

# Influence of Cerium(IV) and Manganese(II) on the Oxidation of *D*-Galactose by Chromium(VI) in the Presence of $\text{HClO}_4$ <sup>1</sup>

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**Abstract**—The kinetics and mechanism of the oxidation of *D*-galactose by chromium(VI) in the absence and presence of cerium(IV) and manganese(II) were studied spectrophotometrically in aqueous perchloric acid media. The reaction is first order in both [*D*-galactose] and  $[\text{H}^+]$ . The cerium(IV) inhibits the oxidation path, whereas manganese(II) catalyzes the reactions. The observed inhibitory role of cerium(IV) suggests the formation of chromium(IV) as an intermediate. In the manganese(II) catalyzed path, the *D*-galactose–manganese(II) complex was considered to be an active oxidant. In this path, the complex forms a ternary chromate ester with chromium(IV) which subsequently undergoes acid catalyzed redox decomposition (one-step three-electron transfer: *Indian J. Chem.*, 2004, vol. 42A, p. 1060; *Colloids and Surfaces*, 2001, vol. 193, p. 1) in the rate determining step. On the basis of kinetic data, the mechanism of *D*-galactose oxidation is proposed for parent, the manganese(II) catalyzed and cerium(IV)–inhibited reactions. The activation parameters  $E_a = 59 \text{ kJ}$   $\Delta H^\# = 57 \text{ kJ mol}^{-1}$ , and  $\Delta S^\# = -119 \text{ J K}^{-1} \text{ mol}^{-1}$  are calculated and discussed. Reaction products are also examined.

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## INTRODUCTION

The oxidation of organic substrates by hexavalent chromium involves both one-electron and two-electron transfer mechanisms [1, 2], and the reaction must proceed through the formation of chromium(V) species and hydrated chromium(IV). The intermediacy of these oxidation states has been presented on several occasions [3, 4]. Espenson et al. [5] first reported a method for the preparation of aqueous chromium(IV) in the absence of stabilizing ligands. This species was the same as the proposed intermediate in the reaction of chromium(VI) with a number of organic reductants [1–4]. The reactivity of chromium(IV) in various possible reactions, i.e., disproportionation, reduction, oxidation, and coordination, has been discussed [3].

The kinetics of chromium(VI) oxidation by several reducing sugars is well documented in the literature [6–10], but the use of manganese(II) in a similar study is rare [11–13]. The effect of cerium(IV) on the sugars–chromium(VI) reaction has not been reported. It has been established that chromium(IV) is a strong oxidant which will react rapidly with any available reducing agent [14, 15]. Manganese(II) and cerium(IV) play an important role in chromium(VI) oxidations, where they have been recognized as a frequently used tool to determine the involvement of chromium(IV) as an intermediate [16–18]. Doyle et al. [17] have observed the role of cerium(III) and cerium(IV) in the chromium(VI)–alcohol oxidation. The present study was undertaken to

compare the role of manganese(II) and cerium(IV) in the oxidation of *D*-galactose by chromium(VI).

## EXPERIMENTAL

**Materials.** *D*-Galactose (S.D.Fine), potassium dichromate (99%, Merck, India), manganese(II)chloride (99%, Qualigens, India), ceric ammonium nitrate (99%, Merck, India), and perchloric acid (Fisher, 70% reagent) were used as received. The solution of potassium dichromate was stored in a dark glass bottle. The *D*-galactose solution was freshly prepared by direct weighing of the sample. Double distilled (first time from alkaline  $\text{KMnO}_4$ ), deionized, and  $\text{CO}_2$  free water was used to prepare the stock solutions of the reactants.

**Kinetic procedure.** Requisite volumes of *D*-galactose,  $\text{HClO}_4$ , and other additives (if needed) were placed into a three-necked reaction flask fitted with a spiral double-walled condenser, and the contents were thermally equilibrated at the desired temperature in a constant temperature paraffin oil bath of  $\pm 0.1 \text{ K}$  accuracy. The reaction was started by adding the chromium(VI) solution as the last component. Progress of the reaction was followed by measuring the absorbance of the remaining chromium(VI) at definite time intervals at 350 nm against blanks containing all the constituents except chromium(VI) on a Spectronic 21D-spectrophotometer. The pseudo-first order conditions were maintained by keeping the  $[\text{D-galactose}] \gg [\text{Cr(VI)}]$ . The values of pseudo-first order rate constants ( $k_{\text{obs}}$ ,  $\text{s}^{-1}$ ) were calculated from the slopes of the plots of

<sup>1</sup> This article was submitted by the authors in English.

$\log A$  versus time (regression coefficient,  $r \geq 0.996$ ). Other experimental details were the same as described elsewhere [19, 20].

**Product Identification.** UV-VIS studies showed that the spectrum of the aqueous chromium(VI) solution consists of one band ( $\lambda_{\text{max}} = 350 \text{ nm}$ ) and a shoulder at 450 nm. The color of the reaction mixture containing chromium(VI), *D*-galactose, and  $\text{HClO}_4$  changed from pale orange to violet blue, and the spectrum at the end of the reaction showed two *d-d* transitions at 408 and 572 nm corresponding to an aqua chromium(III) ion (the most characteristic part of chromium(III) spectrum is the two *d-d* transitions observable in the 350–600 nm regions [21, 22]). Lactone and aldonic acid were identified by the  $\text{FeCl}_3$ –HCl blue test and  $\text{FeCl}_3$ –phenol bright-yellow test, respectively, as the other reaction products [20, 23].

**Polymerization studies.** The formation of white precipitate was detected by adding acrylonitrile ( $10 \text{ cm}^3$ ) in a reaction mixture containing *D*-galactose ( $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ), chromium(VI) ( $4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ), and  $\text{HClO}_4$  ( $0.69 \text{ mol dm}^{-3}$ ). This result indicates the involvement of a free radical during the oxidation process. Control experiments (with *D*-galactose or chromium(VI) only) did not show any precipitate formation.

## RESULTS AND DISCUSSION

**Reaction in the absence of cerium(IV) and manganese(II).** The reactions were studied at various [*D*-galactose] keeping other variables constant, i.e.,  $[\text{Cr(VI)}]$ ,  $[\text{HClO}_4]$ , and temperature. The observed results are summarized in Table 1. The linear plot between the observed rate constant and [*D*-galactose] passes through the origin confirming first order dependence in [*D*-galactose]. The reaction is catalyzed by  $[\text{H}^+]$  (Table 1) and proceeds with an induction period at low  $[\text{HClO}_4]$ . These results are depicted graphically as the log (absorbance)-time profile in Fig. 1. The dependence of  $k_{\text{obs}}$  on  $[\text{HClO}_4]$  is more than unity (Fig. 2). The invariance of rate constants over a variation in the initial  $[\text{Cr(VI)}]$  is indicative of first-order dependence of the reaction in  $[\text{Cr(VI)}]_T$  (Table 1). These observations lead to rate law (1)

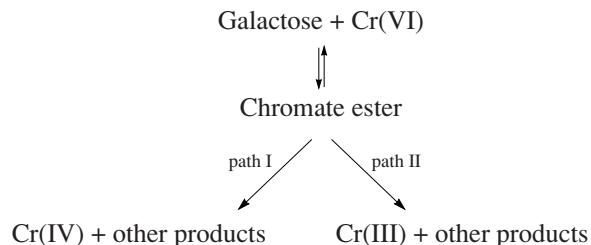
$$-\frac{d[\text{Cr(VI)}]_T}{dt} = k[\text{D-galactose}]_T[\text{Cr(VI)}]_T, \quad (1)$$

where T denotes total concentration. In order to calculate the activation parameters, the kinetic runs were carried out within the 40–60°C range. The values of rate constants are summarized in Table 1. Activation parameters were calculated from Arrhenius and Eyring equations and found to be  $E_a = 59 \text{ kJ/mol}$ ,  $\Delta H^\# = 57 \text{ kJ/mol}$ , and  $\Delta S^\# = -119 \text{ J mol}^{-1} \text{ K}^{-1}$ . The fairly high positive value of  $\Delta H^\#$  indicates that the transition state is highly solvated, and negative  $\Delta S^\#$  also suggests the existence of a compact activated state stabilized by strong hydrogen bonding and large solvation in the electron-transfer step.

**Table 1.** Effect of variation of [D-galactose],  $[\text{HClO}_4]$ ,  $[\text{Cr(VI)}]$ , and temperature on the rate of oxidation of *D*-galactose by chromium(VI)

$[\text{D-galactose}] \times 10^2, \text{ mol dm}^{-3}$	$[\text{HClO}_4] \times 10, \text{ mol dm}^{-3}$	$[\text{Cr(VI)}] \times 10^4, \text{ mol dm}^{-3}$	Temp., °C	$k_{\text{obs}} \times 10^4, \text{ s}^{-1}$
1.0	6.9	4.0	40	2.0
2.0	6.9	4.0	40	3.4
3.0	6.9	4.0	40	4.6
4.0	6.9	4.0	40	8.0
5.0	6.9	4.0	40	9.2
6.0	6.9	4.0	40	11.4
2.0	4.6	4.0	40	1.6
2.0	6.9	4.0	40	3.4
2.0	9.3	4.0	40	6.1
2.0	13.9	4.0	40	15.2
2.0	16.2	4.0	40	27.7
2.0	6.9	1.0	40	3.8
2.0	6.9	2.0	40	3.6
2.0	6.9	3.0	40	3.8
2.0	6.9	4.0	40	3.7
2.0	6.9	4.0	40	3.4
2.0	6.9	4.0	45	5.2
2.0	6.9	4.0	50	6.9
2.0	6.9	4.0	55	10.2
2.0	6.9	4.0	60	15.3

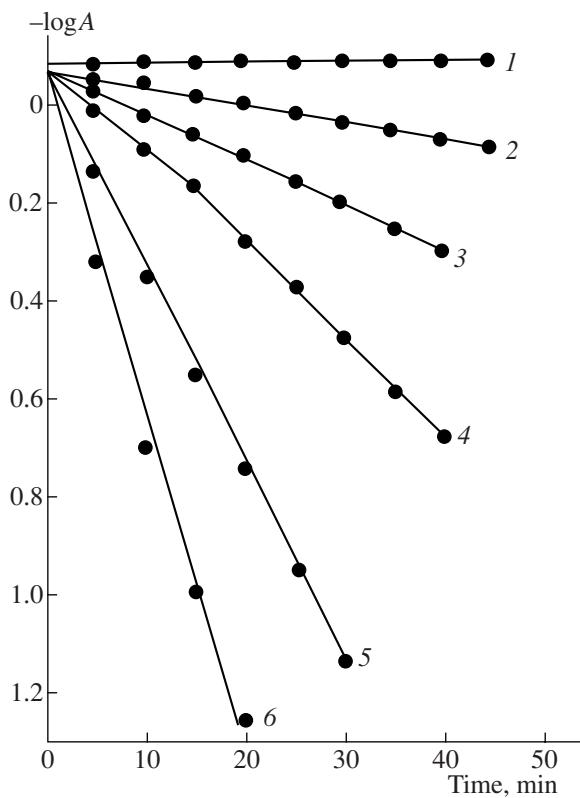
On the basis of the above results and previous observations, the Scheme 1 mechanism can be proposed:



**Scheme 1.**

In Scheme 1, the first step represents formation of a chromate-ester between chromium(VI) and *D*-galactose. In analogy to previous studies, we assume that chromate-ester decomposes by one-step, two-electron (Path I, chromium(IV) formation) or one-step three-electron (Path II, chromium(III) formation) redox mechanisms.

**Reaction in presence of cerium(IV).** To confirm the formation of chromium(IV) as an intermediate (path I),

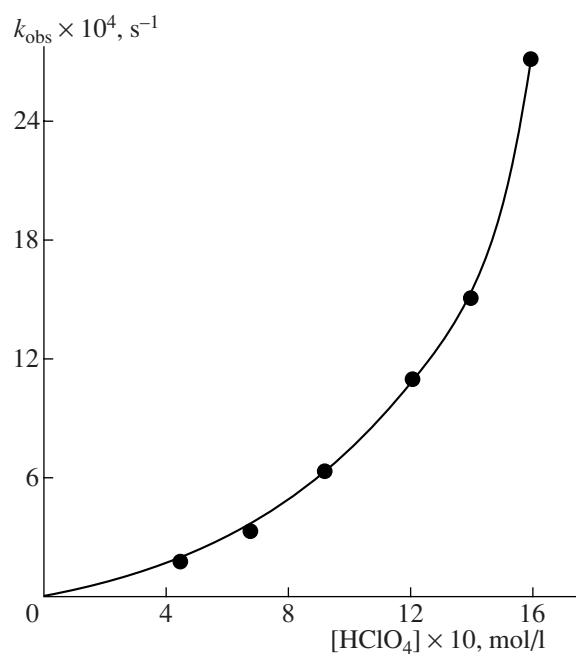


**Fig. 1.** Plots of  $\log$  (absorbance) versus time for the oxidation of *D*-galactose ( $2.0 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ) by chromium(VI) ( $4.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) at  $40^\circ\text{C}$  as a function of  $[\text{HClO}_4] = 0.0$  (1),  $0.46$  (2),  $0.69$  (3),  $0.93$  (4),  $1.39$  (5), and  $1.62$  mol  $\text{dm}^{-3}$  (6).

Scheme 1), a series of kinetic runs were performed at different  $[\text{Ce(IV)}]$  where  $[\text{Cr(VI)}] = 4.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ,  $[\text{HClO}_4] = 0.69$  mol  $\text{dm}^{-3}$ ,  $[\text{D-galactose}] = 2.0 \times 10^{-2}$  mol  $\text{dm}^{-3}$ , and temperature =  $40^\circ\text{C}$ . The

**Table 2.** Effect of variation of  $[\text{Ce(IV)}$ ] and  $[\text{Mn(II)}$ ] on the rate of oxidation of *D*-galactose ( $= 2.0 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ) by chromium(VI) ( $= 4.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) in the presence of  $\text{HClO}_4$  ( $= 0.69$  mol  $\text{dm}^{-3}$ ) at  $40^\circ\text{C}$

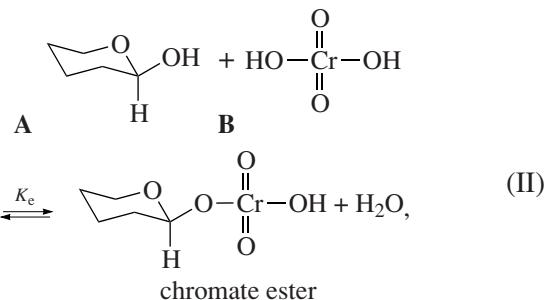
$[\text{Ce(IV)}] \times 10^4$ , mol $\text{dm}^{-3}$	$k_{\text{obs}} \times 10^4$ , $\text{s}^{-1}$	$[\text{Mn(II)}] \times 10^2$ , mol $\text{dm}^{-3}$	$k_{\text{obs}} \times 10^4$ , $\text{s}^{-1}$
0.0	3.4	0.0	3.4
0.4	3.2	0.5	3.6
0.8	3.0	1.0	3.6
1.2	2.6	1.5	3.7
1.6	2.1	2.0	3.8
2.0	1.7	2.5	4.0
3.0	1.3	3.0	4.1
4.0	1.1	4.0	4.3

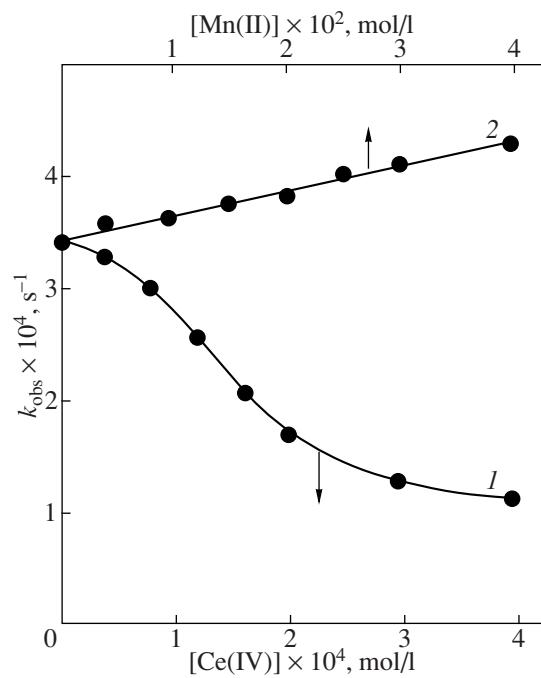


**Fig. 2.** Dependence of  $k_{\text{obs}}$  on  $[\text{HClO}_4]$ . Reaction conditions:  $[\text{D-galactose}] = 2.0 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ,  $[\text{Cr(VI)}] = 4.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ , temperature =  $40^\circ\text{C}$ .

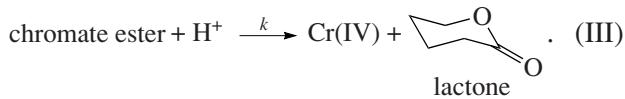
cerium(IV) concentration was varied in the range  $0.4 \times 10^{-4}$  to  $4.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ . A variation in cerium(IV) decreased the rate constants (Table 2, Fig. 3). The plots of  $\log$  (absorbance) versus time (Fig. 4, curve 2) was linear in the absence of cerium(IV). Surprisingly, as the cerium(IV) added from  $0.4 \times 10^{-4}$  to  $0.8 \times 10^{-4}$  mol  $\text{dm}^{-3}$ , deviations from the linearity in the plots of  $\log$  (absorbance) versus time were observed (Fig. 4, curves 3, 4). Interestingly, at higher cerium(IV) concentrations ( $\geq [\text{Cr(VI)}]$ ), the decrease in absorbance of the reaction mixture is very slow. The decrease in  $k_{\text{obs}}$  of chromium(VI) reduction on addition of cerium(IV) has been attributed to the removal of chromium(IV) which is in conformity with the reduction  $\text{Cr(VI)} \rightarrow \text{Cr(IV)}$ .

From the above observations, the Scheme 2 mechanism can be proposed in the presence of cerium(IV).





**Fig. 3.** Dependence of  $k_{\text{obs}}$  on [Ce(IV)] and [Mn(II)]. Reaction conditions:  $[\text{Cr(VI)}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 0.69 \text{ mol dm}^{-3}$ ,  $[\text{D-galactose}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ , temperature =  $40^\circ\text{C}$ .



The overall reaction rate is given by Eq. (2).

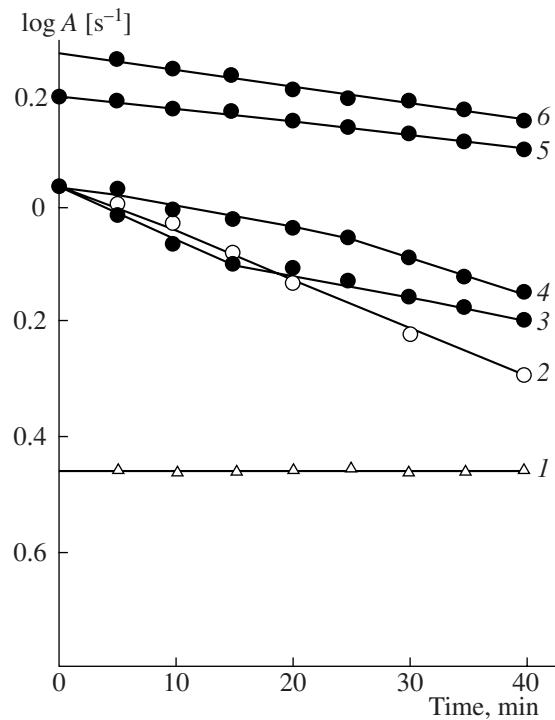
$$v = \frac{k K_{\text{es}} K_a [\text{H}^+]^2 [\text{Cr(VI)}]_t [\text{D-galactose}]}{[\text{H}^+] + K_a} \quad (2)$$

and

$$k_{\text{obs}} = \frac{k K_{\text{es}} K_a [\text{H}^+]^2 [\text{D-galactose}]}{[\text{H}^+] + K_a} \quad (3)$$

According to Eq. (3), the plot of  $k_{\text{obs}}$  versus  $[\text{D-galactose}]$  should be linear with zero intercept; this was found to be so (Fig. 5).

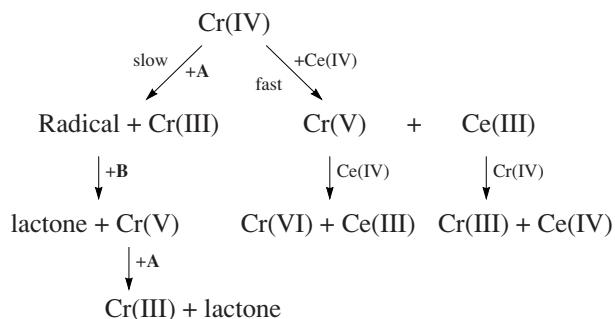
In Scheme 2, the inhibitory effect occurs due to the competition existing between *D*-galactose and cerium(IV) to react with chromium(IV). The *D*-galactose–chromium(IV) reaction involves the cleavage of a C–H bond in the *D*-galactose molecule by transfer a hydrogen atom. On the other hand, the chromium(IV)–cerium(IV) (one-electron transfer) reaction does not involve the bond cleavage. Therefore, chromium(IV) reduction by cerium(IV) is faster than the *D*-galactose. Chromium(IV) and (V) are strong oxidants (the redox potentials of the couples Cr(VI)/Cr(IV) and Cr(VI)/Cr(V) are 0.95 and  $< 1.0$  (also less than



**Fig. 4.** Plots of log (absorbance) versus time. Reaction conditions: (1) Ce(IV) + *D*-galactose; (2) Cr(VI) + *D*-galactose; (3–6) Ce(IV) + Cr(VI) + *D*-galactose. Reaction conditions:  $[\text{Cr(VI)}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{D-galactose}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 0.69 \text{ mol dm}^{-3}$ , temperature =  $40^\circ\text{C}$ ,  $[\text{Ce(IV)}] = 4.0$  (1), 0 (2), 0.4 (3), 0.8 (4), 4.0 (5), and  $6.0 \times 10^{-4}$  (6).

Cr(VI)/Cr(IV), respectively, at  $25^\circ\text{C}$ ). The reaction of chromium(V) and chromium(IV) with the substrate will be fast as compared to the decomposition of chromate-ester. Thus, we may safely conclude that, after addition of cerium(IV) in a reaction mixture containing chromium(VI) and organic substrate, a series of reactions may take place which complicate the oxidation path of *D*-galactose.

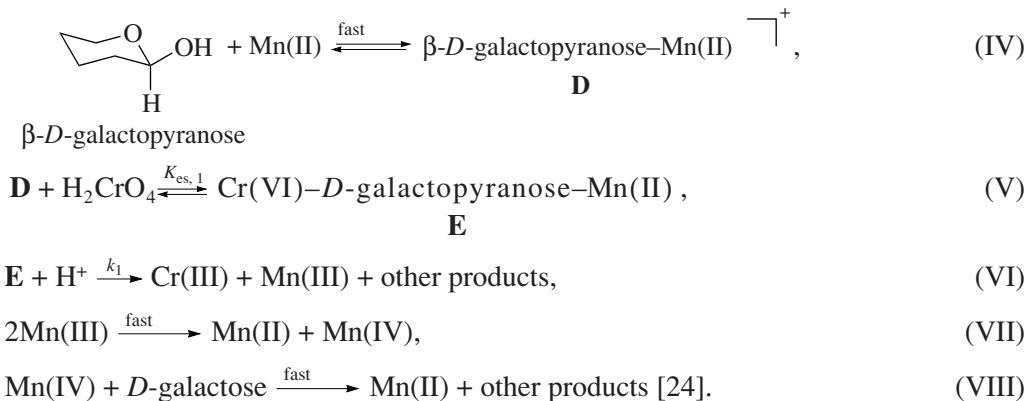
**Reaction in presence of manganese(II).** Manganese(II) has been used as an analytical tool to determine the involvement of chromium(IV), if formed in the rate-



**Scheme 2.**

determining step [3, 16]. Therefore, to substantiate the formation of chromium(IV) during the reduction of chromium(VI) by *D*-galactose, the effect of manganese(II) was investigated at fixed concentrations of other variables. It is seen that  $k_{\text{obs}}$  increases with increase in  $[\text{Mn}^{\text{II}}]$  (Table 2, Fig. 3). The observed posi-

tive catalytic effect rules out the possibility of formation of chromium(IV) (path(i)) in the rate-determining step (in presence of manganese(II), the oxidation rate by chromium(VI) would decrease by half). The following mechanism is, therefore, proposed in the presence of manganese(II) (Scheme 3).



Scheme 3.

The catalytic effect of manganese(II) is considered as due to the formation of an active  $\text{Mn}(\text{II})$ -*D*-galactose complex [11–13, 18]. The equilibrium between  $\beta$ -*D*-galactopyranose and manganese(II) is fast. In the presence of chromium(VI), the equilibrium shifts towards the right-hand side because the complex (**D**) is converted to a ternary chromate-ester complex (**E**) ( $\text{Cr(VI)}\text{-D-galactose--Mn(II)}$ ). As the reaction proceeds, the complex **E** decomposes by a one-step, three-electron oxidation-reduction mechanism directly to chromium(III). One of the electrons transferred is

donated by the manganese atom and the other two by the *D*-galactose. In this situation, Mn(II) is not a true catalyst; it acts as a coreductant. The probability of the direct reaction between chromium(VI) and manganese(II) without the participation of *D*-galactose can be excluded. The reaction product of Eq. (VI) is manganese(III). Therefore, it would also participate in the reaction as an autocatalyst. In the presence of a large amount of *D*-galactose, the manganese(III) immediately gets converted into the stable products (Eqs. (VII) and (VIII)). In the presence of manganese(II), the same kinetic experiments were also performed at 480 nm (characteristic of manganese(III)) [25] but failed to detect any build up of manganese(III) during the course of the redox reaction.

From the Scheme 3 mechanism, the following rate equation was derived conforming to the observed catalytic behavior with respect to [manganese(II)].

$$k_{\text{obs}} = \frac{k_1 K_{\text{es},1} [\text{H}^+]^2 [\text{D-galactose}][\text{Mn}(\text{II})]}{[\text{H}^+] + K_a}. \quad (4)$$

Equation (4) clearly accounts for the first-order dependence on  $[\text{D-galactose--Mn(II)}]$ . The inhibitory and catalytic effect of cerium(IV) and manganese(II), respectively, on the oxidation of *D*-galactose by chromium(VI) was observed. The *D*-galactose-Mn<sup>II</sup> complex formed in situ, is considered to be the active species of reductant. The observed catalytic effect rules out the possibility of chromium(IV) formation in the rate-determining step. The inhibition effect is due to the capture of chromium(IV) by cerium(IV). Thus, we may conclude that cerium(IV) is involved after the rate-determining step in the chromium(VI) oxidation of *D*-galactose. It is suggested that organic reductants that

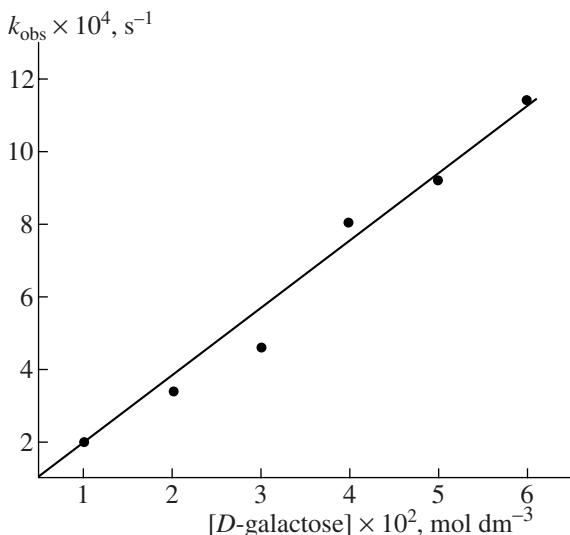


Fig. 5. Plots of  $k_{\text{obs}}$  versus  $[\text{D-galactose}]$ . Reaction conditions:  $[\text{Cr(VI)}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 0.69 \text{ mol dm}^{-3}$ , temperature = 40°C.

are not able to form a complex with added trapping agents act as two equivalent reducing agents.

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