

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

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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°. 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  $\pi$ -complex formation between manganese(III) acetate and the double bond of the substrate is proposed for the first time.

THE efficiency of manganese(III) acetate (MTA) as one-electron transfer oxidant in the oxidation of organic compounds and other compounds containing atoms like phosphorus<sup>1</sup> is well known. Oxidation by manganese(III) pyrophosphate<sup>2,3</sup>, sulphate<sup>4</sup> and perchlorate<sup>5</sup> occurs through free radical mechanism. Sometimes a cyclic complex may be formed which decomposes to a free radical which is further oxidised to various products<sup>6,7</sup>. The oxidation of both saturated mono- and dicarboxylic acids<sup>2,3,6</sup> and of olefins<sup>8-10</sup> has been reported. However, Julien<sup>11</sup> and Vieböck<sup>12</sup> failed to obtain reaction with crotonic, itaconic or oleic acids which may be due to the presence of water in the reaction mixture and failure to go to high enough temperature or variability in the reactivity of manganese(III) acetate. In the oxidation of alkylarenes by manganese(III) and cobalt(III) in acetic acid, the oxidation is enhanced by strong acids so that extensive reaction occurs at room temperature<sup>9</sup>. For example, no reaction takes place when MTA is heated in acetic acid at 70° for 30 min in the presence of dimethylbenzene. But in the presence of 1.0 M sulphuric acid, total reduction occurs just in 10 min at only 25°. The state of manganese(III) in sulphuric acid and perchloric acid solutions has been investigated<sup>13</sup>. Hexaaquamanganese(III) ion or its counterparts in sulphuric acid solution may be responsible for the formation of free radicals or free radical ions. In many cases the MTA attack on the substrate is direct, involving the formation of inner-sphere or outer-sphere complexes. These complexes subsequently dissociate giving radicals and other products. No detailed kinetic study has so far been made for the oxidation of cinnamic acid (CA) and crotonic acid (CRA) by Mn<sup>3+</sup>.

### Materials and Methods

Manganese(III) acetate was prepared by known methods<sup>14</sup>. 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<sup>15</sup>. Sulphuric acid (Basynt, AR, sp. gr., 1.8) and manganese(II) acetate (LR, BDH) were used as such.

**Procedure**—The reaction system consisted of manganese(III) acetate ( $5 \times 10^{-3} M$ ), the unsaturated acid ( $4 \times 10^{-2}$  to  $3.2 \times 10^{-1} M$ ) and [H<sup>+</sup>] (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<sup>2+</sup> is added to stabilise Mn<sup>3+</sup>. 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 specord 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

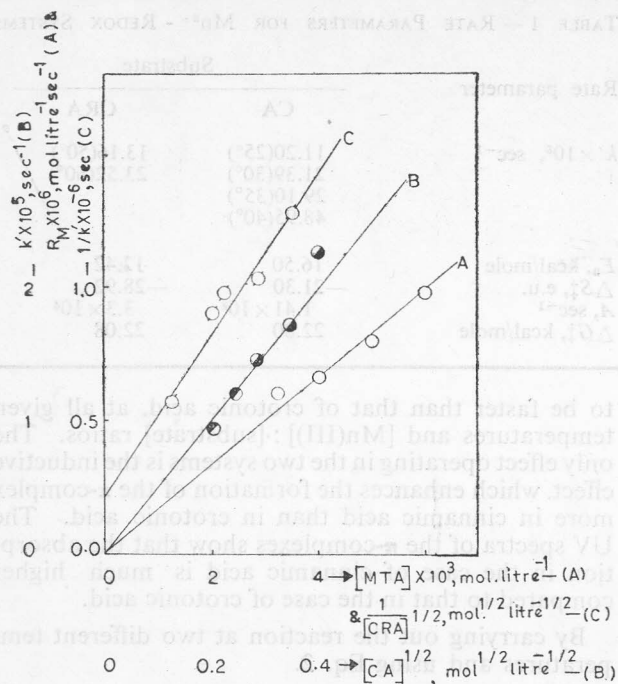


Fig. 1 — Rate plots for  $\text{Mn}^{3+}$  - CA and  $\text{Mn}^{3+}$  - CRA systems {Curve A :  $-R_{\text{Mn}}$  vs  $[\text{Mn}^{3+}]$ ;  $[\text{H}^+] = 0.5 \text{ M}$ ;  $[\text{HOAc}] = 90\%$ ;  $[\text{CA}] = 0.16 \text{ M}$ ;  $[\text{Mn}^{2+}] = 0.05 \text{ M}$ ; temp. =  $30^\circ$ ; curve B :  $k'$  vs  $[\text{CA}]^{1/2}$ ;  $[\text{H}^+] = 0.5 \text{ M}$ ;  $[\text{HOAc}] = 90\%$ ;  $[\text{MTA}] = 0.005 \text{ M}$ ;  $[\text{Mn}^{2+}] = 0.05 \text{ M}$ ; temp. =  $30^\circ$ . Curve C :  $1/k'$  vs  $[\text{CRA}]^{-1/2}$ ;  $[\text{H}^+] = 0.5 \text{ M}$ ;  $[\text{HOAc}] = 90\%$ ;  $[\text{MTA}] = 0.005 \text{ M}$ ;  $[\text{Mn}^{2+}] = 0.05 \text{ M}$ ; temp. =  $40^\circ$ .

to thermal oxidation in the presence of dissolved oxygen.

**Rate of  $\text{Mn}^{3+}$  disappearance ( $-R_{\text{Mn}^{3+}}$ )** — At constant [substrate] ( $0.12 \text{ M}$ ),  $[\text{H}_2\text{SO}_4]$  ( $0.5 \text{ M}$ ), HOAc ( $90\%$ ) and temperature, a first order dependence with respect to  $[\text{Mn}^{3+}]$  was observed (Fig. 1). At constant  $[\text{Mn}^{3+}]$  ( $5 \times 10^{-3} \text{ M}$ ),  $[\text{H}_2\text{SO}_4]$  ( $0.5 \text{ M}$ ), HOAc ( $90\%$ ) and temperature ( $30^\circ$  for CA and  $40^\circ$  for CRA), variation in [substrate] ( $4 \times 10^{-2}$  to  $1.6 \times 10^{-1} \text{ M}$  of cinnamic acid and  $4 \times 10^{-2}$  to  $3.2 \times 10^{-1} \text{ M}$  of crotonic acid) gave increasing rates with increasing [substrate]. Plot of  $k'$  vs  $[\text{CA}]^{1/2}$  is linear and passes through the origin indicating that order of the reaction with respect to substrate is 0.5 (Fig. 1). In the case of CRA,  $1/k'$  is plotted against  $[\text{CRA}]^{-1/2}$  and same results are obtained.

At constant temperature ( $50^\circ$ ), [acetic acid] ( $90\%$ ) and [sulphuric acid] ( $0.5 \text{ M}$ ), equal concentrations of substrate and oxidant were allowed to react. A plot of  $1/(a-x)$  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,  $[\text{MTA}]$  : [substrate] =  $0.005 \text{ M}$  :  $0.2 \text{ M}$  or  $1 : 40$  and constant sulphuric acid concentration ( $0.5 \text{ M}$ ), the rate increases with increasing [acetic acid] ( $50\%$  to  $90\%$ ).

**Effect of sulphuric acid** — As the  $[\text{H}_2\text{SO}_4]$  is increased the rate of oxidation is found to increase. In

sulphuric acid the species present are  $\text{Mn}(\text{H}_2\text{O})_6^{3+}$  and  $\text{Mn}(\text{H}_2\text{O})_5\text{OH}^{2+}$  (ref. 16). It is inferred that the active species in the present studies is  $\text{Mn}(\text{H}_2\text{O})_5\text{OH}^{2+}$ .

**Effect of manganese(II) ion** — Whereas Mn(III) solution remains stable with increasing ratio of  $[\text{Mn(III)}] : [\text{Mn(II)}]$  ( $1 : 10$  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  $\pi$ -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  $275 \text{ nm}$ . 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<sup>17</sup>.

Reduction of  $\text{HgCl}_2$  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<sup>18,19</sup>. 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 replanishing 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 enyl radical (I) does

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%) in the case of CRA and CA respectively. The formation of  $\gamma$ -lactones is ruled out on similar grounds as in the case of oxidation of olefins in non-aqueous media<sup>10</sup>, 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:

The unstable diol intermediate with the carbonium ion rearranges with cleavage of the carbon-carbon bond. Stable diol intermediates, which rearrange to carbonyl compounds, have been reported in the oxidation of olefins by thallium (III) acetate<sup>20</sup>. For both the products only a single Tl(III) ion is used up. Tl(III) being a two-electron transfer oxidant, it is finally reduced to Tl(I). It can be expected that two manganese(III) acetate molecules in aqueous solutions could bring about similar reactions at the double bond through an outersphere or innersphere complex and a  $\pi$ -complex between manganese (III) acetate and double bond of the substrate.

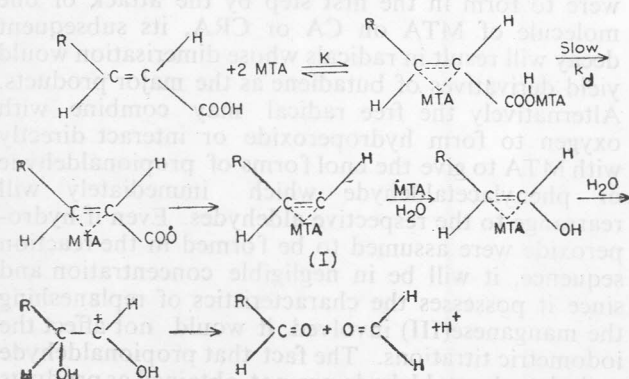
$\pi$ -complexes with  $\text{Co}^{3+}$  have already been reported<sup>21,22</sup>. Chemical evidence for such  $\pi$ -complexes, as in the case of  $\text{Co}^{3+}$  and olefin comes from the methanolysis of 2-acetoxyethyl-2-<sup>13</sup>C (pyridine) cobaloxime and reaction between Cob(III) alamins of Cob(III) aloximes and vinyl ethers<sup>23</sup>.

The direct evidence for the formation of the complex and 0.5 order with respect to the substrate is derived from the obeying of the following kinetic equation (Eq. 1).

$$\frac{1}{k'} = \frac{1}{k_d K [\text{CRA}]^{1/2}} + \frac{1}{k_d} \quad \dots(1)$$

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


 TABLE 1—RATE PARAMETERS FOR  $\text{Mn}^{3+}$ -REDOX SYSTEMS

Rate parameter	Substrate	
	CA	CRA
$k' \times 10^5, \text{ sec}^{-1}$	11.20(25°)	13.16(50°)
	21.39(30°)	23.52(60°)
	29.10(35°)	
	48.95(40°)	
$E_a, \text{ kcal/mole}$	16.50	12.42
$\Delta S^\ddagger, \text{ e.u.}$	-21.30	-28.92
$A, \text{ sec}^{-1}$	$1.41 \times 10^8$	$3.3 \times 10^4$
$\Delta G^\ddagger, \text{ kcal/mole}$	22.80	22.08

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.

$$\ln k_2/k_1 = -E/R [1/T_1 - 1/T_2] \quad \dots(2)$$

the Arrhenius energy of activation,  $E_a$ , entropy of activation  $\Delta S^\ddagger$  and free energy of activation  $\Delta G^\ddagger$  have been calculated (Table 1). The  $\Delta G^\ddagger$  values in both the cases are almost the same and may be understood in terms of isokinetic relationship<sup>24</sup>, for the radical moiety in both the cases is almost the same undergoing reaction by the same mechanism, the free energy  $\Delta G^\ddagger$  will be the same with relative changes in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ .

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Excess volumes ( $V_E$ ), excess enthalpies ( $H_E$ ) and excess Gibbs free energies ( $G_E$ ) of mixing of binary mixtures of nitrobenzene with benzene, *o*-, *p*- and *m*-xylenes have been measured at 318.15 K. The  $V_E$ ,  $H_E$  and  $G_E$  values, which are positive for all the systems, throughout the entire concentration range, have been analysed in terms of electron donor-acceptor type of interactions between the components of these mixtures.

data reported for these compounds at various temperatures.<sup>12</sup> However, the corresponding data for nitrobenzene could not be compared because of the non-availability of the literature data at 318.15 K.

TABLE I - EXCESS VOLUMES OF MIXING FOR VARIOUS MIXTURES AT 318.15 K

Mole fr. of Nitrobenzene (A)	Mole fr. of Benzene (B)	Mole fr. of Nitrobenzene (A) + Benzene (B)	Mole fr. of Nitrobenzene (A) + <i>o</i> -Xylene (B)	Mole fr. of Nitrobenzene (A) + <i>p</i> -Xylene (B)	Mole fr. of Nitrobenzene (A) + <i>m</i> -Xylene (B)
0.000	1.000	0.000	0.000	0.000	0.000
0.010	0.990	0.002	0.003	0.002	0.001
0.020	0.980	0.004	0.006	0.004	0.002
0.030	0.970	0.006	0.009	0.006	0.003
0.040	0.960	0.008	0.012	0.008	0.004
0.050	0.950	0.010	0.015	0.010	0.005
0.060	0.940	0.012	0.018	0.012	0.006
0.070	0.930	0.014	0.021	0.014	0.007
0.080	0.920	0.016	0.024	0.016	0.008
0.090	0.910	0.018	0.027	0.018	0.009
0.100	0.900	0.020	0.030	0.020	0.010
0.110	0.890	0.022	0.033	0.022	0.011
0.120	0.880	0.024	0.036	0.024	0.012
0.130	0.870	0.026	0.039	0.026	0.013
0.140	0.860	0.028	0.042	0.028	0.014
0.150	0.850	0.030	0.045	0.030	0.015
0.160	0.840	0.032	0.048	0.032	0.016
0.170	0.830	0.034	0.051	0.034	0.017
0.180	0.820	0.036	0.054	0.036	0.018
0.190	0.810	0.038	0.057	0.038	0.019
0.200	0.800	0.040	0.060	0.040	0.020
0.210	0.790	0.042	0.063	0.042	0.021
0.220	0.780	0.044	0.066	0.044	0.022
0.230	0.770	0.046	0.069	0.046	0.023
0.240	0.760	0.048	0.072	0.048	0.024
0.250	0.750	0.050	0.075	0.050	0.025
0.260	0.740	0.052	0.078	0.052	0.026
0.270	0.730	0.054	0.081	0.054	0.027
0.280	0.720	0.056	0.084	0.056	0.028
0.290	0.710	0.058	0.087	0.058	0.029
0.300	0.700	0.060	0.090	0.060	0.030
0.310	0.690	0.062	0.093	0.062	0.031
0.320	0.680	0.064	0.096	0.064	0.032
0.330	0.670	0.066	0.099	0.066	0.033
0.340	0.660	0.068	0.102	0.068	0.034
0.350	0.650	0.070	0.105	0.070	0.035
0.360	0.640	0.072	0.108	0.072	0.036
0.370	0.630	0.074	0.111	0.074	0.037
0.380	0.620	0.076	0.114	0.076	0.038
0.390	0.610	0.078	0.117	0.078	0.039
0.400	0.600	0.080	0.120	0.080	0.040
0.410	0.590	0.082	0.123	0.082	0.041
0.420	0.580	0.084	0.126	0.084	0.042
0.430	0.570	0.086	0.129	0.086	0.043
0.440	0.560	0.088	0.132	0.088	0.044
0.450	0.550	0.090	0.135	0.090	0.045
0.460	0.540	0.092	0.138	0.092	0.046
0.470	0.530	0.094	0.141	0.094	0.047
0.480	0.520	0.096	0.144	0.096	0.048
0.490	0.510	0.098	0.147	0.098	0.049
0.500	0.500	0.100	0.150	0.100	0.050

ENNETT and Wain<sup>13</sup> have pointed out that the interactions between polynitro compounds and aromatic hydrocarbons leading to complex formation are of electron donor-acceptor type in which the aromatic hydrocarbons act as potential electron donors. It would therefore be interesting to investigate if this conclusion is valid in the case of nitrobenzene with benzene, toluene and *o*-, *m*- and *p*-xylenes.

**Materials and Methods**  
 Benzene, toluene and *o*-, *m*- and *p*-xylenes (all BDH, AR) were purified as described earlier.<sup>14</sup> Nitrobenzene (BDH, AR) was purified by the method described by Saunders and Spaul.<sup>15</sup> The purity of the final samples was checked by density determination at 298.15±0.01 K which agreed with the corresponding literature values<sup>16</sup> within ±0.0005 g/cm<sup>3</sup>. Excess volumes of mixing ( $V_E$ ) were measured as a function of composition using the direct dilatometric method.<sup>17</sup> The temperature of the thermostat bath was controlled to ±0.01 K. The uncertainty in experimental  $V_E$  values is about 0.5%.

Heats of mixing ( $H_E$ ) were measured in an adiabatic calorimeter described elsewhere.<sup>18</sup> The time was recorded by an electronic timer (type 701 SI No. 010, Sytonic, Adelaide) which could read correct upto ±0.0001 sec. The temperature variation of the thermostat bath was within ±0.01 K. The uncertainty in  $H_E$  values is about 1%.

Vapour pressures of these mixtures were determined by a static method described previously.<sup>19</sup> The apparatus was placed in a water thermostat which was placed in another water thermostat. The temperature of the outer thermostat was controlled to ±0.01 K and the temperature drift in the inner thermostat was found to be less than ±0.003 K. The mercury heights in the manometer were read by a cathetometer which could read upto ±0.001 cm. All vapour pressure measurements were reproducible better than ±0.02 torr.

The measured vapour pressures of aromatic hydrocarbons at 318.15 K compared within 0.3% with the