



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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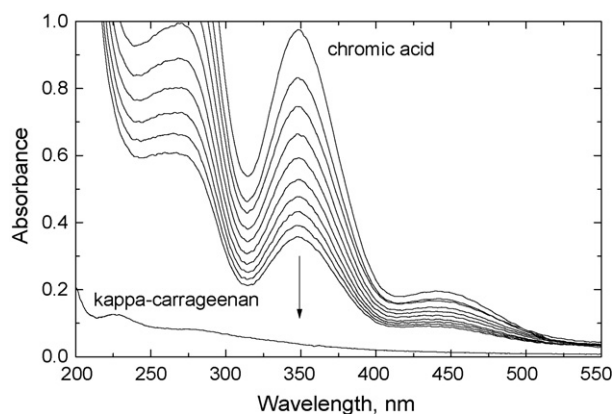


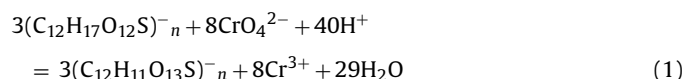
Fig. 1. Spectral changes (200–550 nm) in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , [KCAR] = 4×10^{-3} , $[H^+] = 2.0$ and $I = 4.0 \text{ mol dm}^{-3}$ at 20°C . Scanning time intervals = 4 min.

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).

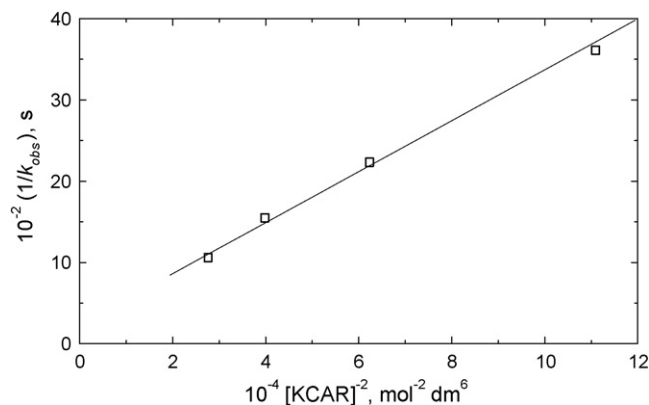


Fig. 2. A reciprocal Michaelis–Menten plot for the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , $[H^+] = 2.0$ and $I = 4.0 \text{ mol dm}^{-3}$ at 20°C .

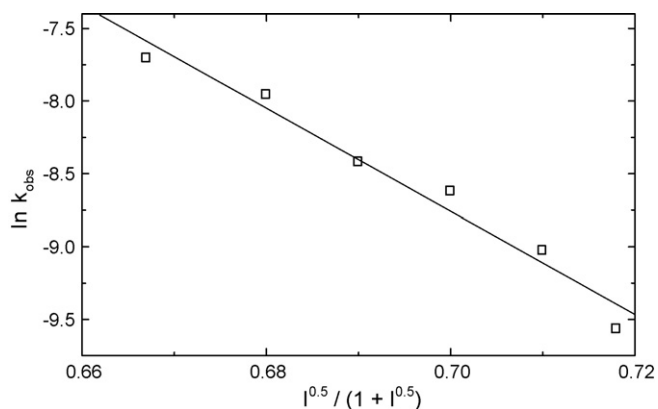


Fig. 3. Dependence of pseudo-first-order rate constant on the ionic strength in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , [KCAR] = 4×10^{-3} and $[H^+] = 2.0 \text{ mol dm}^{-3}$ at 20°C .

3.4. Dependence of reaction rate on ionic strength

To shed some lights on the reactive ionic species in the rate-determining step, kinetic runs were performed at constant $[H^+] = 2.0 \text{ mol dm}^{-3}$ as the NaClO_4 concentration was increased to 6.0 mol dm^{-3} . The values of k_{obs} were found to decrease with increasing the ionic strength. A plot of $\ln k_{\text{obs}}$ against $I^{0.5}/(1 + I^{0.5})$ according to extended Bronsted–Debye–Hückel equation was found to be linear with negative slope (Fig. 3). However, the present measurements, of necessity lie far outside the Bronsted–Debye–Hückel region, covering a range over which the activity coefficients of many electrolytes are known to be fairly dependent on ionic strength. The ionic strength dependence is qualitatively as expected when considering the charges involved [19].

3.5. Dependence of reaction rate on temperature

In order to evaluate the kinetic parameters, kinetic runs were performed at various temperatures and constants of $[H^+]$ and ionic strength. The experimental results were found to fit the Arrhenius and Eyring equations from whose slopes and intercepts the kinetic parameters were evaluated.

3.6. 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), an appreciable white precipitate was observed. Blank experiments from which either chromic acid or KCAR were excluded gave no detectable polymerization during this time. This result indicates that the present oxidation reaction proceeds via free-radical mechanism.

The lack of polymerization observed in chromic acid oxidation of poly(vinyl alcohol) [12] may be attributed to the relative low reactivity and the short lifetime of the radical intermediate involved in that redox system. Therefore, the above reaction was reinvestigated under the same experimental conditions of the present work; a white precipitate was obtained confirming the free-radical mechanism.

4. Discussion

The variety of species of chromium(VI) in acid solution, the presumed passage of chromium through transient unstable species of oxidation numbers (V) and (IV), and the formation of varieties of complexes of chromium(III) all combine to give systems of considerable complexity [20]. Consequently, mechanistic inter-

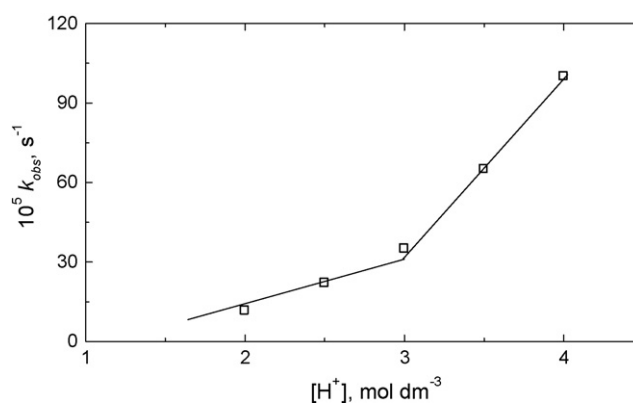


Fig. 4. A plot of $[H^+]$ vs. k_{obs} in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , [KCAR] = 4×10^{-3} and $I = 4.0 \text{ mol dm}^{-3}$ at 20°C .

est of chromium(VI) oxidation began with the inception of chemical kinetics as a tool for studies of mechanism. The hydrogen ion dependence of the rate constant seems to be of complexity. Plots of k_{obs} vs. $[H^+]^n$ ($n = 2, 3$) were fairly linear, but negative intercepts on k_{obs} axis were obtained which clearly have no meaning. Again, when the values of k_{obs} were plotted against $[H^+]$, the rate constant was found to be decreased dramatically below $[H^+] < 3.0 \text{ mol dm}^{-3}$ to give k_{obs} equals approximately zero at $[H^+] \rightarrow 0$ values. A typical plot is shown in Fig. 4.

Therefore, the following equation was suggested in order to fit the kinetic data of the present work (with $n = 4$):

$$k_{\text{obs}} = \frac{a[H^+]^n}{1 + b[H^+]} \quad (2)$$

where a and b are constants. On rearrangement of Eq. (2), the following relationship is obtained:

$$\frac{[H^+]^3}{k_{\text{obs}}} = \frac{1}{a[H^+]} + \frac{b}{a} \quad (3)$$

Eq. (3) requires that plots of $[H^+]^3/k_{\text{obs}}$ vs. $1/[H^+]$ to be linear with positive intercept on $[H^+]^3/k_{\text{obs}}$ axis as is experimentally observed.

Considering the values of protolytic and hydrolytic equilibrium constants for chromium(VI) perchlorate in aqueous solutions [8], one should assume that the main chromium(VI) ions are HCrO_4^- since the quantity of the dimeric form under our experimental conditions is negligible small.

It is not surprising that the reaction rate increases with increasing $[H^+]$ since the net reaction of transformation of oxyanion HCrO_4^- from tetrahedral form to the octahedral configuration in the hydrated cation $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, in acidic solution, consumes hydrogen ions. In view of these interpretations and the experimental observations of both ionic strength and hydrogen ion dependences of the rate constants, the protonated species of the reactants may be considered to be the more reactive species which play the main role in the reaction kinetics. Hence, the influence of the hydrogen ion concentration on the reaction rate acceleration can be explained on the basis of the substrate protonation in acidic medium [16] according to the following equilibria:



where S and SH^+ represent KCAR and its protonated form; while K_1 is the protonation constant of KCAR.

In redox reactions involving chromium(VI) as an oxidant, two reaction mechanisms for electron transfer may be suggested [20,21]. The first one corresponds to successive one-electron-

transfer mechanism:



The second mechanism represents to a simultaneous two-electron changes in a single step:

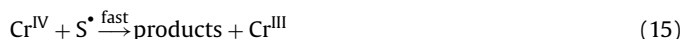


Therefore, chromium(VI) oxidation provide interesting prospects to chemists studying mechanisms. Hence, the most reasonable reaction mechanism which may be suggested, involves a fast complexation between the substrate and the oxidant to give C_1 intermediate which picks up another substrate molecule giving the intermediate C_2 . This intermediate (C_2) decomposes in the rate-determining step to give free-radical substrate with subtraction of H_3O^+ ion as initial oxidation products:



Again, obeying the substrate-dependence of the rate constant to Michaelis–Menten kinetics (Fig. 2) with the formation of 1:2 intermediate complex between chromic acid and KCAR reactants may support this suggestion.

Then, the formed radical is fastly oxidized by either new oxidant molecule or the Cr^{IV} formed to give rise to the reaction products as described by the following equations:



The change of the rate constant with the change in hydrogen ion and substrate concentrations can be expressed by the following rate-equation:

$$\text{Rate} = \frac{-d[\text{HCrO}_4^-]}{dt} = \frac{k_a K_1^2 K_2 K_3 [\text{H}^+]^4 [\text{S}]_T^2 [\text{HCrO}_4^-]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 [\text{HCrO}_4^-] (1 + K_1 K_3 [\text{H}^+] [\text{S}])} \quad (18)$$

where $[\text{S}]_T$ is the analytical total concentration of KCAR. In presence of a large excess of the substrate over that of HCrO_4^- concentration, the rate-law expression is as defined by the following equation:

$$\text{Rate} = \frac{-d[\text{HCrO}_4^-]}{dt} = k_{\text{obs}} [\text{HCrO}_4^-] \quad (19)$$

Comparing Eqs. (18) and (19) and rearrangement, one concludes that²:

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K_1 [\text{H}^+]}{k_a K_1^2 K_2 K_3 [\text{H}^+]^4} \right) \frac{1}{[\text{S}]_T^2} + K' \quad (20)$$

² $K' = \frac{(1 + K_1 K_3 [\text{H}^+] [\text{S}])}{k_a K_1 K_3 [\text{H}^+]^2 [\text{S}]_T^2}$.

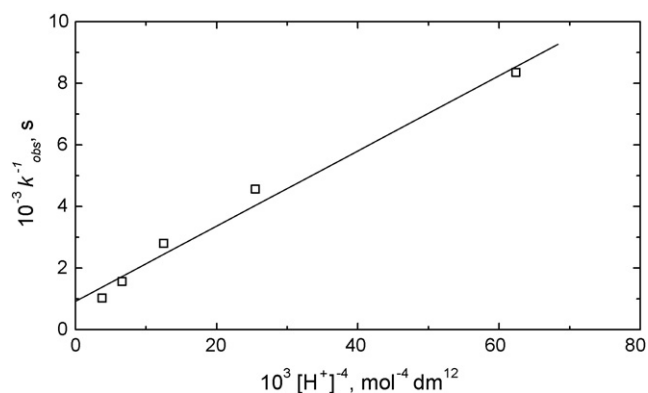


Fig. 5. Plots of $1/k_{\text{obs}}$ vs. $1/[\text{H}^+]^4$ in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: $[\text{chromic acid}] = 7.5 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$ and $I = 4.0 \text{ mol dm}^{-3}$ at 20°C .

Eq. (20) requires that, at constant $[\text{H}^+]$, plots of $(k_{\text{obs}})^{-1}$ against $1/[\text{S}]_T^2$ to be linear with positive intercepts on $(k_{\text{obs}})^{-1}$ axis. The experimental results satisfied this requirement as shown in Michaelis–Menten plot (Fig. 2) indicating the formation of 1:2 intermediate complex between the substrate and the oxidant prior to the rate-determining step. Again, plots of $(k_{\text{obs}})^{-1}$ against $1/[\text{H}^+]^4$ at constant $[\text{S}]$ gave good straight lines with positive intercepts on $1/[\text{H}^+]^4$ as shown in Fig. 5. The small intercept observed in Fig. 2 may lead us to simplify Eq. (20) to the following equation:

$$\frac{[\text{S}]^2 [\text{H}^+]^3}{k_{\text{obs}}} = \left(\frac{[\text{H}^+]^{-1}}{k'_a} + \frac{1}{k''_a} \right) \quad (21)$$

where $k'_a = k_1 K_1^2 K_2 K_3$ and $k''_a = k_1 K_1 K_2 K_3$, respectively. According to Eq. (22), plots of $[\text{S}]^2 [\text{H}^+]^3 / k_{\text{obs}}$ vs. $1/[\text{H}^+]$ gave good straight lines with positive intercepts on $[\text{S}]^2 [\text{H}^+]^3 / k_{\text{obs}}$ axis (Fig. 6), from whose slopes and intercepts the values of the apparent rate constants, k'_a and k''_a , and the protonation constant, K_1 , can be evaluated. These values were calculated by least-square method and are summarized in Table 2.

Unfortunately, the values of the rate constants of the elementary reaction k_a could not be evaluated because of the non-availability of the formation constants (K_2 and K_3) at different temperatures. Therefore, the apparent rate constants (k'_a and k''_a) are considered to be composite quantities of the rate constants, the protonation constants and the formation constants, respectively.

In view of the foregoing experimental observations and the kinetic interpretations, two possible reaction mechanisms for electron transfer may be suggested. The first one corresponds to an

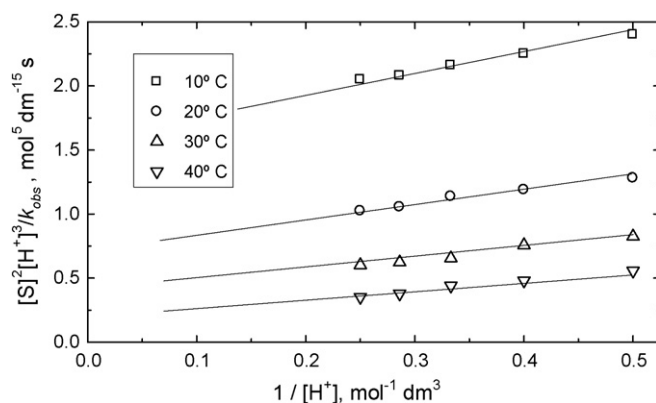
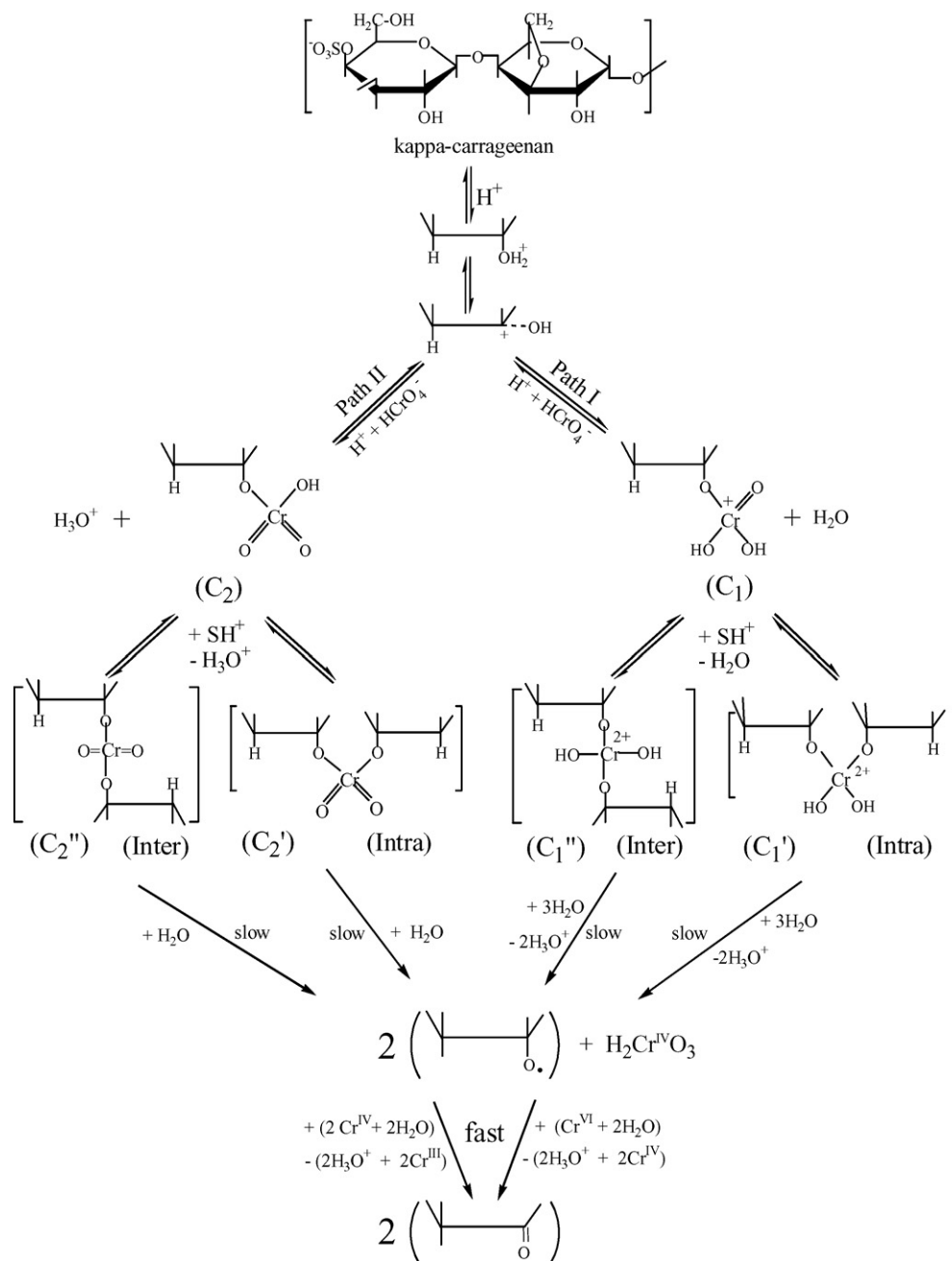


Fig. 6. Plots of $[\text{S}]^2 [\text{H}^+]^3 / k_{\text{obs}}$ vs. $1/[\text{H}^+]$ in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: $[\text{chromic acid}] = 7.5 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$ and $I = 4.0 \text{ mol dm}^{-3}$ at various temperatures.



Scheme 1.

Table 2

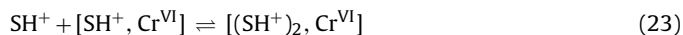
Values of the second-order rate constant (k'), the apparent rate constants (k'_a and k''_a) and the protonation constant (K_1) in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , [KCAR] = 4×10^{-3} and $I = 4.0 \text{ mol dm}^{-3}$.

Constant	Temperature (°C)			
	10	20	30	40
$10^2 k'$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) ^a	1.32	2.50	3.88	5.75
k'_a ($\text{dm}^{18} \text{ mol}^{-6} \text{ s}^{-1}$)	0.89	0.97	1.05	1.17
k''_a ($\text{dm}^{15} \text{ mol}^{-5} \text{ s}^{-1}$)	0.57	1.29	2.80	7.04
K_1 ($\text{dm}^3 \text{ mol}^{-1}$)	1.57	0.75	0.38	0.17

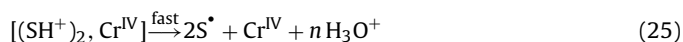
Experimental error $\pm 3\%$.

^a Calculated at $[\text{H}^+] = 2.0 \text{ mol dm}^{-3}$.

outer-sphere mechanism in which the transfer of electrons occurs prior to the protons release. It involves the formation of an outer ion pair:

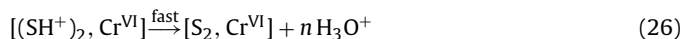
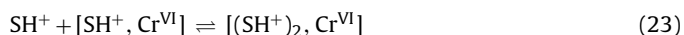
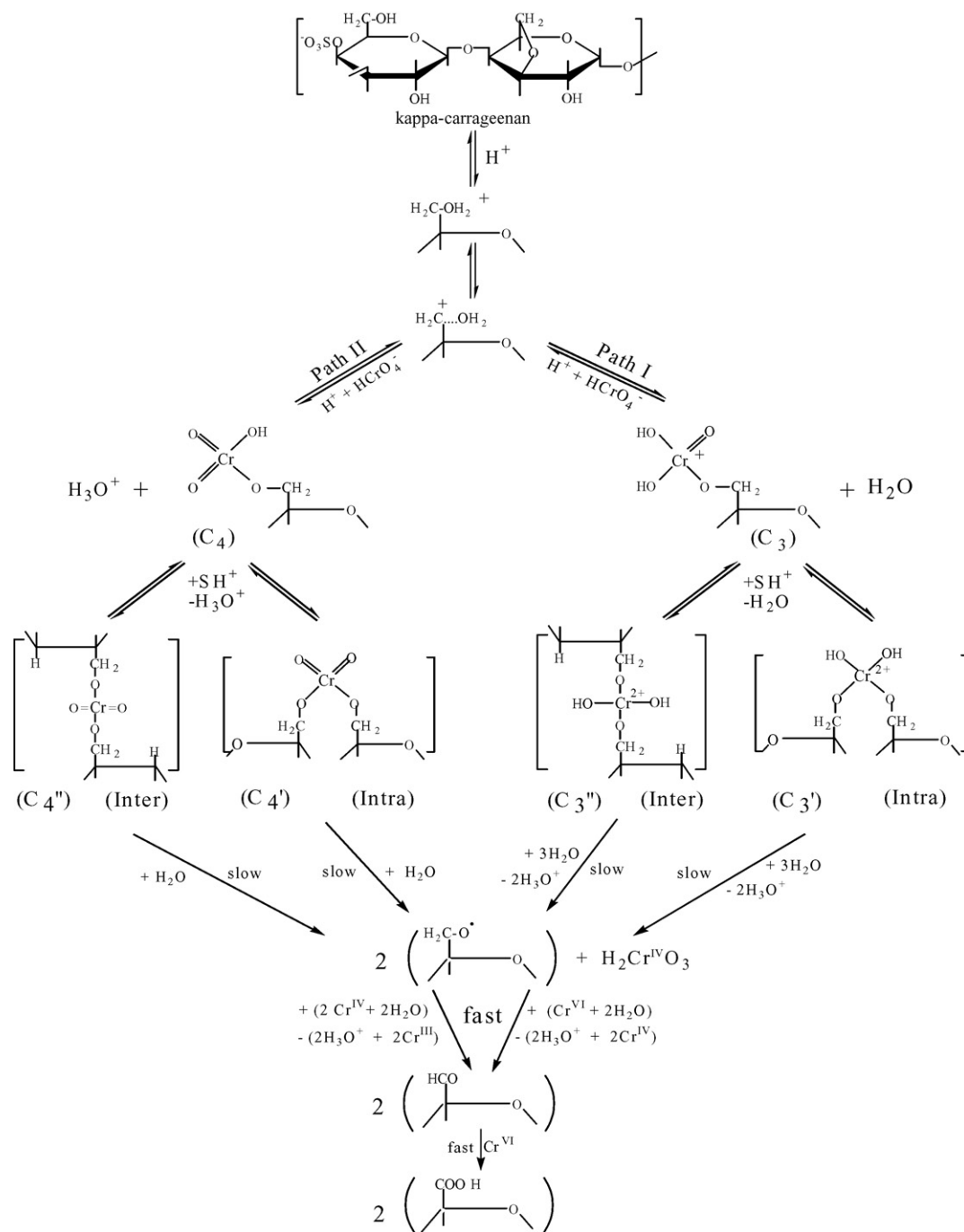


followed by electron transfer process in the rate-determining step:



In the second mechanism, the release of protons precedes the electron-transfer process which corresponds to inner-sphere type as follows:





The former mechanism seems unlikely to account for the present investigation from both thermodynamic and mechanistic points of views since the oxidation reaction was found to proceed via formation of an intermediate complex through free radical mechanism.

The kinetic parameters of the apparent rate constants (k_a and k_a'') were calculated from the temperature dependence of the rate constants by the method of least-squares and are summarized in Table 3. Again, the thermodynamic parameters of the protonation constants are summarized in Table 4. The values of the protona-

tion constants obtained were found to be in good agreement with the same order of magnitude to that obtained for poly(vinyl alcohol) macromolecule when oxidized by chromic acid [12]. This result may be considered as an indirect evidence to support the proposed mechanism.

Stewart [22] and Hassan [23] reported that the entropy of activation, ΔS^\ddagger , is negative for oxidation reactions proceed via complex formation of an inner-sphere nature, which the ΔS^\ddagger values for outer-sphere mechanism tend to be more positive. This suggestion is in good agreement with the observed negative values of ΔS^\ddagger in the present investigation. The value of ΔS^\ddagger obtained may confirm the compactness of the intermediates and it is characterized to one-electron transfer mechanism of inner-sphere nature.

Table 3
Activation parameters of k' , k'_a and k''_a in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , [KCAR] = 4×10^{-3} $l = 4.0 \text{ mol dm}^{-3}$.

Rate constant	Parameter				
	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	E_a^\ddagger (kJ mol ⁻¹)	A (mol ⁻¹ s ⁻¹)
k'^a	33.04	-163.29	81.69	35.85	7.95×10^4
k'_a	4.13	-230.90	72.94	6.60	0.15×10^2
k''_a	58.77	-41.85	71.24	59.86	6.42×10^{10}

Experimental error $\pm 4\%$.

^a Calculated at $[H^+] = 2.0 \text{ mol dm}^{-3}$.

Table 4
Thermodynamic parameters of the protonation constant (K_1) in the oxidation of kappa-carrageenan by chromic acid in aqueous perchloric acid: [chromic acid] = 7.5×10^{-4} , [KCAR] = 4×10^{-3} and $l = 4.0 \text{ mol dm}^{-3}$.

Parameter		
ΔH° (J mol ⁻¹ K ⁻¹)	ΔS°_{293} (J mol ⁻¹ K ⁻¹)	ΔG°_{293} (kJ mol ⁻¹)
-54.62	-184.03	+0.7

Experimental error $\pm 4\%$.

Again, the positive ΔG^\ddagger may confirm the non-spontaneity of complex formation in the rate-determining step, as suggested by the proposed mechanism. Moreover, the protonation values obtained at various temperatures indicated that the prolytic process of carrageenan is an exothermic process.

In view of these arguments and the experimental observations, the oxidation of KCAR by chromic acid can be illustrated by Schemes 1 and 2. Scheme 1 represents the oxidation of secondary alcohols to the corresponding ketone, whereas Scheme 2 refers to the oxidation of primary alcohols to carboxylic acid, respectively.

The hydrogen ion dependence of the rate constant in addition to the high order observed in $[H^+]$ indicated a fast protonation of both the oxidant and substrate. The smaller activation energies observed support that the reaction takes place between ions of different charges or an ion and a neutral molecule. Therefore, the electrostatic attraction between the reactants does not need much energy to bring them together in order to form the activated complex. The protonated substrate is firstly attacked by chromic acid to form the intermediate complex (C_1) which picks up another substrate molecule to give the (C'_2 or C''_2) intermediate complex. Then, the formed intermediate complex decomposes in the rate-determining step to give the initial oxidation products as free radical substrate and Cr^{IV} ion. The substrate radical is further oxidized very fast by either chromic acid or Cr^{IV} oxidants to give rise to the product. The formation of such intermediate complexes has been postulated in

oxidation of some organic substrates containing alcoholic groups by this oxidant [24,25].

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