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Iridium(III) catalysis of oxidation of oxalic acid and malic acid by QFC in acidic medium

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ABSTRACT

Kinetic investigation in Ru(III) catalyzed oxidation of oxalic acid and malic acid in an acidified solution of quinolinium fluorochromate (QFC) has been studied in the temperature range of 30°-45°C. Increase in concentration of oxidant and Cl^- ion showed fractional positive order. First order kinetics was observed in case of catalyst Ir(III) and substrate, $[IrCl_6]^{-3}$ being reactive species of catalyst. The influence of $[H^+]$, and ionic strength on the rate was found to be insignificant. The main product of oxidation of oxalic acid and malic acid are carbon dioxide and oxoacid respectively. The reaction has been studied in ten different solvents. The various thermodynamic parameters were calculated from rate measurements at 30, 35, 40 and 45°C respectively. A suitable mechanism in conformity with the kinetic observations has been proposed and the rate law is derived on the basis of obtained data.

KEYWORDS

Oxidation of acids;
Malic acid;
Oxalic acid;
Quinolinium fluorochromate;
Ir(III) chloride;
Acidic medium.

INTRODUCTION

Quinolinium fluorochromate (QFC) has been used as a mild and selective oxidizing reagent in synthetic organic chemistry[1]. Though few reports on the mechanistic aspects of oxidation reactions of QFC are available in literature[2-4] and nearly no investigation has so far been reported on the catalytic role of Iridium(III) chloride with QFC as an oxidant in acidic medium. The use of Ir(III) chloride as a non-toxic and homogeneous catalyst has been reported by several workers[5-6]. This prompted us to undertake the present investigations, which is focused on the kinetics and mechanism of Ir(III) catalyzed oxidation of oxalic acid and malic acid by QFC in acidic medium.

EXPERIMENTAL

Materials

QFC was prepared by the reported method[1,7]. An aqueous solution of oxalic acid and malic acid (E.Merck), $NaClO_4$ were prepared by dissolving the weighed samples in triple distilled water. Perchloric acid (60%, s.d.fine Chem. Ltd.) was used as a source of H^+ ion. A solution of $IrCl_3$ (Johnson Matthey) was prepared in HCl of known strength. Deuterium oxide (purity 99.4%) was supplied by BARC (Bombay, India). All other reagents were of analytical grade. Sodium perchlorate was used to maintain the ionic strength of the medium. Solvents were purified by the usual methods[8]. Reaction vessels were painted black so as to prevent photochemical decomposition, if any.

Kinetics

A measured waterbath was used to maintain the desired temperature within ±0.1°C. Requisite volume of reagents, including substrate, was taken in a reaction vessel and thermostated at 35±0.1°C for thermal equilibrium. A measured volume of QFC solution, which was also maintained separately at the same temperature, was rapidly poured into the reaction vessel. The kinetics was followed by examining desired portions of reaction mixture for QFC iodometrically using starch as an indicator after suitable time intervals.

STOICHIOMETRY

The stoichiometry of the reaction was determined by equilibrating varying ratios of [QFC] to oxalic acid and malic acid at 35°C for 48 hrs under kinetic condition. Estimation of unconsumed QFC revealed that, one mole of the substrate consumes one mole of the oxidant (TABLE 1). The oxidation of oxalic acid and malic acid leads to the formation of carbon dioxide and oxoacid respectively. The stoichiometric determination indicated the following overall reaction.

TABLE 1 : Stoichiometric results for oxidation of oxalic acid and malic acid

10^3[QFC] M	10^3[Substrate] M	10^3[QFC]*M (residual) Oxalic acid	Malic acid	[QFC]^c/[Substrate] Oxalic acid	Malic acid
12.50	1.00	11.60	11.56	0.09	0.94
10.00	1.00	9.00	9.08	1.00	0.92
5.00	1.00	3.92	3.98	1.08	1.02
2.50	1.00	1.46	1.54	1.04	0.96
10.00	2.00	8.10	8.02	0.95	0.99
10.00	3.00	6.94	7.12	1.02	0.96
10.00	4.00	6.04	5.94	0.99	1.01
10.00	5.00	4.88	5.00	1.02	1.00

$[Ir(III)]_T = 7.20\times10^{-6}$ M (oxalic acid) & 4.80×10^{-6} M (malic acid), [KCl]= 1.0010^{-3} M, [S] = 2.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-3} M, temp. = 323 K, time = 48 h, [QFC]* = [QFC] left unconsumed after 48 h, [QFC]^c = [QFC]-[QFC]* i.e. oxidant consumed during the reaction.

RESULTS AND DISCUSSION

It was observed that the values of k_1 (i.e.-dc/dt/[substrate]) were constant at all initial concentrations of substrate, showing first order dependence on [substrate] (Figure 1). First order dependence on [Ir(III)] is evident from close resemblance between the slope values (3.34×10^{-2} s^{-1} & 6.35×10^{-2} s^{-1} (for oxalic acid) and 3.72×10^{-2} s^{-1} & 7.54×10^{-2} s^{-1} (for malic acid) at 35°C & 45°C respectively) of (-dc/dt) vs. [Ir(III)] plot and average k_1 values (3.30×10^{-2} s^{-1} & 6.50×10^{-2} s^{-1} (for oxalic acid) and 3.82×10^{-2} s^{-1} & 7.62×10^{-2} s^{-1} (for malic acid) at 35°C & 45°C respectively). The oxidation of substrate was studied in 10 different solvents. The choice of solvents was limited due to the solubility of QFC and its reaction with primary and secondary alcohols. There was no reaction between QFC and the solvents chosen. The kinetics was similar in all the solvents. The values of (-dc/dt) and k_1 for different solvents are recorded in TABLE 3. It was observed that the rate of reaction increases with increase in [QFC] and [Cl^-], and thus showing fractional positive order with respect to oxidant and KCl. Negligible effect of variation in [H^+] and ionic strength of the medium on the reaction rate are clear from kinetic data in TABLE 2.

$$(COOH)_2 + O_2CrFO^-QH^+ \xrightarrow[H^+]{IrCl_3} 2CO_2 + H_2O + OCrFO^-QH^+$$

Oxalic acid **QFC** **Carbon dioxide**

$$ArCH(OH)COOH + O_2CrFO^-QH^+ \xrightarrow[H^+]{IrCl_3} ArCOCOOH + H_2O + OCrFO^-QH^+$$

Malic acid **Oxoacid**

The rate measurements were taken at 30°- 45°C and specific rate constant were used to draw a plot of log k vs I/T, which was linear (Figure 3). The values

TABLE 2 : Effect of variation of reactants on the reaction rates

$[QFC]\times10^3$ M	$[KCl]\times10^3$ M	$[HClO_4]\times10^3$ M	$[NaClO_4]\times10^3$ M	$(-dc/dt)\times10^7$ $ML^{-1}s^{-1}$ Oxalic acid	Malic acid
0.83	1.00	0.20	-	2.01	1.56
1.00	1.00	0.20	-	2.36	1.82
1.25	1.00	0.20	-	2.65	2.56
1.67	1.00	0.20	-	3.31	3.20
2.50	1.00	0.20	-	3.87	3.88
5.00	1.00	0.20	-	4.67	4.60
1.00	0.83	0.20	-	2.07	1.74
1.00	1.00	0.20	-	2.36	1.82
1.00	1.25	0.20	-	2.63	1.94
1.00	1.67	0.20	-	3.09	2.18
1.00	2.50	0.20	-	3.35	2.56
1.00	5.00	0.20	-	3.85	2.76
1.00	1.00	0.04	-	2.00	1.80
1.00	1.00	0.08	-	1.89	1.80
1.00	1.00	0.12	-	2.20	1.96
1.00	1.00	0.16	-	2.46	1.78
1.00	1.00	0.20	-	2.36	1.82
1.00	1.00	0.24	-	2.60	1.92
1.00	1.00	0.20	0.83	0.96	1.79
1.00	1.00	0.20	1.00	0.82	1.82
1.00	1.00	0.20	1.25	0.87	1.75
1.00	1.00	0.20	1.67	0.92	1.89
1.00	1.00	0.20	2.50	0.90	1.78
1.00	1.00	0.20	5.00	0.86	1.84

$[Ir(III)]_T = 7.20\times10^{-6}$ M (Oxalic acid) and 4.80×10^{-6} M (Malic acid)
[Substrate] = 2.00×10^{-2} M

TABLE 3 : Rate constants for the decomposition of catalyst-QFC complex in different solvents

Solvents	$(-dc/dt)\times10^7$ $ML^{-1}s^{-1}$ Oxalic acid	Malic acid	$k_1\times10^4$ s^{-1} Oxalic acid	Malic acid
Acetone	2.00	1.82	2.17	1.89
Butanone	2.36	1.96	2.62	2.04
Benzene	2.54	1.90	2.79	1.93
Ethyl acetate	2.05	1.78	2.18	1.79
Nitrobenzene	2.27	1.82	2.46	1.94
Acetic acid	1.85	1.94	2.05	1.97
t-butyl alco.	2.58	2.20	2.89	2.50
Acetophenone	2.14	1.96	2.32	1.97
Choloroform	1.90	1.92	1.87	1.97
Toluene	1.65	2.50	1.85	2.84

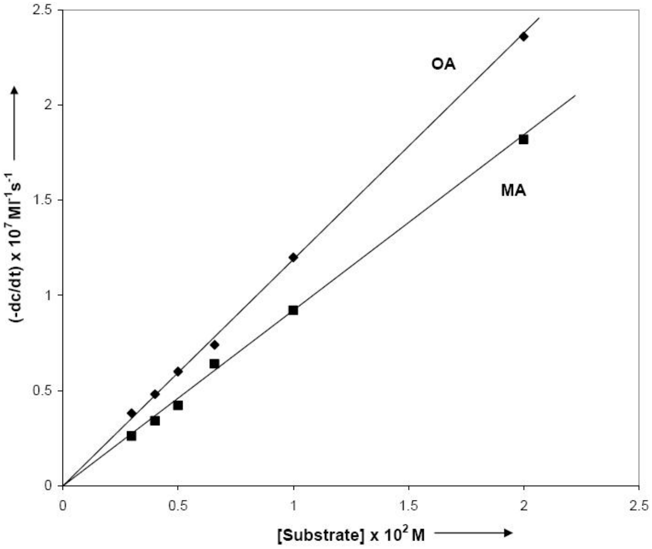


Figure 1 : Plot between [substrate] and (-dc/dt) for oxidation of oxalic acid (OA) and malic acid (MA) at 35°C

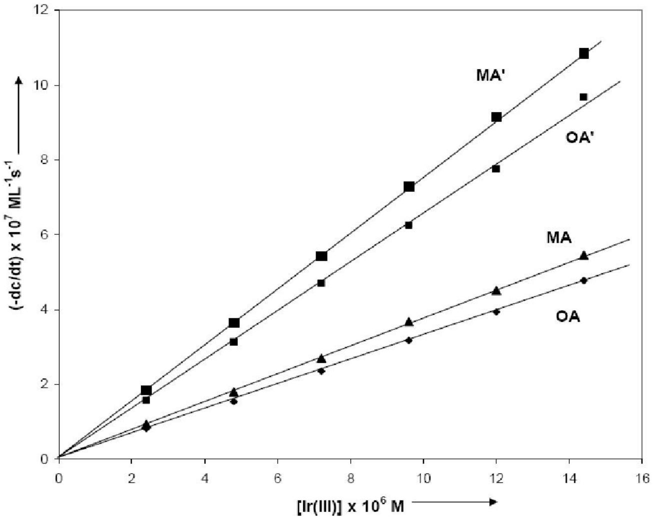


Figure 2 : Plot between [Ir(III)] and (-dc/dt) for oxidation of oxalic acid (OA) & (OA') and malic acid (MA) & (MA') at 35°C and 45°C respectively

TABLE 4 : Rate constants and activation parameters of oxidation of substrate by QFC.

Acid	$10^4 k_r$ (s^{-1}) at (°C) 30	35	40	45	ΔE* $(kJ\ mol^{-1})$	ΔG* $(kJ\ mol^{-1})$	ΔH* $(kJ\ mol^{-1})$	ΔS* $(JK^{-1}mol^{-1})$	log A
Oxalic acid	1.64	2.36	3.24	4.76	56.70	74.51	43.15	-13.77	9.98
Malic acid	1.25	1.80	2.54	3.66	54.39	77.46	50.21	-16.05	9.48

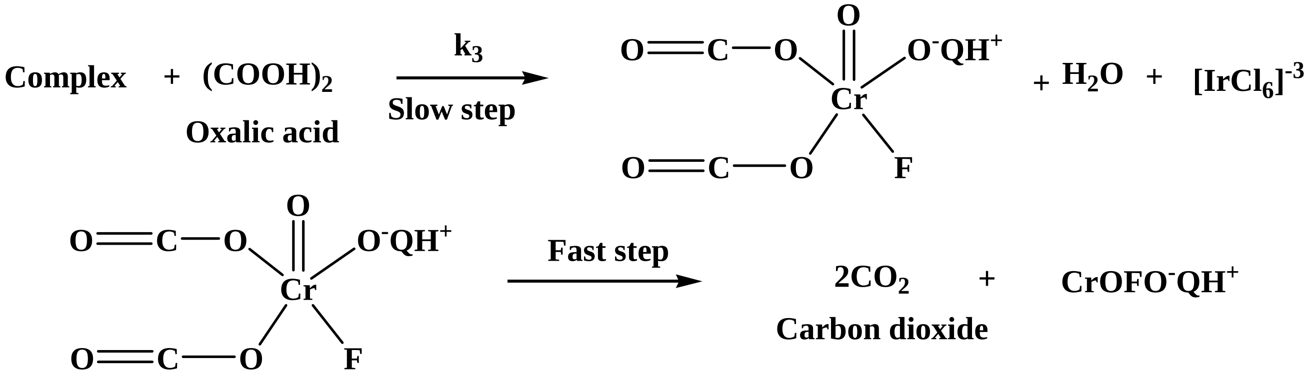
of energy of activation (ΔE*), Arrhenius factor (A), entropy of activation (ΔS*) and free energy of activation (ΔG*) were calculated and these values have been recorded in TABLE 4.

On the basis of above data the following reaction scheme is suggested:

Oxalic acid

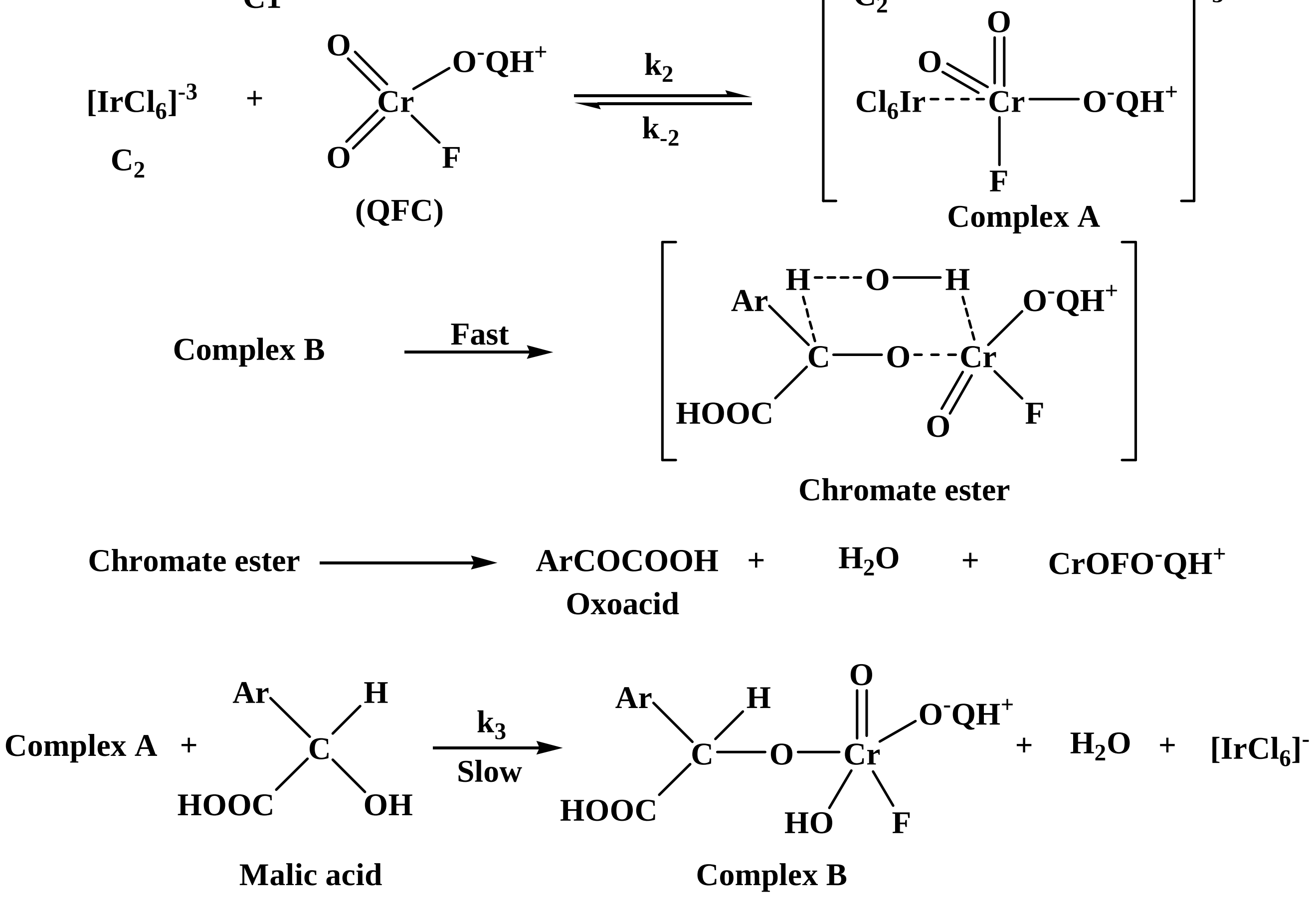
$$\underset{C_1}{[IrCl_5(H_2O)]^{-2}} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C_2}{[IrCl_6]^{-3}} + H_2O$$

$$\underset{C_2}{[IrCl_6]^{-3}} + \underset{QFC}{CrO_2FO^-QH^+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{Complex}{[IrCl_6\text{-----}CrO_2FO\text{-}QH^+]^{-3}}$$



Malic acid

$$\underset{C1}{[IrCl_5(H_2O)]^{-2}} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C_2}{[IrCl_6]^{-3}} + H_2O$$



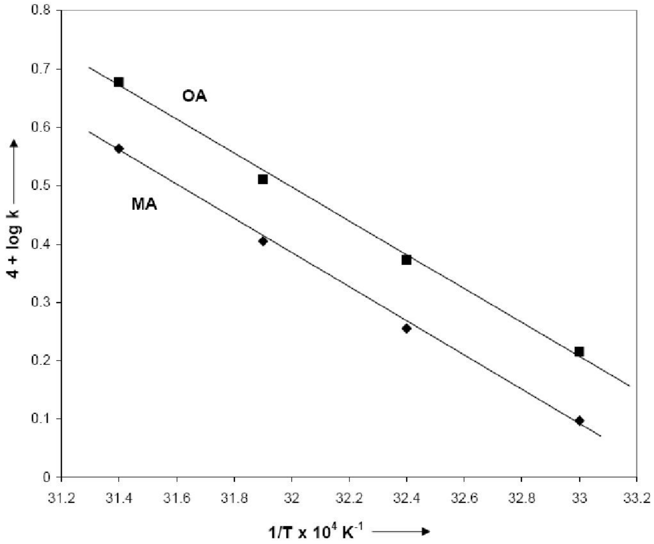


Figure 3 : Plot between 1/T and log k for oxidation of oxalic acid (OA) and malic acid (MA) at 35°C

Considering the above slow steps and applying steady state treatment with a reasonable approximation, the rate law for both oxalic acid and malic acid may be written in terms of consumption of [QFC] as equation.

$$\frac{-d[QFC]}{dt} = \frac{K_1\,K_2\,K_3\,[Cl^-][Ir(III)]_T\,[QFC][S]}{1+K_1\,[Cl^-](1+K_2\,[QFC])}$$

$$[Ir(III)]_T = [C_1] + [C_2]$$

CONCLUSION

The experimental results reveal that the reaction rate doubles when concentration of the catalyst Ir(III) is doubled. The rate law equation is in conformity with all kinetic observations and the proposed mechanistic steps are supported by the negligible effect of ionic strength. The high positive values of change in free energy of activation (ΔG*) indicates highly solvated transition state, while fairly high negative values of change in entropy of activation (ΔS*) suggest the formation of an activated complex with reduction in the degree of freedom of molecules. In the present case Ir(III) chloride is quite soluble in perchloric acid and exists[9] as $[IrCl_6]^{-3}$ which has been reported as the effective catalytic species supported by positive effect of chloride ions. From this investigation it is concluded that $[IrCl_6]^{-3}$ and QFC are the reactive species of Ir(III) chloride and quinolinium fluorochromate in acidic medium respectively.

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REFERENCES

[1] V.Murugesan, A.Pandurangan; Indian J.Chem.B, **31**, 377 **(1992)**.

[2] Itishri Dave, Vinita Sharma, K.Kalyan Benerji; J.Indian Chem.Soc., **79**, 347-350 **(2002)**.

[3] Subbaih Meenakshisundaram, Ramanathan Sockalingam; Collect.Czech.Chem.Commun., **66**, 877-896 **(2001)**.

[4] K.Choudhary, P.K.Sharma, K.K.Benerji; Inter.J.Chem.Kinet., **31(7)**, 469-475 **(1999)**.

[5] Sheila Srivastava, Sarika Singh, Parul Srivastava; Asian J.Chem., **20(1)**, 317-323 **(2008)**.

[6] Sheila Srivastava, Parul Srivastava, Ashish Kumar, Shalini Singh; Bulletin of Catalysis Society of India, **6**, 119-124 **(2007)**.

[7] K.B.Wilberg, R.Stewart; J.Amer.Chem.Soc., **78**, 1214 **(1956)**.

[8] D.D.Perrin, L.Armarego, D.R.Perrin; Purification of Organic Compounds [Oxford : Pergamon]

[9] J.C.Chang, C.S.Garner; Inorg.Chem., **4**, 209 **(1965)**.