

HOMOGENEOUS PERMANGANATE OXIDATION IN NON-AQUEOUS ORGANIC SOLUTION.¹
A STABLE ORGANOMANGANESE INTERMEDIATE IN THE OXIDATION OF ENDO-DICYCLOPENTADIENE

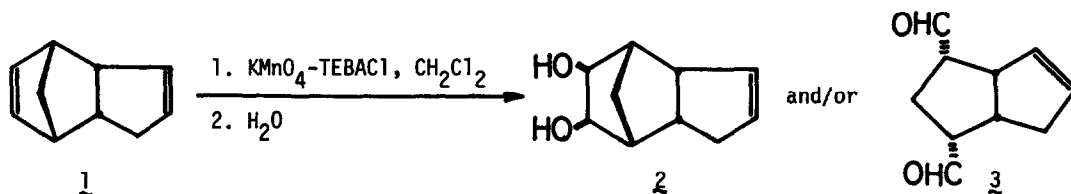
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Summary: The absorption spectrum of a stable organomanganese intermediate in the homogeneously catalyzed permanganate oxidation of endo-dicyclopentadiene in a non-aqueous system was directly determined. The formation and the decomposition of the intermediate were monitored by following the changes of absorbances.

It is generally accepted that cyclic manganese(V) esters are formed in the initial step of the reactions of permanganate ion with olefins.^{2,3} The lifetime of these intermediates is transient in aqueous solutions and the spectrophotometric detections have been accomplished by stopped-flow techniques.^{4,5} A longer-lived manganese(V) ester is known in the oxidation of thymine as the only one example of stable intermediate.⁶ This letter describes the first direct spectrophotometric detection of a stable organomanganese intermediate in non-aqueous organic solution.

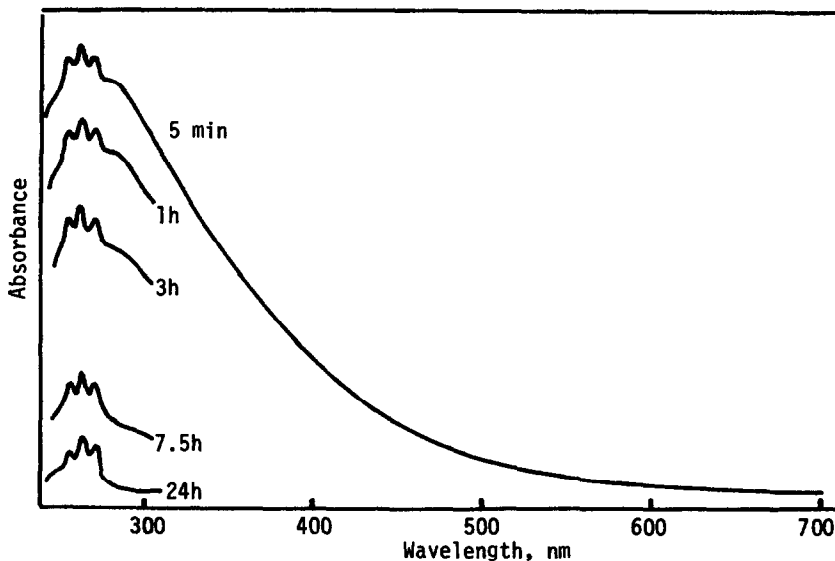
Permanganate ion solubilized in CH_2Cl_2 by use of equimolar amount of triethylbenzylammonium chloride oxidizes **1** to give a homogeneous dark brown solution which gives varying proportions of the diol (**2**) and the dialdehyde (**3**) upon treatments with aqueous solutions.¹ The ratio **2**:**3** is pH dependent and **2** predominates with alkaline conditions.



When a 2-fold excess of **1** was used, MnO_4^- was consumed in few minutes and the absorption spectrum of the reaction mixture was determined 5 minutes after the reaction was complete.⁷ The spectrum exhibits a strong absorption maximum at 275 nm ($\epsilon=8000$)⁸ and a long shoulder in the visible region (Fig. 1). It is of interest to note that the spectrum in the visible region resembles that of the organomanganese(V) intermediate in the oxidation reaction of crotonate anion by aqueous MnO_4^- solution.⁵ The latter spectrum was determined *via* monitoring the spectrum changes at 28 wave lengths by stopped-flow techniques and analyzing the kinetic data. When the reaction mixture was allowed to stand at 0°C , the absorption intensity decreased gradually with the formation of precipitates of MnO_2 , and after 24 hours, the solution became completely colorless (Fig. 1). The change is of first order and the lifetime was found to be *ca.* 3.2 hours.

The product of this anhydrous decomposition of the intermediate was identified as a mixture of the diol (**2**) and the dialdehyde (**3**) in *ca.* 1:1 ratio. However, the dialdehyde was found to be a mixture of stereoisomers at formyl groups, suggesting the occurrence of a basic species

Fig. 1. Absorption spectra of the intermediate in the oxidation of *endo*-dicyclopentadiene.^a

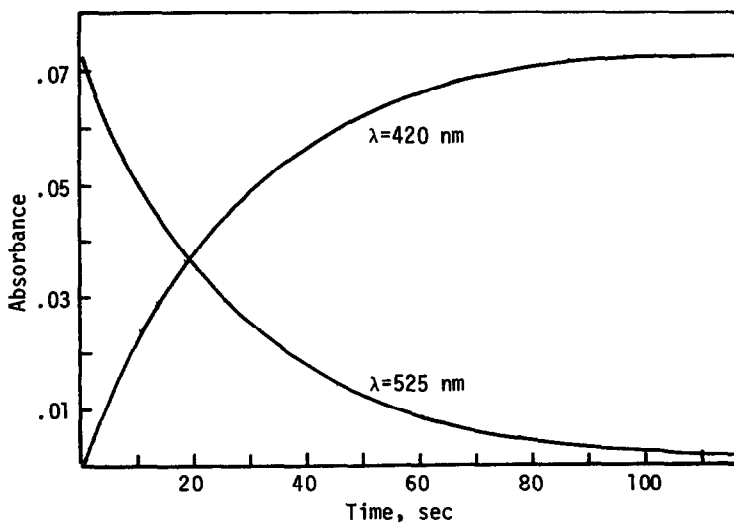


^aSmall peaks around 270 nm are due to triethylbenzylammonium chloride.

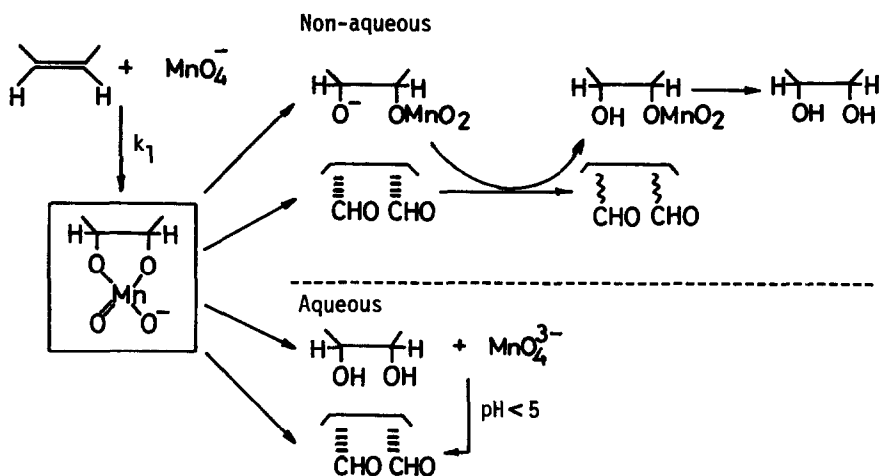
in the course of the reaction (*vide infra*).

The rates of the appearance of the intermediate and the disappearance of permanganate ion could be monitored by following the changes of absorbances at 420 nm⁹ and 525 nm, respectively (Fig. 2). The kinetics was studied under pseudo-first order conditions with the oxidant in an appropriate concentration and with the olefin in 20-60 fold excess.¹⁰ Both rates are directly proportional to the concentration of the olefin and the second order rate constants obtained by monitoring the rate of disappearance of MnO_4^- at 525 nm and those obtained by monitoring the rate of formation of the intermediate at 420 nm are comparable to each other [$k_1 \sim 22 \text{ M}^{-1} \text{ sec}^{-1} (24^\circ)$].

Fig. 2. Reaction rates monitored by following the changes of absorbances at 420 nm and 525 nm.



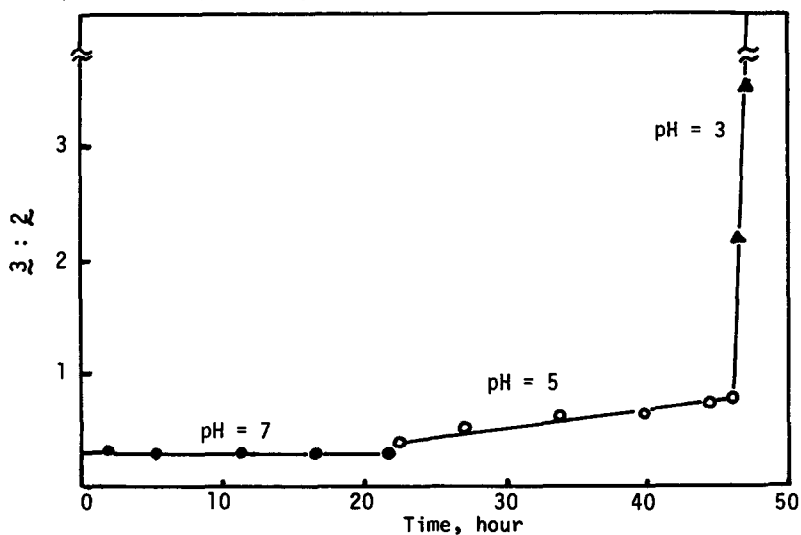
From these observations, a probable scheme for this oxidation reaction is outlined as follows. The stable intermediate which is formed in the initial step is assigned a cyclic hypo-



manganate ester as proposed in aqueous systems and this may be the common intermediate for the diol (2) and the dialdehyde (3) at least in the reaction where excess olefin was used. For the formation of the diol (2) under the anhydrous condition, a proton must be supplied from the dialdehyde (3) to the alkoxide ion derived from the cyclic ester. This is supported by the fact that the aldehyde is obtained as an isomeric mixture (*vide supra*).

In the aqueous decomposition, the formation of the diol (2) predominates under the basic condition and the secondary conversion of the diol to the dialdehyde occurs at low pH. However, the dialdehyde is still a primary product under neutral or weakly acidic conditions. This was

Fig. 3. Effect of pH of the aqueous layer on the product ratio.



supported by the following experiment. In this experiment, the olefin was also used in excess in order to make the reaction complete rapidly. The reaction mixture was immediately quenched by neutral water with vigorous stirring and the ratio of the products was analyzed by glc (Fig. 3). The ratio, $\underline{3}:\underline{2}$, was unchanged in 24 hours at room temperature, supporting the direct formation of the dialdehyde ($\underline{3}$) from the intermediate, but not from the diol ($\underline{2}$) in this condition. When the aqueous layer was made at pH 5, however, the ratio increased slightly in next 24 hours and at pH 3, the ratio increased suddenly with disappearance of the brown precipitates, indicating the secondary conversion of the diol to the dialdehyde by the action of manganese of lower oxidation states.

The evidence for the involvement of the manganese(VI) ester, a possible intermediate of the C-C bond cleavage product,¹¹ *via* an oxidation process whereby the organomanganese(V) intermediate is oxidized by permanganate ion was not obtained, since the ratio $\underline{3}:\underline{2}$ did not vary with the amount of permanganate ion (0.5-2 equiv.) as long as the reaction mixtures were quenched by neutral water.

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References and Notes

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4. D. G. Lee and J. R. Brownridge, *J. Am. Chem. Soc.*, **95**, 3033 (1973); **96**, 5517 (1974).
5. K. B. Wiberg, C. J. Deutsch, and J. Roček, *J. Am. Chem. Soc.*, **95**, 3034 (1973).
6. F. Freeman, C. O. Fuselier, and E. M. Karchefski, *Tetrahedron Lett.*, 2133 (1975).
7. The reaction was carried out in preparative scale at 0° as described in ref. 1 and an aliquot was diluted with CH_2Cl_2 for the spectrophotometric measurement.
8. The value was determined by the reaction of a dilute MnO_4^- -TEBACl solution of known concentration and an excess of $\underline{1}$ in a cell. In this case, the reaction was complete in few seconds.
9. At this wavelength, MnO_4^- has no absorption.
10. $[\text{MnO}_4^- \text{-TEBACl}] = 8.67 \times 10^{-5} \text{ M } (\text{CH}_2\text{Cl}_2)$; $[\text{dicyclopentadiene}] = 1.65 \times 10^{-3}$, 3.30×10^{-3} , and $4.95 \times 10^{-3} \text{ M } (\text{CH}_2\text{Cl}_2)$. Equal volumes of the two solutions were discharged simultaneously into a cell from two syringes equipped with a three-way tube. In the case of Fig. 3, $[\text{dicyclopentadiene}] = 3.30 \times 10^{-3} \text{ M}$.
11. H. O. House, "Modern Synthetic Reactions," 2nd ed., p 275, Benjamin, California (1972); See also ref. 4 and 5.

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