

Kinetics and Mechanism of Permanganate Oxidation of Inositol in Perchloric and Sulfuric Acids Solutions

Ahmed Fawzy^{1,2,*}, Ishaq A. Zaafarany¹, Hatem M. Altass¹, Moataz H. Morad¹, Jabir Alfahemi¹

¹Chemistry Department, Faculty of Applied Science, Umm Al-Qura University, Makkah, Saudi Arabia

²Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

Email address:

afsaad13@yahoo.com (A. Fawzy), iazaafarany@uqu.edu.sa (I. A. Zaafarany), hatem1401@hotmail.com (H. M. Altass), mhmorad@uqu.edu.sa (M. H. Morad), jhfhahemi@uqu.edu.sa (J. Alfahemi)

*Corresponding author

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Abstract: The kinetics of oxidation of inositol (INOS) by permanganate ion in both perchloric and sulfuric acids solutions was studied using a spectrophotometric technique at a constant ionic strength of 1.0 mol dm⁻³ and at 25°C. In both acids, the reactions showed a first order dependence with respect to [permanganate], whereas the orders with respect to [INOS] were found to be less than unity. The effect of acids concentrations suggests that the reactions were acid-catalyzed with fractional-second order kinetics in [H⁺]. Variation of either ionic strength or dielectric constant of the medium had no effect significantly on the oxidation rates. The reactions mechanism adequately describing the kinetic results was proposed. In both acids, the main oxidation products of inositol were identified by spectral and chemical tools as the corresponding monoketone derivative, namely inosose. Under comparable experimental conditions, the oxidation rate in sulfuric acid was approximately three times higher than that in perchloric acid. Regarding to the second order rate constants of these reactions, the activation parameters have been evaluated and discussed.

Keywords: Inositol, Oxidation, Acid, Permanganate, Kinetics, Mechanism

1. Introduction

Oxidation reactions are very important in organic synthesis. Among the important oxidizing agents, permanganate ion is widely used in the oxidation of many organic compounds in acidic, neutral and alkaline media [1-11]. The mechanism of oxidation reactions by permanganate ion is governed by pH of the medium [12]. 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 (MnO₄⁻) can exist in several different forms, HMnO₄, H₂MnO₄⁺, HMnO₃, and Mn₂O₇. The oxidant has been assigned with an inner-sphere and an outer-sphere mechanism pathways in their redox reactions [13, 14]. In general, reduction of permanganate ion in acidic media goes to either 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 [15].

Inositol is a water soluble six membered cyclic polyol, which is synthesized by both eukaryotes and prokaryote [16]. In humans most inositol is synthesized in the kidneys. Inositol and some of its mono and polyphosphates function as the basis for a number of signaling and secondary messenger molecules [17, 18]. These are involved in insulin signal transduction, gene expression, breakdown of fats and reducing blood cholesterol [19]. Oxidation of inositol was studied by different oxidants like alkaline potassium periodate [20], alkaline diperiodatocuprate(III) [21], alkaline permanganate [22], V(V) in acid medium [23] and chromic acid [24]. A literature survey revealed that there is a lack of literature on the kinetics of oxidation of inositol by permanganate ion in acidic media. This observation prompted us to investigate the title reactions. The objectives of the present study are to check the reactivity of inositol towards

3.3. Dependence of Reaction Rate on $[MnO_4^-]$

The concentration of permanganate ion was varied in the range of $1.0 - 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ while the rest of the reactant concentrations were kept constant. It has been found that, plots of $\ln(\text{Abs.})$ versus time were linear up to about 70% of the reactions completion. Furthermore, the increase in the oxidant concentration did not change the oxidation rates as listed in Table 1. These results indicate that the order of the reactions with respect to the oxidant is confirmed to be one.

3.4. Dependence of Reaction Rate on $[INOS]$

The observed first order rate constants were measured at various concentrations of inositol keeping others constant. In both perchloric and sulfuric acid solutions, plots of k_{obs} versus $[INOS]$ were found to be linear with positive intercepts on k_{obs} axes as shown in Fig. 2 confirming the less than unit order dependences with respect to inositol concentration.

3.5. Dependence of Reaction Rate on $[H^+]$

The influence of both perchloric and sulfuric acids on the

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

$10^4 [MnO_4^-]$ (mol dm^{-3})	$10^2 [INOS]$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	I (mol dm^{-3})	$10^5 k_{\text{obs}}$ (s^{-1})	
				Perchloric	Sulfuric
1.0	1.0	0.5	1.0	23.9	73.4
2.0	1.0	0.5	1.0	24.5	74.1
4.0	1.0	0.5	1.0	23.7	72.6
6.0	1.0	0.5	1.0	25.6	69.8
8.0	1.0	0.5	1.0	22.1	71.0
4.0	0.2	0.5	1.0	8.7	21.5
4.0	0.6	0.5	1.0	15.8	48.5
4.0	1.0	0.5	1.0	23.7	72.6
4.0	1.4	0.5	1.0	28.8	94.0
4.0	1.8	0.5	1.0	35.5	115.1
4.0	1.0	0.1	1.0	3.1	7.6
4.0	1.0	0.3	1.0	12.8	37.2
4.0	1.0	0.5	1.0	23.7	72.7
4.0	1.0	0.7	1.0	39.3	99.8
4.0	1.0	0.9	1.0	53.2	133.0
4.0	1.0	0.5	1.0	23.7	72.7
4.0	1.0	0.5	1.5	24.1	74.3
4.0	1.0	0.5	2.0	22.0	71.8
4.0	1.0	0.5	2.5	23.7	75.0
4.0	1.0	0.5	3.0	25.2	73.7

Experimental error $\pm 3\%$

rates was investigated by varying the hydrogen ion concentration in the range of $0.1 - 0.9 \text{ mol dm}^{-3}$, keeping all other reactants concentrations constant. The rate constants increased with increasing acid concentration (Table 1). Plots of $\log k_{\text{obs}}$ versus $\log [H^+]$ were also linear with slopes of 1.62 and 1.57 in both acids, respectively, Fig. 3, suggesting that the orders of reactions with respect to $[H^+]$ were fractional-second.

3.6. Effect of Ionic Strength and Dielectric Constant

The effect of ionic strength has been investigated by varying the concentration of NaClO_4 in case of perchloric acid and Na_2SO_4 in case of sulfuric acid solutions in the reactions media at constant concentrations of permanganate, inositol and acids. It was found that variation in ionic strength did not affect the rates as observed from the data listed in Table 1. Furthermore, the effect of 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 constants did not significantly affected by the decrease in dielectric constant of the solvent mixture; i.e. increase in acetic acid content.

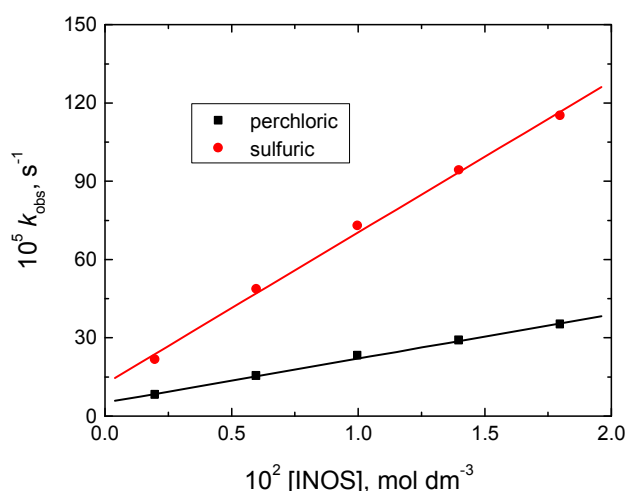


Figure 2. Plots of the observed first order rate constants (k_{obs}) versus $[INOS]$ in the oxidation of inositol by permanganate ion in perchloric and sulfuric acids solutions. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[H^+] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

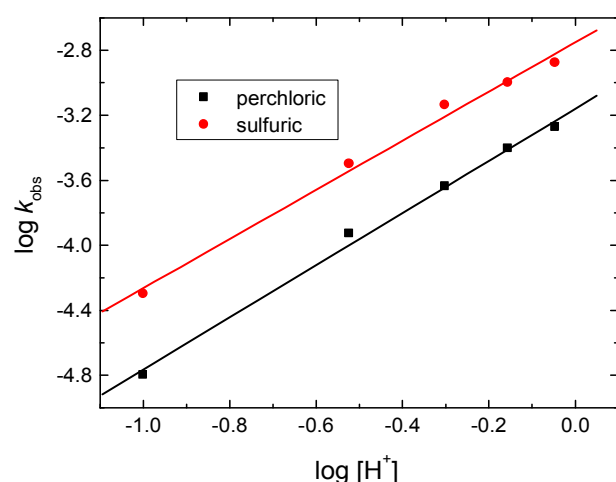


Figure 3. Plots of $\log k_{obs}$ versus $\log [H^+]$ in the oxidation of inositol by permanganate ion in perchloric and sulfuric acids solutions. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[INOS] = 1.0 \times 10^{-2}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

3.7. Effect of Temperature

The rates of the reactions were carried out at five different temperatures between 283 and 308 K at constant concentrations of the reactants and other conditions being constant. The results indicate that the rate constants increased with rise in temperature. The activation parameters of the second order rate constant (k_2) are calculated using Eyring and Arrhenius plots and are listed in Table 2.

Table 2. Activation parameters of the second order rate constant (k_2) in the oxidation of inositol by permanganate ion in perchloric and sulfuric acids solutions. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[INOS] = 1.0 \times 10^{-2}$, $[H^+] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$.

Acid	$\Delta S^\ddagger, \text{J mol}^{-1}\text{K}^{-1}$	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta G^\ddagger_{298}, \text{kJ mol}^{-1}$	$E_a^\ddagger, \text{kJ mol}^{-1}$
Perchloric	-77.87	62.30	85.50	65.07
Sulfuric	-81.02	57.81	81.91	59.93

3.8. Polymerization Study

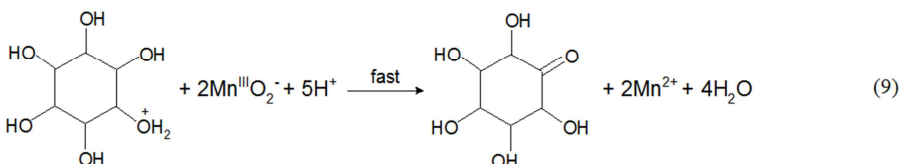
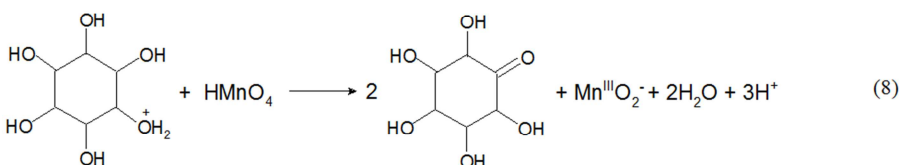
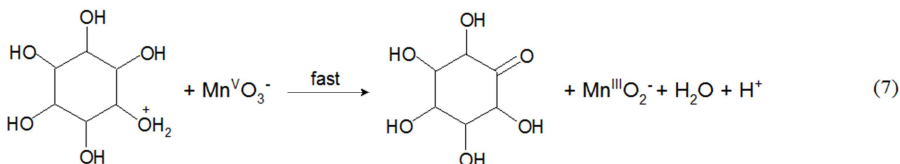
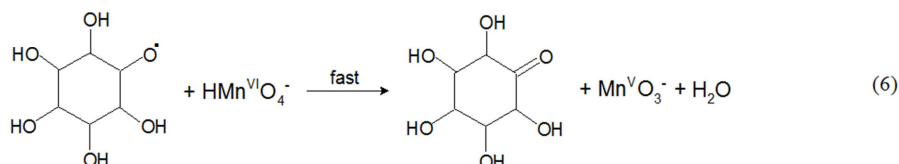
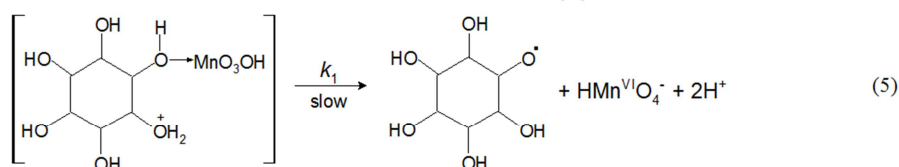
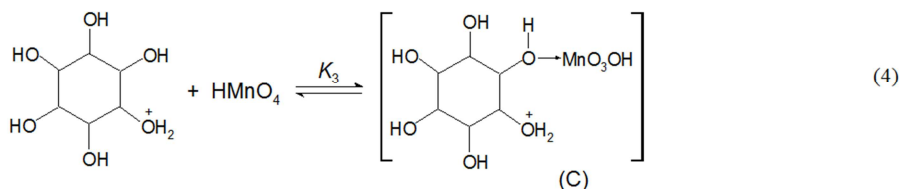
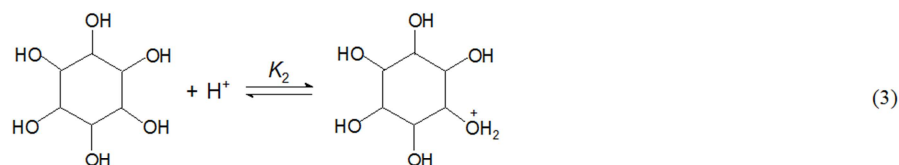
To check the existence of free radicals in the reactions under investigations, the reactions mixtures were mixed with identified quantities of acrylonitrile and kept for 8 hours under nitrogen. On dilution with methanol, white precipitates were formed, indicating the participation of free radicals in the oxidation reactions. The blank experiments which were carried out with either permanganate or inositol with acrylonitrile did not induce polymerization under the same experimental conditions.

4. Discussion

It was reported [3-11] that most permanganate oxidation reactions proceed through intermediate complex formation between the oxidant and substrate. The investigated reactions between inositol and permanganate ion in both perchloric and sulfuric acids solutions have a stoichiometry of 5:2, $INOS : MnO_4^-$. The reactions exhibited a first order dependence with respect to $[MnO_4^-]$ and less than unit order dependences with respect to $[INOS]$. The reactions exhibited fractional-second order kinetics in $[H^+]$ suggesting protonation of both permanganate ion [29,30] and inositol in the first steps of the reactions (illustrated by steps (1) and (2) in Scheme 1) to form more reactive species of both reactants. On the other hand, the less than unit order dependences with respect to inositol concentration in both acids suggest formation of intermediate complexes (C) between the kinetically active species of inositol substrate and permanganate oxidant prior to the rate-determining step. Complexes formation was also proved kinetically by the non-zero intercept of the plots of $1/k_{obs}$ versus $1/[INOS]$, Fig. 4, in favor of possible formation of a transient complex flanked by oxidant and substrate comparable with the well-known Michaelis-Menten mechanism for enzyme-substrate reactions [31]. The observed insignificant effect of either ionic strength or dielectric constant of the reactions media on the oxidation rates implies association of two neutral molecule or between a neutral molecule and an ion [32,33], i.e. between acid permanganate and protonated inositol.

Owing to the experimental results, a plausible reactions mechanism has been proposed which involves protonation of both permanganate ion and inositol in the first two steps followed by complexation of the protonated reactants prior to the rate-determining step. Such complex decomposes yielding a free radical intermediate derived from inositol substrate and manganate(VI) intermediate. The free radical is attacked by manganate(VI) to give the corresponding mono ketone (inosose) as the final oxidation product of inositol. In a further fast step the intermediate Mn(V), being very active and unstable in acidic medium, reacts with another inositol substrate to form also inosose product and an intermediate Mn(III) species. This step is followed by other fast steps including reactions of inositol with acid permanganate species to form again the final oxidation products and

Mn(III) species. The last step is the attack of Mn(III) species on another inositol molecule to give the final oxidation product and Mn(II) satisfying the obtained stoichiometry.



Scheme 1. Mechanism of oxidation of inositol by permanganate ion in acidic media.

Owing to the proposed mechanistic Scheme 1, the oxidation rate can be expressed by the following rate law:

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_1[\text{C}] \quad (10)$$

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

$$\text{Rate} = \frac{k_1 K_1 K_2 K_3 [\text{MnO}_4^-] [\text{INOS}] [\text{H}^+]^2}{1 + K_1 [\text{H}^+] + K_1 K_2 K_3 [\text{INOS}] [\text{H}^+]^2} \quad (11)$$

Under pseudo-first order condition, the ratelaw can be expressed by Eq. (12),

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}} [\text{MnO}_4^-] \quad (12)$$

Comparing Eqs. (11) and (12) and rearrangement, the following equation is obtained:

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[H^+]}{k_1 K_1 K_2 K_3 [H^+]^2} \right) \frac{1}{[INOS]} + \frac{1}{k_1} \quad (13)$$

According to Eq. (13), other conditions being constant, plots of $1/k_{obs}$ versus $1/[INOS]$ at constant $[H^+]$ and $1/k_{obs}$ versus $1/[H^+]^2$ at constant $[INOS]$ should be linear with positive intercepts on the $1/k_{obs}$ axes and are indeed found to be so as shown in Figs. 4 and 5. The slopes and intercepts of such plots lead to calculate the values of k_1 , K_1 and K_2 .

The activation parameters listed in Table 2 may be interpreted as follows. The obtained large negative values of ΔS^\ddagger suggest compactness of the formed complexes [34]. Also, the obtained values of ΔS^\ddagger are within the range of radical reactions. The positive values of both ΔH^\ddagger and ΔG^\ddagger confirm endothermic formation of the intermediate complexes and their non-spontaneities, respectively.

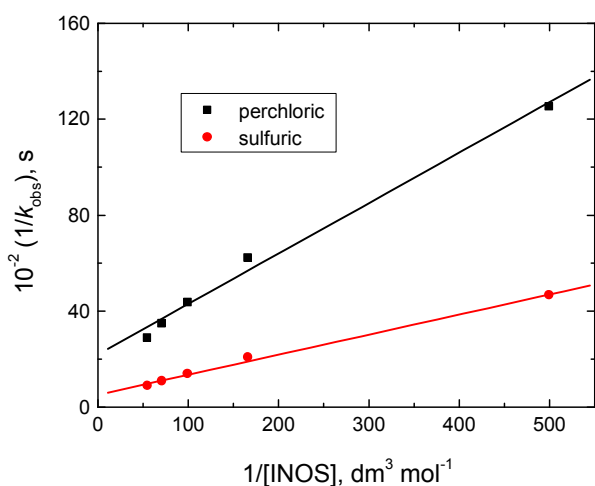


Figure 4. Plots of $1/k_{obs}$ versus $1/[INOS]$ in the oxidation of inositol by permanganate ion in perchloric and sulfuric acids solutions. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[H^+] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

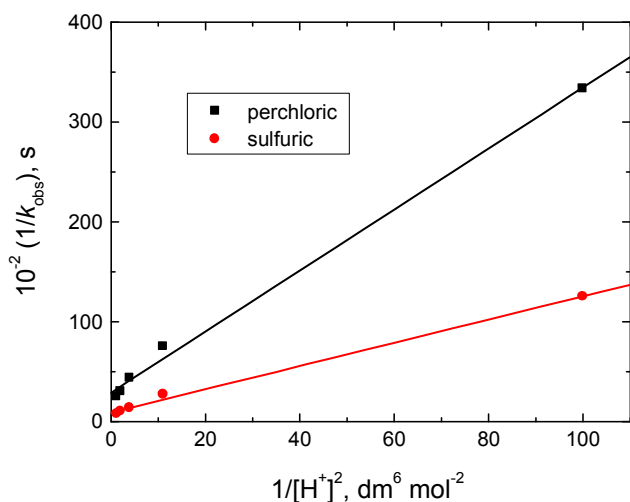


Figure 5. Plots of $1/k_{obs}$ versus $1/[H^+]^2$ in the oxidation of inositol by permanganate ion in perchloric and sulfuric acids solutions. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[INOS] = 1.0 \times 10^{-2}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

5. Conclusions

The kinetics of oxidation of inositol by permanganate ion in both perchloric and sulfuric acids solutions has been studied. The final oxidation product of inositol was identified in both cases as the corresponding monoketone, namely inosose. Under comparable experimental conditions, the oxidation rate in sulfuric acid was about three times higher than that in perchloric acid. The activation parameters have been evaluated and discussed.

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