



Oxidation-reduction reaction of chromium (VI) and iron (III) with paracetamol: Kinetics and Mechanistic studies

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ABSTRACT

Kinetics of the oxidation of paracetamol (PCM), $C_8H_9NO_2$, by Cr (VI) and Fe (III) were carried out in aqueous HNO_3 (0.06 mol dm^{-3}) medium at ionic strength of 0.01 mol dm^{-3} ($NaNO_3$). The stoichiometries of the reactions were determined to be 1:3 ($Cr_2O_7^{2-} : C_8H_9NO_2$) and 2:1 ($Fe^{3+} : C_8H_9NO_2$). The reaction products were identified as sodium acetate, ammonium ions and benzoquinone. The following infrared stretching frequencies; $\nu_{(C=O)}$, 1623.15 cm^{-1} and 1644.37 cm^{-1} ; $\nu_{(C-H)}$, 880.77 cm^{-1} and 875.71 cm^{-1} (out of plane bending); and $\nu_{(C=C)}$, 474.63 cm^{-1} and 453.41 cm^{-1} were observed for the oxidized products of Cr(VI) and Fe(III), respectively. The reactions were found to follow the rate equation:

$$\frac{-d[M^{n+}]}{dt} = k_2[M^{n+}][C_8H_9NO_2]$$

The second-order rate constants, k_2 , were determined to be $1.31 \pm 0.12 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $1.16 \pm 0.26 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for Cr(VI) and Fe(III), respectively. The reaction rates were dependent on $[H^+]$ but independent of ionic strength. The activation energy (E_a), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) were determined to be $49.45 \text{ kJ mol}^{-1}$, $46.73 \text{ kJ mol}^{-1}$, and $-131.23 \text{ J mol}^{-1} \text{ K}^{-1}$ for Cr(VI); and $42.73 \text{ kJ mol}^{-1}$, $40.01 \text{ kJ mol}^{-1}$ and $-154.27 \text{ J mol}^{-1} \text{ K}^{-1}$ for Fe(III). The mechanism of the reaction was proposed to involve an ester formation and/or a precursor complex leading to the formation of benzoquinone.

Keywords: Paracetamol oxidation, iron (III), chromium (VI), Kinetics, Mechanism.

INTRODUCTION

Paracetamol (acetaminophen) is an effective oral analgesic, with few adverse effects when used at the recommended dose. Nevertheless, paracetamol poisoning is potentially fatal and is the leading cause of acute liver failure according to recent findings [1, 2]. Therefore, the development of simple, sensitive, and accurate methods for determination of its active ingredients in pharmaceutical formulations has become critical in drug quality control. Generally, oxidation of paracetamol by metal ions has been used for the estimation of paracetamol [3]. Thus the kinetics and mechanisms of the interaction of these metal ion oxidants with paracetamol would be very useful for industrial and commercial applications [3]. Methods that have been developed for its assay include fluorimetry [4], capillary electrophoresis [5], the official pharmacopeia [6,7], Sultan method [8], among others. However, these methods usually require pre-concentration and take long time to perform. The official pharmacopeia [6], and the Sultan method [8] for instance, require about 60 and 15 minutes reflux and heating of the reaction mixture, respectively. The main disadvantages of these methods are high concentration (6 mol/dm^3) of sulphuric acid and high temperature (80°C) are required for the oxidation of the paracetamol by chromium (VI) [8].

Transition metal ions are highly oxidizing agents and the oxidation-reduction chemistry of paracetamol with these metal ions can form a basis for understanding the “redox” chemistry of this drug. In this study we investigated the kinetics and mechanisms of oxidation-reduction reactions of paracetamol with two transition metal ions, namely Cr (VI) and Fe (III).

MATERIALS AND METHODS

2.1 Materials

Potassium dichromate, $K_2Cr_2O_7$, (BDH chemicals) trioxonitrate (V) acid, HNO_3 , (BDH chemicals) ferric chloride hexahydrate, $FeCl_3 \cdot 6H_2O$, (BDH chemicals) and sodium trioxonitrate (V), $NaNO_3$, (BDH chemicals); acrylamide, methanol and Ethanol, were obtained from Qualikems and dichloromethane, from Hopkins and Williams Ltd, and Litmus red (export quality Ex-701), paracetamol, 500 mg (Emzor). All reagents were received in analytical grade and used without further purification. Distilled-deionised water was used for all solution preparations. However, the solution of paracetamol was freshly prepared and used immediately to avoid auto-oxidation. FTIR spectrophotometer (Shimadzu FTIR 8400s), Analytical balance (Ohaus Adventure Pro AV313C), Kenko sport timer (Kenko K/F 5853) Thermostated water bath (Clifton 60978) and UV-visible spectrophotometer (Jenway 6305).

2.2 Methods

2.2.1 Determination of UV-Visible Spectrum of the Transition Metal Salts

0.009 M solutions of the salts of Cr (VI) and Fe (III) were prepared by dissolving 0.263 g of $K_2Cr_2O_7$, and 0.608 g of $FeCl_3 \cdot 6H_2O$ each in 250 cm^3 of water. The absorbance of each solution was taken with the UV-visible spectrophotometer (Jenway 6305) in the wavelength range of 300 – 750 nm. The wavelength of maximum absorption was obtained by a plot of absorbance versus wavelength [9] from where the λ_{max} of each solution was determined.

2.2.2 Stoichiometric Studies

The Stoichiometries of the reactions were determined by spectrophotometric titration. Reaction mixtures containing fixed volume, 10.00 cm^3 (6.0×10^{-5} mol/ dm^3) of paracetamol and varying concentrations of the metal salts (1.0×10^{-3} to 1.4×10^{-2} mol/ dm^3 of Cr (VI) and Fe (III)) each at constant ionic strength of 0.01 mol/ dm^3 ($NaNO_3$), temperature of 298 ± 1 K and acid (HNO_3) concentration of 0.06 mol/ dm^3 were allowed to go to completion. The absorbances of the solutions were taken at $\lambda_{max} = 351$ nm for Cr (VI) and $\lambda_{max} = 520$ nm for Fe (III) and the equivalent points determined from the plot of absorbances against the solution concentrations [9].

2.2.3 Kinetic Studies

Rate measurements were made using the UV-visible spectrophotometer at wavelengths λ_{max} for each ion; the reaction rates were monitored at these wavelengths by noting the decrease in absorbance of the reaction mixture with time in each case. All kinetic measurements were made under pseudo-first order conditions with the concentration of paracetamol at least 60 times greater than that of the [Cr (VI)] and [Fe (III)] solutions.

The pseudo-first order rate constants, k_{obs} , were then obtained from the plots of $\ln(A_t - A_\infty / A_0 - A_\infty)$ against time (where A_t , A_0 and A_∞ are the absorbances of the reaction mixtures at times t, zero and infinity, respectively) at constant temperature of 298 ± 1 K, $[H^+] = 6.0 \times 10^{-2}$ M and $I = 0.01$ M. Plot of $\log k_{obs}$ vs. $\log [PCM]$ was then made in each case.

2.2.4 Acid Dependence Studies

The second order rate constants for the PCM/Cr(VI) and PCM/Fe(III) reactions were determined at $[H^+]$ in the range of 0.005-0.025 mol/ dm^3 while keeping the concentration of the reactants and ionic strengths (0.01 mol/ dm^3) constant. Plots of $\log k_{H^+}$ versus $\log [H^+]$ were obtained.

2.2.5 Product Analysis

0.045 M solution of paracetamol was added to an acidified solution of potassium dichromate salt, containing 0.015 M Cr (VI). This was allowed to stand for one hour, in order to obtain the oxidized product. The mixture was then divided into three portions. To the first portion was added 0.02 M sodium hydroxide solution and the formation of precipitate was observed. To the second portion a wet blue litmus paper was dipped and the colour was observed. The third portion was then mixed with dichloromethane and agitated for 45 minutes to isolate/separate benzoquinone (the oxidized product of paracetamol) from the reaction mixture. The two layers were separated using separating funnel, and the organic layer was evaporated to recover the oxidized product. The same procedure was repeated for iron (III) but with 0.09 M of the salt in 1 dm^3 of water, and UV-visible and FTIR spectrophotometers were used to ascertain the formation of the product.

RESULT AND DISCUSSION

The result of the analyses are shown below in figures 1(a, b) – 4 (a, b) and Tables 1– 4

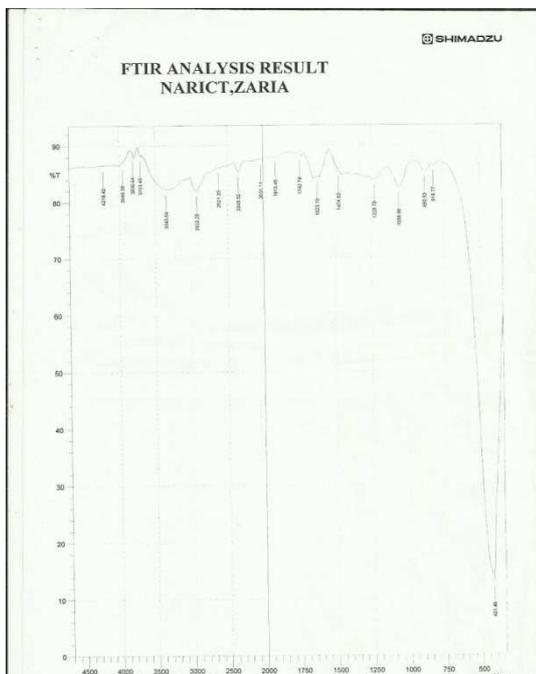


Fig 1a IR spectrum for oxidation product of PCM from Cr (VI) ion.

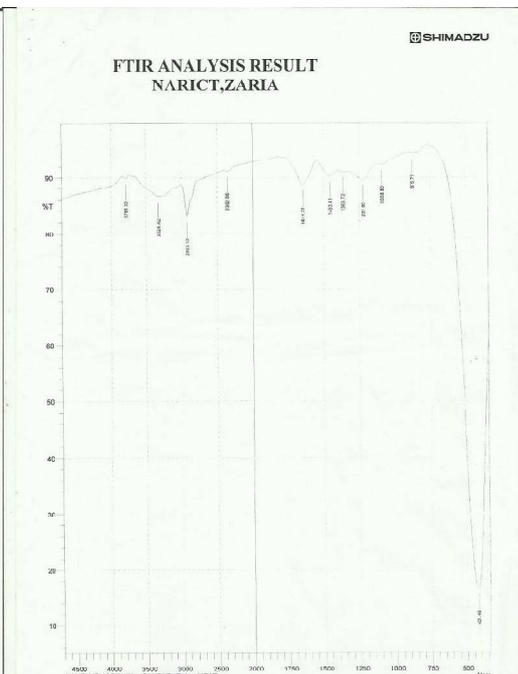


Fig 1b IR spectrum for oxidation product of PCM from Fe (III) ion

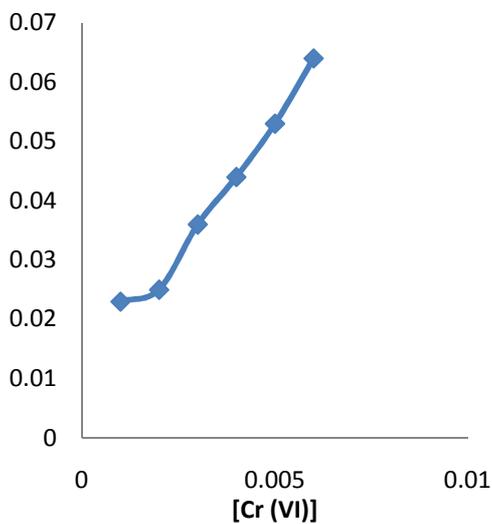


Fig 2a Plot of Absorbance vs [Cr (VI)]

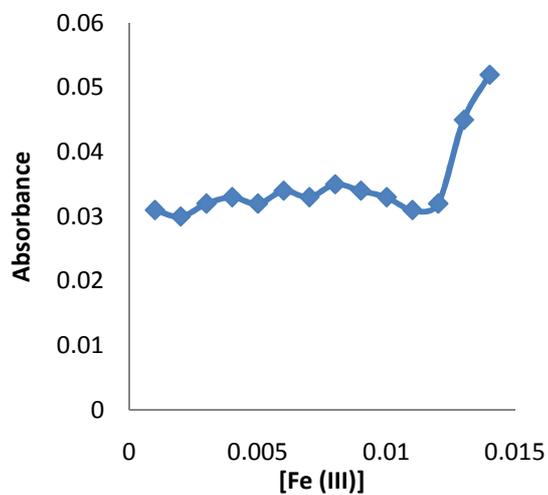


Fig 2b Plot of absorbance vs [Fe (III)]

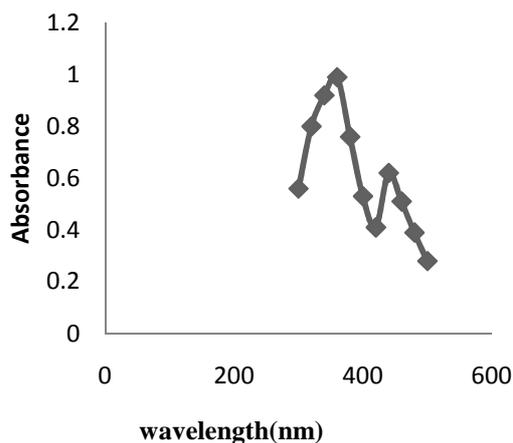


Fig 1a Plot of absorbance vs. wavelength for Cr (VI) ion

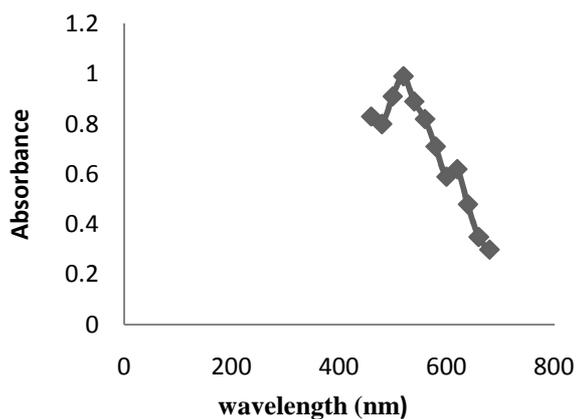


Fig 1b Plot of absorbance vs. wavelength for Fe (III) ion

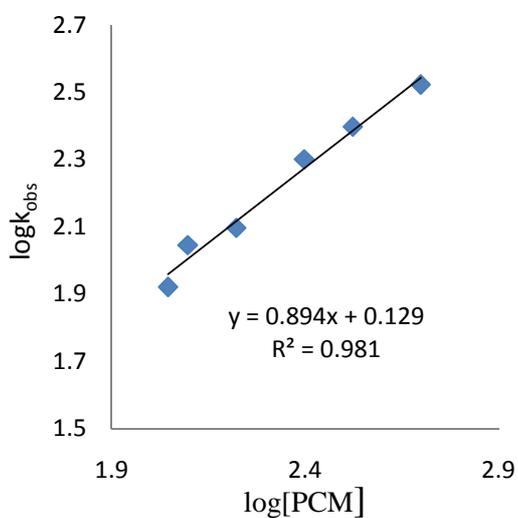


Fig 4a Order with respect to PCM in Cr (VI) ion oxidation

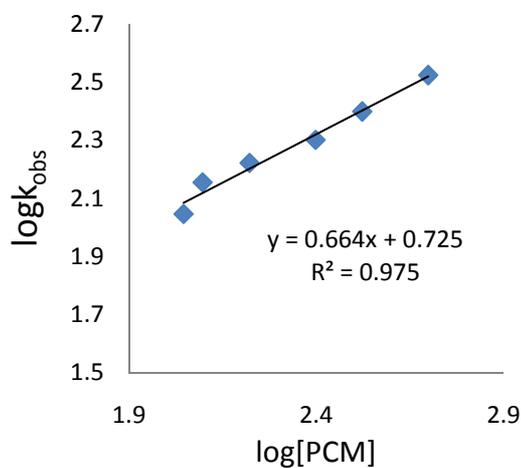


Fig 4b Order with respect to PCM in Fe (III)

Table 1: Infrared and UV-visible spectral data for the oxidation product with Cr(VI) and Fe(III) with paracetamol

Metal Ions	Infrared Frequencies			λ_{\max}
	$\nu(\text{C=O})$	$\nu(\text{C-H})$	$\nu(\text{C=C})$	
Cr(VI)	1623.15	880.77	474.63	543
Fe(III)	1644.37	875.71	453.41	545

Table 2a: Pseudo-first order and second order rate constant data for the reaction involving PCM and Cr⁶⁺ at $\lambda_{\max} = 351 \text{ nm}$, $T = 298 \pm 0.1 \text{ K}$, $[\text{HNO}_3] = 0.06 \text{ mol/dm}^3$, $[\text{Cr (VI)}] = 7.20 \times 10^{-5} \text{ mol/dm}^3$

$[\text{PCM}]/(10^{-4})$ mol/dm^3	I mol/dm^3	$k_{\text{obs}}/(10^{-4})$ s^{-1}	k_2 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
9.00	0.01	12.00	1.33
8.00	0.01	9.00	1.13
6.00	0.01	8.00	1.33
4.00	0.01	5.00	1.25
3.00	0.01	4.00	1.33
2.00	0.01	3.00	1.50

Table 2b: Pseudo-first order and second order rate constant data for the reaction involving PCM and iron (III) ion at $\lambda_{\max} = 520$ nm, T = 298 ± 0.1 K, $[\text{HNO}_3] = 0.06$ mol/dm³, $[\text{Fe (III)}] = 7.20 \times 10^{-5}$ mol/dm³

[PCM]/(10 ⁻⁴) mol/dm ³	I mol/dm ³	k _{obs} /(10 ⁻⁴) s ⁻¹	k ₂ dm ³ mol ⁻¹ s ⁻¹
9.00	0.01	9.00	1.00
8.00	0.01	7.00	0.88
6.00	0.01	6.00	1.00
4.00	0.01	5.00	1.25
3.00	0.01	4.00	1.33
2.00	0.01	3.00	1.50

Table 3a: Pseudo-first order, k_{H⁺} and second order rate constant data for the reaction involving PCM and Cr⁶⁺ at $\lambda_{\max} = 351$ nm, T = 298 ± 0.1 K, $[\text{Cr (VI)}] = 7.20 \times 10^{-5}$ mol/dm³, $[\text{PCM}] = 4.00 \times 10^{-3}$ mol/dm³

[H ⁺]/10 ⁻⁴ mol/dm ³	I mol/dm ³	k _{H⁺} /10 ⁻⁴ s ⁻¹	k ₂ dm ³ mol ⁻¹ s ⁻¹
25.00	0.01	25.00	6.29
21.00	0.01	18.00	4.50
17.00	0.01	14.00	3.50
13.00	0.01	11.00	2.75
9.00	0.01	10.00	2.50
5.00	0.01	7.00	1.75

Table 3b: Pseudo-first order, k_{H⁺} and second order rate data for the reaction involving PCM and Fe³⁺ at $\lambda_{\max} = 520$ nm, T = 298 ± 0.1 K, $[\text{Fe (III)}] = 7.20 \times 10^{-5}$ mol/dm³, $[\text{PCM}] = 4.00 \times 10^{-3}$ mol/dm³

[H ⁺]/10 ⁻⁴ mol/dm ³	I mol/dm ³	k _{H⁺} /10 ⁻⁴ s ⁻¹	k ₂ dm ³ mol ⁻¹ s ⁻¹
25.00	0.01	25.00	6.29
21.00	0.01	17.00	4.25
17.00	0.01	14.00	3.50
13.00	0.01	10.00	2.50
9.00	0.01	7.00	1.70
5.00	0.01	6.00	1.50

Table 4: Pseudo-first order rate constants, k_{obs} for the oxidation-reduction reaction involving PCM with Cr(VI) and Fe(III).; $[\text{M}^{\text{III}}] = 7.20 \times 10^{-5}$ mol/dm³, $[\text{PCM}] = 8.00 \times 10^{-3}$ mol/dm³ and T = 298 K.

[NaNO ₃]/(10 ⁴) mol/dm ³	k _{obs} /(10 ⁻⁴) s ⁻¹	
	Cr(VI)	Fe (III)
21.00	9.00	8.00
17.00	10.00	7.00
13.00	9.00	7.00
9.00	9.00	7.00
5.00	9.00	6.00
1.00	9.00	7.00

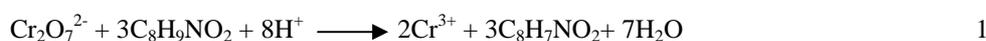
Table 5 Activation parameters (enthalpy, entropy and activation energy) of the oxidation-reduction reaction involving PCM with Cr(VI) and Fe(III)

Metal ion	ΔH^* (kJmol ⁻¹)	ΔS^* (Jmol ⁻¹ K ⁻¹)	E _a (kJmol ⁻¹)
Cr (VI)	46.73	-131.23	49.45
Fe (III)	40.01	-154.27	42.73

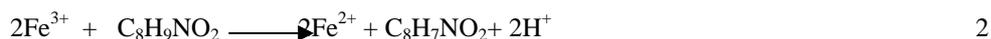
In figures 1 (a) and 1 (b) above, the bands correspond to the d–d transitions; the redistribution of electrons among orbitals that are mainly localized on the metal atom. Similar spectra were obtained in related work [10]. The bands above 300 nm and below 700 nm; involve the motion of electrons from a ligand-based orbital to an essentially metal-based, or vice versa. This makes charge to be transferred from one atom to another. In general, it is referred to as ligand – to – metal charge – transfer (LMCT), and occurs within the visible or near UV region [11, 12].

From the calculation of the concentrations at the equivalence points of the spectrophotometric titrations the stoichiometries of the reactions were obtained as follows: 1:3 for [Cr (VI)] to [C₈H₉NO₂] and 2:1 for [Fe (III)] to [C₈H₉NO₂] as shown in figures 2a and 2b above, respectively.

The dichromate ion – paracetamol oxidation reaction can then be stoichiometrically represented thus;



while iron (III) ion-paracetamol oxidation reaction as;



The addition of acrylamide to the partially oxidized reaction mixture of PCM/Cr (VI) and PCM/Fe (III) at $[\text{H}^+] = 0.06 \text{ mol/dm}^3$, $T = 298 \text{ K}$ and $I = 0.01 \text{ mol/dm}^3$, showed gel formation on addition of excess methanol to the reaction mixture. This is suggestive formation of free radicals as intermediates in the reaction [13].

On addition of 0.02 M solution of sodium hydroxide to the mixture containing 0.045 M solution of PCM and 0.015 M solution of potassium dichromate (VI), a white precipitate of sodium acetate was observed, indicating the presence of acetic acid, CH_3COOH [27]. On immersing a wet red litmus paper into the beaker the colour changed to blue, showing the presence of ammonia also in the solution [14]. The same test was repeated with the mixture containing 0.02 M PCM with 0.09 M ferric chloride hexahydrate.

The characteristic energy of a transition and the wavelength of radiation absorbed are properties of a group of atoms rather than of electrons themselves. The group of atoms producing such absorption is called a chromophore [15]. The UV-visible spectral data of benzoquinone, the oxidized product of paracetamol were recorded in ethanol in the wavelength range 300-750 nm at room temperature ($33 \pm 1^\circ\text{C}$). The electronic spectra data of the compound has λ_{max} at 540 nm [46, 47]. This band is attributed to $n \rightarrow \pi^*$ transitions [16]. The oxidized product (benzoquinone) showed similar band at 543 nm and 545 nm for Cr (VI) and Fe (III), respectively (Table 1). These bands are in complete agreement with the literature values, which showed the oxidation of paracetamol by the various metals to benzoquinone

The oxidation of paracetamol to benzoquinone by the metal ions was further confirmed by infra-red studies. Quinones, which have both carbonyl groups in the same ring, absorb in the 1690 -to- 1635cm^{-1} region [16]. Similar bands were observed in the infra-red spectra of the oxidized product of paracetamol by the metal ions; 1623.15 cm^{-1} and 1644.37 cm^{-1} for Cr (VI) and Fe (III), respectively (Table 1 and Figures 1a and 1b). IR bands in the spectra of ring compounds occur in the low frequency range between 900 cm^{-1} and 650 cm^{-1} . These strong absorption bands result from the out-of-plane bending 'oop' of the ring C-H bonds [17]. In the spectra of the oxidized product were observed bands at 880.77 cm^{-1} and 875.71 cm^{-1} for Cr (VI) and Fe (III), respectively. The product, benzoquinone, was further confirmed by the stretching frequencies, $\nu_{(\text{C}=\text{C})}$ observed at 1474.63 cm^{-1} and 1453.41 cm^{-1} for Cr (VI) and Fe (III), respectively. On the basis of the ultra-violet and infra-red spectrophotometric analysis, it is confirmed that paracetamol was, indeed, oxidized to p-benzoquinone by the metal ions: Cr (VI) and Fe (III).

Tables 2a and 2b summarize the values of k_{obs} and k_2 for the oxidation-reduction reaction involving PCM and the transition metal ions. The results show an increase in k_{obs} values with increase in concentration of PCM. Also, plots of $\log k_{\text{obs}}$ vs. $\log[\text{PCM}]$ in figures 4a and 4b showed a linear relationship, with the slope of 1.00, implying that the reactions are first order with respect to PCM. Hence, the reactions are second order overall, which is in agreement with other works [8]. Therefore the rate equation for the reactions is as given in equation 3 below;

$$-\frac{d[\text{M}^{n+}]}{dt} = k_2[\text{M}^{n+}][\text{PCM}] \quad 3$$

where, M^{n+} is the metal ion.

The second order rate constants, k_2 were determined as $k_{\text{obs}}/[\text{PCM}]$ and found to be $1.31 \pm 0.12 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $1.16 \pm 0.24 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for Cr (VI) and Fe (III) ions, respectively. The second order rate constants as seen in tables 2a and 2b above are fairly constant, further suggesting that the reactions are first order with respect to [PCM] [18]. The second order rate constants for these metal ions are fairly the same with Cr (VI) being higher. This may mainly be because the oxidizing power of the oxyanions rises as a result of both the kinetic and thermodynamic factors [18]. The reaction pathway even though involves the M - O bond rupture, and the bond strength was observed to be $\text{Cr}^{6+} > \text{Fe}^{3+}$, which seems to be more consistent with the oxidation potential values of these metal ions which follow the order $\text{Cr}^{6+} > \text{Fe}^{3+}$ [19]. Therefore, the oxidizing power in this case is more of thermodynamic than kinetic.

Within the range $0.005 - 0.025 \text{ mol/dm}^3$ with other parameters kept constant, the rate of reactions increased with increase in $[\text{H}^+]$ as shown in tables 3a and 3b above. Plots of $\log k_{\text{obs}}$ vs. $\log[\text{H}^+]$ in this acid concentration range are linear with a slope of 1 implying that the reactions are first order with respect to hydrogen ions for dichromate ion and iron (III) ion. The increase in rate constant with increasing $[\text{H}^+]$ seems to suggest the protonation of $\text{Cr}_2\text{O}_7^{2-}$ and Fe^{3+} to give H_2CrO_4 and $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, respectively [17]. The nature of these ions in solution is dependent on the pH of the solution. $\text{Cr}_2\text{O}_7^{2-}$ for instance, exists in equilibrium with HCrO_4^- at pH between 2 and 6, and at pH below, the main species is H_2CrO_4 . This is however dependent on the nature of the acid used, as HCl results to the formation of chlorochromate ion, CrO_3Cl , while sulphuric acid gives a sulfato complex, $\text{CrO}_3(\text{OSO}_3)^{2-}$, hence the

choice of HNO₃ acid for this research [20]. Also, from the constants for the equilibria of iron (III) salts hydrolysis, it can be seen that even at the acid pH of 2 to 3, the extent of hydrolysis is much, and in order to have solutions containing Fe³⁺ ions to a greater extent, the pH must be decreased significantly [18].

The results of temperature dependence studies showed that as the temperature was increased, the reaction rate increased. The value of activation energy (E_a) was calculated from the slope of Arrhenius plots. A high E_a value signifies that the rate constant depends strongly on temperature [20], and that a slow reaction would require a higher energy of activation [5]. The positive ΔH* values are indicative of the endothermic nature of the metal-paracetamol oxidation, which conforms to the high temperature requirement of the traditional methods of paracetamol determination [7]. A similar research of kinetics and mechanism of paracetamol oxidation by chromium (VI) in absence and presence of manganese (II) and sodiumdodecylsulphate was reported. The activation enthalpies, entropies and activation energies for the oxidation-reduction reaction of paracetamol by chromium (VI) were found as 29 kJ/mol (ΔH*) and 26 kJ/mol (ΔH*), -298 JK⁻¹mol⁻¹ (ΔS*) and -297 JK⁻¹mol⁻¹ (ΔS*) and 31 kJ/mol (E_a) and 28 kJ/mol (E_a) in manganese (II) and sodiumdodecylsulphate [8].

Table 6 Pseudo-first order rate constants, k_{obs}, for the oxidation-reduction reaction involving PCM and transition metal ions; [Mⁿ⁺] = 7.20 x 10⁻⁵ mol/dm³, [PCM] = 8.00 x 10⁻³ mol/dm³ and T = 298 K

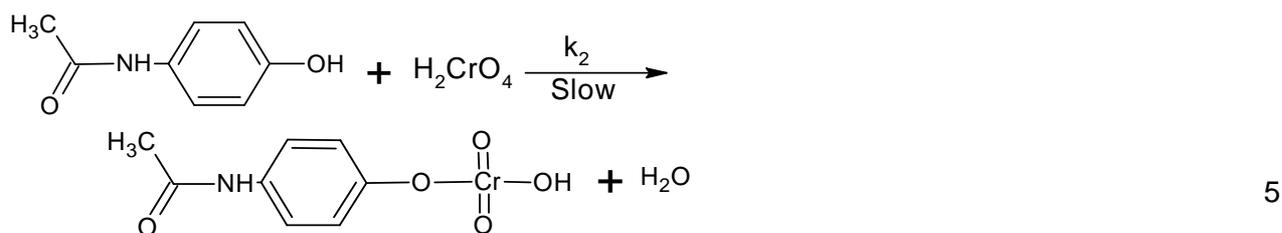
[NaNO ₃]/(10 ⁴) mol/dm ³	k _{obs} /(10 ⁻⁴) s ⁻¹ Cr(VI)	k _{obs} /(10 ⁻⁴) s ⁻¹ Fe (III)
21.00	9.00	8.00
17.00	10.00	7.00
13.00	9.00	7.00
9.00	9.00	7.00
5.00	9.00	6.00
1.00	9.00	7.00

Effect of Ionic Strength on the reaction rate was investigated over the range of 0.001 to 0.021 mol/dm³. The results as presented in table 6 above showed that the reaction rates are fairly constant which showed that the reactions were independent of the ionic strength changes in these range. The independence of the reaction rates on the ionic strength changes suggests that the intermediate is likely a union of the two neutral reactant molecules (paracetamol and the inorganic acid). The negative change in entropy of activation for the reactions further supports the formation of a binuclear activated complex [21].

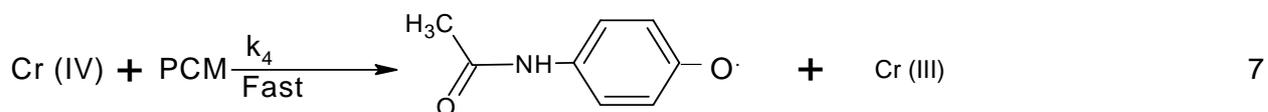
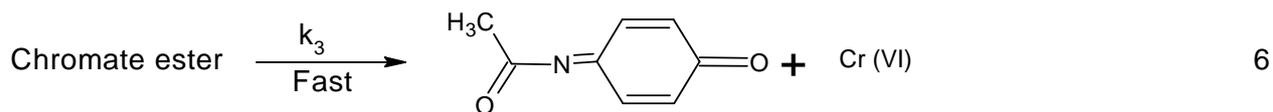
On the basis of these findings, the following mechanisms are proposed for the metal-paracetamol oxidation. Schemes 1 and 2, involve the oxidation of paracetamol by dichromate ion and Fe(III), the reactive species of the metal and paracetamol combine to form an inorganic acid ester; chromate ester and a complex (rate determining steps) [8]. These esters undergo oxidative decomposition in the next step, leading to the formation of an intermediate and Cr (IV). In scheme 2, which involves Fe (III) ion, the reactive species of the Fe (III) ion and paracetamol combine to form a complex C, which oxidatively decomposed to Fe (II) and a radical [13]. Further oxidation of the radical by Fe (III), leads to the formation of the intermediate and Fe (II) ion. The proposed mechanism is further supported by the analysis of the products; ammonia was found as ammonia gas while, acetic acid was detected as sodium acetate in aqueous solution and benzoquinone was confirmed by ultra-violet and infra-red spectrophotometries. Similar products using similar oxidants have been also suggested by Sultan [8].

Proposed Mechanisms for the Reactions

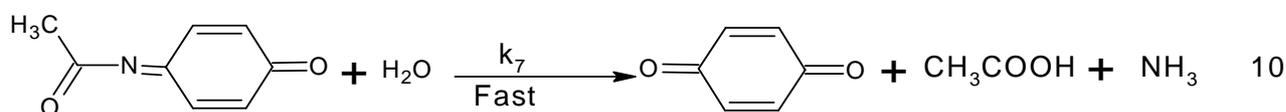
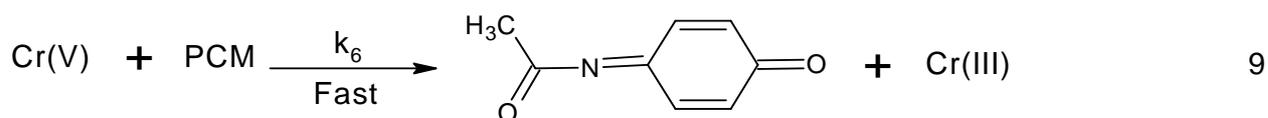
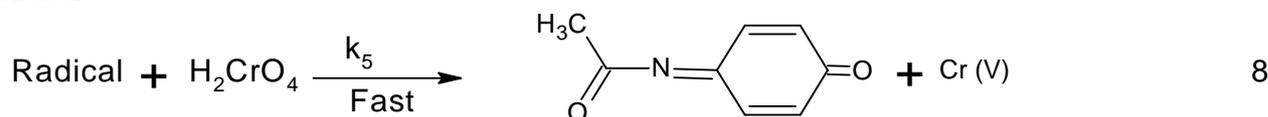
Scheme 1 -Dichromate ion-paracetamol oxidation.



Chromate ester



Radical



Thus,

$$\text{Rate} = k_2[\text{PCM}][\text{H}_2\text{CrO}_4] \quad 11$$

But,

$$K_1 = \frac{[\text{H}_2\text{CrO}_4]}{[\text{HCrO}_4^-][\text{H}^+]}$$

$$\text{and, } [\text{H}_2\text{CrO}_4] = K_1[\text{HCrO}_4^-][\text{H}^+] \quad 12$$

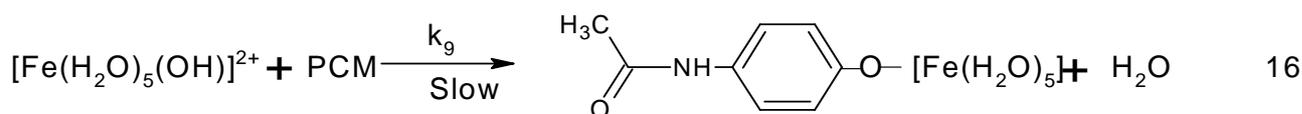
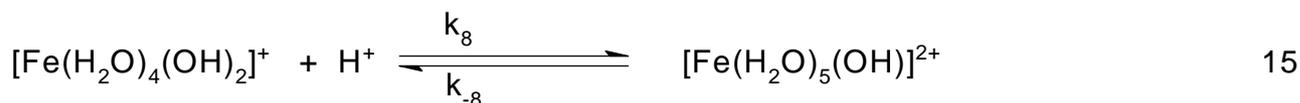
Substituting equation (9) into equation (8) gives

$$\text{Rate} = k_2 K_1 [\text{PCM}][\text{HCrO}_4^-][\text{H}^+] \quad 13$$

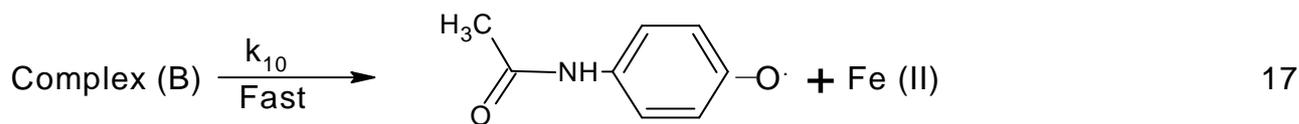
$$= k[\text{PCM}][\text{HCrO}_4^-][\text{H}^+] \quad 14$$

Where $k = k_2 K_1$

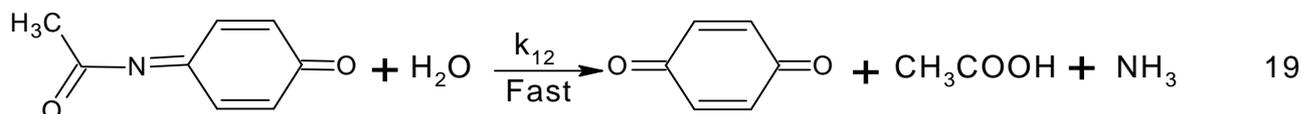
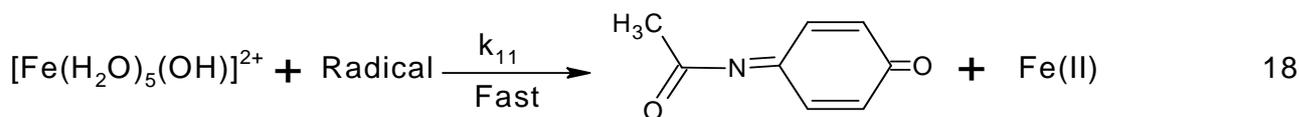
The rate equation seems to be consistent with the experimental data.

Scheme 2: Iron (III) ion – Paracetamol oxidation

Complex (B)



Radical



Here,

$$\text{Rate} = k_9[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}[\text{PCM}] \quad 20$$

It follows from equation (12) that,

$$K_8 = \frac{[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}}{[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+[\text{H}^+]}$$

Therefore,

$$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} = K_8[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+[\text{H}^+] \quad 21$$

Substituting equation (18) into equation (17) gives

$$\text{Rate} = K_9K_8[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+[\text{PCM}][\text{H}^+] \quad 22$$

$$= K[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+[\text{PCM}][\text{H}^+] \quad 23$$

where, $k = K_9K_8$.

CONCLUSION

In the research work, kinetic of the electron transfer reaction of paracetamol with Cr(VI) and Fe(III) ion were carried out in acidic medium at constant ionic strength and within the temperature range of 288 K to 313 K. The metal ion evidently oxidized paracetamol, as there was changes in colour of the metal salt solution and variation in absorbencies on addition of paracetamol and was also observed by the IR spectra. The rate of oxidation of paracetamol by the transition metal ions was found out to be first order with both ions and second order overall in each case. Plausible mechanistic pathways were deduced for the two reactions.

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