

Kinetics and mechanism of oxidation of chitosan polysaccharide by permanganate ion in aqueous perchlorate solutions

Gamal Abdel-Whab Ahmed^{a*}, Khalid Suliman Khairou^b and Refat Moustafa Hassan^b

^a Department of Chemistry, Faculty of Science, Assiut University, Assiut 71516, Egypt.

^b Department of Chemistry, Faculty of Applied Sciences, Umm Al-Qura University, Makkah Al-Mukarramah 5576, Kingdom of Saudi Arabia

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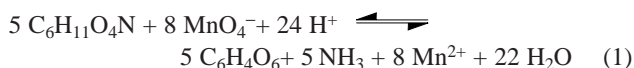
The kinetics of oxidation of chitosan as polysaccharide by permanganate in aqueous perchlorate media at a constant ionic strength was found to have second-order overall kinetics and to be first-order in the concentration of both reactants, the results obtained showed that the reaction is acid catalysed.

Keywords: chitosan, polysaccharide, permanganate, perchlorate media

Chitosan is a polysaccharide consisting of [2-amino-2-deoxy-(1→4) β-D-glucopyranan; poly (1→4 β-D-glucopyranosamine)].² On the other hand, permanganate ion is a powerful oxidising agent for many organic^{7,8} and inorganic compounds.^{11,12} Hassan and coworkers studied the kinetics of oxidation of alginates¹⁵ and pectates¹⁷ as polyelectrolyte macromolecules by permanganate ion in alkaline solutions (pH ≥ 12). They reported that the oxidation processes proceed through the formation of intermediate complexes of manganate (VI) as transient species, followed by slow decomposition of these intermediates to give the reaction products. The present study investigates the reaction of permanganate ion with chitosan in non-complexing perchloric acid media to shed some light on the mechanism of oxidation, the nature of radicals and/or ions formed and the effect of media on the rate of this redox reaction.

Chitosan was converted into water-soluble perchlorate salts (Chitosan-HClO₄) by stepwise addition of the requisite amount of the reagent to perchloric acid. Preparation, storage and standardisation of permanganate ion solution were as described earlier.⁸ All kinetic runs were conducted under pseudo-first-order conditions where [chitosan] ≥ 10 [KMnO₄] at a constant ionic strength of 1.0 mol/dm³. The course of reaction was followed by recording the decrease in absorbance of permanganate ion at its absorption maximum, 525 nm, as a function of time. Pseudo-first-order rate constants (*k*_{obs}) were evaluated from plotting ln (absorbance)₅₂₅ versus time.

A stoichiometric ratio of (1.6 ± 0.1([MnO₄⁻]_{consumed} / [Chitosan]₀) was obtained at several initial concentrations of MnO₄⁻ in 0.5 mol/dm³ HClO₄ adjusted to a constant ionic strength of 1.0 mol/dm³. This indicates that the stoichiometry of the overall reaction conforms to



where C₆H₁₁O₄N and C₆H₄O₆ represent the chitosan and its diketo-acid derivatives, respectively. Diketo-acid derivatives was identified by elemental analysis, IR spectra and formation of 2, 4- dinitrophenyl hyrazone derivative.

Plots of ln (A_t - A_∞) versus time, where A_t and A_∞ represent the absorbance at time *t* and infinite time, respectively, were linear over three half-lives of the reaction completion. This linearity indicated that the reaction is first order with respect to permanganate ion concentration. This first-order dependence was also indicated by the independence of the observed first-order rate constants on different initial [MnO₄⁻]₀. The dependence of the observed first-order rate constants, *k*_{obs}, on the

chitosan concentration was found to follow Michaelis–Menten kinetics.²² The good linearity obtained in addition to the positive intercept on *k*_{obs}⁻¹ axis indicates the formation of an intermediate complex between MnO₄⁻ and chitosan. An increase in the acid concentration was found to accelerate the reaction rate. This dependence was found to be of fractional first-order in the hydrogen ion concentration ([H⁺]₀).

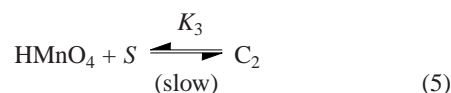
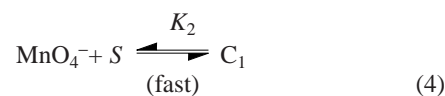
It was found that the variation of [Mn²⁺] had an appreciable effect on the rate of reaction. Similarly, the experimental observations indicated that the reaction rate was not affected remarkably by addition of F⁻ ions.

No polymerisation of acrylonitrile was observed by adding acrylonitrile to the partially oxidised reaction mixture. This shows that the redox reaction was not proceeding through a free-radical mechanism.

The increase of the rate constant with increasing the hydrogen ion concentration is most probably due to the protonation of permanganate ion in acidic solutions as follows:



Again the negative salt effect and the absence of an induction period may further indicate that HMnO₄ is the reactive species in the oxidation process, but not Mn³⁺ and/or Mn⁴⁺ ions. A consistent mechanism involving two competitive reactions in the rate-determining step may be suggested as follows,



where *S*, *K*₂ and *K*₃ represents the chitosan and the formation constants of the intermediate complexes C₁ and C₂, respectively. The change in the rate constant with change in the hydrogen ion concentration may be expressed by equation (8)

* To receive any correspondence. E-mail: gam@aun.eun.eg

$$\text{Rate} = -\frac{d[\text{MnO}_4^-]}{dt} = \frac{(k_a'K_2 + k_b K_1 K_3 [\text{H}^+]) [\text{S}] [\text{MnO}_4^-]_T}{1 + K_1[\text{H}^+] + [\text{S}] (K_2 + K_1 K_3 [\text{H}^+])} \quad (8)$$

$$k_{\text{obs}} = \frac{(k_a K_2 + k_b K_1 K_3 [\text{H}^+]) [\text{S}]}{1 + K_1 [\text{H}^+] + [\text{S}] (K_2 + K_1 K_3 [\text{H}^+])} \quad (10)$$

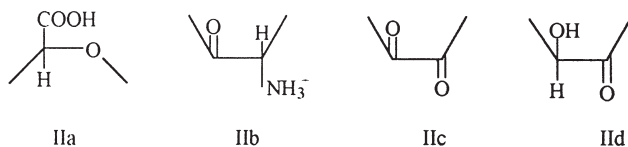
where k_{obs} is the observed first-order rate constant. On rearrangement, Eqn (10) may be written in the form:

$$\frac{1}{k_{\text{obs}}} = \left[\frac{(1 + K_1 [\text{H}^+])}{(k_a K_2 + k_b K_1 K_3 [\text{H}^+])} \right] \frac{1}{[\text{S}]} + K' \quad (11)$$

According to Eqn (11), at constant $[\text{H}^+]$ a plot of k_{obs}^{-1} against $[\text{S}]^{-1}$ should be a straight line with positive intercept on k_{obs}^{-1} axis as is experimentally observed.

The apparent rate constants k_a' and k_b' were calculated at 25°C using the method of least-squares and found to be $1.23 \times 10^{-3} \text{ dm}^9/\text{mol}^3/\text{s}^1$ and $1.83 \times 10^{-3} \text{ dm}^{12}/\text{mol}^4/\text{s}^1$, respectively.

In the light of the above observations and under our experimental conditions, one might expect formation of complex mixtures of the reaction products (II_a–II_d) in the oxidation of chitosan by MnO_4^- .



Techniques used: UV, IR spectrometry, Elemental Analysis.

References: 26

Schemes: 1

Table 1: The observed first-order rate constants for the oxidation of chitosan polysaccharide by permanganate ion

Table 2: Hydrogen ion dependency for the oxidation of chitosan polysaccharide by permanganate ion

Table 3: The activation parameters of the second-order rate constant, k_s for the oxidation of chitosan polysaccharide by permanganate ion

Figure 1. Reciprocal Michaelis-Menten plot for the oxidation of chitosan polysaccharide by permanganate ion.

Figure 2. A typical plots of $k_s'[\text{H}^+]^{-1}$ versus $[\text{H}^+]^{-1}$ for the oxidation of chitosan polysaccharide by permanganate ion.

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