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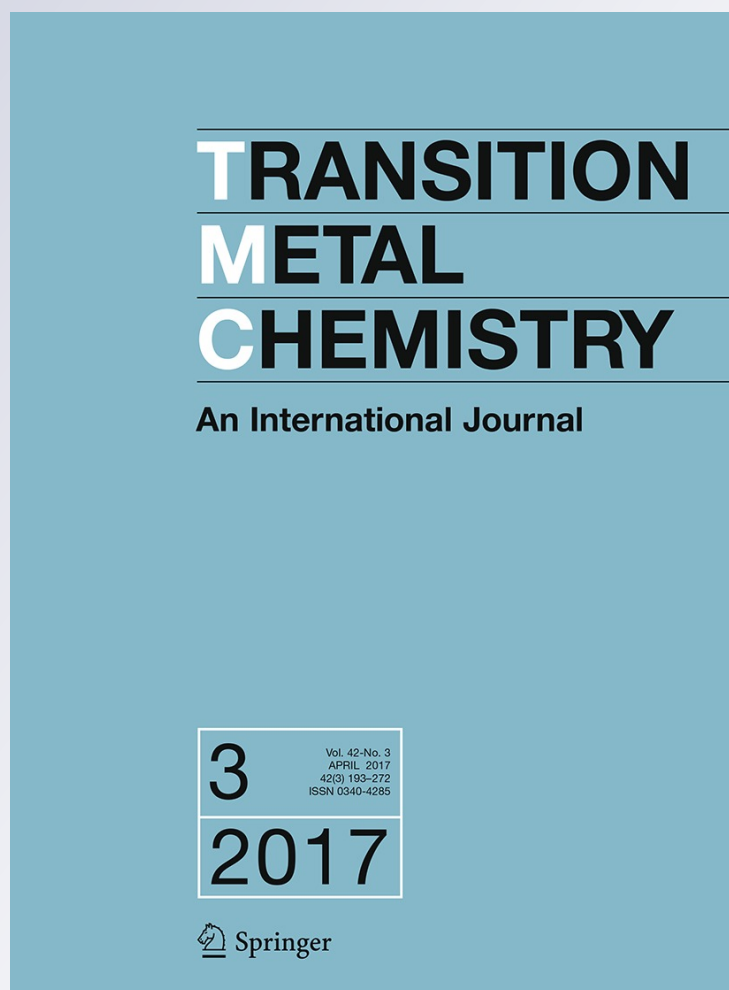# A study of the kinetics and mechanism of chromic acid oxidation of isosorbide, a chiral biomass-derived substrate, in aqueous perchlorate solution

Ahmed Fawzy[1,2] · Nizar El Guesmi[1,3] · Ismail I. Althagafi[1] · Basim H. Asghar[1]

Abstract The oxidation of isosorbide (S) by chromic acid (Cr^{VI}) has been studied in aqueous perchlorate solution at a constant ionic strength of 3.0 mol dm^{-3} and temperature of 25 °C. The course of the reaction was followed spectrophotometrically. The reaction exhibited first-order dependence on [Cr^{VI}], less than unit order with respect to [S], and fractional-second-order dependence with respect to [H^+]. Variation of the ionic strength or dielectric constant of the medium had no significant effects on the oxidation rate. Addition of Mn^{II} inhibited the oxidation rate. The oxidation product of isosorbide was identified as the corresponding monoketone derivative, namely (1S,4S,5R)-4-hydroxy-2,6-dioxabicyclo[3.3.0] octan-8-one. A mechanism for the oxidation is proposed, and the corresponding rate-law expression has been deduced. The activation parameters associated with the second-order rate constant are presented and discussed.

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Introduction

In recent years, the development of materials from renewable resources has gained increasing interest, due to considerations such as environmental impact, sustainability and production costs. In this context, isosorbide (4,8-di-hydroxy-2,6-dioxabicyclo [3.3.0] octane (IR, 4S, 5R, 8R) or (1,4:3,6-dianhydro-D-sorbitol), a chemically and thermally stable and rigid bicyclic diol that can ultimately be obtained from glucose-based polysaccharides such as starch and cellulose, is considered to be versatile intermediate due to its attractive chemical properties [1, 2] particularly the two hydroxyl groups which are interesting candidates for further transformations since they possess different configurations and thus, different reactivities.

Apart from isosorbide, in which the hydroxyl groups on C2 and C5 are in the *exo* and *endo* positions, respectively, two other isohexides are known (Fig. 1): the symmetrical *exo–exo* isomer isoidide (1,4:3,6-dianhydroiditol) and the *endo–endo* isomer isomannide (1,4:3,6-dianhydromannitol), derived from L-iditol and D-mannitol, respectively [2].

The use of isosorbide for synthesis and characterization has been reported [3–5]. Isosorbide is considered to be a versatile biogenic platform compound for the production of chemicals and has been widely used for the synthesis of elaborate molecules including chiral ionic liquids [6, 7], phase-transfer catalysts [8] and ligands (amino alcohols, amines, mono- and diphosphines, diphosphites, bis diaminophosphites, etc.) (Scheme 1) [9, 10].

Interestingly, isosorbide has been used as a starting material for pharmaceutical applications as well as for organic solvents or fuels, and as a building block for biopolymers [11]. Moreover, isosorbide has been used as a chiral auxiliary and chiral ligand in several reactions, among which alkylation, Diels–Alder reactions and
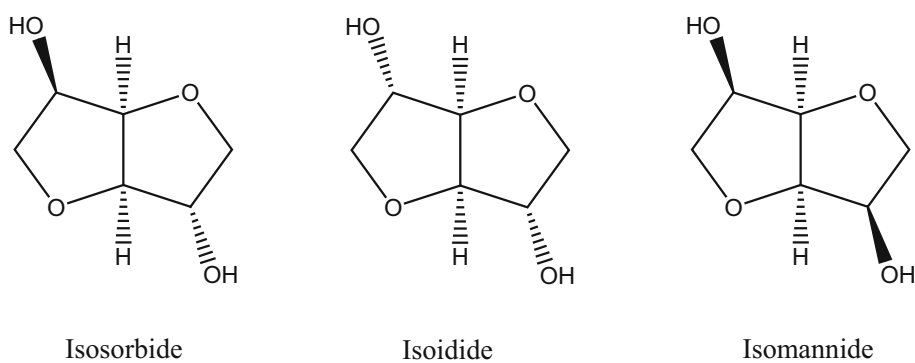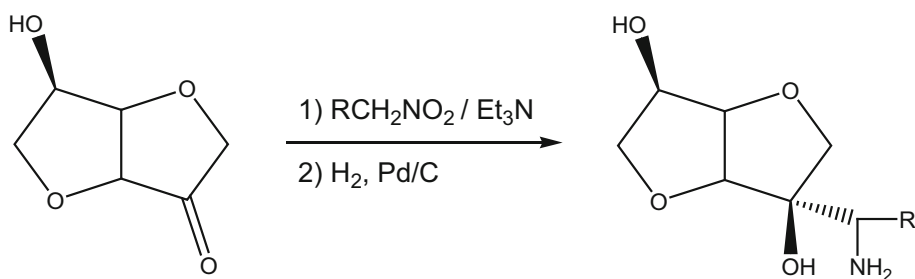
Fig. 1 Three isomeric isohexides

Isosorbide   Isoidide   Isomannide

Scheme 1 Preparation of β-amino alcohol derivatives

1) RCH₂NO₂ / Et₃N

2) H₂, Pd/C

asymmetric hydrogenation are the most important [12]. Isosorbide was selected as a chiral template for investigation of the effects of substituents at the *exo* and *endo* positions in asymmetric alkylation reactions [8]. Some di-O-alkylated products from isosorbide have been described when employing very reactive electrophilic reagents such as alkyl halides, or allyl and benzyl bromide [13]. As with most biomass-derived substrates, isosorbide is hydropholic and is only poorly soluble in most organic solvents. Moreover, there are well-known advantages in using water as a solvent in green synthesis.

Oxidations are of fundamental importance in nature and are regarded as a key transformation in organic synthesis. Chromium(VI) is one of the most versatile agents for the oxidation of both organic and inorganic compounds [14–20]. It can be reduced to lower oxidation states by various biological and chemical reductants [21]. The chemistry of the intermediate oxidation states of chromium, Cr^V and Cr^{IV}, which are observed during the oxidation of organic substrates by chromium(VI), has attracted many researchers because of their possible involvement in the mechanism of chromium-induced cancers [22].

Although some work on the oxidation of isosorbide diol by different techniques has been performed [23–25], there is a lack of information on the kinetics of oxidation of this diol by any oxidant. This observation prompted us to investigate the title reaction. The objectives of the present study were to investigate the reactivity of isosorbide toward chromium(VI) in perchlorate medium, to understand the active reactant species in such medium and to

deduce the mechanism of oxidation of isosorbide by chromium(VI).

Experimental

Materials

A stock solution of isosorbide was prepared by dissolving the sample (Sigma-Aldrich 98%) in doubly distilled water. Solutions of chromic acid (99.9%) were freshly prepared before each experiment and standardized spectrophotometrically. Sodium perchlorate (Sigma-Aldrich 98%) and acetic acid (Sigma-Aldrich 99.8%) were used to attain the required ionic strength and dielectric constant, respectively.

Kinetic measurements

The kinetic runs were performed under pseudo-first-order conditions, such that isosorbide was present in a large excess over chromic acid. The course of the reaction was monitored by following the decrease in absorbance of chromium(VI) as a function of time at $\lambda = 348$ nm, its absorption maximum. The absorbance measurements were taken with a thermostatted Shimadzu UV–VIS–NIR-3600 double-beam spectrophotometer.

First-order plots of ln(absorbance) versus time were linear up to about 70% of the reaction and the observed first-order rate constants (k_{obs}) were calculated from the gradients of the plots. Time-resolved spectra throughout

oxidation of isosorbide by chromic acid in perchlorate solution are shown in Fig. 2. These show gradual decay of the Cr^{VI} band with time, as a result of its reduction by isosorbide.

Reaction orders were determined from the slopes of log k_{obs} versus log(concentration) plots obtained by changing the concentrations of isosorbide and perchloric acid, in turn, while keeping other conditions constant.

Some kinetic runs were carried out after bubbling purified nitrogen through the solution, and compared with those taken under air. The results were found to be the same, suggesting that dissolved oxygen did not have any effect on the oxidation rate.

Results and discussion

Reaction stoichiometry and product analysis

Different sets of reaction mixtures containing various amounts of Cr^{VI} and isosorbide at constant $[H^+]$, temperature and ionic strength were allowed to react for 24 h in closed vessels for completion of the reaction. The unconsumed $[Cr^{VI}]$ was determined spectrophotometrically at 348 nm. The results indicated that two moles of Cr^{VI} are consumed by three moles of isosorbide to yield the oxidation products, as shown in Scheme 2.

The stoichiometric equation shown in Scheme 2 is also consistent with the results of product identification. The oxidation product of isosorbide was identified by spectroscopic tools (Mass and IR spectra) as the corresponding monoketone derivative, namely (1S,4S,5R)-4-hydroxy-2,6-dioxabicyclo[3.3.0]octan-8-one. Furthermore, the product was detected analytically as its 2,4-dinitrophenylhydrazone and dioxime derivatives [26]. Similar oxidation product of isosorbide under different conditions was reported earlier [23–25].
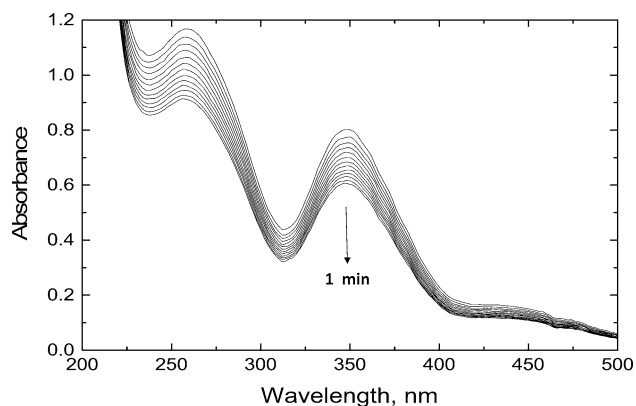

Fig. 2 Time-resolved spectra for the oxidation of isosorbide by chromic acid in perchlorate solution. $[S] = 1.0 \times 10^{-2}$, $[Cr^{VI}] = 5.0 \times 10^{-4}$, $[H^+] = 2.0$ and $I = 3.0$ mol dm^{-3} at 25 °C

Rate dependence on $[Cr^{VI}]$, $[S]$ and $[H^+]$

The concentration of chromium(VI) oxidant was varied in the range $(1.0–11.0) \times 10^{-4}$ mol dm^{-3} keeping other variables constant. Variation of the oxidant concentration does not change the rate, as shown in Table 1. Hence, the order of reaction with respect to the oxidant is unity. The first-order dependence was also confirmed by the linearity of plots of ln(absorbance) versus time up to about 70% of the reaction.

Next, the effect of isosorbide (S) concentration on the rate was examined by varying the initial concentration of isosorbide while other variables were kept constant at different temperatures. It was found that increasing isosorbide concentration increases the oxidation rate, as shown in Table 1. A plot of log k_{obs} versus log[S] at constant $[H^+]$ was found to be linear with a positive intercept, as shown in Fig. 3.

To examine the effect of hydrogen ion concentration on the oxidation rate, kinetic runs were carried out by varying the perchloric acid concentration in the range 0.5–3.0 mol dm^{-3} while maintaining other variables constant. Increasing $[H^+]$ found to increase the oxidation rate (Table 1). A plot of log k_{obs} versus log $[H^+]$ was linear with a slope of 1.65 (Fig. 4), confirming the fractional-second-order dependence with respect to $[H^+]$.

Effects of ionic strength and dielectric constant

The effect of ionic strength on the rate was studied by varying the ionic strength in the range 3.0–4.5 mol dm^{-3} using sodium perchlorate, keeping the concentrations of all other reactants constant. Increasing ionic strength had a negligible effect on the oxidation rate, as shown in Table 1. The effect of the dielectric constant (D) was also studied by varying the acetic acid–water content in the reaction mixture, with all other conditions being kept constant. The data clearly revealed that the rate constant remained essentially unchanged, even at higher acetic acid concentrations.

Effect of manganous ion

To examine the possible contribution of Cr^{IV} as an intermediate species of chromium in the reaction, various concentrations of manganous ion, Mn^{II}, were added to the reaction mixture, up to 0.01 mol dm^{-3}. The rate of reaction was found to decrease linearly with $[Mn^{II}]$, as shown in Fig. 5.

Effect of temperature and free radical test

The oxidation rate was studied at four temperatures between 15 and 45 °C, all other conditions being constant. The activation parameters for the second-order rate

Scheme 2 Stoichiometric equation of oxidation of isosorbide by chromic acid
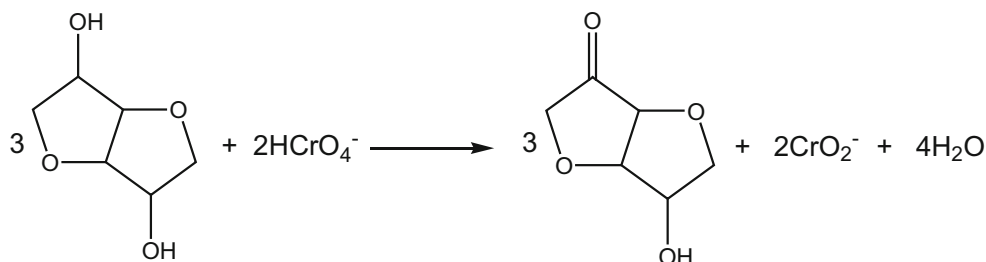
Table 1 Effects of [Cr^{VI}], [S] and [H^+] and ionic strength (I) on the observed first-order rate constant values, k_{obs}, in the oxidation of isosorbide by chromic acid in perchlorate solution at 25 °C

10^4 [Cr^{VI}] (mol dm^{-3})	10^2 [S] (mol dm^{-3})	[H^+] (mol dm^{-3})	I (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})
1.0	1.0	2.0	3.0	33.5
3.0	1.0	2.0	3.0	31.9
5.0	1.0	2.0	3.0	33.4
7.0	1.0	2.0	3.0	36.0
9.0	1.0	2.0	3.0	34.1
11.0	1.0	2.0	3.0	32.4
5.0	**0.2**	2.0	3.0	11.9
5.0	**0.6**	2.0	3.0	23.2
5.0	**1.0**	2.0	3.0	33.4
5.0	**1.4**	2.0	3.0	41.3
5.0	**1.8**	2.0	3.0	51.0
5.0	**2.2**	2.0	3.0	59.4
5.0	1.0	**0.5**	3.0	3.3
5.0	1.0	**1.0**	3.0	10.2
5.0	1.0	**1.5**	3.0	20.5
5.0	1.0	**2.0**	3.0	33.4
5.0	1.0	**2.5**	3.0	48.2
5.0	1.0	**3.0**	3.0	61.0
5.0	1.0	2.0	**3.0**	33.4
5.0	1.0	2.0	**3.3**	36.2
5.0	1.0	2.0	**3.6**	35.6
5.0	1.0	2.0	**3.9**	37.1
5.0	1.0	2.0	**4.2**	35.9
5.0	1.0	2.0	**4.5**	34.7

Bold values indicate specific effect

Experimental error ±4%

constant (k_2) were calculated using Arrhenius and Eyring plots and are listed in Table 2.

The possible intervention of free radicals in the reaction was tested by addition of a known quantity of acrylonitrile monomer to the reaction mixture and keeping the mixture for about 8 h in an inert atmosphere. When diluting the reaction mixture with methanol, no white precipitate was observed, indicating the absence of free radicals in this reaction.

Mechanism of chromic acid oxidation of isosorbide

There are currently two suggested reaction mechanisms for electron transfer in chromium transfer (VI) redox reaction

[27]. The first is a successive one-electron transfer in two steps, while the second involves a simultaneous two-electron transfer in a single step. Both suggested mechanisms may operate during reduction of chromium(VI), leading to formation of either Cr^V or Cr^{IV} intermediate species, respectively [28, 29]. In the present investigation, the negative result for free radical participation provides evidence against the formation of Cr^V intermediate species. On the other hand, the contribution of Cr^{IV} as an intermediate is implied by the observed inhibition of the rate upon addition of Mn^{II} to the reaction medium [30] as shown in Fig. 5. In aqueous acidic media, chromium(VI) was suggested [31] to exist mainly as acid chromate, H_2CrO_4, as represented by the first step in
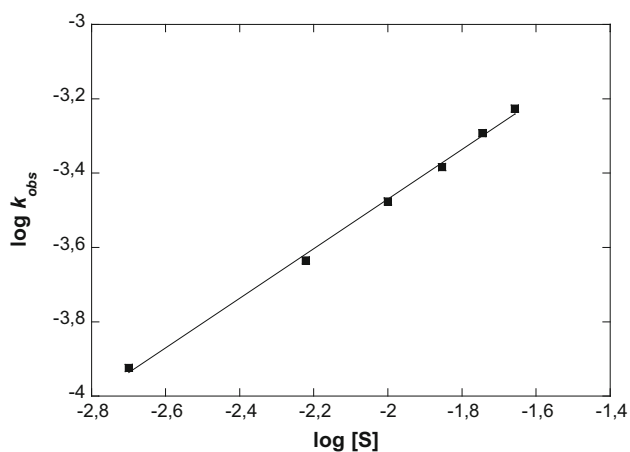
Fig. 3 A plot of log k_{obs} versus log[S] for the oxidation of isosorbide by chromic acid in perchlorate solution. $[Cr^{VI}] = 5.0 \times 10^{-4}$, $[H^+] = 2.0$ and $I = 3.0$ mol dm^{-3} at 25 °C

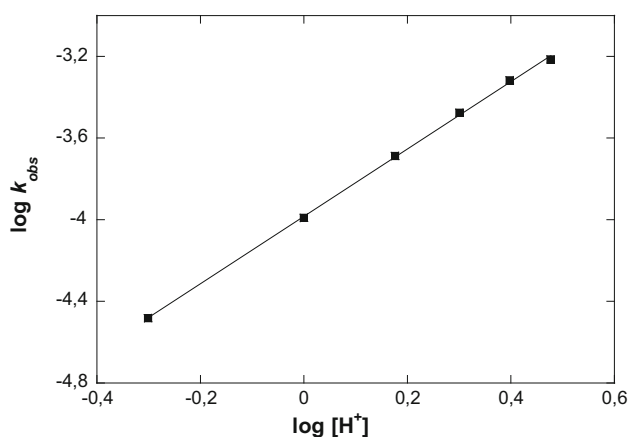**Fig. 4** A plot of log k_{obs} versus log[H$^+$] for the oxidation of isosorbide by chromic acid in perchlorate solution. $[S] = 1.0 \times 10^{-2}$, $[Cr^{VI}] = 5.0 \times 10^{-4}$ and $I = 3.0$ mol dm^{-3} at 25 °C
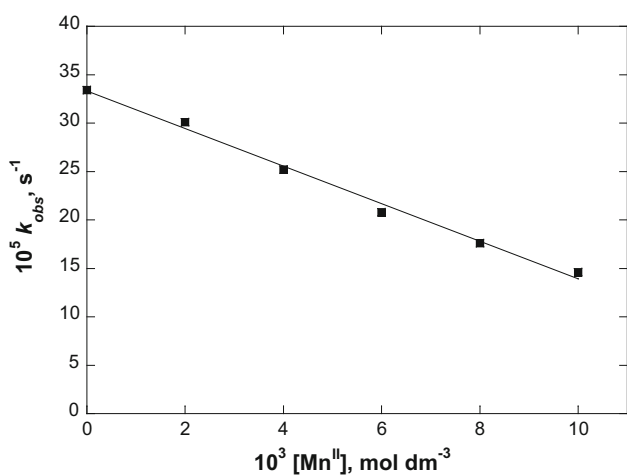

Fig. 5 Effect of Mn(II) on the rate of oxidation of isosorbide by chromic acid in perchlorate solution. $[Cr^{VI}] = 5.0 \times 10^{-4}$, $[S] = 1.0 \times 10^{-2}$, $[H^+] = 2.0$ and $I = 3.0$ mol dm^{-3} at 25 °C

Scheme 3. The enhancement of the oxidation rate upon increasing hydrogen ion concentration indicates a protolytic process involving the chromate ion, i.e., the protonated species of the chromate oxidant (H$_2$CrO$_4$) may be considered as the kinetically reactive species which plays the main role in the oxidation kinetics.

The title reaction between chromic acid and isosorbide (S) in aqueous perchlorate showed a stoichiometry of 2:3 (Cr^{VI}:S), with first-order dependence on [Cr^{VI}], fractional-first-order kinetics with respect to [S] and fractional-second-order dependences on [H$^+$]. The fractional-second-order dependences of the rate constant on [H$^+$] can be explained by protonation of both oxidant and substrate in the first step to form more reactive species, i.e., H$_2$CrO$_4$ and SH$^+$, respectively. On the other hand, the fractional-order dependence on isosorbide concentration can be attributed to complex formation between isosorbide and chromic acid in a pre-equilibrium step, as illustrated by step (III) of Scheme 3. The formation of the complex is indicated kinetically by the observed nonzero intercept of the plot of $1/k_{obs}$ versus $1/[S]$, similar to Michaelis–Menten kinetics [32], as shown in Fig. 6a. Complex formation between chromium(VI) and different organic compounds in acid media has been observed previously [18–20]. Furthermore, the negligible effects of ionic strength and solvent polarity of the medium are consistent with a reaction between an ion and a neutral molecule, or between two neutral molecules [33, 34]; i.e., between SH$^+$ and H$_2$CrO$_4$.

Hence, the most reasonable reaction mechanism which may be suggested is illustrated in Scheme 3. This involves fast complexation of the protonated isosorbide with chromic acid to give an intermediate complex (C). The latter is slowly decomposed in the rate-determining step, followed by a fast step to give the final oxidation products.

The rate-law expression describing the relationship between the reaction rate and the oxidant, reductant and hydrogen ion concentrations was derived according to the suggested mechanism as follows:

$$\text{Rate} = \frac{k_1 K_1 K_2 K_3 [HCrO_4^-][S][H^+]^2}{1 + K_1[H^+] + K_2[H^+] + K_1 K_2[H^+]^2 + K_1 K_2 K_3 [S][H^+]^2} \quad (1)$$

Under pseudo-first-order condition,

$$\text{Rate} = \frac{-d[HCrO_4^-]}{dt} = k_{obs}[HCrO_4^-] \quad (2)$$

Comparison of Eqs. (1) and (2) leads to,

$$k_{obs} = \frac{k_1 K_1 K_2 K_3 [S][H^+]^2}{1 + K_1[H^+] + K_2[H^+] + K_1 K_2[H^+]^2 + K_1 K_2 K_3 [S][H^+]^2} \quad (3)$$

Rearrangement of Eq. (3) gives,

Table 2 Activation parameters of the second-order rate constant k_2 in the oxidation of isosorbide by chromic acid in perchlorate solution

$\Delta S^{\neq}$ (J mol^{-1}K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}_{298}$ (kJ mol^{-1})	$E^{\neq}_a$ (kJ mol^{-1})
−146.91	33.17	76.94	36.07

Experimental error ±4%

$[S] = 1.0 \times 10^{-2}$, $[Cr^{VI}] = 5.0 \times 10^{-4}$, $[H^+] = 2.0$ and $I = 3.0$ mol dm^{-3}
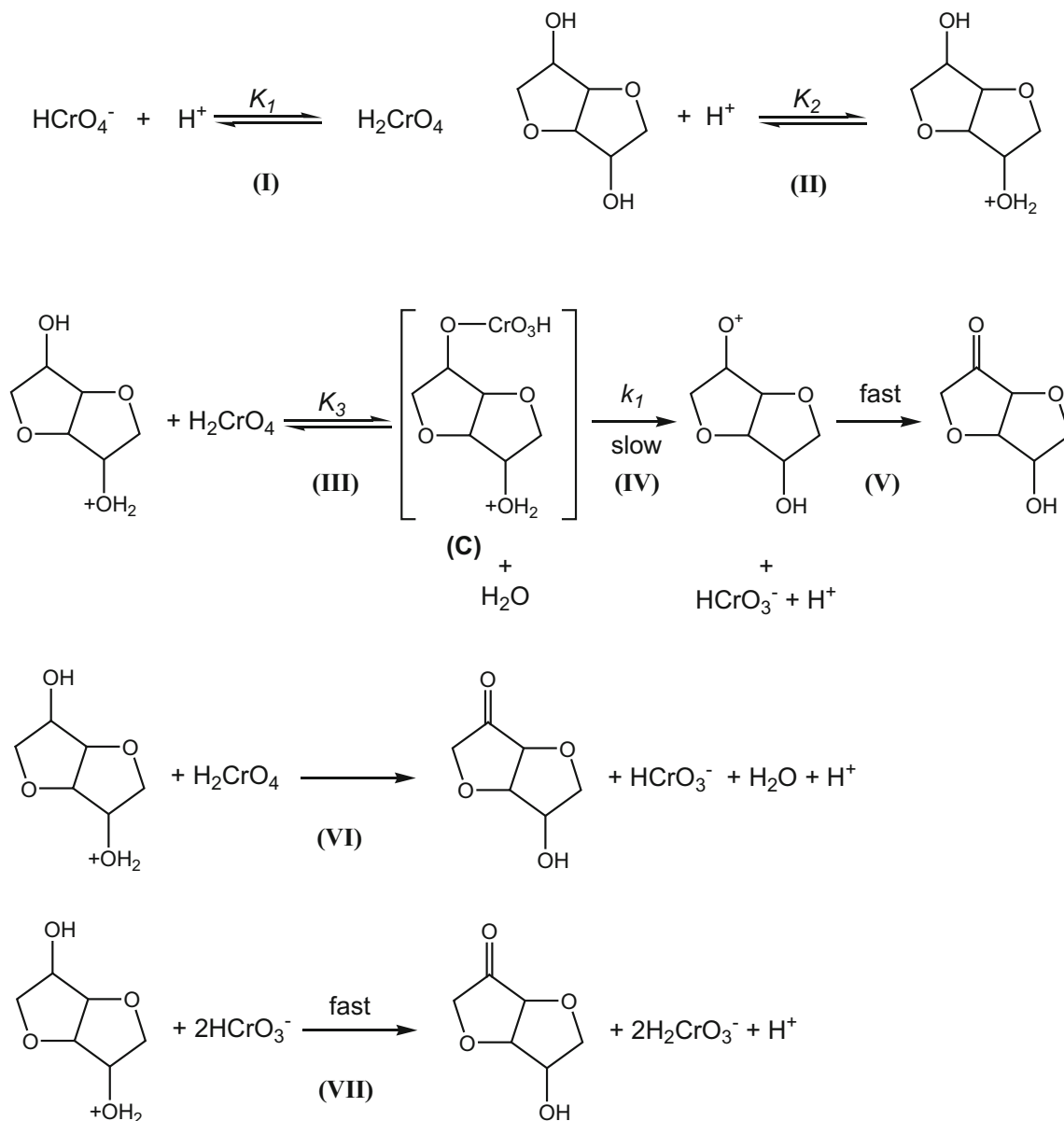
Scheme 3 Proposed mechanism of the chromic acid oxidation of isosorbide in aqueous perchlorate solution

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[H^+]}{k_1 K_1 K_2 K_3 [H^+]^2} \right) \frac{1}{[S]} + \frac{1 + K_1[H^+]}{k_1 K_1 K_3 [S][H^+]} + \frac{1}{k_1} \quad (4)$$

In view of Eq. (4), plots of $1/k_{obs}$ versus $1/[S]$ at constant $[H^+]$, and of $1/k_{obs}$ versus $1/[H^+]^2$ at constant $[S]$,

should be linear with positive intercepts. This is verified in Fig. 6a, b, respectively.

The calculated activation parameters are listed in Table 2. The observed large negative value of the entropy of activation, $\Delta S^\#$, suggests that the reactants form an
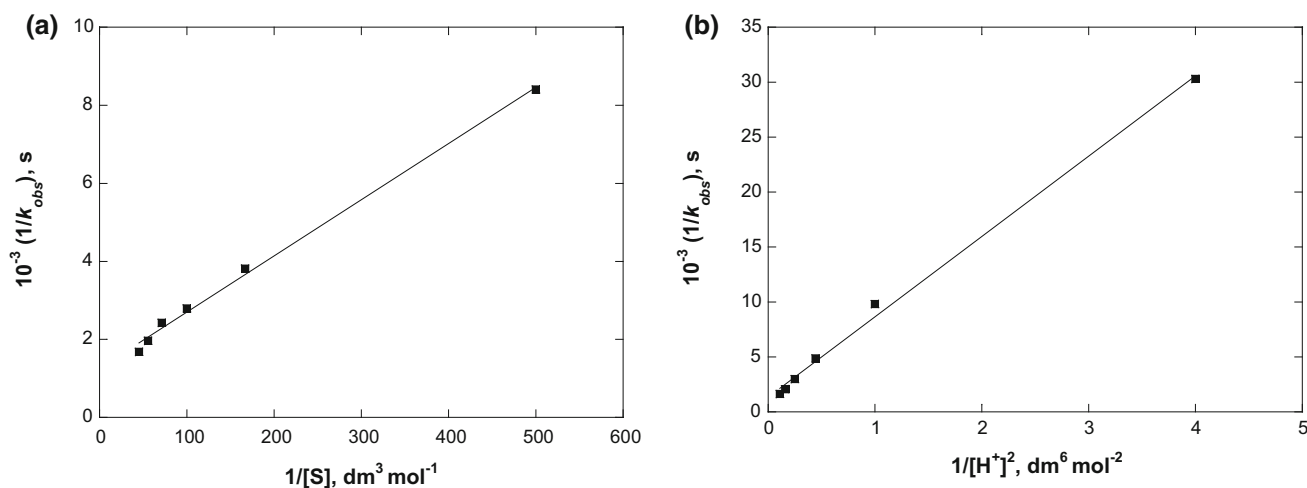
Fig. 6 (**a**, **b**) Verification of Eq. (4) in the oxidation of isosorbide by chromic acid in perchlorate solution. $[Cr^{VI}] = 5.0 \times 10^{-4}$ and $I = 3.0$ mol dm^{-3} at 25 °C

intermediate complex which is more ordered than the reactants [35]. On the other hand, the positive values of both $\Delta H^{\neq}$ and $\Delta G^{\neq}$ confirm the endothermic formation of the intermediate complex.

Conclusions

The kinetics of oxidation of isosorbide by chromic acid in perchlorate solution has been studied by spectrophotometric techniques. The oxidation product of isosorbide was identified as (1S,4S,5R)-4-hydroxy-2,6-dioxabicyclo[3.3.0] octan-8-one, similar to the observations made in earlier studies. Our proposed oxidation mechanism involves formation of a 1:1 intermediate complex between the protonated isosorbide and chromic acid.

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