl ketones as compared to gallic acid alone. As such the following trend with respect to the oscillatory parameters with and without methyl ketones is established.



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Since additives (acetone, butanone and pentanone) also get brominated, but the rate of bromination of gallic acid decreases in presence of methyl ketones and hence adds to the increase in the induction and time periods of the oscillations observed in such systems. The bromination with respect to pentanone is greater than that of the acetone, resulting in increase of the induction period for the former.

A series of experiments were performed with the reaction system in presence and absence of methyl ketones, with different concentrations of sulphuric acid as aqueous acid medium in the range of 0.55-1.75 mol L<sup>-1</sup> to establish the upper and lower limits with respect to the role of H<sup>+</sup> ion on the oscillatory behavior of the system. The data obtained as oscillatory parameters is reported in Table-2. It is apparent that with increase in the acid concentration, the protonation of the benzene ring increases and hence makes it feasible for the bromination of the substrate to attain limiting bromo-gallic acid concentration more quickly, reducing the induction period and thus the oscillation frequency increases but life time decreases.

**Table 1:** Effect of [Media] on the oscillatory parameters of the system: [GA]=0.0059 mol L<sup>-1</sup>, [BrO<sub>3</sub><sup>-</sup>]=0.0333 mol L<sup>-1</sup>, [Mn<sup>2+</sup>]=0.0003 mol L<sup>-1</sup>; acetone=butanone=pentanone=5% (v/v), Temperature=35±0.1°C.

Acid Media	Conc. (M)	t <sub>in</sub> (min)				t <sub>p</sub> (min)				t <sub>l</sub> (min)			
		GA	GAA	GAB	GAP	GA	GAA	GAB	GAP	GA	GAA	GAB	GAP
H <sub>2</sub> SO <sub>4</sub>	1.1	3.25	3.80	4.20	4.65	2.10	2.51	2.78	3.36	52.90	67.90	84.50	89.70
HNO <sub>3</sub>	2.0	3.85	4.24	4.69	5.21	3.15	3.43	3.81	4.34	50.00	45.50	64.50	86.00
H <sub>3</sub> PO <sub>4</sub>	3.0	2.90	3.28	3.60	4.05	2.70	2.76	3.73	3.85	107.00	211.00	238.50	250.00
HClO <sub>4</sub>	1.5	4.93	5.24	5.60	5.97	3.68	3.97	4.39	4.81	85.00	101.00	126.00	144.00

**Table 2:** Effect of [H<sub>2</sub>SO<sub>4</sub>] on the oscillatory parameters of the system: [GA]=0.0059 mol L<sup>-1</sup>, [BrO<sub>3</sub><sup>-</sup>]=0.0333 mol L<sup>-1</sup>, [Mn<sup>2+</sup>]=0.0003 mol L<sup>-1</sup>; acetone=butanone=pentanone=5% (v/v), Temperature=35±0.1°C.

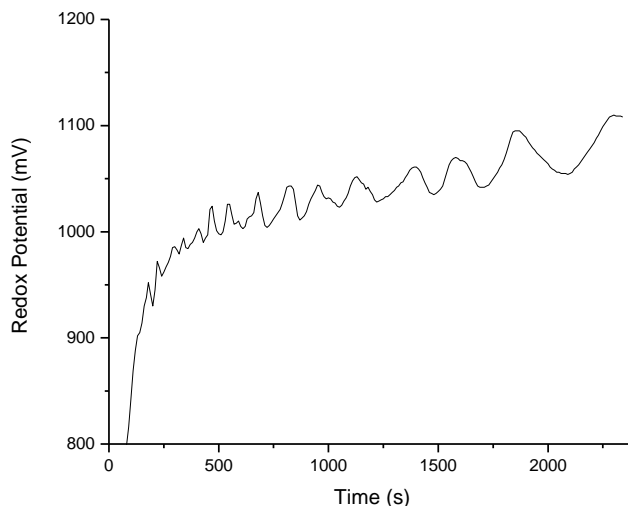
H <sub>2</sub> SO <sub>4</sub> (M)	t <sub>in</sub> (min)				t <sub>p</sub> (min)				t <sub>l</sub> (min)			
	GA	GAA	GAB	GAP	GA	GAA	GAB	GAP	GA	GAA	GAB	GAP
0.549	3.75	4.17	4.43	4.71	2.85	3.16	3.54	3.91	67.00	79.00	89.00	102.00
1.099	3.25	3.56	4.01	4.29	2.10	2.54	3.00	3.49	56.10	68.00	76.00	90.00
1.500	2.60	3.05	3.49	3.78	1.40	1.90	2.55	3.02	41.00	55.50	70.00	79.00
1.750	1.85	2.50	2.87	3.28	0.80	1.43	1.91	2.40	26.00	40.00	56.00	68.00

### Effect of Catalyst

Four different metal ions Fe(phen)<sub>3</sub><sup>2+</sup>, Ce<sup>3+</sup>, Ce<sup>4+</sup> and Mn<sup>2+</sup> were used as catalysts in the reaction system under investigation with and without methyl ketones as additives. The data obtained with respect to the effect on induction period, time period, and life time of oscillations is shown in Table-3. It is observed that pure reaction system (GA) shows prominent oscillatory parameters with ferroin as catalyst i.e., lesser induction period (Figure 1) as compared to Mn(II), wherein the reactivity is significantly lower i.e; greater induction period before the onset of oscillations. Reactivity of the polyphenols (GA) with iron is concentration dependent (Jaen *et al* 2003). Reactivity in this system underlines the reaction that led to formation of bromosubstrate. The more concentrated the solution, the faster the reaction. The effect of these metal ions was also studied in presence of methyl ketones as additives keeping the concentrations of other reagents constant. The mixed reaction systems like GAA, GAB and GAP show better response with Ce<sup>4+</sup> ion as compared to Fe(phen)<sub>3</sub><sup>2+</sup> as catalyst and with Mn<sup>2+</sup> ion the reactivity is quite low. On comparing the overall reactivity of the reaction system with and without methyl ketones in all of the four metal ions, the order of reactivity with respect to oscillatory behavior follows as under:



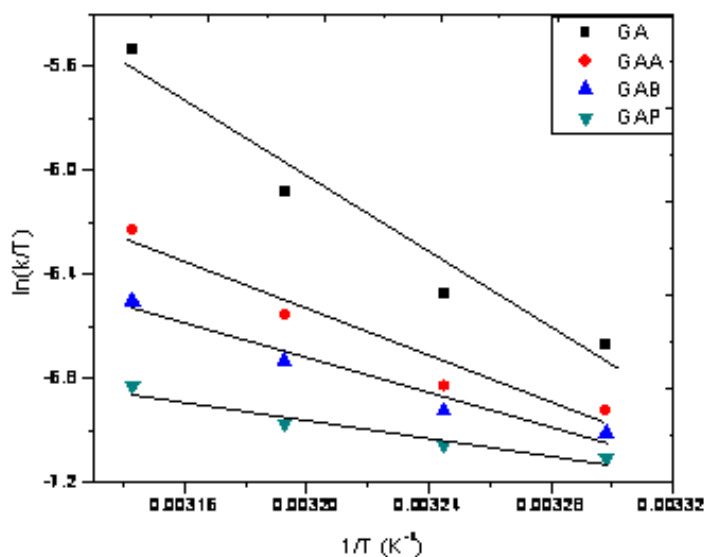
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**Figure 1:** Oscillatory behavior of the system:  $[GA]=0.0059 \text{ mol L}^{-1}$ ,  $[BrO_3^-]=0.0333 \text{ mol L}^{-1}$ ,  $[Fe(phen)_3^{2+}]=0.00025 \text{ mol L}^{-1}$ ; Temperature= $35\pm 0.1^\circ\text{C}$ .

**Table 3:** Effect of  $[M^{n+}]$  as catalyst on the oscillatory parameters of the system:  $[GA]=0.0059 \text{ mol L}^{-1}$ ,  $[BrO_3^-]=0.0333 \text{ mol L}^{-1}$ ; acetone = butanone = pentanone=5% (v/v), Temperature =  $35\pm 0.1^\circ\text{C}$ .

Metal ion	Conc. (M); $10^{-4}$	$t_{in}$ (min)				$t_p$ (min)				$t_l$ (min)			
		GA	GAA	GAB	GAP	GA	GAA	GAB	GAP	GA	GAA	GAB	GAP
$Fe(phen)_3^{2+}$	2.5	2.50	2.91	3.54	4.24	1.60	1.95	2.41	2.92	61.00	66.00	74.30	83.00
$Ce^{4+}$	8.0	2.51	2.80	3.37	3.73	1.90	2.22	2.64	2.92	58.00	64.50	71.80	85.00
$Ce^{3+}$	5.0	2.84	2.99	3.44	3.90	2.09	2.36	2.71	3.06	60.90	68.00	78.69	85.80
$Mn^{2+}$	3.0	3.25	3.53	3.98	4.50	2.10	2.44	2.90	3.40	60.00	68.65	79.00	86.00



**Figure 2:** Linear fit of  $1/T$  versus  $\ln k/T$  showing second order dependence of the rate.

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**Table 4:** Evaluation of  $E_a$ ,  $\Delta H^*$  and  $\Delta S^*$  for the system:  $[GA]=0.0059 \text{ mol L}^{-1}$ ,  $[BrO_3^-]=0.0333 \text{ mol L}^{-1}$ ,  $[Mn^{2+}]=0.0003 \text{ mol L}^{-1}$ ; acetone = butanone = pentanone=5% (v/v) at different temperatures.

System	Temperature (K)	Time period, $t_p$ (min)	Apparent rate constant, $(\text{min})^{-1}$	$E_a^\ddagger$ (kJ/mol)	$\Delta H^*\ddagger$ (kJ/mol)	$\Delta S^*\ddagger$ (kJ/mol)
GA	303	2.60	0.385	63.021	60.439	-62.733
	308	2.10	0.476			
	313	1.40	0.714			
	318	0.80	1.250			
GAA	303	3.35	0.298	40.040	37.459	-140.431
	308	3.00	0.033			
	313	2.25	0.444			
	318	1.60	0.625			
GAB	303	3.65	0.274	29.855	27.273	-174.535
	308	3.30	0.303			
	313	2.68	0.373			
	318	2.10	0.476			
GAP	303	4.01	0.249	17.106	14.525	-194.541
	308	3.76	0.266			
	313	3.41	0.293			
	318	2.90	0.345			

$\ddagger$  using Arrhenius and Eyring equations.

The observed trend shows the least reactivity of the GAP, which is significant in its greater induction period, as compared to GAA, with lesser induction period. This may be attributed to the highest scavenging ability of the pentanone as compared to acetone for the bromine and hence prolongs the formation of limiting bromo-gallic acid concentration.

**Effect of Temperature**

It is observed that with the increase in temperature the oscillatory parameters like induction period ( $t_{in}$ ), time period ( $t_p$ ) and life time ( $t_l$ ) decreases, typically following the Arrhenius equation. As a general rule a BZ reaction is preceded by an induction period which is characterized by the accumulation of sufficient amount of brominated substrate. In case of gallic acid with methyl ketones the comparatively high induction periods indicate that large amount of activation energy is required for there bromination. This activation energy barrier decreases with increase in temperature resulting in the quick bromination to accumulate the bromoderivative and hence there is decrease in the induction period and time period with increase in temperature. The observed trend with respect to the magnitude of oscillatory parameters for the reaction systems containing pure gallic acid (GA) and in presence of methyl ketones is:

$$GA < GAA < GAB < GAP$$

The comparatively higher magnitude of oscillatory parameters with gallic acid in presence of methyl ketones is justified because the methyl ketones also get brominated, owing to which they act as bromine scavengers (Misra *et al* 1998) for the original system i.e., gallic acid. It seems that amongst the three methyl ketones pentanone behaves as a potent scavenger for bromine, thus the system with pentanone shows higher values of oscillatory parameters as compared with that of butanone and acetone and hence control the concentrations of various intermediates generated *in situ* like  $Br_2$ ,  $HOBr$ ,  $Br^-$  etc, which have a key role in the generation of oscillations.. The experimentally obtained oscillatory parameters were used to calculate the apparent kinetic parameters like apparent rate constant ( $k$ ), activation energy ( $E_a$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and entropy of activation ( $\Delta S^\ddagger$ ) using Arrhenius and Eyring equations:

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$$k = Ae^{\frac{-E_a}{RT}} \quad (6)$$

$$k = \frac{kT}{h} e^{\frac{(T\Delta S^\ddagger - \Delta H^\ddagger)}{RT}} \quad (7)$$

A plot of  $\ln k/T$  versus  $1/T$  gave a straight line (Figure 2). From the slope of the straight lines the apparent values of activation energies were obtained.

The order of  $E_a$  for the reaction system with and without methyl ketones, as additives is as follows:



This trend is justified owing to the fact that during the oxidation process (formation of bromoderivative) the additives also get brominated which paves a way for increase in induction and time periods (Harati *et al* 2007; 2009; Rauscher *et al* 2011). This is because the auto-catalysis process starts only when there is limiting concentration of bromo-gallic acid formed; therefore the methyl ketones act as negative feedback for the progression of autocatalysis process.

The present investigation on gallic acid shows that methyl ketones have a fascinating role in the kinetics of gallic acid as a substrate in BZ reaction with different metal ions like  $\text{Fe}(\text{phen})_3^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Ce}^{4+}$  and  $\text{Mn}^{2+}$  as catalysts. It is observed that the magnitude of oscillatory parameters for pure gallic acid system are smaller than for the gallic acid in presence of methyl ketones, hence confirming the faster rate of reaction for the former.

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