



Acid-catalysis of chromic acid oxidation of kappa-carrageenan polysaccharide in aqueous perchlorate solutions

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ABSTRACT

The acid-catalyzed oxidation of kappa-carrageenan (KCAR) polysaccharide as a natural polymer by chromic acid in aqueous perchloric acid at a constant ionic strength of 4.0 mol dm^{-3} have been investigated spectrophotometrically. A first-order reaction in chromic acid and a fractional-order with respect to KCAR concentrations were revealed. A kinetic evidence for the formation of 1:2 complex between chromic acid and KCAR is presented. The influence of hydrogen ion concentrations on the reaction rates showed that the oxidation process is acid-catalyzed. The kinetic parameters have been evaluated and a tentative reaction mechanism consistent with the kinetic results is discussed.

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1. Introduction

Carrageenans are water-soluble sulfated polysaccharides of linear block copolymer structures build up of alternating 1,3 linked β -D-galactopyranosyl and 1,4-linked α -D-galactopyranosyl units. In kappa-carrageenan (KCAR), the 1,3- and 1,4-linked units are D-galactose-4-sulfate and 3,6-anhydro-D-galactose [1–4], respectively.

Although, chromic acid has been extensively used for oxidation of inorganic [5,6] and organic compounds [7–11], a little attention has been focused on the oxidation of macromolecules in particularly polysaccharides by this oxidant. This fact may be attributed to the complexity resulting from the existence of various species of chromium(VI) in acidic medium as well as the existence of various unstable Cr^{V} and Cr^{IV} oxidation states through the reduction of chromium ion from hexavalent to trivalent state. This fact may not allow a mechanistic conclusion. Indeed, Hassan and co-workers studied the kinetics of the oxidation of poly(vinyl alcohol) as a synthetic polymer containing secondary alcoholic groups in acidic medium by this oxidant [12]. They reported that the oxidation processes lead to the oxidation of secondary –OH group to the keto-form with kinetic evidence of 1:1 complex formation. A non-free radical mechanism was suggested for that reaction based on the negative result obtained for the polymerization test when acrylonitrile 5% (v/v) was added to the partially oxidized mixtures.

In view of the above aspects in addition to our interest in the oxidation of macromolecules [13–16], the present investigation of acid-catalyzed oxidation of kappa-carrageenan polysaccharide as a natural polymer containing both primary and secondary alcoholic groups by chromic acid seems to be of great significant and has been undertaken with a view at shedding some light on the influence of the type of oxidant, structure and the functional groups of substrate on the kinetics and mechanistics of acidic oxidation in these redox systems.

2. Experimental

2.1. Materials

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

Kappa-carrageenan (Fluka) was used without further purification. The measured inherent viscosity was found to be 2.25 dL g^{-1} for a 1% (w/w) solution in water at 70°C (the reduced viscosity is 9.5 dL g^{-1} measured under the same conditions). The preparation of the stock solution of KCAR was the same as described elsewhere [14].

2.2. Kinetic measurements

The kinetic measurements were conducted under pseudo-first-order conditions where KCAR was present in a large excess over

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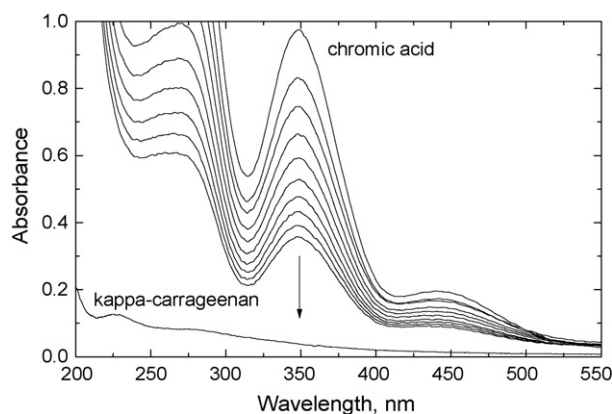


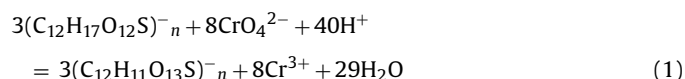
Fig. 1. Spectral changes (200–550 nm) in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , [KCAR] = 4×10^{-3} , $[H^+] = 2.0$ and $I = 4.0 \text{ mol dm}^{-3}$ at 20°C . Scanning time intervals = 4 min.

that of chromic acid concentration at a constant ionic strength of 4.0 mol dm^{-3} . The procedure for measurements was the same as described elsewhere [12–16]. The course of reaction was followed by recording the decrease in absorbance of chromic acid at its absorption maximum, 350 nm, as a function of time. It was verified that there is no interference from other reagents at this wavelength. The absorbance measurements were made in a thermostated cell compartment at the desired temperature within $\pm 0.05^\circ\text{C}$ on a Shimadzu UV-2101/3101 PC automatic scanning double-beam spectrophotometer fitted with a wavelength program controller using cells of a path length 1 cm. The spectral changes during the oxidation reaction are shown in Fig. 1.

3. Results

3.1. Stoichiometry

The stoichiometry of the overall reaction of KCAR with excess chromic acid in 2.0 mol dm^{-3} HClO_4 and at 4.0 mol dm^{-3} ionic strength was determined spectrophotometrically. Reaction mixtures containing different initial concentrations of the reactants were equilibrated for about 48 h at room temperature. The unreacted chromic acid was estimated periodically until it reached a constant value, i.e. completion of the reaction. A stoichiometric ratio of ($[\text{chromic acid}]_{\text{consumed}}/[\text{KCAR}]$) was found to be 2.7 ± 0.1 mol. This result indicates that the stoichiometry of the overall reaction conforms to 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 keto-acid oxidation derivative, respectively. The reaction products were identified by the spectral data and microanalysis as described elsewhere [17,18].

When this oxidation reaction has been carried out in nitrogen atmosphere in order to decide whether chromic acid or dissolved oxygen is the reactive oxidizing agent at the final stage, the same keto-acid derivative was obtained as a final product. This means that the keto-aldehyde derivative intermediate formed is oxidized by chromic acid rather than by dissolved oxygen at the final stage of oxidation.

¹ In case of the hydrolysis of sulfate group ($[H^+] > 4.0 \text{ mol dm}^{-3}$): $3(\text{C}_{12}\text{H}_{17}\text{O}_{12})^-_n + 8\text{CrO}_4^{2-} + 40\text{H}^+ = 3(\text{C}_{12}\text{H}_{10}\text{O}_9)_n + 8\text{Cr}^{3+} + 29\text{H}_2\text{O} + 3\text{HSO}_4^-$ (1).

Table 1

Dependence of the observed first-order rate constant (k_{obs}) on [KCAR] in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , $[H^+] = 3.0$ and $I = 4.0 \text{ mol dm}^{-3}$ at 30°C .

10^3 [KCAR] (mol dm^{-3})	3	4	5	6
$10^5 k_{\text{obs}}$ (s^{-1})	26	44	65	86

Experimental error $\pm 3\%$.

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

Plots of $\ln(A_t - A_\infty)$ vs. time, where A_t and A_∞ represents the absorbance at time t and infinity, respectively, were found to be linear for more than two half-lives of the reaction completion. This linearity indicates that the reaction is first-order kinetics in chromic acid concentration. The first-order dependency was confirmed not only by the linearity of the pseudo-first-order plots, but also by the independence of these rate constants on the different initial concentrations of chromic acid ($(5-10) \times 10^{-4} \text{ mol dm}^{-3}$) in a number of steps at constant concentration of all other reagents. The pseudo-first-order rate constants (k_{obs}) were obtained from the gradients of these plots. The dependence of k_{obs} values on the KCAR were deduced from the measurements of the observed first-order rate constants at several [KCAR]₀ and fixed chromic acid concentration. The values of k_{obs} were calculated by the least-square method and are summarized in Table 1. The order with respect to kappa-carrageenan concentration was determined from the well-known relationship; $k_{\text{obs}} = [C]^n$ and was found to be of fractional-second-order (1.76 ± 0.05). Furthermore, when the reciprocal of the observed first-order rate constants, $(k_{\text{obs}})^{-1}$, were plotted against the $[\text{KCAR}]^2$, straight lines with positive intercepts on the $(k_{\text{obs}})^{-1}$ axis were observed. This behaviour obeys Michaelis–Menten kinetics for the formation of 1:2 complex between chromic acid and KCAR reactants. A typical plot is shown in Fig. 2.

3.3. Dependence of reaction rate on $[H^+]$

To clarify the influence of $[H^+]$ on the rate of reaction and to elucidate the reaction mechanism, kinetic measurements were performed in HClO_4 – NaClO_4 solutions of different $[H^+]$ and constants of ionic strength and temperature. An increase in acid concentration was found to accelerate the reaction rate. The hydrogen ion dependency of the rate constants was found to be complicated. The reaction order with respect to $[H^+]$ was found to be of fractional-fourth-order 3.5 ± 0.3 ($\log k_{\text{obs}} - \log [H^+]$ plot).

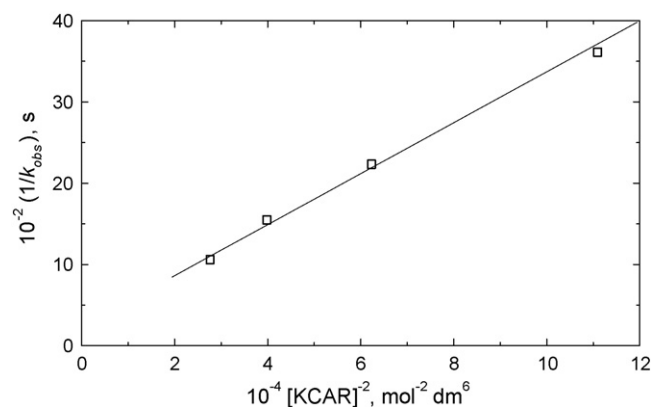


Fig. 2. A reciprocal Michaelis–Menten plot for the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , $[H^+] = 2.0$ and $I = 4.0 \text{ mol dm}^{-3}$ at 20°C .

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