

Mn(VII) oxidation using cetyltrimethylammonium permanganate: Oxidation of alkyl cinnamates

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The kinetics and mechanism of Mn(VII) oxidation of substituted alkyl (E) cinnamates by cetyltrimethylammonium permanganate have been studied spectrophotometrically at 524 nm in chloroform medium. From the formation of aldehydes and Mn(III) a mechanism for the oxidation reaction has been proposed. The formation of cyclic manganate(V) diester intermediate is supported by a large negative entropy of activation. A negatively charged transition state is also supported by the Hammett plot.

The oxidation of unsaturated compounds by permanganate ion using phase transferring agents has received considerable attention. The process of phase transfer catalysis is a method introduced in recent years to utilize the possibility of transferring anions or cations into an organic layer. With the help of a phase transfer agent it is possible to perform reactions in a two-phase system at a rate which is often comparable to anhydrous dipolar aprotic solvents¹.

Mn(VII) oxidation of various organic substrates have been done in organic media using the phase transferring methods². From the kinetic studies with quaternary ammonium permanganate as the oxidant, Lee *et al.*³ have proposed a mechanism where the ground state is a highly delocalised anion in which the charge is spread over the four permanganate oxygens, while the transition state is a more localised enolate ion. Further, they have suggested that since the interaction with the quaternary ammonium ion would be stronger for the structure in which there is greater localization of the negative charge a smaller cation would favour the transition state and thus would promote a faster reaction.

In our earlier communication⁴ we have reported the synthesis, characterization and self-oxidation of cetyltrimethylammonium permanganate (CTAP) along with its use in oxidising benzyl alcohol. We have also compared the oxidation kinetics of styryl pyridinium dyes using KMnO_4 and CTAP⁵. Herein we report the detailed oxidation kinetics of alkyl cinnamate by CTAP in chloroform medium.

Materials and Methods

Cetyltrimethylammonium permanganate was obtained by precipitation from an aqueous mixture of cetyltrimethylammonium bromide and potassium permanganate⁴. The substituted cinnamic acids and corresponding methyl cinnamates were prepared and recrystallised⁶. The alkyl cinnamates were prepared by condensing the respective alcohols with cinnamates. Compounds were purified by distillation or recrystallization. The purity of the compounds were checked on tlc plate. Melting points were determined in open capillary tubes in a sulphuric acid bath and are uncorrected. Elemental analysis were performed on a C H N analyser. The experimental values correspond to the elemental values.

The solvent used for kinetics, chloroform, was purified by treatment with cetyltrimethylammonium permanganate for 48 hours, followed by distillation from the mixture. Chloroform was distilled again just before each experiment.

Rates of reaction

The reactions were followed as previously described⁴ by monitoring spectral changes at 524 nm at various temperatures using a Hitachi-200 UV-VIS spectrophotometer, attached with a MK-70 cryostat. Rate constants were obtained from the plots of $\log(\text{OD}_0/\text{OD}_t)$ with time. All calculations were made using a sigma plot programme in an AT-386 computer. All rate constants are the average of two to three experiments.

The oxidation state of manganese in the product mixture was determined by evaporating the chloroform and adding water to the mixture followed by acidified (HCl) potassium iodide and titrating the iodine released against standard sodium thiosulphate solution^{7,8}. Manganese dioxide was isolated from reaction mixtures after reactions were completed. The spectra of manganese dioxide treated with cetyltrimethylammonium bromide (CTAB) were also recorded in chloroform medium in the colloidal state to compare with that of the product mixture. The solution was made completely CTAB-free.

In separate experiments, the product mixtures were isolated by filtering off the colloidal MnO₂ through a G-4 crucible and evaporating chloroform on a water bath. The products in each experiment showed a positive test for the 2,4-dinitrophenyl hydrazone of benzaldehyde for all cinnamates and substituted benzaldehydes for substituted cinnamates. The melting points of the 2,4-dinitrophenyl hydrazones corresponded with the literature values⁹.

Results

Kinetics

The kinetics of the oxidation of alkyl cinnamates were determined in chloroform medium. The rates of disappearance of the Mn(VII) peaks at 524 nm were monitored. The second order rate constants (k_s) were calculated by dividing the first order rate constants (k_{ψ}) by the concentration of substrates. First order dependence on the concentration of substrates as well as oxidant is observed. The second order rate constants of oxidation at various temperatures and the corresponding thermodynamic parameters ΔH^\ddagger , ΔS^\ddagger and ΔF^\ddagger are given in Table 1.

Sequential scans obtained during the oxidation

reaction are shown in Fig. 1. The isosbestic points at 584 and 494 nm suggest that the reaction does not involve a complicated sequence of events⁷. Similar

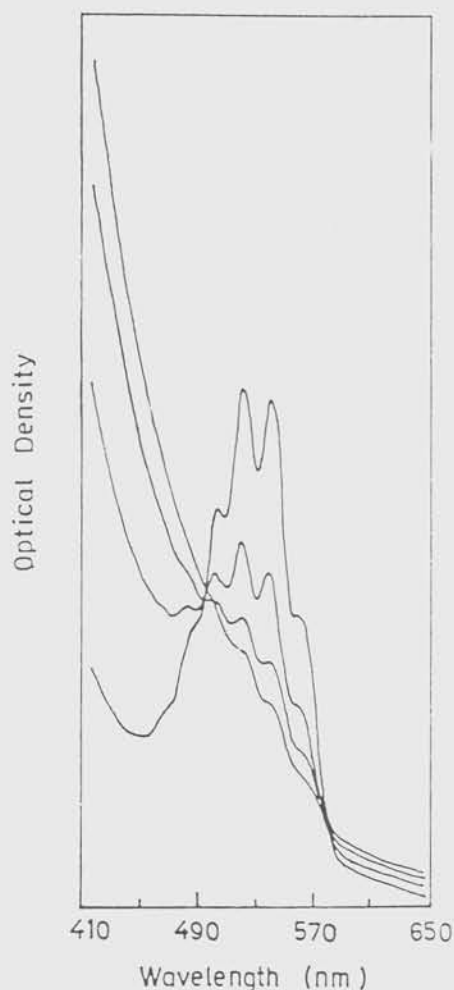


Fig. 1—Successive absorption spectra (Chart speed 30 mm/min, scan interval 4 min) for the oxidation of methyl cinnamate ($0.2 \times 10^{-3} M$) by CTAP ($0.2 \times 10^{-3} M$) in chloroform at 30°C. Isosbestic points at 584 and 494 nm.

Table 1—Second order rate constants (k_s in lit. mol^{-1}) and thermodynamic parameters (at 30°C) for the oxidation of alkyl cinnamates ($0.2 \times 10^{-3} M$) by CTAP ($0.2 \times 10^{-3} M$) in chloroform medium at 524 nm

Substrate	Rate in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$				ΔH^\ddagger kJ/mol	$-\Delta S^\ddagger$ kJ/mol	ΔF^\ddagger kJ/mol
	25°	30°	35°	40°C			
Methyl cinnamate	3.35	3.88	4.60	5.05	19.80	0.168	70.85
Methyl- <i>p</i> -methyl-cinnamate	2.21	2.69	3.42	4.08	30.66	0.135	71.77
Methyl- <i>p</i> -methoxy cinnamate	1.96	2.30	2.78	3.32	25.69	0.153	72.17
Methyl- <i>m</i> -nitro-cinnamate	13.12	16.12	19.49	24.10	29.63	0.124	67.26
Ethyl cinnamate	2.91	3.78	4.60	5.88	34.19	0.121	70.92
Isopropyl cinnamate	1.81	2.17	2.65	3.13	26.84	0.150	72.32
Isobutyl cinnamate	2.71	2.97	3.31	3.65	13.44	0.191	71.53
<i>n</i> -Butyl cinnamate	2.78	3.01	3.35	3.68	12.59	0.194	71.49
Isoamyl cinnamate	2.62	2.88	3.23	3.59	14.36	0.189	71.60

curves were obtained by Lee *et al.*³ while monitoring the oxidation of methyl(E) cinnamate by tetrabutylammonium permanganate. From the iodometric titration of the reaction products, the oxidation state of manganese was found to be 3.05 ± 0.15 . The emergence of a peak at 486 nm during the oxidation process corresponds to the peak, characteristic of Mn(III). Lee *et al.*¹⁰ have observed an absorption maximum at 478 nm at the end of the oxidation reaction of ethyl cinnamate by methyltributylammonium permanganate in dichloromethane due to Mn(III).

Plots of $\ln k_s$ versus $1/T$ ($k_s = k_p/[\text{Substrate}]$) were linear in all the cases. The activation parameters have been calculated and summarized in Table 1.

Addition of cetyltrimethylammonium bromide (10^{-4} - 10^{-3} M) to the reaction mixture had no effect on the rate of the oxidation reaction.

Discussion

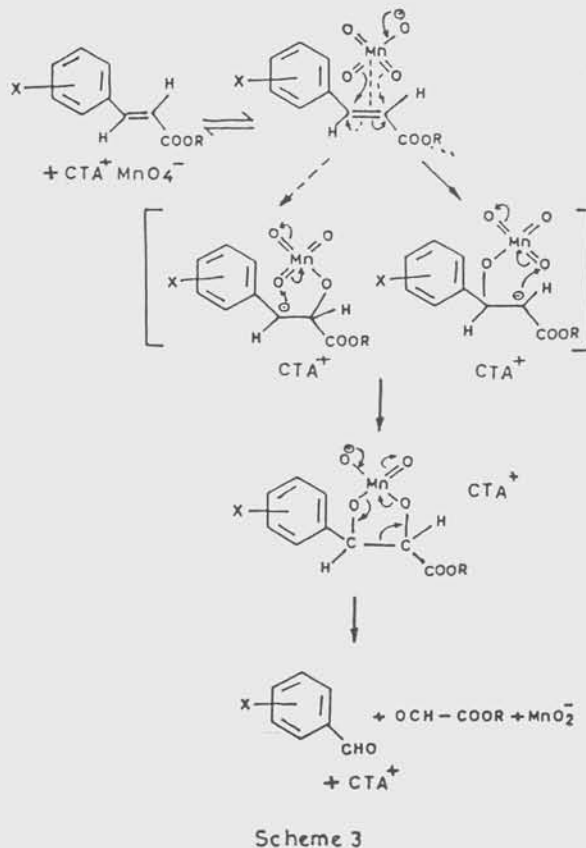
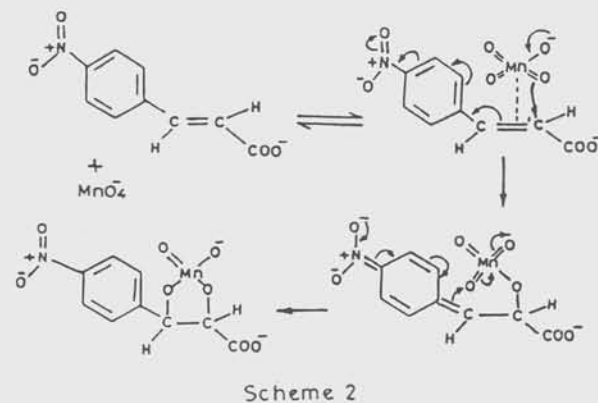
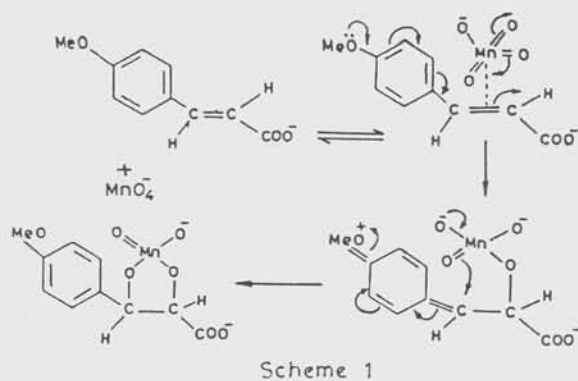
Effect of substituent

The introduction of a substituent in the aromatic ring of methyl cinnamate causes a significant effect on the rate of oxidation. Freeman and Kappos¹¹ have observed a rate enhancement in the permanganate oxidation of (E)-3-aryl-2-propionates having both electron donating and electron withdrawing substituents as compared to that of an unsubstituted substrates. To explain this they have suggested an ambiphilic nature of permanganate ion and have explained it as shown in Schemes 1 and 2.

The data in Table 1 indicate that the electron donating group decreases the rate constants whereas the electron withdrawing group increases the values. Accordingly a mechanism has been proposed (Scheme 3). This mechanism involves a negatively charged transition state. Had the mechanism proposed in Scheme 1 been correct, then the transition state would have been partially charged.

Similar type of observation has been made by Lee *et al.*¹² who have compared the proximity of the quaternary ammonium ion by varying its size. They have also proposed that the proximity of the quaternary ammonium ion increases the stability of the transition state in nonpolar solvents which is less pronounced in more polar solvents due to a greater separation of both the ions by solvation of the cation.

The Hammett plot is linear with a positive ρ value of 0.86. With increase in σ -value, the $\log k_s$



value increases indicating a charge at the vicinity of aromatic ring in the transition state than that in the ground state which is generally inferred for a positive ρ -value.

Regarding the Hammett plot for the oxidation of C-C double bond, several observations have been made by different workers. Toyoshima *et al.*¹³ have observed a negative ρ value for the KMnO_4 oxidation of vinyl ether in aqueous THF, whereas Brownridge *et al.*¹⁴ have found the ρ -value to be zero for the oxidation of cinnamic acids in aqueous acetic acid/ HClO_4 medium.

Lee *et al.*¹² have observed a Hammett plot with a concavity upward for the oxidation of substituted β -bromo and β -methoxy systems. Consequently, they have proposed a mechanism where the reaction proceeds by way of a continuum of transition states that can vary from electron-rich to electron-poor depending upon the capacity of the substrate structures to accommodate either negative or positive charges.

The linear graph with a positive ρ -value in this case, indicates a negatively charged transition state. The probable sites of the negative charge is β -position with respect to the aromatic ring (Scheme 3). At this position it can be stabilized due to the carbonyl group of the ester.

Product of oxidation

The products obtained are Mn(III) and aldehydes. The cycloaddition-type mechanism for the C-C bond cleavage is supported by the large negative values for the entropy of activation¹⁵ (Table 1). Formation of aromatic aldehydes is established from the 2,4-dinitrophenyl hydrazone derivatives obtained after isolating the products. The manganese species in the product mixture after the oxidation of substrate was found to be colloidal in nature. Freeman and Chang¹⁵, Lee and Perez-Benito¹⁶, and Mata-Perez and Perez-Benito¹⁸ have independently observed that the colloidal manganese products (MnO_2) obey Rayleigh's law¹⁹. They have, further, observed a rate enhancement in the oxidation of the substrate when the product mixture (after t_∞) is added to the freshly prepared reaction mixture¹⁷. They have attributed this phenomenon to the catalytic effect of MnO_2 due to adsorption of substrate on MnO_2 particles. In the present study no change in the rate of oxidation was observed when fresh reaction mixture was added to the solution in which the permanganate ion is completely reduced.

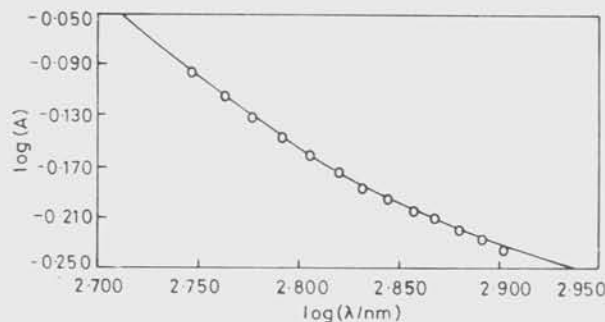
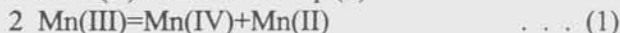


Fig. 2—Plot of $\log A$ versus $\log \lambda$ for the product formed from the reaction of methyl-*p*-methoxy cinnamate ($0.2 \times 10^{-3} M$) with cetyltrimethylammonium permanganate ($0.2 \times 10^{-3} M$) in chloroform at 30°C

Further, the plot of $\log A$ versus $\log \lambda$ was found to be a curve (Fig. 2). These observations suggest that colloidal MnO_2 was not formed as the final product. Rather, MnO_2^- is found to be the reduced form of manganese. The colloidal MnO_2 , obtained after keeping the reaction mixture for an hour, is the result of disproportionation of Mn(III) to Mn(IV) and Mn(II) as shown in Eq. (1)



Effect of alkyl chain

Substitution at the ester end by different alkyl groups at the alcohol side of the ester provides both inductive and steric effects on the rate of oxidation.

Freeman and Kappos²⁰ have studied the kinetics of permanganate ion oxidation of alkyl substituted $\alpha:\beta$ -unsaturated carboxylate ions and observed that although the rate of oxidation is not very sensitive to electronic effects, steric factors appear to be important. Table 1 shows that CTAP reacts very fast with methyl cinnamate and the rate decreases with increasing chain length to three methylene groups. With higher alkyl groups the rate increases a little and remains almost constant for *n*-butyl, iso-butyl and iso-amyl cinnamates. The relative reactivities of the first three alkyl cinnamates correlate with the number of carbon atom linearly.

The activation enthalpies and entropies are found to correlate well with an isokinetic temperature of 280.81 K. The regression equation is found to be $\Delta H^\ddagger (\text{kJ mol}^{-1}) = (68.48 \pm 1.46) + (280.81 \pm 18.04) \times \Delta S^\ddagger (\text{kJ mol}^{-1})$ and $r = 0.987$.

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