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Note

Spectrophotometric evidence for the formation of short-lived hypomanganate(V) and manganate(VI) transient species during the oxidation of *K*-carrageenan by alkaline permanganate

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Dedicated to the memory of Professor Issa M. Issa

Abstract—Spectrophotometric detection of the formation of short-lived hypomanganate(V), [KCAR–$Mn^{V}O_4^{3-}$], and manganate(VI), [KCAR–$Mn^{VI}O_4^{2-}$], intermediates has been confirmed through the oxidation of *K*-carrageenan (KCAR) by potassium permanganate in alkaline solutions of pH's $\geqslant 12$ using a conventional spectrophotometer. The short-lived transient species were characterized and a mechanism consistent with experimental observations is suggested.

Keywords: Carbohydrates; Carrageenans; UV–vis spectra; Hypomanganate(V); Manganate(VI); Oxidation

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Little attention has been paid to the conventional spectrophotometric detection of hypomanganate(V) and manganate(VI) short-lived transient species. This fact can be ascribed to the extremely short lifetime owing to fast disproportionation.[1–5] However, Shaker[6,7] and El-Khatib[8] pointed out the rapid formation of Mn^{V} as a short-lived intermediate complex during kinetic studies on the oxidation of some polysaccharides containing secondary hydroxyl groups such as carboxymethyl cellulose and methyl cellulose. Information about the characteristics of these transient species and the mechanism of oxidation is still lacking.

Therefore, the present work aims at presenting spectrophotometric evidences for the formation of such short-lived intermediates through the oxidation of *K*-carrageenan (KCAR) as a polysaccharide containing both primary and secondary hydroxyl groups by alkaline permanganate. In addition, this work also aims at shedding light on the nature of these short-lived transient species and the aqueous chemistry of carrageenan macromolecule as well as extending our investigation on the oxidation of carbohydrate macromolecules.[9–13]

Preliminary experiments indicated that the oxidation of *K*-carrageenan by alkaline permanganate proceeded via detectable intermediate complexes and the rates of formation and decomposition were of such magnitude that they could be monitored using a conventional spectrophotometer. The initial step was found to be fast involving the formation of complexes, followed by a slower step corresponding to the decomposition of these complexes at the final stage of the reaction to give rise to the products.

As is shown in Figure 1, most of the spectral features of MnO_4^- ion are displayed, but superposition of other species appeared. There is a gradual disappearance of MnO_4^- ion at λ 525 nm, its absorption maximum, with the formation of new intermediates absorbing at wavelengths of 606, 435, 350, and 315 nm. These spectral changes of the reaction mixtures were provided by repetitive spectral scans of the reaction at suitable time intervals. To our knowledge, the 606 nm absorption band corresponds to manganate(VI).[14–16] At this wavelength, the absorption of MnO_4^- is much weaker, thus the detection of $Mn^{VI}O_4^{2-}$ was not difficult. The molar

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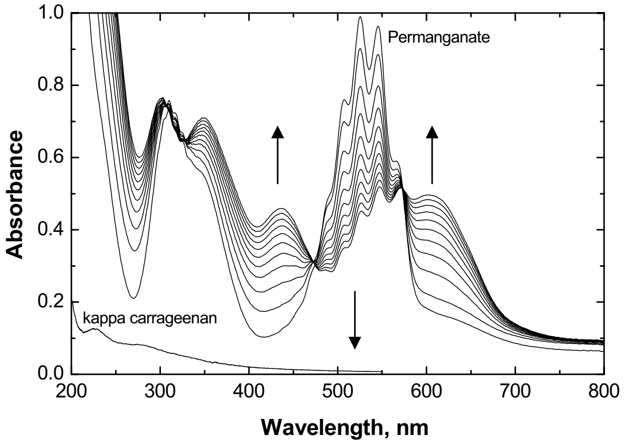


Figure 1. Spectral changes (200–800 nm) in the oxidation of *K*-carrageenan by the permanganate ion. $[MnO_4^-] = 4 \times 10^{-4}$, $[KCAR] = 4 \times 10^{-3}$, $[OH^-] = 1 \times 10^{-2}$, $I = 0.1$ mol dm^{-3} at 20 °C. Scanning time intervals = 4 min.

extinction coefficient (ε_{mix}) of $[KCAR–Mn^{VI}O_4^{2-}]$ intermediate was found to be 1150 ± 50 dm^3 mol^{-1} cm^{-1} at $[KCAR] = 4 \times 10^{-3}$, $[MnO_4^-] = 4 \times 10^{-4}$, $[OH^-] = 0.01$, and $I = 0.1$ mol dm^{-3} at 20 °C. This value was found to be in good agreement with that reported elsewhere.[17–19]

On the other hand, the naked eye observation on the change in color of the solution mixture as the reaction proceeded from purple-pink (Mn^{VII}), to blue (Mn^{V}), to green (Mn^{VI}), to yellow (Mn^{IV}), may suggest the formation of hypomanganate(V) at the first-stage of oxidation. Again, the interconversion of MnO_4^- to $Mn^{VI}O_4^{2-}$ and $Mn^{V}O_4^{3-}$ was apparent from isobestic points at the absorption maxima of 475 and 580 nm, respectively. Therefore, some experimental attempts have been made at low concentration of the reactants and at lower temperatures in order to detect the formation of hypomanganate(V), spectrophotometrically.

As is shown in Figure 2, beside the band which was observed at λ 606 nm, a new band appeared at 738 nm as the reaction begins (initial scans). As the reaction evolved, this new band disappeared. It was reported[1,15,16] that hypomanganate(V) has a band at a wavelength around 700 nm which may disappear by one of the following fast reactions:

$$2Mn^{V} = Mn^{VI} + Mn^{IV} \tag{1}$$

$$Mn^{V} + Mn^{VII} = 2Mn^{VI} \tag{2}$$

The disproportionation process defined by Eq. 1 is autocatalyzed by the presence of Mn^{IV}.[1,5] The formation of Mn^{VI} and/or Mn^{V} as short-lived intermediates have been postulated by many investigators during the oxidation of macromolecules[6–8,17–22] or organic substrates[14,16] by permanganate ion in alkaline solutions. The formation of long-lived hypomanganate(V) is conceivable only with sterically rigid olefines,[4,23] and sulfite ion.[24] The details of the oxidation kinetics of $KCAR–MnO_4^-$ are to be published elsewhere.[25]

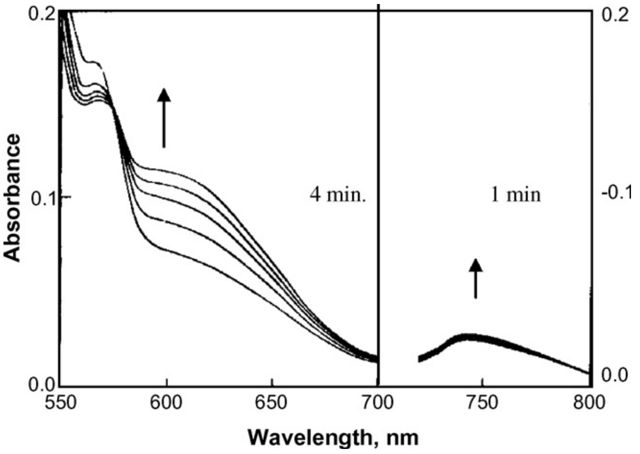


Figure 2. Spectral changes (550–800 nm) in the oxidation of *K*-carrageenan by the permanganate ion. $[MnO_4^-] = 1 \times 10^{-4}$, $[KCAR] = 4 \times 10^{-4}$, $[OH^-] = 0.02$, $I = 0.1$ mol dm^{-3} at 0 °C.

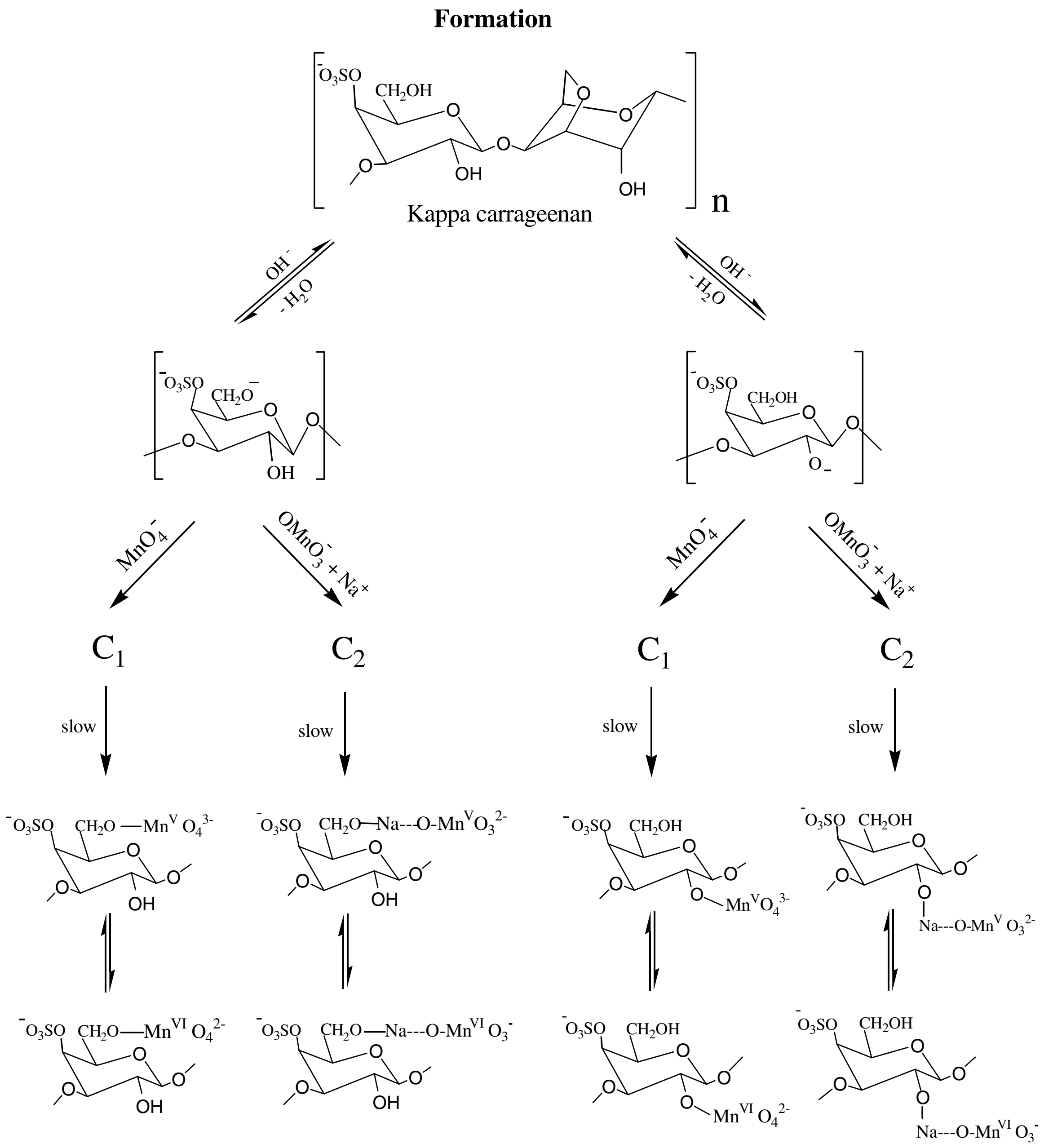
The yellow color persists even after completion of the oxidation reaction while the disappearance of the MnO_4^- ions may suggest the formation of stable soluble manganese(IV) as a final product rather than a colloidal suspension of MnO_2 precipitate.[26–28] The latter can be isolated from the reaction mixture during the oxidation process by adding a stoichiometric amount of NaF with continuous stirring. After completion of the reaction, the formed MnF_4 can be filtered off from the reaction mixture leaving the keto-acid biopolymer derivative. Of course, the formed Mn^{IV} can coagulate on ageing to form a brown MnO_2 precipitate.

In view of the experimental results and the kinetic interpretations,[20] a tentative reaction mechanism consistent with experimental observations may be suggested. This mechanism involves a fast deprotonation of the substrate by alkali in order to produce an alkoxide form prior to the oxidation process. Then, the formed alkoxide is attacked by permanganate to give intermediates involving manganate(VI) and/or hypomanganate(V) short-lived transient species. As the intermediate builts up, a slow decay of it takes place to give rise to the oxidation product. The mechanisms of formation and decomposition of the intermediates are illustrated in more detail in Schemes 1 and 2, respectively.

1. Experimental

1.1. Chemicals and reagents

All materials used were of analytical grade, and doubly distilled degassed conductivity water was employed in all preparations. The temperature was controlled within ±0.05 °C. The *K*-carrageenan (KCAR) used in the present work is from Fluka and was used without further



Scheme 1.

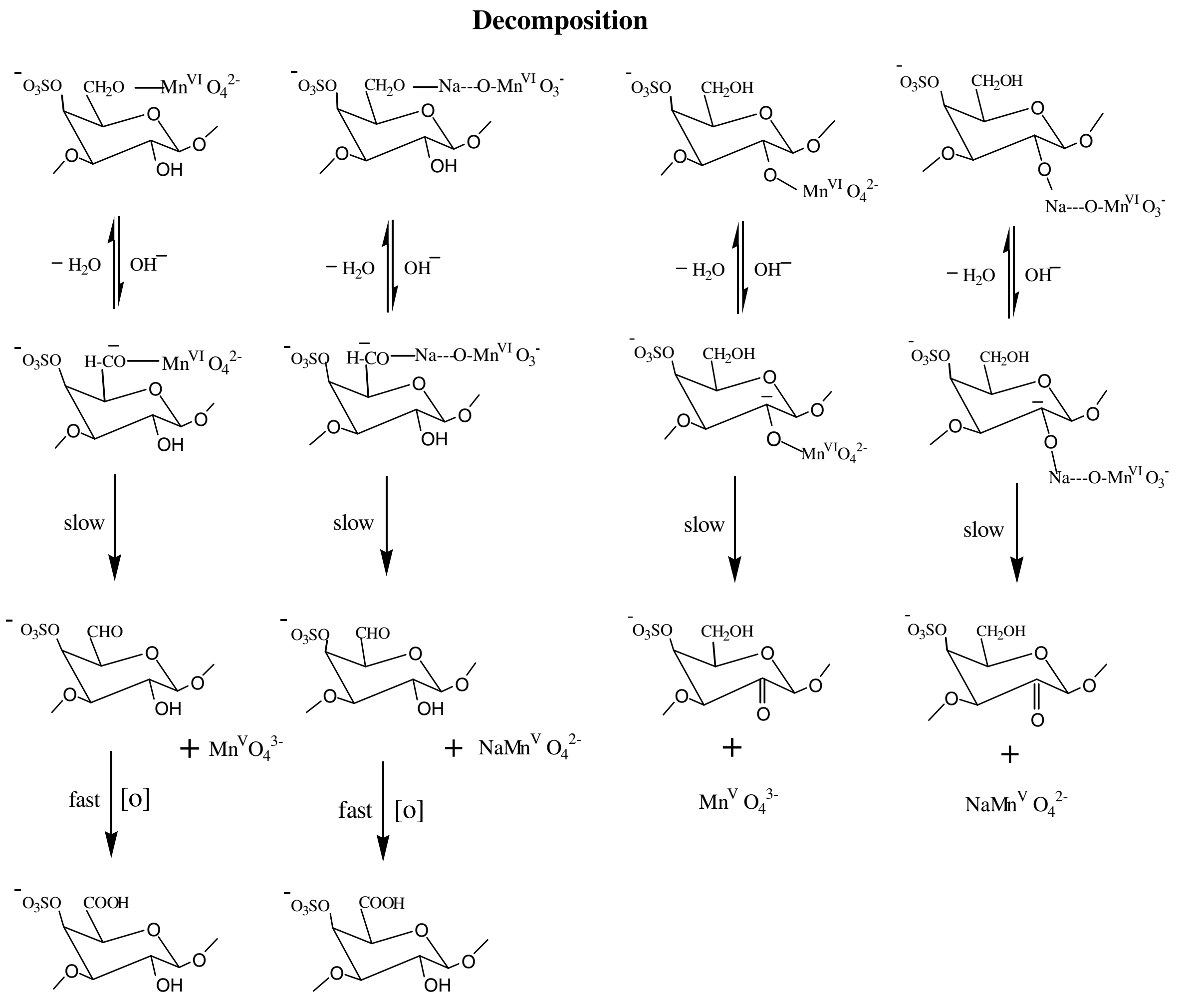
purification. A stock soln of carrageenan was prepared by stepwise addition to doubly distilled water whilst rapidly stirring the soln to avoid the formation of lumps which swell with difficulty. A stock soln of $KMnO_4$ was prepared and standardized by conventional methods as described elsewhere.[9,10] All other reagents were prepared by dissolving the requisite amount of sample in doubly distilled water.

1.2. Instruments and spectrophotometric measurements

The spectral changes during the oxidation of *K*-carrageenan by alkaline permanganate at pH's $\geqslant 12$ was monitored in a thermostated cell compartment within ±0.05 °C using Shimadzu UV-2101/3101 PC and Cecil CE 7200 automatic scanning spectrophotometers with wavelength program controllers.

1.3. Stoichiometry and product analysis

Different ratios of *K*-carrageenan and permanganate (in excess) solns were mixed at 0.01 mol dm^{-3} NaOH and a constant ionic strength of 0.1 mol dm^{-3}, then equilibrated for 48 h at room temperature. Estimation of unreacted MnO_4^- was made as described elsewhere.[4,6] The stoichiometric ratio, $[MnO_4^-]$ consumed/$[\text{KCAR}]_0$,



Scheme 2.

was found to be 2.0 ± 0.1. Hence, the stoichiometric reaction can be represented by the following equation:

$$(C_{12}H_{17}O_{12}S)_n^- + 2MnO_4^- + 1/2O_2 = (C_{12}H_{11}O_{13}S)_n^- + 2MnO_2 + 2OH^- + 2H_2O \quad (3)$$

where $(C_{12}H_{17}O_{12}S)_n^-$ and $(C_{12}H_{11}O_{13}S)_n^-$ are *K*-carrageenan and its keto-acid oxidation product, respectively. The oxidation product of *K*-carrageenan was identified by IR spectroscopy and chemical analysis as described elsewhere.[11–13]

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