Carbohydrate Polymers 82 (2010) 880–886

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Kinetics and mechanism of disproportionation of $Mn^{(VI)}O_4{}^{2-}$ induced by decomposition of intramanganato-polygalacturonate methyl ester coordination polymer precursor: Medium-substituent effects on reactivity

Lobna Abdel-Mohsen Ebaid Nassr*

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

ARTICLE INFO

Article history:
Received 12 March 2010
Received in revised form 29 May 2010
Accepted 7 June 2010
Available online 19 June 2010

Keywords:
Kinetics
Oxidation
Polysaccharides
$KMnO_4$
UV–vis spectroscopy

ABSTRACT

During the oxidation of polygalacturonate methyl ester polysaccharide by $MnO_4{}^-$ in highly basic medium, the formation of the green polygalacturonate methyl ester (PGME-$Mn^{(VI)}O_4{}^{2-}$) and the blue (PGME-$Mn^{(V)}O_4{}^{3-}$) intermediates were followed spectrophotometrically. In this paper, the kinetics of the decay of the green (PGME-$Mn^{(VI)}O_4{}^{2-}$) intermediate, the second stage of the oxidation process, were followed spectrophotometrically at different concentrations of NaOH and temperatures ranging from 10 to 30 °C. The decay of the green intermediate (PGME-$Mn^{(VI)}O_4{}^{2-}$) follows pseudo-first-order kinetics, $d[\text{PGME-Mn}^{(VI)}O_4{}^{2-}]/dt = k_{obs.}[\text{PGME-Mn}^{(VI)}O_4{}^{2-}]$ where $k_{obs.} = k_2[OH^-]$. The reaction was found to be base catalyzed. The obtained linear Michaelis–Menten kinetics proves the formation of intermediates during the decay process. A reaction mechanism involving a deprotonation pre-equilibrium step followed by a rate determining decay of the deprotonated green intermediate (PGME-$Mn^{(VI)}O_4{}^{2-}$) is proposed. Moreover, the activation parameters were consistent with the assumed reaction mechanism. The positive salt effect indicates the ionic character of the transient species. The decay and formation rates increase in the following order of polysaccharides: $\text{MC-Mn}^{(VI)}O_4{}^{2-} < \text{CMC-Mn}^{(VI)}O_4{}^{2-} \ll \text{PGME-Mn}^{(VI)}O_4{}^{2-}$.

1. Introduction

Many plant polysaccharides have been used for the clean up of industrial wastes (Benguella & Benaissa, 2002; Trimukhe & Varma, 2008; Varma, Deshpande, & Kennedy, 2004) and as inhibitors of the corrosion of some metals (Khairou & El-Sayed, 2003). Moreover, natural polysaccharides are considered to be biopolymers which are biocompatible and environmentally friendly. These natural polymers are generally non-toxic, cheap and freely available compared to the synthetic polymers. Moreover, natural polysaccharides are amongst the richest renewable sources of biopolymers and have potential applications in many fields such as food, cosmetics, and pharmaceutical industries (Murphy, 1997). Recently, some studies have shown that many plants used in traditional medicine to treat various types of diseases contain polysaccharides exhibiting biological activity of different kinds. Pectins are an example of complex polysaccharides possessing such an activity when used in traditional medicines (Paulsen & Barsett, 2005; Ridley, O'Neill, & Mohnen, 2001). Moreover, pectins are widely used in food industry as thickening and gelling agents for the preparation of jams and jellies (May, 1990). Pectin is the methyl ester of pectic acid and is composed of long chains of galacturonic acid (Whistler & Smart, 1953). Pectins are found mainly between the cells and in the primary cell wall in most plants (O'Neill, Albersheim, & Darvill, 1990; Stephen, 1983).

In the view of the reported above and the current interest of redox reactions of polysaccharides (El-Khatib, 2002; Khairou, 2001, 2003; Khairou & Hassan, 2000; Shaker, 2001a, 2001b; Shaker, El-Khatib, & Makran, 2007; Shaker, El-Khatib, & Nassr, 2009), the oxidation of polygalacturonate methyl ester (PGME) (pectin) by permanganate has been undertaken employing a wider range and higher concentration of OH^- (from 8×10^{-3} to 2×10^{-2} mol dm^{-3}) and PGME (from 2×10^{-3} to 6×10^{-3} mol dm^{-3}) compared with those applied in the previous publication (Khairou & Hassan, 2000). This research project was done in an attempt to establish a more probable mechanism and to search for the new blue coordination precursor of hypomanganato-PGME intermediate containing Mn(V) recently established by Shaker et al. (2009). This has been achieved by proper control of both temperature and concentration. The first-stage kinetics of the formation of the green PGME-manganato(VI) during the oxidation of poly galacturonate methyl ester by permanganate in strong alkaline medium, pH ≥ 12, has been determined by Shaker et al. (2009).

In this work, the second-stage kinetics of the decomposition of green intermediate (PGME-$Mn^{(VI)}O_4{}^{2-}$) are presented and a mechanism suggested according to the obtained data. Moreover, there

---

* Tel.: +2 0101244189; fax: +2 093 4601159.
E-mail address: lobna.nassr@hotmail.com.

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.06.008

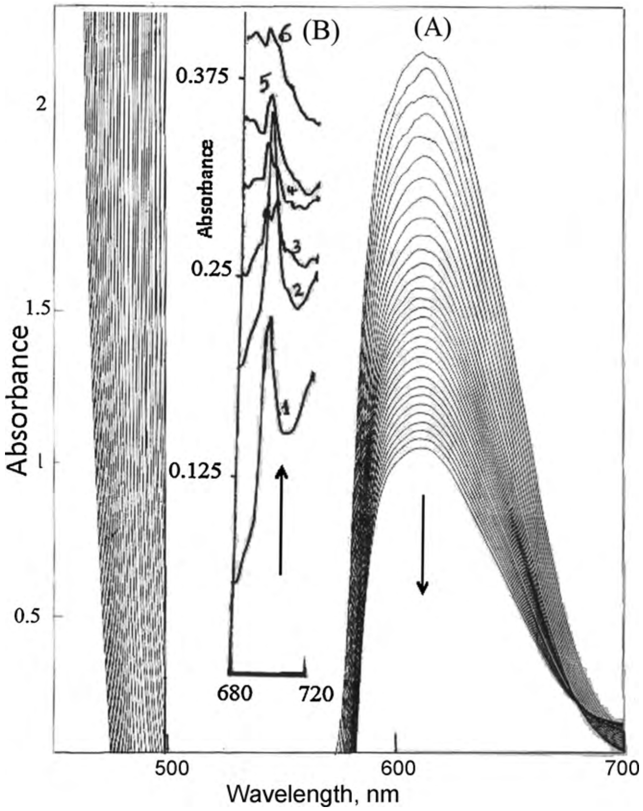


Fig. 1. Repeated spectral scans of the oxidation of PGME by $KMnO_4$ in basic medium ($pH \geq 12$). (A) Decomposition of (PGME-$Mn^{(VI)}O_4^{2-}$) intermediate at $\lambda = 610$ nm, interval time = 3 min, temperature = 20 °C. (B) Formation of metastable (PGME-$Mn^{(V)}O_4^{3-}$) at $\lambda = 700$ nm, interval time = 0.5 min, temperature = 10 °C.

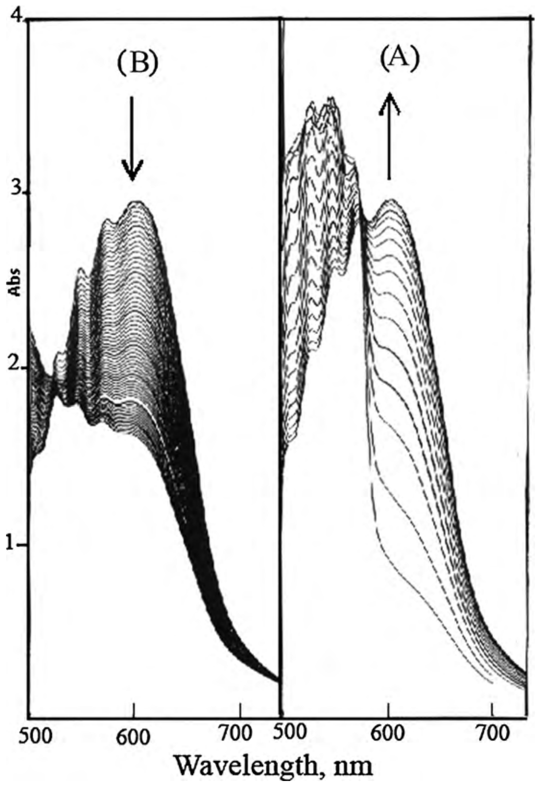


Fig. 2. Repeated spectral scans of the oxidation of PGME by $KMnO_4$ in basic medium ($pH \geq 12$). (A) Formation of (PGME-$Mn^{(VI)}O_4^{2-}$) intermediate (interval time = 3 min), (B) decomposition of (PGME-$Mn^{(VI)}O_4^{2-}$) intermediate (interval time = 1 min).

is a comparison between the data obtained in this work with that from other publications concerning the oxidation of other polysaccharides by alkaline $KMnO_4$ (El-Khatib, 2002; Hassan, 1993a, 1993b, 1993c; Hassan, E1-Gaiar, & El-Summan, 1993; Khairou, 2001, 2003; Khairou & Hassan, 2000; Shaker, 2001a, 2001b; Shaker et al., 2007, 2009) to shed more light on this oxidation reaction.

2. Experimental

2.1. Materials and reagents

Stock solutions were prepared by dissolving the calculated amounts of BDH Analar samples (NaOH, perchlorate salt or $KMnO_4$) in redistilled water. Clear solution from pectin (polygalacturonate methyl ester) solution (BDH) was prepared by stepwise addition of the sample reagent to the deionized water with continuous and rapidly stirring of the solution.

2.2. Kinetic measurements

The decay reaction kinetics were followed by tracing the decrease in the absorbance at $\lambda = 610$ nm, the absorption peak of the green intermediate complex PGME-$Mn^{(VI)}O_4^{2-}$, as a function of time (cf. Fig. 1A). Fig. 2A shows spectra scans for the first-stage formation kinetics of the green intermediate complex PGME-$Mn^{(VI)}O_4^{2-}$ at $\lambda = 610$ nm. The recent second-stage kinetics of the decay of the green (PGME-$Mn^{(IV)}O_4^{2-}$) intermediate were achieved under pseudo-first-order conditions in [MnO_4^-], where [PGME] $\ggg$ [MnO_4^-], and constant ionic strength of 0.1 mol dm^{-3} by using inert $NaClO_4$. The suitable amounts of the reagent solutions were thermostatted at the desired temperature before mixing together. The values of k_2 at various temperatures and the activation parameters have been cited in Table 1.

3. Results

3.1. Stoichiometry of the reaction and free radical formation test

As shown previously (Shaker et al., 2009), the stoichiometry of the oxidation reaction of pectin by MnO_4^- in high alkaline medium was found to be PGME:$KMnO_4$ = 1:2 and the reaction equation presented as:

$$2\left(\tfrac{1}{n}(C_7H_{10}O_6)_n\right) + 4MnO_4^- = 2\left(\tfrac{1}{n}(C_7H_6O_6)_n\right) + 4MnO_2 + 4OH^- + 2H_2O + O_2$$

Table 1
Second-order rate constant values (k_2, $mol^{-1}\,dm^3\,s^{-1}$) at various temperatures, the activation parameters and Arrhenius factors for the formation and decomposition of (PGME-MnO_4^{2-}) intermediate at [OH^-] = 0.02 mol dm^{-3}, [PGME] = 4×10^{-3} mol dm^{-3}, MnO_4^- = 2×10^{-4} mol dm^{-3}, I = 0.1 mol dm^{-3} and λ_{max} = 610 nm.

	Temperature (°C)					E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} K^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	A (mol^{-1} s^{-1})	Reference
	10	15	20	25	30						
Formation (k_2)	2.02	2.54	3.71	5.04	6.38	42.61	40.18	−96.79	68.54	1.45×10^8	Shaker et al. (2009)
Decomposition (10^2k_2)	2.66	3.63		8.04	9.41	47.41	44.98	−115.60	78.85	1.51×10^7	Present paper

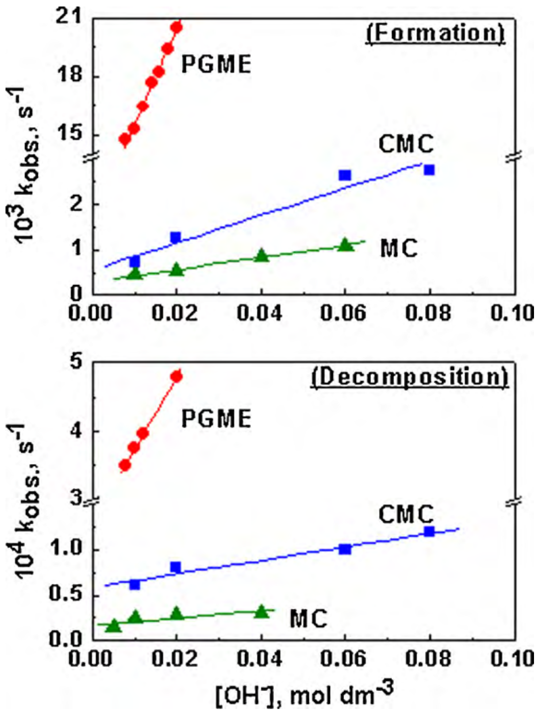
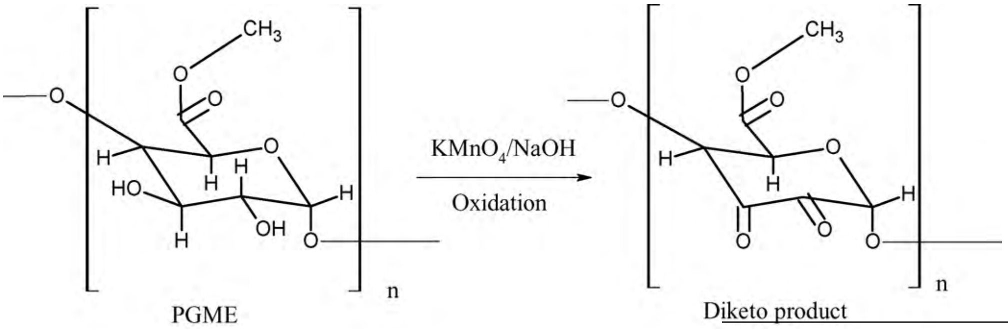


Fig. 3. $k_{obs.}$ *vs.* $[OH^-]$ plot of the formation and the decomposition of polysaccharide-$Mn^{(VI)}O_4{}^{2-}$ intermediate complexes in the presence of different $[OH^-]$ at [polysaccharide] = 4×10^{-3} mol dm^{-3}, $[MnO_4{}^-] = 2 \times 10^{-4}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3} and 20 °C.

where $(C_7H_{10}O_6)_n$ and $(C_7H_6O_6)_n$ correspond to PGME and the oxidation product (diketo) respectively:



The second-stage decay reaction of PGME-$Mn^{(VI)}O_4{}^{2-}$ green intermediate does not occur via free radicals just as its first-stage formation in the oxidation of PGME by $KMnO_4$ at pH ≥ 12 (Shaker et al., 2009).

3.2. *Effect of base concentration on the reaction rate*

The decay of the intermediate (PGME-$Mn^{(VI)}O_4{}^{2-}$) was found to be base catalyzed reaction as shown from Fig. 3.

3.3. *Effect of the oxidant concentration on the reaction rate*

The independence of observed rate constant values ($k_{obs.}$) of the decay of the intermediate (PGME-$Mn^{(VI)}O_4{}^{2-}$) at 610 nm on the initial concentration of $MnO_4{}^-$, indicated the first-order kinetics in $[KMnO_4]$.

3.4. *Effect of [PGME] on the reaction rate*

The relation between $k_{obs.}$ *vs.* [PGME] was a linear plot. Moreover, a linear Lineweaver–Burk plot was obtained ($1/\nu_{0.}$ *vs.* 1/[PGME]).

3.5. *Dependence of reaction rate on the ionic strength*

The values of k_{obs}. were found to increase with increasing ionic strength at constant $[OH^-]$ and the relation of $\log k_{obs.}$ *vs.* $(I)^{0.5}$ is linear (cf. Figs. 4 and 5). Moreover, the activation free energy of transfer for the reaction, $\delta_m \Delta G^{\#}$, from aqueous solution into aqueous solutions containing different concentrations of salt was calculated (cf. Fig. 6).

3.6. *Activation parameters of (PGME-$Mn^{(VI)}O_4{}^{2-}$) intermediate decay*

The observed rate constant ($k_{obs.}$) values increased with increasing the temperature. The activation parameters were obtained by least squares of Arrhenius and Eyring plots (cf. Table 1).

4. Discussion

In the first-stage kinetics of the oxidation of polygalacturonate methyl ester polysaccharide by $MnO_4{}^-$ in highly basic medium resulted in the slow formation of the green (PGME-$Mn^{(VI)}O_4{}^{2-}$) intermediate through the rapid formation and decomposition of a blue hypomanganate(V) intermediate (cf. Figs. 1 and 2). In the current work, the second-stage kinetics of the decay of the green intermediate (PGME-$Mn^{(VI)}O_4{}^{2-}$) were followed spectrophotometrically at 610 nm in pH ≥ 12. Under the implemented conditions of the studied reaction that $[OH^-]$ and $[PGME] \ggg [MnO_4{}^-]$, the pseudo-first-order rate law is suggested to be:

$$\frac{-d[\text{PGME-Mn}^{(VI)}O_4{}^{2-}]}{dt} = k_{obs.}[\text{PGME-Mn}^{(VI)}O_4{}^{2-}] \qquad (1)$$

where, $k_{obs.} = k_2[OH^-]$.

As revealed from Fig. 3; the recent decomposition of the green intermediate complex (PGME-$Mn^{(VI)}O_4{}^{2-}$) is a base catalyzed reaction that would confirm the deprotonation of the intermediate as a first step in the reaction mechanism as follows:

$$\underset{A}{\text{PGME-Mn}^{(IV)}O_4{}^{2-}} + OH^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \underset{A^-}{(\text{PGME-Mn}^{(IV)}O_4{}^{2-})} + H_2O \qquad (2)$$

The decomposition reaction of the green intermediate (PGME-$Mn^{(VI)}O_4{}^{2-}$) exhibits Michaelis–Menten kinetics (the relation between $1/\nu_0$ against 1/[PGME] gives linear plot). This suggests that the decay reaction occurs via the formation of intermediates followed by an intramolecular electron transfer process. From Lineweaver–Burk plot, the Michaelis–Menten constant (K_M) was calculated and found to be $K_M = 0.31$ mol dm^{-3} where the maximum rate (ν_{max}) = 5.40×10^{-3} mol dm^{-3} s^{-1}. The large value of K_M indicates the formation of an intermediate during the reaction

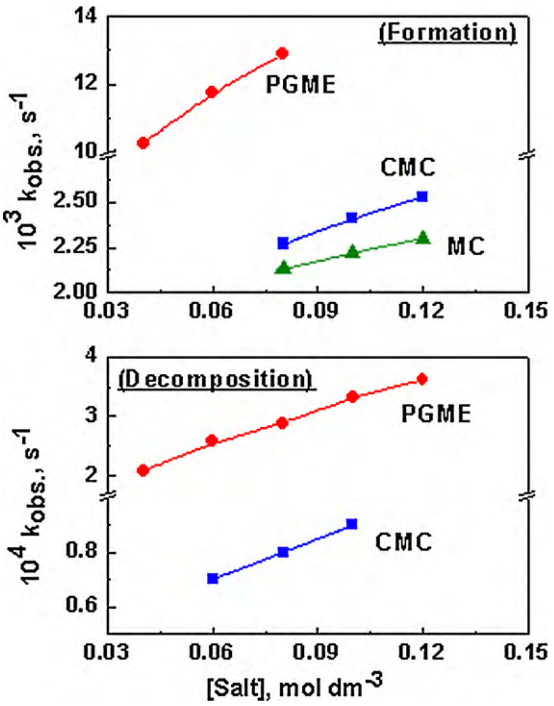


Fig. 4. $k_{obs.}$ *vs.* [Salt] plots of the formation and the decomposition of polysaccharide-$Mn^{(VI)}O_4{}^{2-}$ intermediate complex at $[OH^-] = 0.02$ mol dm^{-3}, $[Poly] = 4 \times 10^{-3}$ mol dm^{-3}, $[MnO_4{}^-] = 2 \times 10^{-4}$ mol dm^{-3} and 20 °C.

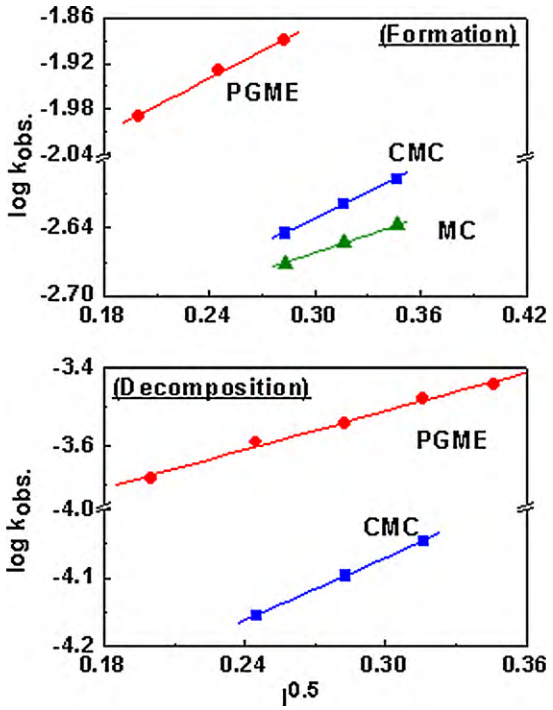


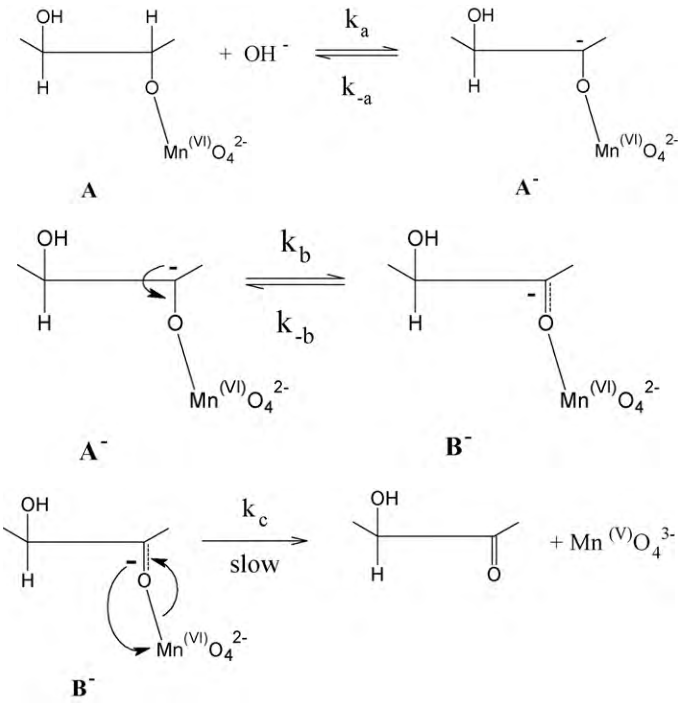
Fig. 5. $\log k_{obs.}$ *vs.* $\sqrt{I}$ plot of the formation and the decomposition of polysaccharide-$Mn^{(VI)}O_4{}^{2-}$ intermediate complex at $[OH^-] = 0.02$ mol dm^{-3}, $[\text{polysaccharide}] = 4 \times 10^{-3}$ mol dm^{-3}, $[MnO_4{}^-] = 2 \times 10^{-4}$ mol dm^{-3} and 20 °C.

progress (Awad, Shaker, Zaki, & Nassr, 2008):

$$A^- \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} B^- \qquad (3)$$

$$B^- \underset{\text{slow}}{\overset{k_c}{\rightleftharpoons}} P \qquad (4)$$

The suggested mechanism can be represented schematically as follows:



The slow decay of (B^-) intermediate is the rate determining step gateway with rate constant k_c.

After the completion of the decomposition of PGME-$Mn^{(VI)}O_4{}^{2-}$, a yellow colour appears, which may be an evidence of the decomposition of $Mn^{(V)}O_4{}^{3-}$ to $Mn^{(IV)}$, followed by aggregation of the latter to a sol of MnO_2 (Shaker, 2001a).

The molar absorptivity (ε) of the intermediate complex (PGME-$Mn^{(VI)}O_4{}^{2-}$) was found to be about 1400 dm^3 mol^{-1} cm^{-1} at the used concentrations; $[PGME] = 4 \times 10^{-3}$ mol dm^{-3}, $[MnO_4{}^-] = 2 \times 10^{-4}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3} and 20 °C. This value of ε is similar to the corresponding values for other polysaccharide-$Mn^{(VI)}O_4{}^{2-}$ intermediates reported before: Sodium alginate; 1300 ± 50 (Hassan, 1993a), chitin and chitosan, 1250 ± 75(Khairou, 2001), carboxymethyl cellulose, 1400 (Shaker, 2001b), methyl cellulose; 1300 ± 50 (El-Khatib, 2002).

By applying the steady state approximation for the concentrations of the intermediates A^- and B^- and putting the total concentration of (PGME-$Mn^{(VI)}O_4{}^{2-}$) $[A]_T$ as:

$$[A]_T = [A] + [A^-] + [B^-] \qquad (5)$$

$$\text{Rate} = \frac{-d[\text{PGME-}Mn^{(VI)}O_4{}^{2-}]}{dt} = \frac{K_a k_b k_c [OH^-][\text{PGME-}Mn^{(VI)}O_4{}^{2-}]_T}{(k_{-b} + k_c)(1 + K_a[OH^-] + K_a K_b[OH^-])} \qquad (6)$$

On comparing Eqs. (1) and (6):

$$k_{obs.} = \frac{K_a k_b k_c [OH^-]}{(k_{-b} + k_c)(1 + K_a[OH^-] + K_a K_b[OH^-])} \qquad (7)$$

and

$$k_2 = \frac{K_a k_b k_c}{(k_{-b} + k_c)(1 + K_a[OH^-] + K_a K_b[OH^-])} \qquad (8)$$

and the relation between $1/k_{obs.}$ against $1/[OH^-]$ is a straight line.

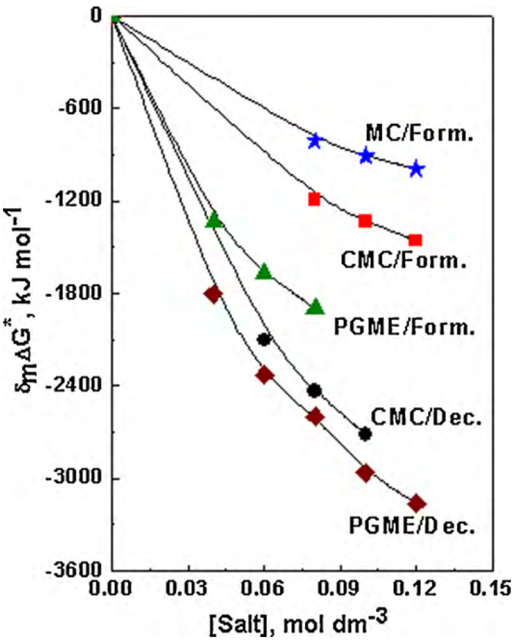


Fig. 6. Plots of the change in the activation barrier ($\delta_m \Delta G^\#$) for the formation (Form.) and the decomposition (Dec.) of polysaccharide-$Mn^{(VI)}O_4^{2-}$ intermediate complexes during the oxidation of polysaccharides by alkaline $KMnO_4$ at different [Salt].

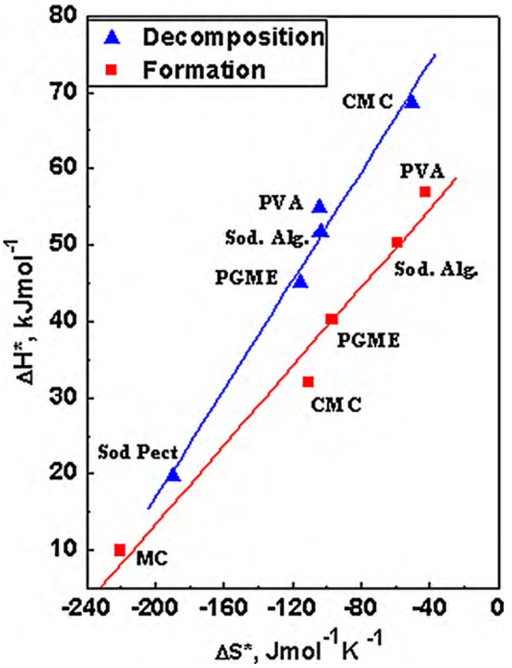
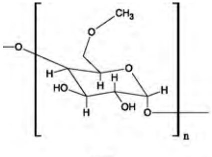
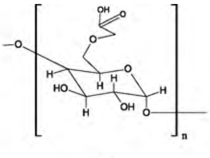


Fig. 7. Isokinetic plots ($\Delta H^\#$ *vs.* $\Delta S^\#$) for the formation and the decomposition of some polysaccharide-$Mn^{(VI)}O_4^{2-}$ intermediate complexes during the oxidation of polysaccharides by alkaline $KMnO_4$.

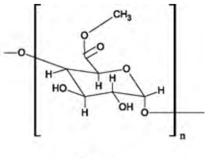
The relation between the values of $k_{obs.}$ *vs.* [OH^-] for the formation and the decomposition of some (polysaccharide-MnO_4^{2-}) intermediate complexes are shown in Fig. 3. It was found that, the reactivity of the formation and the decay of (polysaccharide-MnO_4^{2-}) was largely enhanced for PGME-$Mn^{(VI)}O_4^{2-}$ compared with the corresponding values for CMC-$Mn^{(VI)}O_4^{2-}$ and MC-$Mn^{(VI)}O_4^{2-}$ intermediates (CMC = carboxymethylcellulose, MC = methylcellulose). The reactivity increases in the following order: MC-$Mn^{(VI)}O_4^{2-}$ < CMC-$Mn^{(VI)}O_4^{2-}$ ≪ PGME-$Mn^{(VI)}O_4^{2-}$. It appears that the nature of the terminal groups (CH_2OCH_3, CH_2OCH_2COOH or $COOCH_3$) – in the main structure of the above mentioned polysaccharides – play a crucial role in controlling their reactivity. The reactivity order may be presumably interpreted as due to increasing polarity of the terminal groups $CH_2OCH_3 < CH_2OCH_2COOH < COOCH_3$, this in turn leads to increase hydrophilicity and solubility, as well as, the concentration of free polysaccharide. It may be a substituent effect on the reactivity of the polysaccharides:



MC



CMC



PGME

The positive salt effect obtained in Figs. 4 and 5 may support the ionic nature of the reactants in the rate determining step as suggested in the proposed mechanism (Arnaut, Formosinho, & Burrows, 2007). Fig. 4 shows the change in $k_{obs.}$ values with increasing the concentration of added $NaClO_4$ to the reaction medium in both the formation and the decomposition of polysaccharide-MnO_4^{2-} intermediates (polysaccharide = MC, CMC or PGME). It was found that the order of increase of the reactivity at different [Salt] is: MC-$Mn^{(VI)}O_4^{2-}$ < CMC-$Mn^{(VI)}O_4^{2-}$ ≪ PGME-$Mn^{(VI)}O_4^{2-}$ similar to that reactivity order obtained at different [OH^-] (cf. Fig. 3).

The relation of $\log k_{obs.}$ against $(I)^{0.5}$ for the formation and the decomposition of some (polysaccharide-$Mn^{(VI)}O_4^{2-}$) intermediate complexes is linear (cf. Fig. 5) according to the following equation:

$$\log k = \log k_0 + 2AZ_AZ_B(I)^{0.5} \tag{9}$$

where k_0 is the rate constant value in the absence of added salt and the parameter A in water at 25 °C has the value $A = 0.51\ \mathrm{mol}^{-1/2}\,\mathrm{dm}^{3/2}$ (Arnaut et al., 2007). From the slope and the intercept of the lines in Fig. 5, the constant values in Eq. (9) were determined: MC-MnO_4^{2-}/formation ($k_0 = 1.53 \times 10^{-3}$ and $Z_AZ_B = 0.50$), CMC-MnO_4^{2-}/formation ($k_0 = 1.39 \times 10^{-3}$ and $Z_AZ_B = 0.74$), PGME-MnO_4^{2-}/formation ($k_0 = 5.92 \times 10^{-3}$ and $Z_AZ_B = 1.18$), CMC-MnO_4^{2-}/decomposition ($k_0 = 2.95 \times 10^{-5}$ and $Z_AZ_B = 1.50$) and PGME-MnO_4^{2-}/decomposition ($k_0 = 9.89 \times 10^{-5}$ and $Z_AZ_B = 1.62$).

The activation free energy of transfer for the reaction, $\delta_m \Delta G^\#$, from aqueous solution into aqueous solution containing different concentrations of salt is calculated from reaction rates in the appropriate media, using the relationship:

$$\delta_m \Delta G^\# = -RT \ln\left(\frac{k_s}{k_0}\right) \tag{10}$$

where k_0 is obtained from Eq. (9) and k_s is that for the aqueous solutions containing different [Salt]. The variation of $\delta_m \Delta G^\#$ with [Salt] is shown in Fig. 6. It was found that the activation free energy of transfer decreases with increasing the added salt concentration. Moreover, the values of $\delta_m \Delta G^\#$ for the decomposition reactions of the polysaccharide-MnO_4^{2-} intermediate complexes are more negative than those for the formation reactions.

The second-order rate constants for both formation and decomposition reactions of the green intermediate (PGME-$Mn^{(VI)}O_4^{2-}$) and the activation parameters of these reactions are listed in Table 1. It is clear that the rate constants of the formation process (cf. Fig. 2A) of (PGME-$Mn^{(VI)}O_4^{2-}$) are as 63–76 folds greater than the corresponding values of the decay process (cf. Fig. 2B) under the same conditions (cf. Fig. 2). Moreover, the activation energy (E_a) and enthalpy of activation ($\Delta H^\#$) values, for the formation of (PGME-$Mn^{(VI)}O_4^{2-}$) intermediate, are less than the corresponding activation parameters for the decomposition of this intermediate by (≈5 kJ mol^{-1}). Furthermore, the free energy of activation ($\Delta G^\#$)

for the formation step is greater than that of the decomposition step (≈10 kJ mol^{-1}). These presume that the final decomposition products are more stable than the formed green intermediate (PGME-Mn$^{(VI)}$O$_4$$^{2-}$) and support the proposed mechanism. The negative entropy of activation ($\Delta S^{\#}$) values in both formation and decomposition of the green (PGME-Mn$^{(VI)}$O$_4$$^{2-}$) intermediate suggest that the referenced processes occur via the formation of intermediates as reported in recent and previous publications (Shaker et al., 2009) and are characteristic of inner-sphere electron transfer mechanism (Freeman et al., 1981).

That the plot of the isokinetic relation; $\Delta H^* = C + B\Delta S^*$ (10) (Leffler & Grunwald, 1963) is linear (cf. Fig. 7), indicates similarity to mechanisms of oxidation of the studied polysaccharides (polygalacturonate methyl ester (pectin), sodium pectate, methylcellulose, carboxymethylcellulose, sodium alginate and polyvinyl alcohol) with alkaline permanganate. The constant values are $C = 65.15$ kJ mol^{-1}, $B = 25.84$ K (for the formation of polysaccharide-Mn$^{(VI)}$O$_4$$^{2-}$) and $C = 88.14$ kJ mol^{-1}, $B = 35.60$ K (for the decomposition of polysaccharide-Mn$^{(VI)}$O$_4$$^{2-}$).

5. Conclusion

(1) It was found that, the oxidation of polysaccharides containing secondary alcoholic –OH groups by MnO$_4$$^-$ at high pH (pH ≥ 12) occurs via two stages. The first stage consists of the formation of both polysaccharide-Mn$^{(V)}$O$_4$$^{3-}$ and polysaccharide-Mn$^{(VI)}$O$_4$$^{2-}$. The unstable intermediate complex polysaccharide-Mn$^{(V)}$O$_4$$^{3-}$ (blue colour) is formed very fast and can be detected spectrophotometrically at $\lambda_{max.} = 700$ nm at specific reactant concentrations and temperatures (cf. Fig. 1; Shaker, 2001a). Then polysaccharide-Mn$^{(V)}$O$_4$$^{3-}$ disproportionates slowly to the green polysaccharide-Mn$^{(VI)}$O$_4$$^{2-}$ intermediate complex which can be studied kinetically at $\lambda_{max.} = 610$ nm (cf. Fig. 2; El-Khatib, 2002; Shaker, 2001b; Shaker et al., 2009). The second stage is the decomposition of the green intermediate complex polysaccharide-Mn$^{(VI)}$O$_4$$^{2-}$ (PGME-Mn$^{(VI)}$O$_4$$^{2-}$ in this work) to give Mn$^{(IV)}$ and keto-derivatives as final product (cf. Figs. 1 and 2; El-Khatib, 2002; Shaker, 2001a).

(2) The rate of the decay reaction is base catalyzed and follows Michaelis–Menten kinetics, which suggests a deprotonation pre-equilibrium step and a decay process that progresses through the formation of intermediates.

(3) The rate of the decay reaction obeys pseudo-first-order kinetics: $d[\text{PGME-Mn}^{(VI)}\text{O}_4{}^{2-}]/dt = k_{obs.}[\text{PGME-Mn}^{(VI)}\text{O}_4{}^{2-}]$ and $k_{obs.} = k_2[\text{OH}^-]$.

(4) The addition of a salt to the reaction medium enhances the tested reaction reactivity. This presumes the ionic character of the reactants in the rate determining step.

(5) The terminal groups (COOCH$_3$, CH$_2$OCH$_2$COOH or CH$_2$OCH$_3$) in the main structure of the polysaccharide play an effective role in the enhancement of the reactivity of either the formation or the decomposition of polysaccharide-Mn$^{(VI)}$O$_4$$^{2-}$. The decay rate increases in the following order: MC-Mn$^{(VI)}$O$_4$$^{2-}$ < CMC-Mn$^{(VI)}$O$_4$$^{2-}$ ≪ PGME-Mn$^{(VI)}$O$_4$$^{2-}$.

(6) The values of the activation parameters Ea and $\Delta H^{\#}$ are larger for the decay reaction than for formation of the intermediate. The free energy of activation $\Delta G^{\#}$ for the formation of the green intermediate is greater than the corresponding value for the decomposition, confirming the greater stability of the final product in the oxidation of the polysaccharides.

(7) Studying the kinetics of the formation and the decay of the complexes resulted from the interaction between natural polysaccharides and Mn$^{(VII)}$ ions will give more data about the stability of similar interactions with other metals and will extend the applications of the polysaccharides in industry (Benguella & Benaissa, 2002; Trimukhe & Varma, 2008; Varma et al., 2004) and as biopolymers (Chen, Remondetto, & Subirade, 2006; Emerich & Thanos, 2007; Goldberg, Langer, & Jia, 2007; Kulkarni, Gowthamarajan, Dhobe, Yohanan, & Suresh, 2005; Ubbink & Kruger, 2006).

References

Arnaut, L., Formosinho, S., & Burrows, H. (2007). *Chemical kinetics from molecular structure to chemical reactivity*. Oxford: Elsevier.

Awad, A. M., Shaker, A. M., Zaki, A. B., & Nassr, L. A. E. (2008). Novel mechanistic aspects on the reaction between low spin Fe(II) Schiff base amino acid complexes and hydrogen peroxide—spectrophotometric tracer of intraperoxo intermediate catalyzed reaction. *Spectrochimica Acta A*, *71*, 921–928.

Benguella, B., & Benaissa, H. (2002). Cadmium removal from aqueous solutions by chitin: Kinetic and equilibrium studies. *Water Research*, *36*, 2463–2474.

Chen, L. Y., Remondetto, G. E., & Subirade, M. (2006). Food protein-based materials as nutraceutical delivery systems. *Trends in Food Science & Technology*, *17*(5), 272–283.

El-Khatib, R. M. (2002). Spectrophotometric detection of methyl cellulose-manganate(VI) intermediate complex in the oxidation of methyl cellulose by alkaline permanganate. *Carbohydrate Polymers*, *47*, 377–385.

Emerich, D. F., & Thanos, C. G. (2007). Targeted nanoparticle-based drug delivery and diagnosis. *Journal of Drug Targeting*, *15*(3), 163–183.

Freeman, F., Fuselier, C. O., Armstead, C. R., Dalton, C. E., Davidson, P. A., Karchesfski, E. M., et al. (1981). Permanganate ion oxidations. 13. Soluble manganese(IV) species in the oxidation of 2,4(1H,3H)-pyrimidinediones (Uracils). *Journal of American Chemical Society*, *103*, 1154–1159.

Goldberg, M., Langer, R., & Jia, X. Q. (2007). Nanostructured materials for applications in drug delivery and tissue engineering. *Journal of Biomaterials Science—Polymer Edition*, *18*(3), 241–268.

Hassan, R. M. (1993a). Alginate polyelectrolyte ionotropic gels. XIV. Kinetics and mechanism of formation of intermediate complex during the oxidation of alginate polysaccharide by alkaline permanganate with spectrophotometric evidence of manganate(VI) transient species. *Journal of Polymer Science: Part A: Polymer Chemistry*, *31*, 51–59.

Hassan, R. M. (1993b). Alginate polyelectrolyte ionotropic gels. XVIII. Oxidation of alginate polysaccharide by potassium permanganate in alkaline solutions: Kinetics of decomposition of intermediate complex. *Journal of Polymer Science: Part A: Polymer Chemistry*, *31*, 1147–1151.

Hassan, R. M. (1993c). New coordination polymers. 3. Oxidation of poly (vinyl alcohol) by permanganate ion in alkaline-solutions—kinetics and mechanism of formation of intermediate complex with a spectrophotometric detection of manganate(VI) transient species. *Polymer International*, *30*(1), 5–9.

Hassan, R. M., E1-Gaiar, S. A., & El-Summan, A. M. (1993). New coordination polymers. 4. Oxidation of poly(vinyl alcohol) by permanganate ion in alkaline-solutions—kinetics and mechanism of decomposition of intermediate complex. *Polymer International*, *32*, 39–42.

Khairou, K. S. (2001). Spectrophotometric evidence for the formation of short-lived Mn(VI) as transient species intermediate during the permanganate oxidation of chitin and chitosan polysaccharides in alkaline solutions. *Spectroscopy Letters*, *34*(6), 721–728.

Khairou, K. S. (2003). Kinetics and mechanism of decomposition of intermediate complex during oxidation of pectate polysaccharide by potassium permanganate in alkaline solutions. *International Journal of Chemical Kinetics*, *35*, 67–72.

Khairou, K. S., & El-Sayed, A. (2003). Inhibition effect of some polymers on the corrosion of cadmium in a hydrochloric acid solution. *Journal of Applied Polymer Science*, *88*, 866–871.

Khairou, K. S., & Hassan, R. M. (2000). Pectate polyelectrolyte ionotropic gels. 1. Kinetics and mechanisms of formation of manganate(VI)-pectate intermediate complex during the oxidation of pectate polysaccharide by alkaline permanganate. *European Polymer Journal*, *36*, 2021–2030.

Kulkarni, G. T., Gowthamarajan, K., Dhobe, R. R., Yohanan, F., & Suresh, B. (2005). Development of controlled release spheriods using natural polysaccharide as release modifier. *Drug Delivery*, *12*(4), 201–206.

Leffler, L., & Grunwald, E. (1963). *Rates and equilibria of organic reactions*. New York: Wiley.

May, C. (1990). Industrial pectins: Sources, production and applications. *Carbohydrate Polymers*, *12*, 79–99.

Murphy, R. M. (1997). Static and dynamic light scattering of biological macromolecules: What can we learn? *Current Opinion in Biotechnology*, *8*, 25–30.

O'Neill, M., Albersheim, P., & Darvill, A. (1990). P. M. Dey, & J. B. Harbourne (Eds.), *Methods in 336 plants biochemistry* (p. 415). London: Academic Press.

Paulsen, B. S., & Barsett, H. (2005). Bioactive pectic polysaccharides. *Advanced Polymer Science*, *186*, 69–101.

Ridley, B. L., O'Neill, A. M., & Mohnen, D. (2001). Pectins: Structure, biosynthesis, and oligogalacturonide-related signaling. *Phytochemistry*, *57*, 929–967.

Shaker, A. M. (2001a). Novel carboxymethyl cellulose ionotropic gels II. Kinetics of decomposition of the manganate(VI) intermediate-novel spectrophotometric tracer of the preformed short lived hypomanganate(V) coordination polymer sol. *Journal of Colloid and Interface Science*, *244*, 254–261.

Shaker, A. M. (2001b). Base-catalyzed oxidation of carboxymethyl-cellulose polymer by permanganate. *Journal of Colloid and Interface Science*, *233*, 197–204.

Shaker, A. M., El-Khatib, R. M., & Makran, H. S. (2007). Kinetics and mechanism of the decay of methyl cellulose-manganate(VI) polysaccharide transient species—Novel spectrophotometric kinetic trace of methyl cellulose hypomangate(V) gel intermediate polysaccharide. *Journal of Applied Polymer Science*, *106*, 2668–3267.

Shaker, A. M., El-Khatib, R. M., & Nassr, L. A. E. (2009). Further mechanistic orientation for the oxidation reaction between alkaline permanganate and poly galacturonate methyl ester. Novel spectrophotometric tracer of intrahypomanganate(V)-intermediate. *Carbohydrate Polymers*, *78*, 710–716.

Stephen, A. M. (1983). In G. O. Aspinall (Ed.), *The polysaccharides* (p. 97). London: Academic Press.

Trimukhe, K. D., & Varma, A. J. (2008). Complexation of heavy metals by crosslinked chitin and its deacetylated derivatives. *Carbohydrate Polymers*, *71*, 66–73.

Ubbink, J., & Kruger, J. (2006). Physical approaches for the delivery of active ingredients in foods. *Trends in Food Science & Technology*, *17*(5), 244–254.

Varma, A. J., Deshpande, S. V., & Kennedy, J. F. (2004). Metal complexation by chitosan and its derivative: A review. *Carbohydrate Polymers*, *55*, 77–93.

Whistler, J. R. L., & Smart, C. L. (1953). *Polysaccharide chemistry*. New York: Academic Press.