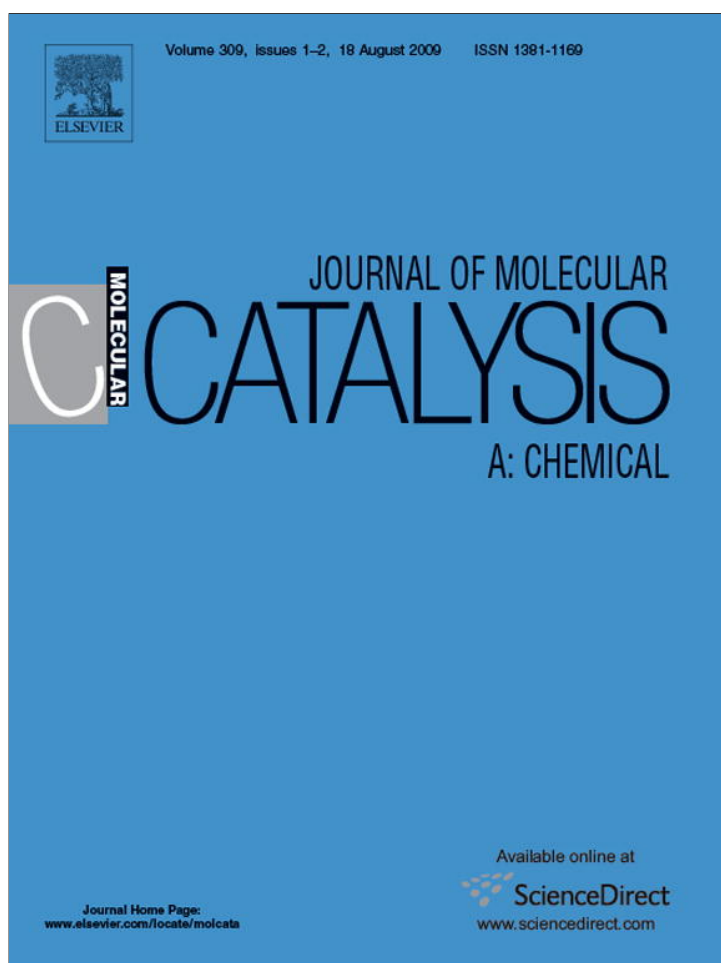




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Acid-catalyzed oxidation of some sulfated macromolecules. Kinetics and mechanism of oxidation of kappa-carrageenan polysaccharide by permanganate ion in acid perchlorate solutions

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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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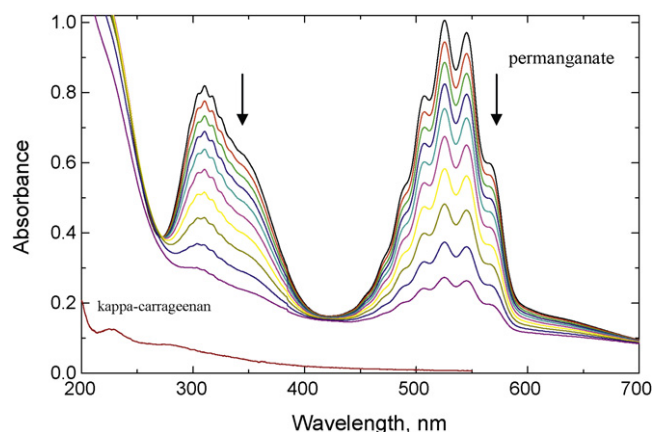


Fig. 1. Spectral changes (200–700 nm) in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$, $[\text{H}^+] = 1.0$, $I = 2.0 \text{ mol dm}^{-3}$ at 20°C . Scanning time intervals = 4 min.

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].

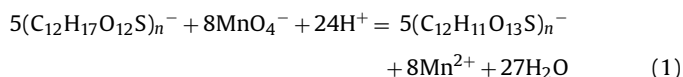
2.3. Polymerization test

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 ± 0.1 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].

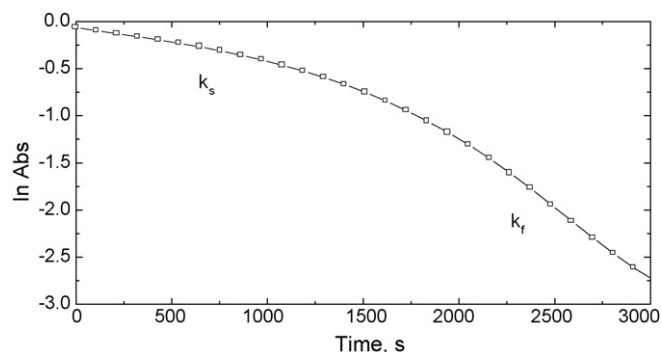


Fig. 2. A plot of ln Abs. vs. time in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$, $[\text{H}^+] = 1.0$, $I = 2.0 \text{ mol dm}^{-3}$ at 20°C .

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

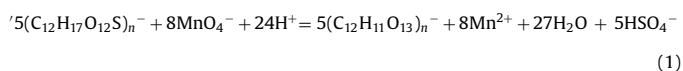
The reaction-time curves were found to be of inverted S-shape throughout the entire range of reaction as shown in Fig. 2. The initial rates were found to be relatively slow in the early stages, followed by an increase in the oxidation rates over longer time periods. As the reaction is of catalytic nature, 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

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



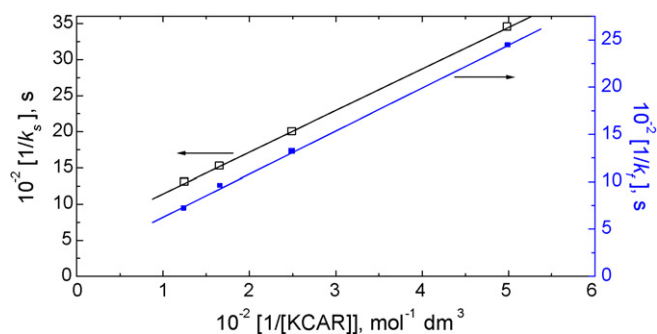


Fig. 3. Reciprocal Michaelis–Menten plots for the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{H}^+] = 2.0$ and $I = 2.0 \text{ mol dm}^{-3}$ at 20°C .

agreement with the Michaelis–Menten kinetics for the formation of intermediate complexes (Fig. 3).

Furthermore, at relatively high concentrations of KCAR ($\geq 10^{-2} \text{ mol dm}^{-3}$), a decrease in the oxidation rate with increasing [KCAR] was observed. This fact may be explained by either the formation of more than one complex and at least one of the complexes appears to resist the oxidation process or the increase in the viscosity results from increasing the substrate concentration will lead to slow down the particles motion and, hence, a decrease in the reaction rate should be observed. Therefore, all the present experiments were performed at $[\text{KCAR}] < 10^{-2} \text{ mol dm}^{-3}$.

3.4. Dependence of reaction rate on $[\text{H}^+]$

In order to clarify the influence of $[\text{H}^+]$ on the rate of reaction and to elucidate a reaction mechanism, kinetic measurements were performed in HClO_4 – NaClO_4 solutions with different $[\text{H}^+]$ and constant ionic strength and temperature. An increase in acid concentration was found to accelerate the rates of both induction and autoacceleration periods. Under our experimental conditions, the order with respect to $[\text{H}^+]$ was found to be unity (calculated from $\log k_s - \log[\text{H}^+]$) at $[\text{H}^+] \leq 2.0 \text{ mol dm}^{-3}$.

Some experimental kinetics have been performed at the higher acidities ($[\text{H}^+] = 2.0$ – 3.5 mol dm^{-3}) with constant ionic strength of 4.0 mol dm^{-3} . Here, second-order dependence in $[\text{H}^+]$ was revealed.

3.5. Dependence of reaction rate on ionic strength

To investigate the effect of ionic strength on the reaction rate, kinetic runs were performed at constant $[\text{H}^+] = 2.0 \text{ mol dm}^{-3}$ as the NaClO_4 concentration was increased to 3.5 mol dm^{-3} . The values of k_s and k_f were found to increase with increasing the ionic strength. The results indicated the catalytic salt effect and showed a good linearity of the extended Bronsted–Debye–Hückel relationship ($\ln k_s$ vs. $I^{0.5}/(1+I^{0.5})$) plot as shown in Fig. 4. 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 [19]. The ionic strength dependence is qualitatively as expected when considering the charges involved [20].

3.6. Dependence of reaction rate on added salts

Since Mn^{2+} ion is expected to be one of the oxidation products, its effect on the reaction rate should be examined. It reported [21] that acidified permanganate is reduced by the addition of Mn^{2+} to give Mn^{3+} and Mn^{4+} according to the following equation:

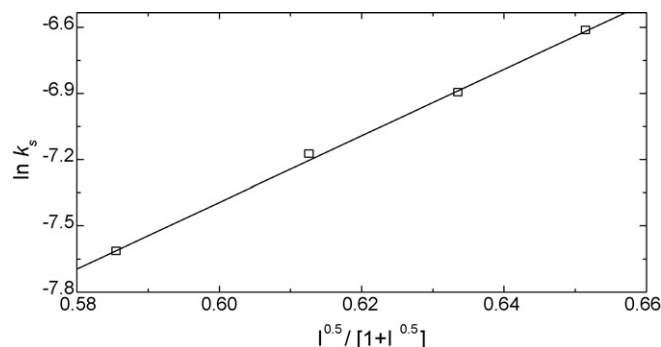
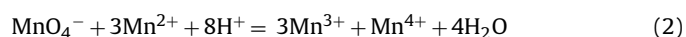


Fig. 4. Dependence of pseudo-first-order rate constant on the ionic strength in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$ and $[\text{H}^+] = 2.0 \text{ mol dm}^{-3}$ at 20°C .

Table 1

Effect of added salts on the autoacceleration rate in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$, $[\text{H}^+] = 2.0$ and $I = 2.0 \text{ mol dm}^{-3}$ at 20°C .

$[\text{Mn}^{2+}] (\text{mol dm}^{-3})$	$10^3 k_f (\text{s}^{-1})$	$[\text{F}^-] (\text{mol dm}^{-3})$	$10^3 k_f (\text{s}^{-1})$
0.00	0.76	0.00	0.76
4×10^{-4}	5.78	4×10^{-4}	0.68
1×10^{-3}	6.41	1×10^{-3}	0.63
4×10^{-3}	8.90	4×10^{-3}	0.48

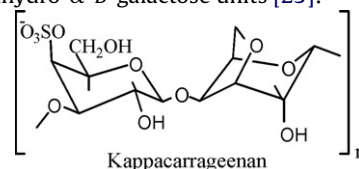
Experimental error $\pm 4\%$.

If MnO_4^- ions are primarily responsible for oxidation, a reduction in the initial rate should be observed in the presence of Mn^{2+} ions, which reduce the concentration of MnO_4^- ions [22]. If, on the other hand, the intermediates Mn^{3+} and/or Mn^{4+} are the reactive oxidizing species, addition of Mn^{2+} should cause an acceleration of the reaction rate. Similarly, the addition of F^- ions should retard the rate of reaction if the intermediates manganese(III) and (IV) ions are mainly responsible for the oxidation owing to the formation of stable complexes with these ions [18], but should cause no significant change if MnO_4^- ions are the principle oxidizing entities.

The experimental observations indicated that the reaction rate increased with increasing $[\text{Mn}^{2+}]$ with a complete disappearance of the induction period, while a decrease in the reaction rate was observed on addition of F^- ions. The results are summarized in Table 1.

4. Discussion

Kappa-carrageenan (KCAR) is a major structural red algae polysaccharide consisting of $(1 \rightarrow 3)$ - β -D-galactose-4-sulfate and $(1 \rightarrow 4)$ -3,6-anhydro- α -D-galactose units [23]:



It has a high degree of polymerization (DP), so that it forms viscous colloidal solutions in water. The solubility in water is owing to the presence of both $-\text{OH}$ and $-\text{OSO}_3^-$ moieties, which have high tendencies to react with water (hydrophilic groups). In aqueous solutions, the orientation (swelling) resulting from the spherical or coiled colloids converts the macromolecule to a linear-block copolymer structure.

The increase in the reaction rates with increasing the hydrogen ion concentration at constant ionic strength may indicate that the protonated species of the reactants are the most reactive species for oxidation in the rate-determining step. Under our experimental

conditions, both permanganate ion and kappa-carrageenan substrate may be suggested to the polytic process in accordance to the following equilibria:



where S and SH⁺ denote the kappa-carrageenan and its protonated form and K and K' are the protonation constants of MnO₄[−] and KCAR, respectively.

The dependence of the observed pseudo-first-order rate constants on [KCAR] which obeys Michaelis–Menten kinetics suggests the formation of an intermediate complex as shown in Fig. 3. The formation of this intermediate complex in the initial slow stage is confirmed not only through Michaelis–Menten plot, but also by the increase in the initial absorbance observed in the UV region on mixing of the substrate with permanganate ion in particularly at lower temperatures. The spectrophotometric failure for detection of such an intermediate complex may be interpreted by either lower concentration of the reactants used and, hence, the expected lower absorptivity of the formed complex and/or the fast subsequent decomposition of the intermediate in comparison to its formation.

In view of the foregoing aspects, the reaction–time curves may be interpreted in terms of two parallel reactions:



or two consecutive reactions:



where k_s and k_f are the observed pseudo-first-order rate constants for the induction and autoacceleration periods, respectively. However, the second mechanism cannot be exclusively eliminated from the kinetic points of view, the experimental results seems to be interpreted in favor of the former mechanism.

The kinetics of the present reaction seems to be of complexity since the reaction order with respect to [H⁺] was found to be first-order at the lower acidities and second-order at the higher ones. The observed first-order dependence in [H⁺] at the lower acidities indicates that, at least, one of the reactants should be in the protonated form in the rate-determining step of the oxidation process. Under our experimental conditions of lower hydrogen ion concentrations used, MnO₄[−] ion has a low tendency to be protonated compared to that of KCAR substrate. This suggestion is based on the pK value of the polytic process of permanganate, which equals to 2.52 and 0.12 dm³ mol^{−1} for permanganate and KCAR, respectively, at 25 °C [24]. Hence, the protonated form of KCAR (SH⁺) is suggested to be the more predominant species in the rate-determining step. On the other hand, the second-order dependence in [H⁺] which observed at the higher acidities may suggest that the protonated forms of both reactants will be considered as the reactive species in the rate-determining step.

Consequently, two competitive reactions may be suggested to proceed in the rate-determining step at the slow initial stage either at the lower [H⁺]:



or at the higher acidity as follows:

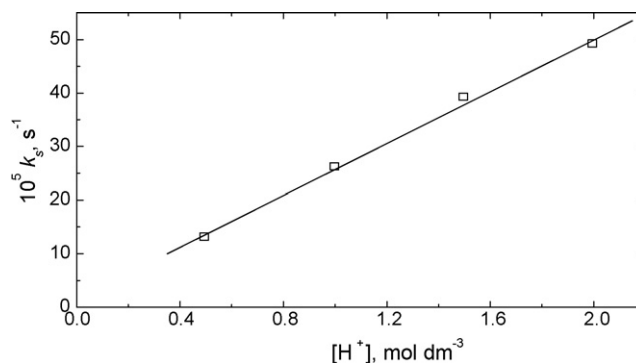


Fig. 5. Dependence of k_s on [H⁺] at lower acidities in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. [MnO₄[−]] = 4 × 10^{−4}, [KCAR] = 4 × 10^{−3} and I = 2.0 mol dm^{−3} at 20 °C.



Since, plots of k_s vs. [H⁺] at lower acidities (Fig. 5) and k_s vs. [H⁺]² at the higher ones (Fig. 6) gave good straight lines passing through the origin. Hence, reaction (8) may be neglected. Therefore, reactions (9) and (10) can be considered as the sole reactive species in the rate-determining steps with respect to the oxidation process at lower and higher acidities, respectively. The ionic strength dependence of the rate constant shown by Bronsted–Debye–Hückel plot (Fig. 4) may support this suggestion with respect to the charges involved [19,20].

The change of the rate constants with the change in the substrate and hydrogen ion concentrations in the rate-determining steps at lower and higher acidities can be expressed by Eqs. (11) and (12), respectively:

$$\text{rate} = \frac{k_b K' K_2 [\text{H}^+] [\text{S}]_T [\text{MnO}_4^-]}{1 + K' [\text{H}^+] + K' K_2 [\text{H}^+] [\text{MnO}_4^-]} \quad (11)$$

$$\text{rate} = \frac{k_c K' K K_3 [\text{H}^+]^2 [\text{S}]_T [\text{MnO}_4^-]}{1 + K' [\text{H}^+] + K' K K_3 [\text{H}^+]^2 [\text{MnO}_4^-]} \quad (12)$$

where [S]_T represents the analytical total concentration of the substrate. In the presence of a large excess of [KCAR] over that of permanganate concentration and rearrangement, one concludes that

$$\frac{1}{k_s} = \left(\frac{1 + K' [\text{H}^+]^2}{k_n [\text{H}^+]^2} \right) \frac{1}{[\text{S}]_T} + C \quad (13)$$

where k_n equals to $k_b K' K_2$ (with $z = 1$) and equals to $k_c K' K K_3$ (with $z = 2$); whereas C equals [MnO₄[−]]/ k_b [S]_T and equals [MnO₄[−]]/ k_c [S]_T, at lower and higher [H⁺], respectively.

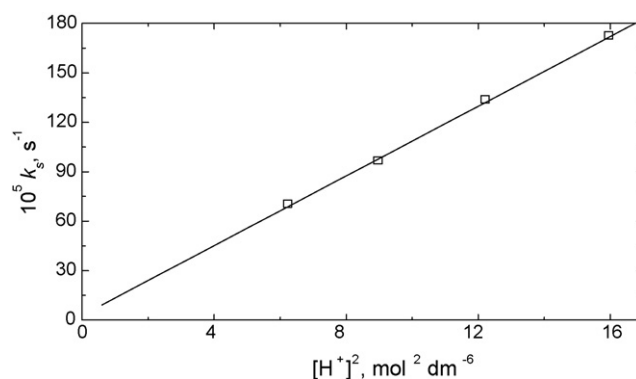


Fig. 6. Dependence of k_s on [H⁺]² at higher acidities in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. [MnO₄[−]] = 4 × 10^{−4}, [KCAR] = 4 × 10^{−3} and I = 4.0 mol dm^{−3} at 20 °C.

Table 2

Values of the apparent rate constants (k'_n and k''_n) and the protonation constant (K') in the induction and autoacceleration periods in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$ mol dm⁻³ and $\lambda = 525$ nm at 20 °C.

	Induction				Autoacceleration	
	Lower $[\text{H}^+]$		Higher $[\text{H}^+]$			
Rate constants (k)	k'_b (mol ⁻³ dm ⁹ s ⁻¹)	k''_b (mol ⁻² dm ⁶ s ⁻¹)	k'_c (mol ⁻³ dm ⁹ s ⁻¹)	k''_c (mol ⁻² dm ⁶ s ⁻¹)	k'_d (mol ⁻³ dm ⁹ s ⁻¹)	k''_d (mol ⁻² dm ⁶ s ⁻¹)
Value	0.081	0.541	0.033	0.60	0.23	1.45
Protonation constant K' (mol ⁻¹ dm ³)	0.150		0.055		0.159	
Ionic strength (I) (mol dm ⁻³)	2.0		3.5		2.0	
Hydrogen ion, $[\text{H}^+]$ (mol dm ⁻³)	$2 < [\text{H}^+] > 0$		$4 < [\text{H}^+] > 2$		$2 < [\text{H}^+] > 0$	

Table 3

Activation parameters of k_2 , k'_b and k''_b in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions for the induction period. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$, $I = 2.0$ mol dm⁻³ and $\lambda = 525$ nm.

Constant	Parameter				
	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$E_a^\ddagger$ (kJ mol ⁻¹)	$10^{-4} A$ (mol ⁻¹ s ⁻¹)
k_2^a	-161.30 ± 3.1	29.63 ± 0.4	77.70 ± 1.3	32.70 ± 0.63	8.67
k'_b	-187.00 ± 1.8	23.45 ± 0.6	79.20 ± 1.15	26.00 ± 0.6	0.30
k''_b	-183.00 ± 1.8	18.13 ± 0.33	71.27 ± 0.87	20.10 ± 0.7	0.83

^a Second-order rate constant measured at $[\text{H}^+] = 1.0$ mol dm⁻³.

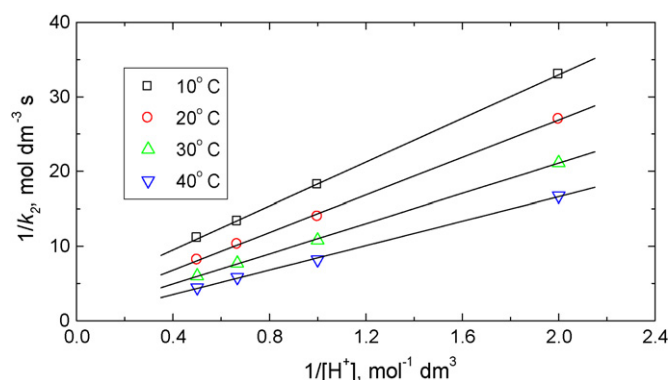


Fig. 7. Plots of $1/k_2$ vs. $1/[\text{H}^+]$ in the oxidation of kappa-carrageenan by permanganate ion in aqueous perchlorate solutions for the induction period. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{KCAR}] = 4 \times 10^{-3}$ and $I = 2.0$ mol dm⁻³.

According to Eq. (13), plots of $1/k_s$ against $1/[\text{S}]_T$ at constant $[\text{H}^+]$ should be straight lines with positive intercepts on $1/k_s$ axis as is experimentally observed (Fig. 3). This behaviour was found to be in a good agreement with Michaelis–Menten kinetics for the formation of intermediate complexes. Again, plots of $1/k_s$ against $1/[\text{H}^+]^2$ at constant $[\text{S}]_T$ should be linear. The experimental results were found to satisfy this requirement. The small intercepts observed in Fig. 3 leads us to simplify Eq. (13) to

$$\frac{[\text{S}]_T}{k_s} = \frac{1}{k_2} = \left(\frac{1}{k'_n[\text{H}^+]^2} + \frac{1}{k''_n} \right) \quad (14)$$

where k'_n and k''_n are the apparent rate constants² and k_2 is the second-order rate constant ($k_2 = k_s/[\text{S}]_T$).

Eq. (14) requires that plots of $1/k_2$ vs. $1/[\text{H}^+]^2$ to be linear with positive intercepts on $1/k_2$ axis as is experimentally observed. A typical plot at lower acidity is shown in Fig. 7. The protonation constant of the substrate, K' , and the apparent rate constants, k'_n and k''_n , can be evaluated from the slopes and intercepts of those plots. These values were calculated by the least-square method and listed in Table 2.

² $k'_n = k_b K' K_2$ and $k''_n = k_b K_2$ at lower acidities, while $k'_n = k_c K K' K_3$ and $k''_n = k_c K K_3$ at higher acidities.

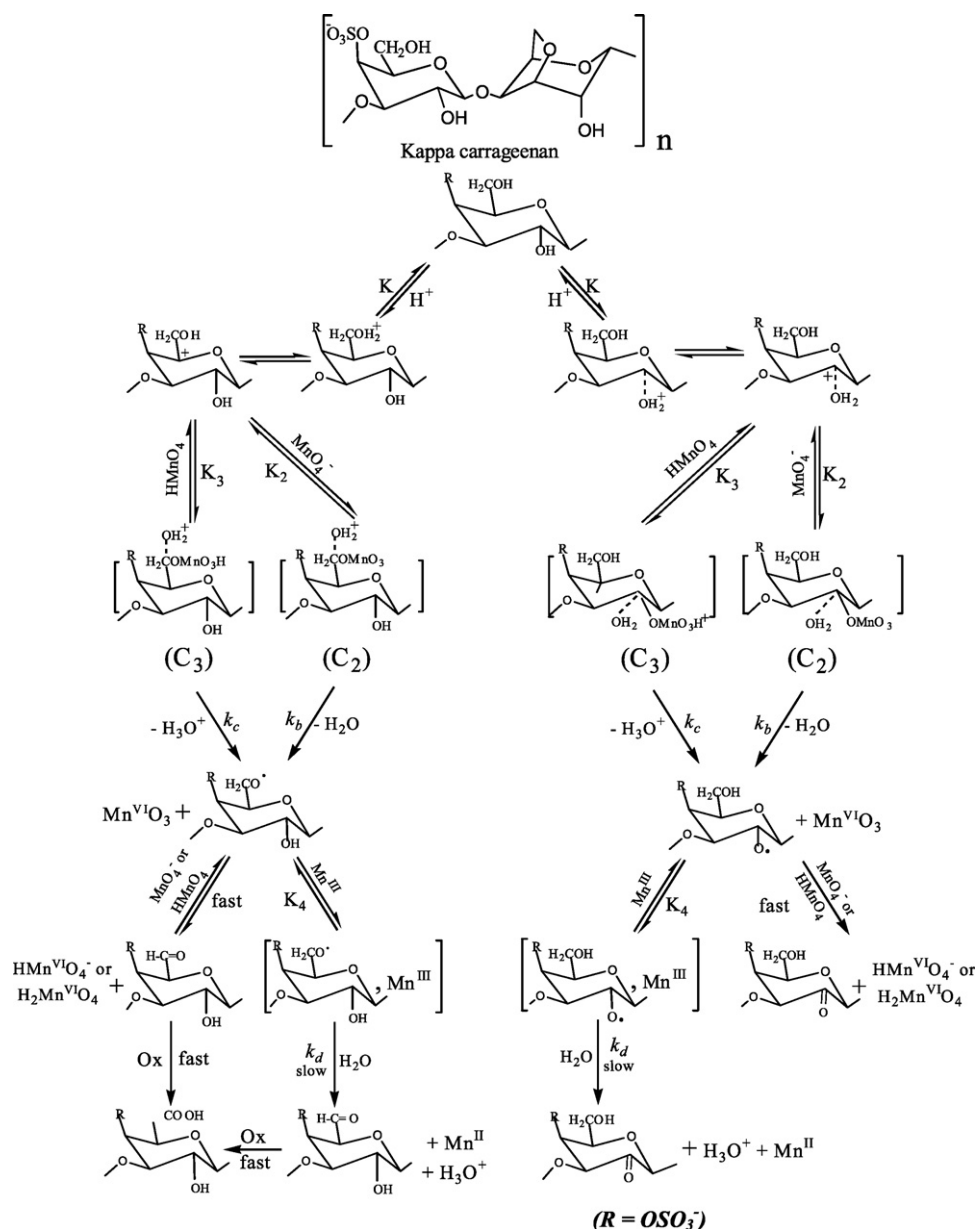
Unfortunately, the values of the rate constants of the elementary reaction k_n could not be calculated because of the non-availability of the formation constants K_2 and K_3 . Some attempts have been made to calculate these formation constants from the experimental data, but the results were not encouraged. Therefore, the values of k'_n and k''_n are considered as the products of the second-order rate constants, the protonation constants and the formation constants, respectively.

The kinetic parameters of k_2 , k'_b and k''_b were calculated from the temperature-dependence of the rate constants using the Arrhenius and Eyring equations by the least-square method and listed in Table 3.

In view of the foregoing kinetic interpretations and experimental observations, the most reasonable reaction mechanism which may be suggested throughout the initial induction period involves a rapid complexation between the reactive species of the reactants (depending on the $[\text{H}^+]$), followed by electron-transfer from the substrate to the oxidant in order to form the initial oxidation product. Here, a question of basic interest may be arisen is whether electron-transfer proceeds through successive one-electron-changes, $\text{Mn}^{\text{VII}} \rightarrow \text{Mn}^{\text{VI}} \rightarrow \text{Mn}^{\text{V}}$ or by a simultaneous two-electron-changes in a single step, $\text{Mn}^{\text{VII}} \rightarrow \text{Mn}^{\text{V}}$. The positive catalytic effect of Mn^{2+} on the rate of reaction may reflect the one-electron-transfer mechanism. Again, the formation of free radicals during the course of reaction as well as the high negative entropy of activation obtained may considered as an evidence to support one-electron-transfer mechanism of inner-sphere nature [25,26].

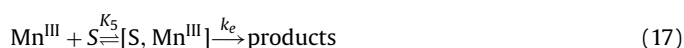
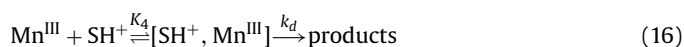
On the other hand, the effect of the added salts on the reaction rates (Table 1) indicates the disappearance of the induction period even at lower concentrations of added Mn^{2+} , in addition to the observed decrease in the reaction rate on addition of F^- ion; thus may suggest that Mn^{3+} and/or Mn^{4+} are the sole oxidants throughout the autoacceleration final stage. However, it is difficult to decide whether Mn^{III} or Mn^{IV} was the reactive species in the autoacceleration period. However, in similar redox reactions involving MnO_4^- as an oxidant, the continuous increase in the oxidation rate with increasing added Mn^{2+} in addition to the formation of free radicals suggested that Mn^{III} is the more predominant ion [21]. Otherwise, if Mn^{IV} is the sole reactive species, addition of Mn^{2+} to the reaction mixture will cause a decrease in the concentration of Mn^{IV} and, hence, a decrease in the rate constant should be observed [21,27] according to the equation:





Scheme 1. Speculated reaction mechanism for oxidation of the primary and secondary alcoholic groups by MnO_4^- ion.

The influence of the hydrogen ion concentration on the reaction rate of the autoacceleration period indicates that the reaction is first-order in $[\text{H}^+]$. Again, the plot of $1/k_f$ vs. $1/[\text{S}]$ indicates the formation of intermediate complexes between the reactants prior to the rate-determining step according to Michaelis–Menten kinetics as shown in Fig. 3. Therefore, the great similarity between the reaction kinetics of the autoacceleration and induction periods in the present investigation, leads us to suggest a similar reaction mechanism for the fast final stage. It involves a rapid complexation between the formed intermediate manganese with the substrate and/or with the formed initial oxidation radical, followed by an electron-transfer process in the rate-determining step as follows:



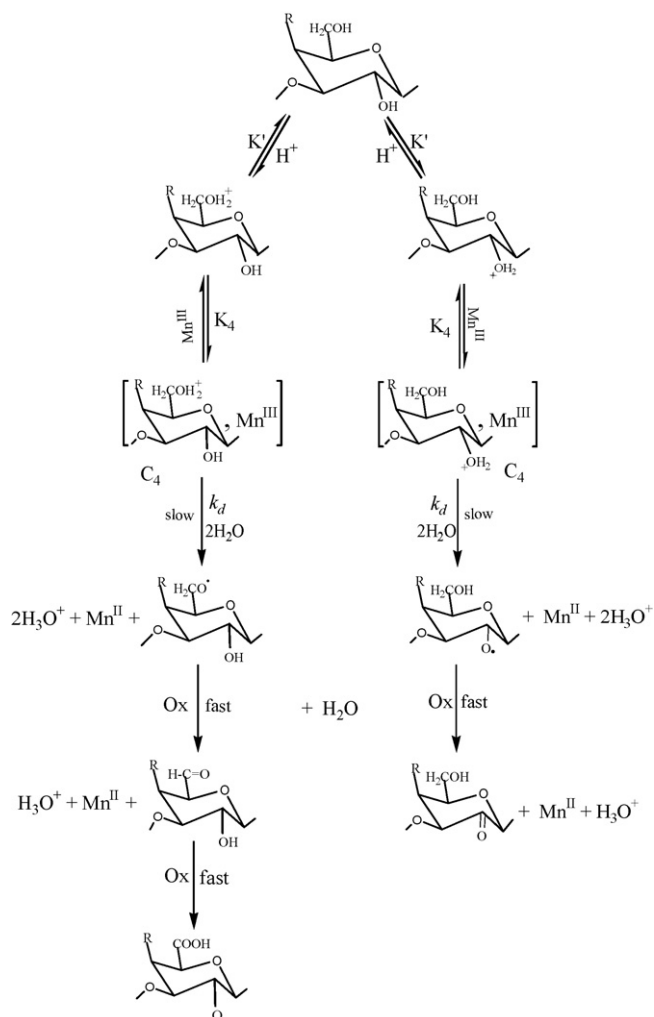
Since the oxidation reaction showed a first-order dependence in $[\text{H}^+]$ through this final stage, reactions (17) and (18) may be neglected and, hence, reaction (16) may be considered as the main pathway in the rate-determining step. Accordingly, the change of the rate constant with the change in the substrate and hydrogen ion concentrations can be written as follows:

$$\text{rate} = \frac{k_d K' K_4 [\text{H}^+] [\text{S}]_T [\text{Mn}^{\text{III}}]}{1 + K' [\text{H}^+] + K' K_4 [\text{H}^+] [\text{Mn}^{\text{III}}]} \quad (19)$$

Considering that the concentration of Mn^{III} is approximately equals to the initial $[\text{MnO}_4^-]_0$, thus yields

$$\frac{1}{k_f} = \left(\frac{1 + K' [\text{H}^+]}{k_d K' K_4 [\text{H}^+]} \right) \frac{1}{[\text{S}]_T} + C' \quad (20)$$

The relationship (20) is quite similar to Eq. (13), which requires that plotting $1/k_f$ against $1/[\text{S}]_T$ at constant $[\text{H}^+]$ to be linear with a positive intercept on $1/k_f$ axis. This requirement is experimentally satisfied as shown in the reciprocal Michaelis–Menten plot (Fig. 3). Again, the small intercept observed in $1/k_f - 1/[\text{S}]$ plot (Fig. 3), leads



Scheme 2. Speculated reaction mechanism for oxidation of the primary and secondary alcoholic groups by Mn^{III} ion.

us to simplify Eq. (20) to Eq. (21):

$$\frac{1}{k'_2} = \frac{[\text{H}^+]^{-1}}{k'_d} + \frac{1}{k''_d} \quad (21)$$

where $k'_d = k_d K' K_4$, $k''_d = k_d K_4$ and k'_2 is the second-order rate constant for the autoacceleration period ($k'_2 = k_f/[S]$). According to Eq. (21), a plot of $1/k'_2$ against $1/[\text{H}^+]$ should be linear with positive intercept on $1/k'_2$ axis as is observed experimentally. A typical plot is shown in Fig. 5; from whose slope and intercept, the values of the apparent rate constants, k'_d and k''_d , as well as the protonation constant, K' , can be evaluated. These values were calculated using the least-squares method and are summarized in Table 2. The calculated value of protonation constant (K') obtained in this stage was found to be in good agreement with that evaluated throughout the induction period as well as with that obtained through the oxidation of KCAR by chromic acid [28] within the experimental errors. This result may be considered as a good support for the validity of the proposed mechanism.

In view of the above kinetic interpretations and the experimental observations throughout the entire range of the overall reaction, a tentative reaction mechanism for oxidation of kappa-carrageenan by acidic permanganate can be suggested as illustrated by Schemes 1 and 2, respectively. It involves a fast protonation of the substrate, followed by the attack of permanganate oxidant on the

protonated substrate giving the intermediate complexes (C_2 and C_3) prior to the rate-determining step. Such complexation is followed by the transfer of electrons from the substrate to the oxidant in the rate-determining step to give free-radical substrates with the subtraction of H_3O^+ and Mn^{III} as initial oxidation products through the initial slow stage of oxidation (Scheme 1).

Then, the formed Mn^{III} reacts with either the substrate radical (Scheme 1) or with another protonated substrate molecule (Scheme 2) to form an intermediate complex (C_4), followed by electron-transfer in the rate-determining step to give rise to the oxidation products throughout the autoacceleration period.

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