

Kinetic Studies on the Effect of Mn(II) on the Oxidation of α -Hydroxy Carboxylic Acids by Cr(VI)

S.L. BIKANERIA† and B.L. HIRAN*

Department of Chemistry

University College of Science, M.L.S. University, Udaipur-313 001, India

Mn(II) catalysis in the chromic acid oxidation of lactic acid (LA), malic acid (MA), tartaric acid (TA) and citric acid (CA) in 50% acetic acid-50% water medium has been studied. Mn(II) retards oxidation at low $[\text{Mn(II)}]/[\text{Cr(VI)}]$ ratio but in H_2SO_4 ($\approx 1.0 \text{ M}$) at high $[\text{Mn(II)}]/[\text{Cr(VI)}]$ ratio 200 for lactic acid, 200 for malic acid and 500 for tartaric acid, rate of oxidation increases while for citric acid it is very low ratio (≈ 10). Rate under the positive catalysis is linearly proportional to $[\text{Mn(II)}]$, $[\text{H}_2\text{SO}_4]$ at $\geq 1.0 \text{ M}$, HCrO_4^- and obey Michaelis-Menten kinetics. Addition of sodium pyrophosphate decreases rate of oxidation. Energy of activation for uncatalysed, Cr(VI)-Mn(II) and catalysed reactions have been given.

INTRODUCTION

The well known effect of manganese (II) ions in diminishing the rates of oxidations of alcohols, α -hydroxy carboxylic acids and aldehydes by chromic acid has been of diagnostic theoretical importance in establishing the mechanism. Less attention has been paid to the positively catalysed manganese (II) oxidations affected by chromic acid.

Kemp and Water¹ have examined Mn(II) catalysis in the oxidation of α -hydroxy-isobutyric acid and malonic acid by chromic acid. Some detailed studies of the effect of Mn(II) in the oxidation of mandelic acid was reported by Beckwith and Water². Bakore and Jain³ have investigated Mn(II) catalysed oxidation of oxalic acid by chromic acid. Bhatnagar⁴ studied the Mn(II) catalysis in some details in the oxidation of malonic acid and their esters by chromium (VI) under acid conditions. Chatterjee and Gyani⁵ and Gyani and Prasad⁶ examined Mn(II) catalysis of chromic acid oxidation of lactic acid and citric acid. Bhalekar *et al.*⁷ have also studied some aspects of manganese (II) catalysed oxidation of lactic acid. In view of the incomplete information on manganese (II) catalysed oxidation of α -hydroxy acids by chromic acid, a detailed kinetic investigation study of oxidation of lactic, malic, tartaric and citric acids by chromic acid in presence of manganese (II) ion was undertaken.

EXPERIMENTAL

All chemicals used either A.R. Grade or were purified using standard methods and purity checked by m.p./b.p. A photochemical oxidation of α -hydroxy carboxylic acids by chromic acid has been reported. However, we observed that the rate of oxidation in dark and in diffused day light were identical. Hence, all

†Excise Laboratory, Government of Rajasthan, Udaipur (Raj) India.

the kinetic work was undertaken in diffused day light. Order of mixing of the reagents in this system was found to affect the rate.⁸ To obtain comparable results the following procedure was adopted. Reaction solutions were separately placed in glass stoppered bottles in a thermostatic bath ($\pm 0.02^\circ\text{C}$) and allowed to attain the thermostat temperature. Solutions of α -hydroxy carboxylic acids, manganese (II) and sulphuric acid were mixed in required proportions and allowed to stand in the thermostat for 0.5 h. The reactions were started by adding thermostated potassium dichromate solution. Aliquots were withdrawn at known interval of time and the gross concentration of chromium (VI) was estimated by iodometric methods, taking precautions to minimize oxidation of iodide by air⁹.

When the concentration of substrate (α -hydroxy carboxylic acids) and sulphuric acid were kept high as compared to that of chromium (VI), it was observed that the rate at which chromium (VI) disappears follows first order rate law upto about 70–75 % of the reaction (Table-1. Fig. 1). However, in presence of manganese (II), there is initial deviation from the linearity for the $\log(a-x)$ versus time plot, because of the induction period (Table 2 and Fig. 2). The first order rate constants have been calculated for the part after the induction period was over.

TABLE-1
OXIDATION OF LACTIC ACID BY Cr(VI)

[Lactic acid]: 0.02 M;	[Cr(VI)]: 8.0×10^{-4} M;	H ₂ SO ₄ : 2 M;	Temp.: 26.5°C
Time (minutes)	(a - x) mL of hypo	$k_1 \times 10^2$ (min ⁻¹)	
0	13.5	—	
1	12.6	6.90	
3	10.8	7.40	
5	9.2	7.64	
7	7.9	7.62	
9	6.8	7.62	
11	5.9	7.50	
13	5.0	7.62	
16	4.1	7.56	
20	3.0	7.50	

Average value: $7.50 (\pm 0.20) \times 10^{-2} \text{ min}^{-1}$,

Graphical Value: $7.60 \times 10^{-2} \text{ min}^{-1}$

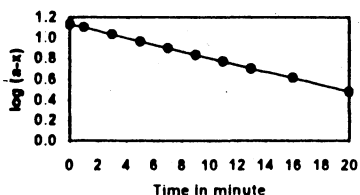


Fig. 1 (cf. Table-1) Typical run: Oxidation of lactic acid by Cr (VI)

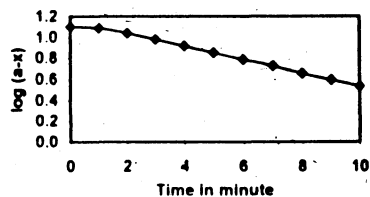


Fig. 2 (cf. Table-2) Typical run: Oxidation of lactic acid by Cr (VI) catalysed by Mn(II)

TABLE-2
OXIDATION OF LACTIC ACID BY Cr(VI) CATALYSED BY Mn(II)

[LACTIC ACID]: 0.02 M; [Cr(VI)]: 8.0×10^{-4} M; [H₂SO₄]: 2 M; [Mn(II)]: 0.75 M
Temp.: 30°C

Time in minutes	(a-x) mL of hypo	$k_1 \times 10^2$ (min ⁻¹)
0	12.6	—
1	12.2	—
2	10.9	—
3	9.5	—*
4	8.2	14.70
5	7.1	14.55
6	6.1	14.78
7	5.3	14.60
8	4.5	14.98
9	3.9	14.84
10	3.4	14.66

*Considering 9.5 mL (at time 3 minutes) as zero (initial) reading;

Average value: $14.7 (\pm 0.20) \times 10^{-2} \text{ min}^{-1}$; Graphical Value: $14.7 \times 10^{-2} \text{ min}^{-1}$

RESULTS AND DISCUSSION

Effect of Mn(II): For low values of [Mn(II)]/[Cr(VI)] the rate diminished in presence of Mn(II) but at sufficiently high values of [Mn(II)]/[Cr(VI)] ratio there is positive catalysis by Mn(II). In case of citric acid the uncatalysed reaction is extremely slow but addition of Mn(II) in the ratio of [Mn(II)]/[Cr(VI)] as low as 10 catalyse the reaction. The results are summarised in (Table 3 and Fig. 3).

Effect of substrate concentration: The effect of the substrate concentration was studied under the conditions of positive catalysis by Mn(II). Results are summarised in Table 4. A plot of $1/k_1$ v/s $1/[S]$ gives a straight line in all the cases. A representative graph of malic acid has been given fig. 4. The results show that with respect to substrate Michaelis-Menten kinetics is observed.

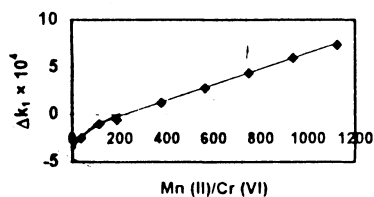


Fig. 3 (cf. Table-3) Effect of Mn(II)/Cr(VI) on rate, lactic acid

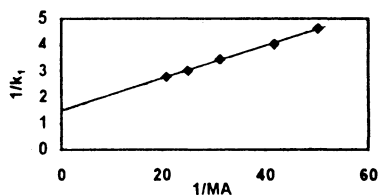


Fig. 4 (cf. Table-4) Effect of substrate variation on rate, malic acid

TABLE-3
EFFECT OF [Mn(II)]/[Cr(VI)] ON RATE OF OXIDATION

[Lactic acid]: 0.02 M; [Cr(VI)]: 8.0×10^{-4} M; [H ₂ SO ₄]: 2 M; Temp.: 30°C				
[Mn(II)]/ [Cr(VI)]	$k_1 \times 10^{-2} \text{ mn}^{-1}$			
	Lactic Acid	Malic Acid	Tartaric acid	Citric acid (0.1 M), 35°C
–	8.74	10.1	3.73	0.10
37.5	5.25	7.1	1.96	31.12
112.5	7.70	8.5	2.22	97.20
375.0	9.96	12.4	3.22	303.25
562.35	11.50	15.7	3.98	468.70
750.0	13.10	18.9	4.73	600.00
937.5	14.70	21.6	–	–
1125.0	16.10	24.8	6.15	–

TABLE-4
EFFECT OF SUBSTRATE CONCENTRATION ON RATE OF REACTION

[Cr(VI)]: 8.0×10^{-4} M; [Mn(II)]: 0.75 M; [H ₂ SO ₄]: 2.00 M; Temp. 30°C							
[LA] $\times 10^2$ moles dm ⁻¹	1.60	2.0	2.4	2.8	3.2	4	
$k_1 \times 10^2 \text{ mn}^{-1}$	12.70	14.7	—	18.0	20.3	23	
[MA] $\times 10^2$ moles dm ⁻¹	2.0	2.4	3.2	4	4.8		
$k_1 \times 10^2 \text{ mn}^{-1}$	21.6	25.0	29.0	33.2	36.0		
[Tartaric Acid] $\times 10^2$ moles dm ⁻¹	0.1	0.16	0.20	0.24	0.30		H ₂ SO ₄ = 1 M
$k_1 \times 10^2 \text{ mn}^{-1}$	6.15	9.77	11.71	13.80	13.8	16.6	
[Citric Acid] $\times 10^2$ moles dm ⁻¹	5	10	20	30	40		
$k_1 \times 10^2 \text{ mn}^{-1}$	2.00	4.00	4.70	10.0	13.2		

(at 35°C [Mn(II)] = 0.10 M and Cr(VI) = 2×10^{-3} M)

$$\frac{1}{k_1} = \frac{1}{k \cdot K[\text{MnII}]} \cdot \frac{1}{[\text{S}]} + \frac{1}{k[\text{MnII}]}$$

The values of k and K (formation constant for substrate-Mn(II) complex estimated from plot $(1/k_1 \text{ v/s } 1/[\text{S}])$ are summarised in Table 5 (Fig. 5)

TABLE-5

Substrate	k	K	Temp. (°C)
Lactic Acid	0.70	19.300	30
Malic Acid	1.00	34.400	30
Tartaric Acid	1.11	0.667	27
Citric Acid	6.67	0.617	35

The results show that reactions involves a fast oxidation of substrate-Mn(II) complex by chromic acid to a corresponding Mn(II) complex which breaks down in the rate determining step.

Effect of H_2SO_4 : It is found that in case of lactic acid malic acid and citric acid the rate constant linearly increases with $[H_2SO_4]$ if acid concentration is greater than 0.9 M, 0.7 M and 0.675 M respectively. A representative Table 6 for citric acid showing effect of H_2SO_4 on rate of oxidation at different $[Mn(II)]$ has been given. In case of tartaric acid the rate increases slowly up $[H_2SO_4]=1.50$ M but rapidly increases at higher concentration of H_2SO_4 (Fig. 6).

TABLE-6
INFLUENCE OF $[H_2SO_4]$ ON RATE OF REACTION WITH CITRIC ACID

$[Mn(II)]$ moles dm^{-1}	$[H_2SO_4]$ moles dm^{-1}	$k_1 \times 10^3 \text{ min}^{-1}$	$k_1 \times 10^3$
			$\{[H_2SO_4]-0.675\}$ $dm \text{ mole}^{-1} \text{ min}^{-1}$
0.04	2.0	17.0	12.83
	2.5	23.0	12.60
	3.0	30.0	12.90
0.06	2.0	25.0	18.86
	2.5	34.0	18.63
	3.0	4.0	18.92
0.10	2.0	40.0	30.19
	2.5	55.0	30.13
	3.0	70.0	30.11
0.15	2.0	60.0	45.28
	2.5	81.0	44.38
	3.0	105.0	45.16
0.20	2.0	80.0	60.37
	2.5	110.0	60.27
	3.0	140.0	60.21

Effect of Cr(VI): The results show that rate is independent of Cr(VI) but proportional to $[HCrO_4^-]$. The concentration of $[HCrO_4^-]$ at each concentration of chromium (VI) was calculated from

$$k' = [HCrO_4^-]^2/[CrO_7^{2-}]$$

$$k' = 24 \times 10^{-2} \text{ (25-30}^\circ\text{C)} \quad (\text{Ref. No. 9})$$

and

$$k' = 1.6 \times 10^{-2} \text{ at } 35^\circ\text{C} \quad (\text{Ref. No. 10})$$

Table 7 represents dependence of rate of oxidation of citric acid with $[HCrO_4^-]$.

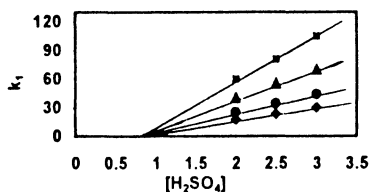
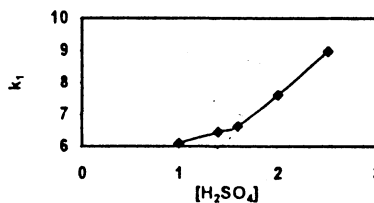
Fig. 5 (cf. Table-5) Effect of $[H_2SO_4]$ on rate, citric acidFig. 6 (cf. Table-6) Effect of $[H_2SO_4]$ on rate, tartaric acid

TABLE-7
EFFECT OF Cr(VI) ON RATE OF OXIDATION OF CITRIC ACID

[Citric Acid]: 0.10 M; [Mn(II)]: 0.10 M;	[H ₂ SO ₄]: 2 M; Temp.: 35°C					
[Cr(VI) × 10 ⁴] moles dm ⁻¹	8	12	16	20	24	28
[HCrO ₄ ⁻] × 10 ⁴ moles dm ⁻¹	7.32	10.60	13.70	16.60	19.30	22.00
k ₁ × 10 ² mn ⁻¹	4.40	4.25	4.16	4.00	3.25	3.70

Thus result is different from the observation of Kemp and Waters¹ in the oxidation of α -hydroxy isobutyric acid that in presence of large [Mn(II)] rate is proportional to $[HCrO_4^-]^{1/3}$ and in case of oxalic acid³ rate was found to be proportional to $[HCrO_4^-]^{0.65}$.

Effect of Sodium Pyrophosphate (SPP): Rate of reaction decreases with SPP but no quantitative relation could be established. Pyrophosphate forms a stable complex with Mn(II) and Mn(III) pyrophosphate (redox potential 1.10 V) is less reactive than Mn(II) sulphate (redox potential 1.50 V). Hence decrease in rate of reaction due to decreasing in oxidizing power.

Effect of Temperature: Rate of reaction increases with increase in temperature; $\log k_1$ vs $1/T$ gives straight line. The energy of activation for uncatalysed, Cr(VI)-Mn(II) and catalysed reactions are summarised in Table 8.

TABLE-8

Substrate	ΔE_a^\ddagger kJouls/mole		
	Uncatalysed	Cr(VI)-Mn(II)	Catalysed
Lactic Acid	34.42	66.75	96.97
Malic Acid	37.78	63.81	110.41
Tartaric Acid	110.75	95.29	95.29
Citric Acid	—	96.97	

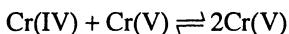
In case of lactic acid and malic acid the energy of activation for catalysed reaction is higher than that for uncatalysed reaction. Similar results were reported by Bakore and Jain³ in manganese(II) catalysed oxidation of oxalic acid by chromium(VI). The results suggest that the catalytic reaction is entropy control-

led. In case of tartaric acid catalysis appears to be the result of decrease in the energy of activation from 100.75 kJ/mole to 95.29 kJ/mole.

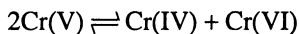
Kemp and Waters¹ have shown that for oxidation of α -hydroxy carboxylic acid (mandelic acid), C—H cleavage must occur with chromic acid but plays a minor part in the oxidations by manganese(III). The kinetic isotope effect of oxidation of mandelic acid by chromic acid at high [Mn(II)] : [Cr(VI)] ratios falls towards that for direct oxidation by manganese(III) sulphate¹¹, shows that at high [Mn(II)] : [Cr(VI)] ratios, the oxidations are virtually oxidations by manganese(III).

Work of Rocek and Radkowsky^{11, 12} and of Rahman and Rocek¹³ have shown that chromium(IV) plays an important role in chromic acid oxidations and that chromium(IV) is responsible for C—C bond cleavage. The work of Wiberg and Schafer^{14, 15} has demonstrated the similarity between the behaviour of chromium(VI) and chromium(V). This has led to the conclusion that Cr(VI) and Cr(V) brings about C—H cleavage and that only chromium(IV) is responsible for C—C cleavage in those oxidations.

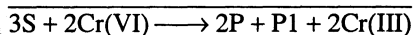
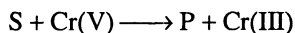
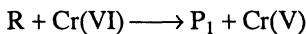
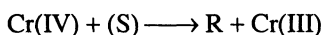
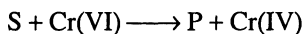
Further Rahman and Rocek¹³ have shown that, the equilibrium constant for the reaction.



is of the order of 4×10^{-4} . Thus, the thermodynamically favoured reaction is:

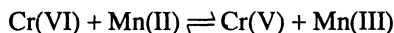


Hence, the mechanism of uncatalysed oxidations by chromic acid can be written as

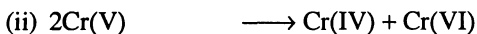
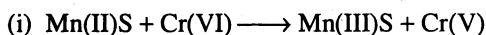


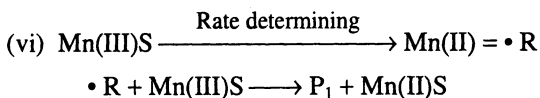
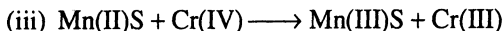
where P is the product of two electron oxidation and P₁ is the product of one electron oxidation.

In view of the fact that the rate of catalysed chromium (VI) oxidation of α -hydroxy carboxylic acids is proportional to HCrO_4^- the equilibrium

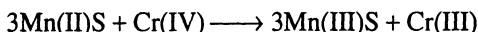


which leads to zero order reaction with respect to chromium (VI)¹² does not play an important role in the manganese (II) catalysed chromic acid oxidation of α -hydroxy carboxylic acids. The rate laws for manganese (II) catalysed chromic acid oxidations observed here can be satisfactorily explained on the following mechanism.





R is radical produced from S and P₁ is the product of one electron oxidation. Steps (i)–(iii) which are relatively fast can be written as



redox potential for Mn(II)/Mn(III) uncomplexed is 1.5 V while that for Cr(VI)/Cr(III) is 1.3 V. This would explain why Mn(II) cannot be oxidized to Mn(III) by Cr(VI) in aqueous solutions. However in presence of complexing substrate and high concentration of sulphuric acid and high [Mn(II)] : [Cr(VI)] ratio, the redox potential of Mn(II) to Mn(III) is sufficiently lowered to permit oxidation of substrate-Mn(II) complex by Cr(VI).

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REFERENCES

1. T.J. Kemp and W.A. Waters, *J. Chem. Soc.* 1192, 3193 (1964); *Proc. Roy. Soc.*, **274A**, 480 (1962); W.A. Waters, *Quart. Rev. Chem. Soc.*, **12**, 277 (1958).
2. F.B. and Beckwith and W.A. Waters, *J. Chem. Soc (B)*, 929 (1969).
3. G.V. Bakore and C.L. Jain, *J. Inorg. & Nucl. Chem.*, **31**, 2527 (1969); G.V. Bakore and S. Narain, *J. Chem. Soc.*, 3419 (1963).
4. Miss Tara Bhatnagar, Ph.D. Thesis, Udaipur University (1978).
5. K. Chatterji and B.P. Gyani, *J. Indian Chem. Soc.*, **35**, 605 (1958).
6. B.P. Gyani and Prasad, *J. Indian Chem. Soc.*, **39**, 765 (1962).
7. A.A. Bhalekar, C.L. Jain, R. Shanker and G.V. Bakore, *Z. Naturforsch.*, **30b**, 73 (1975).
8. A.K. Bhattacharya and N.R. Dhar, *Z. Anorg. Chem.*, **169**, 38 (1928).
9. F.H. Westheimer, *Chem. Rev.* **45**, 419 (1949).
10. K.B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 36022 (1958).
11. J. Rocek and A.E. Radkowsky, *J. Am. Chem. Soc.*, **90**, 2986 (1968).
12. ———, *J. Am. Chem. Soc.* **95**, 7123 (1973); *J. Org. Chem.* **38**, 89 (1973).
13. M. Rahman and J. Rocek, *J. Am. Chem. Soc.*, **93**, 5455 5462 (1971).
14. K.B. Wiberg and H. Schafer, *J. Am. Chem. Soc.*, **87**, 455 (1967).
15. ———, *J. Am. Chem. Soc.*, **91**, 927, 933 (1969).

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