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Study of oxidation of Benzoin in acidic Medium by Ce (IV)

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Abstract
The objective of this paper is to the kinetic study of oxidation of Benzon in acidic medium by Ce. (IV). Effect of variation in Concentration of Benzoin, Ce (IV), $HClO_4$, % Acetic acid, temperature variation etc. were studied. Product study was carried out by the suggesting a free radical mechanism. Reaction was of consecutive type and products formed proceed through stable intermediate Benzil. Increase in dielectric constant decrease the rate of reaction. Oxidation of Benzoin proceeds through formation of stable intermediate and thus oxidation studies of these intermediates can also be carried out.

Keywords: oxidation of Benzoin, acidic Medium, Ce (IV)

Introduction
Oxidation of ketones may prefer two routes, attack at kentone site or at its enol form. ceric salt have been used as one electron oxidizing agent and volumetric reagents in determination of organic and inorganic compounds [1-4]. Kinetic studies of Ag(I) catalysed Ce(IV) oxidation of L(+)-Alanine, L(+)-Valine and L(+)-Lucine was carried out in HNO_3 medium [5]. Ce(IV) is used as an oxident in oxidation of four epimeric forms of 4. Amino oxanes in presence of nitric acid [6]. In oxidation of Diacetone alcohol by Ce(IV), transition metal ions like Ag^+, Cu^{2+} etc. are used as homogenous catalysts [7]. Tetra butyl ammonium cerium (IV) nitrate [8] also acts as mild dehydrogenating agent. Oxidants are also classified as one or two electron abstracting oxidants [9]. Benzoin occurs in ketc and enol both forms [10]. Intermediate formed in oxidation of benzoins by Cr(VI) as an oxidant are benzyl and other products [11].

Materials and Methods
All reagents and compound used were of L.R. and A.R. grade. 625cc of 95% alchol, 500cc of water, 500gm of pure benzeldehyde and 50gm of sodium cyanide were placed in a round bottom flask fitted with a reflux condenser and was heated for two hours. This mixture was then cooled. Crude product was washed with water and re-crystallized by 95% alcohol. The melting point of product was 129 ^{0}C.
Stock solution of cerric ammonium nitrate was prepared in distilled water. Stock solution of Benzoin was prepared in distilled acetic acid and these were then diluted by distilled water as required. All the solutions except that of oxidants were mixed and kept in thermostat.
After attaining constant temperature two solution were mixed and transferred rapidly to a 1 cm quartz cuvette kept in thermostat cell holder. Reaction was followed at 325nm in Shimadzu U.V. spectrophotometer. Temperature of curvette was recorded after completion of reaction.
After completion of reaction, mixture was treated with sodium bicarbonate to neutrilize acetic acid. This was then extracted with ether and on evaporation, only liquid left behind was subjected to tlc with eluent n-Heane : Methanol :: 9:1 Blank spot suggested the product to be benzyl.
Aqueous layer was acidified and extracted with ether. On evaporation of ether, left behind solid was suggested to be Benzoic acid by tlc. The product formed were also confirmed by melting and mixed melting points.

Result and Discussion
A tipical run of the reaction is shown in Table-1 and Graph-1. Rate constant K_1 was calculated by

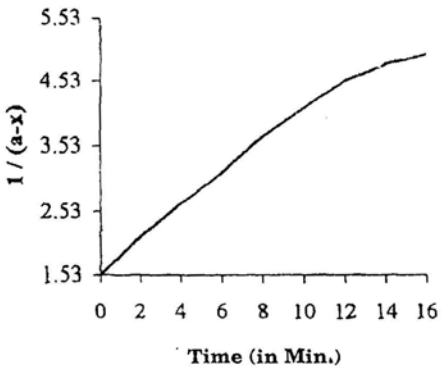
$$k_1 = \frac{O.D.}{t \times \in \times [Ce(IV)]}$$

Here t is time course of reaction, $\in$ is molar extinction coefficient at 325nm and [Ce(IV)] is concentration of Ce(IV) in acidic medium.

Table 1: [Ce(IV)]=2×10^{-4}M, [Benzoin]=2×10^{-4}M, Temp.=25^{0}C, [$HCLO_4$]=2.302M, AcOH=60%(v/v)

S. No	Time (Min)	(a-x) in terms of O.D.	1/(a-x)
1.	0.0	0.650	1.50
2.	2.0	0.471	2.12
3.	4.0	0.377	2.63
4.	6.0	0.319	3.11
5.	8.0	0.280	3.55
6.	10.0	0.253	3.95
7.	12.0	0.236	4.22
8.	14.0	0.220	4.74
9.	16.0	0.210	5.00

K_1=13.3x 10^{-4} (Sec^{-1})



Graph 1: A Typical Run

Varitation of rate with concentratior of Ce(IV) does not show any change in K_1 suggesting first order dependence of reaction rate on concentration of Ce(IV). (Table-2)

Varitation of rate with concentration of Ce(IV)

Table-2: [Benzoin]=2×10^{-4}M, [H$^+$]=2.302M, Temp.=25 ^{0}C, AcOH=60%(v/v)

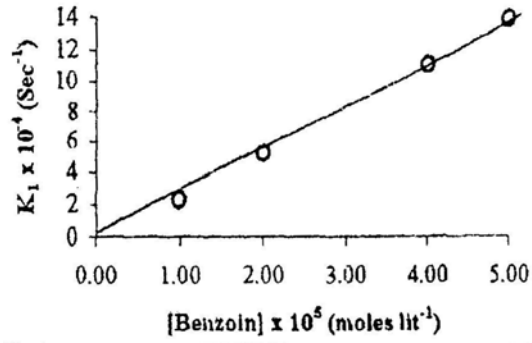
S. No.	Conc. of Ce(IV) (moles lit^{-1})	K^{1}x10^4(Sec^{-1})
1.	8×10^{-5}	13.2
2.	1×10^{-4}	13.1
3.	3×10^{-4}	13.3
4.	5×10^{-4}	13.2

Variation of rate with concentration of Benzoin (Table-3 and Graph-2 and 3) was carried out. Oxidation of Benzoin by Ce(IV) follow first order rate law with concentration of substrate. Plot of log K_1 v/s log [substrate] is linear with slope 1±0.1. Plot of K_1 v/s [substrate] passing through origin suggests that complex formation does not take place between Ce(IV) and Benzoin and thus Micheles-Mentin type of kinetics is not followed.

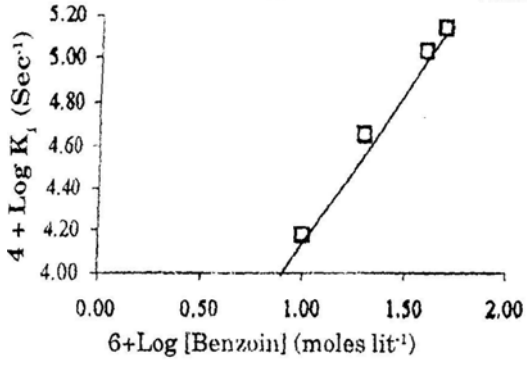
Variation of rate with concentration of Benzoin

Table 3: [Ce(IV)]=2×10^{-4}M, [H$^+$]= 2.302 M, Temp. =25 ^{0}C, AcOH= 60% (v/v)

S. No.	Conc of Benzoin (moles lit^{-4})	K$_1$x10^4 (Sec^{-1})
1.	1x10^{-5}	1.50
2.	2x10^{-5}	4.50
3.	4x10^{-5}	10.60
4.	5x10^{-5}	13.80



Graph 2



Graph 3

Keeping ionic strength constant of $HClO_4$, concentration of H^+ ions was varied. Result are reported in Table 4, 5, 6 and Graph 4 and 5.

Variation of rate with concentration of H$^+$ ions

Table 4: [Ce(IV)]=2×10^{-4} M, [Benzoin] = 2×10^{-4} M, Temp.= 15^{0}C, AcOH=60% (v/v) [HClO$_4$+NaClO$_4$]=0.462 M

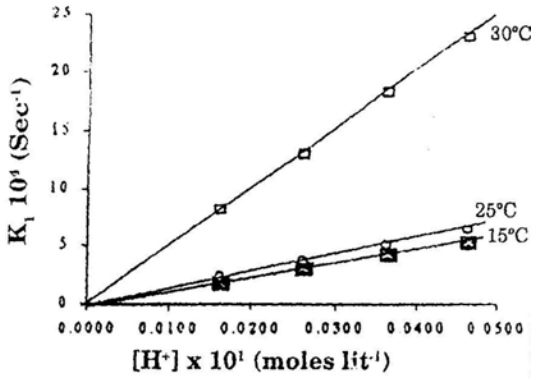
S.No.	[H$^+$] (moles lit^{-1})	K$_1$x10^5 (Sec^{-1})
1.	0.162	8.30
2.	0.262	13.00
3.	0.362	18.20
4.	0.462	23.20

Table 5: [Ce(IV)]=2×10^{-4} M, [Benzoin] = 2×10^{-4} M, Temp.= 25 ^{0}C, [HClO$_4$+NaClO$_4$]=0.462 M AcOH=60% (v/v)

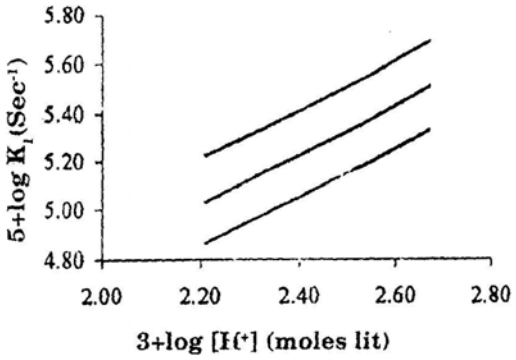
S. No.	[H$^+$] (moles lit^{-1})	K$_1$x10^5 (Sec^{-1})
1.	0.162	1.90
2.	0.262	3.10
3.	0.362	4.25
4.	0.462	5.40

Table 6: [Ce(IV)]=2×10^{-4} M, [Benzoin] = 2×10^{-4} M, Temp.= 15 ^{0}C, [HClO$_4$+NaClO$_4$]=0.462 M AcOH=60% (v/v)

S. No.	[H$^+$] (moles lit^{-1})	K$_1$x10^5 (Sec^{-1})
1.	0.162	2.30
2.	0.262	3.75
3.	0.362	5.20
4.	0.462	6.55



Graph 4



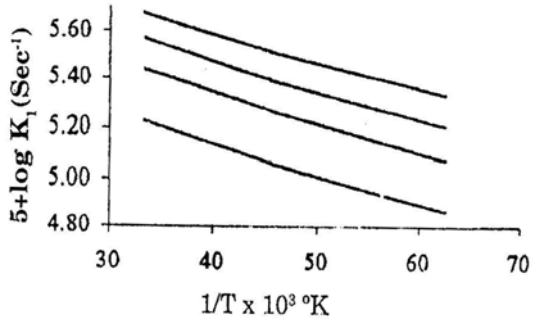
Graph 5

Variation of rate was also studied with temperature and concentration of H^+ ions reported in Graph-6. Linearity of graph of Log K_1 v/s 1/T suggests that only one mode of reaction predominates.

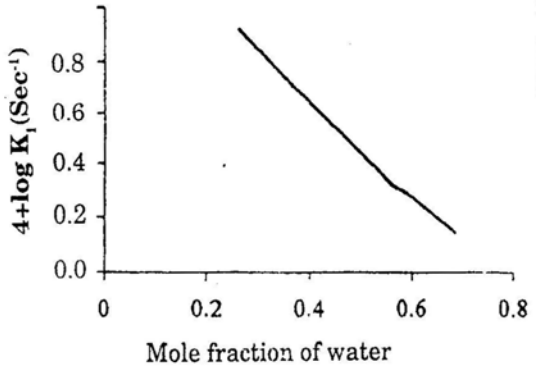
Solution of substrate was prepared in acetic acid water mixture. Dielectric constant was calculated by mixture law. Plot of log K_1 v/s mole fraction of water (Table-7 and

Graph-7) are straight line proving the increase in rate with increase in proportion of acetic acid.

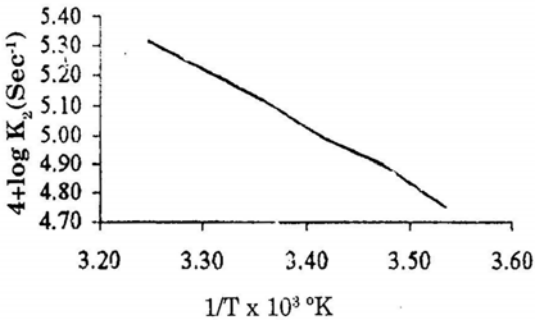
Straight line of plot of log K_1 v/s mole fraction of water suggest the solvating of more polar component to predominate rather than dielectric constant region generated near solute particles.



Graph 6



Graph-7



Graph 8

Effect of temperature variation was studied (Table-8 and Graph-8). Specific rate constant was

$$K_s = \frac{K_1(Sec^{-1})}{[H^+][Substrate]}$$

Table 7: [Ce(IV)]=2×10^{-4} M, [Benzoin] =2×10^{-4} M, Temp. 25^{0}C, [H$^+$]= 0.462 M

S. No.	% AcOH	K_1×10^{-4} (Sec^{-1})	1/D ×10^2	Mole fraction of
1.	60	9.44	2.90	0.6855
2.	70	11.1	3.65	0.5834
3.	80	11.5	4.91	0.4400
4.	90	2.9	7.53	0.2666

Table 8: [Ce(IV)]= 2x10+$^{-4}$ M, [Benzoin]= 2x10^{-4} M, [H$^+$]= 2.302 M, AcOH=60% (v/v)

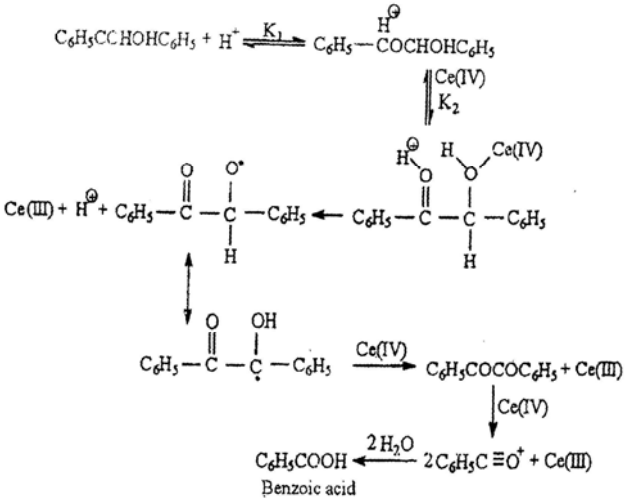
S.No.	Temp. (^{o}K)	K_1x10^{-4} (Sec^{-1})	ΔE* (K.Cal Mole^{-1})	ΔS* (K.Cal Mole^{-1})
1.	283	4.08		
2.	288	5.83		
3.	298	13.3		
4.	308	20.8	11.3	-55.70

Activation parameters are calculated by eyring eqution. Plot of Log K_1 v/s 1/T was straight line.

Conclusion

Plot K_1 v/s [Benzoin] passes through origin suggesting that there is no complex formation beyween Ce(IV) and Benzoin. Linearity of plot K_1 v/s [H$^+$] suggests that Ce(IV) and not it hydrate form $CeOH^{3+}$ attack the Benzoin. Plot of log K_1 v/s 1/D are linear suggesting the reaction to be an iondipole and not affected by Dielectric field generated near solute particles. Product study through tlc show no spot corresponding to benzeldehyde & and this rules out the possibility of C-C bond cleaved production. Reaction proceeds through formation of stable intermediate benzyl, which oxidises at a greater rate to form benzoic acid. The rate of oxidation of Benzoin is too fast and does not provide sufficient time to produce ene-diol form which is not detected by bromination and by reduction through cupric acetate.

Only route thus remaining was protonation of Eenzoin in acidic medium. The mechanism proposed was :-



The stoichiometry suggested is–

$C_6H_5COCHOHC_6H_5+4Ce^{4+}+2H_2O\rightarrow 2C_6H_5COOH+4Ce^{+3}+4H^+$

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