

Kinetics and Mechanism of the Decay of Methyl Cellulose-Manganate(VI) Polysaccharide Transient Species—Novel Spectrophotometric Kinetic Trace of Methyl Cellulose Hypomanganate(V) Gel Intermediate Polysaccharide

Ali M. Shaker, Rafat M. El-Khatib, Hossnia S. Mahran

Chemistry Department, Faculty of Science, Sohag University, Sohag 82524, Egypt

Received 21 December 2005; accepted 12 October 2006

DOI 10.1002/app.26907

Published online 30 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Kinetics of the decay of methyl cellulose-manganate(VI) intermediate polysaccharide [MC-MnO₄²⁻] have been followed spectrophotometrically in different strong basic solutions at different temperatures, as well as, in the presence of different concentrations of perchlorate salt. The reaction is base-catalyzed. Salt never affects the reactiv-

ity. The activation parameters have been evaluated and discussed in connection with the proposal mechanism. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2668–2674, 2007

Key words: polysaccharide; decay; hypomanganate; mechanism; methyl cellulose

INTRODUCTION

Literature showed many reports on the oxidation of organic compounds by permanganate, in particular, in acidic solutions^{1,2} reported by Hassan³ and Shaker⁴ showed that the details of the mechanism, for the oxidation of polysaccharide containing secondary alcoholic groups, have escaped full detection, this would be ascribed to the difficulties arising from over oxidation. The last mechanism suggested by Shaker⁴ assumed that the oxidation of carboxymethyl cellulose proceeds via two stages. The first stage is the formation of the blue hypomanganate(V) metastable complex in a relatively kinetically fast pre-equilibrium, then the second stage is slower interconversion of the latter into the green manganate(VI) polysaccharide intermediate complex. The blue hypomanganate(V) complex has been detected elsewhere^{5–9} by stopped-flow techniques. Shaker¹⁰ could detect and for the first time, spectroscopically observable trace for hypomanganate(V) intermediate complex of carboxymethyl cellulose at 700 nm. El-Khatib¹¹ published before kinetics and mechanism of the oxidation of methyl cellulose via the formation of its manganate(VI) transient species. In the present publication, we managed to continue and undertake kinetics and mechanistic study for the decomposition

of green manganate(VI) intermediate complex of methyl cellulose (MC), as well as, to show the development of the spectrophotometric peak corresponding to the blue hypomanganate(V)-MC complex at 700 nm. This is to present complete imagination about reasonable pathways of the overall oxidation of polysaccharides by permanganate and to confirm the nature of both transient species and oxidation ketopolymer products. The importance of this study stems from the formation of new metastable coordination carbohydrate polymer gels viz. green manganate(VI) and blue hypomanganate(V) transient species. Again, monoketo or a diketobiopolymer, the final oxidation products of industrially importance, are prepared.^{3,4,11,12}

EXPERIMENTAL

All chemicals used are of Sigma and BDH AnalaR samples. Characteristics of methyl cellulose (MC) have been detailed in the previous publication.¹¹ To characterize MC and its oxidation product, IR spectra were monitored.¹¹ Again, the decay of the band at 3450 and the disappearance of that at 1700 cm⁻¹, would suggest the transformation of secondary (—OH) to a (—C=O) group.

Stock solutions of MC (Sigma), NaOH (BDH), perchlorate salt (BDH), and KMnO₄ (BDH) were prepared by dissolving the calculated amounts of BDH Analar samples in redistilled water. The stock solution of KMnO₄ was standardized against As₂O₃,

Correspondence to: A. M. Shaker (shaker-ali@lycos.com).

after which the permanganate ion concentration was determined spectrophotometrically, immediately prior to each run at $\lambda_{\max} = 525$ nm. The stock KMnO_4 was diluted to a suitable concentration before mixing with appropriate amount of NaOH and NaClO_4 solutions.

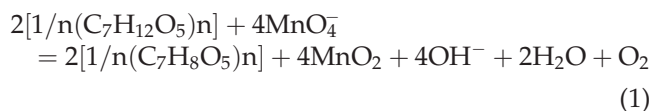
KINETIC MEASUREMENTS

The kinetic measurements were executed under pseudofirst order conditions in $[\text{MnO}_4^-]$. Sodium hydroxide and MC were mixed in large excess over MnO_4^- . Total ionic strength was maintained at 0.1 mol dm^{-3} with inert NaClO_4 and temperature controlled within $\pm 0.1^\circ\text{C}$ in a Haake F3 ultrathermostat. The suitable amounts of the reagents, at the desired temperature, were mixed in the thermostated reaction cell adjusted at the same temperature. The reaction kinetics were followed by monitoring the decrease in the absorbance at 610 nm , the absorption peak of the green $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{3-}]$ intermediate complex as a function of time. As reported elsewhere^{4,10,11} when the green intermediate builds up to maximum concentration, it commences to decompose and the corresponding absorbance at $\lambda_{\max} = 610 \text{ nm}$ decreases. Absorbance values and spectral scans were recorded in a Cecil CE 599 automatic scanning spectrophotometer connected to a CE 836 cell and wavelength programmer. No interference exists from other reagents at the wavelength of measurements, cf. Figures 1, 2.

RESULTS

Stoichiometry and product analysis

The stoichiometric reaction equation, cf. elsewhere publication details in Ref. 11 can be formulated as:



$(\text{C}_7\text{H}_{12}\text{O}_5)_n$ is the methyl cellulose polymer (MC) and $(\text{C}_7\text{H}_8\text{O}_5)_n$ is the diketomethyl cellulose polymer, the oxidation product. The diketobiopolymer would be presented as:

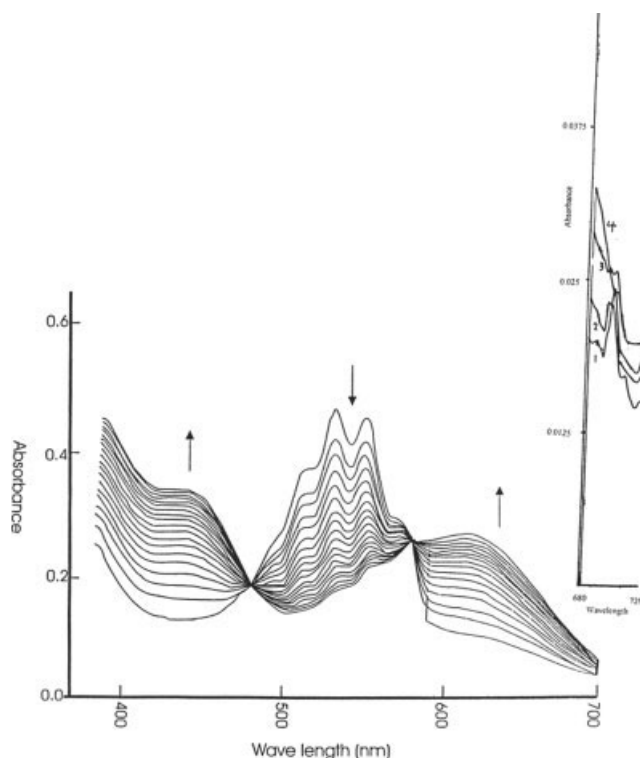
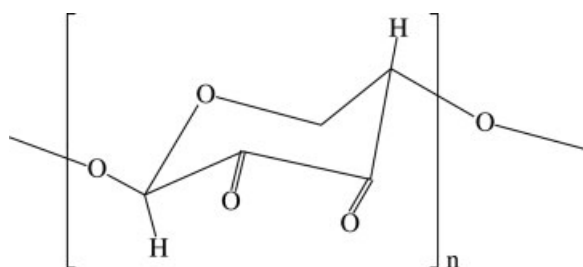


Figure 1 Spectral scans (380–720 nm) during the oxidation of methyl cellulose by alkaline permanganate ion at $[\text{MC}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$ and 20°C . Figure shows on the right scans for the formation and decay of MC-MnO_4^{3-} at 10°C .

The yellow color remaining after the end of the kinetic oxidation run is due to the formation of MnO_2 . This color reaction would indicate that the blue hypomanganate(V) formed and disproportionated to MnO_2 sol, then coagulated to MnO_2 precipitate after long time. Because of the difficulty of the filtration of the colloidal MnO_2 , the latter is separated from its solution by the addition of excess NaF and stirring for 24 h, and then MnF_4 formed is filtered off. The diketobiopolymer can be obtained from the concentrated filtrate via gelation with dilute acetic acid at $\text{pH} = 6$. The acid of diketomethyl cellulose was precipitated from ethanol, filtered off, washed several times with ethanol, and dried under vacuum.¹² The separated dried solid was characterized by IR spectral analysis and a red dinitro-phenylhydrazone test.¹¹

Effect of $[\text{MnO}_4^-]$ on the decomposition reaction

The reaction obeys first-order kinetics in $[\text{MnO}_4^-]$ as evidenced from the independence of k_{obs} values on $[\text{MnO}_4^-]$.

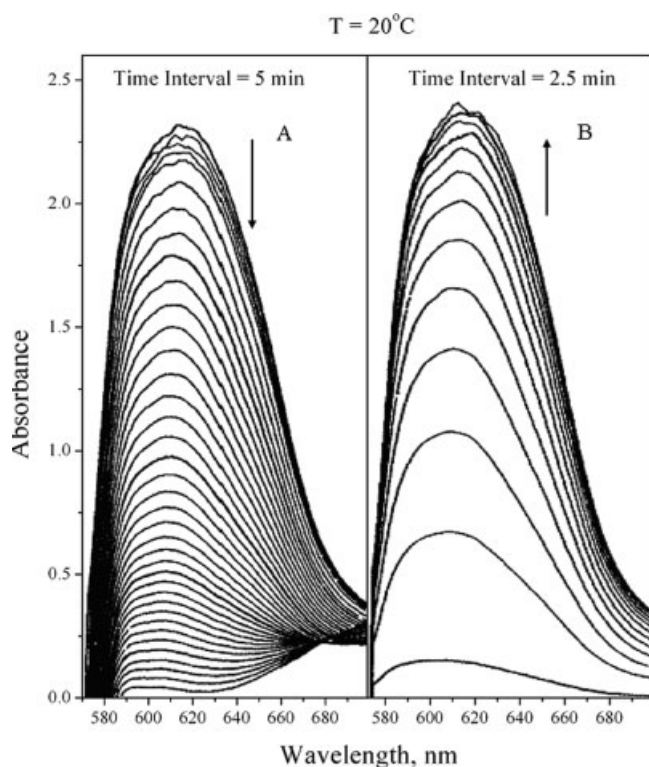


Figure 2 Spectral scans during: (a) the formation and (b) the decomposition of the intermediate MC-MnO_4^{2-} at 610 nm in the oxidation of methyl cellulose by alkaline permanganate at $[\text{MC}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$ and 20°C .

The base catalyzed decomposition reaction

The decomposition rate of the green intermediate $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ was base catalyzed as shown in Figure 4. Linear plot of k_{obs}^{-1} versus $[\text{OH}^-]^{-1}$ was obtained.

The dependence of reaction rate on the ionic strength, I

The rate of reaction never depends on the ionic strength and this issue is consistent with the electrically neutral nature of the slowly decomposed intermediate.

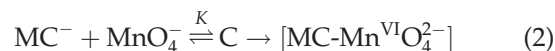
Effect of methyl cellulose MC

k_{obs}^{-1} versus $[\text{MC}]^{-1}$ showed straight lines of Lineweaver–Burk plot (Fig. 5).

DISCUSSION

El-Khatib¹¹ reported the mechanism of formation of the spectrophotometrically observable green intermediate $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ at 610 nm. In the present contribution, and in continuation, kinetics of decom-

position of green $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$, in strong alkaline solution, was followed spectrophotometrically at 610 nm, the absorption peak wavelength of the intermediate.



K is the formation constant of the intermediate species $\text{C} = [\text{MC-Mn}^{\text{V}}\text{O}_4^{3-}]$, MC^- is enolate of methyl cellulose



K' is the dissociation constant of secondary OH in MC. Additively, in this article, it has been feasible to observe a novel spectrophotometric tracer of the short lived blue hypomanganate transient species C, $[\text{MC-Mn}^{\text{V}}\text{O}_4^{3-}]$ which decays rapidly to liberate the green intermediate in concern. Shaker^{4,10} suggested that the blue hypomanganate(V) intermediate interconverts into the green species via metastable state, probably of the form $[\text{MC-Mn}^{\text{V}}\text{O}_4^{3-} \dots \dots \text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$. Repeated spectral scans in Figure 1 show the building up of these intermediates, green at 610 nm and blue at 700 nm. Evidence for the formation of Mn(VI) green and Mn(V) blue as transient polymer precursors was the formation of the blue color at the earliest stages of the oxidation, i.e., after just

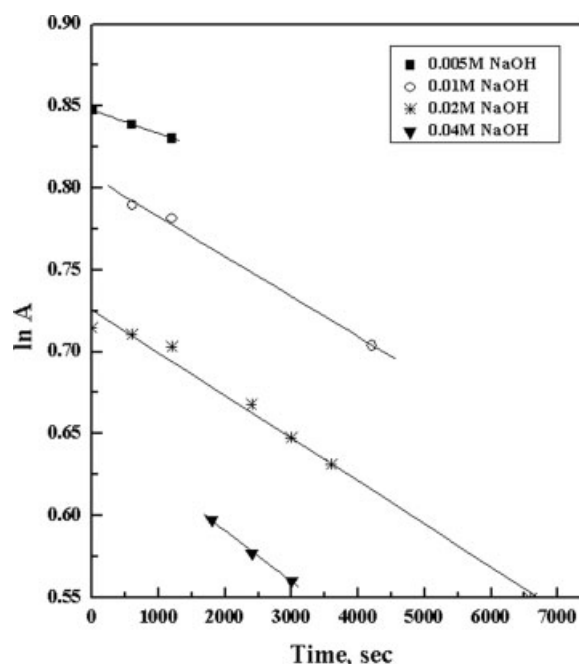


Figure 3 First-order rate plots during the decomposition of MC-MnO_4^{2-} intermediate in the oxidation of MC by alkaline permanganate in the presence of different $[\text{OH}^-]$ at $[\text{MC}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$ and 20°C .

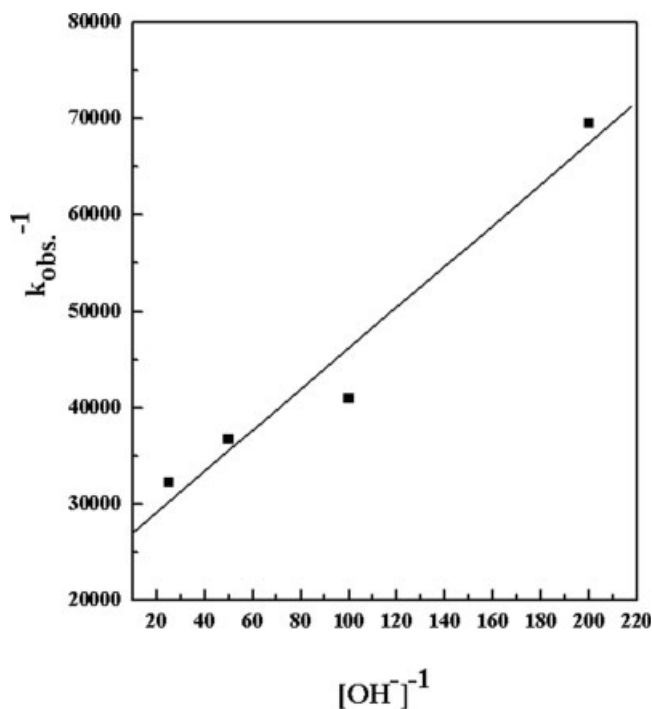


Figure 4 k_{obs}^{-1} versus $[\text{OH}^-]^{-1}$ plot during the decomposition of MC- MnO_4^{2-} complex in the oxidation of MC by alkaline permanganate in the presence of different $[\text{OH}^-]$ at $[\text{MC}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$ and 20°C .

mixing of MC with strong alkaline permanganate ($\text{pH} \geq 12$) then the latter decomposes rapidly leading to the immediate growth of somewhat more stable green color polymer sol. To get scans in Figure 1, several trials have been done through cooling of the reaction mixture, as well as, changing $[\text{MC}]/[\text{MnO}_4^-]$ folds. These scans showed a signal tracer for the blue hypomanganate precursor sol intermediate with MC. Despite its modest sharpness, but anyway presented something like fade light spots in that almost full misleading area, the area of detection of these useful metastable reactive intermediate coordination polymers by conventional and tenable spectrophotometric tools. The weak signal shown at 700 nm, the convenient maximum of the blue hypomanganate(V) intermediate, would be due to the very rapid disproportionation of blue $[\text{MC-Mn}^{\text{V}}\text{O}_4^{3-}]$ hypomanganate(V) intermediates into the relatively more stable green $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ manganate intermediate. Probably, the 700 nm band is obscured by the broad 610 nm band.

The importance of the present contribution is due to throwing more light on the mechanism, the nature of the oxidation of methyl cellulose polymer with strong alkaline KMnO_4 via the cited intermediate polymers. The yellow color persisting even after the end of the kinetic run is due to the formation of MnO_2 sol as a side product of the oxidation.

The observed color reaction changing from blue Mn(V) to green Mn(VI) which are spectrophotometrically observable at 700 and 610 nm, respectively, support the above oxidation proposal. The molar absorptivity of the green manganate(VI) $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ intermediate ϵ_{max} , was evaluated as $1.3 \times 10^3 \pm 50$ at $[\text{MC}] = 4 \times 10^{-3}$, $[\text{MnO}_4^-] = 2 \times 10^{-4}$, $[\text{OH}^-] = 0.02$ and $I = 0.1 \text{ mol dm}^{-3}$ at 20°C . This value is in the order of magnitude of the corresponding values reported for similar intermediates, and can be used in the determination of MC polysaccharide. The green manganate(VI) builds up to its maximum amount as its absorbance reaches its limiting value A_∞ at 610 nm. At this point, the intermediate decays and similarly its corresponding absorbance A_t at arbitrarily time.

The pseudo first-order rate law is formulated as;

$$\frac{-d[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]}{dt} = k_{\text{obs}}[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}] \quad (4)$$

where,

$$k_{\text{obs}} = k_2[\text{OH}^-] \quad (5)$$

The values of k_{obs} of decomposition have been estimated from least squares of the slopes of linear first-order $\ln A_t$ versus t plots, cf. Figure 3.

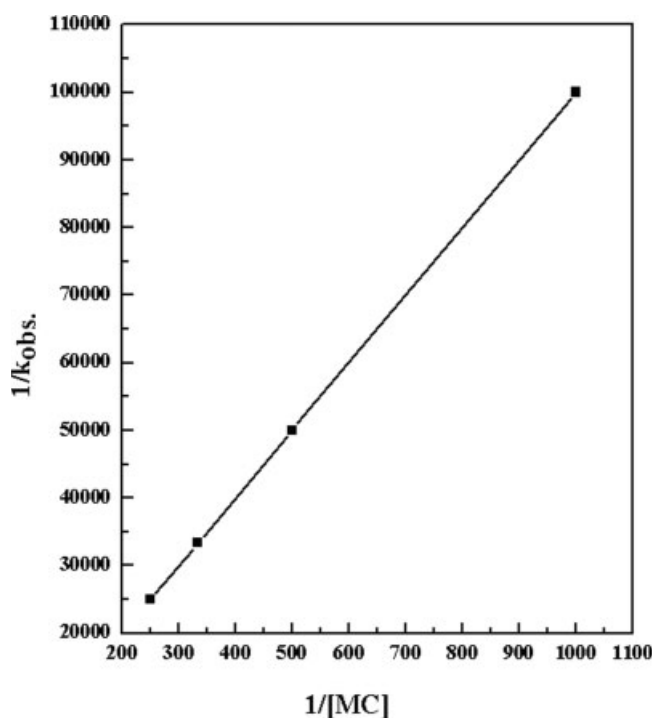


Figure 5 k_{obs}^{-1} versus $[\text{MC}]^{-1}$ plot during the decomposition of MC- MnO_4^{2-} complex in the oxidation of MC by alkaline permanganate at $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$ and 20°C .

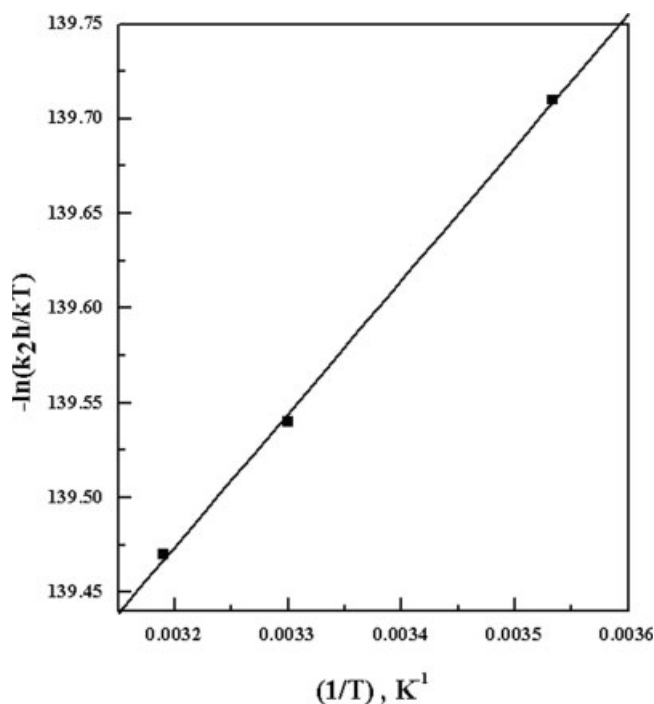
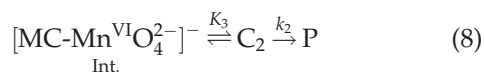
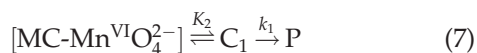


Figure 6 Eyring plot during the decomposition of MC- MnO_4^{2-} in the oxidation of MC by alkaline permanganate at $[\text{MC}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$ and 20°C .

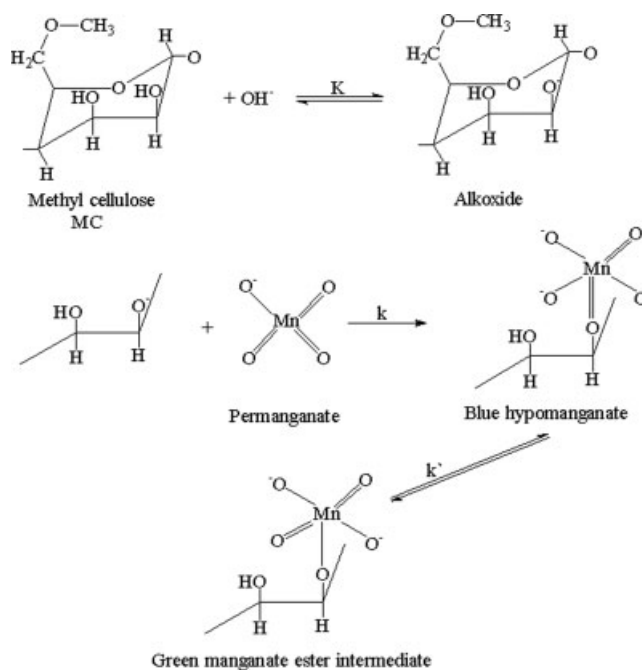
In light of the results that the decay of the intermediate is base catalyzed, thus it deprotonates prior to its decomposition step;



K_1 is the deprotonation constant of the intermediate (Int.). The reaction exhibits Michaelis Menten kinetics, i.e., $[k_{\text{obs}}]^{-1}$ versus $[\text{MC}]^{-1}$ gives linear plots, therefore this suggests that the decomposition of the green manganate(VI) precursors occurs via intermediates. Thus, a reasonable mechanism has been proposed as follows:



The suggested mechanism provides that the decomposition of $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ or $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]_{\text{Int.}^-}$ intermediates (Int. and/or Int.⁻) takes place via transient species (C_1, C_2) in two equilibrium steps. Then C_1 or C_2 decay in the rate-controlling pathways with rate constants k_1 and k_2 .

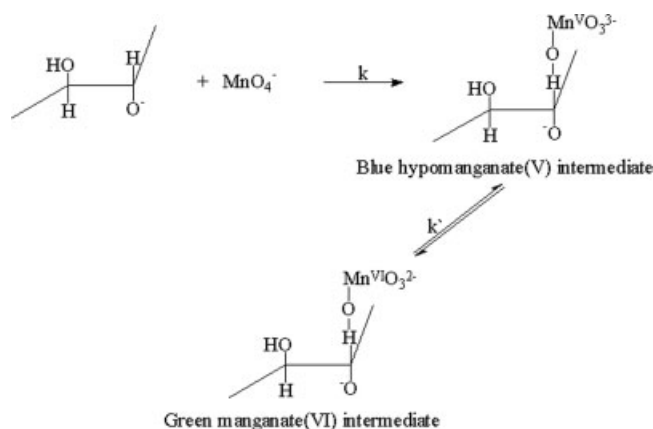


Scheme 1

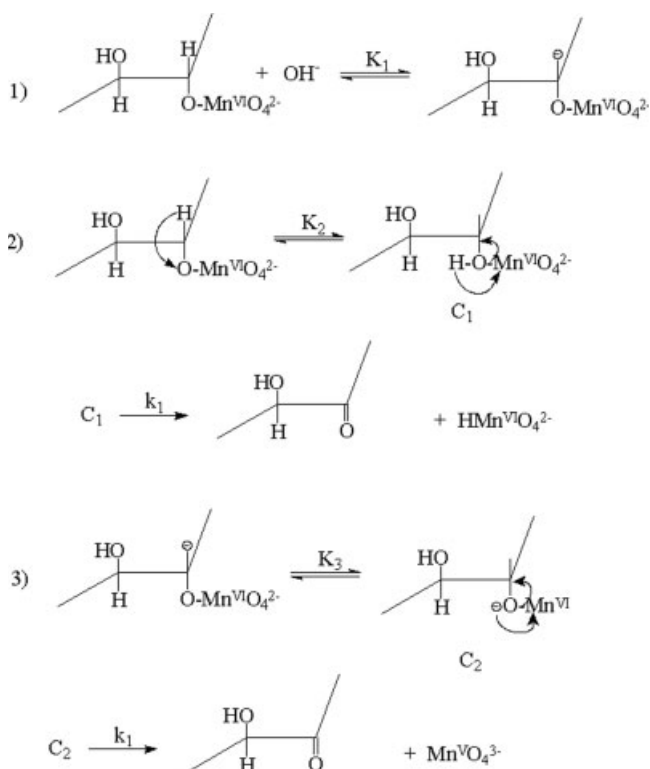
Again, the established Michaelis Menten kinetics for the present decomposition reaction supplement the proposal pathways, as well as, the existence of a permanent equilibrium as follows:



As reported previously⁴ that in the presence of increasing amounts of MC in excess over $[\text{MnO}_4^-]$, the free concentration of the intermediate increases. K_2 and K_3 are the formation constants of the intermediates C_1 and C_2 . There has been a time lag between the complete formation of the intermediates Int. and Int.⁻ and their decay. This probably assumes the establishment of the transient species C_1 and C_2 .



Scheme 2



Scheme 3

The derived rate equation satisfying the above mechanism is given as:

$$\frac{-d[\text{Int.}]_T}{dt} = \frac{(k_1 K_2 + K_1 k_2 K_3 [\text{OH}^-]) [\text{Int.}]_T}{1 + K_1 [\text{OH}^-] + K_2 + K_3} \quad (10)$$

$$[\text{Int.}]_T = [\text{Int.}] + [\text{Int.}^-] + [\text{C}_1]_{\text{ss}} + [\text{C}_2]_{\text{ss}} \quad (11)$$

$[\text{C}_1]_{\text{ss}}$ and $[\text{C}_2]_{\text{ss}}$ are the steady state concentrations of C_1 and C_2 . On matching both of Eq. (10) and (11) it is deduced that,

$$k_{\text{obs}} = \frac{K'_1 + K_1 k_2 K_3 [\text{OH}^-]}{K'_2} \quad (12)$$

where

$$K'_1 = k_1 K_2; \quad K'_2 = (1 + K_2 + K_3) \quad (13)$$

and

$$k_{\text{obs}}^{-1} = \frac{K'_2 [\text{OH}^-]^{-1}}{2K_1 k_2 K_3} + \frac{K'_2}{2K'_1} \quad (14)$$

Thus, the linear plots of k_{obs}^{-1} versus $[\text{OH}^-]^{-1}$ with positive intercepts (cf. Fig. 4) confirm the mechanism proposal. The observed rate independence on the added NaClO_4 salt supports the monelectrolytic nature of the decomposed transient species C_1 and C_2 , it appears that their has probably been a counterbalancing between the enhancement of solvation of the hydrophobic C_1 and C_2 species, on one hand, and the large effective electrostatic interactions between NaClO_4 and OH^- ions. The former effect presumably enhances rate by increasing the reactive concentration of the transient species while the latter effect retards the reactivity due to lowering the chemical potential of the reaction catalyzing OH^- ions. The deprotonation step may be easier, in the case of the decomposition of the more polar carboxymethyl cellulose, than in the case of less polar methyl cellulose green intermediates. This issue renders the nucleophilicity (chemical potential) of the OH^- ion in the former case not as much important as in the latter case. Thus, this behavior may be the reason for that the rate constant values of the decomposition of $[\text{CMC-MnO}_4^{2-}]$ green intermediate increase with increasing the added amount of NaClO_4 ,¹⁰ while the rate constant values of the decomposition of the corresponding MC intermediate remain constant against the amount of the same added salt.

According to the previous publication,¹¹ the first stage of the oxidation of methyl cellulose consists of prealkoxide formation in an equilibrium step followed by the attack of MnO_4^- on the oxygen carrying a negative charge in the alkoxide to afford the blue $[\text{MC-Mn}^{\text{V}}\text{O}_4^{3-}]$ then the green $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ intermediates (Scheme 1).

It is reported before³ the possibility of hydrogen bonding between alkoxide hydrogen and MnO_4^- as in Scheme 2.

The high negative entropy of activation of the intermediate formation and its rather slow decay suggest the former pathway by Mn—O ionic character

TABLE I
Second-Order Rate Constant Values at Different Temperatures, Activation Parameters and Arrhenius Factor for the Formation and the Decomposition of $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ Intermediate Complex at $[\text{MnO}_4^-] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{MC}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$

	$k_2 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{)}$				$E_a \text{ (kJ M}^{-1}\text{)}$	$\Delta H^\ddagger \text{ (kJ M}^{-1}\text{)}$	$\Delta G^\ddagger \text{ (kJ M}^{-1}\text{)}$	$\Delta S^\ddagger \text{ (kJ M}^{-1}\text{)}$	$A \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	Ref.
	10°C	20°C	30°C	40°C						
Formation	0.255	–	0.345	0.428	14.90	9.93	75.97	–220.40	135.5	11
Decomposition	0.0125	–	0.016	0.0175	19.01	13.97	55.90	–138.40	–	Recent paper

Maximum error is $\pm 2\%$ in activation parameters and $\pm 1\%$ in rate constant values.

TABLE II
Second-Order Rate Constant Values at Different Temperatures, Activation Parameters for the Formation and the Decomposition of $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ and $[\text{CMC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ Intermediate Complexes at $[\text{MnO}_4^-] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{MC}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$

Macromolecule	$K_2 (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$				E_a (kJ M^{-1})	ΔG^\ddagger (kJ M^{-1})	ΔS^\ddagger (J K^{-1})	Ref.
	10°C	20°C	30°C	40°C				
CMC, Carboxymethyl cellulose								
Formation	–	19.00	28.00	–	36.95	64.06	–110.60	4
Decomposition	–	8.60	21.76	–	66.26	53.75	–50.20	10
MC, Methyl cellulose								
Formation	0.26	–	0.34	0.43	14.90	75.97	–220.40	11
Decomposition	0.012	–	0.016	0.018	19.01	55.90	–138.40	Recent paper

Maximum error is $\pm 2\%$ in activation parameters and $\pm 1\%$ in rate constant values.

bonding in the intermediate formation (Fig. 6). Again, in Figure 2, a document for this slow decay and thus for the strong intermediate formed is clarified. From the scans in this Figure, it has been observed that the decomposition is notably slower than the formation of the green $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ intermediate.

As the green intermediate forms completely, it commences in the decomposition in the presence of excess NaOH as represented structurally in Scheme 3.

The finally precipitated brown MnO_2 sol, would suggest the formation of hypomanganate(V) which decomposed to Mn(IV) sol, then to MnO_2 particles.

In Table I, there are reported second-order rate constants for both formation and decay of the green methyl cellulose managanate intermediate, as well as, the activation parameters of the whole oxidation process. Examination of this table reveals that the rate constant of the green intermediate formation is as 20- to 25-fold greater as the corresponding rate constant of its decay under the same conditions, cf. Table I and Figure 2. Furthermore, activation energy E_a and enthalpy of activation ΔH^\ddagger , for the formation of the green intermediate, are notably less than the corresponding activation parameters for the decay of this intermediate. The free energy of activation ΔG^\ddagger for the formation of the primary stage is greater than the corresponding value for the secondary decay. This assumes that the final decomposition products, ketopolymer and MnO_2 , are more stable than the green transient species formed and supports the mechanism proposal. The negative entropy of activation in both formation and decomposition of the green $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ intermediate suggests that the referenced processes occur via compact intermediates as reported in recent and previous publication.¹¹ The almost twice fold of negative entropy of activation in the case of the formation of the intermediate

relative to the parallel value in the case of its decay process ensures that the intermediate preformed in the formation of $[\text{MC-Mn}^{\text{VI}}\text{O}_4^{2-}]$ is less adhesive than the intermediate pre-established in the decay. Again, the negative entropy of activation should be much less in the decay than in the formation of the green intermediate associative nature.

Table II shows that the rate constants of the formation and of the decomposition of the green manganese(VI) intermediates have been largely enhanced in the oxidation of carboxymethyl cellulose when compared with the corresponding values reported for the oxidation of methyl cellulose. This result would be ascribed to the electronic structural effects of the studied polysaccharides. The electron withdrawing character of the (C=O) in the carboxymethyl cellulose may enhance the deprotonation steps preceding the formation and the decay of the intermediates formed in the oxidation of these polysaccharides. Then, this effect leads to the enhancement of the reactivity of the whole oxidation process in CMC relative to that of the oxidation in MC.

References

- Kumar, K.; Sakena, L. K. *J Ind Chem Soc* 1970, 47, 435.
- Rao, G. V.; Rajanna, K. C.; Saiprakash, P. K. Z. *Phys Chem (Leipzig)* 1982, 263, 35.
- Hassan, R. M. *J Polym Sci Part A: Polym Chem* 1993, 31, 51.
- Shaker, A. M. *J Colloid Interface Sci* 2001, 233 (Part I), 197.
- Carrington, A.; Symons, M. C. R. *J Chem Soc* 1956, 3373.
- Jacky, M.; Simandy, L. I. *J Am Chem Soc* 1976, 98, 1995.
- Jacky, M.; Simandy, L. I. *J Chem Soc Perkin Trans* 1976, 2, 939.
- Wei, M. M.; Stewart, R. *J Am Chem Soc* 1974, 88, 1966.
- Wiberg, K. W.; Deutsch, C. J.; Rocek, J. *J Am Chem Soc* 1973, 95, 3034.
- Shaker, A. M. *J Colloid Interface Sci* 2001, 244 (Part II), 254.
- El-Khatib, R. M. *Carbohydr Polym* 2002, 47, 377.
- Khairou, K. S.; Hassan, R. M.; Shaker, A. M. *J Appl Polym Sci* 2002, 85, 1019.