Kinetics of Oxidation of Cinnamic & Crotonic Acids by Manganese(III) Acetate in 90% Acetic Acid

R. DEVARAJAN, P. ELAYAPERUMAL, T. BALAKRISHNAN* & M. SANTAPPA
Department of Physical Chemistry, University of Madras, A. C. College of Technology Campus, Madras 600 025

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The kinetics of oxidation of cinnamic and crotonic acids by manganese(III) acetate have been studied in 90% aqueous acetic acid in the temperature range 30-60°C. The overall order of reaction is found to be 1.5; 0.5 with respect to the substrate and 1.0 with respect to the oxidant. The stoichiometry is found to be 1:3, i.e. for every molecule of substrate three molecules of manganese(III) acetate are required for oxidation. The product analysis has been carried out. A suitable mechanism, in accordance with the kinetic results, is proposed. The oxidation experiments have also been conducted at different temperatures to evaluate the kinetic parameters. The free energy of activation for both the substrates is the same (22.8 kcal per mole) suggesting a similar mechanism for both the substrates. The π-complex formation between manganese(III) acetate and the double bond of the substrate is proposed for the first time.

Materials and Methods

Manganese(III) acetate was prepared by known methods. Crotonic and cinnamic acids were recrystallised from water. Acetic acid (LR, BDH) was purified by fractional distillation after refluxing with chromium trioxide and acetic anhydride for 1 hr. Sulphuric acid (Basynth, AR, sp. gr., 1.8) and manganese(II) acetate (LR, BDH) were used as such.

Procedure—The reaction system consisted of manganese(III) acetate (5 × 10^−3 M), the unsaturated acid (4 × 10^−5 to 3.2 × 10^−1 M) and [H+] (0.5 M sulphuric acid) with a total volume of 50 ml in acetic acid. All the components except MTA were placed in a reaction flask which was thermostated. Manganese(III) acetate in 5 M sulphuric acid containing 0.5 M manganese(II) acetate solution was added to the reaction mixtures; Mn^{2+} is added to stabilise Mn^{2+}. The starting time of the reaction is the time when half of the solution has been transferred. At definite intervals, 5 ml aliquots were pipetted out into 1% solution of potassium iodide and the resulting iodine was titrated against sodium thiosulphate solution using starch as the indicator.

Absorption measurements, to determine stoichiometry, were carried out with a C.Z.U.V.—Vis spectrophotometer at 275 nm for cinnamic acid.

Results and Discussion

The oxidation of both the substrates in acetic acid by manganese(III) acetate in sulphuric acid/manganese(II) acetate took place thermally at room temperature. Carrying out the experiments in the presence of dissolved oxygen or in the nitrogen atmosphere did not affect the results. The results reported relate...
substrate and oxidant were allowed to react. A plot of temperature, 
\[ [MTA] : [substrate] = 0.005 \]
showed that the rate of oxidation is found to increase. In the case of CRA, crotonic acid (0.12 M), acetic acid (90 %), and sulphuric acid (0.5 M), equal concentrations of substrate and oxidant were allowed to react. A plot of \( \frac{1}{(a-x)} \) vs time is approximately linear with a large scattering of points. Also the \( k_2 \) value calculated from these plots is not constant.

Effect of solvent medium on rate — At constant temperature, [MTA] : [substrate] = 0.005 M : 0.2 M or 1 : 40 and constant sulphuric acid concentration (0.5 M), the rate increases with increasing [acetic acid] (50 % to 90 %).

Effect of sulphuric acid — As the [H\(_2\)SO\(_4\)] is increased, the rate of oxidation is found to increase. In sulphuric acid the species present are Mn(H\(_2\)O)\(_6\)\(^{2+}\) and Mn (H\(_2\)O)\(_2\)OH\(^{2+}\) (ref. 16). It is inferred that the active species in the present studies is Mn(H\(_2\)O)\(_2\)OH\(^{2+}\).

Effect of manganese(II) ion — Whereas Mn(III) solution remains stable with increasing ratio of [Mn(III)] : [Mn(II)] (1 : 10 to 1 : 20), the reaction mixture added with MTA however gets coagulated, preventing carrying out of any further work, if the [manganese(II) acetate] : [substrate] ratio exceeds the value 1 : 15. In the reaction mixture there was no heterogeneous phase initially. But as the reaction proceeded a fine coating of the oxidant on the surface of the reaction vessel was observed. Under these conditions if the experiments were carried out at different temperatures, a plot of \( \log k' \) vs \( 1/T \) gives a curve which means that both homogeneous and heterogeneous reactions proceed simultaneously. Experiments were carried out at different temperatures only in the concentration range where no heterogeneous phase existed.

Complex formation and stoichiometry — UV spectra of the reaction mixtures of cinnamic acid and crotonic acid, compared to the spectra of the pure compounds in acetic acid, show a strong π-complex formation with high extinction coefficients.

The disappearance of manganese(III) acetate was followed titrimetrically. Simultaneously the disappearance of cinnamic acid for the same time interval was determined spectrophotometrically at 275 nm. Stoichiometry is equal to \(-\Delta [\text{Mn}^{3+}] / -\Delta [\text{Acid}] = 3\). When both the results are considered it is clear that for every molecule of substrate three molecules of MTA are required. Benzaldehyde was detected by TLC as one of the products in the oxidation of CA. The presence of formaldehyde, the other product of oxidation was indicated by the usual tests.

Reduction of HgCl\(_2\) and polymerization of acrylonitrile confirm that the reaction occurs through free radical mechanism. Kinetic and other results obtained could be interpreted as explained below.

The first step of oxidation of both CA and CRA will be the same as that of the oxidation of saturated monocarboxylic acids by MTA\(^{18,19}\). The resulting carboxy radicals however are different in nature and reactivity. As in the oxidation of saturated monocarboxylic acids by MTA, if a 'free' carboxy radical were to form in the first step by the attack of one molecule of MTA on CA or CRA, its subsequent decay will result in radicals whose dimerisation would yield derivatives of butadiene as the major products. Alternatively the free radical may combine with oxygen to form hydroperoxide or interact directly with MTA to give the enol forms of propionaldehyde or phenylacetaldehyde which immediately will rearrange to the respective aldehydes. Even if hydroperoxide were assumed to be formed in the reaction sequence, it will be in negligible concentration and since it possesses the characteristics of reorganizing the manganese(III) involved, it would not affect the iodometric titrations. The fact that propionaldehyde and phenylacetaldehyde are not obtained as products is sufficient to indicate that the enol radical (I) does not participate in the reaction.
not have an independent activity, but it is controlled by steric factors in the near vicinity. Moreover the order in these cases would be 2 and products analysed by TLC indicate that the double bond is certainly cleaved giving acetaldehyde and benzaldehyde as major products (95\%)

The formation of \(\gamma\)-lactones is ruled out on similar grounds as in the case of oxidation of olefins in non-acqueous media\(^1\), the lactones are stable five-membered ring compounds. Again in this case also the order will be 2; which is not in conformity with the observed order of 1.5 and stoichiometry 3. Based on the aforesaid arguments the following mechanism (Scheme 1) is proposed:

\[
\frac{1}{k''} = \frac{1}{k_d} K \text{[CRA]}^{1/2} + \frac{1}{k_d}
\]

where \(K\) is the equilibrium constant for the complex between the substrate and MTA and \(k_d\) is the decomposition rate of the complex. For crotonic acid the values are, \(k_d = 5 \times 10^{-4} \text{sec}^{-1}\) and \(K = 6.45 \times 10^4\).

The rate of oxidation of cinnamic acid is found to be faster than that of crotonic acid, at all given temperatures and \([\text{Mn(III)}] : [\text{substrate}]\) ratios. The only effect operating in the two systems is the inductive effect, which enhances the formation of the \(\pi\)-complex more in cinnamic acid than in crotonic acid. The UV spectra of the \(\pi\)-complexes show that the absorption in the case of cinnamic acid is much higher compared to that in the case of crotonic acid.

By carrying out the reaction at two different temperatures and using Eq. 2.

\[
\ln k_d/k_1 = -E/R \left[1/T_1 - 1/T_2\right]
\]

the Arrhenius energy of activation, \(E_a\), entropy of activation \(\Delta S^\circ\) and free energy of activation \(\Delta G^\circ\) have been calculated (Table 1). The \(\Delta G^\circ\) values in both the cases are almost the same and may be understood in terms of isokinetic relationship\(^4\), for the radical moiety in both the cases is almost the same undergoing reaction by the same mechanism, the free energy \(\Delta G^\circ\) will be the same with relative changes in \(\Delta H^\circ\) and \(\Delta S^\circ\).

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**References**