



Acid-catalyzed oxidation of some sulfated polysaccharides

Kinetics and mechanism of oxidation of kappa-carrageenan by cerium(IV) in aqueous perchlorate solutions

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ABSTRACT

The kinetics of oxidation of kappa-carrageenan (KCAR) as a sulfated polysaccharide by cerium(IV) in aqueous perchlorate solutions at a constant ionic strength of 2.0 mol dm⁻³ have been investigated, spectrophotometrically. The results showed a first-order dependence in [Ce^{IV}] and fractional-first-order kinetics in carrageenan concentration. A kinetic evidence for the formation of 1:1 complex has been revealed. The hydrogen ion dependence of the reaction rate indicated that the oxidation process is acid catalyzed. The oxidation product was identified by the spectral data and elemental analysis. The activation and thermodynamic parameters have been evaluated and a relevant reaction mechanism is suggested and discussed.

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1. Introduction

The study of electron-transfer processes in macromolecules has added a new criterion to the kinetic research [1]. The properties of macromolecules that affect electron-transfer reactions are the localization of the functional groups present in the macromolecular chains. Rate studies provide more information on how the redox process is affected by the hydrophilic and electrostatic attraction between the functional groups and the oxidants.

The kinetics of oxidation of some natural and synthetic polymers by permanganate [2–9] and by chromic acid [10,11] has been investigated and reported previously. It seen that no attempt has been made for the oxidation of these macromolecules by cerium(IV) as a strong oxidant.

This fact prompted us to perform the present investigation for oxidation of kappa-carrageenan (KCAR) by cerium(IV) in aqueous perchlorate solutions with a view to shed some light on the influence of the nature of the oxidant on the reaction kinetics and the

type of products since kappa-carrageenan contains both primary and secondary alcoholic groups.

2. Experimental

2.1. Reagents

All materials employed in the present work were of analytical grade. Doubly distilled water was used in all preparations. The temperature was controlled within ± 0.05 °C.

2.2. Preparation of stock solutions

Kappa-carrageenan (Fluka) was used without further purification. A stock solution of KCAR (0.01 mol dm⁻³) was prepared by stepwise addition of the reagent powder to bidistilled water whilst vigorously stirring the solution to avoid the formation of lumpy precipitate [9–11].

A stock solution of cerium(IV) was prepared as described elsewhere [12,13]. This process was performed by precipitating the hydroxide from cerium ammonium nitrate with NH₄OH. The precipitate was allowed to settle (48 h), leached several times with

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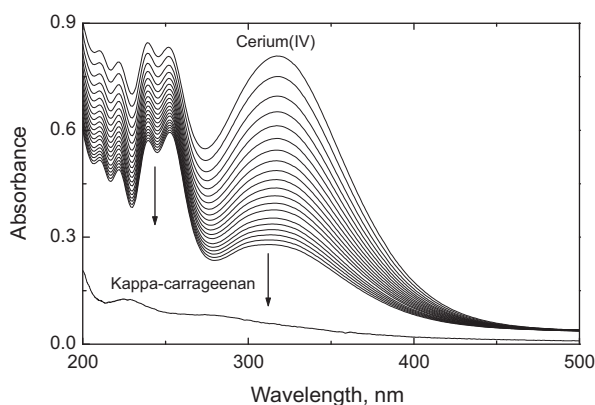


Fig. 1. Spectral changes (200–500 nm) in the oxidation of kappa-carrageenan by cerium(IV) in aqueous perchlorate solutions. $[Ce^{IV}] = 2.0 \times 10^{-4}$, $[H^+] = 1.0$, $[KCAR] = 2.0 \times 10^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25 °C.

bidistilled water, dissolved in $HClO_4$ and filtered off. All cerium(IV) solutions were standardized against ferrous ammonium sulfate using N-phenol anthranilic acid indicator [13]. The solution of cerium(IV) was stored in a dark glass bottle and used after 24 h after (vide infra) since the hydrolysis is negligible small or ruled out after 12 h of preparation [14].

2.3. Kinetic measurements

The kinetic measurements were performed under pseudo-first-order conditions where the substrate (KCAR) was present in a large excess over that of cerium(IV) concentration. The reaction was followed spectrophotometrically at 315 nm, the absorbance maximum of Ce^{IV} , where all other species involved in the reaction have negligible absorbance at this wavelength. The course of reaction was monitored by recording the decrease in absorbance of Ce^{IV} as a function of time using a Shimadzu UV-2101/3101 PC automatic scanning double-beam spectrophotometer fitted with wavelength program controller using cells of path length 1 cm. The spectral changes during the course of reaction are shown in Fig. 1.

Some kinetic runs were carried out under second-order conditions where $[KCAR]_0 \geq [Ce^{IV}]$ to check the producibility of the pseudo-first-order data. The results were found to be in good agreement with each other within the experimental errors indicating the reproducibility of the pseudo-first-order kinetic measurements.

The ionic strength of the reaction mixtures was maintained constant at 2.0 mol dm^{-3} by the addition of $NaClO_4$ as a non-complexing agent.

2.4. 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. Blank experiments from which either Ce^{IV} or KCAR were excluded gave no detectable polymerization. This result indicates the induced free-radical mechanism during the entire course of the present oxidation reaction.

3. Results

3.1. Nature of Ce^{IV} species

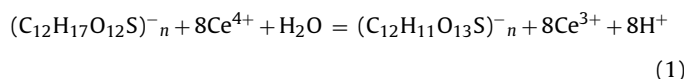
A survey on the earlier literature on the nature of cerium(IV) species in perchloric acid [15] showed that Ce^{IV} exists mainly in the form of monomeric species Ce^{4+} and $Ce(OH)^{3+}$ and partially in the

form of dimeric species $Ce-O-Ce^{6+}$ and $Ce-O-CeOH^{3+}$. However, Offiner and Skoog [16] and after Amzad and McAuely [17] showed from the spectrophotometric studies that the hydrated form, Ce^{4+} , is the predominant species at $[H^+] \geq 1.0 \text{ mol dm}^{-3}$ up to the concentration of $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ of $[Ce^{IV}]$, whereas $Ce(OH)^{3+}$ and dimers are the more predominant at $[H^+] < 0.8 \text{ mol dm}^{-3}$.

Therefore, under our experimental conditions of $[H^+] > 1.0 \text{ mol dm}^{-3}$, Ce^{IV} may be regarded as existing in the form of Ce^{4+}_{aq} (aquacerium(IV)).

3.2. Stoichiometry

It is important to determine the stoichiometric coefficients of the reactants of the overall reaction owing to the complexity of the reaction kinetics. Reaction mixtures containing different initial concentrations of the reactants ($[Ce^{IV}] = (1-4) \times 10^{-4} \text{ mol dm}^{-3}$ and $[KCAR] = 1 \times 10^{-5} \text{ mol dm}^{-3}$) in $1.0 \text{ mol dm}^{-3} HClO_4$ which adjacent to a constant ionic strength of 2.0 mol dm^{-3} were equilibrated in dark. The unreacted $[Ce^{IV}]$ was estimated periodically until it reached a constant value, i.e. completion of the reaction. A stoichiometric ratio of $([Ce^{IV}]_{consumed}/[KCAR]_0)$ was found to be $8.0 \pm 0.1 \text{ mol}$. This result conforms to the following stoichiometric equation



where $(C_{12}H_{17}O_{12}S)^{-n}$ and $(C_{12}H_{11}O_{13}S)^{-n}$ represent to the kappa-carrageenan and its corresponding diketo-acid oxidation derivative, respectively. The products were identified by the spectral data and elemental analysis as described elsewhere [18–20].

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

3.3. Reaction-time curves

Plots of the first-order ($\ln \text{Abs vs. time}$) or the second-order forms ($1/\text{Abs vs. time}$) were found to be fairly linear for more than two-half lives of the reaction completion. The rate constants calculated from the gradients of these plots were found to be in good agreement with each other confirming the reducibility of the performed kinetic measurements.

3.4. Dependence of reaction rate on $[Ce^{IV}]$ and $[KCAR]$

The order with respect to cerium ion was confirmed not only by the linearity of the plots of pseudo-first-order rate constants ($r \geq 0.99$) but also by the independence of the observed rate constants, k_{obs} , on the different initial concentration of cerium(IV) in the range $(1-6) \times 10^{-4} \text{ mol dm}^{-3}$ in a number of steps at constant concentration of all other reagents. The average value of k_{obs} at $[Ce^{IV}] = 2 \times 10^{-4}$, $[KCAR] = 4 \times 10^{-3}$, $[H^+] = 1.0$, and $I = 2.0 \text{ mol dm}^{-3}$ was found to be $8.33 \times 10^{-4} \text{ s}^{-1}$ at 25 °C.

The dependence of k_{obs} values on KCAR were deduced from the measurements of the observed-first-order rate constants at several ratios of $[KCAR]$ and fixed concentration of cerium ion. The order was found to be of fractional-first-order using the relationship ($\log k_{obs} = n \log [KCAR]$). Again, when the reciprocal of the rate constants, $1/k_{obs}$, were plotted against the reciprocal of $1/[KCAR]$, straight lines with positive intercepts on the $1/k_{obs}$ axis were obtained. This behavior obeys the Michaelis–Menten kinetics for the formation of 1:1 intermediate complex. A typical plot is shown in Fig. 2.

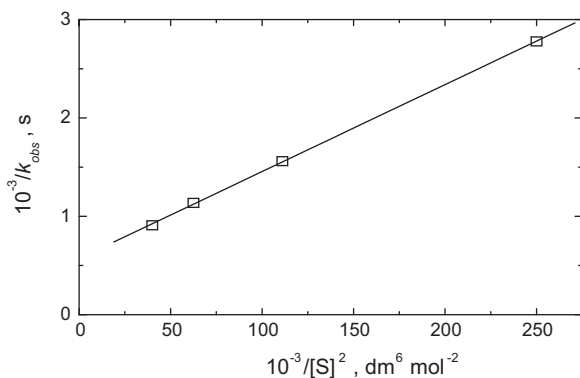


Fig. 2. Plot of $1/k_{obs}$ vs. $1/[H^+]^2$ in the oxidation of kappa-carrageenan by cerium(IV) in aqueous perchlorate solutions. $[Ce^{4+}] = 2.0 \times 10^{-4}$, $[KCAR] = 2.0 \times 10^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25°C .

Furthermore, at relatively high concentrations of KCAR ($>10^{-2} \text{ mol dm}^{-3}$), 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 these complexes appears to resist the oxidation process or the increase in the viscosity as a result of the increase of the substrate concentration. Thus in turn 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 $[KCAR] < 10^{-2} \text{ mol dm}^{-3}$.

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

In order to clarify the influence of $[H^+]$ on the rate of reaction and to elucidate a reaction mechanism, kinetic measurements were performed in $\text{HClO}_4\text{-NaClO}_4$ solutions with different $[H^+]$ and constant ionic strength and temperature. An increase in acid concentration was found to accelerate the rates of the present oxidation reaction. The reaction order with respect to $[H^+]$ was found to be of fractional-second-order (calculated from $\log k_s - \log [H^+]$ plots).

3.6. Dependence of reaction rate on ionic strength

To shed some lights on the reactive species in the rate-determining step, the effect of ionic strength on the reaction rate was examined. Kinetic runs were performed at constant $[H^+] = 1.0 \text{ mol dm}^{-3}$ as the NaClO_4 concentration was increased to 2.5 mol dm^{-3} . The values of k_{obs} were found to increase with increasing the ionic strength. This result indicated the catalytic salt effect and showed a good linearity of the extended Bronsted–Debye–Hückel relationship ($\ln k_{obs}$ vs. $I^{0.5}/(1+I^{0.5})$ plot) as shown in Fig. 3 ($r = 0.99$). 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 [21]. The ionic strength dependence is qualitatively as expected when considering the charges involved [22].

4. Discussion

It has been reported [23–25] that the addition of a polyvalent metal ion electrolyte to an anionic polyelectrolyte such as alginate polysaccharide in either powder or sol forms lead to sol–gel transformation with formation of insoluble cross-linked metal alginate complexes in either granule or gel forms, respectively, depending on the method of preparation [26]. Here, a kind of salt bridge via an egg-carton like structure is formed between the interdiffused polyvalent metal cation and the carboxylate and hydroxyl func-

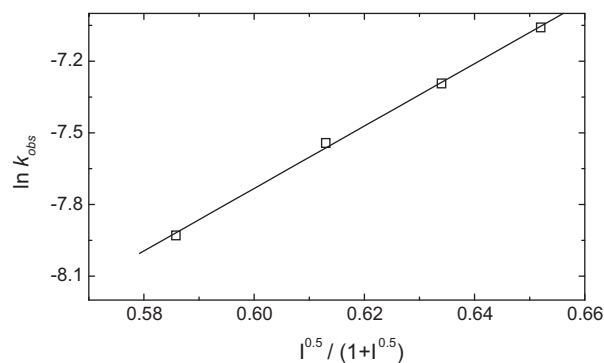


Fig. 3. Plot of $1/k_{obs}$ vs. $1/[KCAR]$ in the oxidation of kappa-carrageenan by cerium(IV) in aqueous perchlorate solutions. $[Ce^{4+}] = 2.0 \times 10^{-4}$, $[H^+] = 1.0$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25°C .

tional groups of alginate macromolecular chains [27–29] through partially ionic and partially coordinate bonds, respectively. Therefore, the failure in gelation occurs through the addition of Ce^{IV} electrolyte to a sol of KCAR polysaccharide as an anionic polyelectrolyte is of interesting. Hence, it may conclude that the presence of carboxylate functional groups in the macromolecular chains of alginate polyelectrolyte is an essential factor for sol–gel transformation phenomenon.

On the other hand, when a reaction mixture of cerium(IV) and KCAR in acidic solution was followed spectrophotometrically, a continuous decrease in the absorbance of Ce^{IV} was observed at its absorption maximum without formation of any precipitate during the entire course of reaction. Since, cerium(IV) is known to be a strong oxidant for most of organic and inorganic substrates [12–17,29–34], the observed decrease in absorbance of cerium(IV) may be interpreted by the oxidation of KCAR macromolecule by the oxidant or the formation of a soluble gel form between the two reactants. Detection of Ce^{III} as a reduced form of Ce^{IV} during the progress of the reaction (on using reference cells containing Ce^{IV} of the same concentration of the reaction mixture) may lead us to exclude the suggestion of a soluble gel formation. Again, the positive polymerization observed on the addition of acrylonitrile to the partially oxidized reaction mixture may confirm the occurrence of an oxidation–reduction reaction.

The increase in the rate constant with increasing the hydrogen ion concentration at constant ionic strength may indicate the protonation of the reactants species. Under our experimental conditions of $[H^+] \geq 1.0 \text{ mol dm}^{-3}$, the hydrolysis of Ce^{IV} is negligible small [14–17] and, hence, KCAR tends to protonate according the following equilibrium



where S and SH^+ represent kappa-carrageenan and its protonated form and K is the protonation constant of kappa-carrageenan.

In view of the foregoing aspects and the experimental observations, the most reasonable reaction mechanism which may be suggested involves a fast complexation between the reactive species of reactants to give an intermediate complex (C) prior to the rate-determining step



where K_1 is the formation constant of the intermediate complex C. This step is followed by the decomposition of the intermediate in the rate-determining step to give rise to the substrate radical (C^*) as initial oxidation product and Ce^{3+} as the reduced form of Ce^{4+} ,

Table 1

Activation parameters of the apparent rate constants in the oxidation of kappa-carrageenan by cerium(IV) in aqueous perchlorate solutions. $[Ce^{4+}] = 2.0 \times 10^{-4}$, $[KCAR] = 2 \times 10^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$.

Rate constant	Parameter				
	$\Delta S^\ddagger \text{ J mol}^{-1} \text{ K}^{-1}$	$\Delta H^\ddagger \text{ kJ mol}^{-1}$	$\Delta G^\ddagger \text{ kJ mol}^{-1}$	$E_a^\ddagger \text{ kJ mol}^{-1}$	$10^{-4} \text{ A mol}^{-1} \text{ s}^{-1}$
k'	-59.80	53.73	71.55	56.21	1.27×10^{10}
k''	+87.25	99.92	73.92	102.41	1.61×10^{17}

Experimental error $\pm 4\%$.

respectively



The substrate radical formed is rapidly oxidized by the oxidant to give rise to the final product.

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

$$\text{Rate} = \frac{-d[Ce^{IV}]}{dt} = \frac{kK_1[H^+]^2[S][Ce^{IV}]}{1 + K[H^+] + K_1[H^+][Ce^{IV}]} \quad (5)$$

where $[S]_T$ represents the analytical total concentration of KCAR substrate, $[S]_T = [S] + [SH^+] + [C]$.

Under pseudo-first-order condition in the presence of a large excess of substrate over that of $[Ce^{IV}]$

$$\text{Rate} = k_{obs}[Ce^{IV}] \quad (6)$$

Comparing Eqs. (5) and (6) and rearrangement, one concludes that

$$\frac{1}{k_{obs}} = \left(\frac{1 + K[H^+]}{kK_1[H^+]^2} \right) \frac{1}{[S]_T} + K' \quad (7)$$

According to Eq. (7), plots of $1/k_{obs}$ against $1/[S]$ at constant $[H^+]$ should be linear ($r > 0.99$) with positive intercepts on $1/k_{obs}$ axis. The experimental results satisfied this requirement as shown in Fig. 2. Again, a plot of $1/k_{obs}$ against $1/[H^+]^2$ at constant $[S]$ should give a straight line with a positive intercept on $1/k_{obs}$ axis as was experimentally observed in Fig. 4. The small intercepts observed in Fig. 2 may lead us to simplify Eqs. (7)–(8) which is considered as the suitable rate-law expression of oxidation of KCAR by Ce^{IV} oxidant

$$\frac{[H^+][S]_T}{k_{obs}} = \left(\frac{1}{k'[H^+]} + \frac{1}{k''} \right) \quad (8)$$

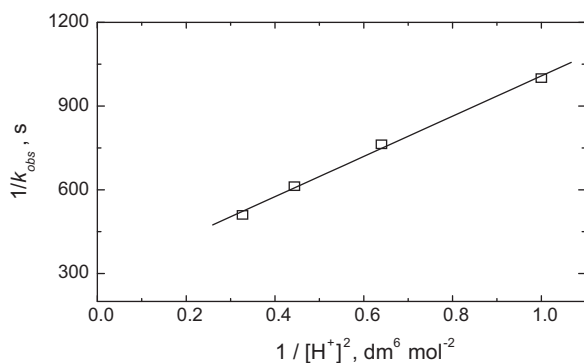


Fig. 4. Plot of $\ln k_{obs}$ vs. $10^{0.5}/(1+10^{0.5})$ in the oxidation of kappa-carrageenan by cerium(IV) in aqueous perchlorate solutions. $[Ce^{4+}] = 2.0 \times 10^{-4}$, $[H^+] = 1.0$ and $[KCAR] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ at 25°C.

Table 2

Values of the protonation constant at different temperatures and its thermodynamic parameters in the oxidation of kappa-carrageenan by cerium(IV) in aqueous perchlorate solutions. $[Ce^{4+}] = 2.0 \times 10^{-4}$, $[KCAR] = 2 \times 10^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$.

	Temp. (°C)			
	25	30	35	40
Value	2.58	1.93	1.42	1.06
Parameter				
	$\Delta H^\circ \text{ kJ mol}^{-1}$	$\Delta S^\circ_{298} \text{ J mol}^{-1} \text{ K}^{-1}$	$\Delta G^\circ_{298} \text{ kJ mol}^{-1}$	
	Value	-74.12	-246.79	-0.58

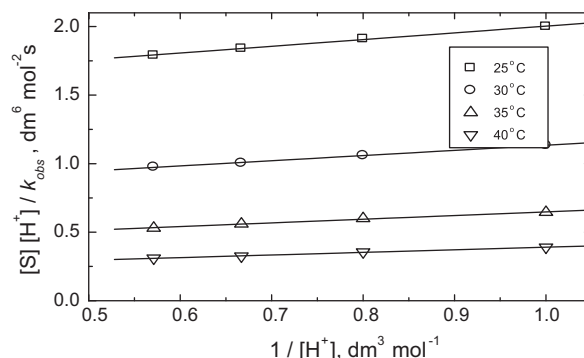


Fig. 5. Plots of $[S][H^+]/k_{obs}$ vs. $[H^+]^{-1}$ in the oxidation of kappa-carrageenan by cerium(IV) in aqueous perchlorate solutions. $[Ce^{4+}] = 2.0 \times 10^{-4}$, $[KCAR] = 2 \times 10^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$.

where k' and k'' are¹ the apparent rate constants and are equal to kK_1 and kK_1 , respectively.

According to Eq. (8), plots of the left hand side against $1/[H^+]$ gave good straight lines ($r > 0.99$) from whose slopes and intercepts, the apparent rate constants and the equilibrium constant can be calculated. Typical plots are shown in Fig. 5. These values were calculated by the least-squares method.

Unfortunately, the values of the rate constants of the elementary reaction k_1 could not be calculated because of the non-availability of the protonation and formation constants K and K_1 values, respectively. However, some attempts have been made to compute these constants from the experimental data, the results obtained were not encouraged. Therefore, the values of the apparent rate constants, k_a' and k_a'' are considered to be composite quantities of the rate constant, formation constant and the protonation constant, respectively.

The activation parameters of k' and k'' (Table 1) along with thermodynamic parameters of K (Table 2) were determined from the temperature-dependence of the reaction rate constants by using the least-square method from the Eyring and Arrhenius equations.

¹ $K' = \frac{[Ce^{IV}]}{[H^+][S]_T}$.

Table 3

The activation parameters of the second-order rate constants in the oxidation of kappa-carrageenan by various oxidants.

Oxidant	Parameter					Conditions		Reference
	ΔS^\ddagger J mol ⁻¹ K ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹	E_a^\ddagger kJ mol ⁻¹	$10^{-4} A$ mol ⁻¹ s ⁻¹	[H ⁺] mol dm ⁻³	I mol dm ⁻³	
MnO ₄ ⁻	-208.31	17.07	79.15	19.42	2.08 × 10 ²	1.0	2.0	9
CrO ₄ ²⁻	-167.93	31.59	81.63	34.05	7.13 × 10 ⁶	2.0	4.0	11
Ce ⁴⁺	+26.67	82.26	74.68	85.11	3.68 × 10 ¹⁴	1.0	2.0	This work

Again, the activation parameters of the second-order rate constants of the present work along with that reported for oxidation of kappa-carrageenan by other various oxidants are listed in Table 3.

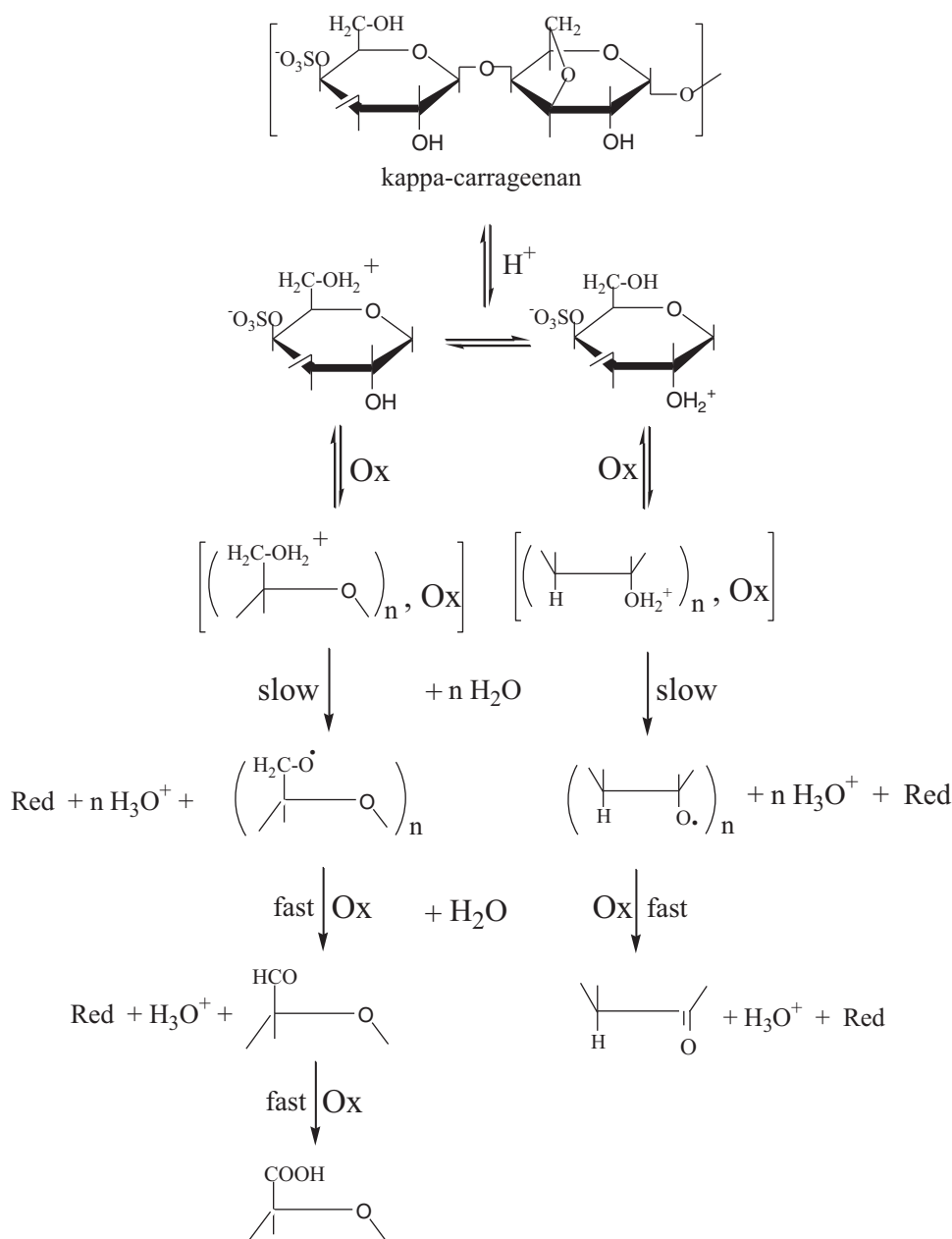
Two reaction mechanisms for electron-transfer may be suggested. The first one is corresponding to an outer-sphere mechanism which proceeds by formation of an outer ion pair,



Then, it followed by an electron-transfer process from the substrate to the oxidant prior to the proton releasing



where SH[•] and S[•] are the free-radical substrates. The second mechanism which may be considered involves the release of protons

**Scheme 1.** Mechanism of oxidation of kappa-carrageenan by cerium(IV) in aqueous perchlorate solutions.

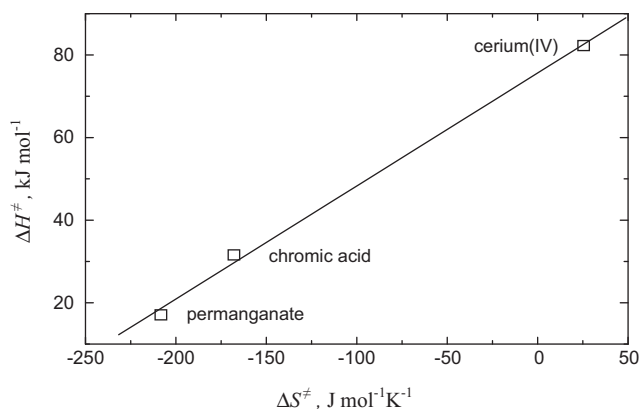


Fig. 6. Exener Isokinetic plot, ΔH^\ddagger vs. ΔS^\ddagger , for oxidation of kappa-carrageenan by various oxidants.

prior to the transfer of electrons and represents to an inner-sphere type as follows



Although, the rate-law expression provides no information on electron transfer, whether it is of inner- or outer-sphere nature, some information may be expected by examining the magnitude of the elementary rate constants and the activation parameters [30–36].

Unfortunately, no data are available about the formation constants in order to evaluate the rate constants of the principal elementary reaction. Indeed, the thermodynamic parameters observed for a series of common reactions may be considered as good evidence to support a certain reaction mechanism [37–40]. It has been suggested that ΔS^\ddagger values tend to be more positive for an outer-sphere type, whereas the reactions of inner-sphere nature tend to possess negative values for entropy of activation [37–40]. The entropy of activation obtained in the present work may suggest the presence of both inner- and outer-sphere mechanisms. Although, the outer-sphere mechanism is the more probable from the thermodynamic ground, the inner-sphere one can not be excluded from the kinetic points of view.

Leffler and Grunwald [41] have pointed out that many reactions show an isokinetic linear relationship $\Delta H^\ddagger = \alpha + \beta \Delta S^\ddagger$. As is shown in Fig. 6, a plot of ΔH^\ddagger against ΔS^\ddagger for the second-order rate constants (k') of the redox reactions involving various oxidants with the same substrate is fairly linear with $\alpha = 75 \text{ kJ mol}^{-1}$ and $\beta = 2.72 \text{ K}$ ($r \geq 0.99$). This linearity indicates that the kinetics of oxidations of these macromolecules may follow similar reaction mechanisms of one electron inner-sphere nature. The β value obtained is significant and reflects the high reactivity of these macromolecule substrates. Again, plots of ΔH^\ddagger vs. ΔS^\ddagger for the apparent rate constants (k_1' or k_1'') were also linear in these oxidation reactions which confirming our suggested mechanism.

In view of the foregoing experimental observations and the kinetic interpretations, a suitable reaction mechanism for the oxidation of KCAR by cerium(IV) may be suggested as shown in Scheme 1.

Appendix A. Appendix A



$$K = \frac{[\text{SH}^+]}{[\text{S}][\text{H}^+]}, \quad [\text{SH}^+] = K[\text{S}][\text{H}^+]$$



$$K_1 = \frac{[\text{C}]}{[\text{Ce}^{4+}][\text{SH}^+]}, \quad [\text{C}] = KK_1[\text{S}][\text{H}^+][\text{Ce}^{4+}]$$



$$\text{Rate} = -\frac{d[\text{Ce}^{4+}]}{dt} = k[\text{C}][\text{H}^+] = kKK_1[\text{S}][\text{H}^+]^2[\text{Ce}^{4+}] \quad (\text{i})$$

Since,

$$[\text{S}]_T = [\text{S}] + [\text{SH}^+] + [\text{C}]$$

$$[\text{S}]_T = [\text{S}] + K[\text{S}][\text{H}^+] + KK_1[\text{S}][\text{H}^+][\text{Ce}^{4+}]$$

$$[\text{S}]_T = [\text{S}](1 + K[\text{H}^+] + KK_1[\text{H}^+][\text{Ce}^{4+}])$$

$$[\text{S}] = \frac{[\text{S}]_T}{[\text{S}](1 + K[\text{H}^+] + KK_1[\text{H}^+][\text{Ce}^{4+}])} \quad (\text{ii})$$

Substituting Eq. (ii) into Eq. (i), gives

$$\text{Rate} = -\frac{d[\text{Ce}^{4+}]}{dt} = \frac{kKK_1[\text{H}^+]^2[\text{S}]_T[\text{Ce}^{4+}]}{1 + K[\text{H}^+] + KK_1[\text{H}^+][\text{Ce}^{4+}]} \quad (\text{A.4})$$

Under pseudo-first-order conditions in the presence of a large excess of KCAR over that of cerium(IV) concentration

$$\text{Rate} = k_{\text{obs}}[\text{Ce}^{4+}] \quad (\text{A.5})$$

Comparing Eqs. (5) and (4) and rearrangement, the following relationship is obtained

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K[\text{H}^+]}{kKK_1[\text{H}^+]^2} \right) \frac{1}{[\text{S}]_T} + \frac{[\text{Ce}^{4+}]}{k_1[\text{S}]_T[\text{H}^+]} \quad (\text{A.6})$$

Michaelis–Menten plot (Fig. 2) leads to simplify Eq. (6) to

$$\frac{[\text{H}^+][\text{S}]_T}{k_{\text{obs}}} = \frac{1}{kKK_1[\text{H}^+]} + \frac{K[\text{H}^+]}{kKK_1[\text{H}^+]} \quad (\text{A.7})$$

References

- [1] Z. Khan, K. Raju, Ud-Din, Colloids Surf. A 225 (2003) 75–83.
- [2] R.M. Hassan, J. Polym. Sci. A 31 (1993) 51–59.
- [3] R.M. Hassan, Polym. Int. 30 (1993) 5–9.
- [4] K.S. Khairou, R.M. Hassan, Eur. Polym. J. 36 (2000) 2021–2030.
- [5] A.M. Shaker, J. Colloid Interface Sci. 233 (2001) 197–204; A.M. Shaker, R.M. El-Khatib, H.S. Mahran, J. Appl. Polym. Sci. 106 (2007) 2668–2674.
- [6] R.M. El-Khatib, Carbohydr. Polym. 47 (2002) 377–385; A.M. Shaker, R.M. El-Khatib, I.A.E. Nassr, Carbohydr. Polym. 78 (2009) 710–716.
- [7] M.I. Abdel-Hamid, K.S. Khairou, R.M. Hassan, Eur. Polym. J. 39 (2003) 381–387.
- [8] R.M. Hassan, D.A. Abdel-Kader, S.M. Ahmed, A. Fawzy, I.A. Zaafarany, B.H. Asghar, H.D. Takagi, Catal. Commun. 11 (2009) 184–190; G.A. Ahmed, K.S. Khairou, R.M. Hassan, J. Chem. Res. 182 (2003) 2003–2008.
- [9] I.A. Zaafarany, A. Al-Arifi, A. Fawzy, G.A. Ahmed, S.A. Ibrahim, R.M. Hassan, H.D. Takagi, Carbohydr. Res. 345 (2010) 1588–1590; R.M. Hassan, A. Fawzy, G.A. Ahmed, I.A. Zaafarany, K.S. Khairou, J. Mol. Catal. 309 (2009) 95–102; G.A. Ahmed, A. Fawzy, R.M. Hassan, Carbohydr. Res. 342 (2007) 1382–1386.
- [10] M.I. Abdel-Hamid, G.A. Ahmed, R.M. Hassan, Eur. Polym. J. 37 (2001) 2201–2206.
- [11] R.M. Hassan, S.A. Ahmed, A. Fawzy, D.A. Abdel-Kader, Y. Ikeda, H.D. Takagi, Catal. Commun. 11 (2010) 611–615; I.A. Zaafarany, K.S. Khairou, R.M. Hassan, J. Mol. Catal. 302 (2009) 112–118.
- [12] S.K. Mishra, Y.K. Gupta, J. Inorg. Nucl. Chem. 30 (1968) 2991–3008.
- [13] S.K. Mishra, Y.K. Gupta, J. Chem. Soc. A (1968) 260–264.
- [14] J.J. Hardwick, E. Roberston, Can. J. Chem. 29 (1951) 818–828.
- [15] L.S.A. Dikshitulu, P. Vani, V.H. Rao, J. Inorg. Nucl. Chem. 43 (1981) 1261–1265.

- [16] H.G. Offiner, D.A. Skoog, *Anal. Chem.* 38 (1966) 1520–1523.
- [17] Z. Amzad, McAuely, *J. Chem. Soc. Dalton Trans.* (1974) 511–518.
- [18] F. Feigl, "Spot Tests", in *Organic Analysis*, Elsevier, London, 1960.
- [19] R.M. Hassan, M.A. Abd-Allah, *J. Mater. Chem.* 2 (1992) 609–611; M.A. Malik, M. Ilyas, Z. Khan, *Ind. J. Chem.* 48 A (2009) 189–193.
- [20] K.S. Khairou, R.M. Hassan, M.A. Shaker, *J. Appl. Polym. Sci.* 85 (2002) 1019–1023; R.M. Hassan, M.A. Abd-Allah, M.F. El-Zohary, *J. Appl. Polym. Sci.* 47 (1993) 1649–1652.
- [21] K.B. Wiberg, R. Stewart, *J. Am. Chem. Soc.* 78 (1956) 1214–1216.
- [22] K. Laidler, *Chemical Kinetics*, McGraw-Hill, New York, 1965.
- [23] A. Haugh, O. Smidsord, *Acta Chem. Scand.* 19 (1965) 341–351.
- [24] R.G. Schweiger, *Koll. Z.* 196 (1965) 47–55.
- [25] H. Thiele, K. Hallich, *Koll. Z.* 151 (1957) 1–12.
- [26] A. Awad, F. El-Cheikh, *J. Colloid Interfaces Sci.* 80 (1980) 107–110.
- [27] D.A. Rees, *Chem. Ind.* 636 (1972).
- [28] R.M. Hassan, *Polym. Int.* 31 (1993) 81–86.
- [29] M.G. Adamson, F.S. Dainton, P. Glenworth, *Trans. Farad. Soc.* 689 (1965).
- [30] F.B. Baker, T.W. Newton, M. Khan, *J. Am. Chem. Soc.* 64 (1960) 109–112.
- [31] L.S.A. Dikshitulu, V.H. Rao, S.N. Dindi, *Ind. J. Chem.* 19A (1980) 203–206.
- [32] A. Prakash, R.N. Mehrotra, B.C. Kapoor, *J. Chem. Soc. Dalton Trans.* (1979) 205–210.
- [33] M. Ardon, *J. Chem. Soc.* (1957) 1811–1815.
- [34] I.C. Tewari, S.R. Tripathi, *J. Inorg. Nucl. Chem.* 39 (1977) 2095–2097.
- [35] F.M. Moore, K.W. Hicks, *Inorg. Chem.* 14 (1975) 413–416.
- [36] K.W. Hicks, D.L. Toppen, R.G. Linck, *Inorg. Chem.* 11 (1972) 310–315.
- [37] N. Sutin, *Acc. Chem. Res.* 1 (1968) 225–231.
- [38] R.M. Hassan, *J. Coord. Chem. Rev.* 27 (1992) 255–266.
- [39] F. Freeman, *J. Am. Chem. Soc.* 103 (1981) 1154–11154.
- [40] K.W. Hicks, G.A. Chappelle, *Inorg. Chem.* 19 (1980) 1623–1631.
- [41] L. Leffler, E. Grunwold, *Rates and Equilibria of Organic Reactions*, Wiley, New York, 1963.