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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

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Abstract

The kinetics of formation of the [Pect $Mn^{VI}O_4^{2-}$] intermediate complex formed during the oxidation of pectate polysaccharide by permanganate ions in alkaline solutions at pH $\geqslant 12$ have been measured by a conventional spectrophotometric technique. The reaction showed a first-order dependence on permanganate concentration and a fractional order with respect to the pectate concentration for the complex formation. Kinetic and spectrophotometric evidence revealed the formation of manganate (VI) transient species. The results obtained indicated that the rate of formation is base catalyzed. Thermodynamic parameters were evaluated and a suitable mechanism consistent with the kinetic results was suggested. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Kinetics; Oxidation; Reduction; Permanganate; Pectate; Polysaccharides; Ionotropic gels

1. Introduction

The structure of pectic acid is closely related to that of alginic acid. The principal structural difference between them is the position of the two C-2 and C-3 hydroxyl groups being *cis* in alginic acid and *trans* in pectic acid or, if the conformation is considered, axial–equatorial and equatorial–equatorial, respectively, the carboxyl groups probably being equatorial in both cases [1,2].

The kinetics of permanganate oxidation of alginate, a natural polymer, in alkaline solution have been reported previously [3,4]. The kinetic results obtained revealed the formation of an intermediate complex involving manganate (VI) as a transient species in the initial stage of oxidation, followed by a slow decomposition of the intermediate at the final stage of reaction to give soluble manganese (IV) and keto-derivatives as final products of the oxidation for the oxidant and substrate, respectively.

Therefore, the present work has been undertaken to examine the influence of OH conformational structure on the reaction kinetics with a view to shedding more light on the oxidation mechanisms of natural polymers and comparing the results obtained with those of synthetic polymers [5,6] containing the same secondary alcoholic groups.

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2. Experimental

All materials used were of analytical grade. Distilled water was redistilled from alkaline permanganate [7] and degassed by bubbling through nitrogen, boiling and cooling under nitrogen atmosphere.

Sodium pectate solutions (BDH) were prepared by stepwise addition of the sample reagent to deionized water whilst rapidly stirring the solution to prevent the formation of lumps, which swell with difficulty. The preparation and analysis of the stock solutions and the procedure for the kinetic runs were the same as described earlier [3,4].

All kinetic measurements were conducted under pseudo first-order conditions where the pectate concentration was maintained in a large excess over that of $[MnO_4^-]_0$. However, some kinetic runs were carried out under the conditions $[MnO_4^-]_0 > [Pect]_0$ in order to check the data obtained from the pseudo first-order kinetics. The results obtained were found to be in good agreement with each other within experimental error (±4%), indicating the reproducibility of the measurements.

3. Results

3.1. Stoichiometry

Since the kinetics of this oxidation reaction are complex owing to the formation of Mn (VI) and/or Mn (V) transient intermediates, determination of the reaction stoichiometry becomes of great importance.

Reaction mixtures containing different initial ratios of the reactants were mixed at pH > 12, to avoid the disproportionation of manganate (VI) ion at lower pH, and equilibrated for about 48 h at room temperature. The unreacted $[MnO_4^-]$ was estimated periodically until it reached a constant value, i.e. completion of reaction. The results confirm that the stoichiometry of the overall reaction holds by the equation

$$3(C_6H_7O_6Na)_n + 4MnO_4^- = 3(C_6H_3O_6Na)_n + 4MnO_2 + 4OH^- + 4H_2O \quad (1)$$

where $C_6H_7O_6Na$ and $C_6H_3O_6Na$ denote the pectate and its keto derivative, respectively. The formation of ketopectates as the final product of pectate oxidation was confirmed by microanalysis and spectral data as the same as described elsewhere [8,9]. The initial reduction product of permanganate was identified from the UV–vis spectrum of manganate (VI) ion. Although this ion may oxidize pectate, the reaction rate seems to be much slower than that of permanganate oxidation based on thermodynamic grounds, and hence it should not influence the kinetics of the initial rate.

3.2. Dependence of reaction rates on $[MnO_4^-]$ and $[Pect]$

Preliminary experiments indicated that the oxidation of pectate by alkaline permanganate proceeds via formation of a detectable intermediate,

$$\text{Pect} + MnO_4^- \xrightarrow[\text{slow}]{k_1} [\text{Pect}\,Mn^{VI}O_4^{2-}] \quad (2)$$

followed by a slower decay of the intermediate complex to give rise to the product,

$$[\text{Pect}\,Mn^{VI}O_4^{2-}] \xrightarrow[\text{slow}]{k_2} \text{products} \quad (3)$$

As shown in Fig. 1, most of the spectral changes of MnO_4^- ion are displayed, but superposition of other species is apparent. A gradual disappearance of the MnO_4^- band at a wavelength of 525 nm, its absorption maximum, with a simultaneous appearance of new intermediate species at wavelengths 606, 435, 350 and 325 nm, is observed.

In the presence of a large excess of pectate over that of permanganate concentration, the absorbance at any time for such a consecutive reaction may be expressed by the relationship [10,11],

$$A_t = A_0 + e^{-k_1 t}\frac{\delta_{\text{int}}[MnO_4^-]k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) + \frac{A_\infty[MnO_4^-]k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \quad (4)$$

where A_0, A_t and A_∞ denote the absorbances of permanganate ion at time = 0, t and infinity, respectively, and k_1 and k_2 are the first-order rate constants for the formation and decomposition of the intermediate complex, respectively.

The rates of formation and decomposition of the intermediate were of such magnitude that they could be monitored separately as shown in Fig. 2. Since the rate of decomposition (k_2) is much smaller than that of formation (k_1), the last two terms in Eq. (4) may be neglected, and hence the initial rate can be expressed by a simple pseudo first-order integrated form.

The rates of the initial reaction were determined by following either the disappearance of permanganate ion or the appearance of the intermediate complex at more suitable wavelengths where no interference from other reagents occur. Identical rate constants within experimental errors were obtained at 606 and 525 nm, indicating that the reaction is first-order with respect to permanganate concentration. The first-order dependency was confirmed

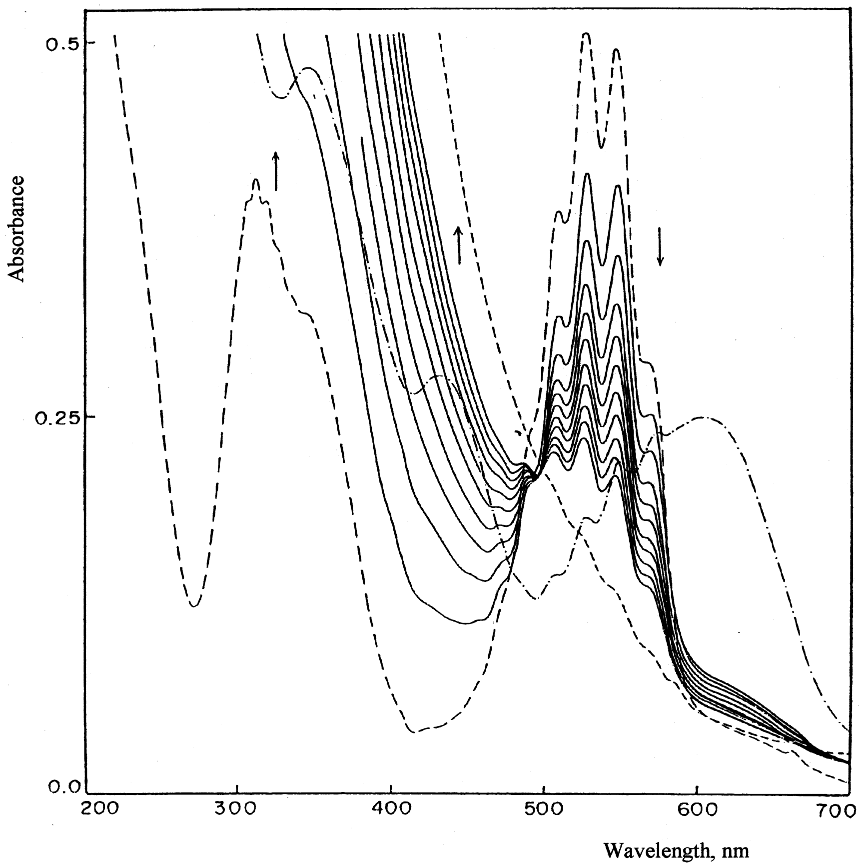


Fig. 1. Spectral changes (200–700 nm) in the oxidation of pectate by permanganate ion at: $[MnO_4^-]=2.2\times10^{-4}$, $[Pect]=2.5\times10^{-3}$ mol dm^{-3} and 5°C; (- - -) MnO_4^- ion; (—) intermediate. (– ·— –) using permanganate ion as a reference.

not only by the linearity of the pseudo first-order plots of ln(absorbance) versus time, but also by the independence of the observed first-order rate constants, k_{obs}, on the initial $[MnO_4^-]_0$ values, varying from 2×10^{-4} to 5×10^{-4} mol dm^{-3} in a number of steps with constant concentrations of all other reagents. The values of k_{obs} were calculated from the gradients of such plots using the method of least-squares and are summarized in Table 1. However, first-order dependence was not maintained with respect to [Pect].

The molar extinction coefficient of the intermediate at a wavelength of 606 nm was calculated by the methods described elsewhere [5,6], and was found to be 1150 ± 30 dm^3 mol^{-1} cm^{-1} at $[MnO_4^-]=2.2\times10^{-4}$, $[Pect]=2.5\times10^{-3}$, $[OH^-]=1\times10^{-3}$, ionic strength $(I)=0.1$ mol dm^{-3} and 5°C.

At relatively high concentrations of pectate, $>10^{-1}$ mol dm^{-3}, a decrease in the initial rate was observed. This fact may be explained by the formation of more than one complex and at least one of the complexes appears to resist the oxidation since increasing the [Pect] decreases the rate. If all complexes undergo oxidation, increases in the pectate concentration should

Table 1
The observed first order rate constant[a] in the oxidation of pectate by permanganate ion: $[MnO_4^-]=2.07\times10^{-4}$; $[OH^-]=3.06\times10^{-3}$, $I=0.1$ mol dm^{-3}, $\lambda=5.25$ nm at 20°C

10^3[Pect] (mol dm^{-3})	1.71	2.29	2.86	3.42
$10^3\ k_{obs}$ (s^{-1})	2.17 (2.11)[b]	2.83(2.78)	3.50(3.52)	4.01(4.05)

[a] Experimental errors ±4%.

[b] The values in parentheses were determined at $\lambda=606$ nm.

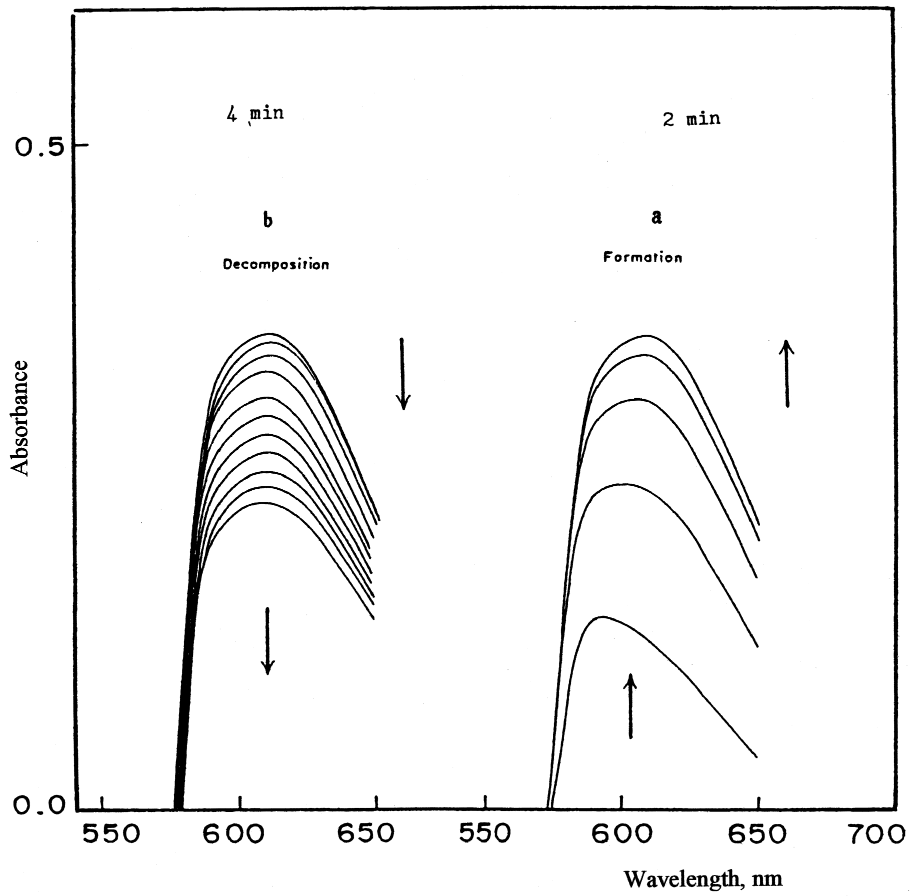


Fig. 2. Spectral changes during (a) the formation and (b) the decomposition of the intermediates in the oxidation of pectate by permanganate ion. $[MnO_4^-] = 2.2 \times 10^{-4}$; $[OH^-] = 1.1 \times 10^{-3}$; $[Pect] = 2.5 \times 10^{-3}$ mol dm^{-3}; 5°C.

increase the rate. Therefore, all of the present experiments were performed under the conditions of $[Pect]_0 < 10^{-2}$ mol dm^{-3}.

Plots of log(absorbance) versus time were fairly linear up to 90% of complete decomposition, giving $k_2 = 2.67 \times 10^{-3}$ s^{-1} at 20°C where $[MnO_4^-] = 2.07 \times 10^{-4}$, $[Pect] = 3.42 \times 10^{-3}$, $[OH^-] = 5.35 \times 10^{-3}$ and $I = 0.1$ mol dm^{-3}. This linearity shows that the reaction is first-order in [Pect $Mn^{VI}O_4^-$]. The first order dependence was confirmed by the observed independence of the decomposition rate constant from either $[MnO_4^-]$ or [Pect].

3.3. Dependence of reaction rates on $[OH^-]$

In order to elucidate the reaction mechanism, kinetic runs were performed for NaOH–$NaClO_4$ solutions with different $[OH^-]$ and constant ionic strength and temperature. The experimental observations showed that both rate constants of formation and decomposition were base catalyzed as an increase in $[OH^-]$ was accompanied by an appreciable increase of the rate constants. Values calculated by the least-squares method are summarized in Table 2.

3.4. Dependence of reaction rates on temperature

The reaction was carried out at four temperatures between 15 and 30°C and at constant $[OH^-]$ and ionic strength in order to determine the thermodynamic parameters. The values of the thermodynamic parameters were calculated by the least-squares method.

Table 2
Dependence of k_{obs} on [OH] in the oxidation of pectate by permanganate ion: $[MnO_4^-] = 2.07 \times 10^{-4}$; $[Pect] = 2.86 \times 10^{-3}$; $I = 0.1$ mol dm^{-3} at 25°C

10^3[OH] (mol dm^{-3})	3.06	3.82	4.59
10^3 k_{obs} (s^{-1})	5.25	7.10	8.51

4. Discussion

Preliminary experiments showed that the kinetics of oxidation of pectate polysaccharide by alkaline permanganate exhibit a similar behavior to that observed in the oxidation of either alginates [3,4] or poly(vinyl alcohol)]5,6] by this oxidant. Permanganate ion reacts with pectate via the formation of an intermediate complex, which displays an absorption maximum at a wavelength of 606 nm. Fig. 1 reveals the formation of manganate (VI) and/or hypomanganate (V) as transient species as the reaction proceeded. The absence of traces having the absorption maximum of Mn (V) around 700 nm [15,16] is considered as evidence against the accumulation of hypomanganate (V), and hence the absorption band observed at 606 nm is due to the transient appearance of manganate (VI) [17,18]. The failure of detection of hypomanganate (V) may be explained by the short life time which is attributed to its rapid disproportionation [19]. The isobestic point seen at a wavelength of 575 nm during the course of disappearance of MnO_4^- ion indicates the conversion of MnO_4^- to MnO_4^{2-}, while that observed at a wavelength of 475 nm reveals that MnO_4^- and formed Mn (IV) do not necessarily exclude the formation of the detectable Mn (VI) intermediate. Again, the change in color of the mixture as the reaction proceeded from purple-pink to blue to green may confirm the reduction of Mn (VII) → Mn (VI) → Mn (V) species, respectively.

In view of these facts and the experimental observations, the absorption spectrum at 606 nm suggests the reduction of $Mn^{VII}O_4^-$ to $Mn^{VI}O_4^{2-}$ at the initial stage which associates with the intermediate complex formed. Again, the dependence of the rate of formation on $[OH^-]$ indicates a deprotonation of the substrate prior to the rate determining step

$$\text{Pect} + \text{OH}^- \underset{\text{fast}}{\overset{k}{\rightleftharpoons}} \text{Pect}^- + \text{H}_2\text{O} \tag{5}$$

followed by the attack of the oxidant to form an intermediate complex defined by Eq. (6)

$$\text{Pect}^- + \text{MnO}_4^- \xrightarrow[\text{slow}]{k} [\text{Pect Mn}^{\text{VI}}\text{O}_4^{2-}] \tag{6}$$

where Pect and Pect^- denote the pectate and the alkoxide form, respectively. The rate of formation of the complex or the disappearance of permanganate ion can be expressed by

$$\text{Rate} = k_a[\text{MnO}_4^-][\text{Pect}^-] \tag{7}$$

Assuming that reaction (6) is the rate-determining step of the initial stage of reaction, the change in the apparent rate constant for the complex formation with change in $[OH^-]$ may be written as follows:

$$\text{Rate} = \frac{k_a K[\text{OH}^-][\text{MnO}_4^-][\text{Pect}^-]_T}{1 + K[\text{OH}^-]} \tag{8}$$

where $[\text{Pect}^-]_T$ is the total concentration of pectate. When the pectate is present in a large excess over the $[MnO_4^-]$, the rate-law is

$$\text{Rate} = k_{\text{obs}}[\text{MnO}_4^-] \tag{9}$$

On comparison of Eqs. (8) and (9), the following relationship is obtained:

$$1/k_{\text{obs}} = \left(\frac{[\text{OH}]^{-1}}{k_a K} + \frac{1}{k_a}\right)\frac{1}{[\text{Pect}]_T} \tag{10}$$

An alternative mechanism could be considered, this being the formation of a transient species (A) before complex formation as follows:

$$\text{Pect}^- + \text{MnO}_4^- \underset{\text{fast}}{\overset{k_1}{\rightleftharpoons}} \text{A} \underset{\text{slow}}{\overset{k}{\rightleftharpoons}} [\text{Pect Mn}^{\text{VI}}\text{O}_4^{2-}] \tag{11}$$

Assuming A to be a reactive intermediate species and applying the steady-state approximation for the concentration of the intermediate, the rate law may be expressed by

$$\text{Rate} = \frac{k_a K K_1[\text{OH}^-][\text{MnO}_4^-][\text{Pect}]_T}{1 + K[\text{OH}^-] + K K_1[\text{OH}^-][\text{MnO}_4^-]} \tag{12}$$

Comparing Eqs. (12) and (9), one concludes that

$$1/k_{\text{obs}} = \left(\frac{[\text{OH}^-]^{-1}}{k'_a} + \frac{1}{k''_a}\right)\frac{1}{[\text{Pect}]} + k' \tag{13}$$

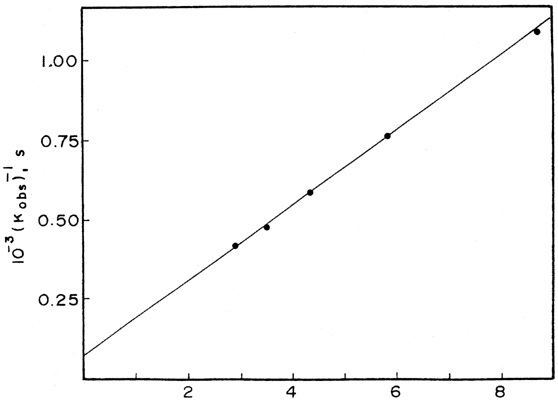


Fig. 3. A reciprocal plot of $1/k_{\text{obs}}$ versus 1/[Pect] in the oxidation of pectate by permanganate ion. $[MnO_4^-] = 2.1 \times 10^{-4}$, $[OH^-] = 1.1 \times 10^{-3}$, $I = 0.1$ mol dm^{-3} at 20°C.

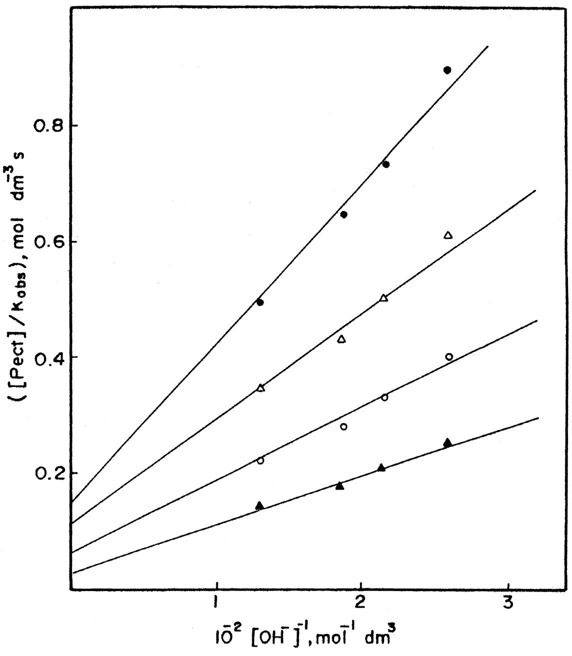


Fig. 4. Plots of $[\mathrm{Pect}]/k_{\mathrm{obs}}$ versus $1/[\mathrm{OH}]$ during the formation of the intermediate complex, $[\mathrm{MnO_4^-}] = 2.1 \times 10^{-4}$, $[\mathrm{Pect}] = 2.86 \times 10^{-2}$, $I = 0.1$ mol dm^{-3}. (●) 10; (△) 15; (○) 20; (▲) 25°C.

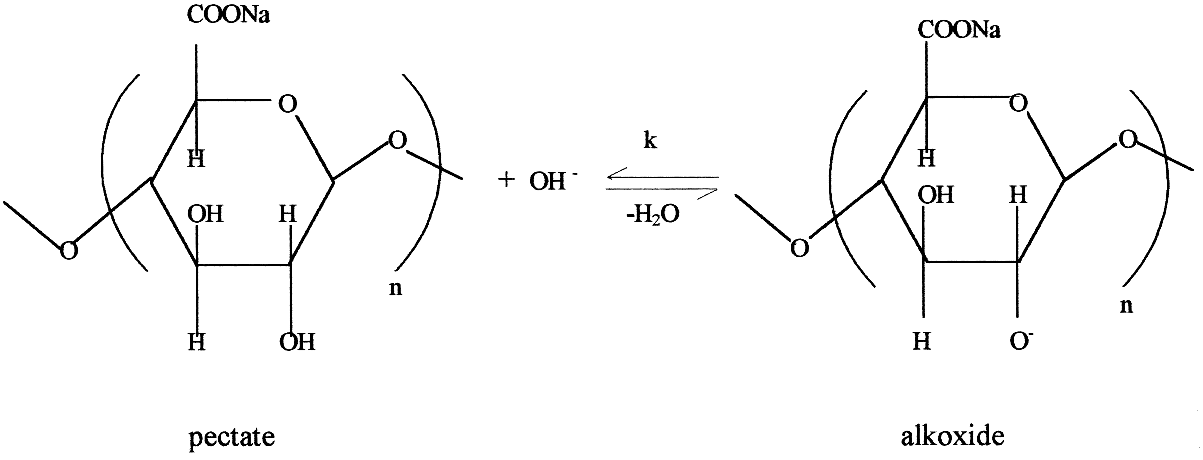
where $k_a' = k_a K K_1$ and $k_a'' = k_a K_1$, respectively. The experimental results are not in agreement with Eq (10) since the plot of $(k_{\mathrm{obs}})^{-1}$ against $[\mathrm{Pect}]^{-1}$ gave a straight line with positive intercept on the $(k_{\mathrm{obs}})^{-1}$ axis. The dependence of k_{obs} on the [Pect] follows Michaelis–Menten kinetics [20] of formation of an intermediate complex of inner sphere nature [21].

Table 3
The values of k_a' and k_a'' in the oxidation of pectate by permanganate ion: $[\mathrm{MnO_4^-}] = 2.07 \times 10^{-4}$; $[\mathrm{Pect}] = 2.86 \times 10^{-3}$, $I = 0.1$ mol dm^{-3}; $\lambda = 5.25$ nm

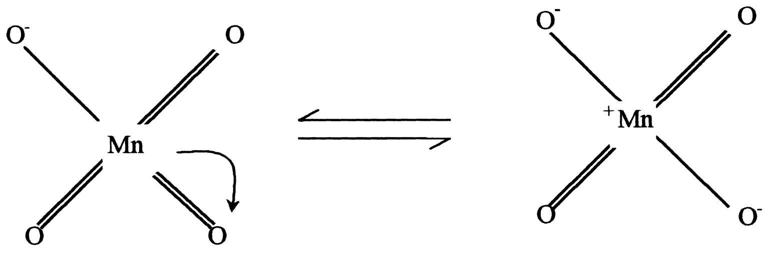
Rate constant	Temperature °C			
	15	20	25	30
$10^2\ k_a'$ (mol^{-1} dm^9 s^{-1})	2.81	4.21	6.10	11.00
$10^2\ k_a''$ (mol^{-2} dm^6 s^{-1})	2.24	3.32	4.64	8.15

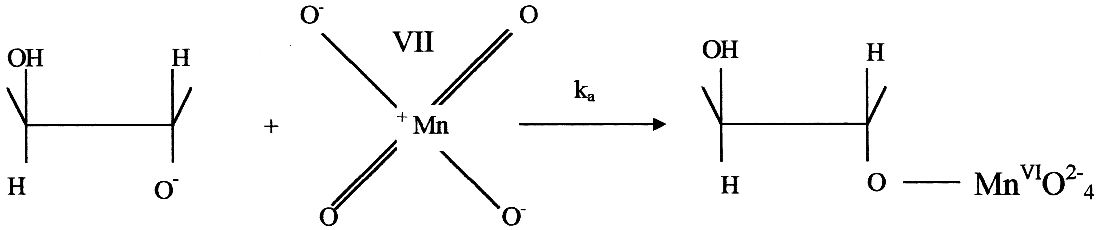
Eq. (13) requires that the plot of $(k_{\mathrm{obs}})^{-1}$ versus $[\mathrm{Pect}]^{-1}$ at constant $[\mathrm{OH^-}]$ should be linear with positive intercept on $1/k_{\mathrm{obs}}$ axis as is experimentally observed (Fig. 3). Again, plots of $[\mathrm{Pect}]/k_{\mathrm{obs}}$ versus $1/[\mathrm{OH^-}]$ gave good straight lines as shown in Fig. 4. The values of k_a' and k_a'' were calculated by the method of least squares and are summarized in Table 3. Values of k_a could not be evaluated owing to the nonavailability of K_2 at various temperatures. The value of K was calculated from the slope and intercept of such plots and found to be 1.31 ± 0.01 dm^3 mol^{-1} at 20°C in good agreement with that calculated by the methods described elsewhere [12–14]. The activation parameters of k_a' and k_a'' were calculated from the temperature-dependence of the rate constant and are summarized along with that for $\mathrm{MnO_4^-}$-alginate reaction in Table 4.

The experimental observations indicated the dependence of the rate constant of formation on the base concentration which leads us to suggest the formation of the alkoxide form of pectate prior to the attack of permanganate ion. This takes place by removal of a proton from OH groups by the alkali:



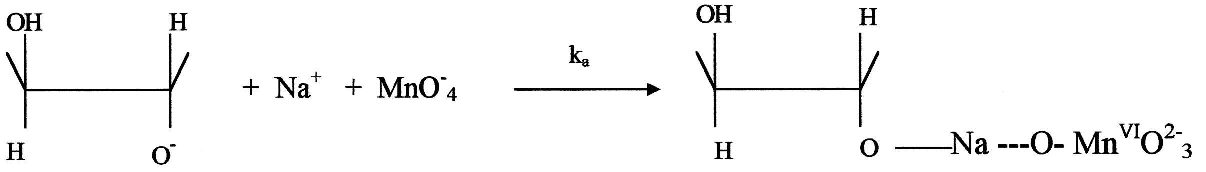
followed by the attack of MnO_4^- ion. In a similar manner to that observed in the oxidation of alginate polysaccharide by this oxidant [3,4], two pathway mechanisms may be suggested for the intermediate complex formation. The first is the attack of MnO_4^- on the alkoxide centre via the formation of intermediate (I) whose formation would be





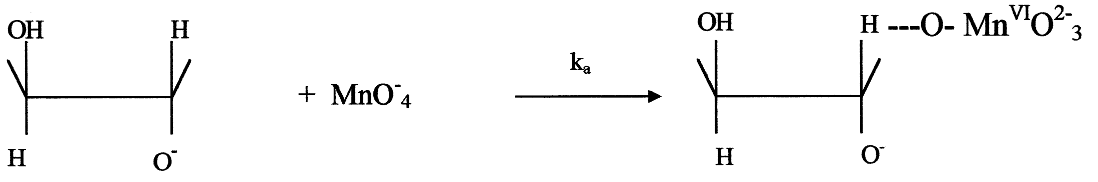
(I)

facilitated by the polarization of the Mn-O bond [22]. Alternatively, attack of MnO_4^- on the alkoxide center may occur via the formation of intermediate (II) whose formation is facilitated by the presence of Na^+ cations that tend to reduce the net charge of intermediate complex as follows:



(II)

The second mechanism corresponds to hydrogen bonding of MnO_4^- to form the intermediate complex (III):



(III)

When the concentration of Mn (VI) builds up, slow decay of the intermediate complex (I), (II) or (III) takes place to give rise to the reaction product. On the basis of [OH$^-$]-dependence of the decomposition rate constant, two possible mechanisms may be suggested for the decomposition of the intermediate complexes (I → III) at the final stage. The first corresponds to a fast deprotonation of the intermediate by the alkali followed by electron transfer from Pect$^-$ to Mn (VI) (intermediates I or II), as illustrated by reaction path A. The second mechanism corresponds to the transfer of hydride ion from Pect$^-$ to MnO$_4^{2-}$ in the rate determining step (intermediate III), as shown in reaction path B.

Path A

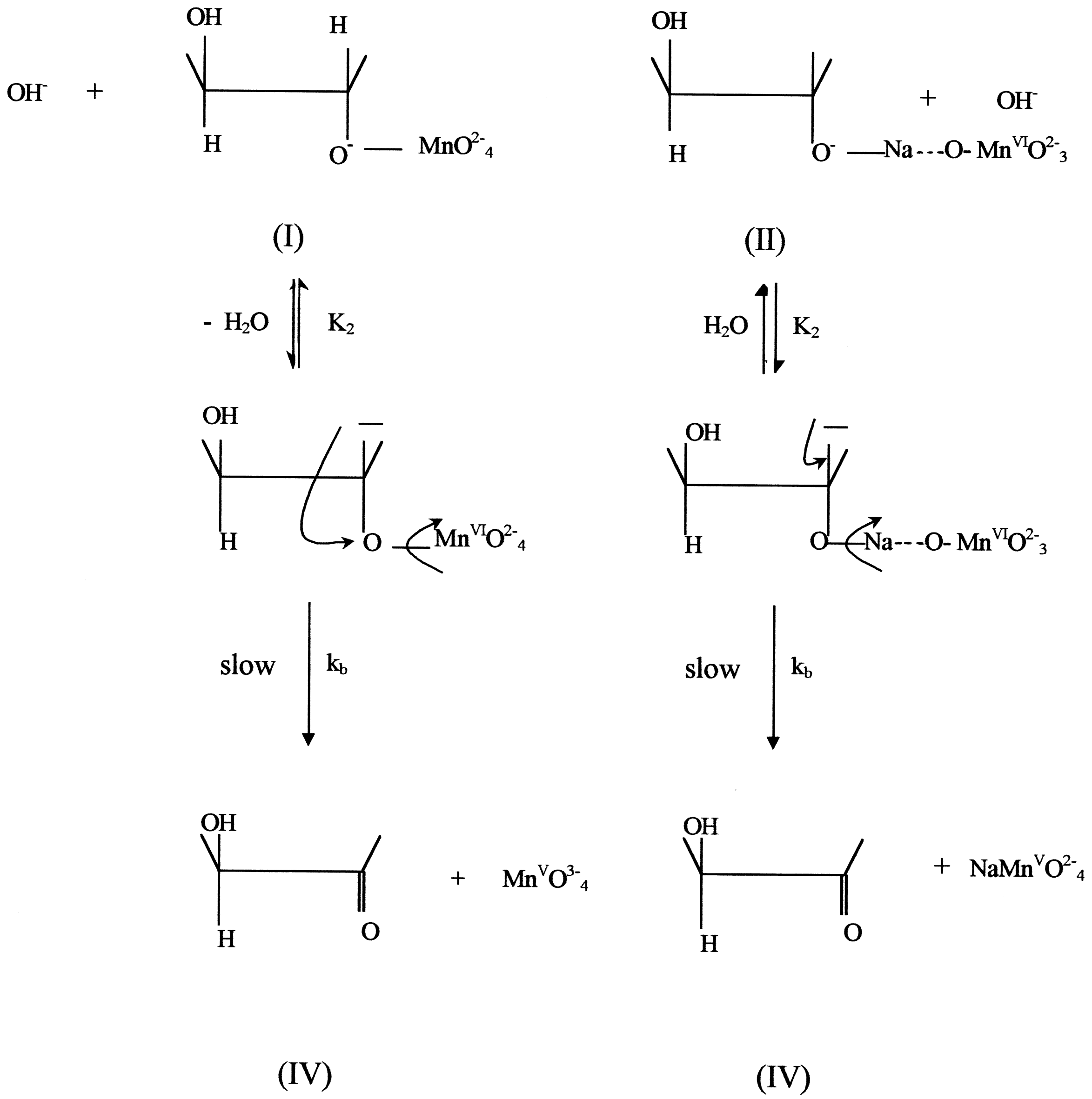
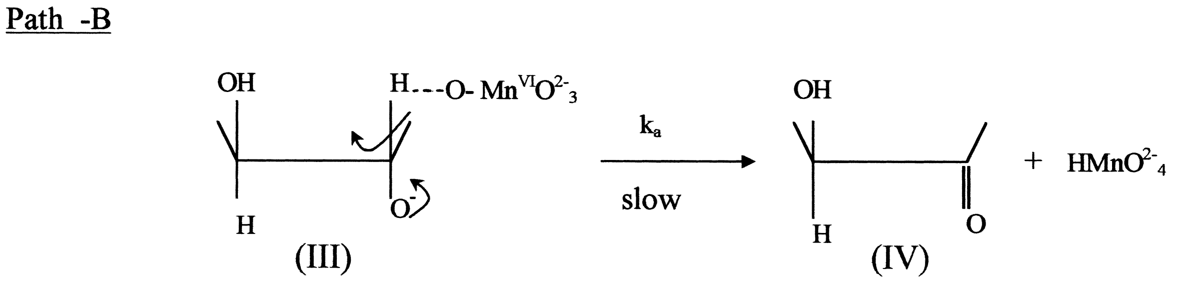


Table 4
Thermodynamic parameters of k'_a in the formation of [Pect $Mn^{VI}O_4^{2-}$] intermediate complex[a]

Rate constant	Parameter		
	$\Delta S^{\pm}$ (J mol^{-1} K^{-1})	$\Delta H^{\pm}$ (kJ mol^{-1} K^{-1})	$\Delta G^{\pm}$ (kJ mol^{-1} K^{-1})
k'_a	-21.44 ± 1.07 (-58.46 ± 1.16)	51.31 ± 1.53 (50.29 ± 0.52)	57.69 ± 1.84 (67.71 ± 0.87)

[a] The values in parentheses were reported for the MnO_4^--alginate reaction [5].

Path B



The reaction mechanism by path A was found to be in good agreement with the experimental observations of the dependence of the decomposition rate constant on the base concentration. This agreement may be considered as an indication that reaction path A is the more reasonable mechanism for the oxidation of pectate by alkaline permanganate. Again, the yellow color which persists even after completion of the oxidation reaction may be considered as evidence of the decomposition of hypomanganate (V) to soluble manganese (IV) rather than the colloidal MnO_2 [23,24]

$$2Mn^{V}O_4^{2-} \rightarrow Mn^{IV}_{sol} + Mn^{V}O_4^{2-} \quad (14)$$

Moreover, the oxidation products (IV) may be monoketo- and/or diketopectates, depending on the molar concentration of the reactants as well as the reaction conditions as follows:

$$(C_6H_7O_6Na)_n + MnO_4^- + OH^- = (C_6H_5O_6Na)_n + HMn^{V}O_4^{2-} + H_2O \quad (15)$$

$$(C_6H_7O_6Na)_n + 2MnO_4^- + 2OH^- = (C_6H_3O_6Na)_n + 2HMn^{V}O_4^{2-} + 2H_2O \quad (16)$$

$$(C_6H_7O_6Na)_n + MnO_4^- + 2OH^- = (C_6H_5O_6Na)_n + Mn^{V}O_4^{3-} + 2H_2O \quad (17)$$

$$(C_6H_7O_6Na)_n + 2MnO_4^- + 4OH^- = (C_6H_3O_6Na)_n + 2Mn^{V}O_4^{3-} + 4H_2O \quad (18)$$

where $C_6H_7O_6Na$, $C_6H_5O_6Na$ and $C_6H_3O_6Na$ denote the sodium pectate, monoketo- and diketopectates, respectively. Under the experimental conditions of the present work, reaction (18) was found to be in good agreement with the obtained kinetic results.

The relatively high rate constants observed for the complex formation, [Pect $Mn^{VI}O_4^{2-}$], in the present work compared with that obtained in the oxidation of alginate, [Alg $Mn^{VI}O_4^{2-}$] by this oxidant [3,4] may be explained on the basis of the position of C-2 and C-3 hydroxylate groups in both substrates. The steric hinderance resulting from the location of OH groups in the *cis*-position with respect to alginate substrate may affect the penetration power of the attacking MnO_4^- ions. This in turn leads to reduction of the magnitude of the rate constant of the complex formation. However, the presence of OH groups in the *trans*-position in the case of pectates may facilitate the attack of

MnO_4^- oxidant and, hence, increases the magnitude of the rate constants.

On the other hand, the tendency of these substrates to be deprotonated in alkaline medium may play a role in the reaction kinetics. The faster the deprotonation is the faster the substrate is oxidized. The experimental results indicated that pectates are more quickly deprotonated and, hence, possess large rate constants of oxidation.

The values of enthalpies of activation may throw some light on the stability of the intermediate complex formed. As is shown in Table 4, the value of $\Delta H^{\#}$ of the complex found in the case of the MnO_4^- alginate reaction is smaller than that observed in the case of the oxidation of pectate by MnO_4^- ion, and hence would be the more stable one.

The great similarity between the kinetics of oxidation of alginates [3,4] and the pectates in the present work as natural polymers to that of poly(vinyl alcohol) [5,6] as synthetic polymer may be considered as indirect evidence that these redox reactions proceed by a similar mechanism. Furthermore, the formation of keto-derivatives as final products with respect to these substrates is consistent with products postulated for the oxidation of other organic substrates containing secondary alcoholic groups by this oxidant.

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Further reading

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