

Acid catalyzed Oxidation: Kinetics of Oxidation of Methyl Cellulose Polysaccharide as A Natural Polymer by Chromic Acid in Aqueous Perchlorate Solutions with Novel Synthesis of Coordination Biopolymer Precursors

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ABSTRACT: The kinetics of chromic acid oxidation of methyl cellulose (MC) in aqueous acidic solutions has been investigated at constant ionic strength of 4.0 mol dm^{-3} , spectrophotometrically. The experimental results showed first-order dependence in chromic acid and fractional first-order kinetics with respect to [MC]. A kinetic evidence for formation of 1:1 intermediate complex was revealed. The hydrogen ion dependence of reaction rates indicated that the oxidation process is acid-catalyzed. The activation parameters have been evaluated and a tentative reaction mechanism consistent with the kinetic results is suggested. The oxidation product of the substrate has been separated as coordination biopolymer chelating agent precursor and was identified by elemental analysis and IR spectra. Its tendency for the oxidation product for chelating the polyvalent metal cations has been examined.

KEYWORDS: Methyl cellulose, Polysaccharide, Chromic acid, Kinetics, Oxidation, Mechanism.

I. INTRODUCTION

Methyl cellulose (MC) is a polysaccharide of amphiphilic character. The associative properties depends on the distribution of methyl substituent (moieties) present in the cellulosic backbone on C-2, C-3 and C-6 positions [1].

The kinetics of oxidation of some polysaccharides as natural polymers [2-7] and pol(vinyl alcohol) as a synthetic polymer [8,9], both of which containing alcoholic groups by using permanganate ion as a multi- equivalent oxidant in either alkaline [2-7] or acidic solutions [10-13] have been previously investigated in more details owing to their great importance and wide applications in industrial technology such as in medicine, pharmaceuticals, food and tissue engineering [14,15].

Although, chromic acid is a strong multi-equivalent oxidizing agent which has been widely used for oxidation of most inorganic and organic substrates in particularly alcohols [16-25], little attention has been focused to the oxidation of alcoholic polysaccharides such as methyl cellulose by this oxidant.

This fact may be attributed to the recognized complexity of kinetics in redox reactions involving chromic acid as an oxidant [26]. This complexity may be arisen from the existence of various species of chromium(VI) in aqueous solutions and the formation of unstable intermediate Cr (V) and Cr(IV) species during the reduction of hexavalent

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chromium ion to its trivalent oxidation state as well as the high tendency of the formed chromium(III) to form complexes with the oxidation product, all together combine to give reactions of considerable complexity. Therefore, a multiplicity of reaction mechanisms have been suggested for the redox systems that involving chromic acid as an oxidant, depending on the nature of the reducing agent and the reaction conditions [27].

Eventhough, Hassan and coworkers studied the kinetics of oxidation of carboxymethyl cellulose (CMC)[28], kappa-carrageenan (KCAR) [12]and chondroitin-4-sulfate (CS) [12] polysaccharides as natural polymers and poly (vinyl alcohol) as synthetic polymer (PVA) (Abdel-Hamid et al. 2001) which containing alcoholic groups by chromic acid in acidic solutions. The oxidation processes were found to proceed via formation of 1:1 intermediate complexes in CMC, PVA and CS reactions, whereas 1:2 intermediate complex was revealed in oxidation in case of oxidation of KCAR substrates. The reaction rates obtained exhibited different orders in hydrogen ion concentration. Again, the oxidation was found to proceed through free-radical intervention mechanism in those redox reactions except of oxidation of PVA reaction. Therefore, the mechanistic pathway, electron-transfer processes and the nature of the transition states in the rate-determining steps in these redox reactions still remain incomplete and controversial.

In view of the above discrepancies and our interest in the kinetics of oxidation of such substrates by various oxidants, the present investigation has been undertaken with the aims of shedding more light on the role of the medium and substrate on the reaction kinetics and mechanistics in terms of the nature of electron-transfer and transition state in the rate determining steps. Moreover, the present work aims to synthesize new keto-derivative as a biodegradable coordination biopolymer precursor chelating agent which can be used for the removal of undesired toxic metal cations from the environment, soil and wastewaters and as a biocatalyst in the technological industry.

II. EXPERIMENTAL SECTION

Materials

All materials employed in the present work were of analytical grade. Doubly distilled conductivity water was used in all preparations. Stock solutions of potassium chromate in doubly distilled water were standardized iodometrically. The solution of potassium chromate was stored in a dark bottle to avoid the influence of sun-light.

Methyl cellulose (MP Biomedicals, LLC) was used without further purification. The viscosity of 2 % solution was found to be 4000 centipoise at 20 °C. The molecular weight is about 50.000 Dalton. The preparation of the stock solution of MC was the same as described elsewhere [28]. This procedure was performed by the addition of methyl cellulose powder reagent to bidistilled water whilst rapidly stirring the solution to avoid the formation of lumps which swell with difficulty.

The temperature was controlled within $\pm 0.05^\circ\text{C}$. Perchloric acid solutions were prepared from 70% perchloric acid (BDH analytical reagent).

Kinetic Measurements

The kinetic measurements were conducted under pseudo-first-order conditions where MC was present in a large excess over that of chromic acid concentration at a constant ionic strength (I) of 4.0 mol dm^{-3} . The procedure of measurements was the same as described elsewhere [11,12,18,28]. The course of reaction was followed by recording the decrease in absorbance of chromic acid at its absorption maximum, 350 nm, as a function of time. It was verified that there is no interference from other reagents at this wavelength. The absorbance measurements were made in a thermostated cell compartment at the desired temperature within $\pm 0.05^\circ\text{C}$ on a Shimadzu UV-2101/3101 PC automatic scanning double-beam spectrophotometer fitted with a wavelength program controller using cells of a path length 1cm. The spectral changes during the progress of oxidation reaction are shown in Fig. 1.

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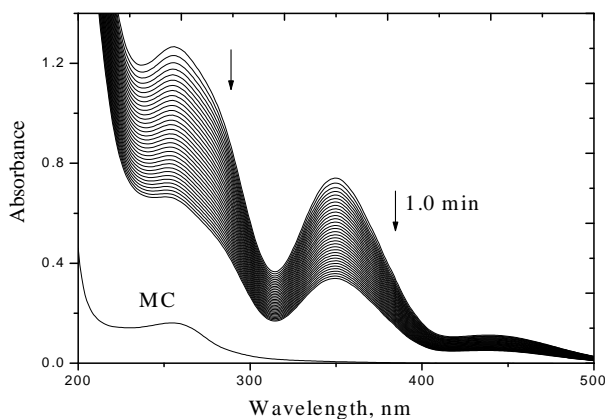
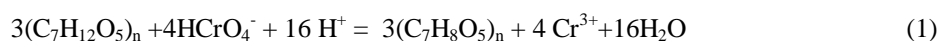


Fig. 1. Spectral changes (200 – 500 nm) in the oxidation of MC by chromic acid in aqueous perchloric acid. [Chromic acid] = 7.0×10^{-4} , [MC] = 3.0×10^{-2} , $[H^+] = 3.0$ and $I = 4.0 \text{ mol dm}^{-3}$ at 35°C .

III. RESULTS

Stoichiometry

Since the reaction kinetics seems to be of complexity, it is important to determine the stoichiometry of the overall reaction of the present work. Reaction mixtures containing different initial concentrations of the reactants in $2.0 \text{ mol dm}^{-3} \text{ HClO}_4$ were equilibrated for about 48 h at room temperature. The unreacted chromic acid was estimated periodically until it reached a constant value, i.e. reaction completion. The estimated stoichiometric ratio of ($[\text{chromic acid}]_{\text{consumed}} / [\text{MC}]_0$) was found to be $1.33 \pm 0.1 \text{ mol}$. This result indicates that the stoichiometry of the overall reaction conforms to the following equation



where $(\text{C}_7\text{H}_{12}\text{O}_5)_n$ and $(\text{C}_7\text{H}_8\text{O}_5)_n$ represent the MC and its corresponding diketo oxidation derivative, respectively. 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 [29-31]. The enhancement of the band of OH group at 1700 cm^{-1} would suggest the transformation of secondary alcohols (-OH) to its corresponding keto (C=O) groups. This would be consistent with the results displayed in Fig.2.

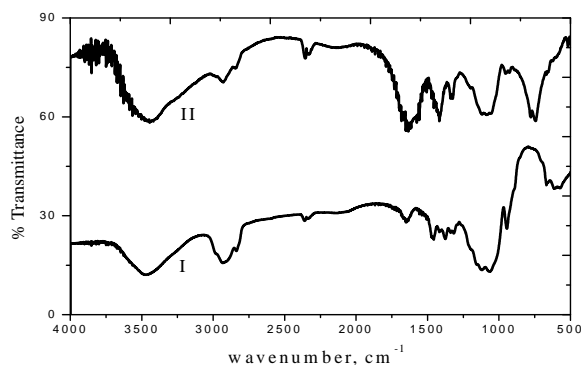


Fig.2. FTIR spectra of MC (I) and its diketo derivative (II).

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Plots of $\ln(\text{absorbance})$ vs. time were found to be linear for more than two-half lives of reaction completion. This linearity indicates that the reaction is first-order kinetics in chromic acid concentration. Pseudo-first-order rate constants (k_{obs}) were obtained from the gradients of such plots using the least-squares method and are summarized in Table 1.

Table 1. Dependence of observed pseudo-first-order rate constants (k_{obs}) on $[\text{H}^+]$ and $[\text{MC}]$ in the oxidation of MC by chromic acid in aqueous perchloric acid. $[\text{Chromic acid}] = 7.0 \times 10^{-4}$ and $I = 4.0 \text{ mol dm}^{-3}$ at 40°C .

$[\text{H}^+]^a$	$10^3 k_{obs}, \text{s}^{-1}$	$10^2 [\text{MC}]^b, \text{mol dm}^{-3}$	$10^3 k_{obs}, \text{s}^{-1}$
2.0	0.37	3.0	0.77
3.0	0.77	5.0	1.27

a- $[\text{MC}] \text{ used} = 3 \times 10^{-2} \text{ mol dm}^{-3}$

b- $[\text{H}^+] \text{ used} = 3.0 \text{ mol dm}^{-3}$

The first-order dependency was confirmed not only by the linearity of the pseudo-first-order plots, but also by the independence of the rate constants obtained at different initial concentrations on chromic acid used ($(5 - 10) \times 10^{-4} \text{ mol dm}^{-3}$) in a number of steps at constant concentrations of all other reagents. The dependence of k_{obs} values on the MC were deduced from the measurements of the observed first-order rate constants at several $[\text{MC}]_0$ and fixed chromic acid concentration. The non-constancy of the second-order rate constants obtained from dividing the observed first-order rate constants by $[\text{MC}]_0$ indicates that the rate is fractional first-order with respect to $[\text{MC}]$. Furthermore, when the reciprocals of the observed first-order rate constants, $(k_{obs})^{-1}$, were plotted against the reciprocals substrate concentration, $[\text{MC}]^{-1}$, straight lines with positive intercepts on the $(k_{obs})^{-1}$ axis were obtained as shown in Fig.3. This behavior indicates that the present redox reaction exhibits the Michaelis-Menten kinetics for formation of 1:1 intermediate complex.

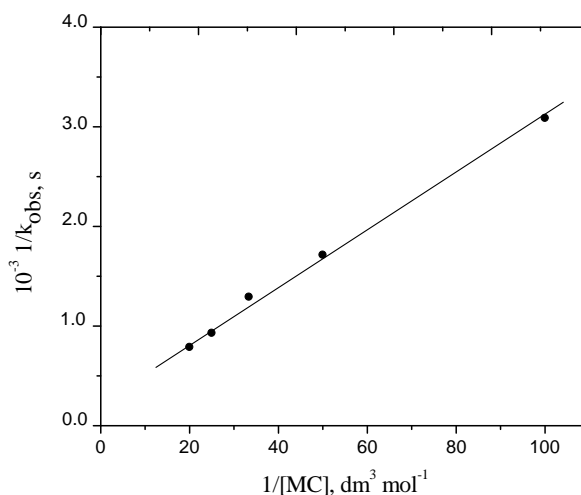


Fig. 3. A reciprocal Michaelis-Menten plot for the oxidation of MC by chromic acid in aqueous perchloric acid. $[\text{Chromic acid}] = 7.0 \times 10^{-4}$, $[\text{H}^+] = 3.0$ and $I = 4.0 \text{ mol dm}^{-3}$ at 40°C .

Influence of $[\text{H}^+]$ on the Reaction Rates

In order to examine the influence of $[\text{H}^+]$ on the reaction rates, some kinetic runs were performed in $\text{HClO}_4\text{-NaClO}_4$ solutions of different $[\text{H}^+]$ and constants of ionic strength and temperature. An increase in the acid concentration was

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found to accelerate the reaction rates as shown in Table 1. The reaction order with respect to $[H^+]$ was found to be of fractional-second-order 1.8 ± 0.1 ($\log k_{obs} - \log [H^+]$ plot).

Influence of Ionic Strength on the Reaction Rates

In order to investigate the effect of ionic strength (I) on the rate of reaction with the aims to throw some light on the reactive species in the rate-determining step, kinetic runs were performed at constant $[H^+] = 3.0 \text{ mol dm}^{-3}$ as the NaClO_4 concentration was increased to 4.5 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 equation was found to be linear with positive slope (Fig. 4). However, lie far outside the Bronsted-Debye-Huckel region over which the activity coefficients of many electrolytes are known to be fairly dependent on the ionic strength, the ionic strength dependence is qualitatively as expected when considering the reactive charges involved [32].

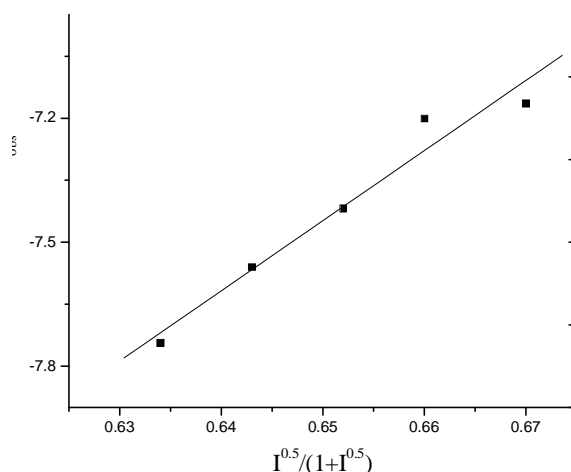


Fig. 4. Dependence of pseudo-first-order rate constant on the ionic strength in the oxidation of MC by chromic acid in aqueous perchloric acid. [Chromic acid] = 7.0×10^{-4} , [MC] = 3.0×10^{-2} and $[H^+] = 3.0 \text{ mol dm}^{-3}$ at 40°C .

Influence of the Added Manganous Ions on the Reaction Rates

Manganese (II) is known to have a high tendency for trapping the Cr (IV) by reducing it to Cr(III) [33,34]. Therefore, in order to check the involvement of chromium (IV) as an intermediate species during the progress of oxidation reactions, the effect of addition of manganous ions on the reaction rates has been studied. It has been noticed that addition of manganous ions to the reaction mixtures leads to a remarkable increase in the oxidation rates. The first-order rate constants obtained were found to increase linearly with increasing the added $[\text{Mn}^{2+}]$ ions as shown in Table 2.

Table 2: Dependence of the observed pseudo-first-order rate constants on the $[\text{Mn}^{2+}]$ in the oxidation of MC by chromic acid in aqueous perchloric acid. [Chromic acid] = 7.0×10^{-4} , [MC] = 3.0×10^{-2} and $I = 4.0 \text{ mol dm}^{-3}$ at 35°C .

$10^3 [\text{MnSO}_4] \text{ mol dm}^{-3}$	0.0	0.5	1.0	5.0
$10^4 k_{obs}, \text{s}^{-1}$	7.74	8.25	8.78	9.0

Influence of Temperature on the Reaction Rate

In order to determine the activation parameters, the reaction was carried out at various temperatures and constants of [MC] and ionic strength. The experimental results were found to fit the Arrhenius and Eyring equations, from whose

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slopes and intercepts the activation parameters can be evaluated. These parameters were calculated by using the least-squares method.

Polymerization Test

Since this oxidation reaction seems to of complementary type, the possibility of formation of free-radicals was examined by adding 10% (v/v) of acrylonitrile to the partially oxidized reaction mixtures. An appreciable white precipitate was observed. Blank experiments from which either chromic acid or MC were excluded gave no detectable polymerization during this time. This result indicates that the present oxidation reaction proceeds via intervention of free-radical mechanism.

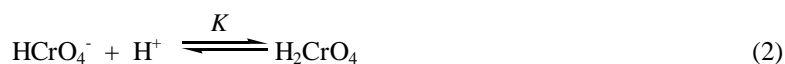
The lack of polymerization noticed in case of chromic acid oxidation of poly (vinyl alcohol) [11] may be attributed to the relative low reactivity and the short lifetime of the radical intermediate involved in such redox reaction. Therefore, that reaction was reinvestigated under the same cited experimental conditions of the present work. A white precipitate was obtained confirming the intervention of free-radical mechanism.

IV. DISCUSSION

Methyl cellulose has a high degree of polymerization, so it forms viscous colloidal solutions in water. The solutions are of hydrophilic sol type, due to the presence of OH moieties which has a remarkable tendency to interact with water (hydrophilic groups). In aqueous systems, orientation (swelling) of the spherical or coiled colloids into linear macromolecules can occur. That is, an interface is formed between MC macromolecules and H₂O via the OH groups [5,6].

It is well established that the formation of variety of unstable oxidation states such as Cr^V and Cr^{IV} species through reduction of chromium (VI) from hexavalent state to the trivalent state in acidic solutions in addition to the tendency of the formed chromium (III) to form a variety of complexes with the oxidation products play an important role in the oxidation kinetics [26,35]. Considering the protolytic and hydrolytic equilibrium processes of chromium (VI) in aqueous perchlorate solutions [36], one should assume that the main chromium (VI) ion is HCrO₄⁻ species since the quantity of the dimeric form is negligible small under our experimental conditions of [H⁺] used. Therefore, it is not surprising to notice the increase in the reaction rates with increasing the hydrogen ion concentration. This is because the net reaction of transformation of the oxyanion HCrO₄⁻ from the tetrahedral form to the octahedral configuration (hydrated cation Cr (H₂O)₆³⁺) consumes hydrogen ions in acidic media [37].

In view of the above interpretations and our experimental observations of the ionic strength and the hydrogen ion concentrations dependences of the rate constants, the protonated species of the reactants may be considered as the more reactive species which play the main role in the reaction kinetics. Hence, the acceleration of the oxidation rates by hydrogen ion can be explained on the basis of the high tendency of the reactants for protonation in acidic solutions according to the following prolytic equilibria



where MC and MCH⁺ represent MC and its protonated form; while *K* and *K*₁ are the protonation constants of chromic acid and methyl cellulose, respectively.

In redox reactions involving chromium (VI) as an oxidant, two reaction mechanisms for electron-transfer may be suggested [38]. The first one corresponds to successive one-electron-transfer mechanism (Cr^{VI} → Cr^V → Cr^{IV}) in a sequence. The second mechanism represents to simultaneous two-electron changes (Cr^{VI} → Cr^{IV}) in a single step. This means that the above two mechanisms may be considered for the cited oxidation process, through formation of either Cr^V or Cr^{IV} intermediates, respectively [27,34,39]. Here, a question of basic interest may be arisen is whether the cited redox reaction proceed by one-electron transfer or two-electron changes mechanism; i.e. via formation of Cr(V) or Cr(IV) intermediate species, respectively.

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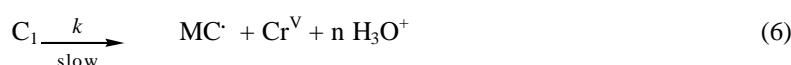
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Involvement of chromium (IV) as an intermediate in these redox reactions has general much debate in the past [33,34]. Therefore, to confirm the involvement of chromium (IV) intermediate during the oxidation processes, the influence of added manganous ion to the reaction mixtures on the oxidation rates is considered as a good evidence for such purpose. The estimated redox potentials of Cr^{VI}/Cr^{III} (E° = 1.33 V) and Mn^{III}/Mn^{II} (E° = 1.54 V) couples indicated that the oxidation of Mn^{II} by Cr^{VI} is slightly endoergic [40]. However, this reaction is believed to occur. Therefore, manganese (II) has been recognized as a frequently tool to determine the involvement of Cr^{IV} as an intermediate [38]. If chromium (IV) intermediate is involved, addition of Mn⁺² should remove it from the reaction mixture as following

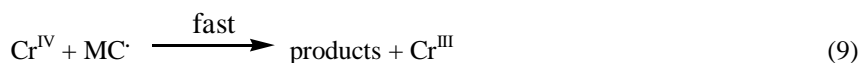


Hence, the reaction rates should be decreased. This behavior was observed in most of oxidation reactions that involving organic substrates by this oxidant [33,38]. On contrary, the observed increase of the rate constants with the increase of the Mn²⁺ ion added in the cited redox system may indicate the absence of Cr^{IV} intermediate involvement.

Therefore, the most reasonable reaction mechanism which may be suggested here, involves a fast complexation between the substrate and the oxidant to give C₁ intermediate, followed by a slow decomposition of such intermediate in the rate-determining step to give free-radical substrate and Cr^V with a subtraction of H₃O⁺ ion as initial oxidation products as follows



Again, the observed obedience of the present reaction to Michaelis-Menten kinetics (Fig. 3) for formation of 1:1 intermediate complex (C₁) may support this suggestion. Then, the formed radical is rapidly oxidized by either picking up a new further oxidant molecule or by the formed Cr^V to give rise to the reaction products as follows,



The disappearance of the hydroxyl groups peak at 3474 cm⁻¹ with the enhancement of the band at 1700 cm⁻¹ in the IR spectrum may be consider as an indirect evidence for the oxidation of the hydroxyl groups to the keto-form. It seems that the oxidation of the substrate radical by chromic acid is easier than that the oxidation of the methyl cellulose itself.

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

$$\text{Rate} = \frac{-d[\text{HCrO}_4^-]}{dt} = \frac{kK_1K_2[\text{H}^+]^2[\text{MC}]_T[\text{Ox}]}{1 + K_1[\text{H}^+] + K_1K_2[\text{H}^+]^2[\text{Ox}]} \quad (10)$$

where [MC]_T is the analytical total concentration of MC. In presence of a large excess of the substrate over that of Cr (VI) concentration, the rate-law expression is expressed by

$$\text{Rate} = k_{\text{obs}} [\text{OX}] \quad (11)$$

Comparing Eqs. (10) and (11) and rearrangement, the following relationship is obtained

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$$\frac{1}{k_{obs}} = \left(\frac{1}{kKK_1K_2[H^+]^2} + \frac{1}{kKK_2[H^+]} \right) \frac{1}{[MC]_T} + \frac{[Ox]}{k[S]} \quad (12)$$

Equation (12) requires that, at constant $[H^+]$ plots of $(k_{obs})^{-1}$ against $1/[MC]_T$ to be linear with positive intercepts on $(k_{obs})^{-1}$ axis. The experimental results were satisfied this requirement as shown by Michaelis-Menten plot (Fig. 3). Again, plots of $(k_{obs})^{-1}$ against $1/[H^+]^2$ at constant $[MC]$ was found to be linear with positive intercepts on $1/[H^+]^2$ as shown in Fig. 5.

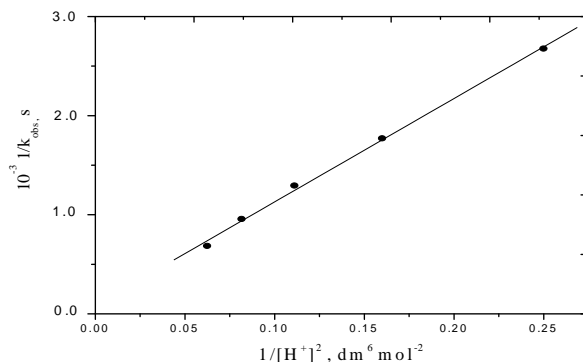


Fig. 5. A typical plot of $1/[H^+]^2$ vs. $1/k_{obs}$ in the oxidation of MC by chromic acid in aqueous perchloric acid. [Chromic acid] = 7.0×10^{-4} , $[MC] = 3.0 \times 10^{-2}$ and $I = 4.0 \text{ mol dm}^{-3}$ at 40°C .

The small intercept observed in Fig. 3 which is related to K' in Eq. (12) may lead us to simplify Eq. (12) to Eq. (13)

$$\frac{[MC][H^+]}{k_{obs}} = \left(\frac{[H^+]^{-1}}{k'} + \frac{1}{k''} \right) \quad (13)$$

where $k' = kKK_1K_2$ and $k'' = kKK_2$, respectively. According to Eq. (13), plots of $[S][H^+]/k_{obs}$ vs. $1/[H^+]$ gave good straight lines with positive intercepts on $[S][H^+]/k_{obs}$ axis (Fig. 6), from whose slopes and intercepts the values of the apparent rate constants, k' and k'' , and the protonation constant, K_1 , can be evaluated. These values were calculated by the least-squares method (Table 3).

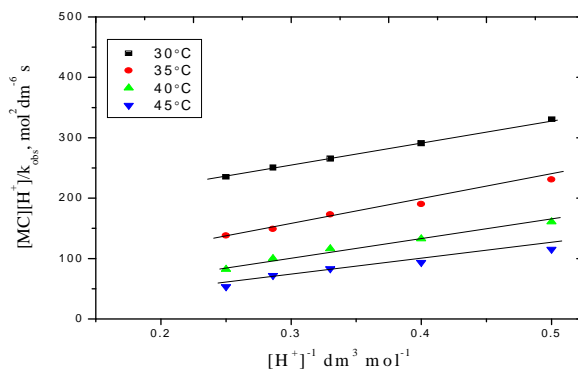


Fig. 6. Plots of $[H^+][MC] / k_{obs}$ vs. $[H^+]^{-1}$ in the oxidation of MC by chromic acid in aqueous perchloric acid. [Chromic acid] = 7.0×10^{-4} , $[MC] = 3 \times 10^{-2}$ and $I = 4.0 \text{ mol dm}^{-3}$ at various $[H^+]$ and temperatures.

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Table 3. The apparent rate constants (k' and k'') and the protonation constant (K_1) in the oxidation of MC by chromic acid in aqueous perchloric acid. [Chromic acid] = 7×10^{-4} , [MC] = 3×10^{-2} and I = 4.0 mol dm^{-3} .

Temp., °C \ Parameter	$10^3 k'$, $\text{dm}^9 \text{mol}^{-3} \text{s}^{-1}$	$10^3 k''$, $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$	K_1 , $\text{dm}^3 \text{mol}^{-1}$
30	1.91	1.30	0.15
35	2.72	2.17	0.13
40	3.74	3.75	0.10
45	5.07	6.12	0.08

Experimental error $\pm 3\%$.

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

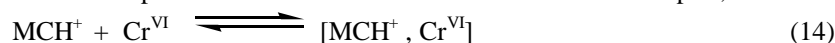
The activation parameters of the apparent rate constants (k' and k'') and second-order rate constant (k_n) were calculated from the temperature dependence of the rate constants by the method of least-squares and are summarized in Table 4. Again, the thermodynamic parameters of the protonation constants were calculated by the well-known thermodynamic methods and are summarized in Table 4.

Constants	Parameters				
	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{K}^{-1}$	ΔG_{303}^\ddagger kJ mol^{-1}	E_a^\ddagger kJ mol^{-1}	A $\text{mol}^{-1} \text{s}^{-1}$
k'	48.17	-83.80	73.14	50.78	1.11×10^6
k''	81.88	+42.82	69.12	84.46	4.61×10^{12}
K_1	ΔH^o kJ mol^{-1}	ΔS_{303}^o $\text{J mol}^{-1} \text{K}^{-1}$	ΔG_{303}^o kJ mol^{-1}		
	-34.33	-128.75	+5.32		

Table 4. Activation parameters of the apparent rate constants (k' and k'') and the thermodynamic parameters of the protonation constant (K_1) in the oxidation of MC by chromic acid in aqueous perchloric acid. [Chromic acid] = 7.0×10^{-4} , [MC] = 3×10^{-2} and I = 4.0 mol dm^{-3} .

Experimental error $\pm 3\%$.

The values of the protonation constants obtained were found to be in good agreement, and with the same order of magnitude, to that previously obtained for other polysaccharides oxidized by chromic acid [11,12,28]. This result may be considered as an indirect evidence to support the cited proposed mechanism. Moreover, the observed magnitude of the protonation constants at various temperatures indicated that the prolytic process of methyl cellulose is an exothermic process in nature. Generally, two possible reaction mechanisms for the nature of electron-transfer in the rate determining step may be suggested. The first one corresponds to an outer-sphere mechanism in which the transfer of electrons occurs prior to the release of protons. It involves the formation of an outer ion-pair,



followed by the transfer of electrons from the substrate to the oxidant in the rate-determining step,

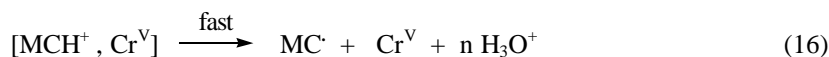


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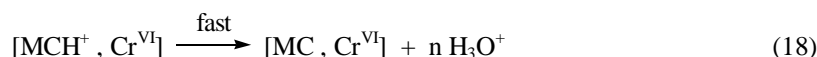
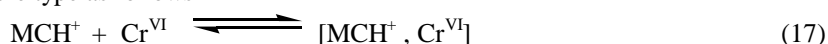
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to give chromium(V) and a free-radical substrate as initial oxidation products



In the second mechanism, the release of protons was preceded the electron-transfer process. This mechanism corresponds to the inner-sphere type as follows



It has been reported [37,41,42] that the entropies of activation, ΔS^\ddagger , are negative for the oxidation reactions which proceeding via complexes formation of inner-sphere nature; while the values of ΔS^\ddagger for the outer sphere mechanisms tend to be more positive. Hence, the former mechanism seems unlikely to account for the present investigation from both mechanistic and thermodynamic points of view since the present oxidation reaction was proceed through formation of an intermediate complex via free-radical intervention mechanism. Therefore, the inner-sphere mechanism is the more probable one for the oxidation of MC by chromic acid. This suggestion was found to be in good agreement with the negative values observed for ΔS^\ddagger in the present investigation. This negative value of ΔS^\ddagger confirms the compactness of the intermediate as well is more characterized to one-electron transfer mechanism of inner-sphere nature. Again, the positive ΔG^\ddagger obtained may confirm the non-spontaneity of the complex formation in the rate-determining step as suggested in the cited proposed mechanism. The hydrogen ion-dependence of the rate-constants in addition to second order magnitude may indicate the fast protonation of both oxidant and the substrate prior to rate determining step. Then the protonated substrate is rapidly attacked by chromic acid oxidant to give an intermediate complex (C_1) which decomposes in the rate-determining step to give the initial oxidation products as free radical substrate and Cr^{V} ion. The substrate radical is further oxidized very rapidly by either picking up a further molecule of chromic acid or by the formed Cr^{V} oxidant to give rise to the final oxidation products. The formation of such intermediate complexes has been postulated in the oxidation of some other organic substrates containing alcoholic groups by this oxidant [19].

Leffler and Grunwald have pointed out that many redox reaction show isokinetic relationship given by $\Delta H^\ddagger = \alpha + \beta\Delta S^\ddagger$. Therefore, the kinetic parameters of the second-order rate constants for oxidation of some macromolecules containing alcoholic groups by this oxidant were examined. As shown in Fig. 7, a plot of ΔH^\ddagger versus ΔS^\ddagger was found to be linear, with $\alpha = 98 \text{ kJ mol}^{-1}$ and $\beta = 361\text{K}$. 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. In view of these arguments and the experimental observations, the oxidation of MC by chromic acid can be illustrated by Schemes (I).

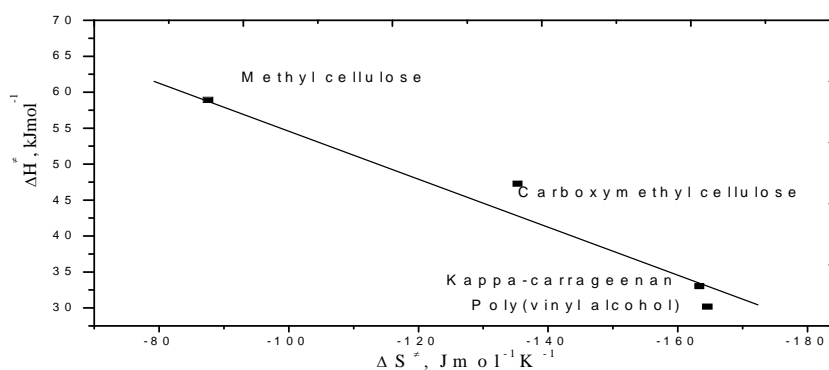


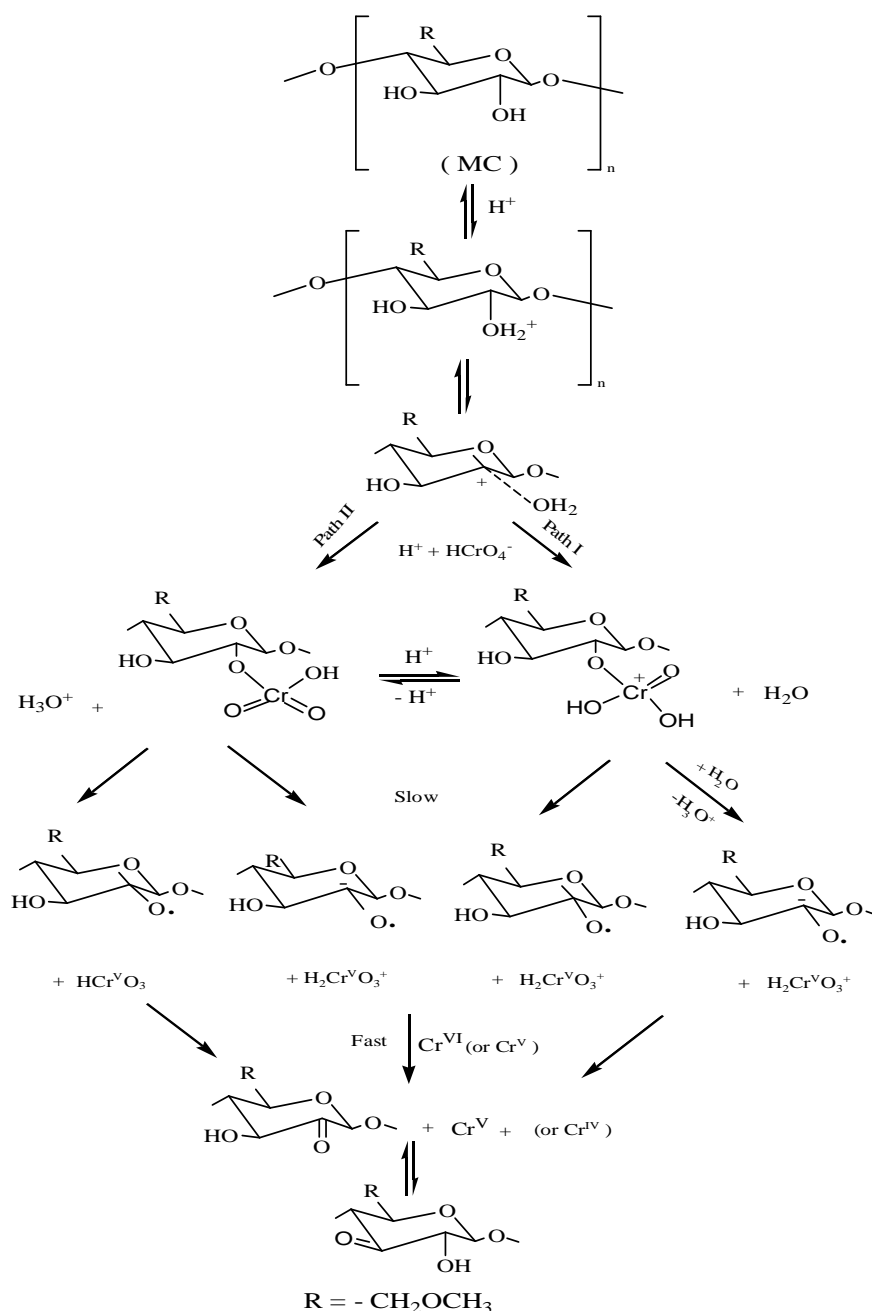
Fig. 7. Isokinetic relationship for oxidation of some macromolecules by chromic acid in aqueous perchlorate solutions.

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In general, biopolymers could be used as biocatalysts and to encapsulate, protect and deliver bioactive or functional components such as drugs, minerals, peptides, proteins, enzymes, lipids or dietary fibers. In addition, the oxidation product of the present work was found to have a high tendency to chelate with Ca (II), Ba(II), Cd(II), Pb(II) and Ag(I) metal cations forming the corresponding coordination biodegradable polymeric complexes. This means that the present oxidation product can be used as a biodegradable chelating agent for the removal of toxic metal cations from the environments, soil and wastewaters. The characteristics of formed biopolymer complexes with metal cations are in progress in our laboratory.



Scheme I. Suggested mechanism of oxidation of MC by chromic acid.

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