Kinetics and mechanism of electron transfer reactions involving pyridinium chlorochromate and α-hydroxy acids in acid medium catalysed by ruthenium(III)

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Summary

The oxidation of α-hydroxy acids (HA), *viz.* glycolic acid (GA), mandelic acid (MA) and lactic acid (LA), by pyridinium chlorochromate (PCC) in aqueous ethanoic acid solution was investigated in the presence and absence of $Ru^{III}Cl_3$. The order in [HA] and [PCC] was found to be unity, with or without ruthenium(III) catalyst, and the order in [Ru^{III}] was found also to be unity. The reaction was acid catalysed also in the presence and absence of ruthenium(III) catalyst, and hence the protonated form of PCC, was assumed to be the active species of oxidant. Added salts, and the change in dielectric constant of the medium, did not affect the oxidation rate. No induced polymerization occurred when acrylamide monomer was added to the reaction mixture. The pseudo-first order rate constants (k'), the formation constants (K_f) of the substrate–catalyst complexes, activation and thermodynamic parameters have been evaluated. Suitable mechanisms in conformity with the experimental observations have been proposed for the uncatalysed and catalysed reactions.

Introduction

Pyridinium chlorochromate (PPC) is a complex of chromium trioxide, pyridine and HCl, known as Corey's reagent. Corey and Suggs[1] reported that this complex converts alcohols into carbonyl compounds smoothly at room temperature in yields well in excess of 80%. Although the kinetics and mechanism of oxidation of alcohols[2,3] and organic sulphur compounds[4,5] have been described, there appears to be no report on the mechanism of oxidation of α-hydroxy acids by PCC. Although the oxidation of α-hydroxy acids by PCC was slow, considerable enhancement in the rate of oxidation occurred in the presence of ruthenium(III). Transition metal ions, such as ruthenium(III), are known to act as effective catalysts in many redox reactions. Complexes of these metal ions are reported to be good hydride ion abstracting agents[6,7] in both acidic and basic solutions. So far, no one has attempted to probe the role of the ruthenium(III) ion as a catalyst in oxidations by PCC. This prompted us to attempt to ascertain the effect of a transition metal ion on the oxidation of α-hydroxy acids by another transition metal ion complex, i.e. PCC.

Experimental

Chemicals used were obtained from BDH or E. Merck (AR). Glycolic, mandelic and lactic acids were of Fluca Puriss grade. PCC was prepared by the Corey and Suggs[1] method and was standardized iodimetrically. Ruthenium(III) chloride (Johnson-Matthey) solution was prepared by dissolving the sample in HCl of known strength. The solution was standardized by the method of Houriuchi *et al.*[8] $MeCO_2H$ was purified by the literature procedure[9]. All the solutions were prepared fresh in double distilled H_2O. The course of reaction was followed by monitoring the disappearance of PCC at $\lambda_{max} = 350$ nm in a U.v.–vis. spectrophotometer (model 140.02 Shimadzu, Japan) equipped with thermostatic cell compartment (1 cm path length). All the reaction flasks were covered with aluminium foil. Requisite amounts of substrate, $MeCO_2H$ and ruthenium(III) chloride (for the catalysed reaction) taken in one flask, and the solution of PCC in another, were thermally equilibrated at the desired temperature for 0.5 h. The requisite amount of PCC was pipetted into the reaction flask containing the substrate to initiate the reaction. The optical density of the unreacted PCC was measured at regular intervals by removing aliquots from the reaction mixture. All the reactions were followed up to at least 80% completion. Oxidation products were identified as the corresponding α-keto acids by characteristic spot tests[10]. The products were also characterized by the m.ps of their 2,4-dinitrophenylhydrazone derivatives. The stoichiometric studies revealed that 1 mol PCC was consumed per mole of hydroxy acid in both the catalysed and uncatalysed reactions. The reaction product from glycolic acid and PCC could be shown as follows:

$$H_2C(OH)CO_2H + C_5H_5N^+HCrO_3Cl^- \longrightarrow HCOCO_2H + CrO_2 + C_5H_5N^+HCl^- + H_2O$$

Pseudo-first order rate constants k' were calculated from the linear least square fit: $-\ln(A_t - A_\infty)/(A_0 - A_\infty) = k't$, where A_0, A_t and A_∞ represent optical density at the commencement of the reaction, at time t and at infinite time, respectively. All the calculations were performed by a Casio PB 110 data bank computer. The correlation coefficients (r) were > 0.995. Duplicate runs indicated that the rate constants were reproducible within 3–5% error.

Results and discussion

Under the experimental conditions PCC ≪ HA, the plots of log(OD) versus time were linear and first order in [PCC]. Pseudo-first order rate constants k' obtained from such plots remained unaffected on changing [PCC], confirming first order in [PCC]. The rate of reaction in the presence and absence of ruthenium(III) was linearly dependent on [HA]. However, the order in [HA] was unity in the absence of ruthenium(III), and was reduced to a fractional order in the presence of ruthenium(III). The plot of $1/k'$ versus 1/[HA] in absence of ruthenium(III) was found to be passing through the origin indicating absence of any complex formation, whereas the plot of $1/k'$ versus 1/[HA] in the presence of ruthenium(III) was also linear but with a definite intercept, indicating complex

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Table 1. Effect of substrate on the oxidation of α-hydroxy acids by PCC[a].

[HA]	GA $10^5 k'$	MA $10^6 k'$	LA $10^5 k'$
0.30	2.14(10.6)[b]	4.56(35.9)	3.86(30.3)
0.45	3.71(15.0)	6.81(43.9)	5.81(39.1)
0.60	5.02(18.3)	9.40(48.4)	7.72(50.3)
0.90	7.39	13.4	11.6
1.20	10.5	18.7	15.4

[a][PCC] = 1.0×10^{-3} mol dm^{-3}; [H^+] = 0.1 mol dm^{-3}; [Ru^{III}] = 1.0×10^{-5} mol dm^{-3}; temperature = 303 K; [b]the figures in parentheses represent catalysed reaction.

Table 2. Effect of [H^+] on the oxidation of α-hydroxy acids by PCC[a].

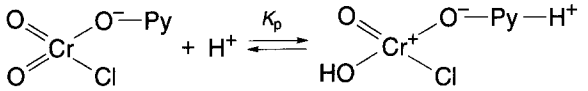
[H^+]	$10^5 k'$ 303 K	313 K	323 K
0.1	2.14	7.7	22.2
0.2	3.71	10.5	33.3
0.3	3.96	13.3	41.5
0.4	4.34	15.4	49.5

[a][PCC] = 1.0×10^{-3} mol dm^{-3}; [GA] = 0.30 mol dm^{-3}; [Ru^{III}] = 1.0×10^{-5} mol dm^{-3}; temperature = 303 K.

formation (Table 1). The rate of oxidation was found to increase with the increase in [H^+] (Table 2). The effect of added salts like $NaClO_4$ on the rate of oxidation in all the reactions was negligible. The reaction rate decreased with increasing polarity of the solvent, i.e. with increasing dielectric constant of the medium. No induced polymerisation was observed when acrylamide monomer was added to the reaction mixture, indicating the absence of a free radical path. The reaction was carried out at three different temperatures and the activation and thermodynamic parameters have been computed.

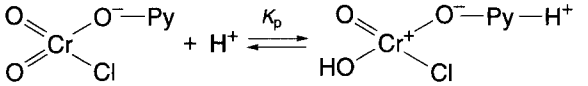
Uncatalysed reaction

Despite the presence of hexavalent chromium in chlorochromate ion, it is a poor oxidising agent relative to acid chromate ion[11]. Nevertheless, it was found to be effective in the oxidation of primary and secondary alcohols in nonaqueous medium[12]. The increase in the oxidation rate with acidity in our study suggests involvement of protonated chromium(VI) species in the rate determining step. The reactivity of $PCCH^+$ can be attributed to the presence of a positively charged chromium, which renders it more electrophilic. The observed effect of [H^+] on the oxidation may be explained by assuming an equilibrium between unprotonated and protonated PCC and that the protonated species is the reactive one.



(I)

The observed dependence in [PCC] as well as in [HA] in the uncatalysed reaction suggests a mechanism shown in Scheme 1.



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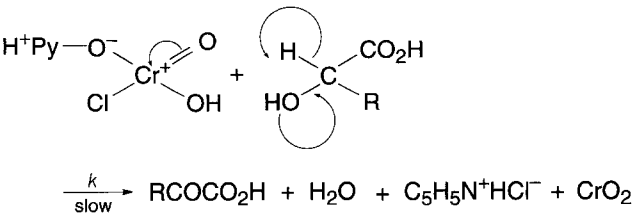


Scheme 1

First order in [HA] can be observed only when step (III) of the above mechanism is slow. Step (III) may be a combination of three indistinguishable steps; these may be (a) formation of precursor complex between HA and PCC, (b) Chemical activation with electron transfer and (c) fission of successor complex. However, such steps cannot be distinguished from one another when outer sphere electron transfer takes place[13]. The mode of electron transfer can be understood from the order of reactivity: lactic > glycolic > mandelic acid. The observed reactivity order indicates that electron releasing groups accelerate the reaction rate, which is commensurate with a hydride ion transfer from the hydroxy acid to give a transient carbocation.

Scheme 1 leads to Rate Law 1:

$$d[PCC]/dt = k[PCCH^+][HA] \quad (1)$$

From step (1)

$$[PCCH^+] = K_p[PCC][H^+]/\{1 + K_p[H^+]\} \quad (2)$$

Substituting for [$PCCH^+$] in Rate Law 1, we get

$$-d[PCC]/dt = \frac{kK_p[PCC][HA][H^+]}{1 + K_p[H^+]} \quad (3)$$

which is in complete accord with observations.

Equation 3 may be written as

$$-d[PCC]_x/dt \times 1/[PCC] = k' = \frac{kK_p[HA][H^+]}{1 + K_p[H^+]} \quad (4)$$

The above rate law accounts for the first order in [PCC] and [HA] and the effect of [H^+]. Taking the reciprocal of Equation 4, we get

$$1/k' = 1/\{kK_p[HA][H^+]\} + 1/k[HA] \quad (5)$$

where k' is the observed pseudo-first order rate constant, k is the second order rate constant for the slow step and K_p is the protonation equilibrium constant for PCC. The above equation envisages a linear relationship between $1/k'$ and $1/[H^+]$. The effect of [H^+] on the rate of oxidation was studied at different temperatures and linear plots were obtained between $1/k'$ and $1/[H^+]$ (Figure 1). k and K_p were calculated from the intercept and slope of these plots at different temperatures (Table 3). The decrease in rate with increasing polarity of the solvent suggests an interaction between a positive ion and dipole and confirms that the rate determining step involves a protonated chromium(VI) species. The reactions were carried out at three different temperatures and the activation parameters were computed (Table 3).

Ruthenium(III) catalysed reaction

A positive catalyst leads to a decrease in the free energy of activation $\Delta G^{\#}$, thereby increasing the reaction rate. In this study, the presence of 10^{-5} mol dm^{-3} ruthenium(III)

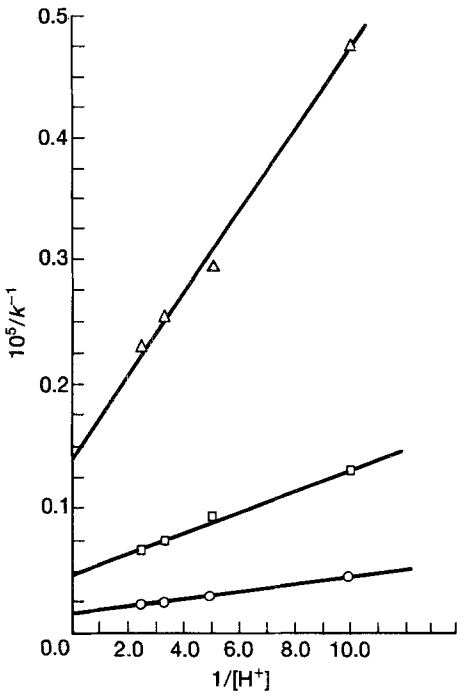
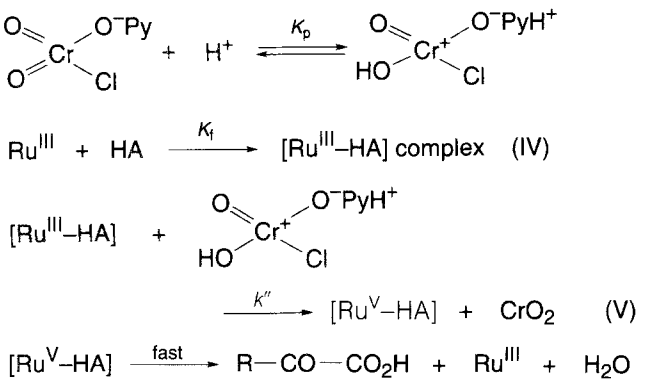


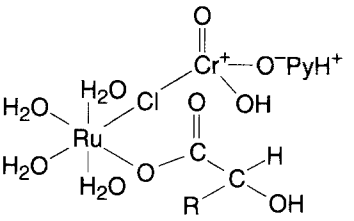
Figure 1. Plots of $10^5/k'$ versus $1/[H^+]$ at 303, 313 and 323 K $[PCC] = 1.0 \times 10^{-3}$ mol dm^{-3}; $[GA] = 0.3$ mol dm^{-3}.

increased the rate significantly. The observed order in [ruthenium(III)] and [HA], one and fractional respectively, indicate complex formation between ruthenium(III) and HA; however, the possibility of complex formation between PCC and HA cannot be completely ruled out, but does not appear probable, as it was not observed in the uncatalysed reaction. A solution of ruthenium(III) in H_2O, exists as octahedral complex with H_2O molecules as ligands, i.e. $[Ru(H_2O)_6]^{3+}$, and is generally substitution labile. Hence, hexaaquoruthenium(III) is more accessible to substrate for the formation of a complex. Based on the experimental observations, a complex formation could be envisaged between ruthenium(III) and the α-hydroxy acid which slowly reacts with PCC in the rate determining step to give products as shown in Scheme 2.



Scheme 2

The first step of protonation of PCC may be explained by the observed $[H^+]$ effect. Hexaaquoruthenium(III) loses one H_2O ligand when hydroxy acid complexes to it. This complex formation may be a slow step as it involves reorganisation of ligands around ruthenium and an inner electron transfer. Though protonated PCC has two groups, viz pyridine and chloro groups, which can bridge the oxidant to the ruthenium(III)–HA complex, chloro group and not pyridine is in a suitable position conducive to electron transfer. Such bridging to form a hetero atomic binuclear compound is common in inner sphere electron transfer[14–17], which can be shown as



The chloro group might be transferred to ruthenium(III) complex from PCC, which is generally observed in inner-sphere electron transfer. Ru^V–HA undergoes decomposition to give ketoacid and ruthenium(III) in the fast step.

Scheme 2 leads to Rate Law 6.

$$-d[PCC]/dt = k''[Complex][PCCH^+] \quad (6)$$

From Equation 3, $[PCCH^+]$ can be written as

$$[PCCH^+] = K_p[PCC][H^+]/\{1 + K_p[H^+]\}$$

$$[Complex] = K_f[Ru^{III}][HA]/\{1 + K_f[HA]\} \quad (7)$$

Substituting for $[PCCH^+]$ and [Complex] in Equation 6 we get

$$d[PCC]/dt = k''K_pK_f[PCC][Ru^{III}][HA][H^+]/\{1 + K_p[H^+]\}\{1 + K_f[HA]\} \quad (8)$$

or

$$d[PCC]/dt \times 1/[PCC] = k' = k''K_pK_f[Ru^{III}][HA][H^+]/\{1 + K_p[H^+]\}\{1 + K_f[HA]\} \quad (9)$$

On multiplying the terms in the denominator and neglecting the product of $K_p[H^+]$ $K_f[HA]$ in comparison to 1, we get

$$k' = k''K_pK_f[Ru^{III}][HA][H^+]/\{1 + K_p[H^+] + K_f[HA]\} \quad (10)$$

Equation 10 explains all the experimental observations such as first order dependence of rate on [PCC] and $[Ru^{III}]$ and the effect of $[H^+]$ and [HA]. Taking reciprocals

Table 3. Activation parameters for the oxidation of α-hydroxy acids by PCC in the absence ruthenium(III).

Substrate		GA	MA	LA
K_p	303 K	4.29	4.29	4.29
	313 K	5.67	5.67	5.67
	323 K	6.66	6.66	6.66
$10^4 k^a$	303 K	1.61	0.63	5.38
	313 K	4.71	1.87	15.7
	323 K	12.8	5.36	42.2
E_a^b		84.6	85.6	83.1
$\Delta H^{\#b}$		82.1	82.9	80.6
$\Delta G^{\#b}$		96.2	98.5	93.1
$-\Delta S^{\#c}$		46.4	51.5	41.1

[a] dm^3 mol^{-1} s^{-1}; [b] kJ mol^{-1}; [c] J mol^{-1} k^{-1}.

Table 4. Activation and thermodynamic parameters for the oxidation of α-hydroxy acids by PCC in the catalysed reaction.

Parameter	Temperature (K)	GA	MA	LA
K_f	303	0.634	4.41	1.22
	313	0.80	5.15	1.99
	323	0.94	5.78	2.56
ΔG^a	303	1.15	−3.73	−0.49
ΔH^a	303	16.4	11.0	30.3
ΔS^b	303	50.3	48.6	101.6
k''^c	303	163	17.5	304
	313	283	33.2	501
	323	474	60.5	799
E_a^a		43.5	50.4	39.4
$\Delta H^{\#a}$	303	41.0	47.9	36.9
$\Delta G^{\#a}$	303	61.4	67.0	59.8
$-\Delta S^{\#b}$	303	67.3	63.1	75.5

[a]kJ mol^{-1}; [b]J mol^{-1} K^{-1}; [c]dm^3 mol^{-1} s^{-1}.

in Equation 10

$$1/k' = 1/[HA]\{1/K_pK_fk''[Ru^{III}][H^+] + 1/K_fk''[Ru^{III}]\} + 1/K_pk''[Ru^{III}][H^+] \quad (11)$$

According to Equation 11, a linear plot should be obtained on plotting $1/k'$ versus $1/[HA]$. From the effect of [HA] at different temperatures, linear plots of $1/k'$ versus $1/[HA]$ were obtained. K_p values from uncatalysed reaction are substituted in the intercept value of these plots to calculate k'' values. Using K_p and k'' values, formation constants K_f at different temperatures were calculated from the slopes of these plots.

Activation and thermodynamic parameters together with K_f and k'' at different temperatures are presented in Table 4. Examination of data shows that the compound with highest rate constant has lowest enthalpy and *vice versa*. A similar trend is observed in the catalysed reaction. One interesting feature is that $\Delta G^{\#}$ for the catalysed reaction is less than that of the uncatalysed reaction. The low values of entropy of activation ($\Delta S^{\#}$) in the uncatalysed reaction indicates absence of complex formation and inner sphere electron transfer. The entropy of activation for catalysed reactions are largely negative, showing involvement of a rigid system in the activated complex. This shows, as shown in the mechanism, a complex formation by which inner sphere electron transfer can take place. The constancy in $\Delta G^{\#}$ in catalysed and uncatalysed reactions indicates that a similar mechanism is operative in all three substrates.

References

(1) E. J. Corey and W. J. Suggs, *Tetrahedron Lett.*, **31**, 2647 (1975).
(2) N. Venkatsubramanian, *Indian J. Chem.*, **16B**, 84 (1978).
(3) E. J. Corey and C. V. Kim, *Tetrahedron Lett.*, **12**, 919 (1973).
(4) G. P. Panigrahi and D. D. Mahapatro, *Int. J. Chem. Kinet.*, **1**, 85 (1981).
(5) K. S. Venkatraman and S. Sundaram, *Indian J. Chem.*, **19A**, 579 (1980).
(6) H. B. Charman, *J. Chem. Soc. B*, 629 (1967).
(7) H. S. Singh, R. K. Singh, S. M. Singh and A. K. Sisodia, *J. Phys. Chem.*, **81**, 1044 (1977).
(8) Y. Houriuchi and Ichiyyo, *Chem. Abstr.*, **72**, 50624 (1970).
(9) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 640 (1924); 983 (1927).
(10) F. Fiegl, *Spot Tests in Organic Analysis*, Elsevier Amsterdam, Vol. II, pp. 482 (1966).
(11) M. Cohen and F. W. Westheimer, *J. Am. Chem. Soc.*, **14**, 4387 (1952).
(12) G. Venkateshwar Rao and P. K. Sai Prakash, *Oxidation Commun.*, **11**, 33 (1988).
(13) K. F. Pureell and J. C. Kotz, *Inorg. Chemistry*, W. B. Saunders, London, pp. 661 (1985).
(14) R. W. Craft and R. G. Gender, *Inorg. Chem.*, **13**, 1005 (1974).
(15) R. W. Craft and R. G. Gender, *Inorg. Chem.*, **14**, 1283 (1975).
(16) R. G. Gender and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).
(17) H. J. Epsenson, *Inorg. Chem.*, **4**, 121 (1965).

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