

## Kinetics and Mechanism of Oxidation of Chloramphenicol by 12-Tungstocobaltate(III) in an Acidic Medium

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The oxidation of Chloramphenicol (CAP) by Keggin-type 12-tungstocobaltate(III) anion was investigated spectrophotometrically under pseudo-first-order conditions in perchloric acid at 303K. Under these reaction conditions, CAP exists in unprotonated form. The reaction was found to proceed via the formation of a weak complex between the reactants. A direct electron transfer from CAP to the 12-tungstocobaltate(III) anion generated a 3-(4-nitrophenyl)-2,2-dichloroacetamido-1-propanol-3-oxy free radical in the rate-determining step. This free radical was further oxidised to give 4-nitrobenzaldehyde, dichloroacetic acid, and glycoaldehyde. The rate constant increased with an increase in concentration of the substrate. The reaction rate remained constant with an increase in hydrogen ion concentration, and was independent of the ionic strength. The products of the reaction were confirmed by LC-MS, FT-IR and <sup>1</sup>H NMR spectroscopy. The thermodynamic parameters were evaluated by temperature variation kinetic data. A detailed mechanism and rate equation are proposed for the reaction.

**Key words:** Keggin type; pseudo-first order; free radical; oxidant; reducing agent

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Chloramphenicol (commercial name Chloromycetin, D-(-)-threo-1-(4-nitrophenyl)-2,2-dichloroacetamido-1,3-propanediol) is a synthetic antibiotic derived firstly from the bacterium *Streptomyces venezuelae*. Chloramphenicol (CAP) shows strong effectiveness against gram-positive and gram-negative bacteria including mostly anaerobic microorganisms. It is a bacteriostatic antimicrobial mainly used for the treatment of a variety of infections of the skin, ear and eye including trachoma, as well as for veterinary purposes [1]. It has been shown that the nitro group in CAP is responsible for its antibacterial activity. CAP is considered a prototypical broad-spectrum antibiotic, alongside the tetracyclines. CAP belongs to the amphenicols, a family of antibiotics mostly used in bovine and aquaculture for many years. CAP has been found to cause bone marrow depression [2]. Recent studies indicate that CAP alone, or in combination with other anticancer drugs, can cause inhibition of growth in several cancer lines including leukemic cell lines. CAP has been used to treat acute fever, dysentery, typhoid, meningitis, plague and pneumonia fever [3].

A recent study focused on electron-transfer processes for pharmaceutical and biological investigations. A unique physico-chemical property of heteropolyacids (HPAs) is that they are used as homogeneous and heterogeneous catalysts for acid-base reactions and redox reactions. Due to their high thermal stability, solubility in various media (aqueous as well as

organic), strong acidity and strong oxidizing ability, Keggin type POMs are widely used for organic transformations [4]. The Keggin structure of 12-tungstocobaltate(III) anion is substitution inert and precludes inner sphere mechanisms because the central Co<sup>III</sup> atom is protected by a sheath of chemically inert oxygen atoms. Electron exchange between the Co<sup>III</sup> and Co<sup>II</sup> compounds in solution is relatively rapid, which supports outer-sphere electron transfer.

The oxidation of certain vital functional groups of drugs have continued to attract the attention of several researchers because investigations into the stability, structural modifications and their influence on the activity of the drugs have always revealed new and interesting factors. A literature survey reveals that POMs have been extensively used for the oxidation of many inorganic and organic substrates in acidic media [5-15]. Kinetic studies of the oxidation of CAP by various oxidants have been carried out under different experimental conditions [16-20].

Antibiotics and their metabolites are continuously released into the aquatic environment. Due to increasing consumption, easy availability, low biodegradability and inimical side effects, the presence of antibiotics residues in the environment has attracted researchers. Effective removal of drugs by water treatment processes is important to minimize the potential health risks [21]. In the last few decades many

attempts have been made to eliminate or inactivate residual CAP in wastewater [22-26]. A literature survey reveals that no kinetic and mechanistic studies of CAP oxidation by POM have been reported. Therefore, understanding the mechanism of CAP decomposition in aqueous solutions becomes important to identify the probable path of its oxidation in the presence of outer-sphere oxidants like the 12-tungstocobaltate(III) anion.

## EXPERIMENTAL

### Materials and Methods

Analytical grade reagents and double-distilled water was used for research work. The preparation of 12-tungstocobaltate(III) anions,  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  and  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{-6}$  was achieved by utilizing sodium tungstate (SD fine), glacial acetic acid (BDH), hydrochloric acid, potassium chloride (Thomas Baker), potassium persulfate (SD fine). Chloramphenicol solution (Sisco Research Laboratory) was freshly prepared each time and kept in Pyrex glassware to avoid degradation by sunlight. Equivalent quantities of  $\text{Na}_2\text{CO}_3$  (BDH, AR) and  $\text{HClO}_4$  (Thomas Baker) were neutralized to obtain  $\text{NaClO}_4$  in water which is used to maintain the ionic strength. The dielectric constant effect was studied using 1,4 Dioxane (BDH, AR) and the effect of  $[\text{H}^+]$  was studied using perchloric acid.

The preparation of the cobalt complex 12-tungstocobaltate(III) anions,  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  and  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{-6}$  was carried out according to literature procedures [27-28]. An Equip-tronics EQ-602 pH meter used to record the pH of the reaction mixture throughout the experiment. IR spectral determinations were performed using a Bruker Model Alpha FT-IR spectrophotometer. The product mass spectra analysis was monitored by 6200 series TOF/6500 series HRMS spectroscopy. A Bruker NMR was used to record  $^1\text{H}$  NMR spectra with  $\text{DMSO-d}_6$  as solvent and tetramethylsilane as internal standard.

### Characterization of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$ :

The complex  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  was characterized spectrophotometrically by a Systronic 119 UV-VIS spectrophotometer. The standardization of

$[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  and  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{-6}$  anions (398 nm for  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  and 624 nm for  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{-6}$  respectively) was carried out [7].

The FT-IR spectrum of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  shows bands at: 3579, 1710, 1601, 1474, 1309, 1230, 1064, 947, 886, 770  $\text{cm}^{-1}$ . Water associated with a Keggin-type structure corresponds to a broad band at 3579  $\text{cm}^{-1}$  and a sharp band at 1601  $\text{cm}^{-1}$ . The characteristic bands for a Keggin unit are observed in the region of 900-700  $\text{cm}^{-1}$ . The fundamental band at 947  $\text{cm}^{-1}$  corresponds to  $\text{W-O}_d$ , 886  $\text{cm}^{-1}$  corresponds to  $\text{W-O}_b\text{-W}$  and 770  $\text{cm}^{-1}$  corresponds to  $\text{W-O}_c\text{-W}$  stretching modes of the Keggin structure.

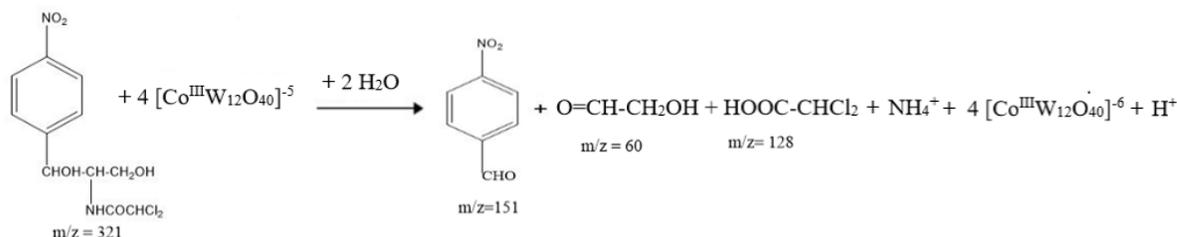
### Kinetic Measurements

CAP was oxidized by the 12-tungstocobaltate(III) anion under pseudo-first-order conditions in a perchloric acid medium. The reaction rate was extremely slow at room temperature and progressed faster at a slightly higher temperature under experimental conditions. So, kinetics is carried out at the slightly elevated temperature.

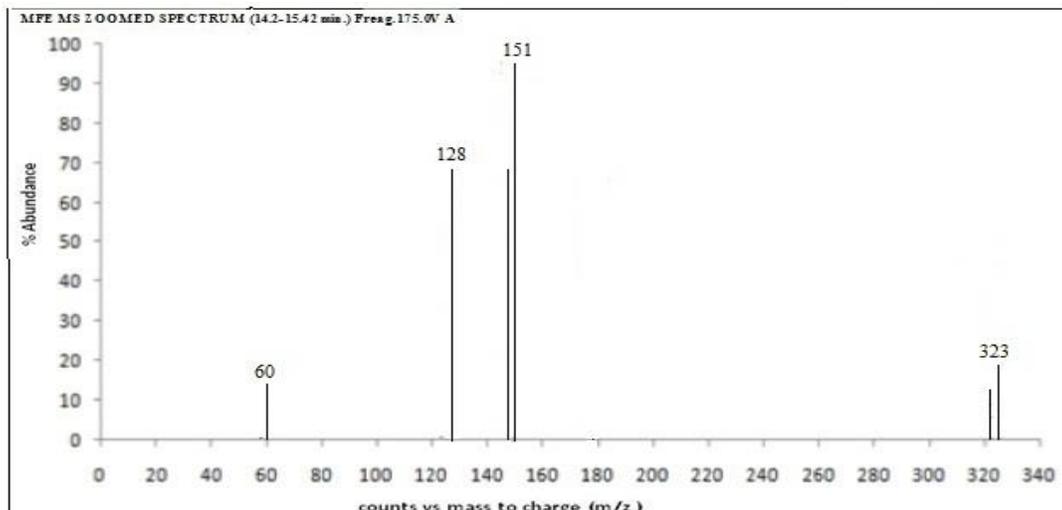
The above solution of 12-tungstocobaltate(III) anion and CAP containing required quantities of perchloric acid and sodium perchlorate were combined into one of a matched pair of 1cm quartz cells. It was then placed in a thermostated cell compartment of the spectrophotometer. An increase in optical density of the 12-tungstocobaltate(III) anion was observed. Pseudo-first-order rate constants were measured by plotting a graph of log Absorbance versus time. The rate constants were reproducible within 4%.

### Product Analysis and Stoichiometry

The reaction mixture containing a known excess of oxidant,  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  anion,  $1 \times 10^{-4}$  mole of chloramphenicol in 0.6  $\text{mol dm}^{-3}$  of  $\text{HClO}_4$  was prepared and was allowed to stand for 48 h at 303K in a thermostated bath. The concentration of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  anion was analyzed spectrophotometrically at 624 nm. The reaction between chloramphenicol and the oxidant,  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  was found to have 1: 4 stoichiometry. (Scheme 1)



Scheme 1. Stoichiometry of the reaction

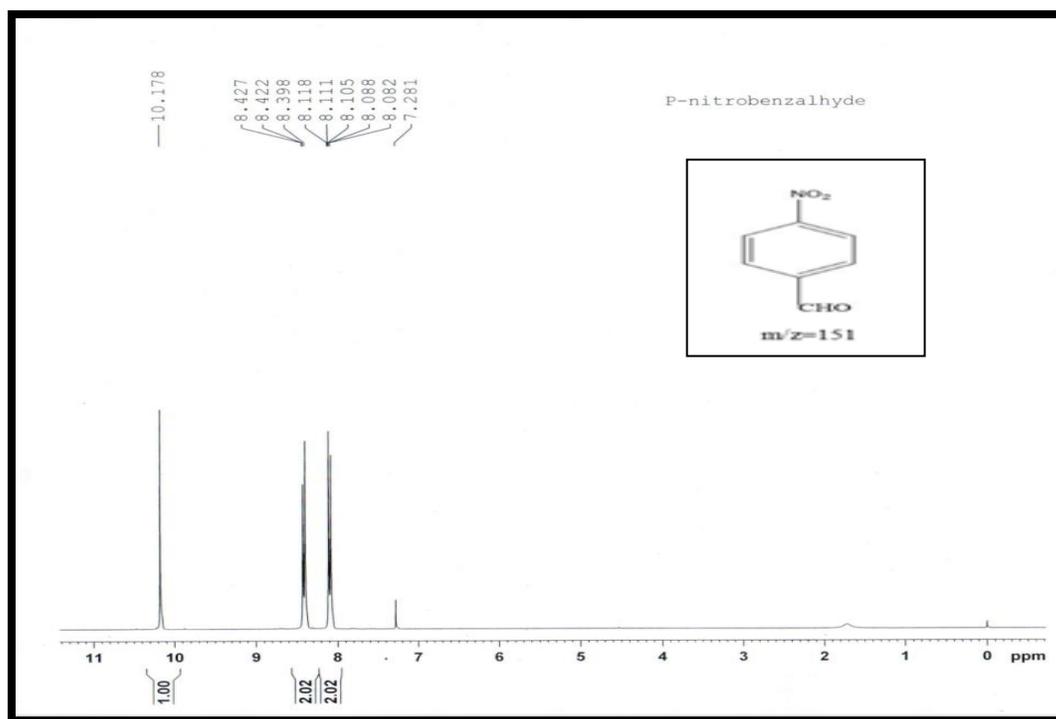


**Figure 1.** LCMS spectra of the products of oxidation of Chloramphenicol

Product analysis was done by LCMS spectroscopy which showed molecular ion peaks at  $m/z$  60, 128, 151, 323 at different time intervals (Figure 1). The main oxidation product was found to be *p*-nitrobenzaldehyde ( $m/z = 151$ ) which was separated by ether extraction. Evaporation of the ether extract yields a crude product, which was recrystallized from ethanol (obs. m.p. 108°C). The formation of *p*-nitrobenzaldehyde was confirmed by  $^1\text{H}$  NMR, FT-IR spectroscopy and mass spectra. The LCMS spectrum

( $m/z = 151$ ) and FTIR spectrum of the product were found to be consistent with *p*-nitrobenzaldehyde.

***p*-nitrobenzaldehyde** (obs. m.p. 108°C) [lit. m. p. 107°C],  $^1\text{H}$  NMR Lit. value ( $\text{CDCl}_3$ , TMS) : 1 H (s) 10.14 ; 2H (d) 8.37; 2H (d) 8.06 (**Figure 2**) Obs. values: 1 H (s) 10.147; 2H (d) 8.44; 2H (d) 8.18. **IR** spectrum: 3745, 2924, 1708 (Aryl CHO), 1531 ( $-\text{NO}_2$  Aromatic structure.), 1178, 1019, 593  $\text{cm}^{-1}$  (**Figure 3**). IR spectrum of chloramphenicol (substrate) (**Figure 4**).



**Figure 2.**  $^1\text{H}$  NMR spectrum of *p*-nitrobenzaldehyde, the product of the oxidation of chloramphenicol by 12-tungstocobaltate(III)

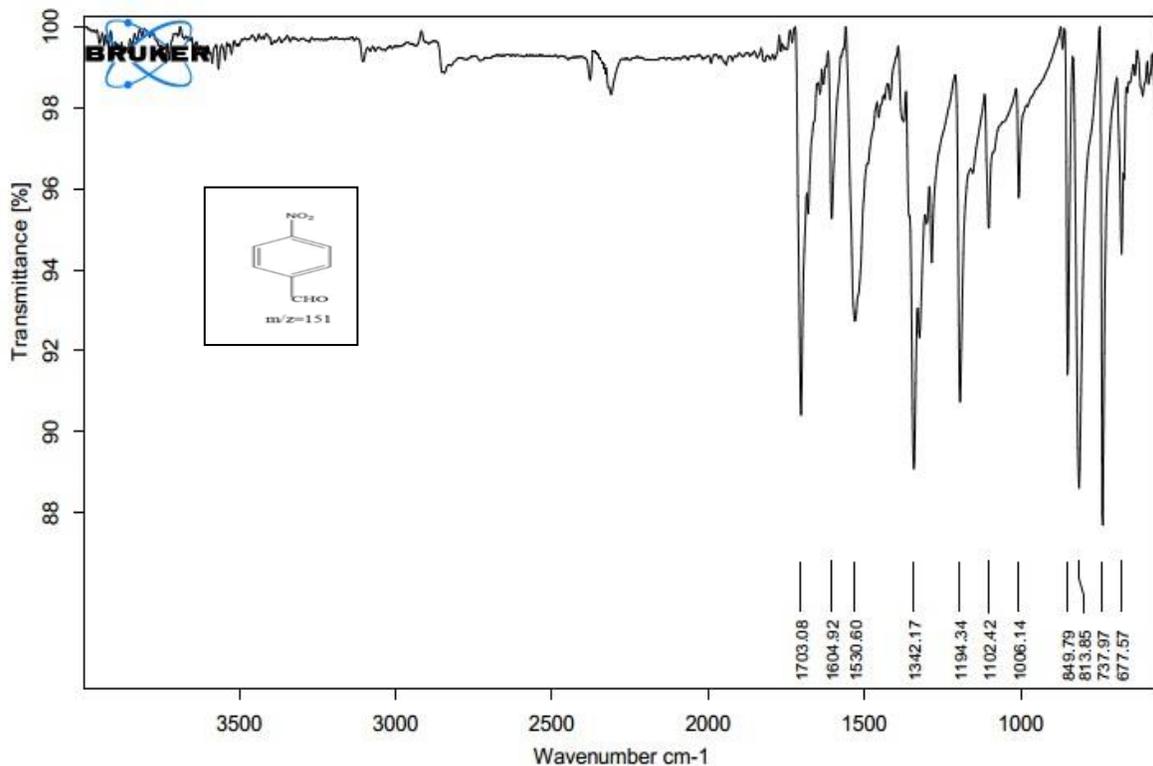


Figure 3. FT-IR spectrum of p-nitrobenzaldehyde

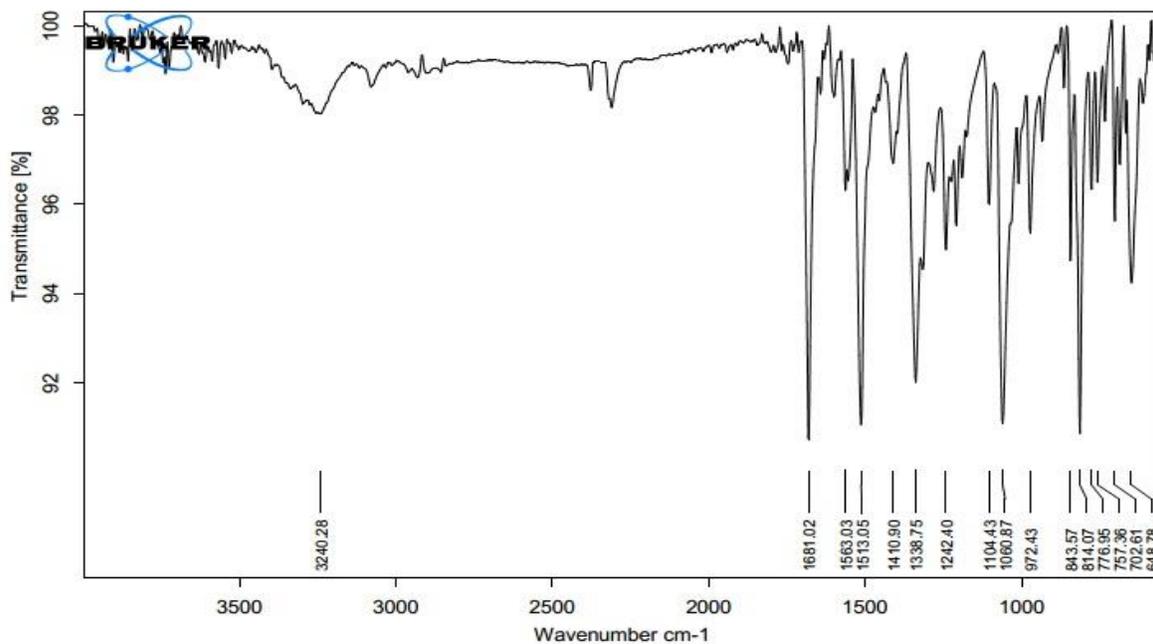
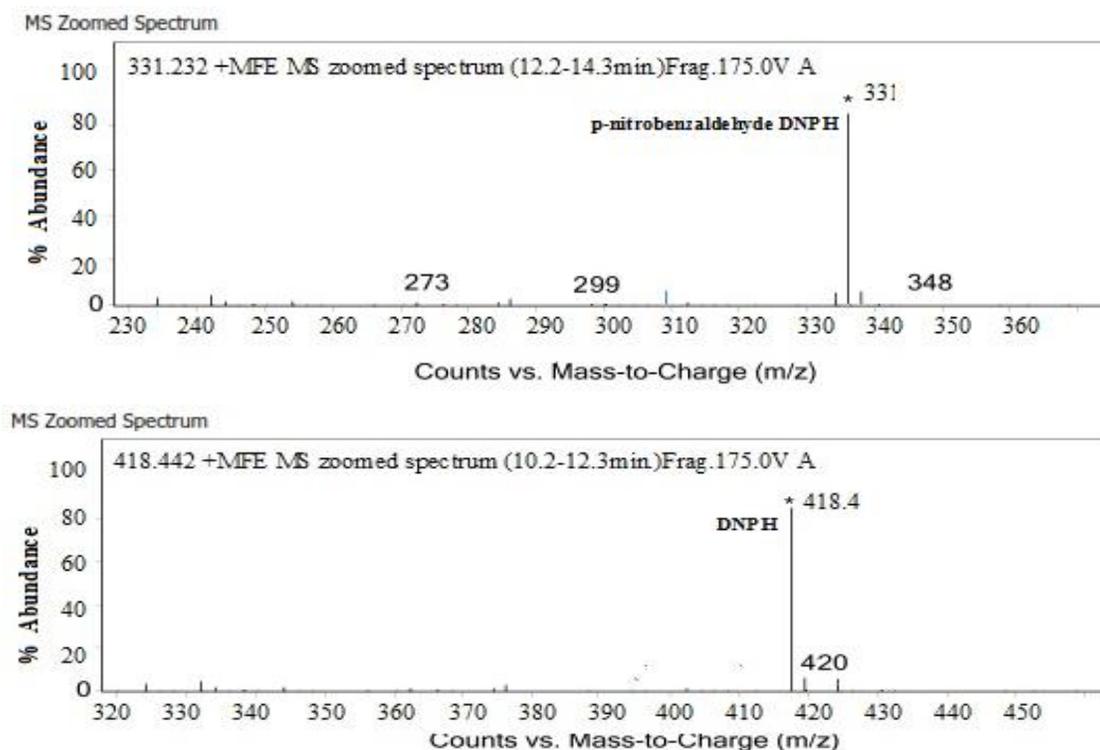


Figure 4. FT-IR spectrum of substrate (Chloramphenicol)



**Figure 5.** Mass spectrum of a DNPH derivative of p-nitrobenzaldehyde and glycoaldehyde

### Interpretation of FTIR and $^1\text{H}$ NMR and Mass Spectra

The FTIR spectrum of the product (p-nitrobenzaldehyde) was compared with that of the substrate (CAP). Both the substrate and the oxidation product showed bands due to aromatic C=C at 1563 and 1604  $\text{cm}^{-1}$  respectively. A band due to the aromatic nitro group showed a symmetric stretching vibration at 1530  $\text{cm}^{-1}$  and an asymmetric stretching vibration at 1342  $\text{cm}^{-1}$  for the product while CAP showed bands at 1513  $\text{cm}^{-1}$  and 1338  $\text{cm}^{-1}$ . Bands due to para disubstituted benzene were observed in the 790-850  $\text{cm}^{-1}$  range. The FTIR spectrum of the product shows a  $\nu_{\text{C=O}}$  stretch at 1703  $\text{cm}^{-1}$  consistent with an aldehydic (-CHO) group (Figure 3), which was absent in substrate. In the  $^1\text{H}$  NMR spectrum of p-nitrobenzaldehyde, an aldehydic proton is furthest downfield (Figure 2). The LCMS spectra shows peaks at m/z 323, 151, 128 and 60. p-nitrobenzaldehyde shows a peak at m/z 151. For aromatic aldehyde, M-1 is a characteristic peak (150) due to the loss of atomic hydrogen from the molecular ion.

### Derivatization Procedure

8 mL of DNPH solution was added to 2 mL of sample using a pipette. Samples were incubated for 1 h before analysis. The mass spectra of the 2,4-DNP derivative of both aldehydes formed at the completion of the reaction showed m/z at 331 and 418 (Figure 5). This supports the formation of p-nitrobenzaldehyde along with glycoaldehyde during the oxidation of chloramphenicol.

### RESULTS AND DISCUSSION:

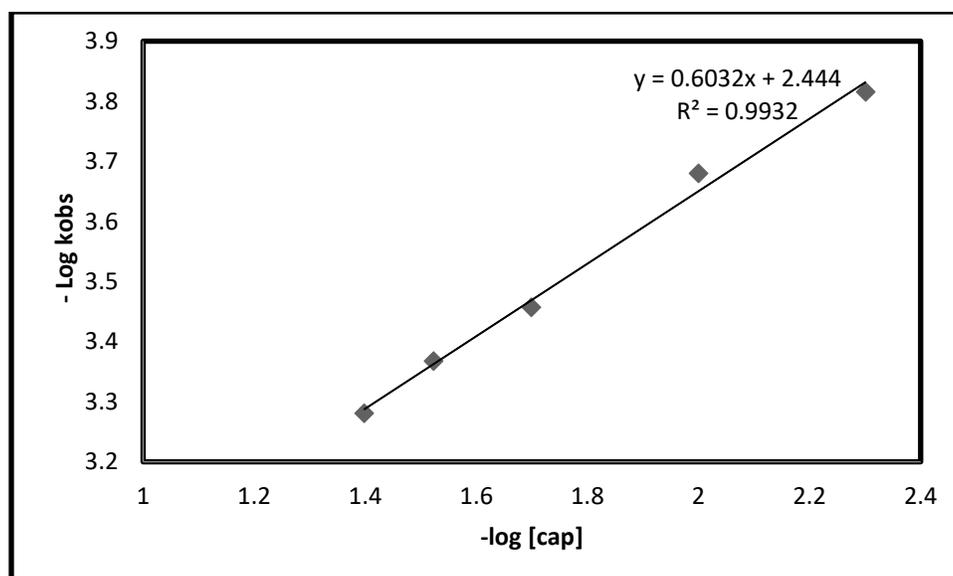
The effects of various parameters on the pseudo-first-order rate constant were studied.

#### Effect of Substrate (Chloramphenicol) Concentration

Velocity constant values of CAP oxidation at 303K increased with an increase in concentration of CAP from  $5.0 \times 10^{-3}$  to  $4.0 \times 10^{-2}$   $\text{mol dm}^{-3}$  while keeping the concentrations of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$ , perchloric acid and sodium perchlorate constant (Table 1).

**Table 1.** Effect of [CAP]  
 $10^4[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5} = 2 \text{ mol dm}^{-3}$      $[\text{HClO}_4] = 0.6 \text{ mol dm}^{-3}$      $I = 0.7 \text{ mol dm}^{-3}$

$10^2[\text{CAP}] \text{ mol dm}^{-3}$	$10^4 k_{\text{obs}} \text{ s}^{-1}$
0.5	1.530
1.0	2.085
2.0	3.498
3.0	4.289
4.0	5.238



**Figure 6.** Plot of  $\log [\text{CAP}]$  against  $\log k_{\text{obs}}$

The plot of  $\log k_{\text{obs}}$  against  $\log [\text{CAP}]$  indicates the dependency of the reaction rate on the concentration of CAP (**Figure 6**).

The Keggin structure of 12-tungstocobaltate(III) anion is substitution-inert and precludes an inner sphere mechanism as the central  $\text{Co}^{\text{III}}$  atom is shielded by chemically-inert oxygen atoms. Electron exchange between  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{II}}$  compounds in solution is relatively rapid, which

supports outer-sphere electron transfer.

#### **Effect of Oxidant 12-tungstocobaltate(III) Concentration**

The rate constant remained unchanged as the concentration of the oxidant,  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  increased from  $5.0 \times 10^{-5}$  to  $4.0 \times 10^{-4} \text{ mol dm}^{-3}$  while the concentrations of CAP, perchloric acid and ionic strength were kept constant. (**Table 2**).

**Table 2.** Effect of variation of oxidant 12-tungstocobaltate(III) concentration

$$10^2[\text{Chloramphenicol}] = 2 \text{ mol dm}^{-3}, \quad [\text{HClO}_4] = 0.6 \text{ mol dm}^{-3}, \quad I = 0.7 \text{ mol dm}^{-3}$$

[Oxidant] mol dm <sup>-3</sup>	10 <sup>4</sup> k <sub>obs</sub> s <sup>-1</sup>
0.5	3.26
1.0	3.51
2.0	3.49
3.0	3.43
4.0	3.47

**Table 3.** Effect of [HClO<sub>4</sub>] variation

$$10^4[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5} = 2 \text{ mol dm}^{-3} \quad 10^2[\text{Chloramphenicol}] = 2 \text{ mol dm}^{-3} \quad I = 0.7 \text{ mol dm}^{-3}$$

[H <sup>+</sup> ] mol dm <sup>-3</sup>	10 <sup>4</sup> K <sub>obs</sub> s <sup>-1</sup>
0.1	3.45
0.3	3.58
0.4	3.36
0.6	3.49
0.8	3.62

### Effect of H<sup>+</sup>

The effect of H<sup>+</sup> of the medium was studied to understand the nature of reactant species present in the solution. The effect of the concentration of H<sup>+</sup> on the reaction between CAP and 12-Tungstocobaltate(III) anion was studied by varying the concentration of HClO<sub>4</sub> while keeping the concentration of CAP, [Oxidant], ionic strength and temperature constant. The concentration of HClO<sub>4</sub> varied from 0.1 to 0.8 mol dm<sup>-3</sup>

while all other conditions were constant (**Table 3**). The rate constant remained practically unchanged with an increase in H<sup>+</sup> concentration.

### Effect of Solvent Polarity

1,4-dioxane was used to observe the solvent polarity effect. The value of the rate constant for the reaction decreased with an increase in concentration of 1,4-dioxane from 0 to 15 % v/v. (**Table 4**)

$$10^4[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5} = 2 \text{ mol dm}^{-3}$$

$$10^2[\text{Chloramphenicol}] = 2 \text{ mol dm}^{-3}$$

$$[\text{HClO}_4] = 0.6 \text{ mol dm}^{-3}$$

$$I = 0.7 \text{ mol dm}^{-3}$$

**Table 4.** Effect of change in the dielectric constant

Dioxane (%)	10 <sup>4</sup> k <sub>obs</sub> s <sup>-1</sup>
0.00	3.49
5 %	3.31
10%	3.15
15 %	2.98

### Effect of Ionic Strength and Temperature

The effect of ionic strength was observed using  $\text{NaClO}_4$ . Reaction rates remained the same with an increase in ionic strength while concentrations of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$ , CAP and  $\text{HClO}_4$  remained constant.

At variable temperatures, the reaction rate was measured while keeping the concentrations of CAP, oxidant, perchloric acid and sodium perchlorate constant. With an increase in

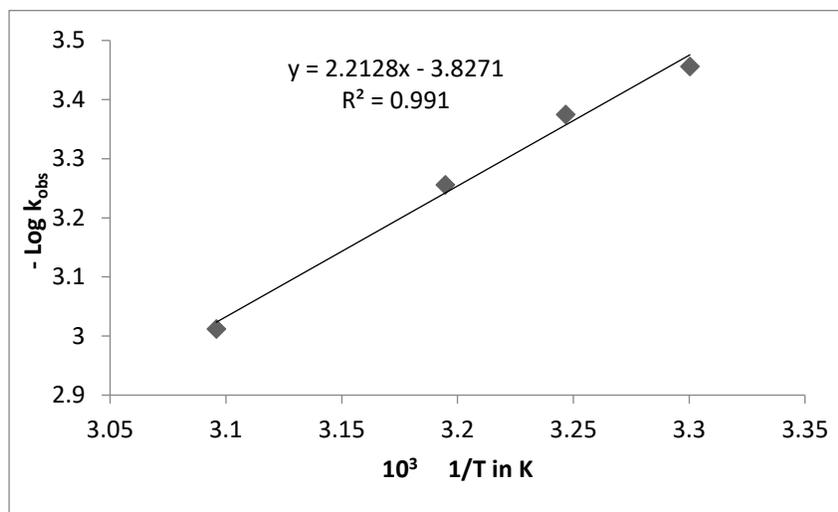
temperature, the reaction rate increased. The rate constants at different temperatures,  $k_{\text{obs}}$  were calculated (Table 5).

A graph of  $\log k_{\text{obs}}$  versus  $1/T$  was plotted and from the slope, the activation energy ( $E_a$ ) was calculated (Figure 7).

Other activation parameters were also determined from this graphically calculated  $E_a$  value and these are given in Table 6.

**Table 5.** Effect of temperature  
 $10^4[\text{Oxidant}] = 2.0 \text{ mol dm}^{-3}$        $10^2[\text{CAP}] = 2.0 \text{ mol dm}^{-3}$   
 $[\text{HClO}_4] = 0.6 \text{ mol dm}^{-3}$        $I = 0.7 \text{ mol dm}^{-3}$

T	$10^4 k_{\text{obs}} \text{ s}^{-1}$
303	3.498
308	4.219
313	5.551
323	9.633



**Figure 7.** Plot of  $\log k_{\text{obs}}$  versus  $1/T$

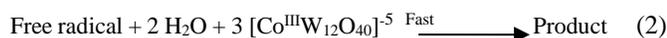
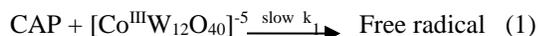
**Table 6:** Activation parameters

Parameters	Calculated values
$E_a \text{ kJ mol}^{-1}$	42.35
$\Delta H^\ddagger \text{ kJ mol}^{-1}$	39.88
$\Delta G^\ddagger \text{ kJ mol}^{-1}$	93.5
$-\Delta S^\ddagger \text{ JK}^{-1}\text{mol}^{-1}$	$176.9 \pm 0.5$

### Test for Free Radicals

Free radical involvement in the oxidation of CAP by 12-tungstocobaltate(III) anion at 303K in acidic media was studied by adding acrylonitrile, which resulted in precipitate formation, suggesting that free radicals may have been produced as intermediates in the reaction.

### Plausible Mechanism

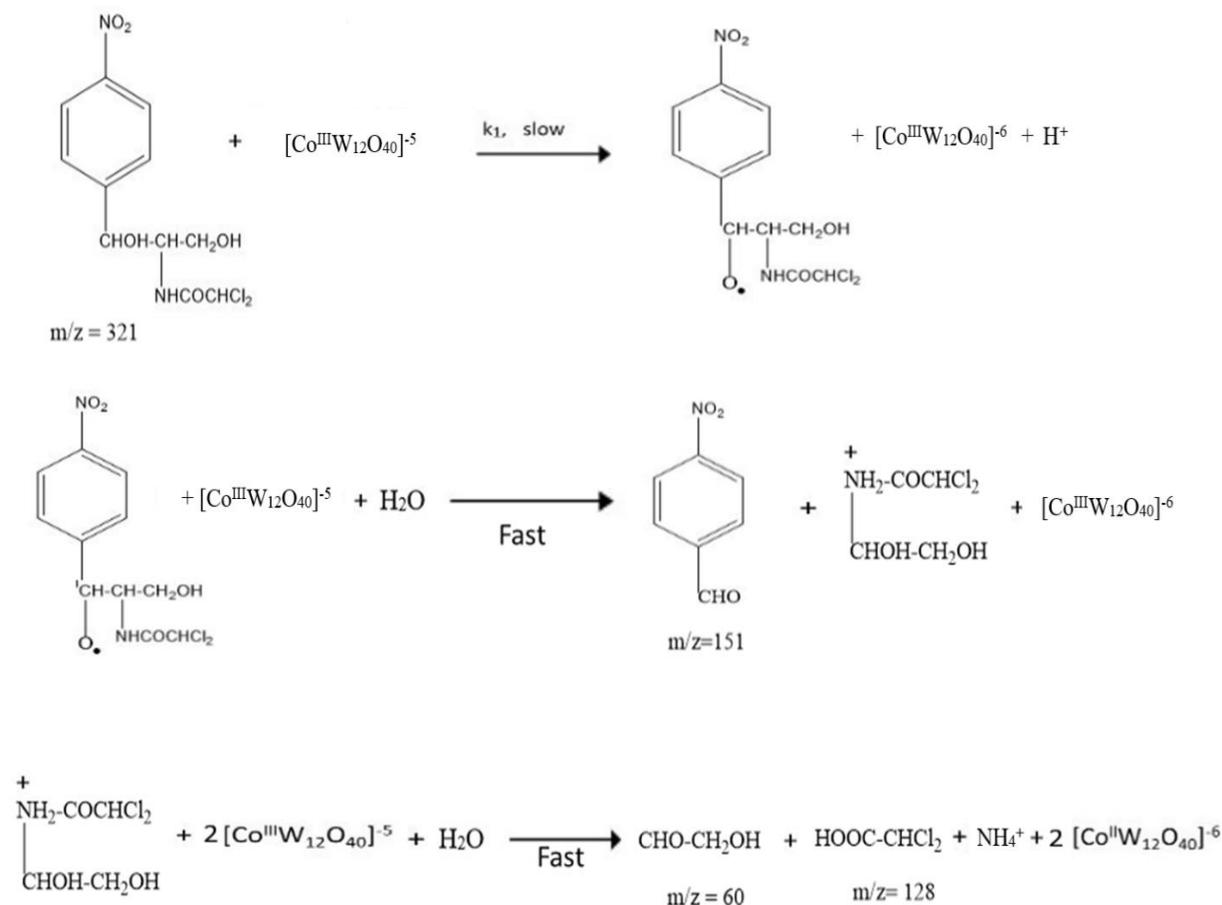


$$\text{Rate} = k_1 [\text{CAP}] \quad (3)$$

The pKa value of CAP is 9. Under the given circumstances, CAP and  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  are the active species in the reaction which generates an oxo-free

radical in the rate determining step. The free radical reacts with another molecule of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  and oxidises to p-nitrobenzaldehyde in a fast step. The complete oxidation requires two more molecules of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{-5}$  which react in further fast steps to obtain the final products. The oxidation of chloramphenicol involves free radical formation in the slow step (RDS). The formed radical further converts to the product in successive fast steps. The products obtained are p-nitrobenzaldehyde, glycoaldehyde, dichloroacetic acid and ammonia. Product analysis was done by using LCMS spectroscopy. Mass spectra of the products obtained by oxidation of Chloramphenicol showed peaks at m/z 151, 128 and 60 after 48 h. The mass spectrum of the DNPH derivative of glycoaldehyde further confirmed formation of glycoaldehyde (Figure 5). Ammonia in the form of ammonium ions was detected using Nessler's reagent.

The proposed reaction pathway is as follows:



## CONCLUSION

The oxidation of chloramphenicol by the 12-tungstocobaltate(III) anion at 303 K was followed spectrophotometrically under pseudo-first-order conditions in a perchloric acid medium. The reaction rate was extremely slow at room temperature but progressed faster with an increase in temperature. So, kinetics was carried out at a slightly elevated temperature.

Oxidation of chloramphenicol by the 12-tungstocobaltate(III) anion followed the first-order dependence of the reaction on substrate concentration. The rate constant remained unchanged as the concentration of the oxidant increased. The reaction rate was found to remain constant despite variations in  $H^+$  concentration. The oxidation of CAP involved free radical formation followed by the attack of other oxidant molecules in an acidic medium. The formation of p-nitrobenzaldehyde was confirmed by IR, NMR and mass spectroscopy. The mass spectrum of the DNPH derivative of glycoaldehyde confirmed the formation of glycoaldehyde. Ammonia formation was confirmed with Nessler's reagent.

Sodium perchlorate and 1,4-dioxane were used to vary the ionic strength and the solvent polarity respectively. Changes in the ionic strength did not affect the rate of reaction; this also supports the initiation of a reaction between a neutral substrate and a charged oxidant. The rate of reaction decreased with 1,4-dioxane concentration. This indicated that the transition state was solvated. With a decrease in relative permittivity, the transition state was less solvated and thus less stable, resulting in a decrease in the rate of reaction. With an increase in temperature, the rate of reaction increased, as seen in the Arrhenius graph. The calculated activation parameters supported the proposed reaction mechanism.

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