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Research Article

Kinetics and Mechanistic Aspects of Oxidation of Iota- And Lambda-carrageenans by Chromium(VI) in Aqueous Perchlorate Solutions

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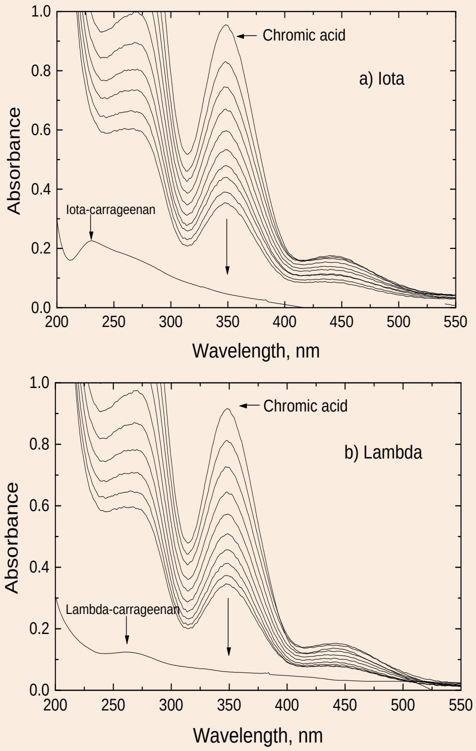
Abstract

The kinetics of chromium(VI) oxidations of iota- and lambda-carrageenans biopolymers have been investigated in aqueous perchlorate solutions at a constant ionic strength of 4.0 mol dm^{-3} and a temperature of 35 °C. The progress of the reactions was followed spectrophotometrically. The reactions showed a first-order dependence in $[Cr^{VI}]$ and fractional-second order kinetics with respect to the concentrations of carrageenans. The influence of hydrogen ion concentration on the oxidation rates showed that the oxidation processes were acid-catalyzed. Increasing ionic strength of the reactions decreased the rates. Kinetic evidence for the formation of 1:2 complexes between chromium(VI) and carrageenans were revealed. The activation parameters of the rate constants along with thermodynamic parameters of the equilibrium constants were computed and discussed. A plausible oxidation mechanism consistent with the kinetic results has been suggested. An isokinetic relationship for some redox reactions involving chromium(VI) as an oxidant was examined. The tendency for formation of coordination polymer complexes between the formed biopolymer precursor chelating agents and some metal cations was investigated.

Keywords*:* Carrageenans, biopolymers, kinetics, chromium(VI), oxidation



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Introduction

Carbohydrates are organic compounds which are regarded as one of the important natural products. The study of carbohydrates is one of the most exciting fields of organic chemistry [1]. Carbohydrates perform numerous roles in living organisms and are also sources of energy for vital metabolic processes [2,3]. The biological and economical importance of carbohydrates is due to their reactivities and their biochemical and physiological properties. Oxidation of carbohydrates is considered as a significant way in which new compounds and materials with interesting properties can be provided [4] and employed as input materials for various chemical industries.

Carrageenans (CAR) are water-soluble polysaccharides extracted from seaweeds [5]. They are regarded as the most important hydrocolloids in the world which have a large list of industrial applications. Carrageenans are valuable gelling agents employed in food applications to improve food texture, gelation, stability and viscosity.

Secondary advantage includes improved palatability and appearance. They are used in both milk and water systems. In medical and pharmaceutical uses, a discovery is that carrageenans even in very great dilution act as an anticoagulant of blood. Despite the potential applications of different types of carrageenans biopolymers in various fields, these biopolymers are frequently subjected to the action of oxidizing agents and their activities depend largely in their redox behavior [6]. Scanning the literature showed a lack of information as to the kinetic studies on the oxidation of such important macromolecules [7-13] which may be resulting from the complexity of their reaction kinetics and mechanistic studies since they contain both primary and secondary alcoholic groups in their macromolecular chains.

Carbohydrates may play an important role in the chemistry of chromium, especially in the environment because of its mutagenic and carcinogenic activity [14,15]. Chromium(VI) is one of the most versatile available oxidizing agents for oxidation of organic compounds. It can be reduced to lower oxidation states by various biological and chemical reductants [16]. Considerably interest has been shown in the chemistry of the intermediate oxidation states, Cr^{V} and Cr^{IV}, due to their observation during the oxidation of organic substrates by Cr^{VI} and implication in the mechanism of Cr-induced cancers [17-19]. Chromium in aqueous solutions exists in both trivalent, Cr^{III}, and hexavalent, Cr^{VI}, species. However, these two oxidation states are characterized by different physical/chemical behavior and toxicity. The compounds of chromium(VI) pose serious dangers to biological systems, whereas those of chromium(III) are relatively non-toxic [18]. Although, chromium(VI) has been extensively used for oxidation of inorganic [20-26] and organic compounds [27-35], a little attention has been focused on the oxidation of carbohydrate biopolymers by this oxidant [28,35]. This may be attributed to the existence of various species of chromium(VI) in acidic medium as well as the instability of Cr^{V} and Cr^{IV} states through the reduction of chromium ion from hexavalent to trivalent state which may not allow a mechanistic conclusion.

Owing to the above discussion, the present work seeks to study the kinetics of oxidation of iota- and lambda-carrageenans (ICAR & LCAR) as biopolymers containing multifunctional alcoholic groups by chromium(VI) in perchlorate solutions. The objectives of this study were to establish the optimum conditions affecting the oxidation of such biopolymers by chromium(VI), to explore the effect of structure of the substrate, and finally to elucidate a plausible oxidation mechanism.

Experimental

Materials

The chemicals used in the present study were reagent grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water. Stock solutions of iota- and lambda-carrageenans were prepared by stepwise addition of the samples (BDH) in double distilled water with rapid and continuous stirring to avoid formation of lumpy aggregates. A fresh solution of chromium(VI) was prepared and standardized spectrophotometrically before each experiment.

Kinetic Measurements

The reactants were formulated such that the reactions were of pseudo-first order kinetics where carrageenans (CAR) were added in a large excess relative to chromium(VI). The progress of the oxidation reactions was followed by tracing the decay in Cr^{VI} absorbance at $\lambda_{max} = 350$ nm, maximum absorption wavelength belonging to Cr^{VI}, whereas the other constituents of the reactions did not absorb significantly at this wavelength. A Shimadzu UV-2101/3101 double-beam spectrophotometer was used for all absorbance measurements.

First order plots of ln (absorbance) versus time were found to be linear up to more than two half-lives of the reactions and the pseudo-first order rate constants (k_{obs}) were evaluated as the gradients of such plots. Average values of at least two independent kinetic runs of the rate constants were taken for the analysis. The kinetic runs were reproducible to within ±4%.

The spectral changes during the oxidations of iota- and lambda-carrageenans biopolymers by chromium(VI) in aqueous perchlorate solutions are shown in Fig. 1(a,b). In both cases, the scanned spectra indicate gradual decay of Cr^{VI} band at its absorption maximum with time as a result of its reduction by the carrageenans substrates.

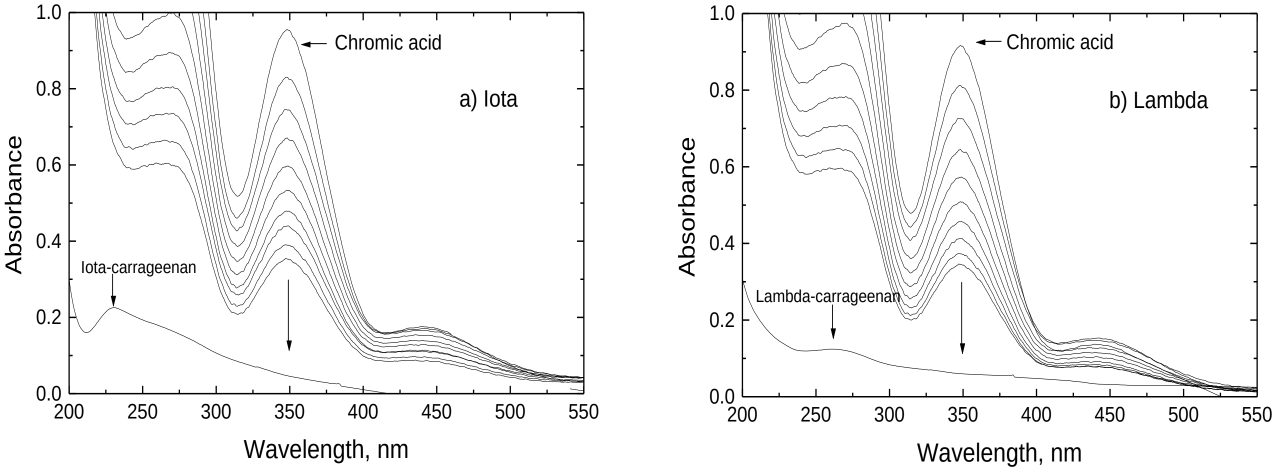


Figure 1 a, b Spectral changes during the oxidations of iota-and lambda-carrageenans by chromium(VI) in perchlorate solutions$[Cr^{VI}] = 7.5 \times 10^{-4}$, $[CAR] = 5.0 \times 10^{-3}$, $[H^+] = 3.0$ and $I = 4.0$ mol dm^{-3} at 35 °C; Scan time intervals = 5 min.

Results

Stoichiometry

Reaction mixtures containing different initial concentrations of the reactants with an excess of chromium(VI) in 2.0 mol dm^{-3} $HClO_4$ and at 4.0 mol dm^{-3} ionic strength, were equilibrated for about 48 h at room temperature. The unreacted chromium(VI) was estimated periodically until it reached a constant value, i.e. completion of the reactions. The ratios of $([Cr^{VI}]_{consumed} / [CAR])$ showed that the overall reactions conform to the following stoichiometric equations,

$$(C_{12}H_{16}O_{15}S_2^{2-})_n + 2CrO_4^{2-} + 10H^+ = (C_{12}H_{12}O_{16}S_2^{2-})_n + 2Cr^{3+} + 7H_2O \quad (1)$$

$$3(C_{12}H_{17}O_{19}S^{3-})_n + 8CrO_4^{2-} + 40H^+ = 3(C_{12}H_{11}O_{20}S^{3-})_n + 8Cr^{3+} + 29H_2O \quad (2)$$

where, $(C_{12}H_{16}O_{15}S_2^{2-})_n$ and $(C_{12}H_{17}O_{19}S_3^{3-})_n$ are iota- and lambda-carrageenans and $(C_{12}H_{12}O_{16}S_2^{2-})_n$ and $(C_{12}H_{11}O_{20}S_3^{3-})_n$ are the corresponding keto-acid oxidation derivatives, respectively. The reaction products were identified by spectral data and elemental analysis as described elsewhere [17-19]. The decay of the bands in the IR spectra at 3430 cm^{-1} as well as the disappearance of the bands at 1710 cm^{-1} suggests transformation of the secondary alcoholic groups (-OH) to its corresponding keto form (-C=O).

The formation of coordination polymeric complexes between the biopolymer precursor oxidation products as chelating agents and some metal cations has been examined. It was found that the oxidation products have a high tendency to chelate with Ba^{II}, Cd^{II}, Pb^{II} and Ag^I metal cations.

Reaction Orders

The reaction orders with respect to the reactants were determined using the plots of log k_C versus log (conc.) by varying the concentrations of the carrageenans substrates and perchloric acid, in turn, while keeping the others constant.

The oxidant, chromium(VI) was varied in the range of 1.0 to 10.0 x 10^{-4} mol dm^{-3} at constant concentrations of all other reagents. Plots of ln(absorbance) versus time were found to be linear for more than two half-lives of the reactions. This linearity indicated that the reactions are first order in chromium(VI) concentration. The first-order dependence was confirmed not only by the linearity of the first order plots, but also by the independence of the first order rate constants (k_{obs}) on the different initial concentrations of chromium(VI) as listed in Table 1.

The observed rate constants were determined at different initial concentrations of the carrageenans biopolymers keeping all other reactant concentrations constant. Plots of k_{obs} versus $[CAR]^2$ were found to be linear with positive intercepts on k_{obs} axes (Fig. 2) indicating that the reactions are fractional-second order with respect to [CAR].

The effect of pH on the oxidation rates was studied by varying the concentration of perchloric acid in the range of 2.0 - 4.0 mol dm^{-3} at constant [CAR], $[Cr^{VI}]$, ionic strength and temperature. An increase in acid concentration was found to accelerate the oxidation rates (Table 1) indicating that the oxidation process is acid-catalyzed. Plots of k_{obs} versus $[H^+]^4$ were found to be linear with positive intercepts on k_{obs} axes (Fig. 3) suggesting that the reactions are fractional-fourth order kinetics in $[H^+]$.

Dependence of Oxidation Rates on the Ionic Strength

The ionic strength of the reactions was varied from 4.0 to 5.6 mol dm^{-3} using sodium perchlorate as an inert electrolyte at constant concentrations of carrageenans and chromium(VI) and at constant pH and temperature. Increasing ionic strength was found to decrease the oxidation rates. Debye-Hückel plots were found to be linear with negative slopes as shown in Fig. 4.

Dependence of Oxidation Rates on Temperature

In order to evaluate the kinetic parameters, kinetic runs were performed at various temperatures and at constant other variables. It was found that raising temperature accelerates the oxidation rates. The obtained results were found to fit the Arrhenius and Erying equations, from whose slopes and intercepts, the kinetic parameters were evaluated and listed in Table 3.

Table 1 Effects of variation of $[Cr^{VI}]$, [CAR], $[H^+]$ and ionic strength (I) on the observed first order rate constant (k_{obs}) in the oxidations of iota- and lambda-carrageenans by chromium(VI) in perchlorate solutions at 35 °C

10^4 $[Cr^{VI}]$ (mol dm^{-3})	10^3 [CAR] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	I (mol dm^{-3})	10^5 k_{obs} (s^{-1})	
				Iota	**Lambda**
1.0	4.0	3.0	4.0	15.4	19.2
3.0	4.0	3.0	4.0	16.2	19.5
5.0	4.0	3.0	4.0	15.9	20.7
7.0	4.0	3.0	4.0	16.1	19.3
10.0	4.0	3.0	4.0	17.3	18.5
5.0	**2.0**	3.0	4.0	5.2	7.1
5.0	**4.0**	3.0	4.0	16.1	19.3
5.0	**6.0**	3.0	4.0	28.9	39.2
5.0	**8.0**	3.0	4.0	50.1	59.9
5.0	**10.0**	3.0	4.0	74.8	90.3
5.0	4.0	**2.0**	4.0	3.9	5.1
5.0	4.0	**2.5**	4.0	8.3	10.4
5.0	4.0	**3.0**	4.0	16.1	19.3
5.0	4.0	**3.5**	4.0	28.0	31.5
5.0	4.0	**4.0**	4.0	41.8	49.7
5.0	4.0	3.0	**4.0**	16.1	19.3
5.0	4.0	3.0	**4.2**	14.8	17.7
5.0	4.0	3.0	**4.5**	13.3	15.7
5.0	4.0	3.0	**4.7**	11.7	14.2
5.0	4.0	3.0	**5.0**	10.4	12.9

Experimental error ± 4%

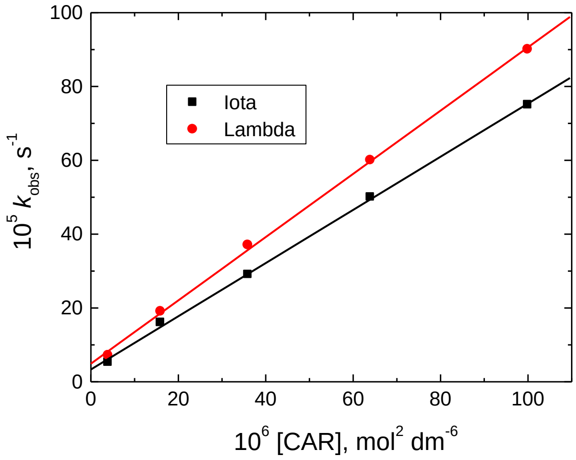


Figure 2 Plots of k_{obs} versus $[CAR]^2$ in the oxidations of iota-and lambda-carrageenans by chromium(VI) in perchlorate solutions. $[Cr^{VI}] = 7.0 \times 10^{-4}$, $[H^+] = 3.0$ and $I = 4.0$ mol dm^{-3} at 35 °C.

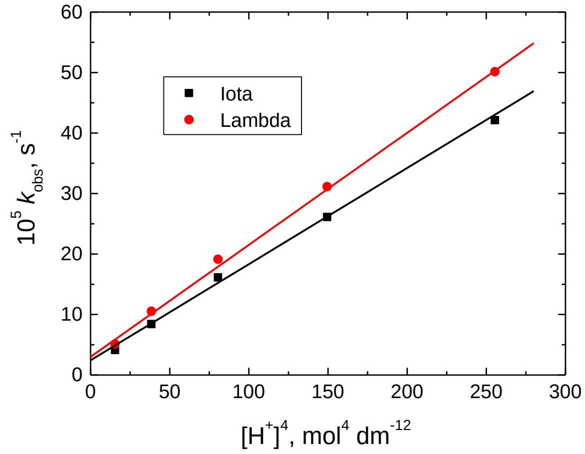


Figure 3 Plots of k_{obs} versus $[H^+]^4$ in the oxidations of iota-and lambda-carrageenans by chromium(VI) in perchlorate solutions. $[Cr^{VI}] = 7.0 \times 10^{-4}$, $[CAR] = 4.0 \times 10^{-3}$ and $I = 4.0$ mol dm^{-3} at 35 °C.

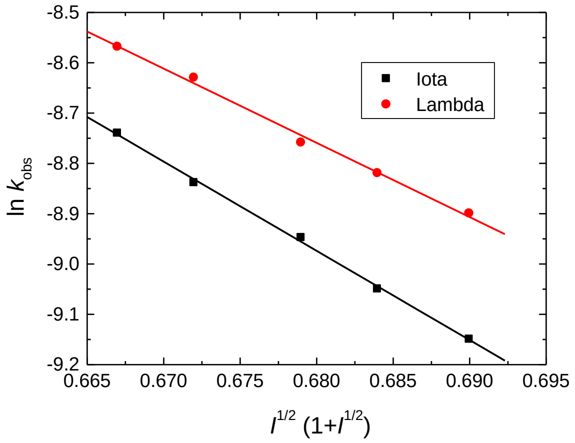


Figure 4 Debye-Huckel plots in the oxidations of iota- and lambda-carrageenans by chromium(VI) in perchlorate solutions. $[Cr^{VI}] = 7.0 \times 10^{-4}$, $[CAR] = 4.0 \times 10^{-3}$ and $[H^+] = 3.0$ mol dm^{-3} at 35 °C.

Discussion

It is reported [36,37] that aqueous solutions of chromium(VI) contain ions such as CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$, besides other protonated species such as H_2CrO_4, $HCr_2O_7^-$ and $H_2Cr_2O_7$. Based on the values of protolytic and hydrolytic equilibrium constants for chromium(VI) species in aqueous perchlorate solutions [38-40], the main chromium(VI) species is $HCrO_4^-$ since the quantity of the dimeric forms is negligibly small under the present experimental conditions. On the other hand, the observed acceleration of the oxidation rates with increasing hydrogen ion concentration in addition to the high order with respect to $[H^+]$ suggesting fast protonation of carrageenans prior to the rate-determining step leading to more reactive species ($HCAR^+$) [6,8,9,12]. The present reactions between carrageenans and chromium(VI) in perchlorate solutions exhibited a first order dependence on $[Cr^{VI}]$ and fractional-second order kinetics with respect to [CAR]. The fractional-second order dependence on carrageenan concentration suggests formation of 1:2 intermediate complexes between chromium(VI) and carrageenans prior to the rate-determining step. Also, the linearity of the plots between $1/k_{obs}$ and $1/[CAR]^2$, Fig. 4, is considered as a kinetic evidence in favor of possible formation of such complexes between oxidant and substrates similar to the well-known Michaelis-Menten mechanism [41] for enzyme-substrate reactions. Furthermore, the observed decrease in the oxidation rates with increasing ionic strength indicates that the oxidation reactions occur between ions of opposite charges, i,e. between $HCAR^+$ and $HCrO_4^-$ [42].

In view of the above discussion, the suggested mechanism involves complex formation between the kinetically active species of both substrate ($CARH^+$) and oxidant ($HCrO_4^-$) to give intermediate complex (C_1). The formed complex attacks another protonated substrate to give a 1:2 intermediate complex (C_2). The latter decomposes in the rate-determining step leading to generation of free radical derived from carrageenan substrate which is rapidly oxidized again by either new oxidant species (Cr^{VI}) or by the formed Cr^{IV} to give rise to the final reaction products. The formation of such intermediate complexes has been postulated in the oxidations of some organic substrates containing alcoholic groups by this oxidant [43,44]. The proposed mechanism is illustrated in Schemes 1 and 2. Scheme 1 shows the oxidation of secondary alcoholic groups in the carrageenans substrates to the corresponding ketones, whereas Scheme 2 refers to the oxidation of primary alcoholic groups to carboxylate groups.

The relationship between the oxidation rate and substrate, hydrogen ion and oxidant concentrations can be expressed by the following rate-law,

$$\text{Rate} = \frac{-d[\mathrm{Cr}^{\mathrm{VI}}]}{dt} = \frac{kK_1^2K_2K_3[\mathrm{CAR}]^2[\mathrm{H}^+]^4[\mathrm{Cr}^{\mathrm{VI}}]}{1+K_1[\mathrm{H}^+]+K_1K_2[\mathrm{H}^+][\mathrm{Cr}^{\mathrm{VI}}](1+K_1K_2[\mathrm{CAR}][\mathrm{H}^+])} \tag{3}$$

Under pseudo-first order conditions, the rate-law expression can be written as follows,

$$\text{Rate} = \frac{-d[\mathrm{Cr}^{\mathrm{VI}}]}{dt} = k_{\mathrm{obs}}[\mathrm{Cr}^{\mathrm{VI}}] \tag{4}$$

Comparing equations (3) and (4) and rearrangement leads to the following relationship,

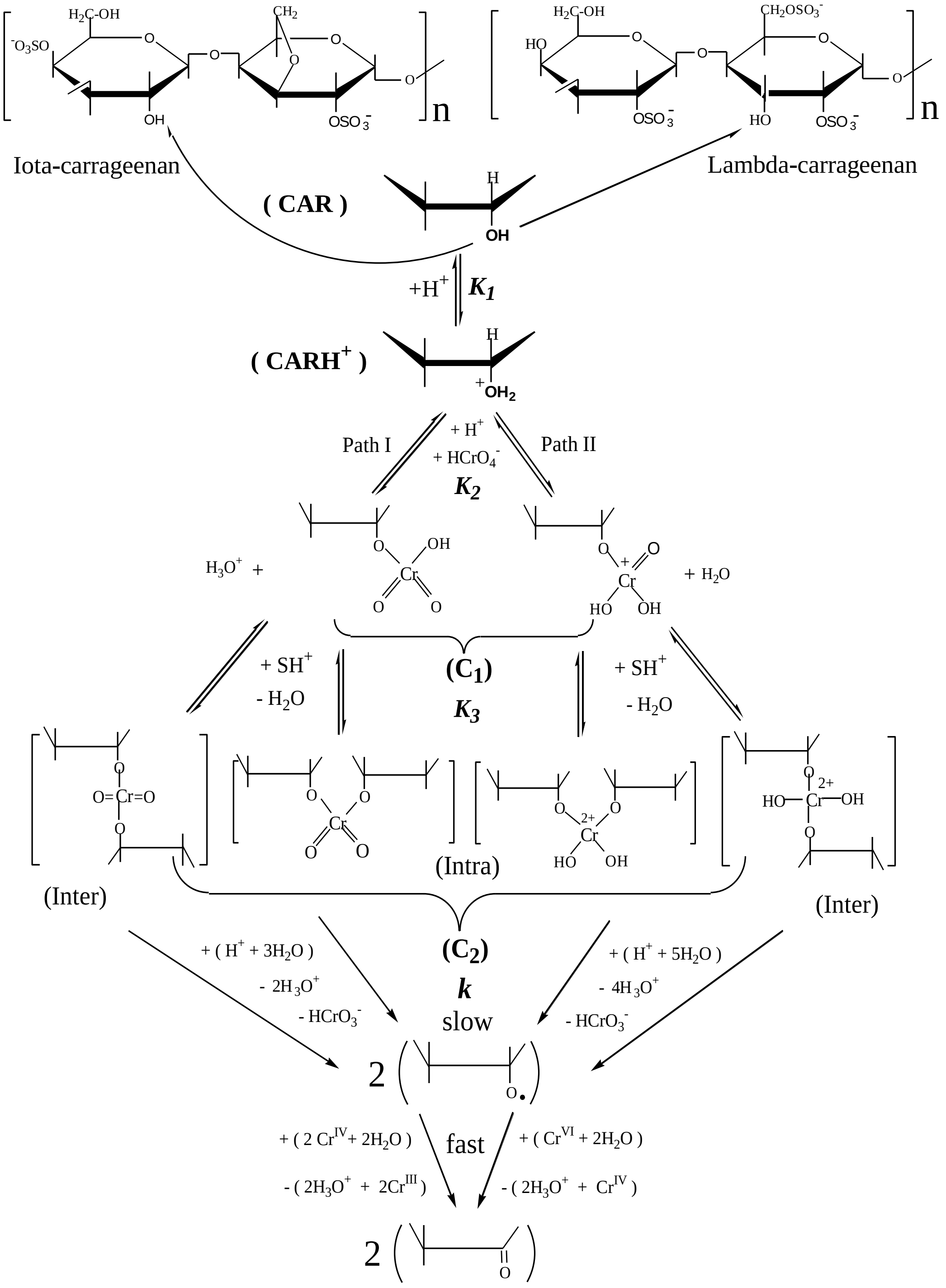
$$\frac{1}{k_{obs}} = \left(\frac{1+K_1[\mathrm{H}^+]}{kK_1^2K_2K_3[\mathrm{H}^+]^4}\right)\frac{1}{[\mathrm{CAR}]^2} + K \tag{5}$$

where $K = [Cr^{VI}](1 + K_1K_2[CAR][H^+]) / kK_1K_3[CAR]^2[H^+]^3$.

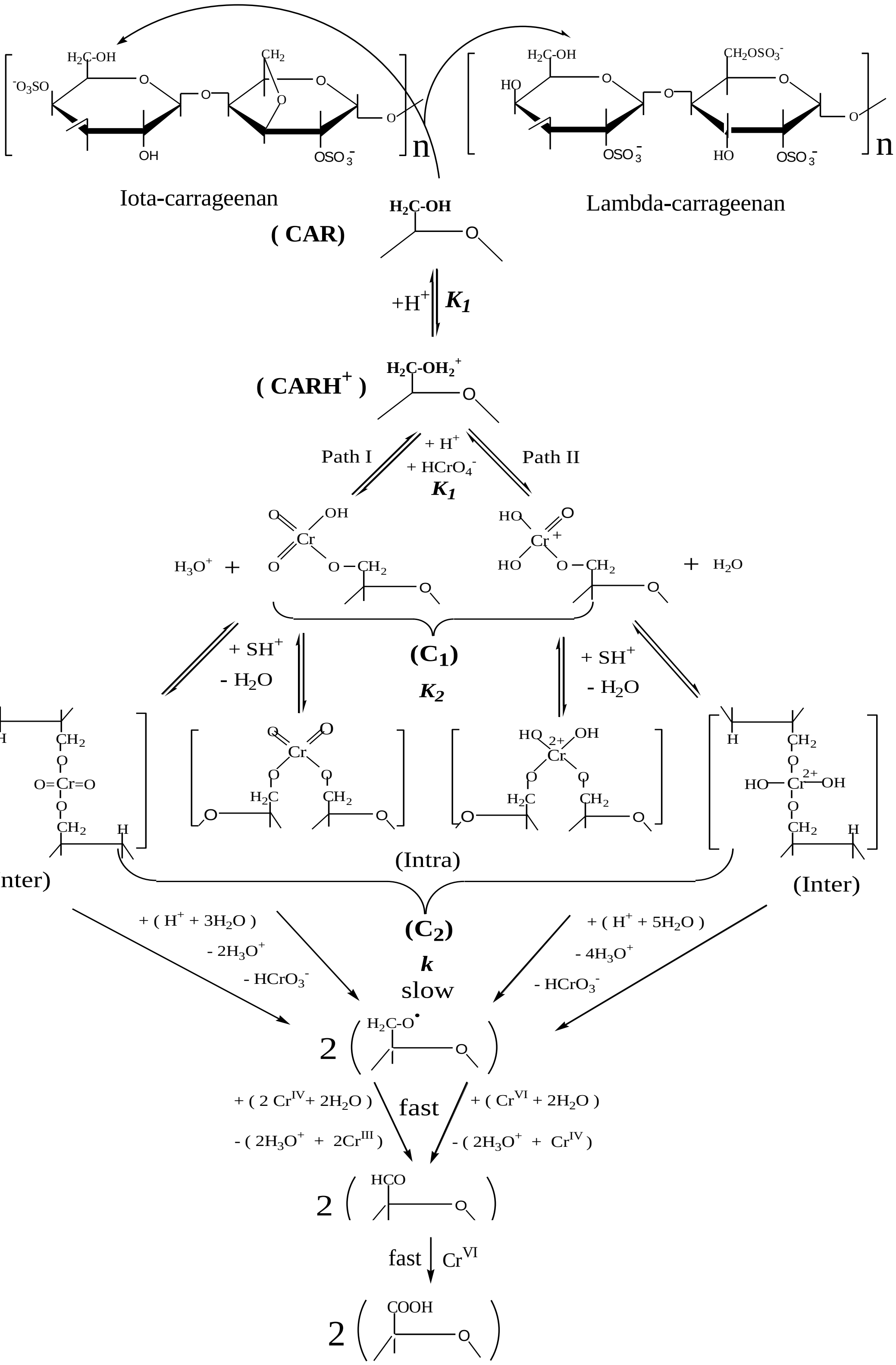
Equation (5) requires that at constant $[H^+]$, plots of $1/k_{obs}$ versus $1/[CAR]^2$ to be linear with positive intercepts on $1/k_{obs}$ axes as were experimentally obtained (Fig. 5). Again, plots of $1/k_{obs}$ versus $1/[H^+]^4$ at constant [CAR] gave good straight lines with positive intercepts on $1/k_{obs}$ axes (Figure not shown). The small intercepts observed in Fig. 5 may lead us to simplify Eq. (5) to Eq. (6),

$$\frac{[\mathrm{CAR}]^2[\mathrm{H}^+]^3}{k_{obs}} = \frac{1}{k'}\frac{1}{[\mathrm{H}^+]} + \frac{1}{k''} \tag{6}$$

where, $k' = kK_1^2K_2K_3$ and $k'' = kK_1K_2K_3$, respectively. According to Eq. (6), plots of $[CAR]^2[H^+]^3/k_{obs}$ versus $1/[H^+]$ gave good straight lines with positive intercepts on $[CAR]^2[H^+]^3/k_{obs}$ axes, Fig. 6(a,b), from whose slopes and intercepts the values of the apparent rate constants, *k*' and *k*", and the protonation constants, K_1, were calculated by the least-squares method and are listed in Table 2. The obtained values of the protonation constants were found to be in good agreement and with the same order of magnitude to that obtained earlier for other biopolymers oxidized by chromium(VI) [6,8,10]. This result may be considered as indirect evidence to support the proposed oxidation mechanism.



Scheme 1 Mechanism of oxidations of the secondary alcoholic groups in iota- and lambda-carrageenans by chromium(VI) in perchlorate solutions



Scheme 2 Mechanism of oxidations of the primary alcoholic groups in iota- and lambda-carrageenans by chromium(VI) in perchlorate solutions

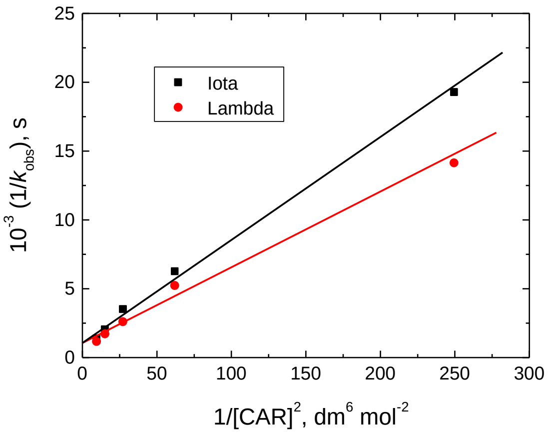


Figure 5 Plots of $1/k_{obs}$ versus $1/[CAR]^2$ in the oxidations of iota- and lambda-carrageenans by chromium(VI) in perchlorate solutions. $[Cr^{VI}] = 7.0 \times 10^{-4}$, $[H^+] = 3.0$ and $I = 4.0$ mol dm^{-3}.

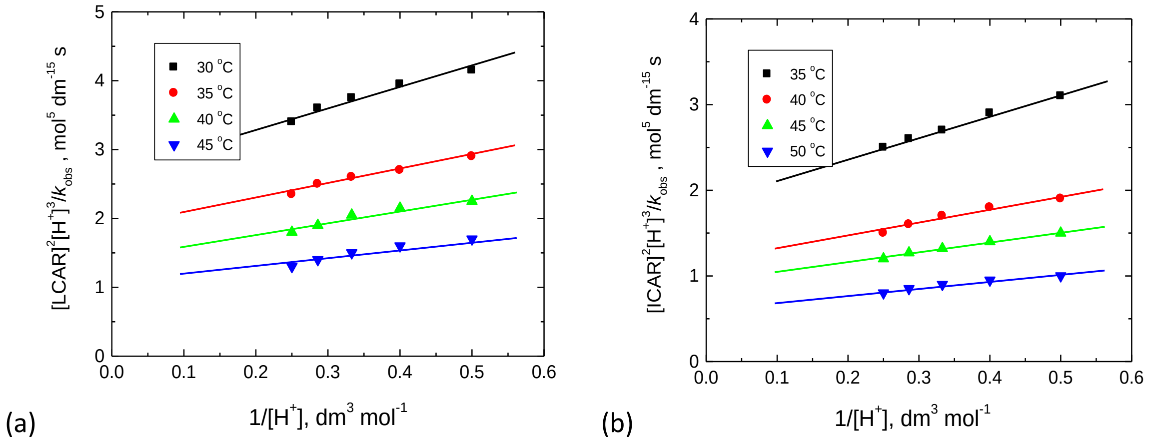


Figure 6 Verification of the rate law (6) at various temperatures in the oxidations of: a) iota-carrageenan, and b) lambda-carrageenan by chromium(VI) in perchlorate solutions. $[Cr^{VI}] = 7.0 \times 10^{-4}$, $[CAR] = 4.0 \times 10^{-3}$ and $I = 4.0$ mol dm^{-3}.

Table 2 Values of the rate constants (k_2, k' and k'') and protonation constants (K_1) at different temperatures in the oxidations of iota- and lambda-carrageenans by chromium(VI) in perchlorate solutions. $[Cr^{VI}] = 7.0 \times 10^{-4}$, $[CAR] = 4.0 \times 10^{-3}$, $I = 4.0$ mol dm^{-3}

CAR	**Constant**	**Temperature (° C)**				
		30	**35**	**40**	**45**	**50**
ICAR	**$10^2\ k_2$ (dm^3 mol^{-1} s^{-1})***	-	4.00	6.75	9.01	12.71
	k' (dm^{18} mol^{-6} s^{-1})	-	0.33	0.51	0.66	0.88
	k'' (dm^{15} mol^{-5} s^{-1})	-	0.60	1.01	1.40	2.04
	K_1 (dm^3 mol^{-1})	-	0.55	0.50	0.47	0.43
LCAR	**$10^2\ k_2$ (dm^3 mol^{-1} s^{-1})***	3.25	5.17	5.98	7.50	-
	k' (dm^{18} mol^{-6} s^{-1})	0.27	0.35	0.41	0.51	-
	k'' (dm^{15} mol^{-5} s^{-1})	0.42	0.68	0.87	1.24	-
	K_1 (dm^3 mol^{-1})	0.63	0.51	0.47	0.41	-

*Calculated at $[H^+] = 3.0$ mol dm^{-3} Experimental error ±3%

Table 3 Activation parameters of the rate constants in the oxidations of iota- and lambda-carrageenans by chromium(VI) in perchlorate solutions. $[Cr^{VI}] = 7.5 \times 10^{-4}$, $[CAR] = 4.0 \times 10^{-3}$, $I = 4.0$ mol dm^{-3}

CAR	ΔH^{o} kJ mol^{-1}	ΔS^{o} J mol^{-1}K^{-1}	ΔG^{o} kJ mol^{-1}
ICAR	-10.86	-40.48	+1.81
LCAR	-24.11	-83.29	+1.96

Experimental error ± 4%

Table 4 Thermodynamic parameters of the protonation constants (K_1) in the oxidations of iota- and lambda-carrageenans by chromium(VI) in perchlorate solutions. $[Cr^{VI}] = 7.5 \times 10^{-4}$, $[CAR] = 4.0 \times 10^{-3}$, $I = 4.0$ mol dm^{-3}

CAR	Rate constant	Parameter				
		$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1}K^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	$E_a^{\neq}$ kJ mol^{-1}	A mol^{-1} s^{-1}
ICAR	k_2	59.69	-77.65	83.60	62.32	1.57×10^{9}
	k'	54.87	-75.95	78.26	57.53	1.91×10^{9}
	k''	64.02	-41.32	76.75	66.51	1.24×10^{11}
LCAR	k_2	40.16	-140.31	81.92	42.76	8.21×10^{9}
	k'	31.26	-152.81	78.33	33.84	1.83×10^{5}
	k''	53.71	-74.82	76.75	56.20	2.17×10^{9}

Experimental error ± 4%

The obtained activation parameters listed in Table 3 can be discussed as follows. The negative values of $\Delta S^{\#}$ suggests formation of intermediate complexes of inner-sphere nature [45,46]. These values are within the range of radical reactions and have been ascribed to the loss of degree of freedom formerly available to the reactants upon formation of a rigid transition state. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are both favorable for electron transfer processes. On the other hand, the positive values of both $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate endothermic formation of the complexes and their non-spontaneities, respectively. On the other hand, the negative values of ΔH^{o} of the protonation constants indicate that the prolytic processes of carrageenans are of exothermic nature.

Leffler and Grunwald [47] have pointed out that many reactions behave an isokinetic relationship, $\Delta H^{\neq} = \alpha + \beta \Delta S^{\neq}$. Therefore, the activation parameters for oxidation of some biopolymers by chromium(VI) [6,48,49] are summarized in Table 5. A plot of $\Delta S^{\neq}$ versus $\Delta H^{\neq}$ of the second-order rate constants is fairly linear with $\alpha = 83.8$ kJ mol^{-1} and $\beta = 311$ K. This linearity indicates that the kinetics of oxidations of these substrates by chromium(VI) may follow similar reaction mechanism. Also, the obtained β value is significant and reflects the high reactivity of the biopolymers.

Table 5 Activation parameters of the second-order rate constants for oxidations of some biopolymers by chromium(VI) in perchlorate solutions

Substrate	Parameter					Reference
	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1}K^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	$E_a^{\neq}$ kJ mol^{-1}	10^{-4} A mol^{-1} s^{-1}	
PVA	30.22	-164.56	79.06	32.52	5.32×10^{6}	48
CMC	47.28	-135.28	87.59	50.26	1.79×10^{6}	49
KCAR	33.04	-163.29	81.69	35.85	7.95×10^{4}	6
ICAR	59.69	-77.65	83.60	62.32	1.57×10^{9}	This work
LCAR	40.16	-140.31	81.92	42.76	8.21×10^{9}	

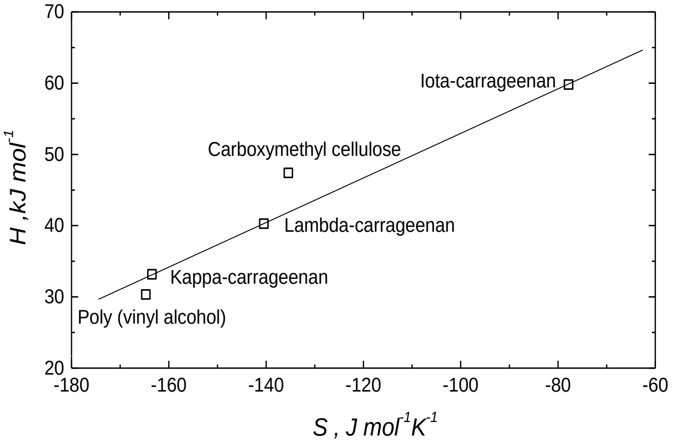


Figure 7 LFER-isokinetic relationship of oxidations of some biopolymers by chromium(VI).

Conclusions

The oxidation reactions between carrageenans and chromium(VI) in perchlorate solutions proceeds by formation of intermediate complexes between the reactants. The rate of oxidation of lambda-carrageenan was found to be higher than that of iota-carrageenan. This may be attributed to the differences in the geometrical structures regarding to the positions of the active functional groups. The reaction mechanism proposed here is consistent with the product, kinetic and mechanistic studies

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