



Acid-catalyzed oxidation of some sulfated macromolecules. Kinetics and mechanism of oxidation of kappa-carrageenan polysaccharide by permanganate ion in acid perchlorate solutions

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ABSTRACT

The kinetics of oxidation of kappa-carrageenan polysaccharide as natural polymer by permanganate ion in aqueous perchlorate solutions at a constant ionic strength of 2.0 mol dm^{-3} have been investigated spectrophotometrically. The experimental observations showed that the pseudo-first-order plots were of inverted S-shape throughout the entire course of reaction. The initial rates were found to be relatively slow in the early stages, followed by an increase in the oxidation rates over longer time periods. A first-order dependence in permanganate and fractional-order kinetics with respect to carrageenan concentration for both the induction and autoacceleration periods were revealed. The results obtained at various hydrogen ion concentrations showed that the oxidation is acid-catalyzed throughout the two stages of reaction. The added salts lead to the prediction that Mn^{III} and/or Mn^{IV} are the reactive species throughout the autoacceleration period. Kinetic evidences for the formation of 1:1 intermediate complexes are presented. The kinetic parameters have been evaluated and a tentative reaction mechanism consistent with the kinetic results is discussed.

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1. Introduction

It well known that the oxidation of organic substrates by permanganate ion depends on the nature of the medium. In alkaline, neutral or weakly acidic solution, Mn^{VII} changes to Mn^{IV} while in strongly acidic media, Mn^{VII} is further reduced forming ultimately Mn^{II} . But the species having the main role as potential oxidants depend on the nature of the substrate as well as the pH of the medium [1–5].

Although, the kinetics of alkaline permanganate oxidation of macromolecules containing secondary alcoholic groups either natural [6–9] or synthetic [10] polymers have received much attention in recent years. A lack of information in the literature survey about the kinetics of oxidation of macromolecules by permanganate ion in acidic solutions still remains [11,12].

In view of the foregoing aspects, in addition to our interest in the oxidation of macromolecules by permanganate ion, we prompted to undertake the present investigation of oxidation of kappa-carrageenan as a polysaccharide containing both primary and secondary alcoholic functional groups in its macromolecular chains by acidic permanganate. The results obtained may shed

some light on the effect of the medium and the functional groups on the kinetics and mechanistics of oxidation in these redox systems.

2. Experimental

2.1. Materials

All materials employed in the present work were of analytical grade. Doubly distilled water was used in all preparations. The temperature was controlled within $\pm 0.05^\circ\text{C}$.

Kappa-carrageenan was Fluka reagent and was used without further purification. Solutions of KCAR (0.01 mol dm^{-3}) were prepared by stepwise addition of the reagent powder to bidistilled water while rapidly stirring the solution to avoid the formation of lumps, which swell with difficulty.

The preparation and standardization of KMnO_4 solution were the same as described elsewhere [13].

2.2. Kinetic measurements

Preliminary experiments indicated that the oxidation reaction is of such a rate to be measured using a conventional spectrophotometer. The spectral changes during the oxidation reaction are shown in Fig. 1.

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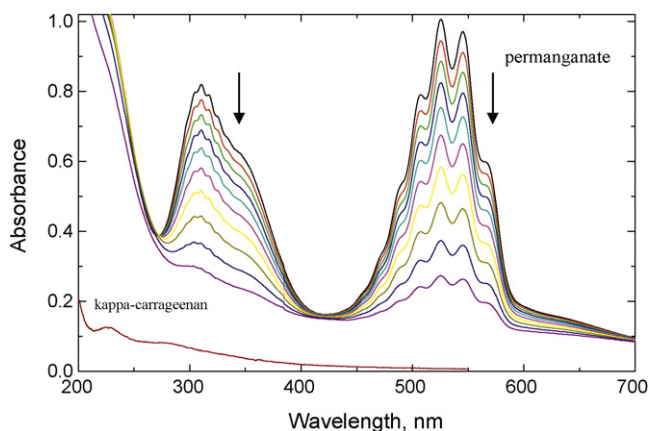


Fig. 1. Spectral changes (200–700 nm) in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$, $[\text{H}^+] = 1.0$, $I = 2.0 \text{ mol dm}^{-3}$ at 20°C . Scanning time intervals = 4 min.

The kinetic measurements were performed under pseudo-first-order conditions where KCAR was present in a large excess over that of permanganate concentration. The ionic strength was maintained constant by the addition of NaClO_4 as an inert electrolyte. The absorbance measurements were made in a thermostated cell compartment at the desired temperature on a Shimadzu UV-2101 double-beam spectrophotometer using cells of path length 1 cm. The procedure for measurements was the same as described elsewhere [13].

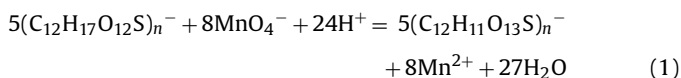
2.3. Polymerization test

The possibility of formation of free radicals was examined by adding 10% (v/v) acrylonitrile to the partially oxidized reaction mixture. After a lapse of 20 min mixing (on warming), a heavy appreciable white precipitate was observed indicating that the oxidation reaction proceeds via generation of free radicals. No detectable polymerization was shown in both experiments in which either of the reactants was absent.

3. Results

3.1. Stoichiometry

Reaction mixtures containing different initial concentrations of the reactants at $[\text{H}^+] = 1.0$ and $I = 2.0 \text{ mol dm}^{-3}$ were equilibrated in dark bottles away from light. The unreacted $[\text{MnO}_4^-]$ was estimated periodically until it reached a constant value, i.e. completion of the reaction. A stoichiometric ratio of $([\text{MnO}_4^-]_{\text{consumed}}/[\text{KCAR}]_0)$ was found to be $1.67 \pm 0.1 \text{ mol}$. This result conforms the following stoichiometric equation¹:



where $(\text{C}_{12}\text{H}_{17}\text{O}_{12}\text{S})_n^-$ and $(\text{C}_{12}\text{H}_{11}\text{O}_{13}\text{S})_n^-$ represent to the kappa-carrageenan and its corresponding diketo-acid oxidation derivative, respectively. The products were identified by the spectral data and microanalysis as described elsewhere [14].

¹ In case of the hydrolysis of sulfate group at higher $[\text{H}^+] > 4.0 \text{ mol dm}^{-3}$:

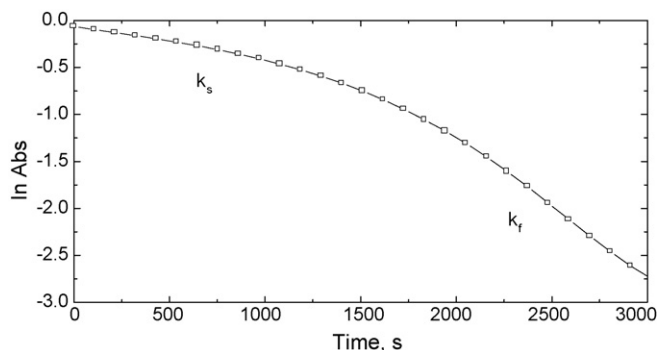
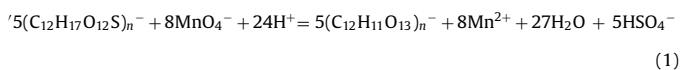


Fig. 2. A plot of $\ln \text{Abs.}$ vs. time in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$, $[\text{H}^+] = 1.0$, $I = 2.0 \text{ mol dm}^{-3}$ at 20°C .

Some experiments have been carried out in nitrogen atmosphere in order to decide whether permanganate ion or dissolved oxygen is the reactive oxidizing agent at the final stage, the same product was obtained. This means that the dissolved oxygen has no influence on the oxidation process.

3.2. Reaction–time curves

The reaction–time curves were found to be of inverted S-shape throughout the entire range of reaction as shown in Fig. 2. The initial rates were found to be relatively slow in the early stages, followed by an increase in the oxidation rates over longer time periods. As the reaction is of catalytic nature, it obeys the rate expression $(A_t - A_\infty) = B_0 e^{-k_s t} + P_0 e^{-k_f t}$ [11] where k_s and k_f are the first-order rate constants for the induction and autoacceleration periods, A_t and A_∞ are the absorbance at times t and infinity; while B_0 and P_0 represent the absorbance change for the slow and fast reacting species, respectively. The rate constants were obtained by drawing a straight line through the slow-time linear portion (k_s) of the first-order plot and extrapolating the time back to zero-time (B_0). The rate of oxidation for the autoacceleration period, k_f , was obtained from plots of the form: $\ln[(A_t - A_\infty) - (A_\infty - A_{t'})] - t$ where the quantity $(A_t - A_\infty)$ represents the experimental point and $(A_\infty - A_{t'})$ is the extrapolated one at time t' [15–17]. The values of pseudo-first-order rate constants (k_s and k_f) were calculated by the least-squares method ($r = 0.99$). All experiments were studied in duplicate and the rate constants were found to be reproducible within $\pm 3\%$. Similar redox reactions involving MnO_4^- as an oxidant, which followed the same behaviour, were reported elsewhere [18].

3.3. Dependence of reaction rate on $[\text{MnO}_4^-]$ and $[\text{KCAR}]$

The order with respect to permanganate ion was determined by studying the reaction rate at different initial concentrations of permanganate ion at constant $[\text{KCAR}]$. The permanganate ion concentration was varied in the range $(2-8) \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{KCAR}] = 4 \times 10^{-3}$, $[\text{H}^+] = 1.0$, and $I = 2.0 \text{ mol dm}^{-3}$ at 20°C . The independence of pseudo-first-order rate constants obtained from the linear portions of $\ln(\text{absorbance})$ -time plots at various $[\text{MnO}_4^-]$, may confirm that the reaction is first-order with respect to permanganate ion concentration.

The order with respect to the KCAR was deduced from the measurement of the initial rate at several ratios of $[\text{KCAR}]$ and fixed concentration of permanganate ion. A fractional-first-order in $[\text{KCAR}]$ was obtained from the plots of double logarithm of the rate constants and concentration ($\log k_{\text{obs}} = n \log[\text{KCAR}]$). Again, when the reciprocal of the rate constants, $1/k_s$ and $1/k_f$, were plotted against the reciprocal of $[\text{KCAR}]$, straight lines with positive intercepts on the $1/k_s$ and $1/k_f$ axes were obtained, respectively, in good

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