Kinetics and mechanism of ruthenium(III) catalyzed oxidation of d-glucose by 12-tungstocobaltate(III) in aqueous hydrochloric acid medium

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ABSTRACT

The oxidation of D-Glucose by 12-tungstocobaltate(III) catalysed by Ruthenium(III) proceeds with transfer of an electron from catalyst to 12-tungstocobaltate(III) generating Ru(IV), which reacts with D-Glucose with the formation of a free radical. The free radical rapidly reacts with second molecule of oxidant to give arabinose. Increase in H^+ ion concentration decreases the rate of reaction, due to acid catalysed enolisation. Decrease in dielectric constant and increase in ionic strength of medium, increases the rate of reaction. Slight decrease in rate is observed by increasing chloride ion concentration, due to conversion of active catalytic species $RuCl_5(H_2O)^{2-}$ into inactive higher chloro-complex, $RuCl_6^{3-}$. The activation parameters were also determined which supports the outer-sphere nature of transition state between catalyst and oxidant.

Key words: 12-Tungstocobaltate(III), Ruthenium(III) Catalysed, Oxidation, D-Glucose Kinetics.

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INTRODUCTION

Most versatile and environmental friendly oxidizing agent comes under the group of polyoxometalates(POMs) like polytungstates, molybdates, silicotungstates and phospotungstates. In recent years these POMs are used in medicines for AIDS treatment[1], radioactive waste treatment, oxidant for polymers, thin film electro-chromic devices[2], transformation of wood-pulp into papers, and many other applications. Hence necessity of understanding the reaction mechanism of POM mediated reactions, motivates this work. Homogenous redox reactions involving polyoxometalates are the best examples of outer-sphere electron transfer processes.[3] One such polyoxometalate, 12-tungstocobaltate(III) has been referred as soluble anode. Oxidation of various organic and inorganic substrates by polyoxometalate containing hetero-atom in its higher oxidation state have been studied.[4] Such oxidations generally proceed with low rates and require high temperatures.[5] Development of multicomponent systems for such slow reactions is desirable to enhance their rates. A three-component redox system including polyoxometalate, hydroquinone and palladium(II) was found to be an efficient homogenous catalyst for Wacker-type of oxidations of alkenes.[6] Therefore in continuation of our work on catalysis of polyoxometalate oxidations,[7] herein we report oxidation of D-glucose by 12-tungstocobaltate(III) in presence of ruthenium(III)

D-glucose is regarded as a representative reducing sugar and is also carbohydrate unit of nucleic acids. These carbohydrate units play important role in mammalian food supply and metabolism. Therefore, interaction of these carbohydrates with metal complexes have been subject of numerous investigations. Oxidation of D-glucose, d-fructose and D-mannose by 12-tungstocobaltate(III) has been studied by Banerjee and co-workers at 60^oC and predicted that the keto-sugar (D-fructose) follow zero-order kinetics, where as the aldo-sugar (D-glucose and D-mannose) follow pseudo-second order kinetics in oxidant concentration.[8] It was observed during present investigation that the reaction in absence of ruthenium(III) occurs to negligible extent at 25^oC and in presence of 2.0 x 10^{-6} mol dm^{-3} of ruthenium(III) it proceeds with measurable rate. Ruthenium(III) also acts as an efficient catalyst[9-11] both in acidic and alkaline medium which is used in present investigation.

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MATERIALS AND METHODS

Materials

Reagent grade chemicals and doubly distilled water were used throughout the work. The glucose solution was freshly prepared every day in water. The cobalt complexes $[Co^{III}W_{12}O_{40}]^{5-}$ and $[Co^{II}W_{12}O_{40}]^{6-}$ were prepared[12,13] by the reported method and standardized spectrophotometrically[14] (at 624 nm , ε_{624}= 180 ± 2 dm^3 mol^{-1} cm^{-1} for $[Co^{II}W_{12}O_{40}]^{6-}$ and at 388 nm, ε_{388}= 1150 ± 2 dm^3 mol^{-1} cm^{-1} for $[Co^{III}W_{12}O_{40}]^{5-}$, respectively) using Elico SL 159 UV-VIS spectrophotometer. The catalyst, ruthenium(III), was prepared by dissolving ruthenium trichloride (Loba) in 0.1 mol dm^{-3} HCl and standardized[15] by EDTA titration. Ionic strength was maintained using $NaClO_4$ and to vary hydrogen and chloride ion concentrations $HClO_4$ (BDH) and NaCl (BDH) were used, respectively.

Kinetic study

The reaction was studied under pseudo-first order condition keeping [Glucose] >> $[Co^{III}W_{12}O_{40}]^{5-}$ in presence of Ru(III) at constant temperature of 25.0 ± 0.1°c, and it was followed by measuring the absorbance of product, $[Co^{II}W_{12}O_{40}]^{6-}$ at 624 nm. The rate constants were determined (Table 1) from the pseudo-first order plots of log $[Co^{II}W_{12}O_{40}]^{6-}$ against time, and the values of rate constants could be reproducible within ± 4%. In an earlier study the reaction was followed by measuring decrease in concentration of $[Co^{III}W_{12}O_{40}]^{5-}$ at 388 nm.[8] It was observed that the oxidation product, $[Co^{II}W_{12}O_{40}]^{6-}$ also shows considerable absorbance at this wavelength.[14] Therefore, increase in the concentration of $[Co^{II}W_{12}O_{40}]^{6-}$ was measured at 624 nm, where $[Co^{III}W_{12}O_{40}]^{5-}$ dose not absorbs considerably.

Stoichiometry

The stoichiometry was studied by keeping the concentration of $[Co^{III}W_{12}O_{40}]^{5-}$ (1.0 X 10^{-2} mol dm^{-3}) constant and varying the concentration D-Glucose from 1.0 x 10^{-4} to 4.0 x 10^{-4} mol dm^{-3} in 0.1 mol dm^{-3} HCl. The reactants were mixed and the concentration of $[Co^{II}W_{12}O_{40}]^{6-}$ was analyzed spectrophotometrically after 48 h at 624 nm. The stoichiometry was found to be 2 moles of $[Co^{III}W_{12}O_{40}]^{5-}$ per mole of D-Glucose.

Reaction order

The order in oxidant is unity as evidenced by the linearity of pseudo-first-order plots of log $[Co^{III}W_{12}O_{40}]^{5-}$ against time and the rate is independent of glucose concentration as the pseudo first-order rate constants were fairly constant (Table 1). There was no effect of the added product $[Co^{II}W_{12}O_{40}]^{6-}$ between the concentration range of 0.2 x 10^{-3} to 5.0 x 10^{-3} mol dm^{-3} keeping all other concentrations constant. The effect of catalyst was studied between the concentration range of 0.2 x 10^{-5} to 6.0 x 10^{-5} mol dm^{-3} keeping all other concentrations constant (Table 2). The order in catalyst, as determined from log k_{obs} against log [(Ru(III)] was also found to be unity.

Effect of hydrogen and chloride ion concentration

The effect of hydrogen and chloride ions was carried out, in order to understand the nature of reactant species present in the solution. The concentration of $[H^+]$ and $[Cl^-]$ were varied between 0.01 to 0.1mol dm^{-3} keeping $[Cl^-]$ and $[H^+]$ constant at 0.1 mol dm^{-3} each respectively (Table 2). To vary the concentration of $[H^+]$ and $[Cl^-]$ sodium chloride and perchloric acid were used respectively. The decrease in rate was observed on increase in concentration of hydrogen ion whereas, the reaction was found to be slightly retarded by chloride ions (Table 2). The order in $[H^+]$ion was found to be -0.45 as determined from the plot of log k_{obs} versus log $[H^+]$.

### Effect of ionic strength, solvent polarity and temperature

The effect of ionic strength and solvent polarity was studied keeping $[Co^{III}W_{12}O_{40}]^{5-}$, and D-Glucose constant at 2.0 x 10^{-3} mol dm^{-3} and 6.0 x 10^{-2} mol dm^{-3} and [HCl] at 0.1 mol dm^{-3} . Sodium perchlorate and 1,4-Dioxan were used to vary the ionic strength and the solvent polarity respectively. The rate of the reaction increases as percentage of 1,4-Dioxan (from 0 to 50 % vol.) and increase in ionic strength (from 0.2 to 1.2 mol dm^{-3}). The relative permitivities of the reaction mixtures were computed from the values of the pure solvents and the plot of log k_{obs} against 1/D was found to be linear with positive slope (Figure 1). The reaction was studied at 25, 30, 35, and 40°C and the kinetic data and the activation parameters $\Delta H^{\#}$, $\Delta G^{\#}$ and $\Delta S^{\#}$ for the reaction are given in Table 3.

Product analysis

The reaction mixture containing 0.1 mole of $[Co^{III}W_{12}O_{40}]^{5-}$, 0.04 mole of glucose, 1 x 10^{-5} mol dm^{-3} of catalyst in 0.1 mol dm^{-3} of HCl was prepared and allowed to stand for two days. The product of reaction, arabinose, was confirmed by paper chromatography[16] and identified by its p-nitroanilide derivative[17] (m.p 206°C). The reaction mixture was after completion of the reaction and distilled, formaldehyde collected was confirmed by its 2-4,DNP derivative[18] (m.p.166 $^{\circ}$C).

RESULTS AND DISCUSSION

The stoichiometry of the reaction was found to be two moles of $[Co^{III}W_{12}O_{40}]^{5-}$ per mole of D-Glucose as given in equation 1 with formaldehyde as one of the product. It was also confirmed, in a separate study, that $[Co^{III}W_{12}O_{40}]^{5-}$ did not further convert formaldehyde to formic acid. The order in oxidant, $[Co^{III}W_{12}O_{40}]^{5-}$ and catalyst, ruthenium(III) are unity each and the reaction is independent on the concentration of glucose. Several mechanisms

$$C_6H_{12}O_6 + 2[Co^{III}W_{12}O_{40}]^{5-} \rightarrow C_5H_{10}O_5 + 2[Co^{II}W_{12}O_{40}]^{6-} + HCHO \quad (1)$$
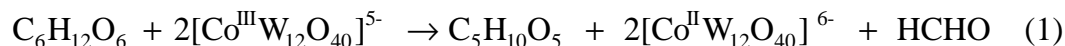
have been proposed for the ruthenium(III) catalysed oxidations by various oxidizing agents which differ in initial step of the reaction.[9-11] The dependence of the rate on the substrate concentration indicate oxidation of the substrate by ruthenium(III) generating ruthenium(II) which will be oxidized back by the oxidant in a subsequent step. On the other hand if the reaction rate is independent of substrate concentration the reaction will be initiated by the oxidation of ruthenium(III) to its higher oxidation states either to ruthenium(IV) or ruthenium(V) which then oxidizes the substrate in a fast succeeding step. In the present study the uncatalysed reaction occurs to negligible extent so that the catalysed path is independent of substrate concentration therefore, the catalysed reaction will be initiated by the reaction between the catalyst, ruthenium(III) and the oxidant, $[Co^{III}W_{12}O_{40}]^{5-}$. For further oxidation of ruthenium(IV) to ruthenium(V), as proposed in some of the reactions, it requires a two electron oxidant or an order greater than unity in case of one electron oxidant. Therefore, from the kinetic results obtained the first step of the reaction is oxidation of ruthenium(III) by $[Co^{III}W_{12}O_{40}]^{5-}$ generating ruthenium(IV) . The next step would be oxidation of substrate either by one electron or by two electron change with the formation of ruthenium(III) or ruthenium(II) respectively. The redox potential[19] of the Ru(IV)/ Ru(III) and Ru(IV)/ Ru(II) couples are 1.3 and 0.3 V respectively due to which ruthenium(II) acts as a very good reducing agent which can be oxidized by the solvent water.[20] Thus, if ruthenium(II) is formed in the reaction it will affect the stoichiometry of the reaction as some of it will be consumed by the solvent where as formation of ruthenium(III) results in generation of free radicals due to one electron oxidation of the substrate. Since there was no change in the stoichiometry of the reaction and free radical formation was confirmed, by polymerization and decrease in the rate of the reaction in presence of added acrylonitrile in the reaction mixture, the reaction involves ruthenium(III)/ ruthenium(IV) catalytic cycle.
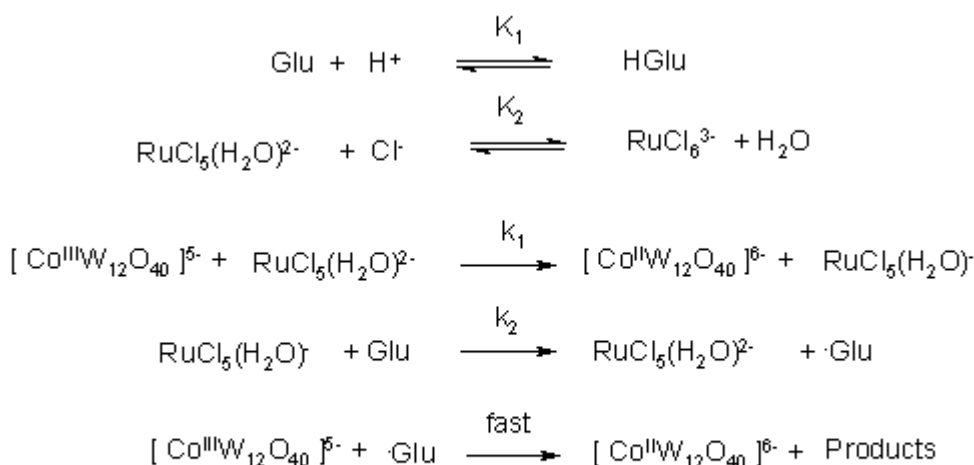
Scheme 1

The rate of the reaction was found to be retarded by increase in both chloride and hydrogen ion concentration. Such retardation is due to the prior equilibria involved in the reaction. In aqueous hydrochloric acid solution the catalyst exists in the form of $RuCl_5(H_2O)^{2-}$ and it will be converted to $RuCl_6^{3-}$ as the chloride ion concentration increases.[21] Since the reaction is inhibited by the chloride ion, $RuCl_5(H_2O)^{2-}$ is the active catalyst species involved in the reaction. Similarly, the effect of hydrogen ion is also due to the protonation equilibria. There are no reports of protonation of the active catalyst species $RuCl_5(H_2O)^{2-}$ and in case of the oxidant it had been shown spectrophotometrically that it does not undergo protonation. Therefore, the acid catalysed enolization of the substrate, glucose, is the reason for the decrease in the rate of the reaction indicating the unprotonated glucose as the active substrate species. The order in oxidant and catalyst was found to be unity each and the reaction zero order dependence on the substrate concentration. Considering all the kinetic data the initiation of the D-glucose oxidation by 12-tungstocobaltate(III) in presence of ruthenium(III) occurs by interaction between the catalyst and the oxidant

forming an intermediate species ruthenium(IV) which the reacts with glucose in a fast step as shown in Scheme 1. According to Scheme 1 the protonation of glucose and substitution of chloride ion of the active catalyst species, $RuCl_5(H_2O)^{2-}$, occurs in prior equilibria. The rate law for Scheme 1 can be derived as follows, which also explains the zero order dependence of the reaction on substrate concentration. The rate of the reaction will be given by

$$Rate = k_2 [RuCl_5(H_2O)^{3-}] [Glucose] \quad\quad (1)$$

Since, glucose undergo protonation its total concentration, $[Glucose]_{Total}$ can be expressed as

$$[Glucose]_{Total} = [Glucose]_{Free} + [Hglucose] \quad\quad (2)$$

then from the protonation equilibria of glucose we get

$$[Glucose]_{Total} = [Glucose]_{Free} + K_1[H+][Glucose]_{Free}$$

$$[Glucose]_{Free} = [Glucose]_{Total} / 1 + K_1[H^+] \qu\quad (3)$$

Substituting the value of $[Glucose]_{Free}$ from equation 3 into the rate law 1 the result is

$$Rate = k_2 [RuCl_5(H_2O)^{3-}][Glucose]_{Total} / 1 + K_1[H^+] \qu\quad (4)$$
Assuming that equilibrium constant protonation of glucose is low we can write equation 4 as

$$Rate = k_2 [RuCl_5(H_2O)^{3-}][Glucose] / 1 + K_1[H^+] \qu\quad (5)$$

Applying steady state approximation to $[RuCl_5(H_2O)^{3-}]$ we get

$$[RuCl_5(H_2O)^{3-}] = k_1[RuCl_5(H_2O)^{2-}] [Co^{III}W_{12}O_{40}]^{5-} / k_2 [Glucose] \qu\quad (6)$$

Considering the chloride substitution on the $RuCl_5(H_2O)^{2-}$ complex the concentration of the active ruthenium complex, $RuCl_5(H_2O)^{2-}$, is given by

$$[RuCl_5(H_2O)^{2-}]_{Free} = [RuCl_5(H_2O)^{2-}]_{Total} / 1 + K_2 [Cl^-] \qu\quad (7)$$

Again assuming that the chloride substitution has a very low equilibrium constant equation 7 can be written as

$$[RuCl_5(H_2O)^{2-}] = [RuCl_5(H_2O)^{2-}]_{Total} / 1 + K_2 [Cl^-] \qu\quad (8)$$

From equation 6 and 8 we get equation 9 and substitution of equation 9 into the rate law 5 gives the equation 10

$$[RuCl_5(H_2O)^{3-}] = k_1[RuCl_5(H_2O)^{2-}]_{Total} [Co^{III}W_{12}O_{40}]^{5-} / (1 + K_2 [Cl^-]) k_2 [Glucose] \quad (9)$$

$$Rate = \frac{\cancel{k_2 [Glucose]}\, k_1[RuCl_5(H_2O)^{2-}]_{Total} [Co^{III}W_{12}O_{40}]^{5-}}{(1 + K_2 [Cl^-]) (1 + K_1[H^+])\,\cancel{k_2 [Glucose]}} \quad\quad (10)$$

the final rate law would be as given in equation 11 and the pseudo-first-order rate constant by equation 12.

$$Rate = \frac{k_1[RuCl_5(H_2O)^{2-}]_{Total} [Co^{III}W_{12}O_{40}]^{5-}}{(1 + K_2 [Cl^-]) (1 + K_1[H^+])} \qu\quad (11)$$

$$k_{obs} = \left\{ \frac{Rate}{[Co^{III}W_{12}O_{40}]^{5-}} \right\} = \left\{ \frac{k_1[RuCl_5(H_2O)^{2-}]_{Total}}{(1 + K_2 [Cl^-]) (1 + K_1[H^+])} \right\} \qu\quad (12)$$

In order to verify the rate law 12 , graphs of $1/k_{obs}$ against [H^+] and [Cl^-] are plotted and they found to be linear (Figure 2) . From the slopes and intercept of these plots the equilibrium constants K_1 and K_2 were calculated as 7.0 x 10^{-2} and 3.11 x 10^{-1} dm^{-3} mol^{-1} respectively and the rate constant k_1 was found to be 14.53 dm^3 mol^{-1} s^{-1}. Therefore, according to Scheme 1 reaction is initiated by interaction between oxidant and catalyst to generate Ru(IV), which oxidizes the substrate, glucose, by two-electron transfer to form Ru(II) . The formation of Ru(II) as a result of two-electron transfer would have affected the stoichiometry of reaction. Since there was no change in the stoichiometry of the reaction, the probable path would be a single electron transfer step generating a glucose free radical, which was detected in the present study. Ruthenium(III) is known to form chloro-complexes of the general formula $RuCl_n^{3-n}$, where n = 1-6 and, ruthenium(III), in aqueous chloride medium exists mainly as $RuCl_5(H_2O)^{2-}$ and as the chloride ion concentration increases it is converted into $RuCl_6^{3-}$.[20] Slight decrease in the rate of the reaction as chloride ion concentration increase may be due to conversion of active $RuCl_5(H_2O)^{2-}$ to inactive $RuCl_6^{3-}$ in prior equilibrium .

The effect of ionic strength on the rate qualitatively explains that one of the step involve reaction between similarly charged ions, as shown in Scheme I. Catalysis by cations was observed in the oxidation of thiosulphate[22] and sugars[8] by $[Co^{III}W_{12}O_{40}]^{5-}$, but in the present case when [Na^+] was varied from 0.01 to 0.1 mol dm^{-3}, no change in the rate occurred indicating no specific cation catalysis. Further, when Li^+ or K^+ replaces Na^+, no significant change in the rate was observed. Increasing the 1,4-dioxan content in the reaction medium leads to an increase in the rate of the reaction and the plot of log k_{obs} against $1/D$, where D is the relative permitivity, is linear with a positive slope (Figure 1). Formation of an inner-sphere complex between the central Co(III) ion and the active catalytic species is unlikely because it is completely shielded by a shell of WO_6 octahedra.[3] Therefore, formation of an outer-sphere complex by the replacement of one of the water molecules of hydration is a more probable transition state. Since the probable transition state is less solvated and as it is larger in size, it will be more stable in the medium of higher relative permitivity,[23] as observed. The decrease in the value of entropy of activation (Table 5.8) also supports formation of such a transition state.

Comparison of oxidation rate with muta-rotation

In aqueous acidic solution, the rate of muta-rotation of D-Glucose is known to be catalysed by H^+ ion. The rate of muta-rotation in presence of acid at 25°C is given by equation (13),[24]

$$k_m = 0.0096 + 0.258 [H^+] \quad \dots \quad (13)$$

therefore, k_m can be calculated as, $k_m = 0.0354 \ s^{-1}$

$$\alpha\text{-D-glucose} \underset{k''}{\overset{k'}{\rightleftharpoons}} \beta\text{-D-glucose}$$
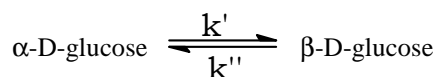
equilibrium constant, $K = k'/k''$ and $k_m = k' + k''$

Using the values of k_m and K (1.77), we can calculate k' and k'' as 1.3×10^{-3} and $2.26 \times 10^{-3} \ S^{-1}$ respectively. Thus the rate of muta-rotation is 100 times greater than the rate of oxidation. Hence, muta-rotation does not interfere the present oxidation reaction.

Effect of enolization on the reaction

Various equilibria of D-glucose, in acidic solution are known.[25] The distribution of these species at room temperature is reported to be 36% of α–D-glucopyranose, 64% β-D-glucopyranose, and the percentage of other forms are negligible. Therefore, in aqueous acidic solutions, conversion of D-glucose into α and β-D-glucopyranose is rapid so that it cannot be rate determining.

Table 1: Effect of reactant concentration on the reaction at 25 °C
[HCl]= 0.1 mol dm⁻³, [Ru^III]= 1 x 10⁻⁵ mol dm⁻³, I = 0.11 mol dm⁻³.

[Glu]= 0.06 mol dm⁻³		[Co^III W₁₂]⁵⁻ = 2 x 10⁻³ mol dm⁻³	
$10^3[Co^{III}W_{12}]^{5-}$ mol dm^{-3}	$10^4 k_s$ s^{-1}	[Glucose] mol dm^{-3}	$10^4 k_s$ s^{-1}
0.5	1.5	0.01	1.3
1.0	1.5	0.02	1.3
2.0	1.3	0.04	1.4
3.0	1.4	0.06	1.3
4.0	1.4	0.08	1.5
5.0	1.4	0.1	1.5

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Table 2: Effect of variation of Ru(III), H$^+$ and Cl$^-$ concentration on reaction
$[Co^{III}W_{12}O_{40}]^{5-}$ = 2 X 10^{-3} mol dm^{-3}, [Glucose] = 6 X 10^{-2} mol dm^{-3}, I = 0.11 mol dm^{-3}

10^5[Ru(III)] mol dm^{-3}	[H$^+$] mol dm^{-3}	[Cl$^-$] mol dm^{-3}	10^4 k$_s$ sec^{-1}
0.2	0.1	0.1	0.2
0.4	0.1	0.1	0.6
0.6	0.1	0.1	0.8
1.0	0.1	0.1	1.3
1.4	0.1	0.1	2.2
2.0	0.1	0.1	3.0
2.4	0.1	0.1	3.5
3.0	0.1	0.1	4.4
4.0	0.1	0.1	5.8
5.0	0.1	0.1	7.2
6.0	0.1	0.1	8.9
1.0	0.08	0.1	1.5
1.0	0.06	0.1	1.8
1.0	0.04	0.1	2.1
1.0	0.02	0.1	2.6
1.0	0.01	0.1	2.8
1.0	0.1	0.05	1.5
1.0	0.1	0.03	1.6
1.0	0.1	0.01	1.8

Table 3: Effect of temperature on the reaction
$[Co^{III}W_{12}O_{40}]^{5-}$ = 2 X 10^{-3} mol dm^{-3}, [Glucose] = 6 X 10^{-2} mol dm^{-3}, [HCl] = 0.1 mol dm^{-3}, [Ru] = 1.0 x 10^{-5}, I = 0.11 mol dm^{-3}

Temperature ºC	10^{4}k$_s$ sec^{-1}
25	1.4
30	1.6
35	1.9
40	2.2
Activation Parameters	
$\Delta H^{\#}$ = 20.92 $\pm$3 kJ mol^{-1}.	
$\Delta S^{\#}$ = - 120.44 $\pm$2 J mol^{-1}.	
$\Delta G^{\#}$ = 87.60 $\pm$2 J mol^{-1}.	

Figure 1: Graph of log k$_s$ against 1/D at 25ºC

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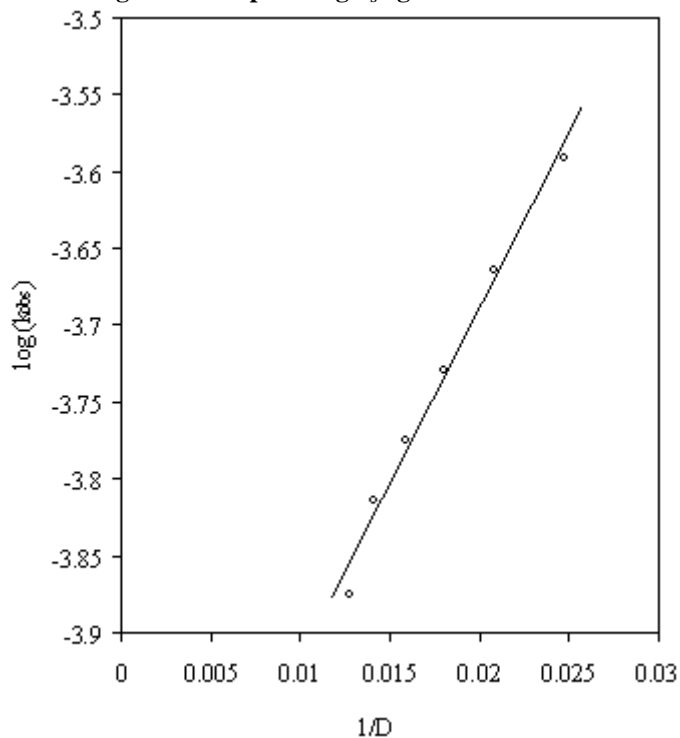
Figure 2: Graph of $1/k_{obs}$ against [H⁺] (O) and [Cl]⁻ (Δ) at 25°C
(Conditions as in table 2)
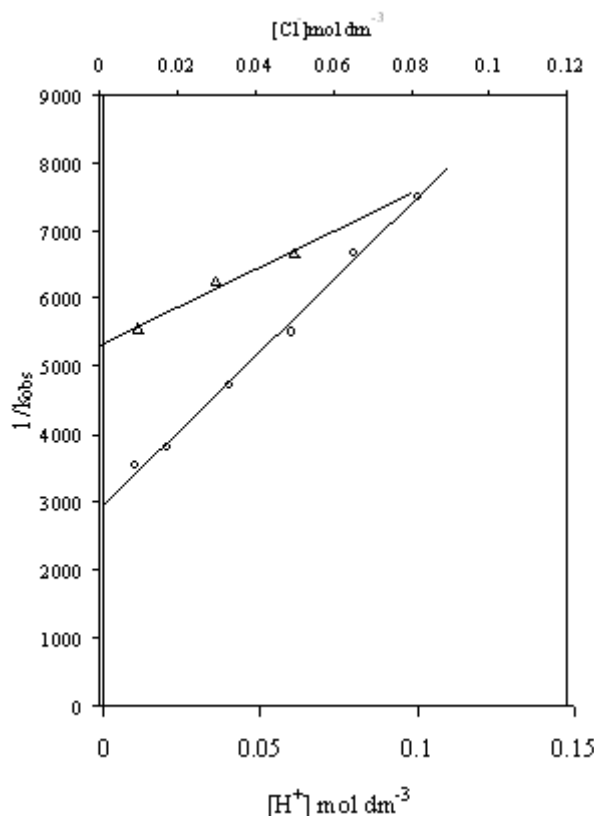
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