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Further mechanistic orientation for the oxidation reaction between alkaline permanganate and poly galacturonate methyl ester. Novel spectrophotometric tracer of intrahypomanganate(V) – Intermediate

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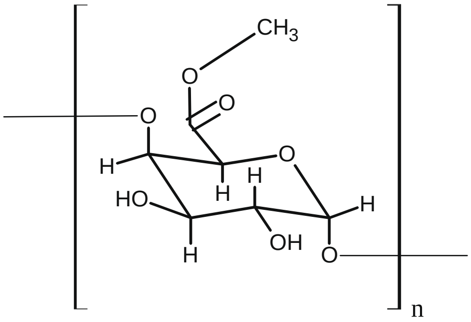
ABSTRACT

The kinetics of formation of the green manganate(VI) intermediate complex formed during the oxidation of pectin polysaccharide (poly galacturonate methyl ester) (PGME) by MnO_4^- in alkaline solution at pH $\geqslant$ 12 have been studied. The rate law was suggested to be: rate = $k_{obs.}[MnO_4^-]$. The reaction was found to be base – catalyzed and fractional second – order in [PGME]. The activation parameters have been evaluated and discussed. A reaction mechanism was suggested according to the experimental data. A new blue hypomanganate(V) coordination polymer intermediate sol was spectrophotometrically detected for the first time for pectin (poly galacturonate methyl ester) oxidation reaction. A further mechanistic presentation was proposed.

1. Introduction

Pectin is the methyl ester of pectic acid and is composed of long chains of galacturonic acid (Whistler & Smart, 1953). Pectin is a polysaccharide derived from the cell wall of higher terrestrial plants. Chemically, pectin is a linear polysaccharide containing from about 300 to 1000 monosaccharide units. D-Galacturonic acid is the principal monosaccharide unit of pectin. The D-galacturonic acid residues are linked together by alpha-1, 4 glycosidic linkages.



The kinetic oxidation of polysaccharides containing secondary alcoholic OH groups by $KMnO_4$ in basic medium were found to occur via the formation of an intermediate complex involving manganate(VI) ($Mn^{(VI)}O_4^{2-}$) as a transient species in the first stage of oxidation followed by a slow decomposition of the intermediate at the last stage of reaction to give soluble manganese(IV) and keto-derivatives as final product of the oxidation for the oxidant and substrate, respectively (El-Khatib, 2002; Hassan, 1993a,b; Khairou, 2001; Shaker, 2001a,b; Shaker, El-Khatib, & Makran, 2007).

The oxidation of sodium pectate polysaccharide was studied previously in alkaline solutions at $[OH^-]$ from 2.55×10^{-3} to 7.65×10^{-3} mol dm^{-3}. The reaction was found to be complicated which proceeded by the formation of Mn(VI)-pectate spectrophotometrically observed intermediate (Khairou, 2003; Khairou & Hassan, 2000). The rate of formation followed a first – order dependence in $[MnO_4^-]$ and fractional – order in sodium pectate concentration (Khairou & Hassan, 2000). Therefore, this complexity in the reaction pathway would deserve further investigation in order to throw more light on the reactive species, as well as, more details in the reaction mechanism.

In view of this and current interest of redox reactions involving polysaccharides as reducing substrates (El-Khatib, 2002; Hassan, 1993a,b; Khairou, 2001; Shaker, 2001a,b; Shaker et al., 2007), the oxidation of poly galacturonate methyl ester (pectin) (PGME) by $KMnO_4$ has been undertaken employing wide range of $[OH^-]$ (from 8×10^{-3} to 2×10^{-2} mol dm^{-3}) and substrate (from 2×10^{-3} to 6×10^{-3} mol dm^{-3}) concentrations. As an attempt to reach a more

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suitable mechanism and spectrophotometrically observed new coordination polymer of hypomanganato – PGME intermediate (containing Mn(V)) which is indeed newly founded in this contribution. This achievement has been undertaken via proper control of both temperature and concentration of reactants. Furthermore, it is tried in the recent presentation to make useful comparison with the data obtained in the previous experiments performed with other polysaccharides by our group {carboxymethyl – cellulose (CMC) (Shaker, 2001a) and methyl – cellulose (MC) (El-Khatib, 2002)} or by other authors {sodium alginate (Hassan, 1993a), pectate (Khairou & Hassan, 2000) and poly vinyl alcohol (Hassan, 1993c)}.

2. Experimental

Stock solutions of NaOH, perchlorate salt and $KMnO_4$ were prepared by dissolving the calculated amounts of BDH Analar samples in redistilled water. Pectin (poly galacturonate methyl ester) (PGME) solution (BDH) was prepared by stepwise addition of the sample reagent to deionized water with rapidly and continuous stirring of the solution to avoid the formation of lumps.

The stock solution of $KMnO_4$ was standardized against As_2O_3 (Vogel, 1989). Stock $KMnO_4$ was diluted to a suitable concentration before mixing with appropriate amount of NaOH and $NaClO_4$ solutions.

2.1. Kinetic measurements

The kinetic measurements were performed under pseudo-first order conditions in $[MnO_4^-]$ where NaOH and pectin (poly galacturonate methyl ester) (PGME) were mixed in large excess over the concentration of MnO_4^-. Total ionic strength was kept constant with inert $NaClO_4$. The suitable amounts of the reagents, at the desired temperature, were mixed in the thermostatted reaction cell adjusted at the same temperature. The reaction kinetics were followed by monitoring the increase in the absorbance at λ = 610 nm, the absorption peak of the green ($PGME - Mn^{VI}O_4^{2-}$) intermediate complex as a function of time. No interference exists from other reagents at that wavelength (cf. Fig. 1).

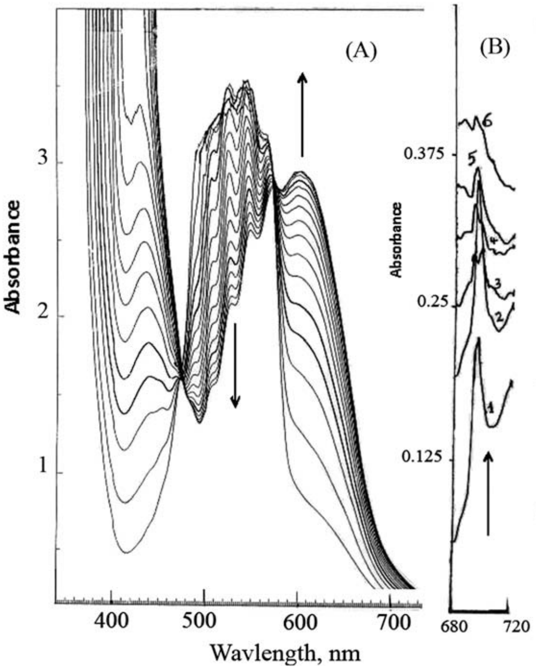


Fig. 1. Repeated Spectral scans during the oxidation of PGME by $KMnO_4$ in basic medium ($pH \geqslant 12$). (A) Formation of ($PGME - Mn^{(VI)}O_4^{2-}$) intermediate at λ = 610 nm, interval time = 3 min., temp. = 20 °C. (B) Formation of metastable Mn(V) at λ = 700 nm, interval time = 0.5 min., temp.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

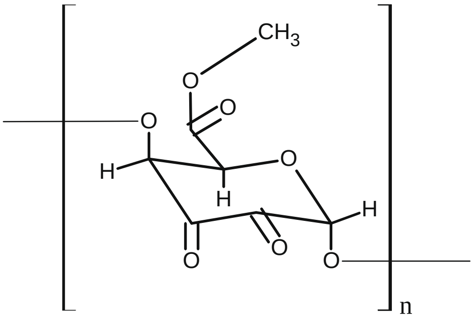
3. Results

3.1. Stoichiometry of the reaction

Different ratios of pectin (PGME) and $KMnO_4$ were mixed at $pH \geqslant 12$ (to avoid disproportionation of MnO_4^- to MnO_2 precipitate) and constant ionic strength, then after 48 h the unreacted $KMnO_4$ was estimated periodically until it reached a constant value, i.e., completion of reaction. The stoichiometry of the reactants was found to be PGME: $KMnO_4$ = 1:2 and the reaction equation can presented as:

$$2(1/n(C_7H_{10}O_6)n) + 4MnO_4^- = 2(1/n(C_7H_6O_6)n) + 4MnO_2 + 4OH^- + 2H_2O + O_2$$

where $(C_7H_{10}O_6)_n$ and $(C_7H_6O_6)_n$ corresponded to poly galacturonate methyl ester (pectin) and the oxidation product (diketo), respectively. The oxidation product may be as:



Moreover, the rate constant values of the growth of the intermediate ($PGME - Mn^{(VI)}O_4^{2-}$) at $\lambda_{max.}$ = 610 nm were often found to be twice those depicted for the decay of MnO_4^- at $\lambda_{max.}$ = 525 nm (cf. Fig. 1). This result is consistent with the evaluated stoichiometric ratio of $[MnO_4^-]/[PGME] = 2$.

3.2. Test of free radical formation

To get more information about the reaction mechanism, acrylonitrile was added to the reaction mixture. No polymerization found, so the oxidation of pectin (PGME) does not occur via free radical formation mechanism.

3.3. Effect of $[MnO_4^-]$ on the reaction rate

It was found that the oxidation of PGME by $KMnO_4$ in alkaline medium ($pH \geqslant 12$) followed first order kinetics in $[MnO_4^-]$:

$$\text{Rate} = -d[MnO_4^-]/dt = k_{obs.}[MnO_4^-]$$

This was indicated by the independence of rate constant values of the formation of intermediate ($PGME - Mn^{(VI)}O_4^{2-}$) at 610 nm on the initial concentration of MnO_4^- (El-Khatib, 2002; Shaker et al., 2007).

3.4. Effect of [PGME] on the reaction rate

A fractional second – order of the reaction rate on [PGME] and linear plots of $k_{obs.}$ *vs.* $[PGME]^2$ and $1/k_{obs.}$ *vs.* $1/[PGME]^2$ were obtained (cf. Figs. 2 and 3).

3.5. Effect of $[OH^-]$ on the reaction rate

The investigated reaction was monitored at different concentrations of OH^- from 8×10^{-3} to 2×10^{-2} mol dm^{-3}. It was found that the formation of the intermediate ($PGME - Mn^{(VI)}O_4^{2-}$) is base catalyzed reaction as shown from Fig. 4.

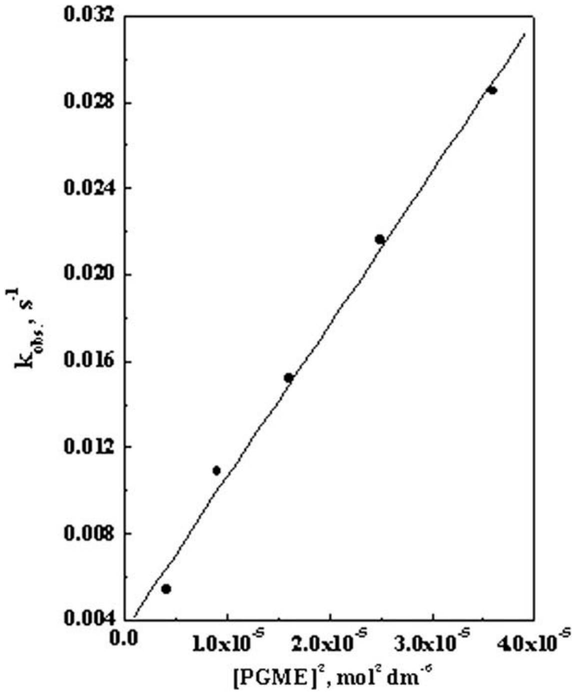


Fig. 2. $k_{obs.}$ *vs.* $[PGME]^2$ plot during the formation of PGME–MnO_4^{2-} complex intermediate in the presence of different [PGME] at $[OH^-] = 0.02\ mol\ dm^{-3}$, $[MnO_4^-] = 2\times10^{-4}\ mol\ dm^{-3}$, $I = 0.1\ mol\ dm^{-3}$ and 20 °C.

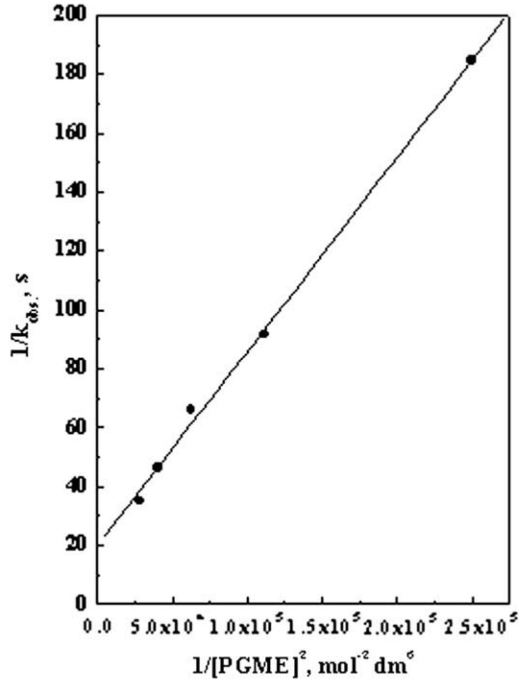


Fig. 3. $1/k_{obs.}$ *vs.* $1/[PGME]^2$ plot during the formation of PGME–MnO_4^{2-} complex intermediate in the presence of different [PGME] at $[OH^-] = 0.02\ mol\ dm^{-3}$, $[MnO_4^-] = 2\times10^{-4}\ mol\ dm^{-3}$, $I = 0.1\ mol\ dm^{-3}$ and 20 °C.

3.6. Effect of ionic strength on the reaction rate

The kinetic runs were executed at constant $[OH^-]$ and different concentrations of $NaClO_4$. The values of $k_{obs.}$ were found to increase with increasing ionic strength giving linear $k_{obs.}$ *vs.* $(\sqrt{I}/(\sqrt{I}+1)$ plot. (cf. Fig. 6).

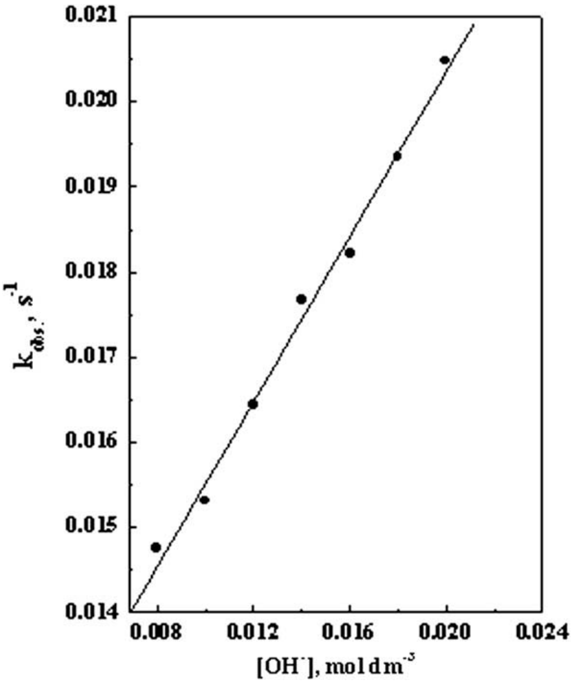


Fig. 4. $k_{obs.}$ *vs* $[OH^-]$ plot during the formation of PGME–MnO_4^{2-} complex intermediate in the presence of different $[OH^-]$ at $[PGME] = 4\times10^{-3}\ mol\ dm^{-3}$, $[MnO_4^-] = 2\times10^{-4}\ mol\ dm^{-3}$, $I = 0.1\ mol\ dm^{-3}$ and 20 °C.

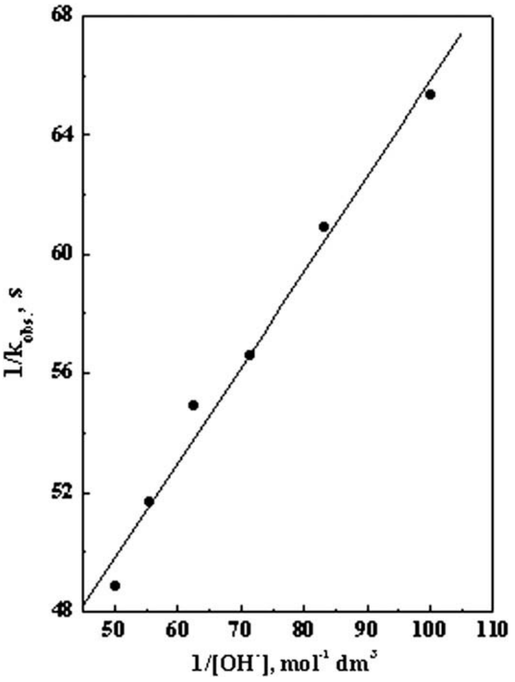


Fig. 5. $k_{obs.}^{-1}$ versus $[OH^-]^{-1}$ plot during the formation of PGME–MnO_4^{2-} complex intermediate in the presence of different $[OH^-]$ at $[PGME] = 4\times10^{-3}\ mol\ dm^{-3}$, $[MnO_4^-] = 2\times10^{-4}\ mol\ dm^{-3}$, $I = 0.1\ mol\ dm^{-3}$ and 20 °C.

3.7. Effect of temperature on the reaction rate

The observed rate constant ($k_{obs.}$) of reaction was estimated at different temperatures, constant $[OH^-]$ and ionic strength. And the activation parameters were calculated and reported in Table 1.

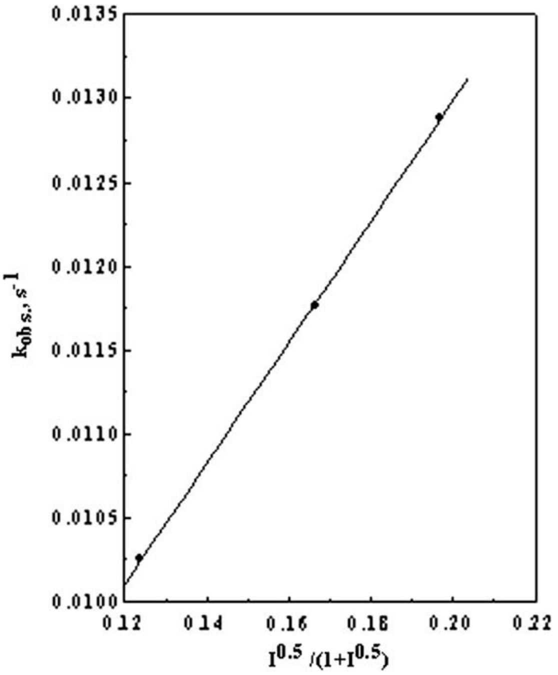


Fig. 6. $k_{obs.}$ *vs* $\sqrt{I}/(\sqrt{I}+1)$ plot during the formation of PGME–MnO_4^{2-} complex intermediate at $[OH^-]$ = 0.02 mol dm^{-3}, [PGME] = 4 × 10^{-3} mol dm^{-3}, $[MnO_4^-]$ = 2 × 10^{-4} mol dm^{-3} and 20 °C.

4. Discussion

The base catalyzed formation of the intermediate complex $(PGME - Mn^{(VI)}O_4^{2-})$ would confirm the deprotonation step of the substrate prior to the rate determining step as follows:

$$PGME + OH^- \overset{K_1}{\rightleftharpoons} PGME^- + H_2O \tag{1}$$

Then this step is followed by the attack of MnO_4^- to form the intermediate complexes C_1 and C_1' from the following competitive steps:

$$PGME^- + MnO_4^- \overset{K_2}{\rightleftharpoons} C_1 \tag{2}$$

$$PGME + MnO_4^- \overset{K_2}{\rightleftharpoons} C_1' \tag{3}$$

The linear plot observed of $k_{obs.}$ *vs.* $[OH^-]$ with a positive intercept refer to these competitive steps (cf. Fig. 4). But the positive salt effect obtained in Fig. 6 ($k_{obs.}$ *vs.* $\sqrt{I}/(\sqrt{I}+1)$) may recast step (3) and enhance step (2).

The fractional second – order dependence in [PGME] would suggest the reaction between C_1 and a further $PGME^-$ ion:

$$C_1 + PGME^- \overset{K_3}{\rightleftharpoons} C_2 \tag{4}$$

This is followed by the decomposition of the intermediate C_2 complex in the following rate – determining step:

$$C_2 \xrightarrow{k_1} \left[PGME - Mn^{(VI)}O_4^{2-}\right] + PGME^- \tag{5}$$

K_2 and K_3 are the first and second formation constants of the intermediates C_1 and C_2, respectively, and k_1 is the apparent first – order constant of the intermediate complex $(PGME - Mn^{(VI)}O_4^{2-})$ formation. It is suggested in these forgoing pathways that C_2 is the primarily formed blue hypomanganate $(PGME - Mn^{(V)}O_4^{3-})$ which is quickly formed and then decomposed to the green manganate intermediate $(PGME - Mn^{(VI)}O_4^{2-})$ complex spectrophotometrically detected at 610 nm (cf. Fig. 1). The former blue hypomanganate $(PGME - Mn^{(V)}O_4^{3-})$ has been spectrophotometrically observed at 700 nm and for the first time in this recent contribution and others by Shaker and his colleagues (El-Khatib, 2002; Shaker, 2001b,c).

C_1 and C_1' are transient intermediates in which inner – sphere one – electron transfer occurs from PGME or $PGME^-$ to MnO_4^- anions in steps (2) and (3), respectively. In step (4), another inner – sphere one – electron transfer undertakes to form the hypomanganate $(PGME - Mn^{(V)}O_4^{3-})$ (C_2) intermediate. In the final stage of manganate $(PGME - Mn^{(VI)}O_4^{2-})$ intermediate formation, a backward inner – sphere one – electron transfer from hypomanganate $(PGME - Mn^{(V)}O_4^{3-})$ to $PGME^-$ polysaccharide occurs.

The short relaxation time of about few seconds elapsed before the first appearance of the blue hypomanganate(V) intermediate complex may forward an evidence for the formation of the transient species C_1 and C_1', as well as, the occurrence of backward electron transfer in step (4) prior to the final formation of the green manganate(VI) intermediate. Fig. 1(A) shows repeat scans with 3 min time intervals illustrating the decay of MnO_4^- at 525 nm whereby growing the band at 610 nm corresponding to the green manganate(VI) intermediate. On the other hand, Fig. 1(B) shows rapid repeat scans with 30 s interval time at 700 nm. As shown in these scans the blue hypomanganate $(PGME - Mn^{(V)}O_4^{3-})$ intermediate could be detected at 700 nm, but is still highly unstable, it can remain for about 3 min at 10 °C, before it reaches a steady state. The stability of $(PGME - Mn^{(V)}O_4^{3-})$ depends on the concentrations of reactants and temperature. It is assumed that the blue intermediate grows rapidly, in the earlier stages, to a steady state and then declines to the green $(PGME - Mn^{(VI)}O_4^{2-})$ transient species. The observed naked eye rapid growth of the blue color and then gradual fading supports this speculation regime. Thereafter, the green intermediate was decomposed much more slowly to the final mono and/or diketo products (colorless solution) and MnO_2. The final products of the oxidation of sodium alginate, CMC and MC were reported elsewhere (El-Khatib, 2002; Hassan, 1993a; Shaker, 2001a).

A further supportive argument for the recent reaction regime is that mentioned before (Hassan, Mousa, & Wahdan, 1988), of initial direct reduction of carboxymethyl cellulose (CMC) of Mn(VII) to Mn(V) without the formation of Mn(VI) as an intermediate in the early stages.

By applying the steady – state approximation for the concentrations of the reactive intermediates C_1 and C_2 and putting the total concentration of poly galacturonate methyl ester (pectin) as:

$$[PGME]_T = [C_1] + [C_2] + [PGME] + [PGME^-] \tag{6}$$

Thus the following reaction rate can be formulated:

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = \frac{k_1K_1K_2K_3[OH^-][PGME]_T^2[MnO_4^-]}{1 + K_1[OH^-] + K_1K_2[OH^-][PGME]_T[MnO_4^-](1 + K_3[PGME]_T)} \tag{7}$$

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

	Temperature, °C					Ea kJmol^{-1}	$\Delta H^{\#}$ kJmol^{-1}	$\Delta S^{\#}$ Jmol^{-1}K^{-1}	$\Delta G^{\#}$ kJmol^{-1}	A mol^{-1} s^{-1}
	10	15	20	25	30					
k_2, mol^{-1} dm^3 s^{-1}	2.02	2.54	3.71	5.04	6.38	42.61	40.18	−96.79	68.54	1.45 × 10^8

Under the adopted conditions of the recent reaction that $[\mathrm{OH^-}]$ and $[\mathrm{PGME}]_T >>> [\mathrm{MnO_4^-}]$ the suitable rate law becomes:

$$-d[\mathrm{MnO_4^-}]/\mathrm{dt} = k_{\mathrm{obs.}}[\mathrm{MnO_4^-}] \tag{8}$$

Then, on comparing Eqs. (7) and (8) and rearrangement, $k_{\mathrm{obs.}}^{-1}$ can be given as:

$$k_{\mathrm{obs.}}^{-1} = \left(\frac{[\mathrm{OH^-}]^{-1}}{k_1K_1K_2K_3} + \frac{1}{k_1K_2K_3}\right)\frac{1}{[\mathrm{PGME}]_T^2} + k' \tag{9}$$

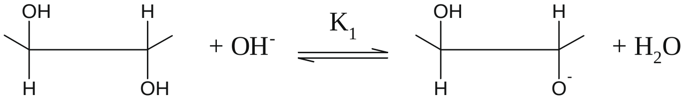
According to Eq. (9) at constant $[\mathrm{OH^-}]$, a plot of $k_{\mathrm{obs.}}^{-1}$ *vs.* $1/[\mathrm{PGME}]^2$ should be straight line with a positive intercept as it is observed experimentally (cf. Fig. 3). The value of the intercept, $k' = 19.93$ s and the slope = 6.59×10^{-4} s mol^2 dm^{-6}.

Again at constant [PGME], a plot of $k_{\mathrm{obs.}}^{-1}$ *vs.* $[\mathrm{OH^-}]^{-1}$ gives a straight line (cf. Fig. 5). Eq. (9) can be simplified as:

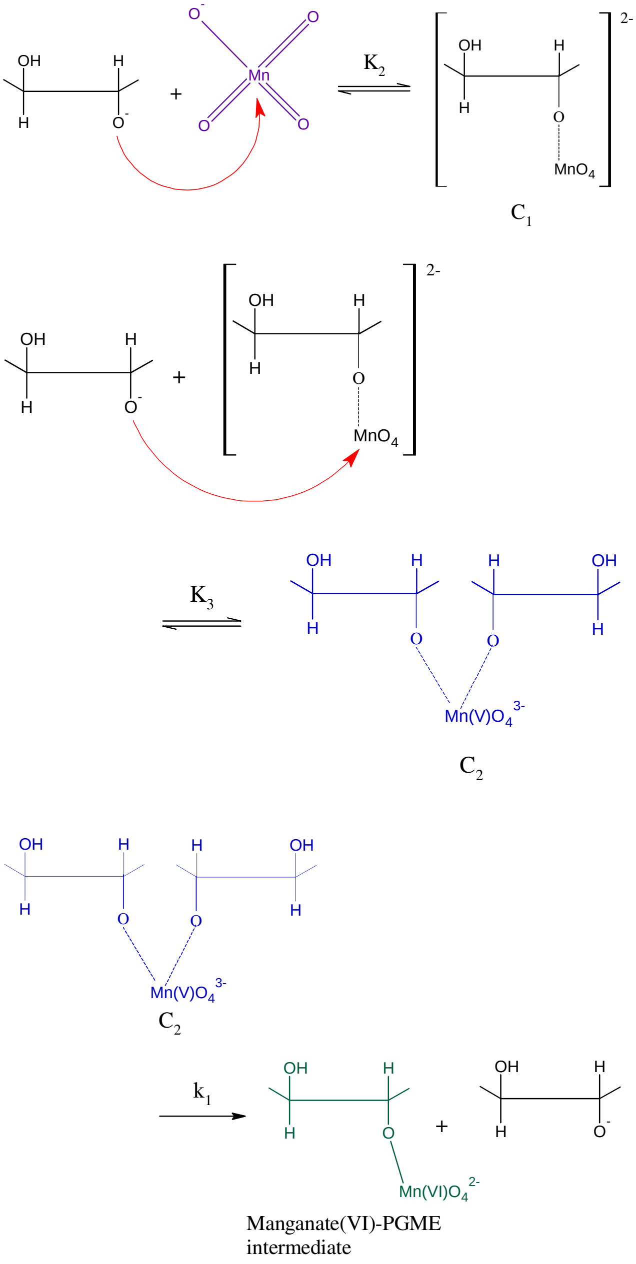
$$k_{\mathrm{obs.}}^{-1}[\mathrm{PGME}]^2 = \frac{[\mathrm{OH^-}]^{-1}}{k_a} + k'' \tag{10}$$

where, $k_a = k_1K_1K_2K_3$, $k'' = k'[\mathrm{PGME}]^2 + 1/k_b$ and $k_b = k_1K_2K_3$. A plot of $k_{\mathrm{obs.}}^{-1}[\mathrm{PGME}]^2$ *vs.* $[\mathrm{OH^-}]^{-1}$ should be a straight line as shown experimentally (cf. Fig. 7) where the value of the intercept, $k'' = 5.40 \times 10^{-4}$ s mol^2 dm^{-6} and the slope = 5.13×10^{-6} s mol^3 dm^{-9}.

The question that remains to be considered is the nature of the intermediates formed from the reaction of $\mathrm{MnO_4^-}$ and the enolate form of the PGME in the early stages. The experimental observations confirmed the base dependence of the rate of formation of the intermediate complex. Thus a prior deprotonation equilibrium step must occur:



This is followed by the attack of $\mathrm{MnO_4^-}$ on the formed alkoxide:



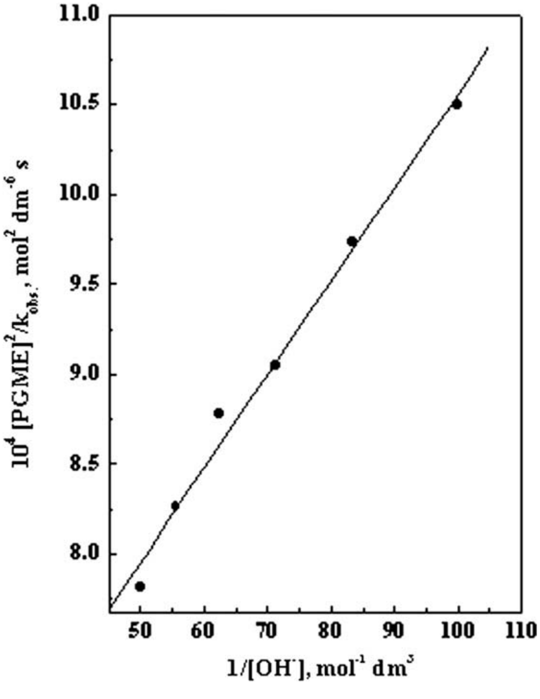


Fig. 7. $[\mathrm{PGME}]^2/k_{\mathrm{obs.}}$ *vs.* $1/[\mathrm{OH^-}]$ plot during the formation of PGME–$\mathrm{MnO_4^{2-}}$ intermediate complex in the presence of different $[\mathrm{OH^-}]$ at [PGME] = 4×10^{-3} mol dm^{-3}, $[\mathrm{MnO_4^-}] = 2 \times 10^{-4}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3} and 20 °C.

Table 2
The activation parameters and Arrhenius factors for the formation of (polysacchride–$\mathrm{MnO_4^{2-}}$) intermediate complexes.

Polysaccharide[a]	Ea kJmol^{-1}	$\Delta H^{\#}$ kJmol^{-1}	$\Delta S^{\#}$ Jmol^{-1} K^{-1}	$\Delta G^{\#}$ kJmol^{-1}	A mol^{-1} s^{-1}	Ref.
Pectin (PGME)	42.61	40.18	−96.79	68.54	1.45 x 10^8	Recent paper
Sodium pectate	–	51.31	−21.44	57.69	–	Khairou & Hassan (2000)
MC	19.90	9.93	−220.40	75.97	135.5	El-Khatib (2002)
CMC	36.95	32.00	−110.60	64.06	9.56 × 10^7	Shaker (2001a)
PVA	–	56.83	−42.17	69.40	–	Hassan (1993c)
Sod. Alg.	–	50.29	−58.46	67.71	–	Hassan (1993a)

[a] MC, methylcellulose; CMC, carboxymethyl cellulose; Sod. Alg., sodium alginate; PVA, polyvinyl alcohol.

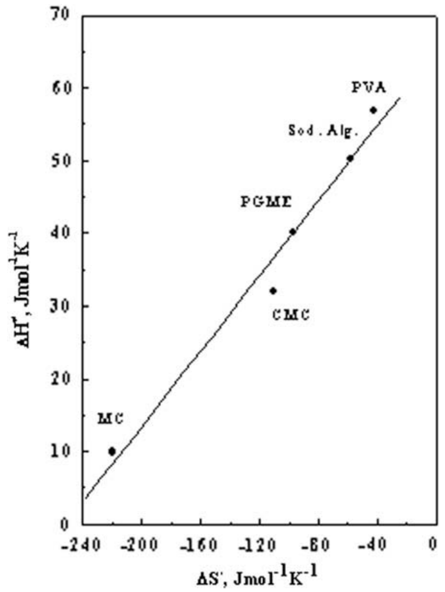


Fig. 8. Isokinetic plot ($\Delta H^{\#}$ *vs.* $\Delta S^{\#}$) for the formation of the intermediate complex during the oxidation of polysaccharides by alkaline $KMnO_4$.

The formation of such intermediates is facilitated by the polarization of the Mn—O bond and presumably pectate free radical firmly bonded to $Mn^{(VI)}O_4^{2-}$ (Sharpless, Teranishi, & Backvall, 1977).

The activation parameters were evaluated from Eyring plot by least squares (cf. Table 1), then collected and compared with the corresponding values reported for the alkaline permanganate oxidation of other polysaccharides containing secondary alcoholic OH groups (cf. Table 2 and Fig. 8).

The activation parameters support the suggested mechanism. The observed large negative values of the entropy of activation $\Delta S^{\#}$ confirm the compactness of the green manganate(VI) intermediate complex and are characteristic of one – and/or two – electron inner – sphere electron transfer (Freeman et al., 1981). Again the positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$ is indicative to the enhanced formation of the intermediates with increasing temperature, as well as, to the non-spontaneity of the complex formation in the rate – determining step as represented by the proposed mechanism. The linear isokinetic plot shown in Fig. 8, indicates similarity of mechanisms of oxidation of polysaccharides (e.g., poly galacturonate methyl ester (pectin), sodium pectate, methylcellulose, carboxymethyl cellulose, sodium alginate and polyvinyl alcohol) with alkaline permanganate, but may be different in some details with consistence in initials of these regimes.

5. Conclusion

Due to the lack of information in literature on the alkaline oxidation of polysaccharides by permanganate (Hassan, 1993a,c; Khairou 2001), we had undertaken a number of kinetic studies programs concerning this respect (El-Khatib, 2002; Shaker, 2001a,b,c; Shaker et al., 2007). Then finally comes to the recent submission to get more focus on the oxidation mechanisms of natural polymers containing secondary alcoholic groups. The recent oxidation reaction of PGME by strong alkaline permanganate implies the primarily and quickly formed blue hypomanganate(V) ($PGME - Mn^{(V)}O_4^{3-}$) intermediate complex, then slowly decomposed to the green manganate(VI) ($PGME - Mn^{(VI)}O_4^{2-}$) transient coordination polymer sol. The former and the latter intermediates have been appeared at 700 nm and 610 nm, respectively. The facile detection of these reactive intermediates of Mn(V) and Mn(VI) coordination precursors by the conventional spectrophotometric tools is supportive in elucidating the mechanism of organic and inorganic substrates by permanganate (Lee, 1982; Semandi, 1983; Stewart, 1965). The detection of these novel intermediate coordination biopolymers would be striking and starting for later vital applications to many aspects. Biopolymers could be used to encapsulate, protect and deliver bioactive or functional components, such as minerals, peptides, proteins, enzymes, drugs, lipids or dietary fibers (Chen, Remondetto, & Subirade, 2006; Emerich & Thanos, 2007; Goldberg, Langer, & Jia, 2007; Kulkarni, Gowthamarajan, Dhobe, Yohanan, & Suresh, 2005; Ubbink & Kruger, 2006).

Furthermore, the diketo-polysaccharide formed in the final second stage of oxidation would be useful as precursors for the synthesis of new biopolymers (Hassan, 1993a), as well as, selective bio-chelating agents for polyvalent cations forming ionotropic gels. These gels would be useful as conductors, selective cation sieves, semi-permeable membranes just as animal bladder, biocatalysts and cation exchange resins (Awad, El-Cheikh, & Shaker, 1980a,b).

As future studies, there will be programs to study the decomposition kinetics of the polymer green intermediate of ($PGME - Mn^{(VI)}O_4^{2-}$), the second stage of the recent paper, as well as, the kinetics of oxidation of other polysaccharides. It would be more interesting to extend these kinetic studies to involve the medium effect on the reaction mechanism.

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