

CHEMICAL KINETICS
AND CATALYSIS

Ruthenium(III) Catalyzed Oxidation of Sugar Alcohols
by Dichloroisocyanuric Acid—A Kinetic Study¹

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Abstract—Kinetics of ruthenium(III) catalyzed oxidation of biologically important sugar alcohols (myo-inositol, *D*-sorbitol, and *D*-mannitol) by dichloroisocyanuric acid was carried out in aqueous acetic acid–perchloric medium. The reactions were found to be first order in case of oxidant and ruthenium(III). Zero order was observed with the concentrations of sorbitol and mannitol whereas, a positive fractional order was found in the case of inositol concentration. An inverse fractional order was observed with perchloric acid in oxidation of three substrates. Arrhenius parameters were calculated and a plausible mechanism was proposed.

Keywords: dichloroisocyanuric acid, sugar alcohols, inositol, sorbitol, mannitol, kinetics, ruthenium(III).

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INTRODUCTION

Sugar alcohols are polyhydric alcohols that represent a group of compounds having a close relation with sugars. They are wide spread in nature in microorganisms, fungi, animals, and plants [1]. Hexitols are the most common alditols. The polyols (inositol, mannitol and sorbitol) are the significant osmolytes in living species [2] and exhibit physiological roles like structural functions, energy storage, coenzyme regulation, and sugar interconversion [3]. Inositol play different vital roles in synthesis of oligosaccharides [4], gene expression [5], signal transduction [6] membrane tethering [7] and auxin perception [8]. *D*-Sorbitol and *D*-mannitol have various medical applications. Both these hexitols are used in food and pharmaceutical industries [9]. Sorbitol is used as a key intermediate in the synthesis of ascorbic acid [10]. *D*-Mannitol plays an important role in stress tolerance in fungi [11]. This polyol is clinically used to reduce acutely raised intracranial pressure and in heart-lung machines [9].

Oxidation of inositol was studied by different oxidants like alkaline hexacyanoferrate(III) ion in presence of osmium(VIII) [12], vanadium (V) in presence of copper(II) [13]. Vanadium(V) oxidation of *D*-sorbitol was studied in the presence of externally added surfactants [14]. Oxidation of *D*-mannitol was carried out using cerium(IV) as an oxidant in presence of ruthenium(III) [15] and iridium(III) [16], NaIO₄ as an oxidant in presence of rhodium(III) [17], by KMnO₄ and hexachloroiridate(IV) in sodium hydrogen carbon-

ate/sodium hydroxide buffer and sodium acetate/ acetic acid buffer respectively [18]. In the presence and absence of surfactants, the oxidation of hexitols (*D*-sorbitol and *D*-mannitol) by cerium(IV) was carried out by Croguennec et al. [19].

The literature survey shows that the oxidation of sugar alcohols has received modest thought compared to studies on the oxidation of sugars. Taking these facts into consideration, recently the present authors have carried out periodate oxidation of inositol, sorbitol and mannitol in alkaline medium and reported substrate inhibition due to stable complex formation between those substrates and periodate [20, 21]. In view of the biological importance of these pure compounds and their derivatives, in continuation, the present paper describes the kinetics and mechanism of ruthenium(III) catalyzed oxidation of three sugar alcohols (myo-inositol, *D*-sorbitol, and *D*-mannitol) by dichloroisocyanuric acid in aqueous acetic acid–perchloric medium.

EXPERIMENTAL

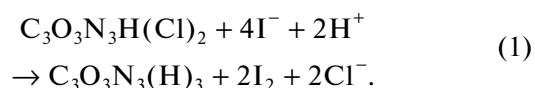
All kinetic measurements were performed under pseudo-first order conditions with higher concentrations of substrates compared to the oxidant. Dichloroisocyanuric acid (DCICA) was purchased from Fluka. Inositol, sorbitol, mannitol, ruthenium chloride and all other chemicals used were of analytical grade and were obtained from SD Fine Chemicals. Essential volumes of oxidant and substrate solutions were thermostated at 35 ± 0.1°C to attain equilibrium.

¹ The article is published in the original.

Table 1. Ruthenium(III) catalyzed oxidation of sugar alcohols by DCICA ([DCICA] = 0.0005 M, [substrate] = 0.02 M, [H⁺] = 0.1 M, temperature = 35°C, solvent composition (AcOH : H₂O) = 20 : 80 (v/v), [Ru(III)] = 5 × 10⁻⁶ M)

Variant	Conc. of variant M	$k_1 \times 10^4 \text{ s}^{-1}$		
		inositol	mannitol	sorbitol
[DCICA] at [Inositol] = 0.005M	0.00025	14.77	5.41	5.75
	0.0005	13.63	5.61	5.80
	0.001	13.65	5.21	5.46
[Substrate]	0.0025	10.99	5.96	5.99
	0.005	13.63	6.66	6.56
	0.01	14.80	5.97	5.56
	0.02	17.03	5.61	5.80
	0.04	20.36	7.00	6.10
	0.08	—	7.12	6.54
	0.1	24.82	7.55	7.29
[H ⁺]	0.05	19.02	7.13	6.38
	0.1	17.03	5.61	5.80
	0.2	13.42	5.22	4.64
	0.4	8.97	4.68	3.85
	0.8	9.36	3.70	—
	5 : 95	—	7.53	5.98
	10 : 90	13.85	6.84	5.89
Solvent composition AcOH : H ₂ O (v/v)	20 : 80	13.28	5.61	5.80
	40 : 60	10.17	5.22	5.55
	35	17.03	5.61	5.80
Temperature (°C)	40	31.01	7.48	8.42
	45	48.05	10.22	10.89
	[Ruthenium(III)]	1.25	2.07	0.80
2.50		5.69	1.84	1.49
5.00		13.63	5.61	5.8
1.00		22.60	11.23	9.21
2.00		46.04	18.02	18.49

After rapid mixing an equal volume of oxidant solution to the substrate solution, progress of the reaction was followed by assaying aliquots of the reaction mixture for dichloroisocyanuric acid, iodometrically using starch as an indicator after suitable time intervals. First order rate constants were evaluated from the linear plots ($r^2 > 0.997$) of $\log[\text{unreacted DCICA}]$ against time. All reactions were generally carried out in duplicate and the rate constants were to $\pm 2\%$. The concentration of unreacted DCICA was determined by iodometry at pH 1–2 in order to follow the reaction.



The ruthenium(III) concentration was assayed by EDTA titration [22].

RESULTS AND DISCUSSION

Reaction Orders of DCICA, Substrate, and Acid

In the ruthenium(III) catalyzed oxidation of inositol, *D*-sorbitol and *D*-mannitol by dichloroisocyanuric acid (DCICA) in aqueous acetic acid—perchloric acid media, the effect of change in concentration of dichloroisocyanuric acid was studied. Plots of $\log(a - x)$ versus time were linear indicating unit dependence with respect to [DCICA] and the first order dependence on [DCICA] was confirmed from the constancy of k_1 values over the range of concentrations of DCICA studied. The rate constants increased on increasing the substrate concentration and a fractional order with [inositol] was observed. But zero order kinetics with respect to concentrations of sorbitol and mannitol was observed as the change in reaction rate is almost negligible with an increase in sub-

strate concentration (Table 1). However, first, fractional and zero order were observed respectively at lower, intermediate and higher concentrations of *D*-mannitol by cerium (IV) in acid medium [23].

A slight decrease in the reaction rates was observed with increase in perchloric acid concentration and the reactions were inverse fractional order with respect to $[H^+]$ in the oxidation of three substrates. Such an inverse fractional order in $[H^+]$ was observed in the oxidation of *D*-mannitol by cerium(IV) in presence of ruthenium(III) [23], whereas, zero effect of $[H^+]$ was observed in the ruthenium(III) catalyzed oxidation of polyhydric alcohols by *N*-bromosuccinimide [24] and bromate [17], Ru(III) catalyzed oxidation of *D*-mannitol by potassium bromate [9], and Rh(III) catalyzed oxidation of ethylene glycol and glycerol by bromate [25]. In the present case, such a minor decrease in the rate of the reaction with an increase in $[H^+]$ is indicating non participation of H^+ in the rate determining step. Out of the possible oxidizing species, HOCl can be considered as the active oxidizing species as the rate of the reaction rate inverse fractional order with respect to $[H^+]$ [26].

Effect of Catalyst and Variation of Solvent Composition

First order dependence on $[Ru(III)]$ was observed in the oxidation of all three substrates (Table 1) which is in corroboration with the first order in ruthenium(III) concentration in the oxidation of *D*-sorbitol and *D*-mannitol by acidic solution of potassium bromate [17] and in Ru(III) catalyzed oxidation of ethylene glycol, glycerol, erythritol and dulcitol by *N*-bromosuccinimide (NBS) [24]. This finding seems to be at variance to the earlier published work [27, 28], where in ruthenium(IV) was active which formed from reaction between oxidant and ruthenium(III).

To find out the effect of dielectric constant on the rates of oxidation, the effect of variation of solvent composition (water-acetic acid mixture) on the rate of reaction was studied in the oxidation of three substrates (inositol, *D*-sorbitol, and *D*-mannitol). The effect of solvent on the reaction rate has been described in detail in the literature. If a plot of $\log k$ versus $1/D$ gives a straight line with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and a positive slope indicates interaction between positive ion and dipole [29]. In the present study, a marginal decrease in reaction rates is observed with an increase in composition of acetic acid in medium in oxidation of all the substrates (Table 1). In other words decrease in dielectric constant of the medium decreases the rate of the reaction. It appears that these reactions are between two neutral molecules, HOCl and complex formed (between ruthenium(III) and substrate molecule). Hence the reactions may be termed as dipole-dipole reactions, which can be further confirmed from linear curves

Table 2. Arrhenius parameters for ruthenium(III) catalyzed oxidation of sugar alcohols

Substrate	ΔE^\ddagger , kJ/mol	ΔH^\ddagger , kJ/mol	$-\Delta S^\ddagger$, J/(mol K)	$\log_{10} P_Z$	ΔG^\ddagger , kJ/mol
Inositol	84.5	81.9	31.9	11.6	91.8
Mannitol	48.8	46.3	157.4	5.0	94.7
Sorbitol	51.3	48.8	148.7	5.5	94.6

with negative slope for the plots of $\log k_1$ versus $1/D$. However, an anion-dipole interaction in the rate-determining step was proposed in Ru(III) catalyzed oxidation of polyhydric alcohols by *N*-bromosuccinimide [24].

Effect of Temperature

The reactions are carried out at three different temperatures to compute various Arrhenius activation parameters. An increase in the rate of reaction was observed with an increase in the temperature in the temperature range 308 to 318 K. Plots of $\log_{10} k$ versus $1/T$ were linear. Activation parameters (E_a , ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger) and $\log_{10} P_Z$ were determined from Arrhenius plot and Gibbs-Helmholtz relationship. Arrhenius parameters are of right order for bimolecular reactions (Table 2). The Moderate values of energy of activation support the proposed mechanisms. The positive values of ΔG^\ddagger and ΔH^\ddagger indicate that transition state is highly solvated in nature. An ordered and compact transition state which has a fewer degrees of freedom is evident from negative values of entropy. Entropy values also explain that a fraction of collisions are stringent leading to a slow decomposition of the rigid activated complex. The values of ΔH and ΔS are both favorable for electron transfer processes. The negative values of entropy indicate that complex between ruthenium(III) and substrates (C) are more ordered than the reactants.

Absence of Induced Polymerization

In presence of added acrylonitrile, the reaction was studied to understand the intervention of free radicals. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 6 h. Upon diluting the reaction mixture with methanol, lack of induced polymerization of the acrylonitrile is evident from non formation of the precipitate as well as zero effect of acrylonitrile on rate of the reaction. The possibility of in situ generation of free radicals during the course of the reaction can be ruled out from the negative polymerization test, whereas, the involvement of free radicals was reported in the oxidation of inositol, sorbitol and mannitol. However, a mechanism involving free

radicals formation was observed in the oxidation of *D*-mannitol by Ce(IV) in aqueous sulphuric acid media [16, 23], and, oxidation of *D*-mannose and *D*-mannitol by KMnO_4 and hexachloroiridate(IV) in sodium hydrogen carbonate/sodium hydroxide buffer and sodium acetate/acetic acid buffer, respectively [18].

Active Oxidizing Species

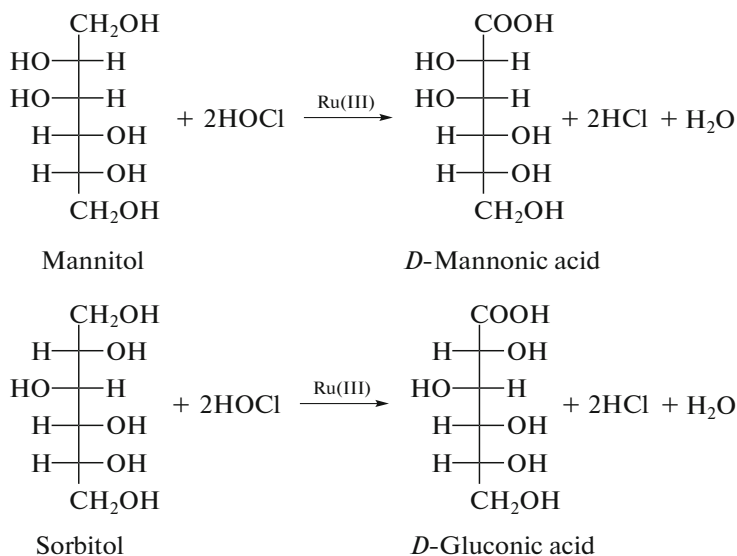
In acidic medium, the active species of DCICA are DCICA itself or HOCl or DCICAH^+ or H_2OCl^+ [30, 31]. In the present case, the possibilities of both unprotonated and protonated forms of undissociated oxidant (DCICA and DCICAH^+) can be ruled out from the negative effect of cyanuric acid on the rate of reaction. Similarly, the role of H_2OCl^+ as oxidizing species in the present reaction can be ruled out from the negative effect of $[\text{H}^+]$ on the rate of reaction. Hence, the only choice left under acidic conditions was HOCl as oxidising species. The decrease in rate with an increase in $[\text{H}^+]$ indicates that probably, HOCl may enter into protonation equilibrium giving H_2OCl^+ and hence the rate of reaction decreased. Thus, reactive species may therefore, be assumed to be HOCl .

Product Analysis and Stoichiometry

The literature collection shows that either aldehyde or acid as the product in the oxidation of sugar alco-

hols by different oxidants. In sulphuric acid medium, inosose was the product in the oxidation of *D*-myoinositol by Cr(VI) [32] and corresponding aldehyde was the product in the oxidation of mannitol by cerium(IV) [33]. In acidic medium, the corresponding monocarboxylic acids were the products like in the ruthenium(III) catalyzed oxidation of *D*-sorbitol and *D*-mannitol by bromate [17], in ruthenium(III) catalyzed oxidation of *D*-mannitol by cerium(IV) [23], in uncatalyzed oxidation of mannitol by potassium bromate [9], rhodium(III) catalyzed oxidation of mannitol by periodate [17] and in ruthenium(III) catalyzed oxidation of erythritol and dulcitol by *N*-bromosuccinimide [24]. Formic acid was one of the product in the oxidation of *D*-mannitol by KMnO_4 and hexachloroiridate(IV) in sodium hydrogen carbonate/sodium hydroxide buffer and sodium acetate/acetic acid buffer respectively [18]. Similarly, formic acid was the product in the reactions between alditols and cerium(IV) in acid medium [34].

In the present study of ruthenium(III) catalyzed oxidation by DCICA in perchloric acid–acetic acid medium, the products are identified as the corresponding monocarboxylic acids (*D*-gluconic acid and *D*-mannonic acid) in the oxidation of *D*-sorbitol and *D*-mannitol as each mole of substrate requires two HOCl or one DCICA in accordance with equations as given below.

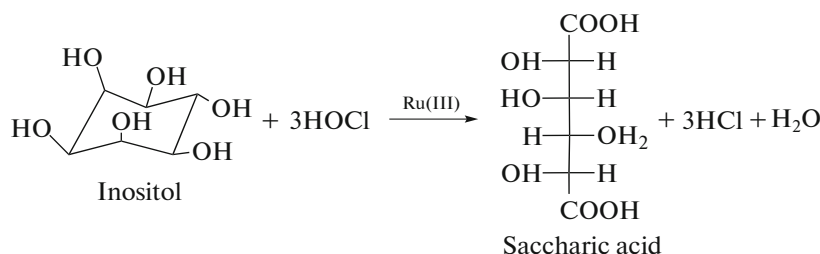


D-Gluconic acid, the product in the oxidation of sorbitol was identified by the spot test [35]. Dinaphthol sulfuric acid test was carried out for further confirmation of gluconic acid by treating a little amount of the final reaction mixture with a few drops of β,β -dinaphthol solution in concentrated sulfuric acid and then was heated to 1 h in a water bath at 85°C. Char-

acteristic green color indicates the presence of *D*-gluconic acid (aldonic acid) [36]. Further, the formation of corresponding aldehydes as products is ruled out from the results of separate experiments carried out in which instantaneous reactions are observed in the ruthenium(III) catalyzed oxidation of the corresponding aldehydes by DCICA. *D*-Mannonic acid

was the product in the oxidation of *D*-mannitol and confirmed by the tests given in literature [37].

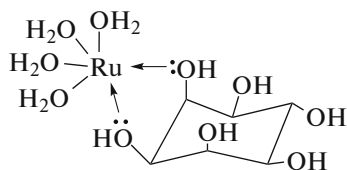
But, in the oxidation by DCICA, the product is a dicarboxylic acid (saccharic acid) in the oxidation of inositol as each mole of substrate requires 3 HOCl or 3/2 DCICA in accordance with equation as given below. Saccharic acid was the product in the oxidation



Higher Reactivity of Inositol

In the present studies of ruthenium(III) catalyzed oxidation of sugar alcohols in acidic medium, the order of reactivity is: inositol > mannitol \cong sorbitol. This report is quite remarkable because the earlier reports demonstrate that sorbitol is the most reactive while mannitol is the least reactive in their oxidation by alkaline KMnO_4 [39] and by vanadium pentoxide (V_2O_5) in acidic medium [40].

In inositol (*cis*-1,2,3,5-*trans*-4,6-cyclohexanehexol), the hydroxyl groups at 1 and 2 positions are in *cis* position as well as alternatively in axial and equatorial. Hence complexation of these two $-\text{OH}$ with Ru(III) is extremely easy. The complex of ruthenium-inositol breaks down due to C–C cleavage to give a dialdehyde initially and leading finally to di-carboxylic acid (saccharic acid). This geometrical difference is reason for higher reactivity in inositol, though the two $-\text{OH}$ groups in general terms are secondary in nature. This is the reason for higher reactivity of inositol compared to mannitol and sorbitol, where primary $-\text{OH}$ groups are oxidized to corresponding acids.



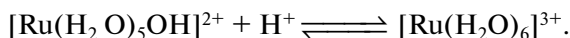
Mechanism and Rate Law

Under the conditions of excess reductant over DCICA, open chain sugar alcohols (*D*-mannitol and *D*-sorbitol) are selectively oxidized at $-\text{OH}$ group on first carbon reflecting the inertness of the secondary $-\text{OH}$ groups of these sugar alcohols compared with primary $-\text{OH}$ groups. This is corroboration with the

of inositol which was confirmed from TLC test with R_f value of 0.59 on cellulose MN 300 HR using the eluting solvent mixture of (isopropanol-ethyl acetate-water—23.5 : 65 : 11.5) using saturated solution of ammonium vanadate in water as chromogenic agent to give a spot of red brown in day light and dark in UV light [38].

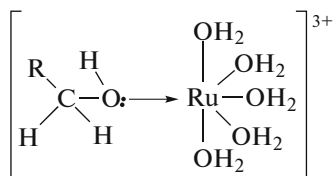
earlier findings that the oxidation takes place at $-\text{OH}$ group of sixth carbon only when anomeric position is blocked as in methyl glycosides [23].

Ruthenium(III) is an efficient catalyst in many redox reactions and exhibits versatile nature due to its multiple oxidation states and formation of intermediate complex involving free radicals [41, 42]. In alkaline media, it is the probable ruthenium(III) chloride species are the $[\text{Ru(III)(OH)}_x]^{3-x}$ where $x < 6$, whereas, at higher pH, the electronic spectra studies have confirmed that the ruthenium(III) chloride exists in the hydrated form as $[\text{Ru(H}_2\text{O)}_6]^{3+}$ [43]. Ru(III) chloride has been reported to give a number of possible chloro species dependent on pH of the solution. In hydrochloric acid medium (having lower pH in the range of 1 to 3), $[\text{RuCl}_6]^{3-}$ has been proposed and confirmed as reactive species dominant [44, 45]. But, in the present case, as the added chloride ions didn't alter the rate of reaction, the probability of participation of chloro-complex ions is excluded. Although the species $[\text{Ru(H}_2\text{O)}_5\text{OH}]^{2+}$ is probable, in the acid medium such a species seem to be remote because of the equilibrium would lie to the right when $[\text{H}^+]$ is much more than $[\text{Ru(III)}]$ [46]. Hence, under the experimental pH range in the present investigation, likely and plausible catalyzing species may be taken to be hexa-aquo species is $[\text{Ru(H}_2\text{O)}_6]^{3+}$ ion.



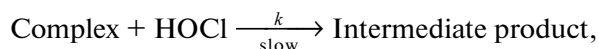
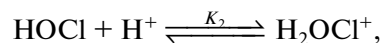
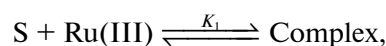
Ruthenium(III) is capable of forming complex with both substrate(s) and oxidant. The lone-pair of electrons on the oxygen atom(s) of polyol can coordinate with Ru(III) to form a $n-n$ complex and alternatively, the n -electrons of oxygen on HOCl form a coordinate bond with Ru(III). In the present case, the Michaelis–Menten type of plot of $1/k_1$ vs. $1/[\text{sugar alcohol}]$ was linear with a non-zero intercept (figure)

and it ascertains the formation of a stable complex between catalyst and substrate, which explains less than unit order in [substrate]. Such a complex formation between substrate and catalyst has been published in the literature [47, 48]. Moreover, the modest activation energy and sizable entropy of activation support a complex transition state in the reaction. The probable structure of the complex between substrate (sorbitol/mannitol) with the catalyst is given below.



The UV-Vis spectra of individual substrates (inositol, sorbitol, and mannitol) and their complexes with ruthenium(III) were taken to establish the complex formation between substrate and catalyst. Bathochromic effects were observed in ruthenium mixtures with a shift in absorption.

The less than unit order in [substrate] presumably results from formation of a complex between the Ru(III) species and substrate. In the case of sorbitol and mannitol, this complex reacts with HOCl (out of the total two HOCl involved or 4 electron transfer reaction) in a slow step with a transfer of two electrons to give aldehyde as an intermediate with regeneration of catalyst. The so formed aldehyde reacts with another HOCl in a fast step to form aldonic acid(s) such as *D*-gluconic acid/*D*-mannonic acid respectively in the oxidation of sorbitol and mannitol respectively. But in the case of inositol oxidation, substrate-ruthenium complex reacts with one HOCl to give an unstable intermediate (CHO-(CHOH)₄-CHO) which rapidly reacts with two more HOCl molecules to give a dicarboxylic acid (saccharic acid) as product.



$$K_1 = \frac{[\text{Complex}]}{[\text{S}][\text{Ru}]},$$

$$K_2 = \frac{[\text{H}_2\text{OCl}^+]}{[\text{HOCl}][\text{H}^+]},$$

$$[\text{HOCl}]_T = [\text{HOCl}] + [\text{H}_2\text{OCl}^+] = [\text{HOCl}] + K_2[\text{HOCl}][\text{H}^+] = [\text{HOCl}]\{1 + K_2[\text{H}^+]\},$$

$$[\text{HOCl}] = \frac{[\text{HOCl}]_T}{\{1 + K_2[\text{H}^+]\}},$$

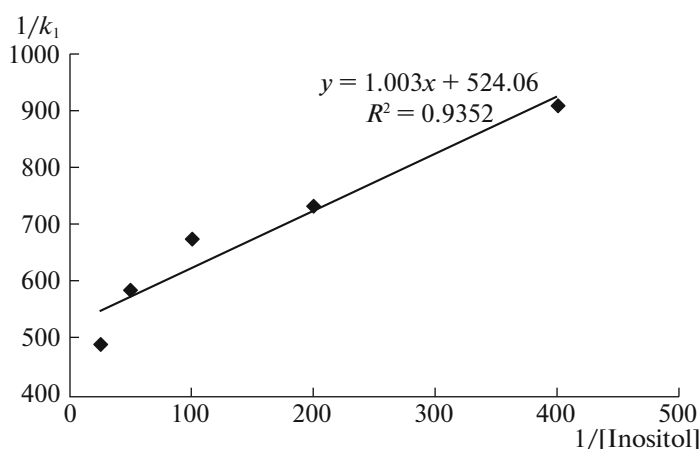
$$[\text{Ru(III)}]_T = [\text{Ru(III)}] + \text{Complex} = [\text{Ru(III)}] + K_1[\text{S}][\text{Ru(III)}] = [\text{Ru(III)}]\{1 + K_1[\text{S}]\},$$

$$[\text{Ru(III)}] = \frac{[\text{Ru(III)}]_T}{\{1 + K_1[\text{S}]\}},$$

$$\begin{aligned} \text{Rate} &= k[\text{Complex}][\text{HOCl}] \\ &= kK_1[\text{S}][\text{Ru(III)}][\text{HOCl}], \end{aligned}$$

$$\begin{aligned} \text{Rate} &= \frac{kK_1[\text{S}][\text{Ru(III)}]_T[\text{HOCl}]}{\{1 + K_1[\text{S}]\}} \\ &= \frac{kK_1[\text{S}][\text{Ru(III)}]_T[\text{HOCl}]_T}{\{1 + K_1[\text{S}]\}\{1 + K_2[\text{H}^+]\}}. \end{aligned}$$

The above rate law explains unit order in [oxidant] and [Ru(III)], fractional order in [substrate] and inverse fractional order in [H⁺] observed in the ruthe-



Michaelis-Menten type of plot for verification of complex between substrate and ruthenium(III).

nium catalyzed oxidation of inositol by DCICA in acetic acid—perchloric acid medium.

When $1 \ll K_1[S]$ i.e., ruthenium(III) exists in mostly in complex form with substrate than in free form, then $\text{Rate} = \frac{k [\text{Ru(III)}]_{\text{T}} [\text{HOCl}]_{\text{T}}}{\{1 + K_2[\text{H}^+]\}}$.

The above rate law explains unit order in [oxidant] and [Ru(III)], zero order in [substrate] and inverse fractional order in $[\text{H}^+]$ observed in the ruthenium catalyzed oxidation of mannitol and sorbitol by DCICA in acetic acid—perchloric acid medium.

CONCLUSION

In the ruthenium(III) catalyzed oxidation of inositol, *D*-sorbitol, and *D*-mannitol by dichloroisocyanuric acid in aqueous acetic acid—perchloric acid media, HOCl is the reactive species which reacts with the complex (formed between substrate and catalyst) in a rate determining step to give fragile intermediate products which decomposes in a fast step to give monocarboxylic acids (gluconic acid and mannonic acids) in the case of sorbitol and mannitol, but it is a dicarboxylic acid (saccharic acid) in the oxidation of inositol.

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