Carbohydrate Polymers 92 (2013) 2321–2326

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Kinetics and mechanism of oxidation of chondroitin-4-sulfate polysaccharide by chromic acid in aqueous perchlorate solutions

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ARTICLE INFO

Article history:
Received 8 August 2012
Received in revised form
20 November 2012
Accepted 21 November 2012
Available online 10 December 2012

Keywords:
Chondroitin-4-sulfate
Polysaccharides
Chromic acid
Catalysis
Oxidation
Kinetics
Mechanisms
Separation

ABSTRACT

The kinetics of chromic acid oxidation of chondroitin-4-sulfate polysaccharide as sulfated carbohydrates at a constant ionic strength of 4.0 mol dm^{-3} has been investigated, spectrophotometrically. The reaction kinetics showed a first-order dependence in chromic acid and fractional-first-order kinetics with respect to the chondroitin-4-sulfate concentration. The influence of [H$^+$] on the reaction rates showed that the oxidation process is acid-catalyzed. Added Mn^{2+} ions indicated the formation of Cr(IV) as intermediate species. A kinetic evidence for formation of 1:1 intermediate complex was revealed. The kinetic parameters have been evaluated and a tentative reaction mechanism in good consistent with the kinetic results obtained is discussed.

1. Introduction

Chondroitin-4-sulfate (CS) is a sulfated glycosaminoglycan (GAG) composed of a chain of alternating sugars (*N*-acetyl-galactosamine and glucuronic acid) (Baeurle, Kiselev, Makarova, & Nogovitsin, 2009).

Although, the kinetics of oxidation of alcohols by chromic acid was the subject of a large number of investigators (Das, 2004; Khan & Ud-Din, 2002; Lee, 1980; Wiberg & Schafer, 1967), a little attention has been focused to the oxidation of carbohydrates containing alcoholic groups by this oxidant. This fact may be attributed to the formation of unstable intermediates such as Cr^{V} and Cr^{IV} species during the reduction of chromium (VI) from hexavalent state to the trivalent ones as well as to the tendency of the formed chromium (III) to give a variety of complexes with the oxidation products of such macromolecules, all combine together to give systems of considerable complexity (Beatewa & Haight, 1972; Mitewa & Bontchev, 1985). Consequently, a mechanistic interest of chromium (VI) oxidation began with the inception of the chemical kinetics as a potential tool for studies of reaction mechanisms.

The kinetics of chromic acid oxidation of poly(vinyl alcohol) as a synthetic polymer (Abdel-Hamid, Ahmed, & Hassan, 2001) and kappa-karrageen (Zaafarany, Khairou, & Hassan, 2009) and carboxmethyl cellulose (Hassan et al., 2010) polysaccharides as natural polymers has been reported by Hassan and coworkers elsewhere. Unfortunately, their suggested reaction mechanisms are not complete owing to the large contrariety noticed in these redox systems.

In view of the above discrepancies and our interest in the kinetic studies of oxidation of macromolecules carrying alcoholic groups by various oxidants in acidic solutions (Abdel-Hamid, Khairou, & Hassan, 2003; Ahmed, Khairou, & Hassan, 2003; Hassan, 1993; Hassan et al., 2009), the present investigation seems to be of great importance to gain more information on the role of the reducing agent and the nature of medium on the kinetics and mechanistic of oxidation in terms of electron-transfer processes. Moreover, this research work aims to synthesize low-cost coordination biopolymer precursors which can be used as new chelating agents for removal of undesired toxic heavy metal cations and radionuclides from the environment, wastewater, soil and other contaminated matters.

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http://dx.doi.org/10.1016/j.carbpol.2012.11.062

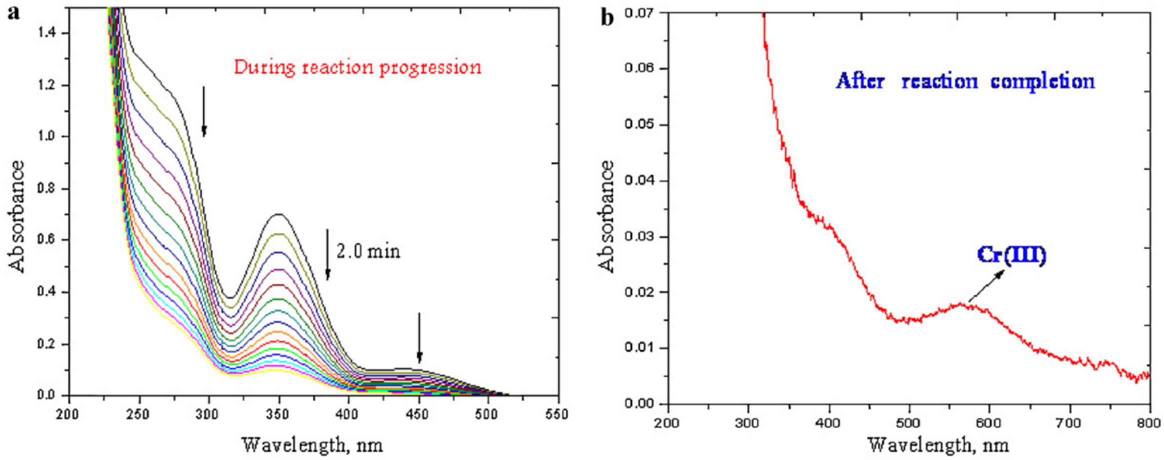

Fig. 1. Spectral changes (200–550 nm) in the oxidation of chondroitin-4-sulfate by chromic acid in aqueous perchloric acid (a) during the reaction progression and (b) after reaction completion. [Chromic acid] = 7.0×10^{-4}, [CS] = 1.5×10^{-2}, [H^+] = 3.0 and I = 4.0 mol dm^{-3} at 40 °C.

2. Experimental

2.1. Materials

Chondroitin-4-sulfate (ICN Biomedicals, Inc.) was used without further purification. Solutions of chondroitin-4-sulfate 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. All other reagents were prepared by dissolving the requisite amount of the reagent in bidistilled water.

2.2. Kinetic measurements

The kinetic measurements were conducted under pseudo-first-order conditions where the CS was present in a large excess over that of chromic acid concentration at a constant ionic strength of 4.0 mol dm^{-3}. The procedure of measurements was the same as described earlier (Abdel-Hamid et al., 2001; Hassan et al., 2010; Zaafarany et al., 2009). 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 ±0.05 °C on a Shimadzu UV-2101/3101 PC automatic scanning double-beam spectrophotometer fitted with a wavelength program controller using cells of a pathlength 1 cm. The spectral changes during the oxidation reaction and after the reaction completion are shown in Fig. 1.

3. Results and discussion

3.1. Stoichiometry

Reaction mixtures containing known different initial concentrations of the reactants were equilibrated for about 48 h at room temperature in a set of experiments. The unreacted chromic acid was estimated periodically until it reached a constant value, i.e. reaction completion. A stoichiometric ratio of ([chromic acid]$_{consumed}$/[CS]$_0$) was found to be 2.62 ± 0.1 mol. This result conforms to the following stoichiometeric overall reaction:

$$3(C_{14}H_{21}NO_{14}S^-)_n + 8H_2CrO_4 + 24H^+ = 3(C_{14}H_{15}NO_{15}S^-)_n + 8Cr^{3+} + 29H_2O \quad (1)$$

where $C_{14}H_{21}NO_{14}S$ and $C_{14}H_{15}NO_{15}S$ represent the chondroitin-4-sulfate and its corresponding keto-acid derivative, respectively. The reaction product was separated and identified by elemental analysis and spectral data. The product was identified by the reaction with 2,4-dinitrophenylhydrazine and hydroxyl amine to afford the formation of the corresponding 2,4-dinitrophenylhydrazone and dioxime, respectively, as described elsewhere (Khairou, Hassan, & Shaker, 2002; Malik, Ilyas, & Khan, 2009). The decay of the band at 3450 cm^{-1} and the disappearance of that at 1700 cm^{-1} would suggest the transformation of secondary alcohols (—OH) to the corresponding keto (=CO) groups. Formation of Cr^{III} as the final reduced form of Cr^{VI} oxidant was detected after the reaction completion (Fig. 1b).

3.2. Dependence of reaction rates on [$HCrO_4^-$] and [CS]

Plots of ln absorbance vs. time were linear for more than three-half lives of reaction completion and found to be independent on the initial concentration of chromic acid varied from $(1–6) \times 10^{-4}$ mol dm^{-3}. This independency confirms that the reaction is first-order in chromic acid concentration. The pseudo-first-order rate constants, k_{obs}, can be evaluated from the gradients of such plots. These values were calculated by the least-squares method. The value of k_{obs} under the condition of [OX] = 7×10^{-4}, [S] = 1.5×10^{-2}, [H^+] = 2.0, [I] = 4.0 mol dm^{-3} and 40 °C was found to be 5.9×10^{-4} s^{-1}.

The non-constancy of the second-order rate constants obtained by dividing the k_{obs} values by [CS]$_0$ at fixed [chromic acid] indicated that the reaction was fractional first-order kinetics in [CS]$_0$. This dependency was found to obey the Michaelis–Menten kinetics for formation of 1:1 intermediate complex. A typical reciprocal Michaelis–Mentent plot is shown in Fig. 2.

Some kinetic experiments were performed by using dichromate ion ($Cr_2O_7^{2-}$) as an oxidant in order to examine the effect of the variation of oxidant conformation on the oxidation rates. The small differences observed between the two rates (Table 1) may be attributed to the large steric hindrance which faces $Cr_2O_7^{2-}$ oxidant of large size during its penetration between the two adjacent

Table 1
Effect of manganous ions on the reaction rate in the oxidation of chondroitin-4 sulfate by chromic acid in aqueous perchloric. [Chromic acid] = 7.0×10^{-4}, [CS] = 1.5×10^{-2}, [H^+] = 3.0 and I = 4.0 mol dm^{-3} at 40 °C.

10^3[$MnSO_4$] (mol dm^{-3})	0.0	0.5	1.0	5.0
10^4 k_{obs} (s^{-1})	8.04	6.66	5.40	5.11

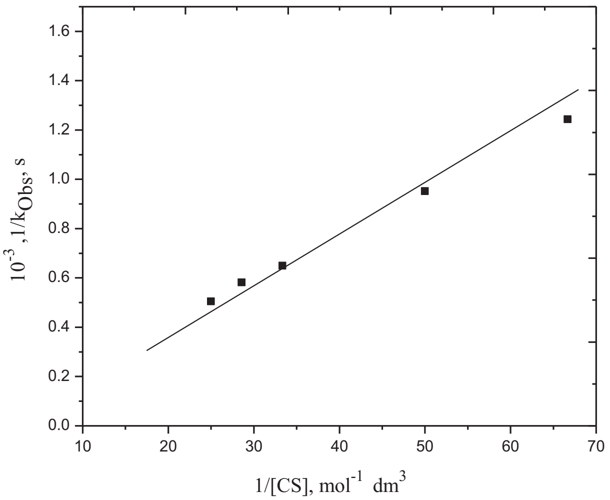

Fig. 2. A reciprocal Michaelis–Menten plot for the oxidation of chondroitin-4-sulfate by chromic acid in aqueous perchloric acid. [Chromic acid] = 7.0×10^{-4}, $[H^+] = 3.0$ and I = 4.0 mol dm^{-3} at 40 °C.

functional alcoholic groups in CS monomers in order to form the intermediate complex (C_1) compared to that observed in case of small size $CrO_4{}^{2-}$ oxidant.

The values of the two rate constants were found to be in the same order of magnitude which may indicate that the reactive attacking species of the oxidants is Cr^{VI} ion in both cases.

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

Kinetic measurements were performed in $HClO_4$–$NaClO_4$ solutions with different hydrogen ion concentrations and constants of ionic strength and temperature in order to clarify the influence of $[H^+]$ on the reaction rates as well as to elucidate a suitable reaction mechanism. An increase in the acid concentration was found to accelerate the oxidation rates indicating that the oxidation process is acid-catalyzed. It is not surprising to notice a such increase in the reaction rates with increasing $[H^+]$ since the net reaction is the transformation of either oxyanion, $HCrO_4{}^-$ or H_2CrO_4, from tetrahedral to octahedral configuration (hydrated cation $Cr(H_2O)_6{}^{3+}$), which needs to consume some hydrogen ions in acidic media (Hicks, 1976).

Some kinetic runs were performed using sulfuric and hydrochloric acids as a source of hydrogen ions in order to examine the influence of the nature of acids on the reaction rates. The kinetic results are summarized in Table 1. The kinetic results indicated that the magnitude of the oxidation rates was decreased in the order $HClO_4 > H_2SO_4 > HCl$, respectively. This means that the anion of the acid may play a role in the oxidation kinetics. Sulfates and chlorides are well-known to have a high tendency to form complexes (Cotton & Wilkinson, 1996), whereas perchlorate anion is known to be extremely inert. Therefore, it may be possible to suggest the formation of some intermediate complexes in case of sulfates and chlorides prior to the rate-determining steps which in turn tend to retard the oxidation process rather than in the former case of inert perchlorate anion (Table 2).

3.4. Dependence of reaction rates on ionic strength

To shed some lights on the reactive species in the rate-determining step, the influence of the ionic strength on the reaction rates was examined. Kinetic runs were performed at constant $[H^+] = 3.0$ mol dm^{-3} as $NaClO_4$ concentration was increased to 5.0 mol dm^{-3}. The values of k_{obs} were found to increase with increasing the ionic strength. A plot of $\ln k_{obs}$ against $I^{0.5}/(1 + I^{0.5})$ according to the extended Bronsted–Debye–Hückel relationship gave good straight line with positive slope (not found). The values of the observed rate constants at ionic strengths of 3, 4 and 5 mol dm^{-3} were found to be 7.5×10^{-4}, 8.1×10^{-4} and 9.0×10^{-4} s^{-1}, respectively. The ionic strength dependence was qualitatively as expected when considering the charges involved (Laidler, 1965).

Table 2
Effect of variation of added mineral acids and variation of Cr(VI) in the oxidation of chondroitin-4-sulfate by chromic acid in aqueous perchloric acid. [CS] = 1.5×10^{-2}, [OX] = 7.0×10^{-4}, $[H^+] = 3.0$, and $I = 4.0$ mol dm^{-3} at 40 °C.

Acid	k_{obs} (s^{-1})	$[Cr^{VI}]$	k_{obs} (s^{-1})
$HClO_4$	8.04×10^{-4}	K_2CrO_4	8.04×10^{-4}
H_2SO_4	1.45×10^{-4}	$K_2Cr_2O_7$	6.54×10^{-4}
HCl	2.10×10^{-5}		

3.5. Polymerization test

Formation of an appreciable white precipitate on adding 10% (v/v) of acylonitrile to the partially oxidized reaction mixtures on warming indicates the intervention of free-radical mechanism.

3.6. Influence of the manganous ions on the rates

In order to check the involvement of Cr^{IV} as an intermediate during the progress of oxidation reaction, the effect of addition of manganous ions to the reaction mixture has been examined (Espenson, 1970; Khan & Id-Din, 2001; Stewart, 1965). The reaction rates were found to decrease linearly with increasing the added Mn^{+2} ions. The experimental results are summarized in Table 2.

In general, two reaction mechanisms for electron-transfer in redox reactions involving chromium (VI) as an oxidant may be suggested. The first one corresponds to successive one-electron-transfer mechanism $Cr^{VI} \rightarrow Cr^{V} \rightarrow Cr^{IV} \rightarrow Cr^{III}$ in a sequence. The second mechanism involves a simultaneous two-electron changes $Cr^{VI} \rightarrow Cr^{IV} \rightarrow Cr^{II}$ in a single step. This means that both one-electron transfer and two-electron changes may be considered for oxidation of carbohydrates by chromium (VI) with formation of either Cr^{V} or Cr^{IV} intermediate species, respectively (Stewart, 1965; Espenson, 1970; Khan & Id-Din, 2001; Zaafarany et al., 2009). The involvement of chromium (IV) as an intermediate in those redox reactions has generated much debate in the past (Khan & Id-Din, 2001). Therefore, the influence of addition of manganous ion on the oxidation rates is considered as good evidence to determine the involvement of chromium (IV) as an intermediate during the progress of reaction. This is because Mn(II) has been recognized as frequently tool for trapping of Cr(IV) intermediate.

The estimated redox potentials of Cr^{VI}/Cr^{III} ($E^\circ = 1.33$ V) and Mn^{III}/Mn^{II} ($E^\circ = 1.\ 51$ V) couples indicated that the oxidation of Mn^{II} by Cr^{VI} is unfavorable based on the thermodynamic grounds (Manhas, Kumar, Mohamed, & Khan, 2008; Milazzo, Caroli, & Sharma, 1978). Therefore, if chromium (IV) intermediate is involved, the addition of Mn^{+2} to the reaction mixture will remove it from the oxidation reaction as follows:

$$Cr^{IV} + Mn^{II} = Cr^{III} + Mn^{III} \qquad (2)$$

Then, addition of manganese (II) to the reaction mixture should be accompanied by a decrease in the oxidation rates as was experimentally observed (Table 2). Such a behavior was observed in most oxidation reactions of organic substrates by this oxidant (Sen Gupta, Chakladar, Chatterjee, & Chakladar, 1973; Sen Gupta & Chakladar, 1974). Although, the formed manganese (III) is a strong competitor oxidant to chromic acid and, hence, is capable to oxidize the protonated substrate, but its oxidation is negligible. This

Table 3

The activation parameters of apparent rate constants and the second-order rate constants in the oxidation of chondroitin-4-sulfate by chromic acid in aqueous perchloric acid. [Chromic acid] = 7.0×10^{-4}, [CS] = 1.5×10^{-3} and I = 4.0 mol dm^{-3}.

Rate constant	Parameter				
	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta G^{\neq}{}_{298}$ (kJ mol^{-1})	$E_a{}^{\neq}$ (kJ mol^{-1})	A (mol^{-1} s^{-1})
k'[a]	37.53	−152.29	82.92	39.70	1.66×10^5
k_a'	31.82	−174.55	83.84	34.52	14.04×10^3
k_a''	56.15	−78.53	79.55	58.76	1.41×10^9

Experimental error ± 4%.

[a] Second-order rate constant measured at [H$^+$] = 3.0 mol dm^{-3}.

fact can be explained by the unstability of Mn(III) which undergoes a rapid disproportionation[1] under our experimental conditions of hydrogen ion used (Adler & Noyes, 1954; Gopalan & Sugumar, 1977).

Considering the values of protolytic and hydrolytic equilibrium constants for chromium (VI) in aqueous perchlorate solutions (Banas, 1981; Espenson & Wang, 1972), it may be reasonable to assume that the main recative chromium (VI) ions are H_2CrO_4 species since the quantity of the dimeric form is negligible small under our experimental conditions. Again, using the reported values for the protonation constants (K) of chromic acid (Banas, 1981; Espenson & Wang, 1972; Tong & King, 1953), the formed H_2CrO_4 was found to range between 80 and 95% of the total analytical concentration of Cr(VI) under our experimental conditions of the hydrogen ion concentrations used. Therefore, the kinetic results obtained from the hydrogen ion dependence of the rate constants can be explained on the basis of prolytic processes of both oxidant and the substrate in acidic medium (Abdel-Hamid et al., 2001; Hassan et al., 2010; Zaafarany et al., 2009) according to the following equilibria

$$HCrO_4^- + H^+ \overset{K}{\rightleftharpoons} H_2CrO_4 \tag{3}$$

$$S + H^+ \overset{K_1}{\rightleftharpoons} SH^+ \tag{4}$$

where S and SH$^+$ represent CS and its protonated form; while K and K_1 are the protonation constants of chromic acid and CS, respectively.

In view of the above interpretations and our experimental results, the most suitable reaction mechanism which may be suggested, involves a fast complexation between chromic acid and the protonated form of the substrate to give the intermediate (C_1), followed by a slow decomposition of such intermediate in the rate-determining step to give free-radical substrate and the reduced form of oxidant, Cr^{IV}, as initial oxidation products with subtraction of H_3O^+ ions as follows

$$H_2CrO_4 + SH^+ \overset{K_2}{\rightleftharpoons} C_1 + H^+ \tag{5}$$

$$C_1 \underset{\text{slow}}{\overset{k_a}{\rightleftharpoons}} S^{\bullet} + Cr^{IV} + n\,H_3O^+ \tag{6}$$

The formed radical is rapidly oxidized by either a further new oxidant molecule or by the Cr^{IV} formed as intermediate species to give rise to the reaction of oxidation products as described by Eqs. (7) and (8)

$$Cr^{VI} + S^{\bullet} \xrightarrow{\text{fast}} \text{products} + Cr^{IV} \tag{7}$$

$$Cr^{IV} + S^{\bullet} \xrightarrow{\text{fast}} \text{products} + Cr^{III} \tag{8}$$

$$2Cr^{IV} = Cr^{III} + Cr^{V} \tag{9}$$

$$Cr^{V} + Cr^{V} = Cr^{IV} + Cr^{VI} \tag{10}$$

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

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[H^+]}{k_a K K_1 K_2 [H^+]} \right) \frac{1}{[S]_T} + *K', \qquad *K' = \frac{[CrO_4{}^{2-}]}{k_a [H^+][S]_T} \tag{11}$$

where $[S]_T$ is the analytical total concentration of the substrate. Eq. (11) requires that at constant [H$^+$] plots of $(k_{obs})^{-1}$ against $1/[S]_T$ should to be linear with positive intercepts on $(k_{obs})^{-1}$ axis as was experimentally observed (Fig. 2). Again, plots of $(k_{obs})^{-1}$ against 1/[H$^+$] at constant [S] gave good straight lines with positive intercepts on $1/k_{obs}$. The small intercept observed in Fig. 2 may lead us to simplify Eq. (11) to (12),

$$\frac{[S]_T}{k_{obs}} = \left(\frac{[H^+]^{-1}}{k'_a} + \frac{1}{k''_a} \right) \tag{12}$$

where $k_a' = k_a K K_1 K_2$ and $k_a'' = k_a K K_2$, respectively. According to Eq. (12), plots of $[S]_T/k_{obs}$ vs. 1/[H$^+$] gave good straight lines with positive intercepts on $[S]_T/k_{obs}$ axis (Fig. 3), from whose slopes and intercepts the values of the apparent rate constants, k_a' and k_a'', and the protonation constants of the substrate, K_1, can be evaluated. These values were calculated by the least-squares method. The calculated values of protonation constants (K_1), at [OX] = 7×10^{-4}, [S] = 1.5×10^{-2} and I = 4.0 mol dm^3, were found to be 0.17 and 0.08 dm^3 mol^{-1} at 25 °C and 45 °C, respectively. These values were found to be in good agreement and with the same order of magnitude to that reported previously for oxidation of some other macromolecules by this oxidant (Abdel-Hamid et al., 2001; Hassan et al., 2010; Zaafarany et al., 2009). This result may be considered as indirect evidence to support the present proposed mechanism. The thermodynamic parameters of the protonation constants were calculated by using the well-known thermodynamic methods and

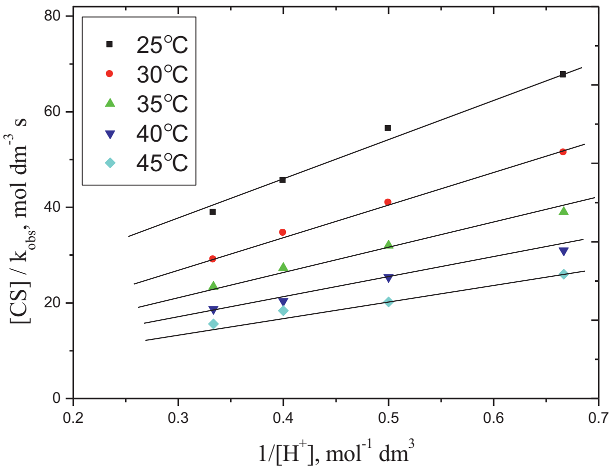

Fig. 3. Plots of [CS]/k_{obs} vs. $[H^+]^{-1}$ in the oxidation of chondroitin-4-sulfate by chromic acid in aqueous perchloric acid. [Chromic acid] = 7.0×10^{-4}, [CS] = 1.5×10^{-2} and I = 4.0 mol dm^{-3} at various temperatures.

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[1] As recommended by the referee.

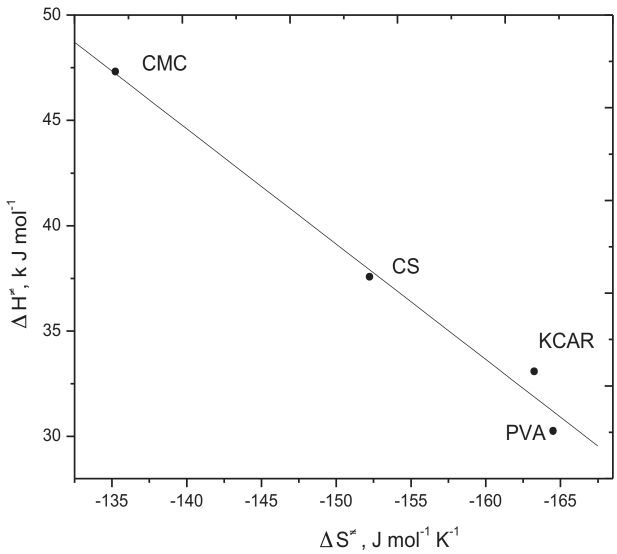


Fig. 4. An isokinetic plot, $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$, of the second-order rate constant in the oxidation of some carbohydrates by chromic acid in aqueous perchloric acid.

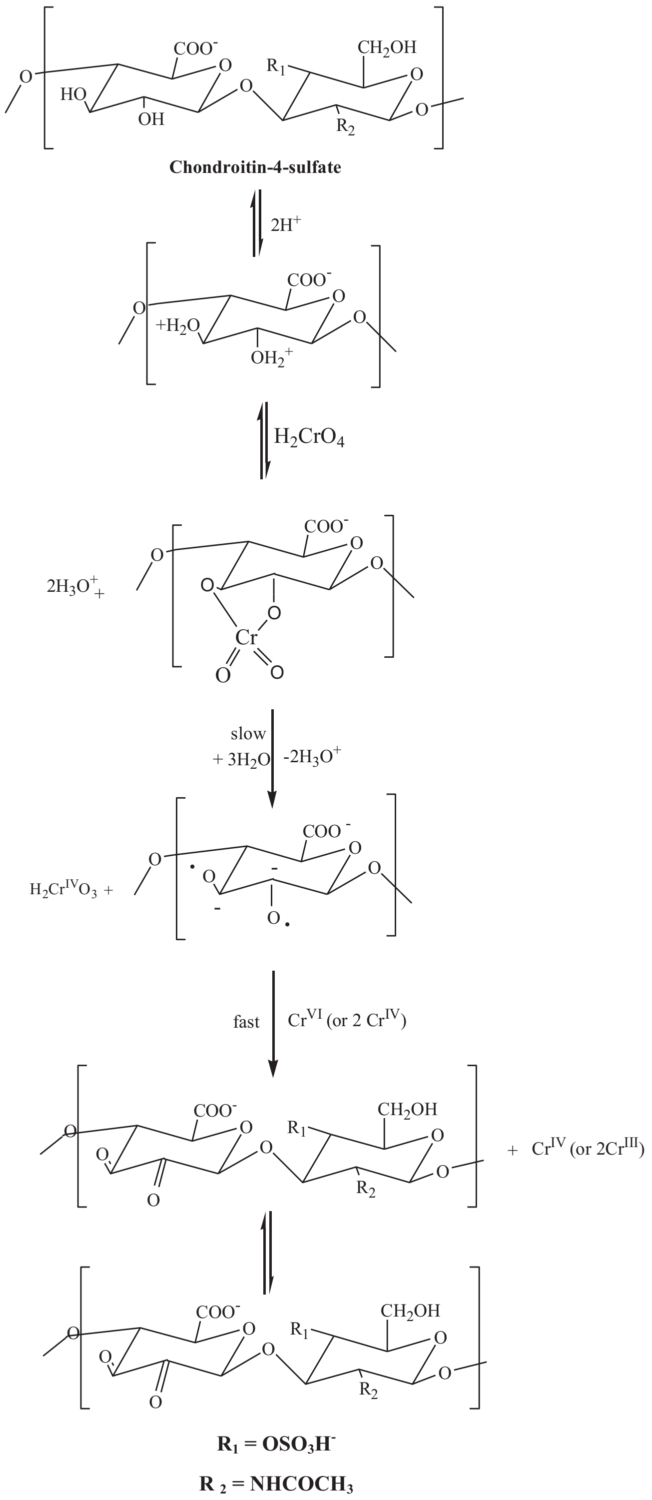
found to be $-23.76\,\text{kJ mol}^{-1}$, $-94.36\,\text{J mol}^{-1}\,\text{K}^{-1}$ and $+4.36\,\text{kJ mol}^{-1}$ for ΔH°, ΔS° and ΔG° values, respectively. The negative value of ΔH° obtained indicates that the prolytic process of substrate is of exothermic nature.

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) 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. The activation parameters of the apparent rate constants ($k_a{}'$ and $k_a{}''$) and second-order rate constant (k') were calculated from the temperature dependence of the rate constants from Arrhenius and Eyring equations by using the method of least-squares and are summarized in Table 3. The positive value observed for $\Delta G^{\neq}$ may confirm the non-spontaneity of the complex formation in the rate-determining step as suggested by the proposed mechanism.

The observed small activation energy value, $E_a{}^{\neq}$ (Table 3), may support that the reaction takes place between a cation and a neutral molecule as was deduced from the ionic strength dependency of the rate constants. Therefore, the electrostatic attraction between the reactants does not need much energy to bring them together in order to form the activated complex.

Stewart (1965), Hassan, Mousa, and Shatoury (1988), Hassan (2011) and Hicks (1976) reported that the entropy on activation, $\Delta S^{\neq}$, is negative for oxidation reactions that proceeding via complex formation of inner-sphere nature; while the values of $\Delta S^{\neq}$ for the outer-sphere mechanisms tend to be more positive. Therefore, the observed negative values of $\Delta S^{\neq}$ obtained in the present investigation may exhibit reactions of inner-sphere mechanism. This means that the oxidation of CS by chromic acid is more favorable to proceed by inner-sphere path rather than by outer-sphere mechanism. In this context, it should be noted that there does not appear to be any experimental confirmation of outer-sphere two-electron transfer process (Hassan, 2011; Hassan et al., 1988). Again, the negative values observed for the entropies of activations, $\Delta S^{\neq}$, may confirm the compactness of the intermediates formed.

Furthermore, Leffler and Grunwald have pointed out that many redox reactions show isokinetic relationship given by $\Delta H^{\neq} = \alpha + \beta \Delta S^{\neq}$. Therefore, these kinetic parameters of the second-order rate constants for oxidation of some macromolecules by this oxidant have been examined. A plot of $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ was found to be linear (Fig. 4) with α and β values equal to 126 kJ and 580 K, respectively. This linearity may indicate that these redox systems follow similar reaction mechanism of inner-sphere nature. Also, the β value obtained is significant and may be considered as a deserved comment.



Scheme 1. Mechanism of oxidation of CS by chromic acid.

A suitable reaction mechanism in good consistent with the observed kinetic results may be suggested by Scheme 1. It involves a rapid attack of the protonated substrate by chromic acid oxidant to form the intermediate complex (C_1). Then, the intermediate is decomposed in the rate-determining step to give free-radical substrate and Cr^{IV} ion as initial oxidation products. The substrate radical is further oxidized very rapidly by either a further molecule of chromic acid or by the formed Cr^{IV} oxidants to give rise to the oxidation products. The formation of such intermediate complexes has been postulated in many redox reactions involving organic alcohols by this oxidant (Hasan & Rocek, 1976).

In general, biopolymers could be used as biocatalysts and to encapsulate, protect and deliver bioactive or functional components such as minerals, peptides, proteins, enzymes, drugs, lipids or dietary fibers. This means that the oxidation products of CS can be used as coordination polymeric biomaterials in such purposes. In addition, the high tendency of the product to chelate with Ca(II), Ba(II), Cd(II), Pb(II) and Ag(I) metal cations forming the corresponding coordination biopolymer complexes can be used for removal of the toxic heavy metal cations from the environment, wastewater and other contaminated resources. The characteristics of the prepared coordination biopolymer complexes are in progress in our laboratory.

Acknowledgment

This work is dedicated to the memories of professor Mohamed A. Abd-Alla, Professor of Polymer Chemistry & Professor Mohamed Tharwat Makhlouf, Professor of Physical Chemistry, Faculty of Science, Assiut University, Assiut, Egypt.

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