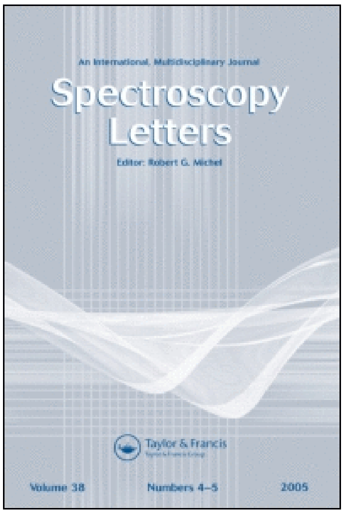


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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

K. S. Khairou[a]
[a] Department of chemistry, Faculty of Applied Sciences, Umm Al-Qura University, Kakkah Al-Mukarramah, Kingdom of Saudi Arabia

To cite this Article 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: 2, 117 — 124

To link to this Article: DOI: 10.1081/SL-100002001

URL: http://dx.doi.org/10.1081/SL-100002001

SPECTROSCOPY LETTERS, 34(2), 117–124 (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

K. S. Khairou

Department of Chemistry, Faculty of Applied Sciences,
Umm Al-Qura University, Kakkah Al-Mukarramah 5576,
Kingdom of Saudi Arabia

ABSTRACT

The formation of a short-lived manganate(VI) intermediate has been confirmed during the oxidation of chitin and chitosan polysaccharides by the permanganate ion at pH's ≥ 12, spectrophotometrically. The Mn(VI) transient species intermediate was characterized by a band at a wavelength of 610 nm, an absorption maximum, with a absorptivity (i.e., molar extinction coefficient) of 1250 ± 75 dm^3 mol^{-1} cm^{-1}.

Key Words: Manganese(VI); Permanganate; Oxidation; Chitin; Chitosan; Polysaccharides.

www.dekker.com

INTRODUCTION

Although, the permanganate ion has been widely used as a powerful oxidizing agent for oxidation of most organic (1–5) and inorganic (6–10) substrates; the oxidation of polyelectrolytes has not received significant attention (11–13).

In alkaline solutions, the reduction of permanganate ion proceeds via formation of detectable short-lived intermediates such as Mn(III) (14), Mn(IV) (15,17), Mn(V) (18,19) and Mn(VI) (1,3,20,21). However, the stopped-flow technique is usually utilized for detection of such intermediates, the conventional spectrophotometric methods have received little attention (22,23).

In view of the above aspects and the current interest in redox reactions involving permanganate ion as an oxidant of polysaccharides (24) in alkaline solutions, the present reaction seems to merit further investigation with a view to gaining unequivocal information on short-lived manganate(VI) intermediate using the conventional spectrophotometric techniques.

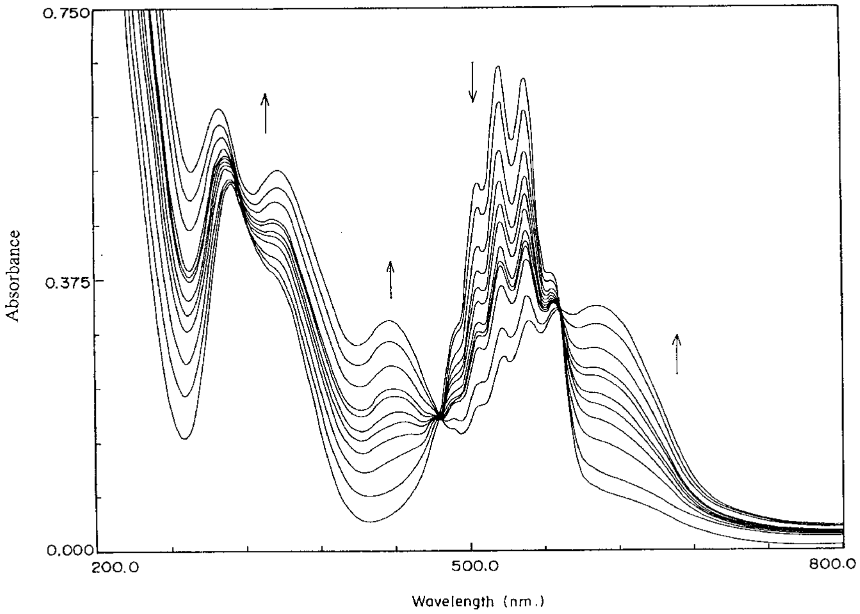


Figure 1. Successive UV-visible spectra for disappearance of permanganate ion and formation of manganate(VI) during the permanganate oxidation of chitin substrate at $[\mathrm{MnO}_4^-] = 3 \times 10^{-4}$, $[\text{chitin}] = 3 \times 10^{-4}$, $[\mathrm{OH}^-] = 3 \times 10^{-2}\ \mathrm{mol \cdot dm^{-3}}$ and 25°C (scanning time intervals between successive curves = 2 min).

EXPERIMENTAL

Chemicals and Reagents

All materials used were of Analar (BDH) grade. Doubly-distilled water was used in all preparations.

Stock solutions of reagents were prepared and standerdized as described elsewhere (22,23).

Instruments and Spectrophotometric Measurements

The spectral change during the reduction of permanganate ion by chitin or chitosan in alkaline solutions (pH $\geq$ 12) was monitored in a thermostated cell compartment at $\pm 0.1^\circ$C on a Shimadzu UV double-beam spectrophotometer using cells of path length 1.0 cm.

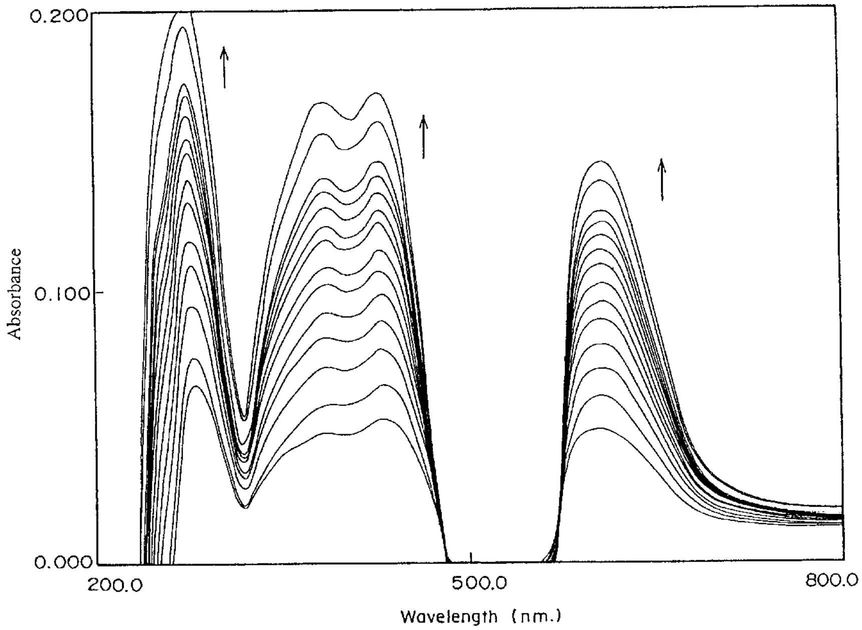


Figure 2. Spectral changes during the formation of the intermediates during the permanganate oxidation of chitin substrate at $[MnO_4^-] = 3 \times 10^{-4}$, $[OH^-] = 3 \times 10^{-2}$ mol · dm^{-3} and 25°C (Reference cell: MnO_4^- and OH^- of the same reaction mixture concentration and scanning time intervals = 2 min).

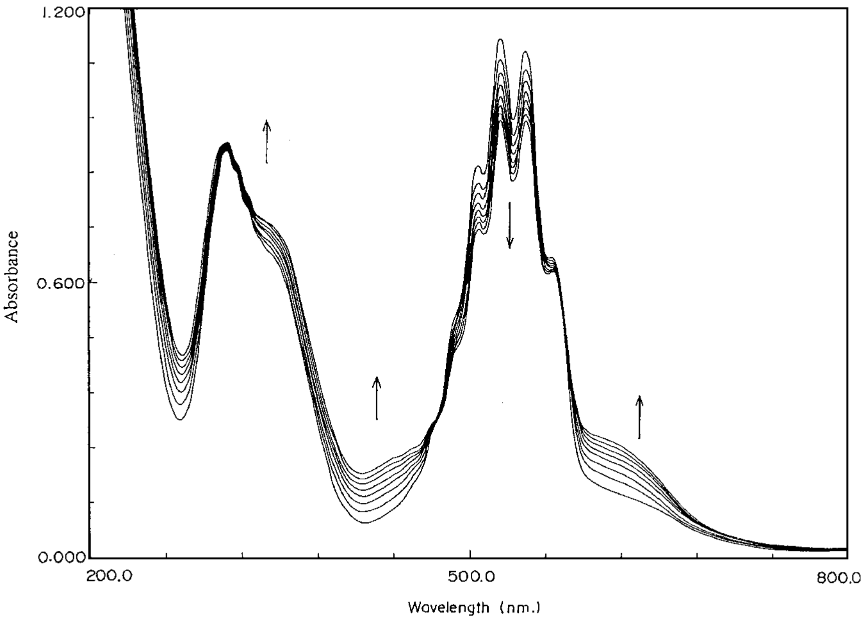


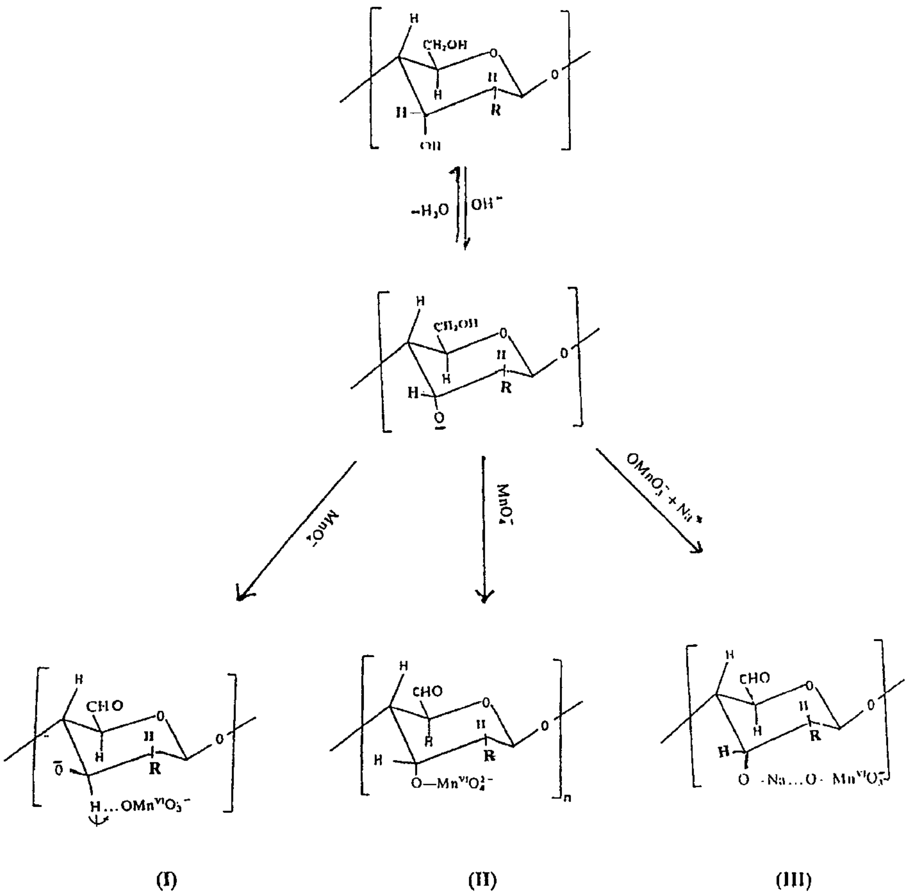
Figure 3. Successive UV-visible spectra for disappearance of permanganate ion and formation of manganate(VI) during the permanganate oxidation of chitosan substrate at $[MnO_4^-] = 4 \times 10^{-4}$, [chitosan] $= 3 \times 10^{-4}$, $[OH^-] = 3 \times 10^{-2}\ mol \cdot dm^{-3}$ and 25°C (scanning time intervals between successive curves = 1 min).

RESULTS AND DISCUSSION

A wealth of information revealing the formation of manganate (VI) and/or hypomanganate (V) are presented in Figures 1 through 3. A gradual decrease in the height of the 525 nm peak with a simultaneous increase in the height of the 610 nm peak is observed. These spectral changes of the reaction mixtures were provided by repetitive spectral scans of the redox reaction at suitable intervals. To our knowledge, the 525 nm band corresponds to the absorption maximum of MnO_4^- ion, whereas that of the 610 nm band corresponds to manganate (VI) (14). At this 610 nm band, the absorption of MnO_4^- is much weaker, thus the detection of MnO_4^{2-} is not difficult. The isobestic point, which is seen at 575 nm during the course of reaction, indicates the conversion of MnO_4^- to MnO_4^{2-}, whereas that of ~475 nm reveals that both Mn(VII) and Mn(IV) formed do not necessarily exclude the detectable Mn(VI) intermediate (11–13). Furthermore, the change in the intensity of the bands observed at wavelengths of 435 and 350 nm is due to the increase of the formed soluble Mn(IV) concentration which does not absorb above 540 nm (22,23).

Evidence against the formation of the hypomanganate(V) intermediate is provided by the absence of an absorption maximum around 700 nm unless observed at very low temperatures (3,19). The failure of detection of Mn(V) may be explained by its extreme short lifetime (3,25), where Mn(V) undergoes a rapid disproportionation, which is autocatalytic in the presence of manganese(IV).

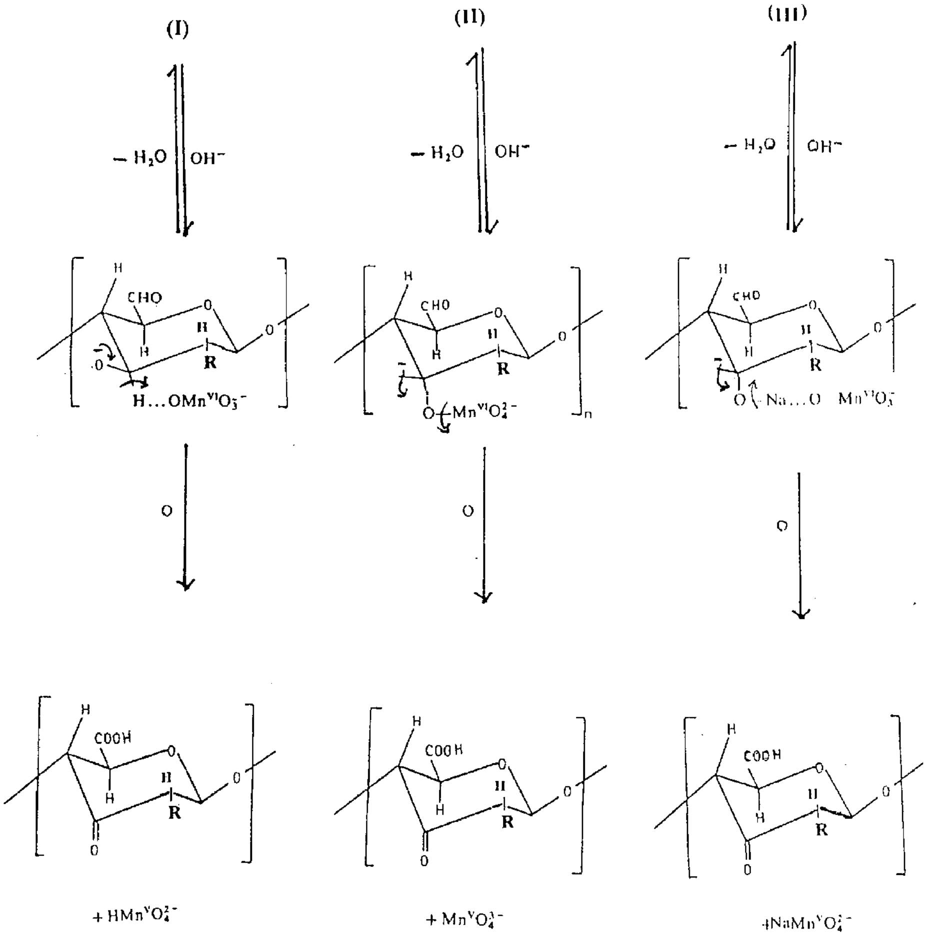
Furthermore, the change in color of the solution mixture as the reaction proceeded, from purple-pink to blue to green may confirm these suggestions for the intermediate. The yellow colour which persists after the disappearance of all the MnO_4^- ions may suggest the formation of a stable soluble manganese(IV) as a final product rather than a colloidal suspension of MnO_2 (2,16,23,28). Many investigators have postulated the formation of Mn(VI) and/or Mn(V) as short lived



Scheme 1. Formation.

intermediates during the oxidation of organic substrates by permanganate ion in alkaline solutions (14,19).

Preliminary experiment indicated the formation of ketoderivatives as reaction products of the oxidation of chitin and chitosan by alkaline permanganate. These products could be separated from the reaction mixtures and its presence confirmed by Infrared and elemental analyses (19). Hence, mechanisms consistent with the experimental observations may be suggested as in Schemes 1 and 2. The first step corresponds to the removal of the H^+ ion from the substrate by the alkali to give an alkoxide form, followed by the attack of MnO_4^- ion to form intermediate



Scheme 2. Decomposition.

complexes involving manganate(VI) transient species in the rate-determining steps as shown in Scheme 1.

Again, these formed intermediates are slowly decayed to give rise to the products. The decay takes place by fast protonation of the intermediates by the alkali, followed by the transfer of either an electron or an hydride ion from the substrates to the manganate(VI) in the rate-determining steps as shown in Scheme (2).

The kinetics and mechanisms of these redox reactions have been discussed in more details and presented elsewhere (29).

REFERENCES

1. Wei, M.M.; Stewart, R. J. Am. Chem. Soc. **1966**, *88*, 1974.
2. Lee, D.G.; Brownridge, R. J. Am. Chem. Soc. **1973**, *95*, 3033.
3. Lee, D.G.; Sebastian, C.F. Cand. J. Chem. **1981**, *59*, 1776.
4. Hassan, R.M.; Mousa, M.A.; Wahdan, M.H. J. Chem. Soc., Dalton Trans. **1988**, 605.
5. Hassan, R.M. Cand. J. Chem. **1991**, *59*, 2018.
6. Hassan, R.M.; Mousa, M.A.; El-Shatoury, S.A. J. Chem. Soc., Dalton Trans. **1988**, 601.
7. Hassan, R.M.; El-Gaiar, S.A.; El-Summan, A.M. Collect. Czech. Chem. Commun. **1993**, *58*, 538.
8. Thomas, L.; Sutter, J.R. J. Phys. Chem. **1967**, *71*, 2767.
9. Rowwof, M.A.; Sutter, J.R. J. Phys. Chem. **1967**, *71*, 2767.
10. Hicks, K.W.; Sutter, J.K. J. Phys. Chem. **1971**, *75*, 1107.
11. Hassan, R.M. Polym. Inter. **1993**, *30*, 5.
12. Hassan, R.M. J. Polym. Sci. **1993**, *31*, 1147.
13. Hassan, R.M. J. Polym. Sci. **1993**, *31*, 51.
14. Stewart, R. *Oxidation in Organic Chemistry*; Wilberg, K.B., Ed.; Part A, Academic Press, New York, 1965.
15. Simandi, L.I.; Jaky, M. J. Am. Chem. Soc. **1976**, *98*, 1995.
16. Jaky, M.; Simaxdi, L.I. J. Chem. Soc., Perkin Trans. **1976**, *2*, 939.
17. San, N.T.; Jaky, M.; Simandi, L.I. Inorg. Nucl. Chem. Lett. **1976**, *12*, 291.
18. Isaacs, N.S.; Hermans, K. Tetrahedron Lett. **1987**, *22*, 4759.
19. Carrington, A.; Symons, M.C.R. J. Chem. Soc. **1956**, 3373.
20. Wiberg, K.W.; Geer, R.D. J. Am. Chem. Soc. **1966**, *88*, 5827.
21. Wiberg, K.W.; Deutsch, C.J.; Rocek, J. J. Am. Chem. Soc. **1973**, *95*, 3034.
22. Makhlouf, M.Th.; El-Shatoury, S.A.; Hassan, R.M. High Perf. Polym. **1992**, *4*, 89.
23. El-Azhari, S.; Hassan, R.M. Spect. Lett. **1999**, *32*, 17.
24. Khairou, K.S.; Hassan, R.M. Eur. Polym. J. **2000**, *36*, 2021.

25. Zimmerman, C.L. Thesis University of Chicago, 1949.
26. Lee, D.G.; Brownridge, J.R. J. Am. Chem. Soc. **1974**, *96*, 5517.
27. Simandi, L.I.; Jaky, M.; Schelly, Z.A. J. Am. Chem. Soc. **1984**, *106*, 6866.
28. Chandler, D.; Anderson, H.C. J. Chem. Phys. **1972**, *57*, 1930.
29. Khairou, K.S. (Forthcoming).

Received July 20, 1999
Accepted November 11, 2000

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 03:12 30 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SL100002001