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Kinetics and Mechanism of Rh(III) Catalyzed Oxidation of Fumaric Acid by Ce(IV) in Acidic Medium

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The kinetics of Rh(III) catalysed oxidation of fumaric acid by Ce(IV) has been investigated in acidic medium. The reaction shows first order kinetics with respect to fumaric acid, Ce(IV) and Rh(III) and no effect of the medium. There is no significant effect of ionic strength and potassium chloride on reaction rate. Elevation of temperature increases the rate of reaction. A mechanism consistent with the above kinetic results has been suggested.

Key Words: Oxidant Ce(IV), Fumaric acid, Sulphuric acid, Rh(III), Kinetics and mechanism.

INTRODUCTION

Kinetics studies on the catalyzed oxidation of unsaturated aliphatic acid with different oxidants like N-bromobenzamide[1], ethyl N-chlorocarbamate[2], pyridinium hydrobromide[3], benzyltrimethyl ammonium chlorobromate[4] using different catalysts like Ru(III), Os(VIII) and Ir(III). However, there is no work on oxidation reaction of fumaric acid by Ce(IV) in acidic medium in presence of Rh(III) catalyst. Rh(III) is rare, lustrous, silvery hard metal. Rh(III) is known to have catalyst reaction in acidic and alkaline medium both[5, 6].

EXPERIMENTAL

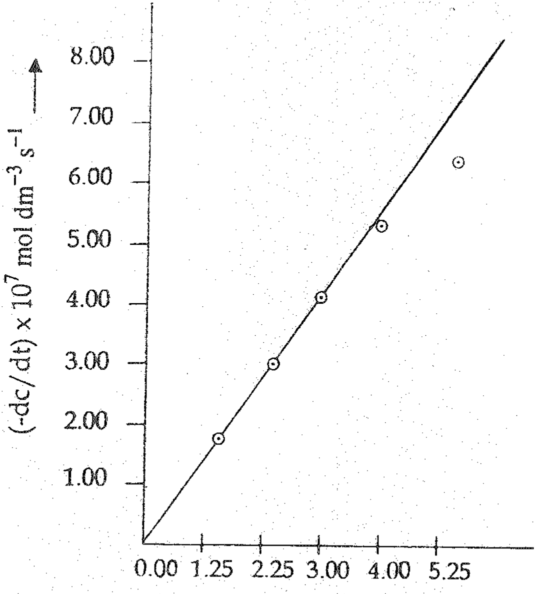
All chemicals were of AR grade and doubly distilled water used throughout. Aqueous solution of fumaric acid (E. Merck) was prepared in doubly distilled water and standardized iodometrically[7]. Stock solution of Ce(IV) was prepared by dissolving the sample in 1 M sulphuric acid. Rhodium trichloride (Johnson Matthey) was dissolved in 0.1 M hydrochloric acid. The reaction was initiated by mixing the preequilibrated reactant solution taken at desired temperature (35°C) and progress of reaction was followed by withdrawing known amount of aliquots (5 mL) of the reaction solution at regular time intervals, quenching the reaction by excess standardized ferrous ammonium sulfate solution and back titrating unreacted ferrous ion with standard Ce(IV) solution using ferrion as an internal indicator[8–13].

RESULTS AND DISCUSSION

The oxidation of fumaric acid by Ce(IV) studied over a wide range of concentrations of the reactant showed that the reaction follows first order dependence on Ce(IV) (Fig. 1). It gives a straight line with unit slope which confirms the first order kinetics. A linear increase in first order rate constant with an increase in the initial concentration of fumaric acid and Rh(III) was observed which shows the order with respect to fumaric acid and [Rh(III)], *i.e.*, one (Fig. 2). Increase in the concentration of $[H^+]$ has no effect of the medium. Addition of K_2SO_4 and KCl has no significant effect on reaction rate.

TABLE-1
EFFECT OF VARIATION OF $[H^+]$, [Ce(IV)], FUMARIC ACID AND [Rh(III)] CATALYSED ON REACTION RATE CONSTANT, AT TEMPERATURE = 35°C, KCl = 1.00×10^{-3} mol dm^{-3}

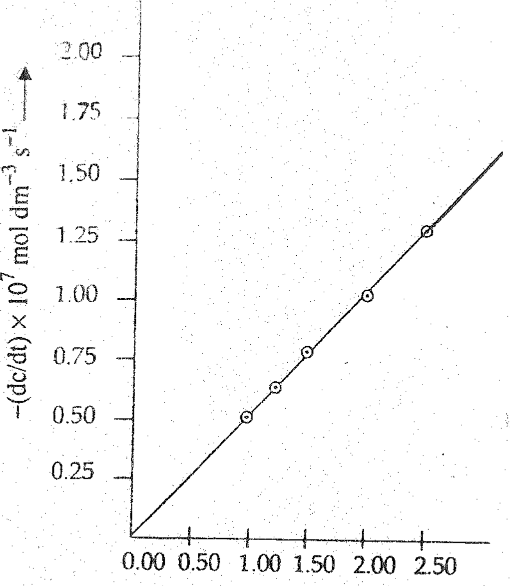
[Fumaric acid] $\times 10^3$ (mol dm^{-3})	Ce(IV) $\times 10^4$ (mol dm^{-3})	$[H_2SO_4] = 0.590$ (mol dm^{-3})	[Rh(III)] $\times 10^6$ (mol dm^{-3})	[–dc/dt] $\times 10^7$ (mol dm^{-3})	$k_1 \times 10^3$ (s^{-1})
1.00	1.25	0.50	5.00	1.60	1.60
1.00	2.25	0.50	5.00	3.00	1.62
1.00	3.00	0.50	5.00	4.30	1.58
1.00	4.00	0.50	5.00	5.30	1.61
1.00	5.25	0.50	5.00	6.25	1.60
1.00	6.00	0.50	5.00	0.58	0.12
1.50	6.00	0.50	5.00	0.80	0.17
2.00	6.00	0.50	5.00	1.13	0.25
2.50	6.00	0.50	5.00	1.35	0.30
3.00	6.00	0.50	5.00	1.66	0.36
1.00	6.00	0.50	1.25	0.52	0.11
1.00	6.00	0.50	1.25	0.65	0.14
1.00	6.00	0.50	1.50	0.77	0.17
1.00	6.00	0.50	2.00	1.05	0.23
1.00	6.00	0.50	2.50	1.34	0.29
1.00	6.00	0.50	5.00	0.68	0.15
1.00	6.00	1.00	5.00	0.66	0.14
1.00	6.00	1.50	5.00	0.69	0.15
1.00	6.00	2.00	5.00	0.67	0.14
1.00	6.00	2.50	5.00	0.65	0.14



[Ce(IV)] × 10^4 mol dm^{-3} ⟶

Fig. 1. Variation of oxidant Ce(IV) at 35°C

[Fumaric acid] × 10^3 = 1.00 mol dm^{-3}; [Rh(III)] × 10^6 = 5.00 mol dm^{-3};
[H_2SO_4] = 0.50 mol dm^{-3}; [KCl] × 10^3 = 1.00 mol dm^{-3};



[Rh(III)] × 10^6 mol dm^{-3} ⟶

Fig. 2. Variation of catalyst at 35°C

[Fumaric acid] × 10^3 = 1.00 mol dm^{-3}; [Ce(III)] × 10^4 = 6.00 mol dm^{-3};
[H_2SO_4] = 0.50 mol dm^{-3}; [KCl] × 10^3 = 1.00 mol dm^{-3};

TABLE-2
EFFECT OF IONIC STRENGTH, CHLORIDE ION AND TEMPERATURE

Temperature (°C)	Ionic strength (μ) × 10^2 (mol dm^{-3})	[KCl] × 10^2 (mol dm^{-3})	$k_1 \times 10^7$ (s^{-1})
—	8.73	0.00	1.15
—	11.73	0.00	1.17
—	18.73	0.00	1.04
—	29.73	0.00	1.14
—	34.73	0.00	1.10
—	41.73	0.00	1.30
—	0.00	1.00	0.26
—	0.00	1.50	0.26
—	0.00	2.00	0.24
—	0.00	2.50	0.28
—	0.00	3.00	0.22
30	0.00	0.00	0.09
35	0.00	0.00	0.19
40	0.00	0.00	0.28
45	0.00	0.00	0.55

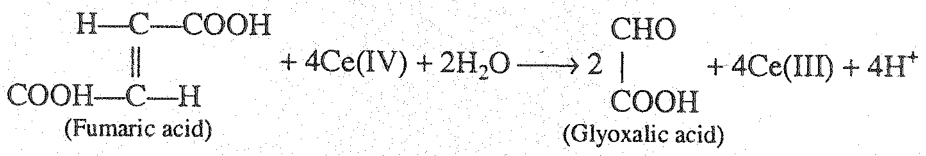
TABLE-3
THERMODYNAMIC PARAMETERS

E_a (kJ mol^{-1})	log A	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
82.84	6.99	80.28	–27.37	88.71

Stoichiometry and product analysis

Reaction mixture containing varying properties of Ce(IV) and fumaric acid under the condition [Ce(IV)]≫ [Fumaric acid] were kept at room temperature for 24 h. Estimation of unreacted Ce(IV) shows that 1 mol of the substrate, *i.e.*, fumaric acid, consumed 4 mol of Ce(IV).

According to stoichiometry, the equation for the oxidation of fumaric acid by Ce(IV) can be written as



$$\underset{\text{(Fumaric acid)}}{\begin{matrix}\text{H—C—COOH}\\ \| \\ \text{COOH—C—H}\end{matrix}} + 4Ce(IV) + 2H_2O \longrightarrow 2\underset{\text{(Glyoxalic acid)}}{\begin{matrix}\text{CHO}\\ | \\ \text{COOH}\end{matrix}} + 4Ce(III) + 4H^+$$

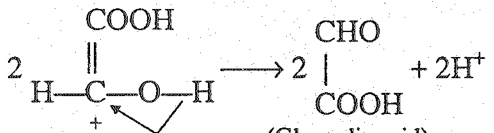
The product glyoxalic acid was detected and estimated gravimetrically as well as by TLC.

Mechanism

$$Rh(III) + S \xrightleftharpoons{K} [RhS]^{3+} \qquad (i)$$

$$[RhS]^{3+} + Ce(IV) + 2H_2O \xrightarrow{k_1} Ce(III) + Rh + \underset{\text{(Intermediate complex)}}{2CH(OH)COOH} + 2H^+ \qquad (ii)$$

$$\mathrm{Rh} + 3\mathrm{Ce(IV)} \longrightarrow 3\mathrm{Ce(III)} + \mathrm{Rh(III)} \qquad \text{(iii)}$$



$$2\ \mathrm{H{-}\underset{+}{\overset{\overset{COOH}{\|}}{C}}{-}O{-}H} \longrightarrow 2\ \begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{COOH}\end{array} + 2H^+$$

(Glyoxalic acid)

Considering the above reaction step, the rate of reaction can be written as rate of loss of Ce(IV). Thus the rate of reaction is expressed as

$$-\frac{d[\mathrm{Ce(IV)}]}{dt} = k[\mathrm{RhS}]^{3+}[\mathrm{Ce(IV)}] \qquad (1)$$

Considering step (1) we have [RhSj'V

$$K = \frac{\mathrm{RhS}^{3+}}{[\mathrm{Rh(III)}][\mathrm{S}]}$$

or

$$[\mathrm{RhS}]^{+3} = K[\mathrm{Rh(III)}][\mathrm{S}] \qquad (2)$$

On substituting the value of $[\mathrm{RhS}]^{3+}$ from eqn. (2) in eqn. (1),

$$-\frac{d[\mathrm{Ce(IV)}]}{dt} = kK[\mathrm{Rh(III)}][\mathrm{S}][\mathrm{Ce(IV)}] \qquad (3)$$

where [S] is an unsaturated aliphatic acid, *i.e.*, fumaric acid.

The rate law (3) is in agreement with all observed kinetics, *i.e.*, first order in case of [Rh(III), [Ce(IV)], [S] and no effect of $[H^+]$, *i.e.*, medium.

REFERENCES

1. A. Agarwal, S. Mittal and K.K. Banerji, *Indian J. Chem.*, **26A**, 339 (1987).
2. A. Pareek, S. Kothari and K.K. Banerji, *Indian J. Chem.*, **35A**, 119 (1996).
3. J. Devi, S. Kothari and K.K. Banerji, *Indian J. Chem.*, **24A**, 116 (1995).
4. R. Ram, V.S. Sharma, K. Pradeep and K.K. Banerji, *Indian J. Chem.*, **39A**, 650 (2000).
5. I.S. Ahmed and C. Mohammad, *J. Chem Kinet.*, **11**, 813 (1985).
6. G.P. Tickhonova and S. Bovkwest, *Russ. J. Inorg. Chem.*, **23**, 1687 (1987).
7. B. Singh and A.K. Singh, *Indian J. Chem.*, **43A**, 1645 (2004).
8. AQ.I. Vogel, Quantitative Organic Analysis, Part-3, ELBS-Longman, London, p. 739 (1958).
9. Ashish, A.K. Singh and B. Singh, *Indian J. Chem.*, **43A**, 1645 (2004).
10. R.A. Singh, S.P. Mishra, V.K. Srivastava and J. Verma, *Asian J. Chem.*, **17**, 2849 (2005).
11. R.A. Singh and R.S. Singh, *Oxid. Comm.*, **26**, 207 (2003).
12. B. Krishna and H.S. Singh, *J. Phys. Chem.*, 231, 399 (1996).
13. S.P. Mishra, A.Singh, J. Verma, V.K. Srivastava and R.A. Singh, *Acta Cienc. Indica*, **31C**, 93 (2005).

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