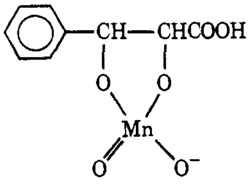
Table I. Isotope Effects on the Rate of Formation (k_2) and Decomposition (k_1) of the Intermediate Hypomanganate Ester During the Oxidation of *trans*-Cinnamic Acid by Acidic Permanganate[a]

Reductant	$k_2 \times 10^{-3}$,[b] M^{-1} sec^{-1}	k_2(H)/k_2(D)	$k_1 \times 10^2$,[b] sec^{-1}	k_1(H)/k_1(D)
trans-Cinnamic acid	1.56 ± 0.03		2.60 ± 0.02	
trans-Cinnamic acid-α-*d*	2.02 ± 0.01	0.77 ± 0.02	2.39 ± 0.02	1.09 ± 0.01
trans-Cinnamic acid-β-*d*	2.08 ± 0.01	0.75 ± 0.02	2.38 ± 0.02	1.09 ± 0.01

[a] [Reductant] = 5.23×10^{-4} *M*, [$KMnO_4$] = 2.20×10^{-4} *M*, [$HClO_4$] = 0.99 *M*, *T* = 30.0°. [b] The average of three or more experiments.

the appearance of the intermediate at 415 nm. Identical rates (within experimental error) are observed at both wavelengths, and the reaction is clearly second order as indicated by the excellent rate plots obtained (correlation coefficients of 0.999). The decomposition of the intermediate, which can be monitored by the decrease in absorption at 415 nm, is a somewhat slower first-order reaction.

The nature of these reactions was further defined by a study of the kinetic isotope effects observed when *trans*-cinnamic acid-α-*d* and *trans*-cinnamic acid-β-*d* were used as substrates. In each case the rate of the reaction was increased by about 30% (Table I), thus suggesting that this reaction involves a rehybridization of the olefinic carbon atoms from sp^2 to sp^3.[1] The fact that an inverse isotope effect of similar magnitude was obtained at both the α and β positions indicates that the transition state is approximately symmetrical with respect to attack of the oxidant at the double bond. An attractive explanation for these observations is to suggest that the yellow intermediate is actually the hypomanganate ester **1**. Such compounds have previously been considered as intermediates in similar reactions[2,3] and the observation that the electronic spectrum has a maximum at 415 nm and a minimum around 530 nm is not inconsistent with the known spectral properties of other Mn^V compounds.[3]



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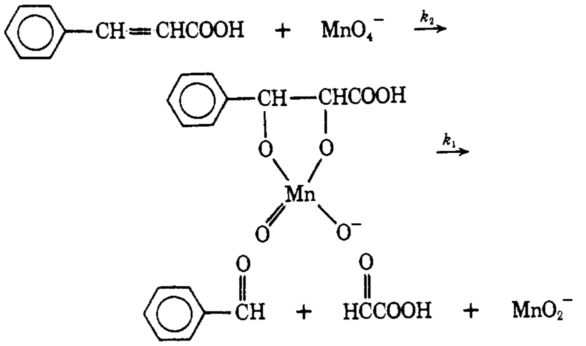
The second step of the reaction exhibited an isotope effect (Table I) of the magnitude usually associated with reactions where the hybridization of carbon is changed from sp^3 to sp^2.[1] Furthermore, benzaldehyde was the major detectable product of the reaction when it was carried out under an inert nitrogen atmosphere, whereas in the presence of oxygen only benzoic acid was obtained. Hence it appears that the intermediate decomposes to give, initially, benzaldehyde which then undergoes further oxidation to the product usually reported from this reaction, benzoic acid.

It was also possible to test for the presence of Mn^{III} in the product solution since it is known to disproportionate to Mn^{II} and MnO_2 under alkaline conditions.[3] When the solution of reaction products was made basic by the addition of sodium hydroxide, a brown precipitate of MnO_2 was indeed obtained. Hence it appears that the intermediate decomposes to give benzaldehyde and Mn^{III} as the initial products. A probable sequence which accounts for all of these observations has been outlined in eq 1.



(1)

Although hypomanganate esters have often been considered as possible intermediates in these reactions,[2-4] we believe that this is the first time their physical detection has been reported. They appear to exhibit distinctly different properties from the Mn^{III} intermediate which has recently been detected during the permanganate oxidation of acetylenedicarboxylic acid.[5]

The kinetics were determined in a routine way with the aid of a Durrum Model D-110 stopped-flow spectrophotometer. The preparation and identification of the deuterated cinnamic acids have been described elsewhere.[6]

Acknowledgments. The authors are pleased to acknowledge the financial assistance of the National Research Council of Canada in the form of an operating grant (D. G. L.) and a scholarship (J. R. B.).

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(4) K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, **79**, 2822 (1957); K. B. Wiberg and R. D. Geer, *ibid.*, **88**, 5827 (1966).

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(6) J. R. Brownridge, M.Sc. Thesis, The University of Saskatchewan, Regina Campus, 1972. D. G. Lee and J. R. Brownridge, *Can. J. Chem.*, in press.

Donald G. Lee,* James R. Brownridge
Department of Chemistry, University of Saskatchewan
Regina Campus
Regina, Saskatchewan, Canada

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Permanganate Oxidation of Crotonic Acid. Spectrometric Detection of an Intermediate[1]

Sir:

In our previous study of the kinetics of the permanganate oxidation of crotonic and cinnamic acids, evi-

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(1) This investigation was supported by the National Science Foundation.

dence was found for the involvement of an intermediate, presumably derived from manganese(V), which could further be oxidized by permanganate.[2] This second oxidation step appeared to be of importance in determining which products are formed. We now wish to present direct spectrometric evidence for such an intermediate.

When a large excess of crotonic acid was used at pH 7 the absorbance at 525 mμ decreased in a normal first-order fashion. However, at 420 mμ, the absorbance increased at a corresponding rate. The kinetic behavior was a function of pH. Using 0.2 M sodium hydroxide, the change in absorbance with time at 525 mμ was unchanged. The absorbance at 420 mμ first increased and then decreased, whereas the absorbance at 584 mμ first decreased and then increased.

The spectral changes were monitored at 28 wavelengths and all of the data were treated simultaneously by the method of least squares.[3] The data were consistent with the following scheme

$$CH_3CH{=}CHCO_2^- + MnO_4^- \xrightarrow{k_1} A$$

$$A + HO^- \xrightarrow{k_2} B$$

where $k_1 = 110\ M^{-1}\ sec^{-1}$ and $k_2 = 10\ M^{-1}\ sec^{-1}$ (0°). The spectra were obtained *via* this analysis and are shown in Figure 1. The species B reacts further at a slow rate giving manganese dioxide. The spectra of both A and B are markedly different than either permanganate or manganate.

When the ratio of crotonic acid to permanganate was reduced, the spectrum indicated that manganate(VI) began to be formed.[4] A detailed kinetic analysis of the data indicated that both A and B were oxidized by permanganate giving manganese(VI) species.[5] The rate of formation of A was unchanged. Since A and B are converted to manganese(VI) by permanganate, they must be derivatives of manganese(V).

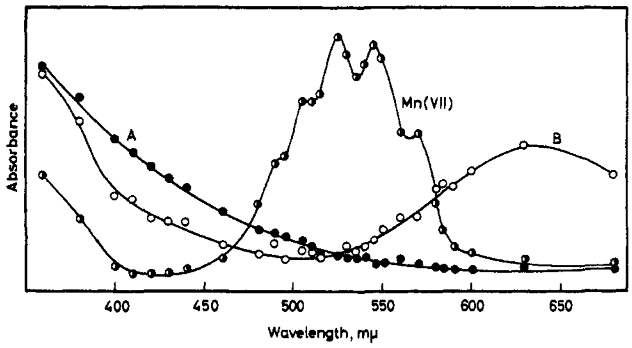
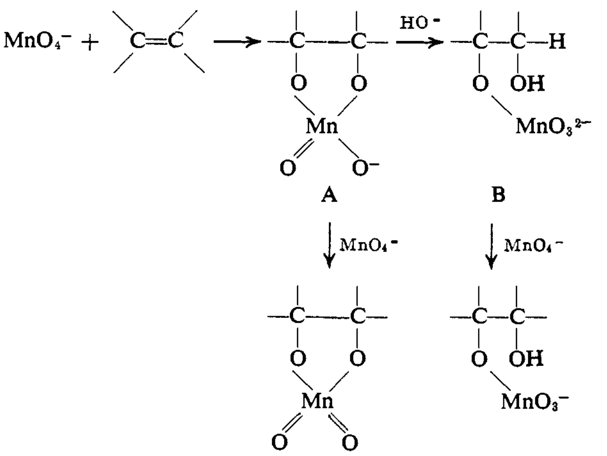


Figure 1. Absorption spectra of permanganate and of the two manganese(V) species, A and B, as determined from an analysis of kinetic data. The absorbance values for B have been multiplied by a factor of two.

Scheme I



These data are in good accord with the scheme (Scheme I) which we proposed previously.[2] The first-formed species, A, is assigned the cyclic structure in accord with the stereochemistry of the diol formation,[6] the observation of oxygen-18 transfer from permanganate,[7] and the present observation that it is converted to another manganese(V) species by base.

The unique observation is the relatively high stability of A in neutral solution. Manganate(V) is stable toward disproportionation only in concentrated potassium hydroxide solutions.[8] Even manganate(VI) is unstable below about pH 10. The high stability of A is probably a result of its being a diester and, thus, being completely ionized even in neutral solution. The base concentrations at which manganate(VI) and manganate(V) are stable are those which would be expected to give essentially complete conversion to the respective anions. Disproportionation may well involve initial anhydride formation which would be facilitated by protonation.

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[2] K. B. Wiberg and R. D. Geer, *J. Amer. Chem. Soc.*, **88**, 5827 (1966).

[3] C. Deutsch, "Computer Programs for Chemistry," Vol. 4, D. F. DeTar, Ed., Academic Press, New York, N. Y., 1972, p 243.

[4] Manganate(VI) has absorption maxima at 439 and 606 mμ. When a 2:1 ratio of permanganate to crotonic acid was used, the spectrum of the reaction solution was the same as that for manganate(VI).

[5] The scheme shown below was employed with a Runge-Kutta numerical integration routine to generate simulated kinetic data. It was possible to adjust the rate constants for oxidation of A and B to give a good fit for a number of crotonate:permanganate ratios ranging from 1000:1 to 1:1. At the high ratio, no manganate(VI) was formed and at the low ratio, manganate(VI) was the only manganese species formed.

[6] J. Böseken, *Recl. Trav. Chim. Pays-Bas*, **40**, 553 (1921); *ibid.*, **47**, 683 (1928).

[7] K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, **79**, 2822 (1957).

[8] The properties of manganate(V) are reviewed by R. Stewart, "Oxidation in Organic Chemistry, Part A," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965.

Kenneth B. Wiberg,* Carol J. Deutsch
Department of Chemistry, Yale University
New Haven, Connecticut 06520

Jan Roček
Department of Chemistry, University of Illinois at Chicago Circle
Chicago, Illinois 60680

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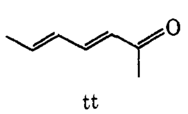
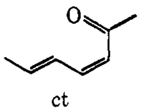
Triplet Sensitized Photoisomerization of 3,5-Heptadienone

Sir:

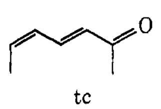
Irradiation of any of the three known isomers of 3,5-heptadienone (tt, ct, and tc) cleanly and rapidly pro-



tt



ct



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