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CATALYSED RU(III) OXIDATION OF GLUCITOL AND OSMITROL WITH CHLORAMINE T IN ALKALINE MEDIUM

Chemistry

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ABSTRACT

Kinetics of oxidation of Glucitol and Osmitrol with alkaline medium in presence of Ru act as a homogenous catalyst is reported. Kinetic data obtained that the rates of oxidation are independent of Chloramine T and are directly catalysed by Ru. The reaction rate shows nearly first order kinetics at lower hydroxide concentration and tends to zero at higher hydroxide concentrations. The dependence of reaction rate on the organic substrate concentration is also complicated. The reaction rate which follow first order kinetics at lower concentration and retards at higher concentration of Glucitol. The reaction rate shows nearly first order kinetics with respect to lower Osmitrol concentrations, reaches to maximum beyond which it falls at still higher concentration. In present scenario these substrates are also oxidised with CAT itself. The empirical rate law in terms of disappearance of CAT might be proposed as follows:

$$\frac{-d[CAT]}{dt}=k_1[CAT]+k_2[Ru]$$

Where k1 is observed first order rate constant in Chloramine T and k2 is the constant depending upon the concentration of substrates and hydroxide ion.

KEYWORDS

Kinetics, Mechanism, Oxidation, Chloramine T and Ruthenium (III) catalyst.

INTRODUCTION:

Chloramine-T (CAT) is the most important member of organic halo-amine family and behaves as an oxidizing agent in both acidic and alkaline media[1-5]. It is versatile oxidizing agent and has shown a variety of kinetic results due to formation of its various oxidizing species depending upon pH of the medium. Many reviews presenting very interesting information have also been written by many authors (S.K. Uppadhaya 1991, S. gupta & V. Ali 1988). Ramchandrappa& Puttaswamy (1998) reported Ruthenium[6-8] act as catalyst in redox reaction involves many complexes but a little attention has been paid to explore the catalytic role of Ru with N-halo compounds as oxidant[9-10].

The mechanism proposed for the oxidation of organic substrates involves the formation of a 1:1 complex of Ru and the anion of organic substrates the first step followed by its decomposition to intermediate products and the Ru(VI) species.

A vast amount of literature is available on the kinetics of oxidation of sugar alcohols[11-13], using various oxidants. Different methods and reaction media include acidic and alkaline media (Okoro & Odebunmi, 2009). Inspite of these much works are yet to be done on catalytically oxidation, especially using homogenous transition metal catalyst[14-20] as Mn(II), Ir (III), Ru(VIII), Hg(II) etc.(Singh etal., 2007; Rahmani etal., 2005; Tripathi & Uppadhya, 2004). Therefore in present communication, an attempt has to be made to study the kinetics and mechanism[21] of Ru(III) catalysed oxidation of glucitol and osmitrol by CAT in alkaline medium. The study of sugar alcohols have been carried out because of its biological importance.

Experimental

All the reagents were of analytical grade, and double distilled water was used throughout the work. The samples of the glucitol and osmitrol used in this investigation were of E. Merck (India). G.R. samples of sodium hydroxide, sodium carbonate and sodium bicarbonate were used by dissolving in distilled water. A stock solution of CAT (loba, AR) was prepared in double distilled water and standardized by the iodometric method, and preserved in brown bottles. A solution of Ruthenium chloride (E. Merck) was prepared by dissolving a known weight of $RuCl_3$ in NaOH of known strength and stored in a black coated bottle to prevent photochemical oxidation. The standard solution of $Hg(OAc)_2$ of known strength are also used without further purification. All other reaction vessels were also coated black from outside to avoid any photochemical degradation.

Kinetics

A thermostatic water bath was used to maintain the desired temperature with in $\pm 0.1^0$ C. Requisite volume of reagents, including substrate, was taken in a reaction vessel and thermo stated at 35 ± 0.1^0C for thermal equilibrium. A measured volume of oxidant solution, which was also maintained separately at the same temperature, was rapidly poured in to the reaction vessel. The kinetics was followed by examining desired portions of reaction mixture for oxidant iodometrically using starch as an indicator after suitable time intervals.

RESULT AND DISCUSSION

The kinetic measurements for the rate of the oxidation of glucitol and osmitrol were carried out with wide range of reactant concentrations. It is worth mentioning here that CAT oxidation of these substrates have also been studied by us in aqueous alkaline medium in the absence of Ru catalyst and it was noticed that uncatalysed route of the reaction takes place up to very low concentrations. Thus, the kinetic study has been made in such a condition where catalysed a well as uncatalysed reaction is occurring simultaneously[22].

The reaction nature shows a zero order plot for the rate of oxidation of glucitol in fig (1). In order to avoid the possible error involved due to interference of the reaction products on the reaction rate, the initial (-dc/dt) has been calculated.

The values of (-dc/dt), obtained at varying concentrations of CAT are presented in fig (2), where (-dc/dt) is plotted against corresponding concentration of CAT. This deviation from the straight line clearly demonstrates that deactivation of the Ruthenium is playing the measure role in the reaction. The straight line intercepting the rate axis leads to use, the idea that a part of the reaction is independent of the CAT concentration while the other part is dependent on it. In the oxidation of glucitol by CAT, the reaction obeyed perfect first order kinetics with respect to it. Thus this confirms that the order with respect to CAT is zero even up to wide range of concentrations. Similarly the kinetic data collected for osmitrol are presented in fig (3) from this data it is again obvious that the reaction is taking place in two part, one in which Ru (VI) catalysed oxidation shows zero order dependence of the reaction rate and other in which uncatalysed oxidation indicates directly proportionately of the reaction rate with respect to CAT in each case. Fig (4) demonstrates that the reaction rate, which follows nearly first order kinetics at low glucitol concentration, tends to decrease at higher concentration.

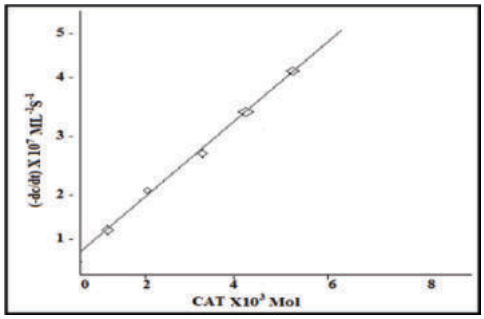


Fig.1 Rate of oxidation of Glucitol

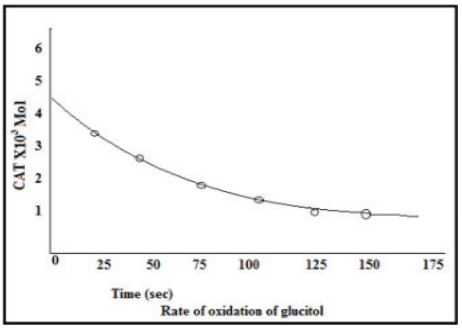
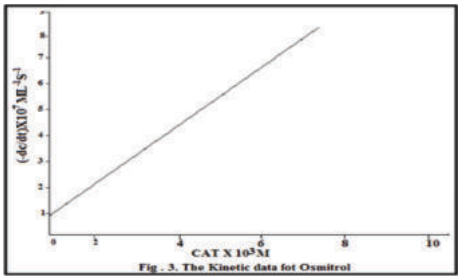
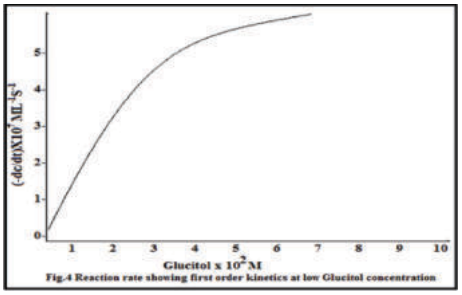
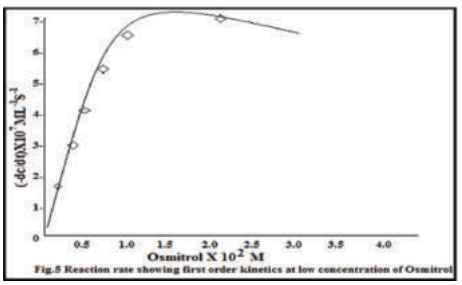


Fig.2 Rate(dc/dt)obtained at varying concentrations of CAT







The result presented in fig (5) again indicates that the reaction rate, which follows nearly first order kinetics with respect to low osmitrol concentration. The kinetic study of glucitol carried out in alkaline buffer containing sodium carbonate and bi-carbonate, indicates that reaction rate follows nearly first order kinetics of low hydroxyl concentration and shows retarding effect at its higher concentration (Table 1). Similarly, hydroxyl ion variation in the oxidation kinetics of osmitrol indicates the same nature as observed in case of glucitol (Fig 6).

Table 1 The Kinetics of Glucitol

$[Na_2CO_3] = 10 \times 10^{-2}$ M [Glucitol] = 5×10^{-2} M
[CAT] = 2.5×10^{-3} M [RuO4] = 4.0×10^{-4} M μ = 1.30 M

PH	(-dc/dt) X 107	(-dc/dt) X 102/[OH]-
10.0	1.40	3.5
10.5	1.46	3.3
11.0	1.51	3.2
11.5	1.56	3.0
12.0	1.60	2.8
12.5	1.63	2.6

Fig 7 indicates the effect of Ru on the oxidation rate of glucitol and osmitrol. The straight line suggests the direct proportionality of the reaction rate with respect to the catalyst concentration and the intercept is for uncatalysed path of the reaction.

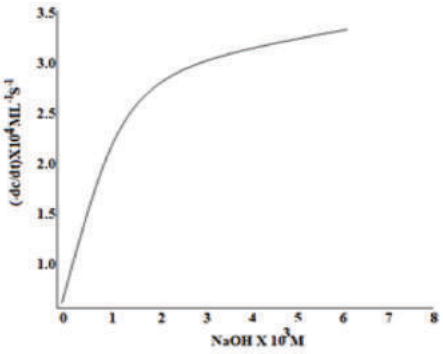


Fig.6 Hydroxyl ion variation in the oxidation kinetics of Osmitrol

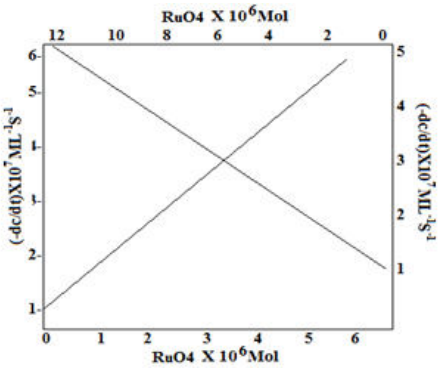


Fig. 7 Effect of Ruthenium Tetraoxide on the oxidation of Glucitol and Osmitrol

Now, on the basis of experimental results it is worth to assume the first order dependence of the reaction rate on catalyst, alcohol and hydroxyl ion at their lower concentrations and zero order on CAT. Thus under these conditions a probable rate law might be given as

$$\frac{-d[CAT]}{dt} = k_1[CAT] + k_2[RuO_4] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where CAT= chloramine T and K_1 is the observed first order rate constant in CAT and K_2 is the constant depending upon the concentration of the substrates and hydroxyl ion. The first term of the right hand side of the equation (1) is due to the part of the oxidation going on without catalyst Ruthenium tetra oxide while the second is due to the oxidation taking place with catalyst Ruthenium tetra oxide.

Mechanism

$$S + Ru(VIII) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Complex } (C_1) \quad \ldots\ldots\ldots\ldots (I)$$

$$C_1 + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Complex } (C_2) \quad \ldots\ldots\ldots\ldots (II)$$

$$C_1 + OH^- \xrightarrow{k_3} Ru(VI) + \text{other products} \quad \ldots\ldots\ldots\ldots (III)$$

$$Ru(VI) + 2[CAT] \xrightarrow[\text{Fast}]{k_4} Ru(VIII) + 2[CAT] \quad \ldots\ldots\ldots\ldots (IV)$$

Where [S] represent the respective polyhydric alcohols. The formation of the complex C_2 is only evidenced for Osmitrol.

Assuming the steady state conditions for the concentration of C_1 and C_2 the above scheme results

$$[C_1] = \frac{k_1[Ru(VIII)][S] + k_{-2}[C_2]}{k_{-1} + k_2[S] + k_2[OH]^-} \quad \ldots\ldots\ldots\ldots (2)$$

$$[C_2] = \frac{k_2[C1][S]}{k_{-2}} = K[C_1][S] \quad \ldots\ldots\ldots\ldots (3)$$

where $K = \frac{k_2}{k_{-2}}$

Eliminating C_2 from equation (2), the concentration of C_1 would be

$$C_1 = \frac{k_1[Ru(VIII)][S]}{k_{-1} + k_3[OH]^-} \quad \ldots\ldots\ldots\ldots (4)$$

The total Ru(VIII) concentration might be obtained from equ.(5)

$$[Ru(VIII)]_0 = [Ru(VIII)] + [C_1] + [C_2] \quad .....(5)$$

Substituting the value of Ru(VIII) in (3) and eliminating C_2, the value of C_1 comes out to be

$$[C_1] = \frac{k_1 [S] [Ru(VIII)]_0}{k_{-1} + k_3 [OH]^- + k_1 [S] [1 + k (S)]} \quad .....(6)$$

Now, rate law in terms of decreasing concentration of CAT would be

$$\frac{-d[CAT]}{dt} = \frac{2d[Ru(VI)}{dt} = 2k_3 [C_1][OH]^- \quad .....(7)$$

From equ. (6) and (7) the rate law comes out to be

$$\frac{-d[CAT]}{dt} = \frac{2k_1 k_3 [S] [Ru(VIII)]_0 [OH]^-}{k_{-1} + k_3 [OH] + k_1 [S] \{1 + k [S]\}} \quad ..... (8)$$

The rate (8) is valid only up to first stage of oxidation of substrate. The actual rate law in terms of Chloramine T (CAT), should be multiplied by the equivalence of CAT as obtained for the respective organic substrates.

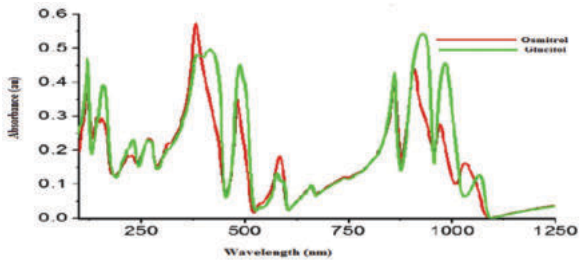
The validity of rate law (8) could be verified under different conditions. When no complex C_2 is formed (K= O), equation (8) reduces to

$$\frac{-d [CAT]}{dt} = \frac{2k_1 k_3 [S] [Ru(VIII)]_0 [OH]^-}{k_{-1} + k_3 [OH]^- + k_1 [S]} \quad ..... (9)$$

Similarly the retarding effect of Glucitol also shows under the conditions

$$\frac{-d[CAT]}{dt} = \frac{2k_1 k_3 [S] [Ru(VIII)_0 [OH]^-}{k_{-1} + k_3 [OH]^-} \quad .....(10)$$

The retarding effect obtained on the variation of hydroxyl ion in osmitrol is very well explained from equation (10). The oxidation products of glucitol and osmitrol could not be determined significantly. The formation of oxalic acid was confirmed by TLC and UV spectral analysis. By UV spectra which showed absorbance band at 256 nm. This indicates that the complex formation has taken place between Ru (VIII) and substrate.



The rate law is in agreement with all kinetic observations and proposed mechanistic steps are supported by negligible effect of ionic strength. From this investigation, it is concluded that CAT and RuO_4 are reactive species of p-TSA and Ruthenium Chloride in alkaline medium.

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