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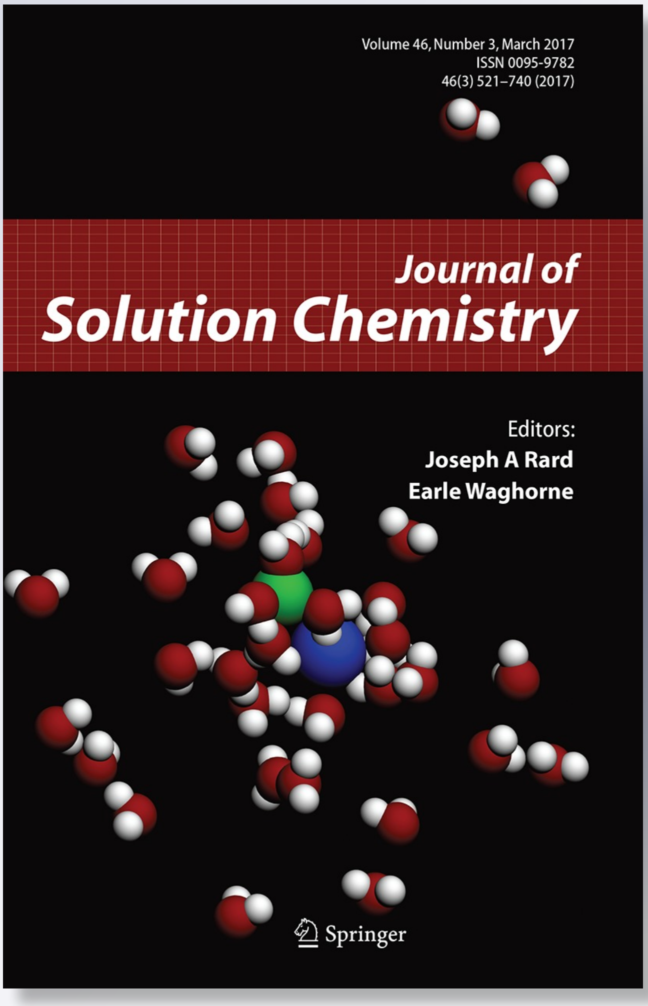

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Kinetics and Mechanism of Permanganate Oxidations of Isosorbide in Different Acidic Media

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Abstract The oxidation kinetics of isosorbide (S) by potassium permanganate in both perchloric and sulfuric acid solutions was investigated spectrophotometrically at a constant ionic strength of 2.0 mol·dm^{-3} and at 25 °C. In both acids, the oxidation reactions showed a first-order dependence on $[\mathrm{MnO_4^-}]$, apparent a less than unit-order dependence with respect to [S] and a fractional-second-order dependence with respect to $[\mathrm{H^+}]$. Variation of either the ionic strength or dielectric constant of the reactions media did not significantly affect the oxidation rates. In both acids, the final oxidation product of isosorbide was identified by both spectroscopic and chemical tools as the corresponding monoketone derivative, namely (1S,4S,5R)-4-hydroxy-2,6-dioxabicyclo[3.3.0] octan-8-one. Under comparable experimental conditions, the oxidation rate of isosorbide in perchloric acid was lower than that in sulfuric acid. The oxidation mechanism describing the kinetic results was proposed and the rate law expression was derived. The activation parameters of the second-order rate constants were computed and are discussed.

Keywords Isosorbide · Acid · Permanganate · Oxidation · Kinetics · Mechanism

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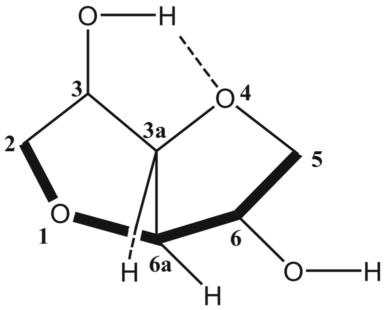
1 Introduction

In recent years, the development of materials from renewable resources is a field that is gaining increased interest due to factors such as environmental impact, sustainability and production costs. Isosorbide is an attractive building block because it is easily accessible from renewable resources in the form of its pure enantiomers. Isosorbide (1,4:3,6-dianhydro-D-glucitol) is easily produced on the industrial scale by double dehydratation of D-glucose. It is thermally stable up to 280 °C, of low cost, and is available in large quantities. Isosorbide is basically comprised of two fused tetrahydrofuran rings having the cis-arrangement at the ring junction, giving a wedge-shaped molecule. The compound bears two hydroxyl groups, one at C6 having the exo-orientation with respect to the wedge-shaped molecule, and the other at C3 having the endo-orientation, which makes possible intramolecular hydrogen bonding with the oxygen atom of the neighboring tetrahydrofuran ring (Fig. 1).

Isosorbide is considered a versatile intermediate due to its chemical structure [1, 2], particularly the two hydroxyl groups that are interesting for further transformations since they possess different configurations and thus, different reactivities. The use of isosorbide for synthesis and characterization has been reported [3–8]. Isosorbide is considered as a versatile biogenic platform compound for the production of chemicals and has been widely used for the synthesis of sophisticated molecules including chiral ionic liquids [9–11], phase-transfer catalysts [12], and ligands (amino alcohols, amines, mono- and diphosphines, diphosphites, *bis*-diaminophosphites, etc.) [13, 14]. It is used as a starting material for pharmaceutical applications as well as for organic solvents or fuels and as a building block for biopolymers [15].

Oxidation reactions are very important in organic synthesis. Among the important oxidizing agents, permanganate ion is widely used in the oxidation of various organic compounds in neutral, alkaline and acidic media [16–29]. The mechanism of oxidation reactions by permanganate ion is governed by the pH of the medium [30]. Although some work on the oxidation of isosorbide diol by different techniques has been performed [31–33], there is a lack of literature on the kinetics of oxidation of isosorbide by permanganate ion as the most efficient oxidant. This observation prompted us to investigate the title reactions. The objectives of the present study are to check the reactivity of isosorbide towards permanganate ion in different acidic media and to propose the oxidation mechanism of such a diol.

Fig. 1 Structure of isosorbide



2 Experimental

2.1 Materials

The chemicals employed in the present work were of reagent grade and their solutions were prepared by dissolving the samples in bidistilled water. The stock solution of isosorbide was prepared by dissolving the sample in doubly distilled water. The potassium permanganate solution was freshly prepared and standardized as reported earlier [34]. Sodium perchlorate and sodium sulfate were used to attain the required ionic strength in perchloric and sulfuric acids, respectively, and acetic acid was also used to vary the dielectric constants of the reaction's media.

2.2 Kinetic Measurements

All kinetic measurements were followed under pseudo-first-order conditions where isosorbide was present in a large excess over that of the oxidant permanganate ion. The course of the reaction was followed by monitoring the decay of the absorbance of permanganate as a function of time at its absorption maximum ($\lambda = 525$ nm); the other constituents of the reaction mixtures did not absorb significantly at this wavelength. The absorption measurements were done in a temperature-controlled Shimadzu UV–VIS-NIR-3600 double-beam spectrophotometer.

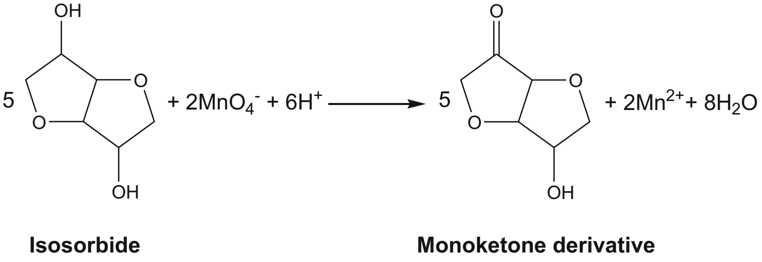
First-order plots of ln(absorbance) versus time were recorded to be straight lines up to at least 70% of the completion of reaction. The observed first-order rate constants (k_{obs}) were calculated using non-linear least-squares fitting to the first-order dependence of the absorbance versus time plots. The reported rate constants are the mean values of at least three kinetic measurements. The rate constants were reproducible to within 3–4%.

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

3 Results

3.1 Stoichiometry and Product Identification

Reaction mixtures containing various amounts of permanganate ion and isosorbide at constant [H$^+$], ionic strength, and temperature were allowed to react for 24 h in closed vessels for completion of the oxidation reaction. The unconsumed [permanganate] was determined spectrophotometrically at 525 nm. The results indicate that two moles of permanganate are consumed by five moles of isosorbide to yield the oxidation products as shown in the following reaction:



The above stoichiometric equation is consistent with the results of product identification. The oxidation product of isosorbide was identified by spectroscopic tools (mass spectra and infra-red 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 via its 2,4-dinitrophenyl-hydrazone and dioxime derivatives [35–37]. A similar oxidation product of isosorbide with different conditions was reported earlier [31–33].

3.2 Spectral Changes

The spectral scans during the oxidation of isosorbide by permanganate ion in perchloric and sulfuric acids solutions are shown in Fig. 2a and b, respectively. It is seen that there is a gradual disappearance of the permanganate band at its absorption maximum ($\lambda = 525$ nm) as a result of its reduction by the isosorbide substrate.

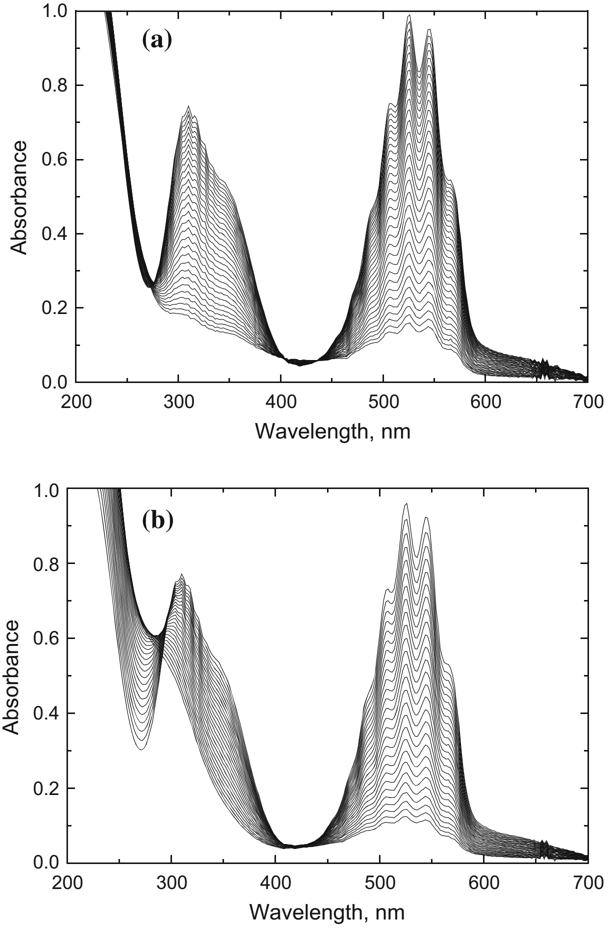


Fig. 2 **a**, **b** Spectral changes during the oxidation of isosorbide by permanganate ion in: **a** perchloric, and **b** sulfuric acid solutions; $[S] = 8.0 \times 10^{-3}$ mol·dm^{-3}, $[MnO_4^-] = 4.0 \times 10^{-4}$ mol·dm^{-3}, $[H^+] = 1.0$ mol·dm^{-3} and $I = 2.0$ mol·dm^{-3} at 25 °C; scanning time intervals = 1.0 min

3.3 Order of Reactions

The orders of the reactions with respect to the reactants were determined from the slopes of $\log_{10} k_{obs}$ versus $\log_{10}$ (concentration) plots by varying the concentrations of isosorbide and the acids, in turn, while keeping the other conditions constant.

The oxidant, permanganate ion, was varied in the concentration range $(1.0–8.0) \times 10^{-4}$ mol·dm^{-3} while the rest of the reactants' concentrations were kept constant and both pH and temperature also remained constant. It was found that the plots of ln(absorbance) versus time were linear up to about 70% completion of reactions. Furthermore, an increase in the oxidant concentration did not significantly affect the oxidation rates as listed in Table 1. These results confirm that the order of the reactions with respect to the oxidant is one.

The observed first-order rate constants were measured at various concentrations of isosorbide while keeping others constant. Plots of $\log_{10} k_{obs}$ versus $\log_{10}$ [S] were found to be linear with slopes of 0.5 and 0.84 in perchloric and sulfuric acids solutions, respectively, as shown in Fig. 3, confirming the less than unit-order dependences with respect to the isosorbide concentration.

Table 1 Effect of $[MnO_4^-]$, [S], $[H^+]$ and ionic strength I on the observed first-order rate constants (k_{obs}) in the oxidations of isosorbide by permanganate ion in perchloric and sulfuric acids solutions at 25 °C

10^4 $[MnO_4^-]$ (mol·dm^{-3})	10^3 [S] (mol·dm^{-3})	$[H^+]$ (mol·dm^{-3})	I (mol·dm^{-3})	10^5 k_{obs} (s^{-1})	
				Perchloric acid	Sulfuric acid
1.0	8.0	1.0	2.0	44.1	68.2
2.0	8.0	1.0	2.0	46.5	65.1
4.0	8.0	1.0	2.0	45.6	67.4
6.0	8.0	1.0	2.0	47.1	66.9
8.0	8.0	1.0	2.0	44.9	71.2
4.0	**2.0**	1.0	2.0	15.9	19.7
4.0	**5.0**	1.0	2.0	30.3	45.2
4.0	**8.0**	1.0	2.0	45.6	67.4
4.0	**12.0**	1.0	2.0	61.4	92.8
4.0	**16.0**	1.0	2.0	75.0	115.2
4.0	8.0	**0.2**	2.0	4.2	6.3
4.0	8.0	**0.6**	2.0	22.3	33.0
4.0	8.0	**1.0**	2.0	45.6	67.4
4.0	8.0	**1.4**	2.0	79.2	93.6
4.0	8.0	**1.8**	2.0	112.0	124.8
4.0	8.0	1.0	**2.0**	45.6	67.4
4.0	8.0	1.0	**2.5**	48.2	63.9
4.0	8.0	1.0	**3.0**	47.8	68.0
4.0	8.0	1.0	**3.5**	45.3	69.1
4.0	8.0	1.0	**4.0**	46.7	69.8

Experimental error ± 3%. The quantities being varied in each series of five experiments are given in bold face font

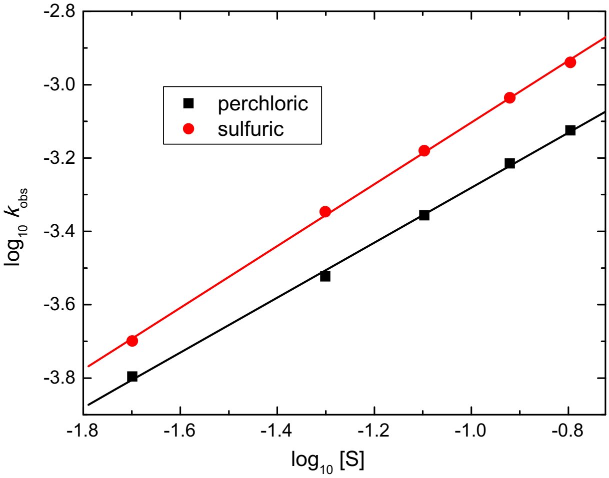


Fig. 3 Plots of $\log_{10} k_{obs}$ versus $\log_{10}$ [S] in the oxidation of isosorbide by permanganate ion in perchloric and sulfuric acids solutions: $[MnO_4^-] = 4.0 \times 10^{-4}$ mol·dm^{-3}, $[H^+] = 1.0$ mol·dm^{-3} and $I = 2.0$ mol·dm^{-3} at 25 °C

The effect of hydrogen ion concentration on the oxidation rates for both perchloric and sulfuric acids was investigated by varying $[H^+]$ in the range of 0.2–1.8 mol·dm^{-3}, keeping all other reactants concentrations constant. The rate constants increase with increasing acid concentration as listed in Table 1. Plots of $\log_{10} k_{obs}$ versus $\log_{10}$ $[H^+]$ also are linear with slopes of 1.76 and 1.71 in perchloric and sulfuric acids solutions, respectively, Fig. 4, suggesting that the orders of the reactions with respect to $[H^+]$ are fractional second order.

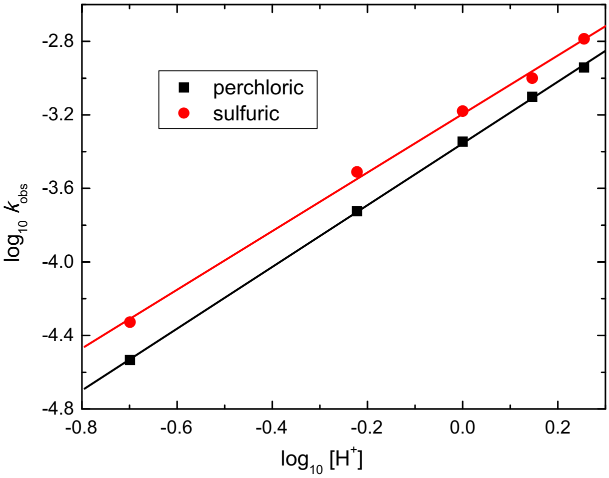


Fig. 4 Plots of $\log_{10} k_{obs}$ versus $\log_{10}$ $[H^+]$ in the oxidations of isosorbide by permanganate ion in perchloric and sulfuric acid solutions: $[MnO_4^-] = 4.0 \times 10^{-4}$ mol·dm^{-3}, [S] = 8.0×10^{-3} mol·dm^{-3} and $I = 2.0$ mol·dm^{-3} at 25 °C

Table 2 Activation parameters of the rate constant k' in the oxidation of isosorbide by permanganate ion in perchloric and sulfuric acids solutions: $[MnO_4^-] = 4.0 \times 10^{-4}$ mol·dm^{-3}, $[S] = 8.0 \times 10^{-2}$ mol·dm^{-3}, $[H^+] = 1.0$ mol·dm^{-3} and $I = 2.0$ mol·dm^{-3}

Acid	$\Delta S^{\neq}$ (J·mol^{-1}·K^{-1})	$\Delta H^{\neq}$ (kJ·mol^{-1})	$\Delta G^{\neq}_{298}$ (kJ·mol^{-1})	$E^{\neq}_a$ (kJ·mol^{-1})
Perchloric	–112.27	37.85	71.30	40.02
Sulfuric	–99.70	33.71	63.42	35.98

Experimental error ± 4%

3.4 Effect of Ionic Strength and Dielectric Constant

The ionic strength effect was investigated by varying the concentrations of sodium pechlorate in the case of perchloric acid and sodium sulfate in case of sulfuric acid, in the reactions media at constant concentrations of permanganate, isosorbide and acid. It was found that variations of the ionic strength did not affect the rates as observed from the data listed in Table 1. Also, the effect dielectric constant (D) was studied by varying the acetic acid–water content in the reaction mixtures with all other conditions being kept constant. The data clearly reveal that the rate constants is not significantly affected by the decrease in dielectric constant of the solvent mixture, i.e., the increase in acetic acid content.

3.5 Effect of Temperature

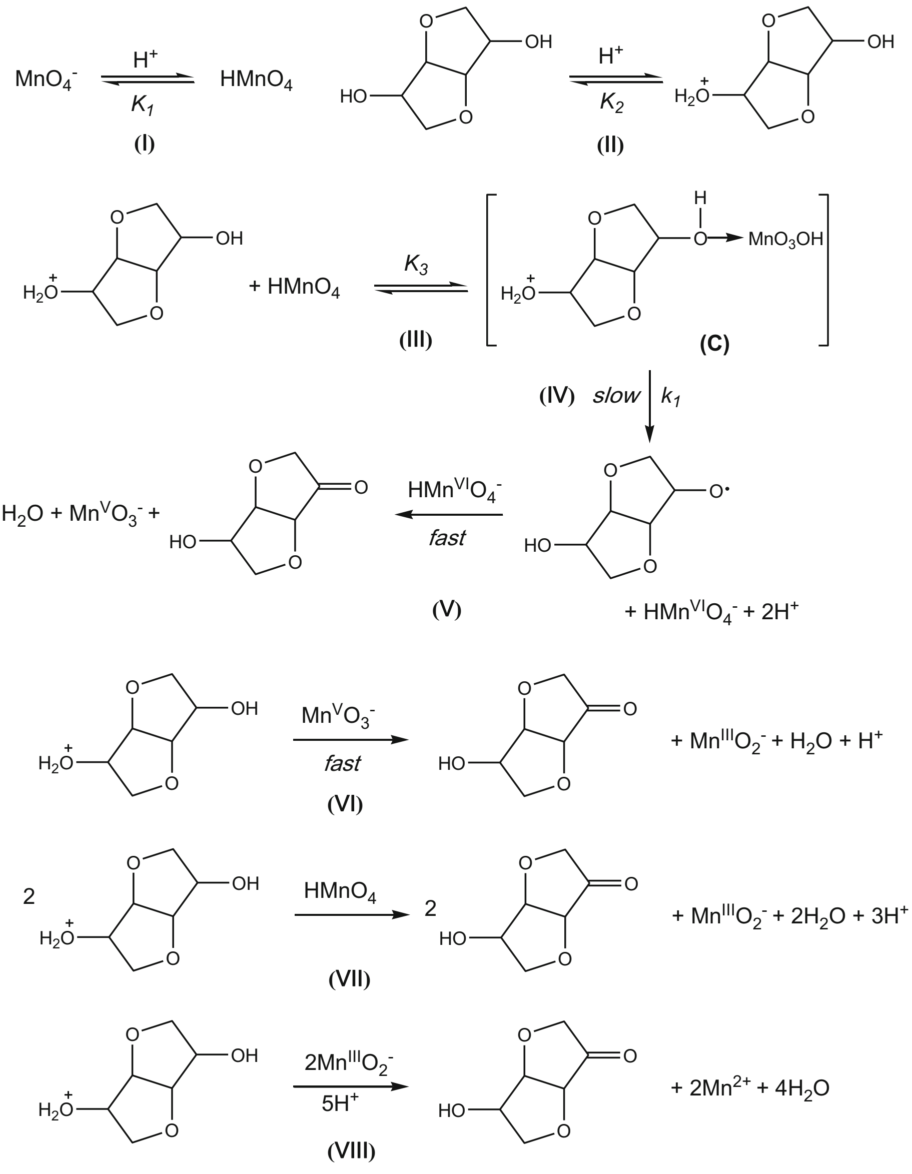
The oxidation rates were measured at five different temperatures between 288 and 318 K at constant concentrations of the reactants with other conditions being constant. The results indicate that the rate constant increases with rise in temperature. The activation parameters of the rate constant k' ($k' = k_{obs}/[S]$) were calculated using Eyring and Arrhenius plots and are reported in Table 2.

3.6 Polymerization Study

To check the presence of free radicals in the reactions under investigations, the reactions mixtures were mixed with specified quantities of acrylonitrile monomer and kept for 6 h under nitrogen. On dilution with methanol, white precipitates were formed, indicating the participation of free radicals in the oxidation reactions. The blank experiments, which were carried out with either permanganate or isosorbide with acrylonitrile, did not induce polymerization under the same experimental conditions.

4 Discussion

During oxidation by permanganate, it is evident that the Mn(VII) in permanganate is reduced to various oxidation states in acidic, neutral and alkaline media. In acidic media, permanganate ion (MnO_4^-) can exist in several different forms, $HMnO_4$, $M_2MnO_4^+$, $HMnO_3$, and Mn_2O_7, depending on the nature of the reductant. The oxidant has been assigned with both inner-sphere and outer-sphere mechanism pathways in their redox reactions [28, 29]. In general, reduction of permanganate ion in acidic medium goes either to Mn^{IV} or Mn^{II}, where the reduction potential of the Mn^{VII}/Mn^{IV} couple is 1.695 V and that of the Mn^{VII}/Mn^{II} couple is 1.51 V [30]. Also, permanganate ion in acidic media tends to protonate to form a more powerful oxidant species, namely permanganic acid [38, 39]. The protonation of permanganate ion shifts the Mn^{VII}/Mn^{VI} couple to a more positive value (+1.3 V), which makes $HMnO_4$ a stronger oxidizing agent than MnO_4^- [38, 39]. In the present work, the increasing oxidation rates upon increasing the hydrogen ion concentration supports this suggestion as illustrated by step (I) in Scheme 1. Furthermore, the fractional-second-order dependence with respect to $[H^+]$ also suggests protonation of the



Scheme 1 Mechanism of oxidation of isosorbide by permanganate ion in acidic media

isosorbide reductant, step (II) in Scheme 1, giving the protonated isosorbide (SH^+) that may be considered as more reactive species in the oxidation reactions.

On the other hand, most of the permanganate oxidation reactions are suggested [18–26] to proceed through intermediate complex formation between the oxidant and substrate. The kinetic evidence that supports complex formation in both acids is the linearity of the plots between $1/k_{obs}$ and 1/[S] with positive intercepts on $1/k_{obs}$ axes, Fig. 5, in favor of possible formation of a transient complex flanked by oxidant and substrate, comparable with the well known Michaelis–Menten mechanism [40] for enzyme–substrate reactions. The observed insignificant effect of either ionic strength or dielectric constant of the reaction media on the oxidation rates implies association of two neutral molecules or a neutral molecule with an ion [41, 42], i.e., between permanganic acid and positively charged protonated isosorbide.

In view of the above arguments, the following reactions mechanism may be suggested. The mechanism involves protonation of both permanganate and isosorbide, followed by attack of the powerful oxidant, permanganate acid, on the protonated isosorbide, step (III), leading to the formation of a complex (C) prior to the equilibrium step. Such a complex decomposes to form a free radical intermediate derived from the isosorbide substrate and Mn(VI) intermediate, step (IV). The latter attacks the isosorbide free radical to yield the oxidation product of isosorbide (monoketone derivative) and Mn(V) intermediate, step (**V**). In a further fast step, the intermediate Mn(V), being very active and unstable in acidic medium, reacts with another molecule of protonated isosorbide to form again the oxidation product of isosorbide, step (VI). This step is followed by other fast steps, including reactions of two molecules of isosorbide with an acid permanganate species to form the monoketone oxidation product and Mn(III) species, step (VII). The last step is the attack of Mn(III) species on another protonated isosorbide to give the monoketone oxidation product and Mn(II), step (VIII), satisfying the obtained stoichiometry as illustrated in Scheme 1.

Based on the proposed mechanistic Scheme 1, the oxidation rate can be expressed by the following rate law:

$$\text{Rate} = \frac{-d[\mathrm{MnO_4^-}]}{dt} = k_1[\mathrm{C}]. \tag{1}$$

The relationship between the oxidation rate and the oxidant, substrate and hydrogen ion concentrations is deduced to give the following equation:

$$\text{Rate} = \frac{k_1 K_1 K_2 K_3 [\mathrm{MnO_4^-}][\mathrm{S}][\mathrm{H^+}]^2}{1 + K_1[\mathrm{H^+}] + K_1 K_2 K_3 [\mathrm{S}][\mathrm{H^+}]^2}. \tag{2}$$

Under pseudo-first-order condition, the rate law can be expressed by Eq. 3:

$$\text{Rate} = \frac{-d[\mathrm{MnO_4^-}]}{dt} = k_{obs}[\mathrm{MnO_4^-}]. \tag{3}$$

Comparing Eqs. 2 and 3 and rearrangement, the following equation is obtained:

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

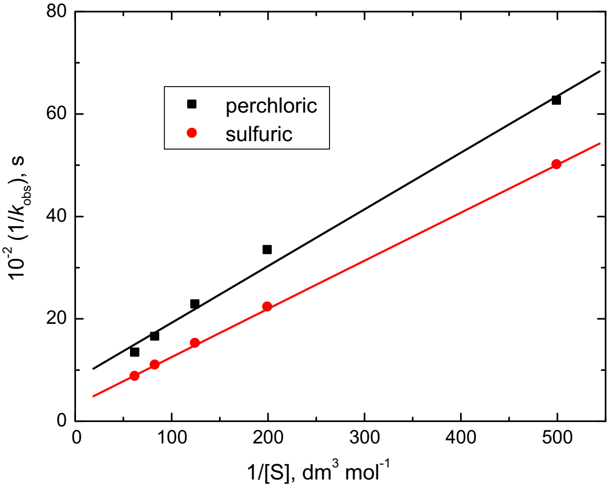


Fig. 5 Verification of Eq. 4 for the oxidation of isosorbide by permanganate ion in perchloric and sulfuric acids solutions: $[\mathrm{MnO_4^-}] = 4.0 \times 10^{-4}$ mol·dm^{-3}, $[\mathrm{H^+}] = 1.0$ mol·dm^{-3} and $I = 2.0$ mol·dm^{-3} at 25 °C

$$\frac{1}{k_{\mathrm{obs}}} = \left(\frac{1}{k_1 K_1 K_2 K_3 [S]}\right) \frac{1}{[\mathrm{H}^+]^2} + \frac{1}{k_1} + K' \tag{5}$$

where $K' = 1/k_1 K_2 K_3 [\mathrm{H}^+][\mathrm{S}]$.

According to Eqs. 4 and 5, with other conditions being constant, plots of $1/k_{\mathrm{obs}}$ versus 1/[S] at constant [H$^+$] and $1/k_{\mathrm{obs}}$ versus $1/[\mathrm{H}^+]^2$ at constant [S] should be linear with positive intercepts on the $1/k_{\mathrm{obs}}$ axes and are found to be so as shown in Figs. 5 and 6, respectively. These results support the proposed mechanism.

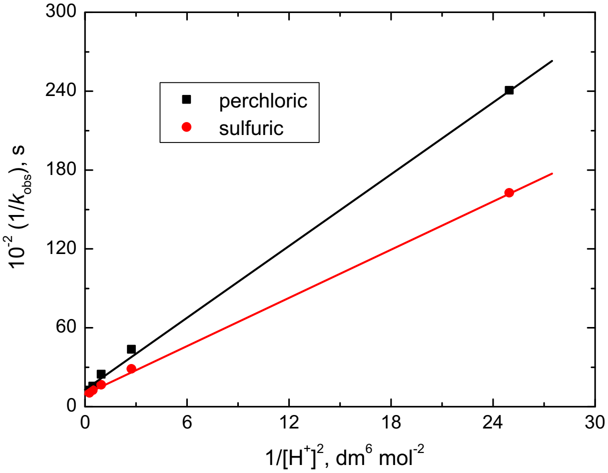


Fig. 6 Verification of Eq. 5 for the oxidation of isosorbide by permanganate ion in perchloric and sulfuric acids solutions: $[\mathrm{MnO_4^-}] = 4.0 \times 10^{-4}$ mol·dm^{-3}, $[\mathrm{S}] = 8.0 \times 10^{-3}$ mol·dm^{-3} and $I = 2.0$ mol·dm^{-3} at 25 °C

The activation parameters listed in Table 2 may be interpreted as follows. The obtained large negative values of entropy of activation, $\Delta S^{\neq}$, suggest compactness of the formed complexes and that such complexes are more ordered than the reactants due to loss of degrees of freedom [43]. It was observed that the value of $\Delta S^{\neq}$ for perchloric acid is larger than that of sulfuric acid, suggesting that the formed intermediate complex in the case of perchloric acid is more compact than that formed in sulfuric acid. Also, the obtained values of $\Delta S^{\neq}$ are within the range of free radical reactions. The positive values of both enthalpy of activation, $\Delta H^{\neq}$ confirms the endothermic formation of the intermediate complexes.

5 Conclusions

The kinetics of oxidation of isosorbide by potassium permanganate was investigated in both perchloric and sulfuric acids solutions. In both acids, the final 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. Under comparable experimental conditions, the oxidation rate of isosorbide in perchloric acid is slightly lower than that in sulfuric acid. An oxidation mechanism was proposed and the activation parameters were computed and discussed.

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