

Kinetics and Mechanism of Oxidation of Cinnamaldehyde by Chromium(VI)

A. CHELLAMANI*, N.M.I. ALHAJI and S. SELVARAJAN†
 Department of Chemistry, Manonmaniam Sundaranar University
 Tirunelveli-627 002, India.

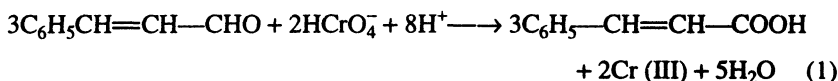
The kinetics of oxidation of cinnamaldehyde by Cr(VI) in 90% (v/v) aqueous acetic acid has been studied. The reaction follows second-order kinetics, first-order each in cinnamaldehyde and Cr(VI), at constant ionic strength and $[H^+]$. A mechanism involving the chromic acid ester of hydrated cinnamaldehyde as intermediate has been suggested.

INTRODUCTION

While Cr(VI) oxidation of chalcone¹ yields an epoxide, aliphatic unsaturated aldehydes² on the contrary are oxidised to their corresponding acids by Cr(VI). Although Cr(VI) has been widely used as an oxidant for the oxidation of organic compounds³, studies with unsaturated aldehydes received little attention. In this paper the results of the kinetics of oxidation of cinnamaldehyde Cr(VI) in 90% (v/v) aqueous acetic acid are reported and discussed.

EXPERIMENTAL

Cinnamaldehyde was purified before use. Acetic acid was purified by the method of Orton and Bradfield⁴. All the other chemicals used were of AnalaR grade. The kinetic studies were carried out in 90% (v/v) aqueous acetic acid under pseudo first-order conditions and the temperature was maintained within $\pm 0.1^\circ\text{C}$. The titrimetric procedure of Wiberg and Mill⁵ was followed for the estimation of unreacted Cr(VI). The pseudo first-order rate constant (k_1) for each run was evaluated from the slope of the linear plot of $\log(a-x)$ vs time (correlation coefficient, $r > 0.995$) by the method of least squares. The second-order rate constants were obtained from $k_2 = k_1/[\text{cinnamaldehyde}]$. The kinetic data fit the Eyring's equation and the activation parameters were evaluated by the method of least-squares. TLC of the reaction mixture of an actual kinetic run showed that cinnamaldehyde was oxidised to cinnamic acid. Stoichiometric studies indicated that three molecules of cinnamaldehyde were oxidised for each two Cr(VI) species reduced to Cr(III) and the reaction could be represented as:



†Department of Chemistry, VHNSN College, Virudhunagar-626 001, India.

RESULTS AND DISCUSSION

The pseudo first-order rate constants and second-order rate constants at different [Cr(VI)] and [cinnamaldehyde] are presented in Table 1. The reaction is first-order in Cr(VI) as shown by the constant values of the pseudo first-order rate constants at different initial concentrations of Cr(VI). The constancy of second-order rate constants at different initial concentrations of cinnamaldehyde shows that the reaction is first-order in cinnamaldehyde. Further a plot of k_1 vs. [cinnamaldehyde] is linear ($r = 0.999$) passing through the origin indicating that the reaction follows second-order kinetics.

TABLE-1
DEPENDENCE OF RATE ON [Cr(VI)] AND [CINNAMALDEHYDE]

$10^3[\text{Cr(VI)}]$ (mol dm ⁻³)	10^2 [cinnamaldehyde] (mol dm ⁻³)	$k_1 \times 10^4$ (s ⁻¹)	$k_2 \times 10^2$ (dm ³ mol ⁻¹ s ⁻¹)
1.00	3.00	15.3	5.09
1.50	3.00	14.8	4.93
2.00	3.00	14.8	4.92
2.50	3.00	13.8	4.61
3.00	3.00	14.0	4.67
1.00	1.00	4.79	4.79
1.00	1.50	7.22	4.82
1.00	2.00	10.0	5.00
1.00	2.50	12.3	4.90

Solvent: 90% (v/v) aqueous acetic acid; $I = 0.120$ mol dm⁻³; $[\text{HClO}_4] = 0.100$ mol dm⁻³;
Temp. = 313K

Kinetic data at different $[\text{H}^+]$, ionic strengths, percentage of acetic acid and [Mn(II)] are presented in Table-2. The rate of the reaction is unaffected by change in ionic strength of the medium. The reaction rate increases with an increase in the concentration of HClO_4 and the order in $[\text{H}^+]$ is around one (plot of $\log k_1$ vs $\log [\text{H}^+]$; $r = 0.997$, slope = 1.22; in evaluating $[\text{H}^+]$ the dissociation of acetic acid is also taken into account). The rate of oxidation increases with an increase in the acetic acid content in the reaction mixture. This may be due to the increased acidity of the medium at higher percentage of acetic acid^{3,5-7}. Alternatively the enhanced rate of oxidation in solutions containing higher percentage of acetic acid may be due to the formation of the acetyl chromate ion³. The acetyl group present in this ion would increase the electron-accepting power of Cr(VI). The rate retardation by the addition of Mn(II) demonstrates the formation of Cr(IV) in the rate-controlling step as a result of two-electron transfer process^{5,8,9}. The addition will generally lead to a decreased rate of oxidation because Mn(II) removes the Cr(VI) formed^{5,8,9}. The second-order rate constants at 298, 303, 308, 313 and 318 K under identical condition are 1.77×10^{-2} , 2.56×10^{-2} , 3.27×10^{-2} , 4.79×10^{-2} and 6.92×10^{-2} dm³ mol⁻¹ s⁻¹ respectively. The enthalpy and entropy of activation are 50.6 KJ mol⁻¹ and -13.4 KJ⁻¹ mol⁻¹ respectively.

TABLE-2
EFFECT OF $[H^+]$, IONIC STRENGTH (I), PERCENTAGE OF ACETIC ACID AND $[Mn(II)]$ ON Cr(VI) OXIDATION OF CINNAMALDEHYDE

[cinnamaldehyde] = 0.010 mol dm ⁻³ ; [Cr(VI)] = 0.001 mol dm ⁻³ Temp. = 303K					
10 $[H^+]^a$ (mol dm ⁻³)	1.16	1.66	2.16	2.66	3.16
$k_2 \times 10^2$ (dm ³ mol ⁻¹ s ⁻¹)	2.44	4.03	5.22	7.20	8.21
10 I ^b (mol dm ⁻³)	1.20	1.50	2.00	2.20	3.20
$k_2 \times 10^2$ (dm ³ mol ⁻¹ s ⁻¹)	2.56	2.40	2.36	2.49	2.44
HOAc—H ₂ O (v/v) ^c %	75–25	80–20	85–15	90–10	
$k_2 \times 10^3$ (dm ³ mol ⁻¹ s ⁻¹)	3.27	4.67	10.1	25.6	
10 ³ [Mn(II)] ^d (mol dm ⁻³)	0.00	1.00	3.00		
$k_2 \times 10^2$ (dm ³ mol ⁻¹ s ⁻¹)	2.56	1.29	1.18		

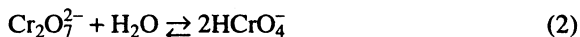
^aSolvent: 90% (v/v) aqueous acetic acid; I = 0.320 mol dm⁻³

^bSolvent: 90% (v/v) aqueous acetic acid; $[HClO_4] = 0.100$ mol dm⁻³

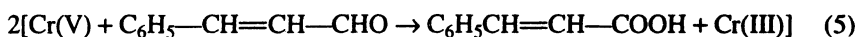
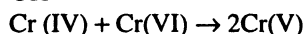
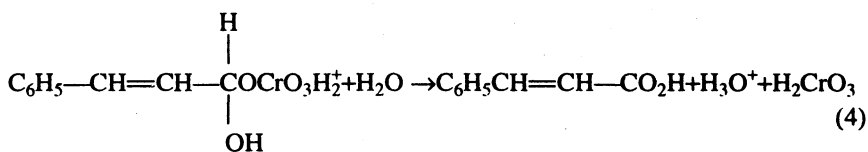
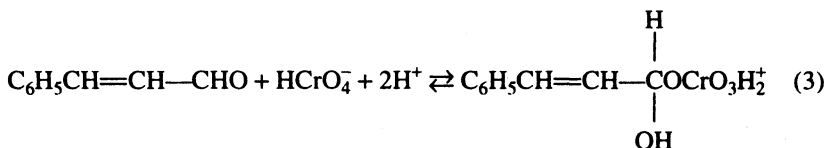
$c_1 = 0.120$ mol dm⁻³; $[HClO_4] = 0.100$ mol dm⁻³

^dSolvent: 90% (v/v) aqueous acetic acid; $[HClO_4] = 0.100$ mol dm⁻³; I = 0.120 mol dm⁻³

At dilute solutions of Cr(VI) (as in the present case) the monomer – dimer equilibrium



is displaced to the right and the monomeric form predominates⁹⁻¹¹ The acid chromate ion $HCrO_4^-$ does not lose a proton until the pH is raised to about 7 and it gains a second proton in the H-range of -1 to -3. At higher concentrations of $HClO_4$, or Cr(VI) mainly exists as $HCrO_3^+$ ^{6,12}, whereas at lower concentrations it exists as $HCrO_4^-$ ^{3,5}. Hence it may be presumed that under the present experimental conditions, where the acid concentration is low, Cr(VI) exists largely as $HCrO_4^-$. On the basis of the foregoing arguments, the following two-electron transfer mechanism has been postulated.



The mechanism envisages the formation of chromic acid ester of hydrated cinnamaldehyde as intermediate. The rate-controlling step (eqn. 4) postulates that the aldehydic hydrogen atom is lost as a proton. Equation (4) has been written as if a water molecule abstracts the proton from the ester. An alternate possibility is that the proton is abstracted in a cyclic process by one of the chromate oxygen atoms⁵. Similar type of mechanism has been postulated in the oxidation of alcohols⁸ and aldehydes^{5, 9} by Cr(VI). The rate law for the oxidation of cinnamaldehyde by Cr(VI) can be written as

$$\frac{-d[\text{Cr(VI)}]}{dt} = k_2[\text{cinnamaldehyde}][\text{HCrO}_4^-] \text{ at constant } [\text{H}^+].$$

ACKNOWLEDGEMENT

The authors are grateful of Prof. C. Srinivasan for helpful discussions.

REFERENCES

1. N.C. Khandual and K.K. Satpathy, *J. Chem. Soc.*, 328 (1974).
2. S.V. Anantkrishnan and V. Sathyabhama, *Indian J. Chem.*, **10**, 168 (1972).
3. C. Srinivasan, A. Chellamani and S. Rajagopal, *J. Org. Chem.*, **50**, 1201 (1985) and references cited therein.
4. K.J.P. Orton and A.E. Bradfield, *J. Chem. Soc.*, 986 (1927).
5. K.B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).
6. V. Baliah and P.V.V. Satyanarayana, *Indian J. Chem.*, **16A**, 966 (1978).
7. _____, *Indian J. Chem.*, **19B**, 620 (1980).
8. W. Watanabe and F.H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949).
9. G.T.E. Graham and F.H. Westheimer, *J. Am. Chem. Soc.*, **80**, 3030 (1958).
10. K.B. Wiberg, *Oxidation in Organic Chemistry*, Academic Press, New York, p. 71, 182 (1965).
11. A. Chellamani and A. Jawahar, *Asian J. Chem.*, **3**, 385 (1991).
12. L.S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

(Received: 26 April 1994; Accepted: 15 September 1994)

AJC-868